The background of the cover features a complex arrangement of abstract molecular models. In the center, a large red sphere with a honeycomb-like internal structure is surrounded by several smaller spheres of varying sizes, some in red and some in gold. These spheres are set against a dark blue background that has a subtle, wavy, grid-like texture.

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1	1A	1 H	2 Hydrogen 1.008
11	1A	Na Sodium	22 Atomic mass

The diagram consists of three adjacent rectangular boxes. The leftmost box is green and labeled "Meta". The middle box is light blue and also labeled "Meta". The rightmost box is light blue and labeled "Non".

58 Ce Cerium 140.1	59 Pr Praseodymium 140.9	60 Nd Neodymium 144.2	61 Pm Promethium (147)	62 Sm Samarium 150.4	63 Eu Europium 152.0	64 Gd Gadolinium 157.3	65 Tb Terbium 158.9	66 Dy Dysprosium 162.5	67 Ho Holmium 164.9	68 Er Erbium 167.3	69 Tm Thulium 168.9	70 Yb Ytterbium 173.0	71 Lu Lutetium 175.0
90 Th Thorium 232.0	91 Pa Protactinium (231)	92 U Uranium 238.0	93 Np Neptunium (237)	94 Pu Plutonium (242)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (249)	99 Es Einsteinium (254)	100 Fm Fermium (253)	101 Md Mendelevium (256)	102 No Ne�rium (256)	103 Lr Lawrencium (257)

The 1–18 group designation has been recommended by the International Union of Pure and Applied Chemistry (IUPAC) but is not yet in wide use. In this text we use the standard U.S. notation for group numbers (1A–8A and 1B–8B). In 2011 IUPAC revised the atomic masses of some elements. The changes are minor and they are not adopted in the present edition of this text.

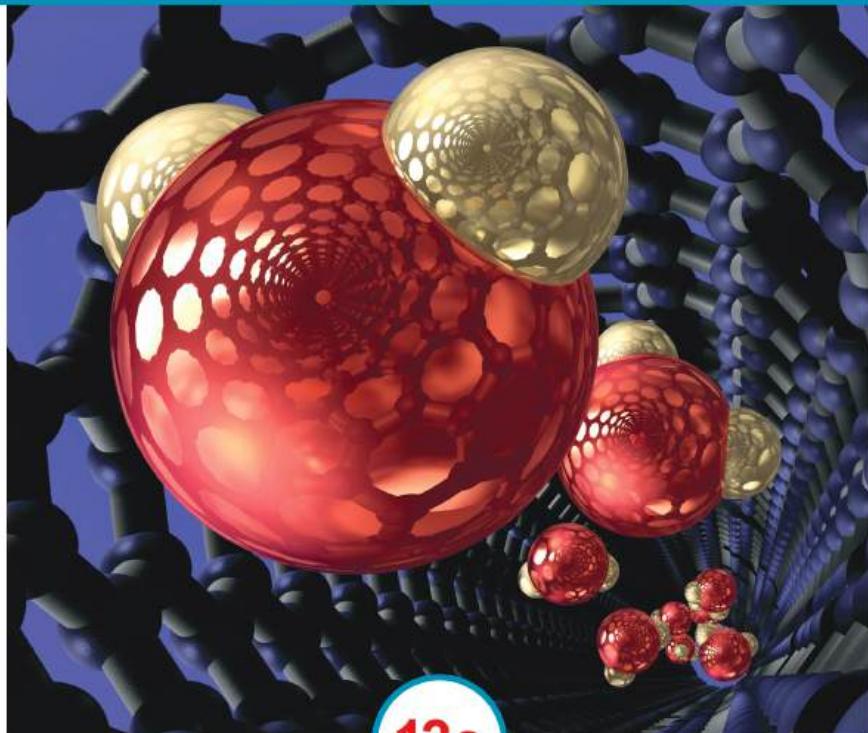
The Elements with Their Symbols and Atomic Masses*

Element	Symbol	Atomic Number	Atomic Mass [†]	Element	Symbol	Atomic Number	Atomic Mass [†]
Actinium	Ac	89	(227)	Mendelevium	101	(256)	
Aluminum	Al	13	26.98	Mercury	Hg	80	200.6
Americium	Am	95	(243)	Molybdenum	Mo	42	95.94
Antimony	Sb	51	121.8	Moscovium	Mc	115	(288)
Argon	Ar	18	39.95	Neodymium	Nd	60	144.2
Arsenic	As	33	74.92	Neon	Ne	10	20.18
Astatine	At	85	(210)	Neptunium	Np	93	(237)
Barium	Ba	56	137.3	Nickel	Ni	28	58.69
Berkelium	Bk	97	(247)	Nihonium	Nh	113	(284)
Beryllium	Be	4	9.012	Niobium	Nb	41	92.91
Bismuth	Bi	83	209.0	Nitrogen	N	7	14.01
Bohrium	Bh	107	(262)	Nobelium	No	102	(253)
Boron	B	5	10.81	Oganesson	Og	118	(294)
Bromine	Br	35	79.90	Osmium	Os	76	190.2
Cadmium	Cd	48	112.4	Oxygen	O	8	16.00
Calcium	Ca	20	40.08	Palladium	Pd	46	106.4
Californium	Cf	98	(249)	Phosphorus	P	15	30.97
Carbon	C	6	12.01	Platinum	Pt	78	195.1
Cerium	Ce	58	140.1	Plutonium	Pu	94	(242)
Cesium	Cs	55	132.9	Polonium	Po	84	(210)
Chlorine	Cl	17	35.45	Potassium	K	19	39.10
Chromium	Cr	24	52.00	Praseodymium	Pr	59	140.9
Cobalt	Co	27	58.93	Promethium	Pm	61	(147)
Copernicium	Cn	112	(285)	Protactinium	Pa	91	(231)
Copper	Cu	29	63.55	Radium	Ra	88	(226)
Curium	Cm	96	(247)	Radon	Rn	86	(222)
Darmstadtium	Ds	110	(269)	Rhenium	Re	75	186.2
Dubnium	Db	105	(260)	Rhodium	Rh	45	102.9
Dysprosium	Dy	66	162.5	Roentgenium	Rg	111	(272)
Einsteinium	Es	99	(254)	Rubidium	Rb	37	85.47
Erbium	Er	68	167.3	Ruthenium	Ru	44	101.1
Europium	Eu	63	152.0	Rutherfordium	Rf	104	(257)
Fermium	Fm	100	(253)	Samarium	Sm	62	150.4
Flerovium	Fl	114	(289)	Scandium	Sc	21	44.96
Fluorine	F	9	19.00	Seaborgium	Sg	106	(263)
Francium	Fr	87	(223)	Selenium	Se	34	78.96
Gadolinium	Gd	64	157.3	Silicon	Si	14	28.09
Gallium	Ga	31	69.72	Silver	Ag	47	107.9
Germanium	Ge	32	72.59	Sodium	Na	11	22.99
Gold	Au	79	197.0	Strontium	Sr	38	87.62
Hafnium	Hf	72	178.5	Sulfur	S	16	32.07
Hassium	Hs	108	(265)	Tantalum	Ta	73	180.9
Helium	He	2	4.003	Technetium	Tc	43	(99)
Holmium	Ho	67	164.9	Tellurium	Te	52	127.6
Hydrogen	H	1	1.008	Tennessine	Ts	117	(294)
Indium	In	49	114.8	Terbium	Tb	65	158.9
Iodine	I	53	126.9	Thallium	Tl	81	204.4
Iridium	Ir	77	192.2	Thorium	Th	90	232.0
Iron	Fe	26	55.85	Thulium	Tm	69	168.9
Krypton	Kr	36	83.80	Tin	Sn	50	118.7
Lanthanum	La	57	138.9	Titanium	Ti	22	47.88
Lawrencium	Lr	103	(257)	Tungsten	W	74	183.9
Lead	Pb	82	207.2	Uranium	U	92	238.0
Lithium	Li	3	6.941	Vanadium	V	23	50.94
Livermorium	Lv	116	(293)	Xenon	Xe	54	131.3
Lutetium	Lu	71	175.0	Ytterbium	Yb	70	173.0
Magnesium	Mg	12	24.31	Yttrium	Y	39	88.91
Manganese	Mn	25	54.94	Zinc	Zn	30	65.39
Meitnerium	Mt	109	(266)	Zirconium	Zr	40	91.22

*All atomic masses have four significant figures. These values are recommended by the Committee on Teaching of Chemistry, International Union of Pure and Applied Chemistry.

[†]Approximate values of atomic masses for radioactive elements are given in parentheses.

CHEMISTRY



13e

Raymond Chang

Williams College

Jason Overby

College of Charleston



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Raymond Chang was born in Hong Kong and grew up in Shanghai and Hong Kong. He received his B.Sc. degree in chemistry from London University, and his Ph.D. in chemistry from Yale University. After doing postdoctoral research at Washington University and teaching for a year at Hunter College of the City University of New York, he joined the chemistry department at Williams College.

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In his free time, he enjoys boating, bowling, and cooking. He is also involved with USA Swimming as a nationally certified starter and stroke-and-turn official. He lives in South Carolina with his wife Robin and two daughters, Emma and Sarah.



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Contents in Brief

- 1** Chemistry: The Study of Change 1
- 2** Atoms, Molecules, and Ions 40
- 3** Mass Relationships in Chemical Reactions 78
- 4** Reactions in Aqueous Solutions 121
- 5** Gases 174
- 6** Thermochemistry 230
- 7** Quantum Theory and the Electronic Structure of Atoms 274
- 8** Periodic Relationships Among the Elements 326
- 9** Chemical Bonding I: Basic Concepts 366
- 10** Chemical Bonding II: Molecular Geometry and Hybridization of Atomic Orbitals 410
- 11** Intermolecular Forces and Liquids and Solids 461
- 12** Physical Properties of Solutions 513
- 13** Chemical Kinetics 556
- 14** Chemical Equilibrium 616
- 15** Acids and Bases 660
- 16** Acid-Base Equilibria and Solubility Equilibria 714
- 17** Entropy, Free Energy, and Equilibrium 770
- 18** Electrochemistry 806
- 19** Nuclear Chemistry 856
- 20** Chemistry in the Atmosphere 896
- 21** Metallurgy and the Chemistry of Metals 926
- 22** Nonmetallic Elements and Their Compounds 952
- 23** Transition Metals Chemistry and Coordination Compounds 990
- 24** Organic Chemistry 1020
- 25** Synthetic and Natural Organic Polymers 1054

Appendix 1 Units for the Gas Constant A-1

Appendix 2 Thermodynamic Data at 1 atm and 25°C A-2

Appendix 3 Mathematical Operations A-7

Contents

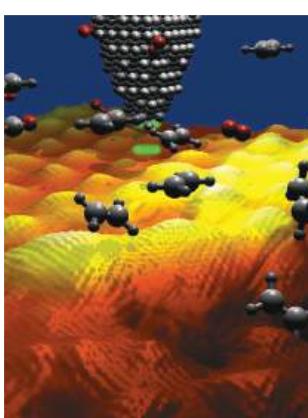
List of Applications xix

List of Videos xx

Preface xxi

Instructor and Student Resources xxvi

A Note to the Student xxx



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Chemistry: The Study of Change 1

1.1 Chemistry: A Science for the Twenty-First Century 2

1.2 The Study of Chemistry 3

1.3 The Scientific Method 4

CHEMISTRY *in Action*

The Search for the Higgs Boson 6

1.4 Classifications of Matter 7

1.5 The Three States of Matter 9

1.6 Physical and Chemical Properties of Matter 10

1.7 Measurement 12

CHEMISTRY *in Action*

The Importance of Units 17

1.8 Handling Numbers 18

1.9 Dimensional Analysis in Solving Problems 23

1.10 Real-World Problem Solving: Information, Assumptions, and Simplifications 27

Learning Objectives 29

Key Equations 29

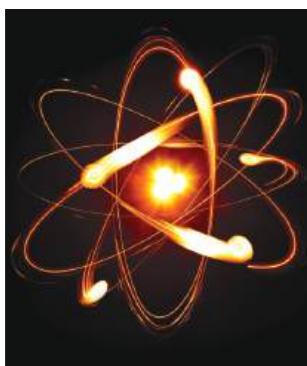
Summary of Concepts & Facts 29

Questions & Problems 30

CHEMICAL *MYSTERY*

The Disappearance of the Dinosaurs 38





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Atoms, Molecules, and Ions 40

- 2.1 The Atomic Theory 41**
 - 2.2 The Structure of the Atom 43**
 - 2.3 Atomic Number, Mass Number, and Isotopes 48**
 - 2.4 The Periodic Table 50**
- CHEMISTRY in Action**
Distribution of Elements on Earth and in Living Systems 51
- 2.5 Molecules and Ions 52**
 - 2.6 Chemical Formulas 54**
 - 2.7 Naming Compounds 58**
 - 2.8 Introduction to Organic Compounds 67**

Learning Objectives 69
Key Equations 69
Summary of Concepts & Facts 69
Questions & Problems 70



NASA

Mass Relationships in Chemical Reactions 78

- 3.1 Atomic Mass 79**
- 3.2 Avogadro's Number and the Molar Mass of an Element 81**
- 3.3 Molecular Mass 84**
- 3.4 The Mass Spectrometer 87**
- 3.5 Percent Composition of Compounds 88**
- 3.6 Experimental Determination of Empirical Formulas 91**
- 3.7 Chemical Reactions and Chemical Equations 93**
- 3.8 Amounts of Reactants and Products 98**
- 3.9 Limiting Reagents 102**
- 3.10 Reaction Yield 106**

CHEMISTRY in Action
Chemical Fertilizers 108

Learning Objectives 109
Key Equations 109
Summary of Concepts & Facts 109
Questions & Problems 110





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Reactions in Aqueous Solutions 121

4.1 General Properties of Aqueous Solutions 122

4.2 Precipitation Reactions 125

CHEMISTRY *in Action*

An Undesirable Precipitation Reaction 129

4.3 Acid-Base Reactions 130

4.4 Oxidation-Reduction Reactions 136

CHEMISTRY *in Action*

Breathalyzer 146

4.5 Concentration of Solutions 147

4.6 Gravimetric Analysis 151

4.7 Acid-Base Titrations 153

4.8 Redox Titrations 156

CHEMISTRY *in Action*

Metal from the Sea 158

Learning Objectives 159

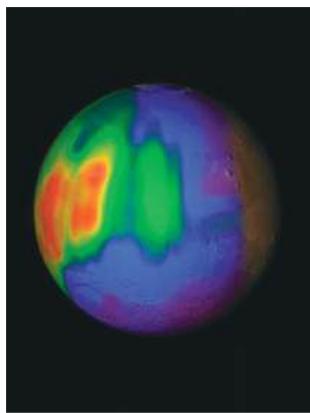
Key Equations 160

Summary of Concepts & Facts 160

Questions & Problems 161

CHEMICAL MYSTERY

Who Killed Napoleon? 172



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Gases 174

5.1 Substances That Exist as Gases 175

5.2 Pressure of a Gas 177

5.3 The Gas Laws 180

5.4 The Ideal Gas Equation 186

5.5 Gas Stoichiometry 195

5.6 Dalton's Law of Partial Pressures 197

CHEMISTRY *in Action*

Scuba Diving and the Gas Laws 202

5.7 The Kinetic Molecular Theory of Gases 203

CHEMISTRY *in Action*

Super Cold Atoms 209

5.8 Deviation from Ideal Behavior 211

Learning Objectives 214

Key Equations 214

Summary of Concepts & Facts 215

Questions & Problems 216

CHEMICAL MYSTERY

Out of Oxygen 228



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Thermochemistry 230

6.1 The Nature of Energy and Types of Energy 231

6.2 Energy Changes in Chemical Reactions 232

6.3 Introduction to Thermodynamics 234

CHEMISTRY in Action

Making Snow and Inflating a Bicycle Tire 240

6.4 Enthalpy of Chemical Reactions 240

6.5 Calorimetry 246

CHEMISTRY in Action

White Fat Cells, Brown Fat Cells, and a Potential Cure for Obesity 250

6.6 Standard Enthalpy of Formation and Reaction 252

CHEMISTRY in Action

How a Bombardier Beetle Defends Itself 256

6.7 Heat of Solution and Dilution 258

Learning Objectives 261

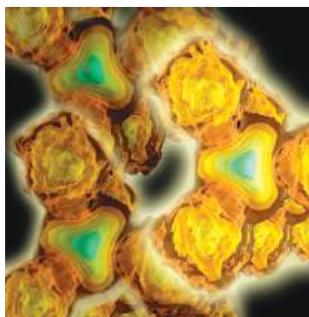
Key Equations 261

Summary of Concepts & Facts 261

Questions & Problems 262

CHEMICAL MYSTERY

The Exploding Tire 272



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Quantum Theory and the Electronic Structure of Atoms 274

7.1 From Classical Physics to Quantum Theory 275

7.2 The Photoelectric Effect 279

7.3 Bohr's Theory of the Hydrogen Atom 282

7.4 The Dual Nature of the Electron 287

CHEMISTRY in Action

Laser—The Splendid Light 288

CHEMISTRY in Action

Electron Microscopy 291

7.5 Quantum Mechanics 292

7.6 Quantum Numbers 294

7.7 Atomic Orbitals 297

7.8 Electron Configuration 301

7.9 The Building-Up Principle 307

CHEMISTRY in Action

Quantum Dots 310

Learning Objectives 312

Key Equations 313

Summary of Concepts & Facts 313

Questions & Problems 314

CHEMICAL MYSTERY

Discovery of Helium and the Rise and Fall of Coronium 324





Periodic Relationships Among the Elements 326



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- 8.1 Development of the Periodic Table 327**
- 8.2 Periodic Classification of the Elements 329**
- 8.3 Periodic Variation in Physical Properties 333**
- 8.4 Ionization Energy 339**

CHEMISTRY in Action

The Third Liquid Element? 340

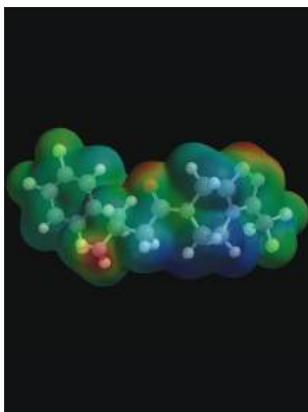
- 8.5 Electron Affinity 344**
- 8.6 Variation in Chemical Properties of the Representative Elements 346**

CHEMISTRY in Action

Discovery of the Noble Gases 355

Learning Objectives 357
Key Equations 357
Summary of Concepts & Facts 357
Questions & Problems 358

Chemical Bonding I: Basic Concepts 366



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- 9.1 Lewis Dot Symbols 367**
- 9.2 The Ionic Bond 368**
- 9.3 Lattice Energy of Ionic Compounds 370**

CHEMISTRY in Action

Sodium Chloride—A Common and Important Ionic Compound 374

- 9.4 The Covalent Bond 375**
- 9.5 Electronegativity 378**
- 9.6 Writing Lewis Structures 381**
- 9.7 Formal Charge and Lewis Structure 384**
- 9.8 The Concept of Resonance 387**
- 9.9 Exceptions to the Octet Rule 389**

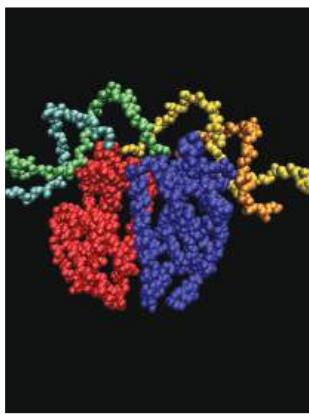
CHEMISTRY in Action

Just Say NO 394

- 9.10 Bond Enthalpy 395**

Learning Objectives 400
Key Equation 400
Summary of Concepts & Facts 400
Questions & Problems 401





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Chemical Bonding II: Molecular Geometry and Hybridization of Atomic Orbitals 410

10.1 Molecular Geometry 411

10.2 Dipole Moments 421

CHEMISTRY in Action

Microwave Ovens—Dipole Moments at Work 422

10.3 Valence Bond Theory 426

10.4 Hybridization of Atomic Orbitals 428

10.5 Hybridization in Molecules Containing Double and Triple Bonds 437

10.6 Molecular Orbital Theory 440

10.7 Molecular Orbital Configurations 443

10.8 Delocalized Molecular Orbitals 448

CHEMISTRY in Action

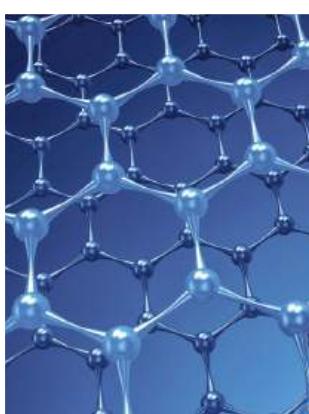
Buckyball, Anyone? 450

Learning Objectives 452

Key Equations 452

Summary of Concepts & Facts 452

Questions & Problems 453



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Intermolecular Forces and Liquids and Solids 461

11.1 The Kinetic Molecular Theory of Liquids and Solids 462

11.2 Intermolecular Forces 463

11.3 Properties of Liquids 469

CHEMISTRY in Action

A Very Slow Pitch 471

CHEMISTRY in Action

Why Do Lakes Freeze from the Top Down? 473

11.4 Crystal Structure 474

11.5 X-Ray Diffraction by Crystals 480

11.6 Types of Crystals 482

CHEMISTRY in Action

High-Temperature Superconductors 484

CHEMISTRY in Action

And All for the Want of a Button 488





11.7 Amorphous Solids 488 11.8 Phase Changes 489 11.9 Phase Diagrams 498

CHEMISTRY *in Action*

Hard-Boiling an Egg on a Mountaintop, Pressure Cookers, and Ice Skating 499

CHEMISTRY *in Action*

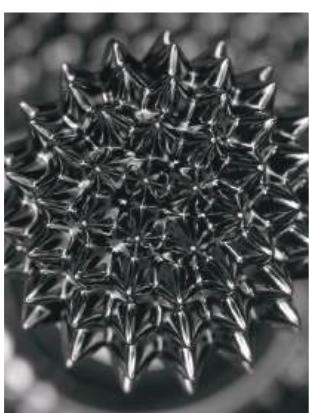
Liquid Crystals 500

Learning Objectives 503

Key Equations 503

Summary of Concepts & Facts 504

Questions & Problems 505



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Physical Properties of Solutions 513

12.1 Types of Solutions 514 12.2 A Molecular View of the Solution Process 515 12.3 Concentration Units 517 12.4 The Effect of Temperature on Solubility 522 12.5 The Effect of Pressure on the Solubility of Gases 524

CHEMISTRY *in Action*

The Killer Lake 526

12.6 Colligative Properties of Nonelectrolyte Solutions 527 12.7 Colligative Properties of Electrolyte Solutions 538

CHEMISTRY *in Action*

Dialysis 539

12.8 Colloids 541

Learning Objectives 543

Key Equations 543

Summary of Concepts & Facts 544

Questions & Problems 544

CHEMICAL MYSTERY

The Wrong Knife 554





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Chemical Kinetics 556

13.1 The Rate of a Reaction 557

13.2 The Rate Law 565

13.3 The Relation Between Reactant Concentration and Time 569

CHEMISTRY *in Action*

Radiocarbon Dating 580

13.4 Activation Energy and Temperature Dependence of Rate Constants 582

13.5 Reaction Mechanisms 588

13.6 Catalysis 593

CHEMISTRY *in Action*

Pharmacokinetics 600

Learning Objectives 602

Key Equations 602

Summary of Concepts & Facts 603

Questions & Problems 603



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Chemical Equilibrium 616

14.1 The Concept of Equilibrium and the Equilibrium Constant 617

14.2 Writing Equilibrium Constant Expressions 620

14.3 The Relationship Between Chemical Kinetics and Chemical Equilibrium 631

14.4 What Does the Equilibrium Constant Tell Us? 632

14.5 Factors That Affect Chemical Equilibrium 638

CHEMISTRY *in Action*

Life at High Altitudes and Hemoglobin Production 644

CHEMISTRY *in Action*

The Haber Process 646

Learning Objectives 647

Key Equations 648

Summary of Concepts & Facts 648

Questions & Problems 649





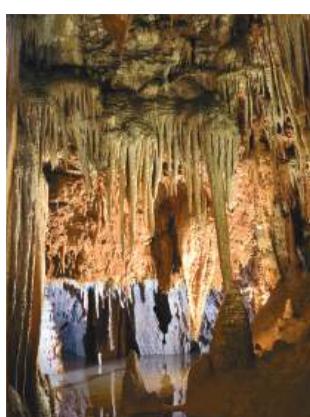
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Acids and Bases 660

- 15.1 Brønsted Acids and Bases 661**
 - 15.2 The Acid-Base Properties of Water 663**
 - 15.3 pH—A Measure of Acidity 664**
- CHEMISTRY in Action**
Antacids and the pH Balance in Your Stomach 668
- 15.4 Strength of Acids and Bases 670**
 - 15.5 Weak Acids and Acid Ionization Constants 674**
 - 15.6 Weak Bases and Base Ionization Constants 681**
 - 15.7 The Relationship Between the Ionization Constants of Acids and Their Conjugate Bases 683**
 - 15.8 Diprotic and Polyprotic Acids 684**
 - 15.9 Molecular Structure and the Strength of Acids 688**
 - 15.10 Acid-Base Properties of Salts 692**
 - 15.11 Acid-Base Properties of Oxides and Hydroxides 697**
 - 15.12 Lewis Acids and Bases 699**

Learning Objectives 701
Key Equations 702
Summary of Concepts & Facts 702
Questions & Problems 703

CHEMICAL MYSTERY
Decaying Papers 712



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Acid-Base Equilibria and Solubility Equilibria 714

- 16.1 Homogeneous versus Heterogeneous Solution Equilibria 715**
 - 16.2 The Common Ion Effect 715**
 - 16.3 Buffer Solutions 719**
 - 16.4 Acid-Base Titrations 724**
- CHEMISTRY in Action**
Maintaining the pH of Blood 726
- 16.5 Acid-Base Indicators 733**
 - 16.6 Solubility Equilibria 736**
 - 16.7 Separation of Ions by Fractional Precipitation 743**
 - 16.8 The Common Ion Effect and Solubility 745**
 - 16.9 pH and Solubility 746**
 - 16.10 Complex Ion Equilibria and Solubility 749**

CHEMISTRY in Action
How an Eggshell Is Formed 753





16.11 Application of the Solubility Product Principle to Qualitative Analysis 754

Learning Objectives 757

Key Equations 757

Summary of Concepts & Facts 758

Questions & Problems 758

CHEMICAL MYSTERY

A Hard-Boiled Snack 768



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Entropy, Free Energy, and Equilibrium 770

17.1 The Three Laws of Thermodynamics 771

17.2 Spontaneous Processes 771

17.3 Entropy 773

17.4 The Second Law of Thermodynamics 777

17.5 Gibbs Free Energy 782

CHEMISTRY in Action

The Efficiency of Heat Engines 784

CHEMISTRY in Action

The Thermodynamics of a Rubber Band 789

17.6 Free Energy and Chemical Equilibrium 791

17.7 Thermodynamics in Living Systems 795

Learning Objectives 796

Key Equations 797

Summary of Concepts & Facts 797

Questions & Problems 798

Electrochemistry 806



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18.1 Redox Reactions 807

18.2 Galvanic Cells 810

18.3 Standard Reduction Potentials 812

18.4 Thermodynamics of Redox Reactions 818

18.5 The Effect of Concentration of Cell Emf 821

18.6 Batteries and Fuel Cells 826

CHEMISTRY in Action

Bacteria Power 831

18.7 Corrosion 832

CHEMISTRY in Action

Dental Filling Discomfort 835

18.8 Electrolysis 836

Learning Objectives 842

Key Equations 842

Summary of Concepts & Facts 842

Questions & Problems 843

CHEMICAL MYSTERY

Tainted Water 854





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Nuclear Chemistry 856

19.1 The Nature of Nuclear Reactions 857

19.2 Nuclear Stability 859

19.3 Natural Radioactivity 865

19.4 Nuclear Transmutation 868

19.5 Nuclear Fission 871

CHEMISTRY *in Action*

Nature's Own Fission Reactor 876

19.6 Nuclear Fusion 877

19.7 Uses of Isotopes 879

19.8 Biological Effects of Radiation 882

CHEMISTRY *in Action*

Food Irradiation 884

CHEMISTRY *in Action*

Boron Neutron Capture Therapy 885

Learning Objectives 885

Key Equations 886

Summary of Concepts & Facts 886

Questions & Problems 887

CHEMICAL MYSTERY

The Art Forgery of the Twentieth Century 894

Chemistry in the Atmosphere 896

20.1 Earth's Atmosphere 897

20.2 Phenomena in the Outer Layers of the Atmosphere 901

20.3 Depletion of Ozone in the Stratosphere 903

20.4 Volcanoes 907

20.5 The Greenhouse Effect 908

20.6 Acid Rain 912

20.7 Photochemical Smog 915

20.8 Indoor Pollution 917

Learning Objectives 920

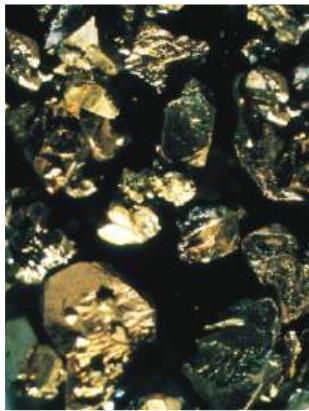
Summary of Concepts & Facts 920

Questions & Problems 921



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Metallurgy and the Chemistry of Metals 926

- 21.1 Occurrence of Metals 927**
- 21.2 Metallurgical Processes 928**
- 21.3 Band Theory of Electrical Conductivity 935**
- 21.4 Periodic Trends in Metallic Properties 937**
- 21.5 The Alkali Metals 938**
- 21.6 The Alkaline Earth Metals 942**
- 21.7 Aluminum 944**

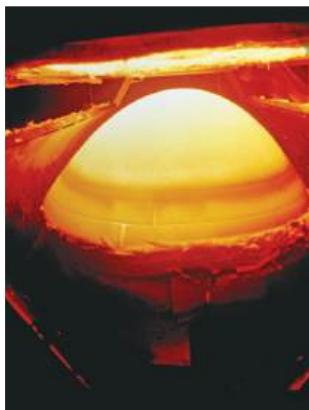
CHEMISTRY in Action

Recycling Aluminum 946

Learning Objectives 948

Summary of Concepts & Facts 948

Questions & Problems 948



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Nonmetallic Elements and Their Compounds 952

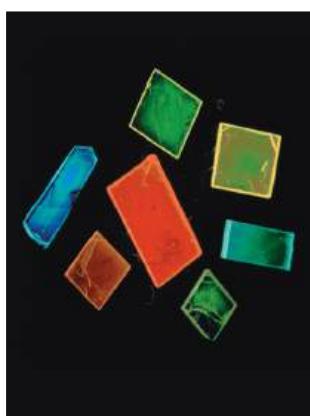
- 22.1 General Properties of Nonmetals 953**
- 22.2 Hydrogen 954**
- CHEMISTRY in Action**
- Metallic Hydrogen 959
- 22.3 Carbon 959**
- CHEMISTRY in Action**
- Synthetic Gas from Coal 962
- 22.4 Nitrogen and Phosphorus 963**
- CHEMISTRY in Action**
- Ammonium Nitrate—The Explosive Fertilizer 967
- 22.5 Oxygen and Sulfur 971**
- 22.6 The Halogens 978**

Learning Objectives 985

Summary of Concepts & Facts 985

Questions & Problems 986





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Transition Metals Chemistry and Coordination Compounds 990

- 23.1 Properties of the Transition Metals 991**
- 23.2 Chemistry of Iron and Copper 994**
- 23.3 Coordination Compounds 996**
- 23.4 Structure of Coordination Compounds 1001**
- 23.5 Bonding in Coordination Compounds: Crystal Field Theory 1004**

CHEMISTRY *in Action*

Coordination Compounds in Living Systems 1010

- 23.6 Reactions of Coordination Compounds 1011**
- 23.7 Applications of Coordination Compounds 1012**

CHEMISTRY *in Action*

Cisplatin—The Anticancer Drug 1014

Learning Objectives 1014

Key Equations 1015

Summary of Concepts & Facts 1015

Questions & Problems 1016



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Organic Chemistry 1020

- 24.1 Classes of Organic Compounds 1021**
- 24.2 Aliphatic Hydrocarbons 1021**

CHEMISTRY *in Action*

Ice That Burns 1023

- 24.3 Aromatic Hydrocarbons 1034**
- 24.4 Chemistry of the Functional Groups 1037**

CHEMISTRY *in Action*

The Petroleum Industry 1042

Learning Objectives 1046

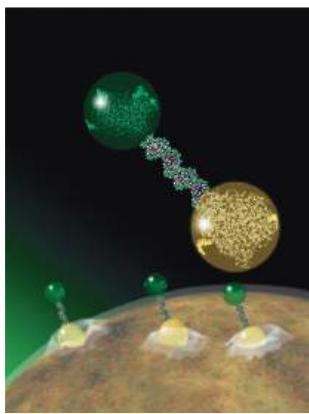
Summary of Concepts & Facts 1046

Questions & Problems 1046

CHEMICAL *MYSTERY*

The Disappearing Fingerprints 1052





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Medicine and Biological Sciences

Synthetic and Natural Organic Polymers 1054

25.1 Properties of Polymers 1055

25.2 Synthetic Organic Polymers 1056

25.3 Proteins 1061

CHEMISTRY in Action

Sickle Cell Anemia—A Molecular Disease 1068

25.4 Nucleic Acids 1069

CHEMISTRY in Action

DNA Fingerprinting 1072

Learning Objectives 1073

Summary of Concepts & Facts 1073

Questions & Problems 1074

CHEMICAL MYSTERY

A Story That Will Curl Your Hair 1078

Appendix 1 Units for the Gas Constant A-1

Appendix 2 Thermodynamic Data at 1 atm and 25°C A-2

Appendix 3 Mathematical Operations A-7

Glossary G-1

Answers to Even-Numbered Problems AP-1

Index I-1



List of Applications



The opening sentence of this text is, “Chemistry is an active, evolving science that has vital importance to our world, in both the realm of nature and the realm of society.” Throughout the text, Chemistry in Action boxes and Chemical Mysteries give specific examples of chemistry as active and evolving in all facets of our lives.

Chemistry in Action

- The Search for the Higgs Boson 6
- The Importance of Units 17
- Distribution of Elements on Earth and in Living Systems 51
- Chemical Fertilizers 108
- An Undesirable Precipitation Reaction 129
- Breathalyzer 146
- Metal from the Sea 158
- Scuba Diving and the Gas Laws 202
- Super Cold Atoms 209
- Making Snow and Inflating a Bicycle Tire 240
- White Fat Cells, Brown Fat Cells, and a Potential Cure for Obesity 250
- How a Bombardier Beetle Defends Itself 256
- Laser—The Splendid Light 288
- Electron Microscopy 291
- Quantum Dots 310
- The Third Liquid Element? 340
- Discovery of the Noble Gases 355
- Sodium Chloride—A Common and Important Ionic Compound 374
- Just Say NO 394
- Microwave Ovens—Dipole Moments at Work 422
- Buckyball, Anyone? 450
- A Very Slow Pitch 471
- Why Do Lakes Freeze from the Top Down? 473
- High-Temperature Superconductors 484
- And All for the Want of a Button 488
- Hard-Boiling an Egg on a Mountaintop, Pressure Cookers, and Ice Skating 499
- Liquid Crystals 500
- The Killer Lake 526

- Dialysis 539
- Radiocarbon Dating 580
- Pharmacokinetics 600
- Life at High Altitudes and Hemoglobin Production 644
- The Haber Process 646
- Antacids and the pH Balance in Your Stomach 668
- Maintaining the pH of Blood 726
- How an Eggshell Is Formed 753
- The Efficiency of Heat Engines 784
- The Thermodynamics of a Rubber Band 789
- Bacteria Power 831
- Dental Filling Discomfort 835
- Nature’s Own Fission Reactor 876
- Food Irradiation 884
- Boron Neutron Capture Therapy 885
- Recycling Aluminum 946
- Metallic Hydrogen 959
- Synthetic Gas from Coal 962
- Ammonium Nitrate—The Explosive Fertilizer 967
- Coordination Compounds in Living Systems 1010
- Cisplatin—The Anticancer Drug 1014
- Ice That Burns 1023
- The Petroleum Industry 1042
- Sickle Cell Anemia—A Molecular Disease 1068
- DNA Fingerprinting 1072

Chemical Mystery

- The Disappearance of the Dinosaurs 38
- Who Killed Napoleon? 172
- Out of Oxygen 228
- The Exploding Tire 272
- Discovery of Helium and the Rise and Fall of Coronium 324
- The Wrong Knife 554
- Decaying Papers 712
- A Hard-Boiled Snack 768
- Tainted Water 854
- The Art Forgery of the Twentieth Century 894
- The Disappearing Fingerprints 1052
- A Story That Will Curl Your Hair 1078

List of Videos



The videos below are correlated to *Chemistry*.

Within the chapter are icons letting the student and instructor know that a video is available for a specific topic. Videos can be found in the Connect ebook.

Absorption of Color (23.5)
Acid Ionization (15.5)
Acid-Base Titrations (16.4)
Activation Energy (13.4)
Alpha, Beta, and Gamma Rays (2.2)
 α -Particle Scattering (2.2)
Aluminum Production (21.7)
Atomic and Ionic Radius (8.3)
Atomic Line Spectra (7.3)
Base Ionization (15.6)
Buffer Solutions (16.3)
Catalysis (13.6)
Cathode Ray Tube (2.2)
Chemical Equilibrium (14.1)
Chirality (23.4, 24.2)
Collecting a Gas over Water (5.6)
Cu/Zn Voltaic Cell (18.2)
Cubic Unit Cells and Their Origins (11.4)
Current Generation from a Voltaic Cell (18.2)
Diffusion of Gases (5.7)
Dissociation of Strong and Weak Acids (15.4)
Dissolution of an Ionic and a Covalent Compound (12.2)
Electron Configurations (7.8)
Emission Spectra (7.3)
Equilibrium Vapor Pressure (11.8)
Formation of a Covalent Bond (9.4)
Formation of Ag_2S by Oxidation-Reduction (4.4)
Formation of an Ionic Compound (2.7)

Galvanic Cells (18.2)
The Gas Laws (5.3)
Heat Flow (6.2)
Hybridization (10.4)
Hydration (4.1)
Influence of Shape on Polarity (10.2)
Ionic and Covalent Bonding (9.4)
Ionic vs. Covalent Bonding (9.4)
Le Châtelier's Principle (14.5)
Limiting Reagent (3.9)
Line Spectra (7.3)
Millikan Oil Drop (2.2)
Molecular Shape and Orbital Hybridization (10.4)
Neutralization Reactions (4.3)
Nuclear Fission (19.5)
Operation of a Voltaic Cell (18.2)
Orientation of Collision (13.4)
Osmosis (12.6)
Oxidation-Reduction Reactions (4.4)
Packing Spheres (11.4)
Phase Diagrams and the States of Matter (11.9)
Polarity of Molecules (10.2)
Properties of Buffers (16.3)
Radioactive Decay (19.3)
Reaction of Cu with AgNO_3 (4.4)
Reaction of Magnesium and Oxygen (4.4, 9.2)
Resonance (9.8)
Rutherford's Experiment (2.2)
Sigma and Pi Bonds (10.5)
Strong Electrolytes, Weak Electrolytes, and
Nonelectrolytes (4.1)
VSEPR Theory (10.1)
VSEPR (10.1)

The thirteenth edition follows the long tradition of sustaining a firm foundation in the concepts of chemical principles and instilling an appreciation of the important role chemistry plays in our daily lives. We believe that it is our responsibility to help both instructors and students in their pursuit of this goal by presenting a broad range of chemical topics in a logical format. At all times, we strive to balance theory and application and to illustrate principles with applicable examples whenever possible.

As in previous editions, our goal is to create a text that clearly and concisely explains abstract concepts yet comprehensive enough that students are prepared to make the move forward in the chemistry curriculum. Encouraging feedback from instructors and students alike reaffirm that this approach is effective.

Review of Concepts and Facts

In previous editions, Review of Facts questions were provided throughout various sections of the book as a way for students to quickly gauge their understanding of a concept just presented. We have now expanded these checks to be a Review of Concepts and Facts provided at the end of most sections in a chapter. Over 170 new questions have been added to the Review of Concepts and Facts boxes ensuring students have ample opportunity to practice and review the major concepts and facts presented in that section. The answers to each of these questions are provided at the end of the chapter.

Summary of Concepts & Facts

- The study of chemistry involves three basic steps: observation, representation, and interpretation. Observation refers to measurements in the microscopic world; representation involves the use of shorthand notation symbols and equations for communication; interpretations are based on atoms and molecules, which belong to the microscopic world.
- The scientific method is a systematic approach to research that begins with the gathering of information through observation and measurements. In the process, hypotheses, laws, and theories are devised and tested.
- Chemists study matter and the changes it undergoes. The substances that make up matter have unique physical properties that can be observed without changing their identity and unique chemical properties that, when they are demonstrated, do change the identity of the substances. Mixtures, whether homogeneous or heterogeneous, can be separated into pure components by physical means.
- The simplest substances in chemistry are elements. Compounds are formed by the chemical combination of atoms of different elements in fixed proportions.
- All substances, in principle, can exist in three states: solid, liquid, and gas. The interconversion between these states can be effected by changing the temperature.
- SI units are used to express physical quantities in all sciences, including chemistry.
- Numbers expressed in scientific notation have the form $N \times 10^n$, where N is between 1 and 10, and n is a positive or negative integer. Scientific notation helps us handle very large and very small quantities.

Student Hot Spots

The adaptive reading tool SmartBook® now gives authors a detailed analysis of student performance on various learning objectives and concepts. With this powerful insight into the ideas and concepts students struggle with, we are now able to provide strategically-placed notifications about access to additional learning resources. Identified areas of particularly difficult content are now denoted with a margin note called “Student Hot Spots”. These are intended to direct students to additional learning resources specific to that

content. Students now have access to over 1,000 digital learning resources throughout the SmartBook® version of this text. Included in these learning resources are over 200 videos of chemistry faculty solving actual problems or explaining concepts.

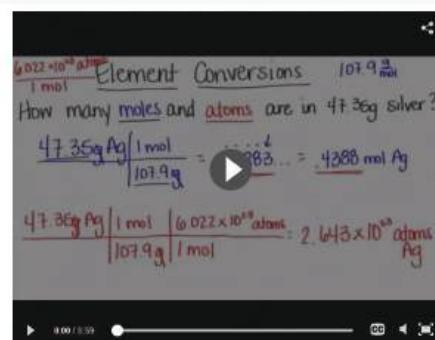
In the electronic version of this text, all the learning resources for the Student Hot Spots are readily available.

Student Hot Spot

Student data indicate you may struggle with significant figures. Access your eBook for additional Learning Resources on this topic.

STUDENT HOT SPOT

Student data indicate you may struggle with this content. View the following video, "Converting Element Mass into Moles and Atoms," to make sure you understand the concept before moving on.



Further, access to student results has guided the editing of content in many chapters. While many of the changes are subtle, some are more comprehensive. The ability to edit based on real time assessment data from students is the new paradigm for textbook authoring. Undoubtedly this changes how we provide and enhance learning materials for our students in the future!

Learning Objectives

All chapters now have a comprehensive list of learning objectives provided to help facilitate instructors' assessment of their students. Every learning objective item is tagged by its location in the chapter. Further, each learning objective is written using only appropriate action verbs based on Bloom's taxonomy.

Learning Objectives

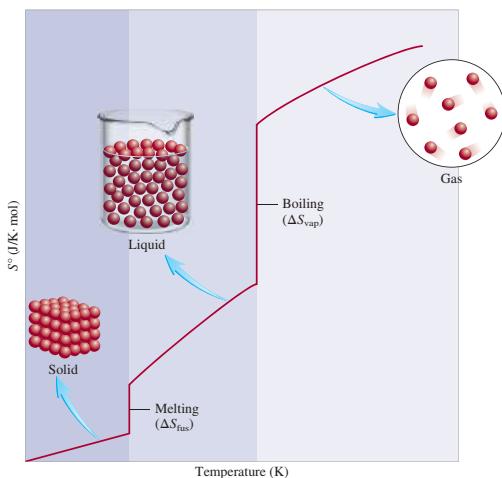
- Outline Dalton's hypotheses about the nature of matter. (Section 2.1)
- Understand the concept of the atom and the nature of an element. (Section 2.2)
- Assess the importance of experiments conducted by Thomson, Millikan, Röntgen, and Rutherford, and how they influenced our understanding of the nature and structure of atoms. (Section 2.2)
- Summarize the different types of radiation that radioactive substances can produce. (Section 2.2)
- Describe the location and physical properties of electrons, protons, and neutrons. (Section 2.2)
- Explain the nature and importance of isotopes. (Section 2.3)
- Calculate the mass number of an isotope. (Section 2.3)
- Utilize the mass number of an isotope to solve for the number of electrons, protons, or neutrons, given other relevant information. (Section 2.3)
- Recognize the general organization of the periodic table with respect to metals, metalloids, nonmetals, groups, and periods. (Section 2.4)
- Differentiate between molecules and ions. (Section 2.5)
- Classify chemical formulas as either molecular or empirical. (Section 2.6)
- Determine formulas of ionic compounds. (Section 2.6)

Questions and Problems

The Review Questions and Problems at the end of each chapter have been reorganized so that they fully correlate to a given section. In many cases, the heading for a group of questions was revised to reflect the title of a section. These changes should increase the ease with which students and instructors alike can identify appropriate questions and problems for practice or assignments.

Art Program and Design

For this edition, the art program was thoroughly revised to impart a more modern look and enhance visibility. Clear graphics are a vital component of the student learning process and as such, all graphs, periodic tables, and other figures have been updated with a new look and color scheme. In some instances, illustrations have been replaced with scientifically accurate photographs for enhanced chemical context. Many chapter opening photographs have been updated for new insights into various chemical topics and applications.



In addition to the more than 170 new Review of Concepts & Facts questions that have been added throughout the chapters, following are just a few of the highlights of the 13th edition content revision.

Chapter 1

- A revised discussion of the difference between intensive and extensive properties is provided.
- Table 1.3 has been expanded to include the common prefix peta-.
- A more detailed discussion of accuracy and precision has been included.

Chapter 3 The language concerning limiting reactants versus limiting reagents has been made consistent.

Chapter 7 A new worked example concerning quantum numbers has been included.

Chapters 2, 7, 8, 19, and 23 Figures and tables throughout have been updated to reflect the newest additions to the periodic table.

Problem Solving

The development of problem-solving skills has always been a major objective of this text. The two major categories of learning are shown next.

Worked examples follow a proven step-by-step strategy and solution.

- Problem statement** is the reporting of the facts needed to solve the problem based on the question posed.
- Strategy** is a carefully thought-out plan or method to serve as an important function of learning.
- Solution** is the process of solving a problem given in a stepwise manner.
- Check** enables the student to compare and verify with the source information to make sure the answer is reasonable.
- Practice Exercise** provides the opportunity to solve a similar problem in order to become proficient in this problem type. The Practice Exercises are available in the Connect electronic homework system. The margin note lists additional similar problems to work in the end-of-chapter problem section.

End-of-Chapter Problems are organized in various ways. Each section under a topic heading begins with Review Questions followed by Problems. The Additional Problems section provides more problems not organized by section, followed by the problem type Interpreting, Modeling & Estimating.

Many of the examples and end-of-chapter problems present extra tidbits of knowledge and enable the student to solve a chemical problem that a chemist would solve. The examples and problems show students the real world of chemistry and applications to everyday life situations.

Visualization

Graphs and Flow Charts are important in science. In *Chemistry*, flow charts show the thought process of a concept and graphs present data to comprehend the concept. A significant number of Problems and Review of Concepts & Facts, including many new to this edition, include graphical data.

Molecular art appears in various formats to serve different needs. Molecular models help to visualize the three-dimensional arrangement of atoms in a molecule. Electrostatic potential maps illustrate the electron density distribution in molecules. Finally, there is the macroscopic to microscopic art helping students understand processes at the molecular level.

Photos are used to help students become familiar with chemicals and understand how chemical reactions appear in reality.

Figures of apparatus enable the student to visualize the practical arrangement in a chemistry laboratory.

Study Aids

Setting the Stage

Each chapter starts with the Chapter Outline and A Look Ahead.

Chapter Outline enables the student to see at a glance the big picture and focus on the main ideas of the chapter.

A Look Ahead provides the student with an overview of concepts that will be presented in the chapter.

Tools to Use for Studying

Useful aids for studying are plentiful in *Chemistry* and should be used constantly to reinforce the comprehension of chemical concepts.

Marginal Notes are used to provide hints and feedback to enhance the knowledge base for the student.

Worked Examples

Practice Exercises are very important tools for learning and mastering chemistry. The problem-solving steps guide the student through the critical thinking necessary for succeeding in chemistry. Using sketches helps student understand the inner workings of a problem. Similar problems in the end-of-chapter problems section are listed at the end of the examples, enabling the student to apply new skill to other problems of the same type. Answers to the Practice Exercises are listed at the end of the chapter problems.

Key Equations are highlighted within the chapter, drawing the student's eye to material that needs to be understood and retained. The key equations are also presented in the chapter summary materials for easy access in review and study.

Summary of Concepts & Facts provides a quick review of concepts presented and discussed in detail within the chapter.

Key Words are a list of all important terms to help the student understand the language of chemistry.

Testing Your Knowledge

Review of Concepts & Facts lets students pause and check to see if they understand the concept presented and discussed in the section occurred.

Answers to the Review of Concepts can be found in the Student Solution Manual.

End-of-Chapter Problems enable the student to practice critical thinking and problem-solving skills. The problems are broken into various types:

- By chapter section. Starting with Review Questions to test basic conceptual understanding, followed by Problems to test the student's skill in

solving problems for that particular section of the chapter.

- Additional Problems uses knowledge gained from the various sections and/or previous chapters to solve the problem.
- Interpreting, Modeling & Estimating problems teach students the art of formulating models and estimating ballpark answers based on appropriate assumptions.

Real-Life Relevance

Interesting examples of how chemistry applies to life are used throughout the text. Analogies are used where appropriate to help foster understanding of abstract chemical concepts.

End-of-Chapter Problems pose many relevant questions for the student to solve. Examples include Why do swimming coaches sometimes place a drop of alcohol in a swimmer's ear to draw out water? How does one estimate the pressure in a carbonated soft drink bottle before removing the cap?

Chemistry in Action boxes appear in every chapter on a variety of topics, each with its own story of how chemistry can affect a part of life. The student can learn about the science of scuba diving and nuclear medicine, among many other interesting cases.

CHEMISTRY *in Action*

An Undesirable Precipitation Reaction

Limestone (CaCO_3) and dolomite ($\text{CaCO}_3 \cdot \text{MgCO}_3$), which are widespread on Earth's surface, often enter the water supply. According to Table 4.2, calcium carbonate is insoluble in water. However, in water containing dissolved carbon dioxide (from the atmosphere), calcium carbonate is converted to soluble calcium bicarbonate [$\text{Ca}(\text{HCO}_3)_2$],

$$\text{CaCO}_3(s) + \text{CO}_2(aq) + \text{H}_2\text{O}(l) \longrightarrow \text{Ca}^{2+}(aq) + 2\text{HCO}_3^-(aq)$$

where HCO_3^- is the bicarbonate ion.

Water containing Ca^{2+} and Mg^{2+} ions is called *hard water*, and water that is relatively free of these ions is called *soft water*. Hard water is unsuitable for some household and industrial uses. When water containing Ca^{2+} and HCO_3^- ions is heated or boiled, the solution is reversed to produce the CaCO_3 .



Chemical Mystery poses a mystery case to the student. A series of chemical questions provide clues as to how the mystery could possibly be solved. Chemical Mystery will foster a high level of critical thinking using the basic problem-solving steps built up throughout the text.

CHEMICAL *MYSTERY*

Who Killed Napoleon?

After his defeat at Waterloo in 1815, Napoleon was exiled to St. Helena, a small island in the Atlantic Ocean, where he spent the last six years of his life. In the 1960s, samples of his hair were analyzed and found to contain a high level of arsenic, suggesting that he might have been poisoned. The prime suspects are the governor of St. Helena, with whom Napoleon did not get along, and the French royal family, who wanted to prevent his return to France.

Elemental arsenic is not that harmful. The commonly used poison is actually arsenic(III) oxide, As_2O_3 , a white compound that dissolves in water, is tasteless, and, if administered over a period of time, is hard to detect. It was once known as the "inheritance powder," because it was added to grandfather's wine to hasten his demise so that his grandson could inherit the estate.

In 1832 the English chemist Marsh devised a procedure for detecting arsenic. This test, now known as Marsh's test, combines hydrogen former to reduce the reaction between zinc and sulfuric acid with a sample of the suspected poison. If As_2O_3 is present, it reacts with hydrogen to form a toxic gas, arsenic (AsH_3). When arsenic is heated, it decomposes to form arsenic, which is recognized by its metallic luster. The Marsh test is an

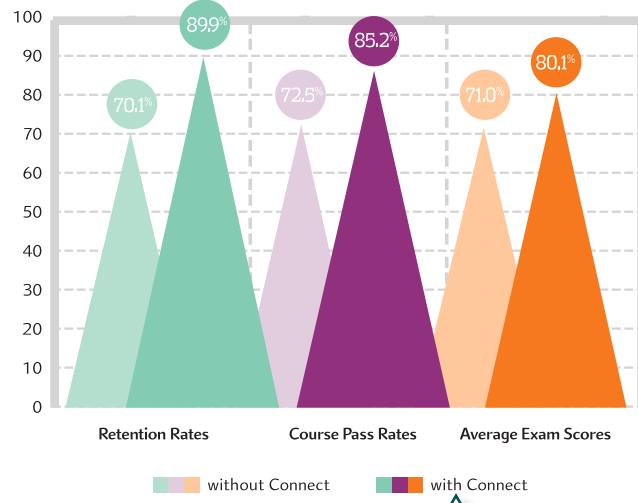
McGraw-Hill Connect® is a highly reliable, easy-to-use homework and learning management solution that utilizes learning science and award-winning adaptive tools to improve student results.

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- The Connect eBook makes it easy for students to access their reading material on smartphones and tablets. They can study on the go and don't need internet access to use the eBook as a reference, with full functionality.
- Multimedia content such as videos, simulations, and games drive student engagement and critical thinking skills.

73% of instructors who use Connect require it; instructor satisfaction increases by 28% when Connect is required.



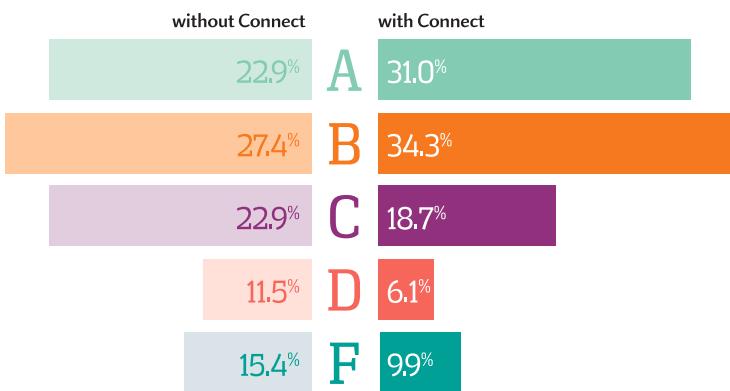
Robust Analytics and Reporting

- Connect Insight® generates easy-to-read reports on individual students, the class as a whole, and on specific assignments.
- The Connect Insight dashboard delivers data on performance, study behavior, and effort. Instructors can quickly identify students who struggle and focus on material that the class has yet to master.
- Connect automatically grades assignments and quizzes, providing easy-to-read reports on individual and class performance.



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Impact on Final Course Grade Distribution



More students earn
As and Bs when they
use Connect.

Trusted Service and Support

- Connect integrates with your LMS to provide single sign-on and automatic syncing of grades. Integration with Blackboard®, D2L®, and Canvas also provides automatic syncing of the course calendar and assignment-level linking.
- Connect offers comprehensive service, support, and training throughout every phase of your implementation.
- If you're looking for some guidance on how to use Connect, or want to learn tips and tricks from super users, you can find tutorials as you work. Our Digital Faculty Consultants and Student Ambassadors offer insight into how to achieve the results you want with Connect.

Instructor and Student Resources



Learn without Limits

A robust set of questions, problems, and interactive figures are presented and aligned with the textbook's learning goals. The integration of **ChemDraw by PerkinElmer**, the industry standard in chemical drawing software, allows students to create accurate chemical structures in their online homework assignments. As an instructor, you can edit existing questions and write entirely new problems. Track individual student performance—by question, assignment, or in relation to the class overall—with detailed grade reports. Integrate grade reports easily with Learning Management Systems (LMS), such as WebCT and Blackboard—and much more. Also available within Connect, our adaptive SmartBook has been supplemented with additional learning resources tied to each learning objective to provide point-in-time help to students who need it. To learn more, visit www.mheducation.com.

The screenshot shows a question titled "Sec. Ex. 4B - Resonance structures of sulfite anion". It includes a ChemDraw interface for drawing chemical structures. The question asks the user to draw arrows on the first structure to show its conversion to the second structure. The first structure is SO_3^{2-} with two double bonds to sulfur and one single bond to each oxygen. The second structure is $\text{S}(\text{O}_2)^2-$ with a triple bond to sulfur and two single bonds to each oxygen. A "Report problem" button is visible at the top right.

Instructors have access to the following instructor resources through Connect.

- **Art** Full-color digital files of all illustrations, photos, and tables in the book can be readily incorporated into lecture presentations, exams, or custom-made classroom materials. In addition, all files have been inserted into PowerPoint slides for ease of lecture preparation.

- **Animations** Numerous full-color animations illustrating important processes are also provided. Harness the visual impact of concepts in motion by importing these files into classroom presentations or online course materials.
- **PowerPoint Lecture Outlines** Ready-made presentations that combine art and lecture notes are provided for each chapter of the text.
- **Computerized Test Bank** Over 3,000 test questions that accompany *Chemistry* are available utilizing the industry-leading test generation software TestGen. These same questions are also available and assignable through Connect for online tests.
- **Instructor's Solutions Manual** This supplement contains complete, worked-out solutions for *all* the end-of-chapter problems in the text.



Fueled by LearnSmart—the most widely used and intelligent adaptive learning resource—**LearnSmart Prep** is designed to get students ready for a forthcoming course by quickly and effectively addressing pre-requisite knowledge gaps that may cause problems down the road. By distinguishing what students know from what they don't, and honing in on concepts they are most likely to forget, LearnSmart Prep maintains a continuously adapting learning path individualized for each student, and tailors content to focus on what the student needs to master in order to have a successful start in the new class.

The screenshot shows a "Particle Description of the Phases of Matter" activity. It features a video player with a thumbnail of a person speaking. Below the video is a text box with the following text:
There are three phases, or states, of matter: solid, liquid, and gas. This image shows a solid, a liquid, and a gas. Solids have a definite shape and volume. Liquids have a definite volume but no definite shape. Gases have neither a definite shape nor a definite volume.
The video player has a progress bar at the bottom. To the right of the video is an illustration of three bottles containing red spheres representing particles. One bottle is labeled "solid", one "liquid", and one "gas". Below the illustration are "NEXT PAGE" and "PREVIOUS" buttons. At the bottom of the screen, a progress bar shows "PROGRESS: Structure of Matter 3%".

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Student Solutions Manual

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A Note to the Student

General chemistry is commonly perceived to be more difficult than most other subjects. There is some justification for this perception. For one thing, chemistry has a very specialized vocabulary. At first, studying chemistry is like learning a new language. Furthermore, some of the concepts are abstract. Nevertheless, with diligence you can complete this course successfully, and you might even enjoy it. Here are some suggestions to help you form good study habits and master the material in this text.

- Attend classes regularly and take careful notes.
- If possible, always review the topics discussed in class the same day they are covered in class. Use this book to supplement your notes.
- Think critically. Ask yourself if you really understand the meaning of a term or the use of an equation. A good way to test your understanding is to explain a concept to a classmate or some other person.
- Do not hesitate to ask your instructor or your teaching assistant for help.

The thirteenth edition tools for *Chemistry* are designed to enable you to do well in your general chemistry course. The following guide explains how to take full advantage of the text, technology, and other tools.

- Before delving into the chapter, read the chapter *outline* and the chapter *introduction* to get a sense of the important topics. Use the outline to organize your note taking in class.
- At the end of each chapter you will find a summary of facts and concepts, the key equations, and a list of

key words, all of which will help you review for exams.

- Definitions of the key words can be studied in context on the pages cited in the end-of-chapter list or in the glossary at the back of the book.
- Careful study of the worked-out examples in the body of each chapter will improve your ability to analyze problems and correctly carry out the calculations needed to solve them. Also take the time to work through the practice exercise that follows each example to be sure you understand how to solve the type of problem illustrated in the example. The answers to the practice exercises appear at the end of the chapter, following the questions and problems. For additional practice, you can turn to similar problems referred to in the margin next to the example.
- The questions and problems at the end of the chapter are organized by section.
- The back inside cover shows a list of important figures and tables with page references. This index makes it convenient to quickly look up information when you are solving problems or studying related subjects in different chapters.

If you follow these suggestions and stay up-to-date with your assignments, you should find that chemistry is challenging, but less difficult and much more interesting than you expected.

—Raymond Chang and Jason Overby

CHAPTER

1

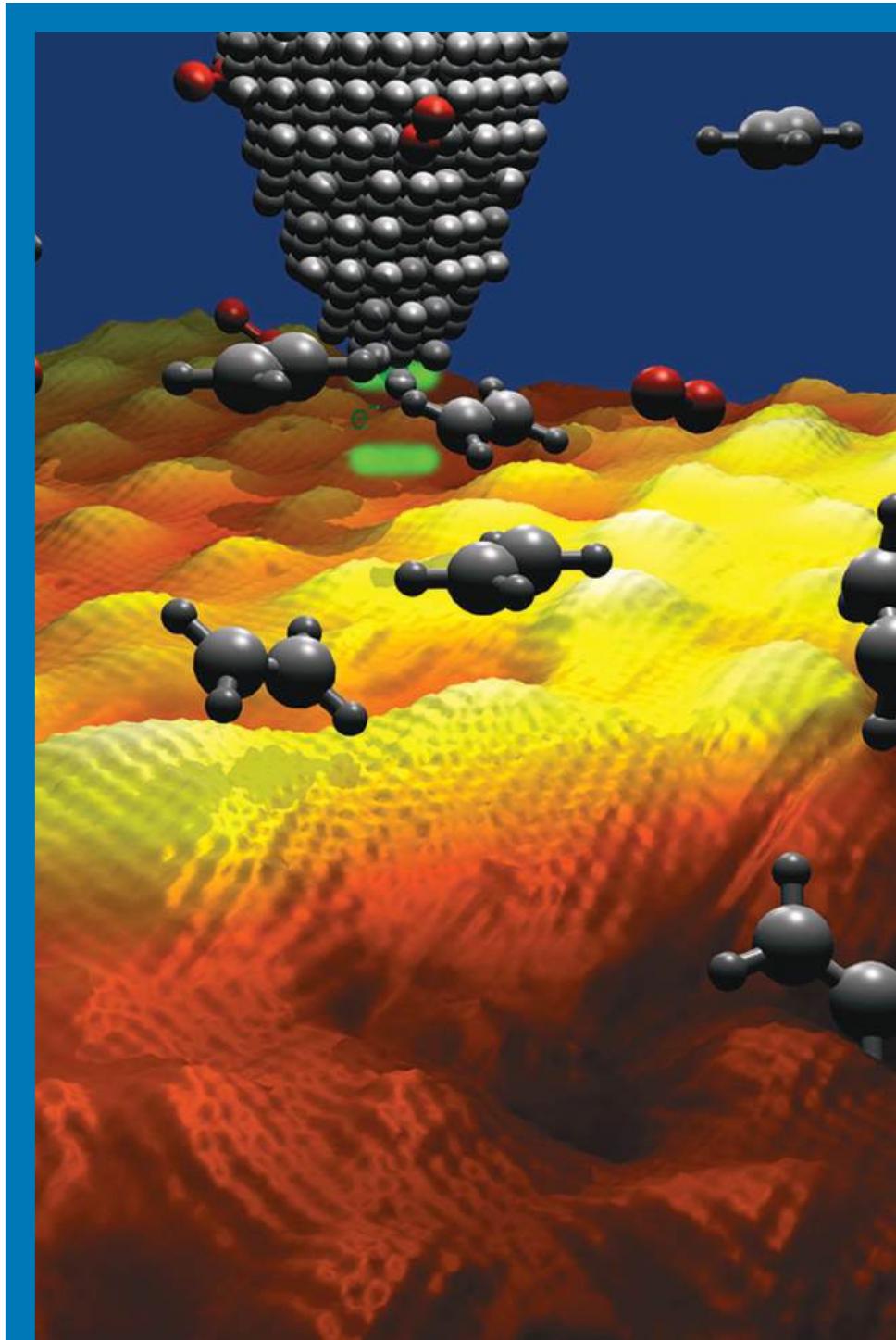
A scanning tunneling microscope probes individual small molecules when they adsorb on graphene, a single-atom thin sheet of carbon atoms.

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CHAPTER OUTLINE

- 1.1** Chemistry: A Science for the Twenty-First Century
- 1.2** The Study of Chemistry
- 1.3** The Scientific Method
- 1.4** Classifications of Matter
- 1.5** The Three States of Matter
- 1.6** Physical and Chemical Properties of Matter
- 1.7** Measurement
- 1.8** Handling Numbers
- 1.9** Dimensional Analysis in Solving Problems
- 1.10** Real-World Problem Solving: Information, Assumptions, and Simplifications

Chemistry The Study of Change



A LOOK AHEAD

- We begin with a brief introduction to the study of chemistry and describe its role in our modern society. (1.1 and 1.2)
- Next, we become familiar with the scientific method, which is a systematic approach to research in all scientific disciplines. (1.3)
- We define matter and note that a pure substance can either be an element or a compound. We distinguish between a homogeneous mixture and a heterogeneous mixture. We also learn that, in principle, all matter can exist in one of three states: solid, liquid, and gas. (1.4 and 1.5)
- To characterize a substance, we need to know its physical properties, which can be observed without changing its identity and chemical properties, which can be demonstrated only by chemical changes. (1.6)
- Being an experimental science, chemistry involves measurements. We learn the basic SI units and use the SI-derived units for quantities like volume and density. We also become familiar with the three temperature scales: Celsius, Fahrenheit, and Kelvin. (1.7)
- Chemical calculations often involve very large or very small numbers and a convenient way to deal with these numbers is the scientific notation. In calculations or measurements, every quantity must show the proper number of significant figures, which are the meaningful digits. (1.8)
- We learn that dimensional analysis is useful in chemical calculations. By carrying the units through the entire sequence of calculations, all the units will cancel except the desired one. (1.9)
- Solving real-world problems frequently involves making assumptions and simplifications. (1.10)

Chemistry is an active, evolving science that has vital importance to our world, in both the realm of nature and the realm of society. Its roots are ancient, but as we will see, chemistry is every bit a modern science.

We will begin our study of chemistry at the macroscopic level, where we can see and measure the materials of which our world is made. In this chapter, we will discuss the scientific method, which provides the framework for research not only in chemistry but in all other sciences as well. Next we will discover how scientists define and characterize matter. Then we will spend some time learning how to handle numerical results of chemical measurements and solve numerical problems. In Chapter 2, we will begin to explore the microscopic world of atoms and molecules.

1.1 Chemistry: A Science for the Twenty-First Century

Chemistry is *the study of matter and the changes it undergoes*. Chemistry is often called the central science, because a basic knowledge of chemistry is essential for students of biology, physics, geology, ecology, and many other subjects. Indeed, it is central to our way of life; without it, we would be living shorter lives in what we would consider primitive conditions, without automobiles, electricity, computers, CDs, and many other everyday conveniences.

Although chemistry is an ancient science, its modern foundation was laid in the nineteenth century, when intellectual and technological advances enabled scientists to break down substances into ever smaller components and consequently to explain many of their physical and chemical characteristics. The rapid development of increasingly sophisticated technology throughout the twentieth century has given us even greater means to study things that cannot be seen with the naked eye. Using computers and special microscopes, for example, chemists can analyze the structure of atoms and molecules—the fundamental units on which the study of chemistry is based—and design new substances with specific properties, such as drugs and environmentally friendly consumer products.

化
学

The Chinese characters for chemistry mean “the study of change.”

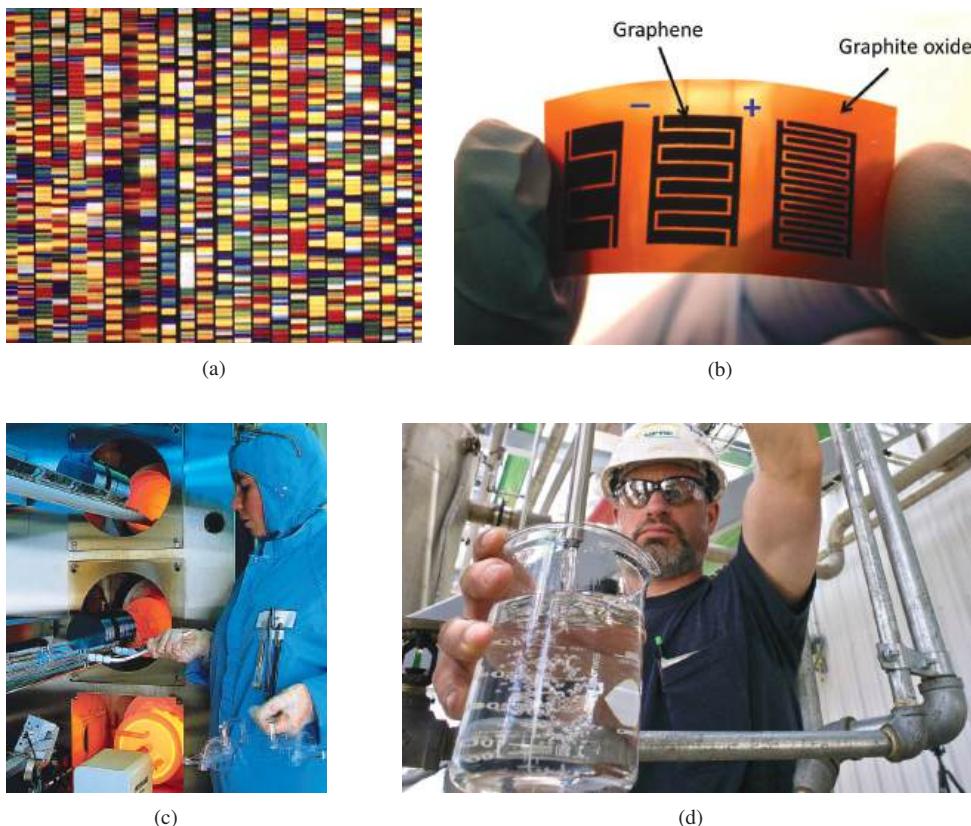


Figure 1.1 (a) The output from an automated DNA sequencing machine. Each lane displays the sequence (indicated by different colors) obtained with a separate DNA sample. (b) A graphene supercapacitor. These materials provide some of the highest known energy-to-volume ratios and response times. (c) Production of photovoltaic cells, used to convert light into electrical current. (d) Ethanol for fuel use is produced by distillation from corn.

(a): ©Science Source; (b): Courtesy of Richard B. Kaner; (c): ©David Parker/Seagate/Science Source; (d): ©David Nunuk/Science Source

It is fitting to ask what part the central science will have in the twenty-first century. Almost certainly, chemistry will continue to play a pivotal role in all areas of science and technology. Before plunging into the study of matter and its transformation, let us consider some of the frontiers that chemists are currently exploring (Figure 1.1). Whatever your reasons for taking general chemistry, a good knowledge of the subject will better enable you to appreciate its impact on society and on you as an individual.

1.2 The Study of Chemistry

Compared with other subjects, chemistry is commonly believed to be more difficult, at least at the introductory level. There is some justification for this perception; for one thing, chemistry has a very specialized vocabulary. However, even if this is your first course in chemistry, you already have more familiarity with the subject than you may realize. In everyday conversations we hear words that have a chemical connection, although they may not be used in the scientifically correct sense. Examples are “electronic,” “quantum leap,” “equilibrium,” “catalyst,” “chain reaction,” and “critical mass.” Moreover, if you cook, then you are a practicing chemist! From experience gained in the kitchen, you know that oil and water do not mix and that boiling water left on the stove will evaporate. You apply chemical and physical principles when you use baking soda to leaven bread, choose a pressure cooker to shorten the time it takes to prepare soup, add meat tenderizer to a pot roast, squeeze lemon juice over sliced pears to prevent them from turning brown or over fish to minimize its odor, and add vinegar

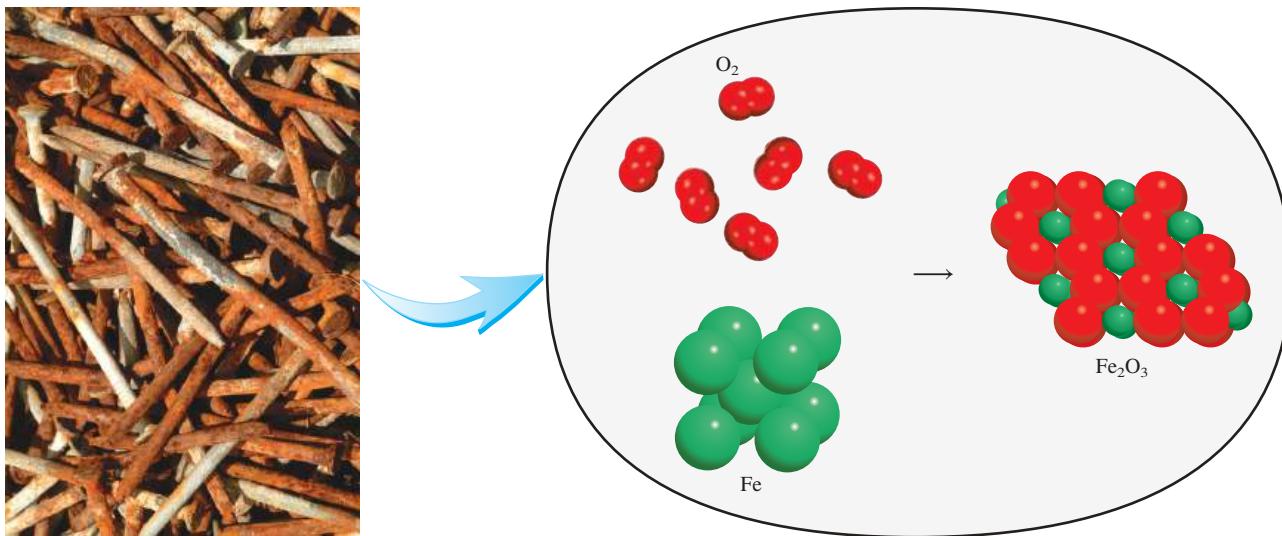


Figure 1.2 A simplified molecular view of rust (Fe_2O_3) formation from iron (Fe) atoms and oxygen molecules (O_2). In reality, the process requires water, and rust also contains water molecules.

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to the water in which you are going to poach eggs. Every day we observe such changes without thinking about their chemical nature. The purpose of this course is to make you think like a chemist, to look at the *macroscopic world*—the things we can see, touch, and measure directly—and visualize the particles and events of the *microscopic world* that we cannot experience without modern technology and our imaginations.

At first some students find it confusing that their chemistry instructor and textbook seem to be continually shifting back and forth between the macroscopic and microscopic worlds. Just keep in mind that the data for chemical investigations most often come from observations of large-scale phenomena, but the explanations frequently lie in the unseen and partially imagined microscopic world of atoms and molecules. In other words, chemists often *see* one thing (in the macroscopic world) and *think* another (in the microscopic world). Looking at the rusted nails in Figure 1.2, for example, a chemist might think about the basic properties of individual atoms of iron and how these units interact with other atoms and molecules to produce the observed change.

1.3 The Scientific Method

All sciences, including the social sciences, employ variations of what is called the **scientific method**, *a systematic approach to research*. For example, a psychologist who wants to know how noise affects people's ability to learn chemistry and a chemist interested in measuring the heat given off when hydrogen gas burns in air would follow roughly the same procedure in carrying out their investigations. The first step is to carefully define the problem. The next step includes performing experiments, making careful observations, and recording information, or *data*, about the system—the part of the universe that is under investigation. (In the examples just discussed, the systems are the group of people the psychologist will study and a mixture of hydrogen and air.)

The data obtained in a research study may be both **qualitative**, consisting of *general observations about the system*, and **quantitative**, comprising numbers obtained by *various measurements of the system*. Chemists generally use standardized symbols and equations in recording their measurements and observations. This form of representation not only simplifies the process of keeping records, but also provides a common basis for communication with other chemists.

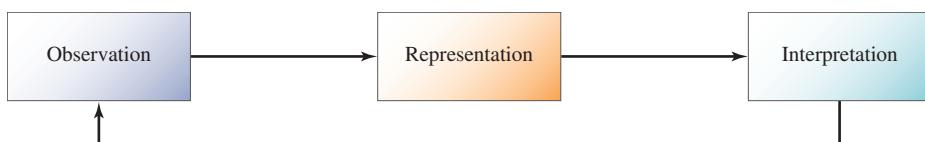


Figure 1.3 The three levels of studying chemistry and their relationships. Observation deals with events in the macroscopic world; atoms and molecules constitute the microscopic world. Representation is a scientific shorthand for describing an experiment in symbols and chemical equations. Chemists use their knowledge of atoms and molecules to explain an observed phenomenon.

When the experiments have been completed and the data have been recorded, the next step in the scientific method is interpretation, meaning that the scientist attempts to explain the observed phenomenon. Based on the data that were gathered, the researcher formulates a ***hypothesis***, a *tentative explanation for a set of observations*. Further experiments are devised to test the validity of the hypothesis in as many ways as possible, and the process begins anew. Figure 1.3 summarizes the main steps of the research process.

After a large amount of data has been collected, it is often desirable to summarize the information in a concise way, as a law. In science, a ***law*** is a *concise verbal or mathematical statement of a relationship between phenomena that is always the same under the same conditions*. For example, Sir Isaac Newton's second law of motion, which you may remember from high school science, says that force equals mass times acceleration ($F = ma$). What this law means is that an increase in the mass or in the acceleration of an object will always increase its force proportionally, and a decrease in mass or acceleration will always decrease the force.

Hypotheses that survive many experimental tests of their validity may evolve into theories. A ***theory*** is a *unifying principle that explains a body of facts and/or those laws that are based on them*. Theories, too, are constantly being tested. If a theory is disproved by experiment, then it must be discarded or modified so that it becomes consistent with experimental observations. Proving or disproving a theory can take years, even centuries, in part because the necessary technology may not be available. Atomic theory, which we will study in Chapter 2, is a case in point. It took more than 2000 years to work out this fundamental principle of chemistry proposed by Democritus, an ancient Greek philosopher. A more contemporary example is the search for the Higgs boson discussed in the Chemistry in Action essay, “The Search for the Higgs Boson.”

Scientific progress is seldom, if ever, made in a rigid, step-by-step fashion. Sometimes a law precedes a theory; sometimes it is the other way around. Two scientists may start working on a project with exactly the same objective, but will end up taking drastically different approaches. Scientists are, after all, human beings, and their modes of thinking and working are very much influenced by their background, training, and personalities.

The development of science has been irregular and sometimes even illogical. Great discoveries are usually the result of the cumulative contributions and experience of many workers, even though the credit for formulating a theory or a law is usually given to only one individual. There is, of course, an element of luck involved in scientific discoveries, but it has been said that “chance favors the prepared mind.” It takes an alert and well-trained person to recognize the significance of an accidental discovery and to take full advantage of it. More often than not, the public learns only of spectacular scientific breakthroughs. For every success story, however, there are hundreds of cases in which scientists have spent years working on projects that ultimately led to a dead end, and in which positive achievements came only after many wrong turns and at such a slow pace that they went unheralded. Yet even the dead ends contribute something to the continually growing body of knowledge about the physical universe. It is the love of the search that keeps many scientists in the laboratory.

The Search for the Higgs Boson

In this chapter, we identify mass as a fundamental property of matter, but have you ever wondered: Why does matter even have mass? It might seem obvious that “everything” has mass, but is that a requirement of nature? We will see later in our studies that light is composed of particles that do not have mass when at rest, and physics tells us under different circumstances the universe might not contain *anything* with mass. Yet we know that *our* universe is made up of an uncountable number of particles with mass, and these building blocks are necessary to form the elements that make up the people to ask such questions. The search for the answer to this question illustrates nicely the process we call the scientific method.

Current theoretical models tell us that everything in the universe is based on two types of elementary particles: bosons and fermions. We can distinguish the roles of these particles by considering the building blocks of matter to be constructed from fermions, while bosons are particles responsible for the force that holds the fermions together. In 1964, three different research teams independently proposed mechanisms in which a field of energy permeates the universe, and the interaction of matter with this field is due to a specific boson associated with the field. The greater the number of these bosons, the greater the interaction will be with the field. This interaction is the property we call mass, and the field and the associated boson came to be named for Peter Higgs, one of the original physicists to propose this mechanism.

This theory ignited a frantic search for the “Higgs boson” that became one of the most heralded quests in modern science. The Large Hadron Collider at CERN in Geneva, Switzerland (described in Chapter 19), was constructed to carry out experiments designed to find evidence for the Higgs boson. In these experiments, protons are accelerated to nearly the speed of light in opposite directions in a circular 17-mile tunnel, and then allowed to collide, generating even more fundamental particles at very high energies. The data are examined for evidence of an excess of particles at an energy consistent with theoretical predictions for the Higgs boson. The ongoing process of theory suggesting experiments that give results used to evaluate and ultimately refine the theory, and so on, is the essence of the scientific method.

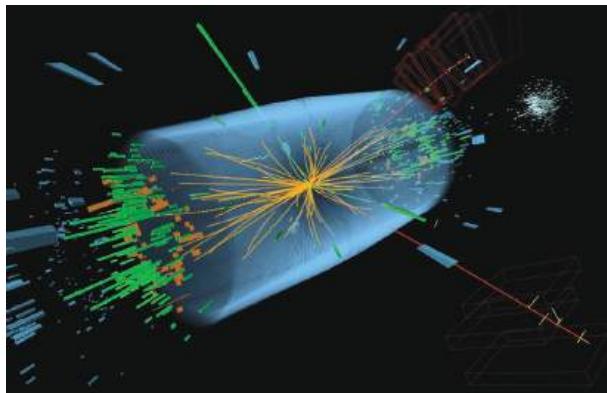


Illustration of the data obtained from decay of the Higgs boson into other particles following an 8-TeV collision in the Large Hadron Collider at CERN.
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On July 4, 2012, scientists at CERN announced the discovery of the Higgs boson. It takes about 1 trillion proton–proton collisions to produce one Higgs boson event, so it requires a tremendous amount of data obtained from two independent sets of experiments to confirm the findings. In science, the quest for answers is never completely done. Our understanding can always be improved or refined, and sometimes entire tenets of accepted science are replaced by another theory that does a better job explaining the observations. For example, scientists are not sure if the Higgs boson is the only particle that confers mass to matter, or if it is only one of several such bosons predicted by other theories.

But over the long run, the scientific method has proven to be our best way of understanding the physical world. It took 50 years for experimental science to validate the existence of the Higgs boson. This discovery was greeted with great fanfare and recognized the following year with a 2013 Nobel Prize in Physics for Peter Higgs and François Englert, another one of the six original scientists who first proposed the existence of a universal field that gives particles their mass. It is impossible to imagine where science will take our understanding of the universe in the next 50 years, but we can be fairly certain that many of the theories and experiments driving this scientific discovery will be very different than the ones we use today.

Review of Concepts & Facts

- 1.3.1 Which of the following statements is true?
- (a) A hypothesis always leads to the formulation of a law.
 - (b) The scientific method is a rigid sequence of steps in solving problems.
 - (c) A law summarizes a series of experimental observations; a theory provides an explanation for the observations.
- 1.3.2 A student collects the following data for a sample of an unknown liquid. Which of these data are qualitative measurements and which are quantitative measurements?
- (a) The sample has a volume of 15.4 mL.
 - (b) The sample is a light yellow liquid.
 - (c) The sample feels oily.
 - (d) The sample has a mass of 13.2 g.

1.4 Classifications of Matter

We defined chemistry in Section 1.1 as the study of matter and the changes it undergoes. **Matter** is *anything that occupies space and has mass*. Matter includes things we can see and touch (such as water, earth, and trees), as well as things we cannot (such as air). Thus, everything in the universe has a “chemical” connection.

Chemists distinguish among several subcategories of matter based on composition and properties. The classifications of matter include substances, mixtures, elements, and compounds, as well as atoms and molecules, which we will consider in Chapter 2.

Substances and Mixtures

A **substance** is *a form of matter that has a definite (constant) composition and distinct properties*. Examples are water, ammonia, table sugar (sucrose), gold, and oxygen. Substances differ from one another in composition and can be identified by their appearance, smell, taste, and other properties.

A **mixture** is *a combination of two or more substances in which the substances retain their distinct identities*. Some familiar examples are air, soft drinks, milk, and cement. Mixtures do not have constant composition. Therefore, samples of air collected in different cities would probably differ in composition because of differences in altitude, pollution, and so on.

All mixtures are classified as either homogeneous or heterogeneous. When a spoonful of sugar dissolves in water we obtain a **homogeneous mixture** in which *the composition of the mixture is the same throughout*. If sand is mixed with iron filings, however, the sand grains and the iron filings remain separate (Figure 1.4). This type of mixture is called a **heterogeneous mixture** because *the composition is not uniform*.

Any mixture, whether homogeneous or heterogeneous, can be created and then separated by physical means into pure components without changing the identities of the components. Thus, sugar can be recovered from a water solution by heating the solution and evaporating it to dryness. Condensing the vapor will give us back the water component. To separate the iron-sand mixture, we can use a magnet to remove the iron filings from the sand, because sand is not attracted to the magnet [see Figure 1.4(b)]. After separation, the components of the mixture will have the same composition and properties as they did to start with.

Elements and Compounds

Substances can be either elements or compounds. An **element** is *a substance that cannot be separated further into simpler substances by chemical methods*. To date, 118 elements have been positively identified. Most of them occur naturally on Earth. The others have been created by scientists via nuclear processes, which are the subject of Chapter 19 of this text.

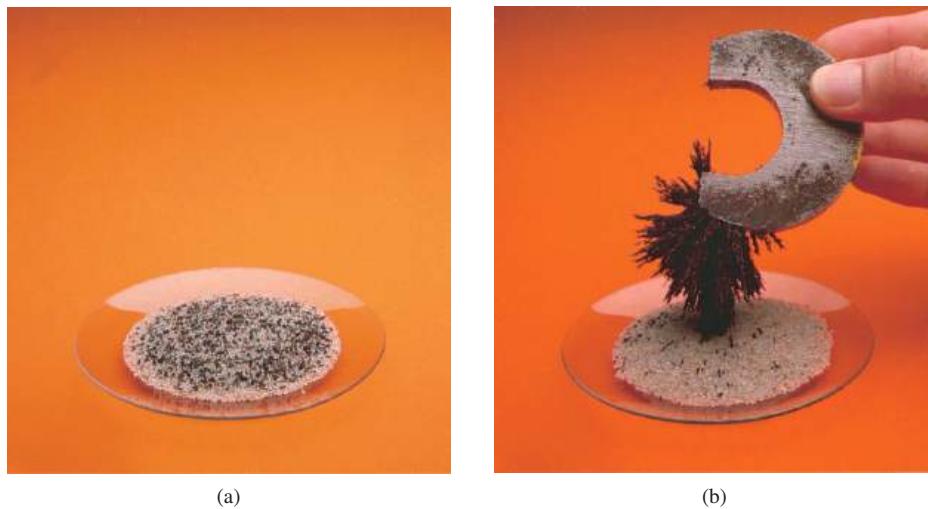


Figure 1.4 (a) The mixture contains iron filings and sand. (b) A magnet separates the iron filings from the mixture. The same technique is used on a larger scale to separate iron and steel from nonmagnetic objects such as aluminum, glass, and plastics.

(a and b): ©McGraw-Hill Education/Ken Karp

For convenience, chemists use symbols of one or two letters to represent the elements. The first letter of a symbol is *always* capitalized, but any following letters are not. For example, Co is the symbol for the element cobalt, whereas CO is the formula for the carbon monoxide molecule. Table 1.1 shows the names and symbols of some of the more common elements. The symbols of some elements are derived from their Latin names—for example, Au from *aurum* (gold), Fe from *ferrum* (iron), and Na from *natrium* (sodium)—whereas most of them come from their English names.

Atoms of most elements can interact with one another to form compounds. Hydrogen gas, for example, burns in oxygen gas to form water, which has properties that are distinctly different from those of the starting materials. Water is made up of two parts hydrogen and one part oxygen. This composition does not change, regardless of whether the water comes from a faucet in the United States, a lake in Outer Mongolia, or the ice caps on Mars. Thus, water is a **compound**, *a substance composed of atoms of two or more elements chemically united in fixed proportions*. Unlike mixtures, compounds can be separated only by chemical means into their pure components.

The relationships among elements, compounds, and other categories of matter are summarized in Figure 1.5.

Table 1.1 Some Common Elements and Their Symbols

Name	Symbol	Name	Symbol	Name	Symbol
Aluminum	Al	Fluorine	F	Oxygen	O
Arsenic	As	Gold	Au	Phosphorus	P
Barium	Ba	Hydrogen	H	Platinum	Pt
Bismuth	Bi	Iodine	I	Potassium	K
Bromine	Br	Iron	Fe	Silicon	Si
Calcium	Ca	Lead	Pb	Silver	Ag
Carbon	C	Magnesium	Mg	Sodium	Na
Chlorine	Cl	Manganese	Mn	Sulfur	S
Chromium	Cr	Mercury	Hg	Tin	Sn
Cobalt	Co	Nickel	Ni	Tungsten	W
Copper	Cu	Nitrogen	N	Zinc	Zn

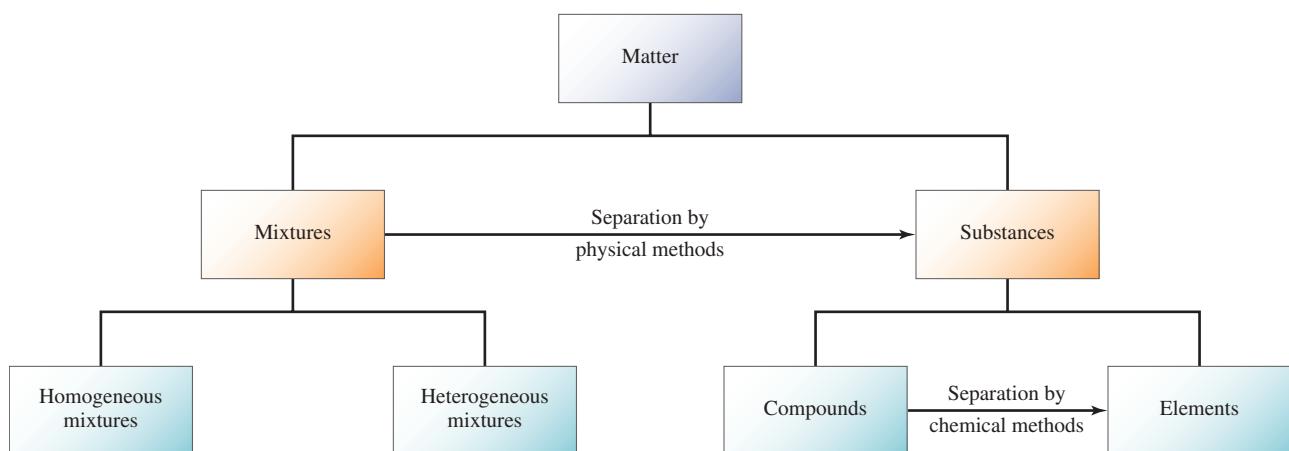
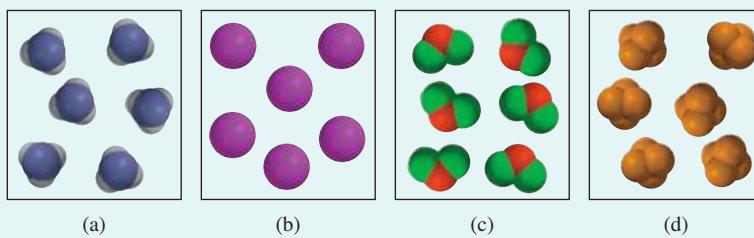


Figure 1.5 Classification of matter.

Review of Concepts & Facts

- 1.4.1** Which of the following diagrams represent elements and which represent compounds? Each color sphere (or truncated sphere) represents an atom. Different colored atoms indicate different elements.



1.5 The Three States of Matter

All substances, at least in principle, can exist in three states: solid, liquid, and gas. As Figure 1.6 shows, gases differ from liquids and solids in the distances between the atoms. In a solid, atoms (or molecules) are held close together in an orderly fashion with little

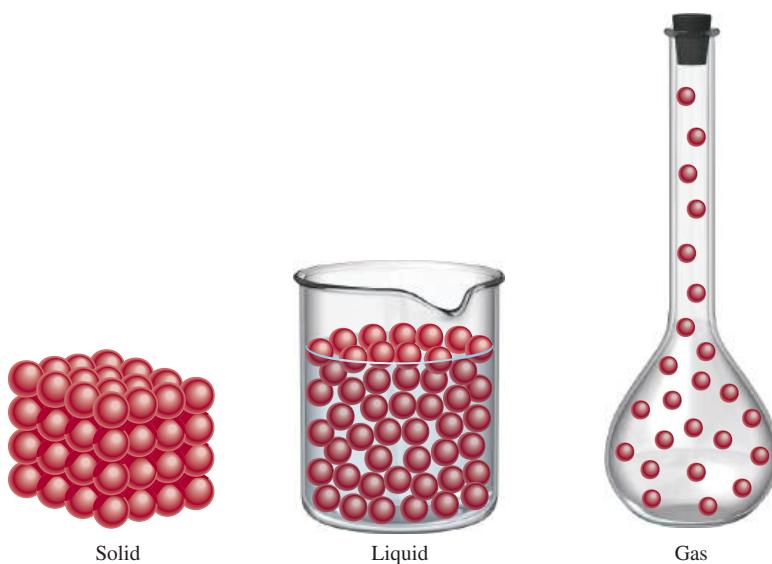
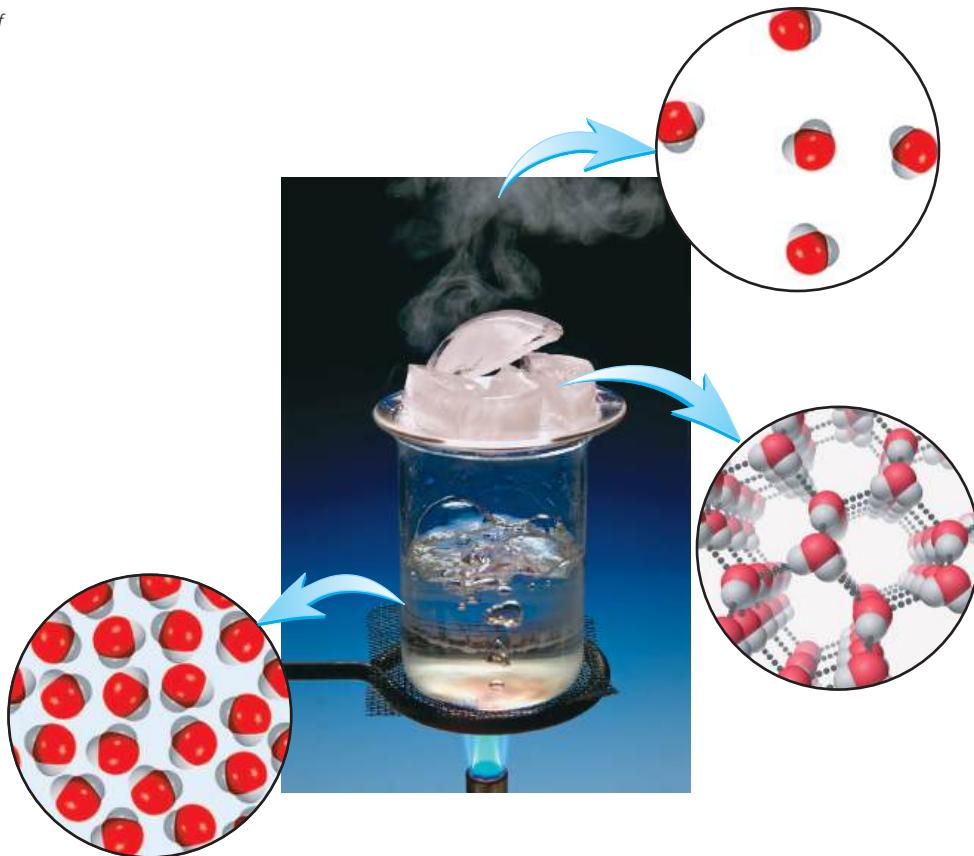


Figure 1.6 Microscopic views of a solid, a liquid, and a gas.

Figure 1.7 The three states of matter. A hot poker changes ice into water and steam.
©McGraw-Hill Education/Charles D. Winters



freedom of motion. Atoms (or molecules) in a liquid are close together but are not held so rigidly in position and can move past one another. In a gas, the atoms (or molecules) are separated by distances that are large compared with the size of the atoms (or molecules).

The three states of matter can be interconverted without changing the composition of the substance. Upon heating, a solid (for example, ice) will melt to form a liquid (water). (The temperature at which this transition occurs is called the *melting point*.) Further heating will convert the liquid into a gas. (This conversion takes place at the *boiling point* of the liquid.) On the other hand, cooling a gas will cause it to condense into a liquid. When the liquid is cooled further, it will freeze into the solid form. Figure 1.7 shows the three states of water. Note that the properties of water are unique among common substances in that the molecules in the liquid state are more closely packed than those in the solid state.

Review of Concepts & Facts

- 1.5.1** An ice cube is placed in a closed container. On heating, the ice cube first melts and the water then boils to form steam. Which of the following statements is true?
- The physical appearance of the water is different at every stage of change.
 - The mass of water is greatest for the ice cube and least for the steam.

1.6 Physical and Chemical Properties of Matter

Substances are identified by their properties as well as by their composition. Color, melting point, and boiling point are physical properties. A **physical property** can be measured and observed without changing the composition or identity of a substance. For example,

we can measure the melting point of ice by heating a block of ice and recording the temperature at which the ice is converted to water. Water differs from ice only in appearance, not in composition, so this is a physical change; we can freeze the water to recover the original ice. Therefore, the melting point of a substance is a physical property. Similarly, when we say that helium gas is lighter than air, we are referring to a physical property.

On the other hand, the statement “Hydrogen gas burns in oxygen gas to form water” describes a **chemical property** of hydrogen. *To observe this chemical property of hydrogen we must carry out a chemical change*—in this case, burning the hydrogen gas in oxygen. After the change, the original chemical substance, the hydrogen gas, will have vanished, and all that will be left is a different chemical substance—water. We *cannot* recover the hydrogen from the water by means of a physical change, such as boiling or freezing.

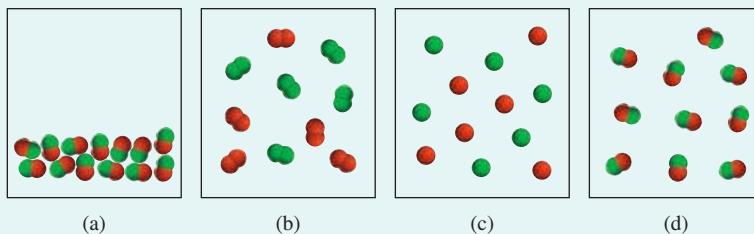
Every time we hard-boil an egg, we bring about a chemical change. When subjected to a temperature of about 100°C, the yolk and the egg white undergo changes that alter not only their physical appearance but their chemical makeup as well. When eaten, the egg is changed again, by substances in the body called *enzymes*. This digestive action is another example of a chemical change. What happens during digestion depends on the chemical properties of both the enzymes and the food.

All measurable properties of matter fall into one of two additional categories: extensive properties and intensive properties. The measured value of an **extensive property** depends on how much matter is being considered. **Mass**, which is the quantity of matter in a given sample of a substance, is an extensive property. More matter means more mass. Values of the same extensive property can be added together. For example, two copper pennies will have a combined mass that is the sum of the masses of each penny, and the length of two tennis courts is the sum of the lengths of each tennis court. **Volume**, defined as *length cubed*, is another extensive property. The value of an extensive quantity depends on the amount of matter.

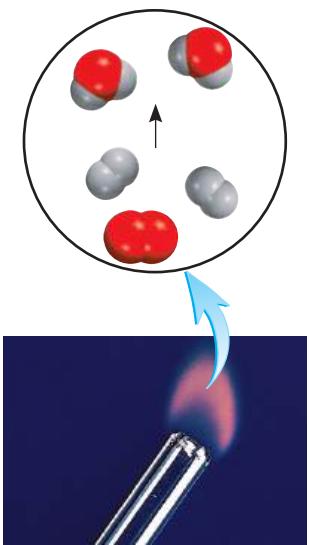
The measured value of an **intensive property** does not depend on how much matter is being considered. **Density**, defined as the mass of an object divided by its volume, is an intensive property. So is temperature. Suppose that we have two beakers each containing 100 mL of water at 25°C. If we combine them to give 200 mL of water in a larger beaker, the temperature of the combined quantities of water will be still be 25°C, the same as it was in two separate beakers. The density of the combined quantities of water will also be the same as the original quantities. The temperature and the density of water do not depend on the amount of water present. Unlike mass, length, and volume, temperature and other intensive properties are not additive.

Review of Concepts & Facts

- 1.6.1** The diagram in (a) shows a compound made up of atoms of two elements (represented by the green and red spheres) in the liquid state. Which of the diagrams in (b)–(d) represents a physical change and which diagrams represent a chemical change?



- 1.6.2** Determine which of the following properties are intensive and which are extensive.
- The hardness of diamond is 10 on the Mohs scale.
 - The melting point of water is 0°C.
 - A cube of lead has an edge length of 2.5 cm.



Hydrogen burning in air to form water.

©McGraw-Hill Education/Ken Karp

1.7 Measurement

The measurements chemists make are often used in calculations to obtain other related quantities. Different instruments enable us to measure a substance's properties: The meterstick measures length or scale; the buret, the pipet, the graduated cylinder, and the volumetric flask measure volume (Figure 1.8); the balance measures mass; the thermometer measures temperature. These instruments provide measurements of ***macroscopic properties***, which *can be determined directly*. ***Microscopic properties***, on the atomic or molecular scale, must be determined by an indirect method, as we will see in Chapter 2.

A measured quantity is usually written as a number with an appropriate unit. To say that the distance between New York and San Francisco by car along a certain route is 5166 is meaningless. We must specify that the distance is 5166 kilometers. The same is true in chemistry; units are essential to stating measurements correctly.

SI Units

For many years, scientists recorded measurements in *metric units*, which are related decimally—that is, by powers of 10. In 1960, however, the General Conference of Weights and Measures, the international authority on units, proposed a revised metric system called the ***International System of Units*** (abbreviated ***SI***, from the French *Système Internationale d'Unités*). Table 1.2 shows the seven SI base units. All other units of measurement can be derived from these base units. Like metric units, SI units are modified in decimal fashion by a series of prefixes, as shown in Table 1.3. We will use both metric and SI units in this book.

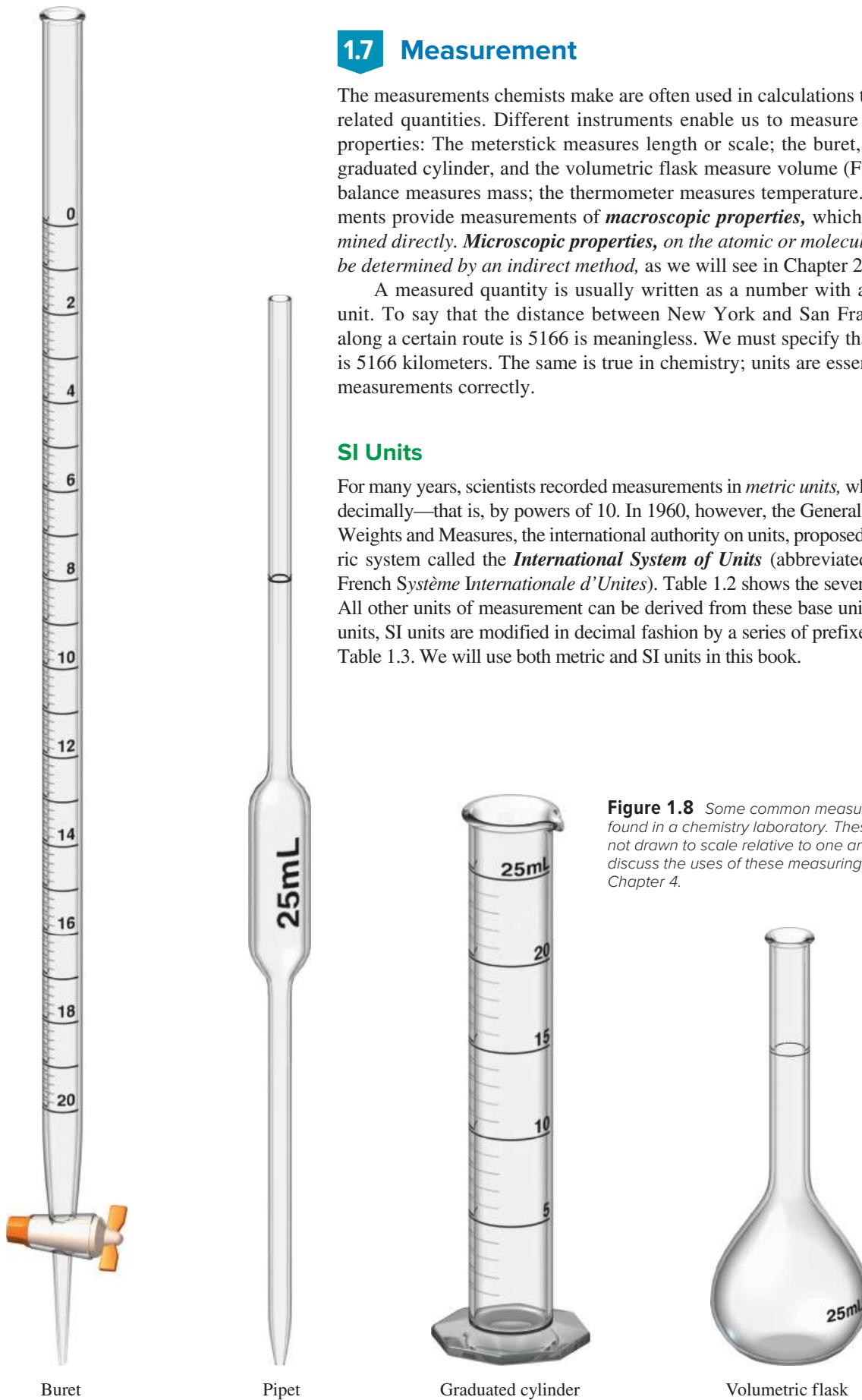


Figure 1.8 Some common measuring devices found in a chemistry laboratory. These devices are not drawn to scale relative to one another. We will discuss the uses of these measuring devices in Chapter 4.

Table 1.2 SI Base Units

Base Quantity	Name of Unit	Symbol
Length	meter	m
Mass	kilogram	kg
Time	second	s
Electrical current	ampere	A
Temperature	K	
Amount of substance	mole	mol
Luminous intensity	candela	cd

Note that a metric prefix simply represents a number:

$$1 \text{ mm} = 1 \times 10^{-3} \text{ m}$$



An astronaut jumping on the surface of the moon.

Source: NASA

Table 1.3 Prefixes Used with SI Units

Prefix	Symbol	Meaning	Example
peta-	P	1,000,000,000,000,000, or 10^{15}	1 petameter (Pm) = 1×10^{15} m
tera-	T	1,000,000,000,000, or 10^{12}	1 terameter (Tm) = 1×10^{12} m
giga-	G	1,000,000,000, or 10^9	1 gigameter (Gm) = 1×10^9 m
mega-	M	1,000,000, or 10^6	1 megameter (Mm) = 1×10^6 m
kilo-	k	1,000, or 10^3	1 kilometer (km) = 1×10^3 m
deci-	d	1/10, or 10^{-1}	1 decimeter (dm) = 0.1 m
centi-	c	1/100, or 10^{-2}	1 centimeter (cm) = 0.01 m
milli-	m	1/1,000, or 10^{-3}	1 millimeter (mm) = 0.001 m
micro-	μ	1/1,000,000, or 10^{-6}	1 micrometer (μm) = 1×10^{-6} m
nano-	n	1/1,000,000,000, or 10^{-9}	1 nanometer (nm) = 1×10^{-9} m
pico-	p	1/1,000,000,000,000, or 10^{-12}	1 picometer (pm) = 1×10^{-12} m
femto-	f	1/1,000,000,000,000,000, or 10^{-15}	1 femtometer (fm) = 1×10^{-15} m
atto-	a	1/1,000,000,000,000,000,000, or 10^{-18}	1 attometer (am) = 1×10^{-18} m

Measurements that we will utilize frequently in our study of chemistry include time, mass, volume, density, and temperature.

Mass and Weight

The terms “mass” and “weight” are often used interchangeably, although, strictly speaking, they are different quantities. Whereas mass is a measure of the amount of matter in an object, **weight**, technically speaking, is *the force that gravity exerts on an object*. An apple that falls from a tree is pulled downward by Earth’s gravity. The mass of the apple is constant and does not depend on its location, but its weight does. For example, on the surface of the moon the apple would weigh only one-sixth what it does on Earth, because the moon’s gravity is only one-sixth that of Earth. The moon’s smaller gravity enabled astronauts to jump about rather freely on its surface despite their bulky suits and equipment. Chemists are interested primarily in mass, which can be determined readily with a balance; the process of measuring mass, oddly, is called *weighing*.

The SI unit of mass is the *kilogram* (kg). Unlike the units of length and time, which are based on natural processes that can be repeated by scientists anywhere, the kilogram is defined in terms of a particular object (Figure 1.9). In chemistry, however, the smaller *gram* (g) is more convenient:

$$1 \text{ kg} = 1000 \text{ g} = 1 \times 10^3 \text{ g}$$



Figure 1.9 The prototype kilogram is made of a platinum-iridium alloy. It is kept in a vault at the International Bureau of Weights and Measures in Sèvres, France. In 2007 it was discovered that the alloy has mysteriously lost about 50 μg !

©Jacques Brinon/AP Images

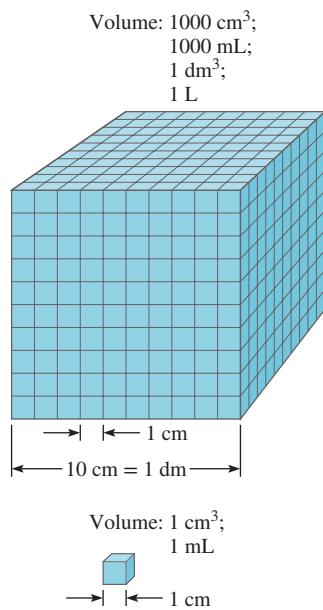


Figure 1.10 Comparison of two volumes, 1 mL and 1000 mL.

Volume

Volume is an example of a measured quantity with derived units. The SI-derived unit for volume is the *cubic meter* (m³). Generally, however, chemists work with much smaller volumes, such as the cubic centimeter (cm³) and the cubic decimeter (dm³):

$$1 \text{ cm}^3 = (1 \times 10^{-2} \text{ m})^3 = 1 \times 10^{-6} \text{ m}^3$$

$$1 \text{ dm}^3 = (1 \times 10^{-1} \text{ m})^3 = 1 \times 10^{-3} \text{ m}^3$$

Another common unit of volume is the liter (L). A *liter* is *the volume occupied by one cubic decimeter*. One liter of volume is equal to 1000 milliliters (mL) or 1000 cm³:

$$1 \text{ L} = 1000 \text{ mL}$$

$$= 1000 \text{ cm}^3$$

$$= 1 \text{ dm}^3$$

and one milliliter is equal to one cubic centimeter:

$$1 \text{ mL} = 1 \text{ cm}^3$$

Figure 1.10 compares the relative sizes of two volumes. Even though the liter is not an SI unit, volumes are usually expressed in liters and milliliters.

Density

Density is another measured quantity with derived units. The equation for density is

$$\text{density} = \frac{\text{mass}}{\text{volume}}$$

or

$$d = \frac{m}{V} \quad (1.1)$$

where d , m , and V denote density, mass, and volume, respectively. Because density is an intensive property and does not depend on the quantity of mass present, for a given substance the ratio of mass to volume always remains the same. In other words, V increases as m does. Density usually decreases with temperature.

The SI-derived unit for density is the kilogram per cubic meter (kg/m³). This unit is awkwardly large for most chemical applications. Therefore, grams per cubic centimeter (g/cm³) and its equivalent, grams per milliliter (g/mL), are more commonly used for solid and liquid densities. Because gas densities are often very low, we express them in units of grams per liter (g/L):

$$1 \text{ g/cm}^3 = 1 \text{ g/mL} = 1000 \text{ kg/m}^3$$

$$1 \text{ g/L} = 0.001 \text{ g/mL}$$

Table 1.4

Densities of Some Substances at 25°C	
Substance	Density (g/cm ³)
Air*	0.001
Ethanol	0.79
Water	1.00
Graphite	2.2
Table salt	2.2
Aluminum	2.70
Diamond	3.5
Iron	7.9
Lead	11.3
Mercury	13.6
Gold	19.3
Osmium [†]	22.6

*Measured at 1 atmosphere.

[†]Osmium (Os) is the densest element known.

Table 1.4 lists the densities of several substances.

Examples 1.1 and 1.2 show density calculations.

Example 1.1

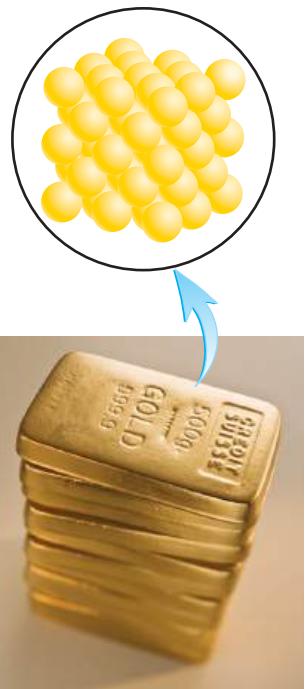
Gold is a precious metal that is chemically unreactive. It is used mainly in jewelry, dentistry, and electronic devices. A piece of gold ingot with a mass of 301 g has a volume of 15.6 cm³. Calculate the density of gold.

Solution We are given the mass and volume and asked to calculate the density. Therefore, from Equation (1.1), we write

$$\begin{aligned} d &= \frac{m}{V} \\ &= \frac{301 \text{ g}}{15.6 \text{ cm}^3} \\ &= 19.3 \text{ g/cm}^3 \end{aligned}$$

Practice Exercise A piece of platinum metal with a density of 21.5 g/cm³ has a volume of 4.49 cm³. What is its mass?

Similar problems: 1.23, 1.24.



Gold bars and the solid-state arrangement of the gold atoms.
©Tetra Images/Getty Images

Example 1.2

The density of mercury, the only metal that is a liquid at room temperature, is 13.6 g/mL. Calculate the mass of 5.50 mL of the liquid.

Solution We are given the density and volume of a liquid and asked to calculate the mass of the liquid. We rearrange Equation (1.1) to give

$$\begin{aligned} m &= d \times V \\ &= 13.6 \frac{\text{g}}{\text{mL}} \times 5.50 \text{ mL} \\ &= 74.8 \text{ g} \end{aligned}$$

Practice Exercise The density of sulfuric acid in a certain car battery is 1.41 g/mL. Calculate the mass of 242 mL of the liquid.

Similar problems: 1.23, 1.24.



Mercury.
©McGraw-Hill Education/Stephen Frisch

Temperature Scales

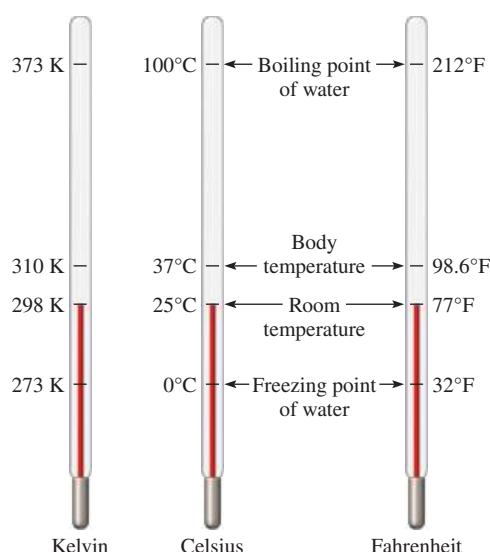
Three temperature scales are currently in use. Their units are °F (degrees Fahrenheit), °C (degrees Celsius), and K (kelvin). The Fahrenheit scale defines the normal freezing and boiling points of water to be exactly 32°F and 212°F, respectively. The Celsius scale divides the range between the freezing point (0°C) and boiling point (100°C) of water into 100 degrees. As Table 1.2 shows, the *kelvin* is the SI base unit of temperature: It is the *absolute* temperature scale. By absolute we mean that the zero on the Kelvin scale, denoted by 0 K, is the lowest temperature that can be attained theoretically. On the other hand, 0°F and 0°C are based on the behavior of an arbitrarily chosen substance, water. Figure 1.11 compares the three temperature scales.

The size of a degree on the Fahrenheit scale is only 100/180, or 5/9, of a degree on the Celsius scale. To convert degrees Fahrenheit to degrees Celsius, we write

$$?^\circ\text{C} = (\text{°F} - 32^\circ\text{F}) \times \frac{5^\circ\text{C}}{9^\circ\text{F}} \quad (1.2)$$

Note that the Kelvin scale does not have the degree sign. Also, temperatures expressed in kelvins can never be negative.

Figure 1.11 Comparison of the three temperature scales: Celsius, Fahrenheit, and absolute (Kelvin) scales. Note that there are 100 divisions, or 100 degrees, between the freezing point and the boiling point of water on the Celsius scale, and there are 180 divisions, or 180 degrees, between the same two temperature limits on the Fahrenheit scale. The Celsius scale was formerly called the centigrade scale.



The following equation is used to convert degrees Celsius to degrees Fahrenheit:

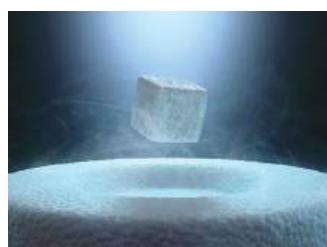
$$\text{?}^{\circ}\text{F} = \frac{9^{\circ}\text{F}}{5^{\circ}\text{C}} \times (\text{?}^{\circ}\text{C}) + 32^{\circ}\text{F} \quad (1.3)$$

Both the Celsius and the Kelvin scales have units of equal magnitude; that is, one degree Celsius is equivalent to one kelvin. Experimental studies have shown that absolute zero on the Kelvin scale is equivalent to -273.15°C on the Celsius scale. Thus, we can use the following equation to convert degrees Celsius to kelvin:

$$\text{? K} = (\text{?}^{\circ}\text{C} + 273.15^{\circ}\text{C}) \frac{1\text{ K}}{1^{\circ}\text{C}} \quad (1.4)$$

We will frequently find it necessary to convert between degrees Celsius and degrees Fahrenheit and between degrees Celsius and kelvin. Example 1.3 illustrates these conversions.

The Chemistry in Action essay, “The Importance of Units,” shows why we must be careful with units in scientific work.



A magnet suspended above a superconductor that is cooled below its transition temperature by liquid nitrogen.

©ktsimage/Getty Images

Example 1.3

- (a) Below the transition temperature of -141°C , a certain substance becomes a superconductor, meaning it conducts electricity with no resistance. What is the temperature in degrees Fahrenheit? (b) Helium has the lowest boiling point of all the elements at -452°F . Convert this temperature to degrees Celsius. (c) Mercury, the only metal that exists as a liquid at room temperature, melts at -38.9°C . Convert its melting point to kelvins.

Solution These three parts require that we carry out temperature conversions, so we need Equations (1.2), (1.3), and (1.4). Keep in mind that the lowest temperature on the Kelvin scale is zero (0 K); therefore, it can never be negative.

- (a) This conversion is carried out by writing

$$\frac{9^{\circ}\text{F}}{5^{\circ}\text{C}} \times (-141^{\circ}\text{C}) + 32^{\circ}\text{F} = -222^{\circ}\text{F}$$

(Continued)

CHEMISTRY *in Action*

The Importance of Units

In December 1998, NASA launched the \$125 million Mars Climate Orbiter, intended as the red planet's first weather satellite. After a 416-million-mile journey, the spacecraft was supposed to go into Martian orbit on September 23, 1999. Instead, it entered the Martian atmosphere about 100 km (62 mi) lower than planned and was destroyed by heat. The mission controllers said the loss of the spacecraft was due to the failure to convert English measurement units into metric units in the navigation software.

Engineers at Lockheed Martin Corporation who built the spacecraft specified its thrust in pounds, which is an English unit. Scientists at NASA's Jet Propulsion Laboratory, on the other hand, had assumed that thrust data they received were expressed in metric units, as newtons. Normally, pound is the unit for mass. Expressed as a unit for force, however, 1 lb is the force due to gravitational attraction on an object of that mass. To carry out the conversion between pound and newton, we start with $1 \text{ lb} = 0.4536 \text{ kg}$ and from Newton's second law of motion,

$$\begin{aligned}\text{force} &= \text{mass} \times \text{acceleration} \\ &= 0.4536 \text{ kg} \times 9.81 \text{ m/s}^2 \\ &= 4.45 \text{ kg m/s}^2 \\ &= 4.45 \text{ N}\end{aligned}$$

because $1 \text{ newton (N)} = 1 \text{ kg m/s}^2$. Therefore, instead of converting 1 lb of force to 4.45 N, the scientists treated it as 1 N.

The considerably smaller engine thrust expressed in newtons resulted in a lower orbit and the ultimate destruction of the spacecraft. Commenting on the failure of the Mars mission, one

scientist said: "This is going to be the cautionary tale that will be embedded into introduction to the metric system in elementary school, high school, and college science courses till the end of time."



Artist's conception of the Martian Climate Orbiter.

Source: NASA/JPL-Caltech

(b) Here we have

$$(-452^\circ\text{F} - 32^\circ\text{F}) \times \frac{5^\circ\text{C}}{9^\circ\text{F}} = -269^\circ\text{C}$$

(c) The melting point of mercury in kelvins is given by

$$(-38.9^\circ\text{C} + 273.15^\circ\text{C}) \frac{1 \text{ K}}{1^\circ\text{C}} = 234.3 \text{ K}$$

Practice Exercise Convert (a) 327.5°C (the melting point of lead) to degrees Fahrenheit; (b) 172.9°F (the boiling point of ethanol) to degrees Celsius; and (c) 77 K , the boiling point of liquid nitrogen, to degrees Celsius.

Similar problems: 1.26, 1.27, 1.28.

Review of Concepts & Facts

- 1.7.1** The density of platinum is 21.45 g/cm^3 . What is the volume of a platinum sample with a mass of 11.2 g?

1.7.2 The melting point of adamantine is 518°F . What is this melting point in kelvins?

1.7.3 The density of copper is 8.94 g/cm^3 at 20°C and 8.91 g/cm^3 at 60°C . This density decrease is the result of which of the following?

 - (a) The metal expands.
 - (b) The metal contracts.
 - (c) The mass of the metal increases.
 - (d) The mass of the metal decreases.

1.8 Handling Numbers

Having surveyed some of the units used in chemistry, we now turn to techniques for handling numbers associated with measurements: scientific notation and significant figures.

Scientific Notation

Chemists often deal with numbers that are either extremely large or extremely small. For example, in 1 g of the element hydrogen there are roughly

602,200,000,000,000,000,000

hydrogen atoms. Each hydrogen atom has a mass of only

0.0000000000000000000000000000166 g

These numbers are cumbersome to handle, and it is easy to make mistakes when using them in arithmetic computations. Consider the following multiplication:

$$0.000000056 \times 0.0000000048 = 0.00000000000000002688$$

It would be easy for us to miss one zero or add one more zero after the decimal point. Consequently, when working with very large and very small numbers, we use a system called *scientific notation*. Regardless of their magnitude, all numbers can be expressed in the form

$$N \times 10^n$$

where N is a number between 1 and 10, and n (the exponent) is a positive or negative integer (whole number). Any number expressed in this way is said to be written in scientific notation.

Suppose that we are given a certain number and asked to express it in scientific notation. Basically, this assignment calls for us to find n . We count the number of places that the decimal point must be moved to give the number N (which is between 1 and 10). If the decimal point has to be moved to the left, then n is a positive integer; if it has to be moved to the right, n is a negative integer. The following examples illustrate the use of scientific notation:

- (1) Express 568.762 in scientific notation:

$$568.762 = 5.68762 \times 10^2$$

Note that the decimal point is moved to the left by two places and $n = 2$.

- (2) Express 0.00000772 in scientific notation:

$$0.00000772 \equiv 7.72 \times 10^{-6}$$

Here the decimal point is moved to the right by six places and $n = -6$.

Keep in mind the following two points. First, $n = 0$ is used for numbers that are not expressed in scientific notation. For example, 74.6×10^0 ($n = 0$) is equivalent to 74.6. Second, the usual practice is to omit the superscript when $n = 1$. Thus, the scientific notation for 74.6 is 7.46×10 and not 7.46×10^1 .

Next, we consider how scientific notation is handled in arithmetic operations.

Any number raised to the power zero is equal to one.

Addition and Subtraction

To add or subtract using scientific notation, we first write each quantity—say, N_1 and N_2 —with the same exponent n . Then we combine N_1 and N_2 ; the exponents remain the same. Consider the following examples:

$$\begin{aligned}(7.4 \times 10^3) + (2.1 \times 10^3) &= 9.5 \times 10^3 \\(4.31 \times 10^4) + (3.9 \times 10^3) &= (4.31 \times 10^4) + (0.39 \times 10^4) \\&= 4.70 \times 10^4 \\(2.22 \times 10^{-2}) - (4.10 \times 10^{-3}) &= (2.22 \times 10^{-2}) - (0.41 \times 10^{-2}) \\&= 1.81 \times 10^{-2}\end{aligned}$$

Multiplication and Division

To multiply numbers expressed in scientific notation, we multiply N_1 and N_2 in the usual way, but *add* the exponents together. To divide using scientific notation, we divide N_1 and N_2 as usual and subtract the exponents. The following examples show how these operations are performed:

$$\begin{aligned}(8.0 \times 10^4) \times (5.0 \times 10^2) &= (8.0 \times 5.0)(10^{4+2}) \\&= 40 \times 10^6 \\&= 4.0 \times 10^7 \\(4.0 \times 10^{-5}) \times (7.0 \times 10^3) &= (4.0 \times 7.0)(10^{-5+3}) \\&= 28 \times 10^{-2} \\&= 2.8 \times 10^{-1} \\ \frac{6.9 \times 10^7}{3.0 \times 10^{-5}} &= \frac{6.9}{3.0} \times 10^{7-(-5)} \\&= 2.3 \times 10^{12} \\ \frac{8.5 \times 10^4}{5.0 \times 10^9} &= \frac{8.5}{5.0} \times 10^{4-9} \\&= 1.7 \times 10^{-5}\end{aligned}$$

Significant Figures

Except when all the numbers involved are integers (for example, in counting the number of students in a class), it is often impossible to obtain the exact value of the quantity under investigation. For this reason, *significant figures*, which are *the meaningful digits in a measured or calculated quantity*, are used to indicate the margin of error in a measurement. When significant figures are used, the last digit is understood to be uncertain. For example, we might measure the volume of a given amount of liquid using a graduated cylinder with a scale that gives an uncertainty of 1 mL in the measurement. If the volume is found to be 6 mL, then the actual volume is in the range of 5 mL to 7 mL. We represent the volume of the liquid as (6 ± 1) mL. In this case, there is only one significant figure (the digit 6) that is uncertain by either plus or minus 1 mL. For greater accuracy, we might use a graduated cylinder that has finer divisions, so that the volume we measure is now uncertain by only 0.1 mL. If the volume of the liquid is now found to be 6.0 mL, we may express the quantity as (6.0 ± 0.1) mL, and the actual value is somewhere between 5.9 mL and 6.1 mL. We can further improve



Figure 1.12 A Fisher Scientific A-200DS Digital Recorder Precision Balance.

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the measuring device and obtain more significant figures, but in every case, the last digit is always uncertain; the amount of this uncertainty depends on the particular measuring device we use.

Figure 1.12 shows a modern balance. Balances such as this one are available in many general chemistry laboratories; they readily measure the mass of objects to four decimal places. Therefore, the measured mass typically will have four significant figures (for example, 0.8642 g) or more (for example, 3.9745 g). Keeping track of the number of significant figures in a measurement such as mass ensures that calculations involving the data will reflect the precision of the measurement.

Guidelines for Using Significant Figures

We must always be careful in scientific work to write the proper number of significant figures. The following rules determine how many significant figures a number has:

1. Any digit that is not zero is significant. Thus, 845 cm has three significant figures, 1.234 kg has four significant figures, and so on.
2. Zeros between nonzero digits are significant. Thus, 606 m contains three significant figures, 40,501 kg contains five significant figures, and so on.
3. Zeros to the left of the first nonzero digit are not significant. Their purpose is to indicate the placement of the decimal point. For example, 0.08 L contains one significant figure, 0.0000349 g contains three significant figures, and so on.
4. If a number is greater than 1, then all the zeros written to the right of the decimal point count as significant figures. Thus, 2.0 mg has two significant figures, 40.062 mL has five significant figures, and 3.040 dm has four significant figures. If a number is less than 1, then only the zeros that are at the end of the number and the zeros that are between nonzero digits are significant. This means that 0.090 kg has two significant figures, 0.3005 L has four significant figures, 0.00420 min has three significant figures, and so on.
5. For numbers that do not contain decimal points, the trailing zeros (that is, zeros after the last nonzero digit) may or may not be significant. Thus, 400 cm may have one significant figure (the digit 4), two significant figures (40), or three significant figures (400). We cannot know which is correct without more information. By using scientific notation, however, we avoid this ambiguity. In this particular case, we can express the number 400 as 4×10^2 for one significant figure, 4.0×10^2 for two significant figures, or 4.00×10^2 for three significant figures.

Example 1.4 shows the determination of significant figures.

Student Hot Spot
Student data indicate you may struggle with significant figures. Access your eBook for additional Learning Resources on this topic.

Example 1.4

Determine the number of significant figures in the following measurements: (a) 394 cm, (b) 5.03 g, (c) 0.714 m, (d) 0.052 kg, (e) 2.720×10^{22} atoms, (f) 3000 mL.

Solution (a) Three, because each digit is a nonzero digit. (b) Three, because zeros between nonzero digits are significant. (c) Three, because zeros to the left of the first nonzero digit do not count as significant figures. (d) Two. Same reason as in (c). (e) Four. Because the number is greater than one, all the zeros written to the right of the decimal point count as significant figures. (f) This is an ambiguous case. The

(Continued)

number of significant figures may be four (3.000×10^3), three (3.00×10^3), two (3.0×10^3), or one (3×10^3). This example illustrates why scientific notation must be used to show the proper number of significant figures.

Practice Exercise Determine the number of significant figures in each of the following measurements: (a) 35 mL, (b) 2008 g, (c) 0.0580 m^3 , (d) 7.2×10^4 molecules, (e) 830 kg.

Similar problems: 1.35, 1.36.

A second set of rules specifies how to handle significant figures in calculations.

1. In addition and subtraction, the answer cannot have more digits to the right of the decimal point than either of the original numbers. Consider these examples:

$$\begin{array}{r} 89.332 \\ + 1.1 \\ \hline 90.432 \end{array} \leftarrow \text{one digit after the decimal point}$$

90.432 \leftarrow round off to 90.4

$$\begin{array}{r} 2.097 \\ - 0.12 \\ \hline 1.977 \end{array} \leftarrow \text{two digits after the decimal point}$$

1.977 \leftarrow round off to 1.98

The rounding-off procedure is as follows. To round off a number at a certain point we simply drop the digits that follow if the first of them is less than 5. Thus, 8.724 rounds off to 8.72 if we want only two digits after the decimal point. If the first digit following the point of rounding off is equal to or greater than 5, we add 1 to the preceding digit. Thus, 8.727 rounds off to 8.73, and 0.425 rounds off to 0.43.

2. In multiplication and division, the number of significant figures in the final product or quotient is determined by the original number that has the *smallest* number of significant figures. The following examples illustrate this rule:

$$2.8 \times 4.5039 = 12.61092 \leftarrow \text{round off to 13}$$

$$\frac{6.85}{112.04} = 0.0611388789 \leftarrow \text{round off to 0.0611}$$

3. Keep in mind that *exact numbers* obtained from definitions or by counting numbers of objects can be considered to have an infinite number of significant figures. For example, the inch is defined to be exactly 2.54 centimeters; that is,

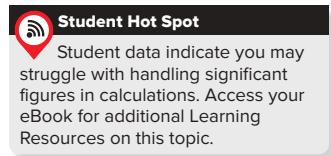
$$1 \text{ in} = 2.54 \text{ cm}$$

Thus, the “2.54” in the equation should not be interpreted as a measured number with three significant figures. In calculations involving conversion between “in” and “cm,” we treat both “1” and “2.54” as having an infinite number of significant figures. Similarly, if an object has a mass of 5.0 g, then the mass of nine such objects is

$$5.0 \text{ g} \times 9 = 45 \text{ g}$$

The answer has two significant figures because 5.0 g has two significant figures. The number 9 is exact and does not determine the number of significant figures.

Example 1.5 shows how significant figures are handled in arithmetic operations.



Example 1.5

Carry out the following arithmetic operations to the correct number of significant figures: (a) $12,343.2 \text{ g} + 0.1893 \text{ g}$, (b) $55.67 \text{ L} - 2.386 \text{ L}$, (c) $7.52 \text{ m} \times 6.9232$, (d) $0.0239 \text{ kg} \div 46.5 \text{ mL}$, (e) $5.21 \times 10^3 \text{ cm} + 2.92 \times 10^2 \text{ cm}$.

(Continued)

Solution In addition and subtraction, the number of decimal places in the answer is determined by the number having the lowest number of decimal places. In multiplication and division, the significant number of the answer is determined by the number having the smallest number of significant figures.

- (a)
$$\begin{array}{r} 12,343.2 \text{ g} \\ + 0.1893 \text{ g} \\ \hline 12,343.3893 \text{ g} \end{array} \leftarrow \text{round off to } 12,343.4 \text{ g}$$
- (b)
$$\begin{array}{r} 55.67 \text{ L} \\ - 2.386 \text{ L} \\ \hline 53.284 \text{ L} \end{array} \leftarrow \text{round off to } 53.28 \text{ L}$$
- (c) $7.52 \text{ m} \times 6.9232 = 52.06246 \text{ m} \leftarrow \text{round off to } 52.1 \text{ m}$
- (d)
$$\frac{0.0239 \text{ kg}}{46.5 \text{ mL}} = 0.0005139784946 \text{ kg/mL} \leftarrow \text{round off to } 0.000514 \text{ kg/mL}$$

or $5.14 \times 10^{-4} \text{ kg/mL}$
- (e) First we change $2.92 \times 10^2 \text{ cm}$ to $0.292 \times 10^3 \text{ cm}$ and then carry out the addition $(5.21 \text{ cm} + 0.292 \text{ cm}) \times 10^3$. Following the procedure in (a), we find the answer is $5.50 \times 10^3 \text{ cm}$.

Practice Exercise Carry out the following arithmetic operations and round off the answers to the appropriate number of significant figures: (a) $26.5862 \text{ L} + 0.17 \text{ L}$, (b) $9.1 \text{ g} - 4.682 \text{ g}$, (c) $7.1 \times 10^4 \text{ dm} \times 2.2654 \times 10^2 \text{ dm}$, (d) $6.54 \text{ g} \div 86.5542 \text{ mL}$, (e) $(7.55 \times 10^4 \text{ m}) - (8.62 \times 10^3 \text{ m})$.

Similar problems: 1.37, 1.38.

The preceding rounding-off procedure applies to one-step calculations. In *chain calculations*—that is, calculations involving more than one step—we can get a different answer depending on how we round off. Consider the following two-step calculations:

$$\begin{array}{l} \text{First step: } A \times B = C \\ \text{Second step: } C \times D = E \end{array}$$

Let's suppose that $A = 3.66$, $B = 8.45$, and $D = 2.11$. Depending on whether we round off C to three or four significant figures, we obtain a different number for E :

Method 1	Method 2
$3.66 \times 8.45 = 30.9$	$3.66 \times 8.45 = 30.93$
$30.9 \times 2.11 = 65.2$	$30.93 \times 2.11 = 65.3$

However, if we had carried out the calculation as $3.66 \times 8.45 \times 2.11$ on a calculator without rounding off the intermediate answer, we would have obtained 65.3 as the answer for E . Although retaining an additional digit past the number of significant figures for intermediate steps helps to eliminate errors from rounding, this procedure is not necessary for most calculations because the difference between the answers is usually quite small. Therefore, for most examples and end-of-chapter problems where intermediate answers are reported, all answers, intermediate and final, will be rounded.

Accuracy and Precision

In discussing measurements and significant figures, it is useful to distinguish between *accuracy* and *precision*. **Accuracy** tells us *how close a measurement is to the true value of the quantity that was measured*. **Precision** refers to *how closely two or more measurements of the same quantity agree with one another* (Figure 1.13).

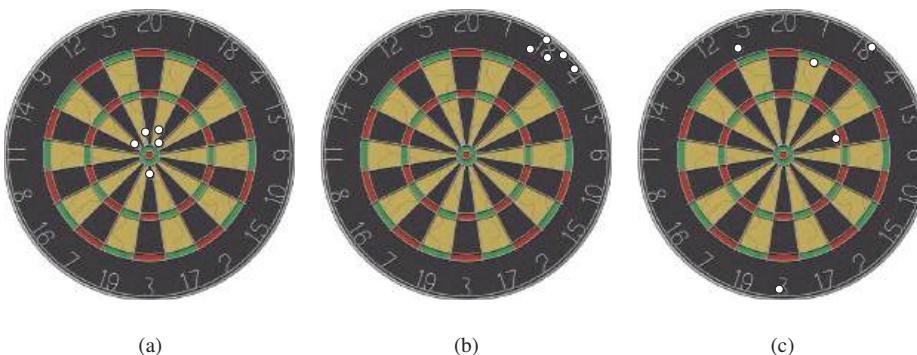


Figure 1.13 The distribution of holes formed by darts on a dart board shows the difference between precise and accurate. (a) Good accuracy and good precision. (b) Poor accuracy and good precision. (c) Poor accuracy and poor precision.

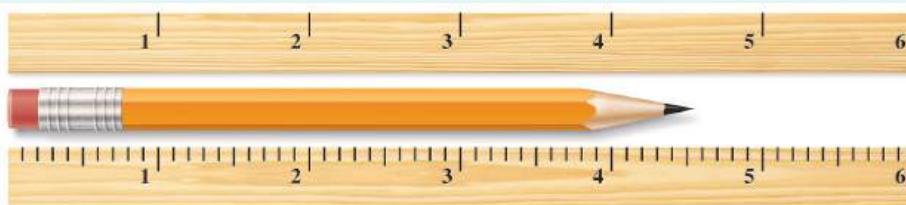
The difference between accuracy and precision is a subtle but important one. Suppose, for example, that three students are asked to determine the mass of a piece of copper wire. The results of three successive weighings by each student are

Student A	Student B	Student C
1.964 g	1.970 g	2.000 g
1.971 g	1.972 g	2.002 g
1.978 g	1.968 g	2.001 g
Average value	1.971 g	2.001 g

The true mass of the wire is 2.000 g. Therefore, Student B's results are more *precise* than those of Student A (1.970 g, 1.972 g, and 1.968 g deviate less from 1.970 g than 1.964 g, 1.971 g, and 1.978 g from 1.971 g), but neither set of results is very *accurate*. Student C's results are not only the most *precise*, but also the most *accurate*, because the average value is closest to the true value. Highly accurate measurements are usually precise, too. On the other hand, highly precise measurements do not necessarily guarantee accurate results. For example, an improperly calibrated meterstick or a faulty balance may give precise readings that are in error.

Review of Concepts & Facts

- 1.8.1** Give the length of the pencil with proper significant figures according to the two rulers you use for the measurement.



- 1.8.2** A student measures the density of an alloy with the following results: 10.28 g/cm^3 , 9.97 g/cm^3 , 10.22 g/cm^3 , 10.15 g/cm^3 , 9.94 g/cm^3 . How should the average value for the density be reported?
- 1.8.3** Four mass measurements of a metal cube were made using a laboratory balance. The results are 24.02 g, 23.99 g, 23.98 g, and 23.97 g. The actual mass of the metal cube is 25.00 g. Are the mass measurements accurate? Are the mass measurements precise?

1.9 Dimensional Analysis in Solving Problems

Careful measurements and the proper use of significant figures, along with correct calculations, will yield accurate numerical results. But to be meaningful, the answers also must be expressed in the desired units. We use *dimensional analysis* (also called the

factor-label method) to convert between units in solving chemistry problems. Dimensional analysis is based on the relationship between different units that express the same physical quantity. For example, by definition 1 in = 2.54 cm (exactly). This equivalence enables us to write a conversion factor as follows:

$$\frac{1 \text{ in}}{2.54 \text{ cm}}$$

Because both the numerator and the denominator express the same length, this fraction is equal to 1. Similarly, we can write the conversion factor as

$$\frac{2.54 \text{ cm}}{1 \text{ in}}$$

which is also equal to 1. Conversion factors are useful for changing units. Thus, if we wish to convert a length expressed in inches to centimeters, we multiply the length by the appropriate conversion factor.

$$12.00 \text{ in} \times \frac{2.54 \text{ cm}}{1 \text{ in}} = 30.48 \text{ cm}$$

We choose the conversion factor that cancels the unit inches and produces the desired unit, centimeters. Note that the result is expressed in four significant figures because 2.54 is an exact number.

Next let us consider the conversion of 57.8 meters to centimeters. This problem can be expressed as

$$? \text{ cm} = 57.8 \text{ m}$$

By definition,

$$1 \text{ cm} = 1 \times 10^{-2} \text{ m}$$

Because we are converting “m” to “cm,” we choose the conversion factor that has meters in the denominator,

$$\frac{1 \text{ cm}}{1 \times 10^{-2} \text{ m}}$$

and write the conversion as

$$\begin{aligned} ? \text{ cm} &= 57.8 \text{ m} \times \frac{1 \text{ cm}}{1 \times 10^{-2} \text{ m}} \\ &= 5780 \text{ cm} \\ &= 5.78 \times 10^3 \text{ cm} \end{aligned}$$

Note that scientific notation is used to indicate that the answer has three significant figures. Again, the conversion factor $1 \text{ cm}/1 \times 10^{-2} \text{ m}$ contains exact numbers; therefore, it does not affect the number of significant figures.

In general, to apply dimensional analysis we use the relationship

$$\text{given quantity} \times \text{conversion factor} = \text{desired quantity}$$

and the units cancel as follows:

$$\frac{\text{given unit}}{\text{given unit}} \times \frac{\text{desired unit}}{\text{given unit}} = \text{desired unit}$$

Remember that the unit we want appears in the numerator and the unit we want to cancel appears in the denominator.

In dimensional analysis, the units are carried through the entire sequence of calculations. Therefore, if the equation is set up correctly, then all the units will cancel except the desired one. If this is not the case, then an error must have been made somewhere, and it can usually be spotted by reviewing the solution.

A Note on Problem Solving

At this point you have been introduced to scientific notation, significant figures, and dimensional analysis, which will help you in solving numerical problems. Chemistry is an experimental science and many of the problems are quantitative in nature. The key to success in problem solving is practice. Just as a marathon runner cannot prepare for a race by simply reading books on running and a pianist cannot give a successful concert by only memorizing the musical score, you cannot be sure of your understanding of chemistry without solving problems. The following steps will help to improve your skill at solving numerical problems.

1. Read the question carefully. Understand the information that is given and what you are asked to solve. Frequently it is helpful to make a sketch that will help you to visualize the situation.
2. Find the appropriate equation that relates the given information and the unknown quantity. Sometimes solving a problem will involve more than one step, and you may be expected to look up quantities in tables that are not provided in the problem. Dimensional analysis is often needed to carry out conversions.
3. Check your answer for the correct sign, units, and significant figures.
4. A very important part of problem solving is being able to judge whether the answer is reasonable. It is relatively easy to spot a wrong sign or incorrect units. But if a number (say, 9) is incorrectly placed in the denominator instead of in the numerator, the answer would be too small even if the sign and units of the calculated quantity were correct.
5. One quick way to check the answer is to round off the numbers in the calculation in such a way so as to simplify the arithmetic. The answer you get will not be exact, but it will be close to the correct one.

 **Student Hot Spot**
Student data indicate you may struggle with conversion factors. Access your eBook for additional Learning Resources on this topic.

Example 1.6

A person's average daily intake of glucose (a form of sugar) is 0.0833 pound (lb). What is this mass in milligrams (mg)? ($1 \text{ lb} = 453.6 \text{ g}$)

Strategy The problem can be stated as

$$? \text{ mg} = 0.0833 \text{ lb}$$

The relationship between pounds and grams is given in the problem. This relationship will enable conversion from pounds to grams. A metric conversion is then needed to convert grams to milligrams ($1 \text{ mg} = 1 \times 10^{-3} \text{ g}$). Arrange the appropriate conversion factors so that pounds and grams cancel and the unit milligrams is obtained in your answer.

Solution The sequence of conversions is

$$\text{pounds} \longrightarrow \text{grams} \longrightarrow \text{milligrams}$$

Using the following conversion factors

$$\frac{453.6 \text{ g}}{1 \text{ lb}} \quad \text{and} \quad \frac{1 \text{ mg}}{1 \times 10^{-3} \text{ g}}$$

(Continued)



Glucose tablets can provide diabetics with a quick method for raising their blood sugar levels.
©Leonard Lessin/Science Source

Conversion factors for some of the English system units commonly used in the United States for nonscientific measurements (for example, pounds and inches) are provided in the list of Useful Conversion Factors and Relationships.

we obtain the answer in one step:

$$\text{? mg} = 0.0833 \text{ lb} \times \frac{453.6 \text{ g}}{1 \text{ lb}} \times \frac{1 \text{ mg}}{1 \times 10^{-3} \text{ g}} = 3.78 \times 10^4 \text{ mg}$$

Check As an estimate, we note that 1 lb is roughly 500 g and that 1 g = 1000 mg. Therefore, 1 lb is roughly 5×10^5 mg. Rounding off 0.0833 lb to 0.1 lb, we get 5×10^4 mg, which is close to the preceding quantity.

Practice Exercise A roll of aluminum foil has a mass of 1.07 kg. What is its mass in pounds?

Similar problem: 1.47.



A cryogenic storage tank for liquid helium.

©Charles Falco/Science Source

Remember that when a unit is raised to a power, any conversion factor you use must also be raised to that power.

As Examples 1.7 and 1.8 illustrate, conversion factors can be squared or cubed in dimensional analysis.

Example 1.7

A liquid helium storage tank has a volume of 275 L. What is the volume in m³?

Strategy The problem can be stated as

$$\text{? m}^3 = 275 \text{ L}$$

How many conversion factors are needed for this problem? Recall that 1 L = 1000 cm³ and 1 cm = 1×10^{-2} m.

Solution We need two conversion factors here: one to convert liters to cm³ and one to convert centimeters to meters:

$$\frac{1000 \text{ cm}^3}{1 \text{ L}} \quad \text{and} \quad \frac{1 \times 10^{-2} \text{ m}}{1 \text{ cm}}$$

Because the second conversion deals with length (cm and m) and we want volume here, it must therefore be cubed to give

$$\frac{1 \times 10^{-2} \text{ m}}{1 \text{ cm}} \times \frac{1 \times 10^{-2} \text{ m}}{1 \text{ cm}} \times \frac{1 \times 10^{-2} \text{ m}}{1 \text{ cm}} = \left(\frac{1 \times 10^{-2} \text{ m}}{1 \text{ cm}} \right)^3$$

This means that $1 \text{ cm}^3 = 1 \times 10^{-6} \text{ m}^3$. Now we can write

$$\text{? m}^3 = 275 \text{ L} \times \frac{1000 \text{ cm}^3}{1 \text{ L}} \times \left(\frac{1 \times 10^{-2} \text{ m}}{1 \text{ cm}} \right)^3 = 0.275 \text{ m}^3$$

Check From the preceding conversion factors you can show that 1 L = 1×10^{-3} m³. Therefore, a 275-L storage tank would be equal to 275×10^{-3} m³ or 0.275 m³, which is the answer.

Practice Exercise The volume of a room is $1.08 \times 10^8 \text{ dm}^3$. What is the volume in m³?

Similar problem: 1.52(d).

Example 1.8

Liquid nitrogen is obtained from liquefied air and is used to prepare frozen goods and in low-temperature research. The density of the liquid at its boiling point (-196°C or 77 K) is 0.808 g/cm³. Convert the density to units of kg/m³.

(Continued)

Strategy The problem can be stated as

$$? \text{ kg/m}^3 = 0.808 \text{ g/cm}^3$$

Two separate conversions are required for this problem: $\text{g} \rightarrow \text{kg}$ and $\text{cm}^3 \rightarrow \text{m}^3$. Recall that $1 \text{ kg} = 1000 \text{ g}$ and $1 \text{ cm} = 1 \times 10^{-2} \text{ m}$.

Solution In Example 1.7 we saw that $1 \text{ cm}^3 = 1 \times 10^{-6} \text{ m}^3$. The conversion factors are

$$\frac{1 \text{ kg}}{1000 \text{ g}} \quad \text{and} \quad \frac{1 \text{ cm}^3}{1 \times 10^{-6} \text{ m}^3}$$

Finally,

$$? \text{ kg/m}^3 = \frac{0.808 \text{ g}}{1 \text{ cm}^3} \times \frac{1 \text{ kg}}{1000 \text{ g}} \times \frac{1 \text{ cm}^3}{1 \times 10^{-6} \text{ m}^3} = 808 \text{ kg/m}^3$$

Check Because $1 \text{ m}^3 = 1 \times 10^6 \text{ cm}^3$, we would expect much more mass in 1 m^3 than in 1 cm^3 . Therefore, the answer is reasonable.

Practice Exercise The density of the lightest metal, lithium (Li), is $5.34 \times 10^2 \text{ kg/m}^3$. Convert the density to g/cm^3 .

Similar problem: 1.53.



Liquid nitrogen is used for frozen foods and low-temperature research.

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Review of Concepts & Facts

- 1.9.1** What is the correct answer with the appropriate number of significant figures and units for the following energy conversion calculation?

$$3.54 \times 10^{12} \text{ erg} \times \frac{1.000 \text{ J}}{1.000 \times 10^7 \text{ erg}} \times \frac{1.000 \text{ cal}}{4.184 \text{ J}} \times \frac{1 \text{ kcal}}{1000 \text{ cal}} =$$

- 1.9.2** What is the volume in L of a 1.24-kg sample of benzene (density = 0.876 g/mL)?
- 1.9.3** The heat of combustion of TNT is 14.5 MJ/kg. What is this heat of combustion in J/g?

1.10 Real-World Problem Solving: Information, Assumptions, and Simplifications

In chemistry, as in other scientific disciplines, it is not always possible to solve a numerical problem exactly. There are many reasons why this is the case—for example, our understanding of a situation is not complete or data are not fully available. In these cases, we must learn to make an intelligent guess. This approach is sometimes called “ball-park estimates,” which are simple, quick calculations that can be done on the “back of an envelope.” As you can imagine, in many cases the answers are only order-of-magnitude estimates.[†]

In most of the example problems that you have seen so far, as well as the questions given at the end of this and subsequent chapters, the necessary information is provided; however, to solve important real-world problems such as those related to medicine, energy, and agriculture, you must be able to determine what information is needed and where to find it. Much of the information you might need can be found in the various tables located throughout the text, and a list of tables and important

[†]An order of magnitude is a factor of 10.

figures is given in the Index of Important Figures and Tables. In many cases, however, you will need to go to outside sources to find the information you need. Although the Internet is a fast way to find information, you must take care that the source is reliable and well referenced. One excellent source is the National Institute of Standards and Technology (NIST).

To know what information you need, you will first have to formulate a plan for solving the problem. In addition to the limitations of the theories used in science, typically assumptions are made in setting up and solving the problems based on those theories. These assumptions come at a price, however, as the accuracy of the answer is reduced with increasing simplifications of the problem, as illustrated in Example 1.9.

Example 1.9

A modern pencil “lead” is actually composed primarily of graphite, a form of carbon. Estimate the mass of the graphite core in a standard No. 2 pencil before it is sharpened.

Strategy Assume that the pencil lead can be approximated as a cylinder. Measurement of a typical unsharpened pencil gives a length of about 18 cm (subtracting the length of the eraser head) and a diameter of roughly 2 mm for the lead. The volume of a cylinder V is given by $V = \pi r^2 l$, where r is the radius and l is the length. Assuming that the lead is pure graphite, you can calculate the mass of the lead from the volume using the density of graphite given in Table 1.4.

Solution Converting the diameter of the lead to units of cm gives

$$2 \text{ mm} \times \frac{1 \text{ cm}}{10 \text{ mm}} = 0.2 \text{ cm}$$

which, along with the length of the lead, gives

$$\begin{aligned} V &= \pi \left(\frac{0.2 \text{ cm}}{2} \right)^2 \times 18 \text{ cm} \\ &= 0.57 \text{ cm}^3 \end{aligned}$$

Rearranging Equation (1.1) gives

$$\begin{aligned} m &= d \times V \\ &= 2.2 \frac{\text{g}}{\text{cm}^3} \times 0.57^3 \\ &= 1 \text{ g} \end{aligned}$$

Check Rounding off the values used to calculate the volume of the lead gives $3 \times (0.1 \text{ cm})^2 \times 20 \text{ cm} = 0.6 \text{ cm}^3$. Multiplying that volume by roughly 2 g/cm^3 gives around 1 g, which agrees with the value just calculated.

Practice Exercise Estimate the mass of air in a ping-pong ball.

Similar problems: 1.105, 1.106, 1.114.

Considering Example 1.9, even if the dimensions of the pencil lead were measured with greater precision, the accuracy of the final answer would be limited by the assumptions made in modeling this problem. The pencil lead is actually a mixture of graphite and clay, where the relative amounts of the two materials determine the softness of the lead, so the density of the material is likely to be different than 2.2 g/cm^3 . You could probably find a better value for the density of the mixture used to make No. 2 pencils, but it is not worth the effort in this case.

Learning Objectives

- Summarize the steps of the scientific method. (Section 1.3)
- Distinguish between qualitative and quantitative data. (Section 1.3)
- Classify matter as substances or mixtures. (Section 1.4)
- Differentiate between homogeneous and heterogeneous mixtures. (Section 1.4)
- Categorize substances as elements or compounds. (Section 1.4)
- Compare and contrast the three states of matter. (Section 1.5)
- Appraise properties of matter as either chemical or physical. (Section 1.6)
- Identify properties of matter as either extensive or intensive. (Section 1.6)
- Use SI unit prefixes. (Section 1.7)
- Employ measurements such as mass, volume, and density in calculations. (Section 1.7)
- Perform conversions among the different temperature scales. (Section 1.7)
- Apply significant figure rules in calculations. (Section 1.8)
- Discriminate between accuracy and precision. (Section 1.8)
- Manipulate conversion factors in dimensional analysis problems. (Section 1.9)
- Solve problems utilizing dimensional analysis. (Section 1.9)

Key Equations

$$d = \frac{m}{V} \quad (1.1)$$

Equation for density

$$\text{?}^{\circ}\text{C} = (\text{?}^{\circ}\text{F} - 32^{\circ}\text{F}) \times \frac{5^{\circ}\text{C}}{9^{\circ}\text{F}} \quad (1.2)$$

Converting $^{\circ}\text{F}$ to $^{\circ}\text{C}$

$$\text{?}^{\circ}\text{F} = \frac{9^{\circ}\text{F}}{5^{\circ}\text{C}} \times (\text{?}^{\circ}\text{C}) + 32^{\circ}\text{F} \quad (1.3)$$

Converting $^{\circ}\text{C}$ to $^{\circ}\text{F}$

$$\text{? K} = (\text{?}^{\circ}\text{C} + 273.15^{\circ}\text{C}) \frac{1 \text{ K}}{1^{\circ}\text{C}} \quad (1.4)$$

Converting $^{\circ}\text{C}$ to K

Summary of Concepts & Facts

1. The study of chemistry involves three basic steps: observation, representation, and interpretation. Observation refers to measurements in the macroscopic world; representation involves the use of shorthand notation symbols and equations for communication; interpretations are based on atoms and molecules, which belong to the microscopic world.
2. The scientific method is a systematic approach to research that begins with the gathering of information through observation and measurements. In the process, hypotheses, laws, and theories are devised and tested.
3. Chemists study matter and the changes it undergoes. The substances that make up matter have unique physical properties that can be observed without changing their identity and unique chemical properties that, when they are demonstrated, do change the identity of the substances. Mixtures, whether homogeneous or heterogeneous, can be separated into pure components by physical means.
4. The simplest substances in chemistry are elements. Compounds are formed by the chemical combination of atoms of different elements in fixed proportions.
5. All substances, in principle, can exist in three states: solid, liquid, and gas. The interconversion between these states can be effected by changing the temperature.
6. SI units are used to express physical quantities in all sciences, including chemistry.
7. Numbers expressed in scientific notation have the form $N \times 10^n$, where N is between 1 and 10, and n is a positive or negative integer. Scientific notation helps us handle very large and very small quantities.

Key Words

Accuracy, p. 22	Homogeneous mixture, p. 7	Macroscopic properties, p. 12	Quantitative, p. 4
Chemical property, p. 11	Hypothesis, p. 5	Mass, p. 11	Scientific method, p. 4
Chemistry, p. 2	Intensive property, p. 11	Matter, p. 7	Significant figures, p. 19
Compound, p. 8	International System of Units (SI), p. 12	Microscopic properties, p. 12	Substance, p. 7
Density, p. 11	Kelvin, p. 15	Mixture, p. 7	Theory, p. 5
Element, p. 7	Law, p. 5	Physical property, p. 10	Volume, p. 11
Extensive property, p. 11	Liter, p. 14	Precision, p. 22	Weight, p. 13
Heterogeneous mixture, p. 7		Qualitative, p. 4	

Questions & Problems

Red numbered problems solved in *Student Solutions Manual*

1.3 The Scientific Method

Review Questions

- 1.1 Explain what is meant by the scientific method.
- 1.2 What is the difference between qualitative data and quantitative data?

Problems

- 1.3 Classify the following as qualitative or quantitative statements, giving your reasons. (a) The sun is approximately 93 million miles from Earth. (b) Leonardo da Vinci was a better painter than Michelangelo. (c) Ice is less dense than water. (d) Butter tastes better than margarine. (e) A stitch in time saves nine.
- 1.4 Classify each of the following statements as a hypothesis, a law, or a theory. (a) Beethoven's contribution to music would have been much greater if he had married. (b) An autumn leaf gravitates toward the ground because there is an attractive force between the leaf and Earth. (c) All matter is composed of very small particles called atoms.

1.4 Classifications of Matter

Review Questions

- 1.5 Give an example for each of the following terms: (a) matter, (b) substance, (c) mixture.
- 1.6 Give an example of a homogeneous mixture and an example of a heterogeneous mixture.
- 1.7 Give an example of an element and a compound. How do elements and compounds differ?
- 1.8 What is the number of known elements?

Problems

- 1.9 Give the names of the elements represented by the chemical symbols Li, F, P, Cu, As, Zn, Cl, Pt, Mg, U, Al, Si, Ne. (See Table 1.1 and the list of The Elements with Their Symbols and Atomic Masses.)

- 1.10** Give the chemical symbols for the following elements: (a) cesium, (b) germanium, (c) gallium, (d) strontium, (e) uranium, (f) selenium, (g) neon, (h) cadmium. (See Table 1.1 and the inside front cover.)

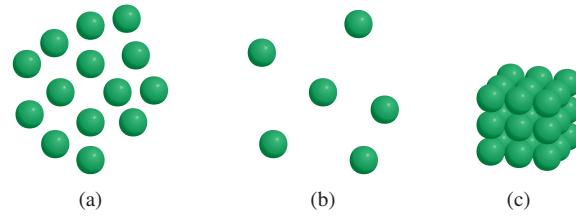
- 1.11** Classify each of the following substances as an element or a compound: (a) hydrogen, (b) water, (c) gold, (d) sugar.

- 1.12** Classify each of the following as an element, a compound, a homogeneous mixture, or a heterogeneous mixture: (a) water from a well, (b) argon gas, (c) sucrose, (d) a bottle of red wine, (e) chicken noodle soup, (f) blood flowing in a capillary, (g) ozone.

1.5 The Three States of Matter

Review Questions

- 1.13** Identify each of the diagrams shown here as gas, liquid, or solid.



- 1.14** Explain how the distances between particles typically change with different states of matter.

1.6 Physical and Chemical Properties of Matter

Review Questions

- 1.15 Using examples, explain the difference between a physical property and a chemical property.
- 1.16 How does an intensive property differ from an extensive property? Which of the following properties are intensive and which are extensive? (a) length, (b) volume, (c) temperature, (d) mass.

Problems

- 1.17** Do the following statements describe chemical or physical properties? (a) Oxygen gas supports combustion. (b) Fertilizers help to increase agricultural production. (c) Water boils below 100°C on top of a mountain. (d) Lead is more dense than aluminum. (e) Uranium is a radioactive element.
- 1.18** Does each of the following describe a physical change or a chemical change? (a) The helium gas inside a balloon tends to leak out after a few hours. (b) A flashlight beam slowly gets dimmer and finally goes out. (c) Frozen orange juice is reconstituted by adding water to it. (d) The growth of plants depends on the sun's energy in a process called photosynthesis. (e) A spoonful of table salt dissolves in a bowl of soup.

1.7 Measurement

Review Questions

- 1.19** Name the SI base units that are important in chemistry. Give the SI units for expressing the following: (a) length, (b) volume, (c) mass, (d) time, (e) energy, (f) temperature.
- 1.20** Write the numbers represented by the following prefixes: (a) mega-, (b) kilo-, (c) deci-, (d) centi-, (e) milli-, (f) micro-, (g) nano-, (h) pico-.
- 1.21** What units do chemists normally use for density of liquids and solids? For gas density? Explain the differences.
- 1.22** Describe the three temperature scales used in the laboratory and in everyday life: the Fahrenheit scale, the Celsius scale, and the Kelvin scale.

Problems

- 1.23** Bromine is a reddish-brown liquid. Calculate its density (in g/mL) if 586 g of the substance occupies 188 mL.
- 1.24** The density of methanol, a colorless organic liquid used as solvent, is 0.7918 g/mL. Calculate the mass of 89.9 mL of the liquid.
- 1.25** Convert the following temperatures to degrees Celsius or Fahrenheit: (a) 95°F, the temperature on a hot summer day; (b) 12°F, the temperature on a cold winter day; (c) a 102°F fever; (d) a furnace operating at 1852°F; (e) -273.15°C (theoretically the lowest attainable temperature).
- 1.26** (a) Normally the human body can endure a temperature of 105°F for only short periods of time without permanent damage to the brain and other vital organs. What is this temperature in degrees Celsius? (b) Ethylene glycol is a liquid organic compound that is used as an antifreeze in car radiators. It freezes at -11.5°C. Calculate its freezing temperature in degrees Fahrenheit. (c) The temperature on the surface of the sun is about 6300°C. What is this temperature in degrees Fahrenheit? (d) The ignition temperature of paper is 451°F. What is the temperature in degrees Celsius?

- 1.27** Convert the following temperatures to kelvin: (a) 113°C, the melting point of sulfur, (b) 37°C, the normal body temperature, (c) 357°C, the boiling point of mercury.

- 1.28** Convert the following temperatures to degrees Celsius: (a) 77 K, the boiling point of liquid nitrogen, (b) 4.2 K, the boiling point of liquid helium, (c) 601 K, the melting point of lead.

1.8 Handling Numbers

Review Questions

- 1.29** What is the advantage of using scientific notation over decimal notation?
- 1.30** Define significant figure. Discuss the importance of using the proper number of significant figures in measurements and calculations.

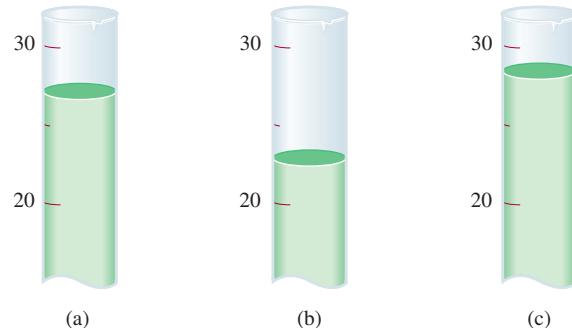
Problems

- 1.31** Express the following numbers in scientific notation: (a) 0.000000027, (b) 356, (c) 47,764, (d) 0.096.
- 1.32** Express the following numbers as decimals: (a) 1.52×10^{-2} , (b) 7.78×10^{-8} .
- 1.33** Express the answers to the following calculations in scientific notation: (a) $145.75 + (2.3 \times 10^{-1})$ (b) $79,500 \div (2.5 \times 10^2)$ (c) $(7.0 \times 10^{-3}) - (8.0 \times 10^{-4})$ (d) $(1.0 \times 10^4) \times (9.9 \times 10^6)$
- 1.34** Express the answers to the following calculations in scientific notation: (a) $0.0095 + (8.5 \times 10^{-3})$ (b) $653 \div (5.75 \times 10^{-8})$ (c) $850,000 - (9.0 \times 10^5)$ (d) $(3.6 \times 10^{-4}) \times (3.6 \times 10^6)$
- 1.35** What is the number of significant figures in each of the following measurements? (a) 4867 mi (b) 56 mL (c) 60,104 tons (d) 2900 g (e) 40.2 g/cm³ (f) 0.0000003 cm (g) 0.7 min (h) 4.6×10^{19} atoms
- 1.36** How many significant figures are there in each of the following? (a) 0.006 L, (b) 0.0605 dm, (c) 60.5 mg, (d) 605.5 cm², (e) 960×10^{-3} g, (f) 6 kg, (g) 60 m.
- 1.37** Carry out the following operations as if they were calculations of experimental results, and express each answer in the correct units with the correct number of significant figures: (a) $5.6792 \text{ m} + 0.6 \text{ m} + 4.33 \text{ m}$ (b) $3.70 \text{ g} - 2.9133 \text{ g}$ (c) $4.51 \text{ cm} \times 3.6666 \text{ cm}$ (d) $(3 \times 10^4 \text{ g} + 6.827 \text{ g}) / (0.043 \text{ cm}^3 - 0.021 \text{ cm}^3)$

- 1.38** Carry out the following operations as if they were calculations of experimental results, and express each answer in the correct units with the correct number of significant figures:
- $7.310 \text{ km} \div 5.70 \text{ km}$
 - $(3.26 \times 10^{-3} \text{ mg}) - (7.88 \times 10^{-5} \text{ mg})$
 - $(4.02 \times 10^6 \text{ dm}) + (7.74 \times 10^7 \text{ dm})$
 - $(7.8 \text{ m} - 0.34 \text{ m}) / (1.15 \text{ s} + 0.82 \text{ s})$
- 1.39** Three students (A, B, and C) are asked to determine the volume of a sample of ethanol. Each student measures the volume three times with a graduated cylinder. The results in milliliters are: A (87.1, 88.2, 87.6); B (86.9, 87.1, 87.2); C (87.6, 87.8, 87.9). The true volume is 87.0 mL. Comment on the precision and the accuracy of each student's results.
- 1.40** Three apprentice tailors (X, Y, and Z) are assigned the task of measuring the seam of a pair of trousers. Each one makes three measurements. The results in inches are X (31.5, 31.6, 31.4); Y (32.8, 32.3, 32.7); Z (31.9, 32.2, 32.1). The true length is 32.0 in. Comment on the precision and the accuracy of each tailor's measurements.
- 1.9 Dimensional Analysis in Solving Problems**
Problems
- 1.41** Carry out the following conversions: (a) 22.6 m to decimeters, (b) 25.4 mg to kilograms, (c) 556 mL to liters, (d) 10.6 kg/m^3 to g/cm^3 .
- 1.42** Carry out the following conversions: (a) 242 lb to milligrams, (b) 68.3 cm^3 to cubic meters, (c) 7.2 m^3 to liters, (d) $28.3 \mu\text{g}$ to pounds.
- 1.43** The average speed of helium at 25°C is 1255 m/s. Convert this speed to miles per hour (mph).
- 1.44** How many seconds are there in a solar year (365.24 days)?
- 1.45** How many minutes does it take light from the sun to reach Earth? (The distance from the sun to Earth is 93 million mi; the speed of light = $3.00 \times 10^8 \text{ m/s}$.)
- 1.46** A jogger runs a mile in 8.92 min. Calculate the speed in (a) in/s, (b) m/min, (c) km/h. ($1 \text{ mi} = 1609 \text{ m}$; $1 \text{ in} = 2.54 \text{ cm}$.)
- 1.47** A 6.0-ft person weighs 168 lb. Express this person's height in meters and weight in kilograms. ($1 \text{ lb} = 453.6 \text{ g}$; $1 \text{ m} = 3.28 \text{ ft}$.)
- 1.48** The speed limit on parts of the German autobahn was once set at 286 kilometers per hour (km/h). Calculate the speed limit in miles per hour (mph).
- 1.49** For a fighter jet to take off from the deck of an aircraft carrier, it must reach a speed of 62 m/s. Calculate the speed in miles per hour (mph).
- 1.50** The "normal" lead content in human blood is about 0.40 part per million (that is, 0.40 g of lead per million grams of blood). A value of 0.80 part per million (ppm) is considered to be dangerous. How many grams of lead are contained in $6.0 \times 10^3 \text{ g}$ of blood (the amount in an average adult) if the lead content is 0.62 ppm?
- 1.51** Carry out the following conversions: (a) 1.42 light-years to miles (a light-year is an astronomical measure of distance—the distance traveled by light in a year, or 365 days; the speed of light is $3.00 \times 10^8 \text{ m/s}$). (b) 32.4 yd to centimeters. (c) $3.0 \times 10^{10} \text{ cm/s}$ to ft/s.
- 1.52** Carry out the following conversions: (a) 70 kg, the average weight of a male adult, to pounds. (b) 14 billion years (roughly the age of the universe) to seconds. (Assume there are 365 days in a year.) (c) 7 ft 6 in, the height of the basketball player Yao Ming, to meters. (d) 88.6 m^3 to liters.
- 1.53** Aluminum is a lightweight metal (density = 2.70 g/cm^3) used in aircraft construction, high-voltage transmission lines, beverage cans, and foils. What is its density in kg/m^3 ?
- 1.54** Ammonia gas is used as a refrigerant in large-scale cooling systems. The density of ammonia gas under certain conditions is 0.625 g/L . Calculate its density in g/cm^3 .
- Additional Problems**
- 1.55** Give one qualitative and one quantitative statement about each of the following: (a) water, (b) carbon, (c) iron, (d) hydrogen gas, (e) sucrose (cane sugar), (f) table salt (sodium chloride), (g) mercury, (h) gold, (i) air.
- 1.56** Which of the following statements describe physical properties and which describe chemical properties? (a) Iron has a tendency to rust. (b) Rainwater in industrialized regions tends to be acidic. (c) Hemoglobin molecules have a red color. (d) When a glass of water is left out in the sun, the water gradually disappears. (e) Carbon dioxide in air is converted to more complex molecules by plants during photosynthesis.
- 1.57** In 2008, about 95.0 billion lb of sulfuric acid were produced in the United States. Convert this quantity to tons.
- 1.58** In determining the density of a rectangular metal bar, a student made the following measurements: length, 8.53 cm; width, 2.4 cm; height, 1.0 cm; mass, 52.7064 g. Calculate the density of the metal to the correct number of significant figures.
- 1.59** Calculate the mass of each of the following: (a) a sphere of gold with a radius of 10.0 cm [the volume of a sphere with a radius r is $V = (4/3)\pi r^3$; the density of gold = 19.3 g/cm^3], (b) a cube of platinum of edge length 0.040 mm (the density of platinum = 21.4 g/cm^3), (c) 50.0 mL of ethanol (the density of ethanol = 0.798 g/mL).
- 1.60** A cylindrical glass bottle 21.5 cm in length is filled with cooking oil of density 0.953 g/mL . If the mass of the oil needed to fill the bottle is 1360 g, calculate the inner diameter of the bottle.
- 1.61** The following procedure was used to determine the volume of a flask. The flask was weighed dry and then filled with water. If the masses of the empty flask and filled flask were 56.12 g and 87.39 g, respectively, and the density of water is 0.9976 g/cm^3 , calculate the volume of the flask in cm^3 .

- 1.62** The speed of sound in air at room temperature is about 343 m/s. Calculate this speed in miles per hour. (1 mi = 1609 m.)
- 1.63** A piece of silver (Ag) metal weighing 194.3 g is placed in a graduated cylinder containing 242.0 mL of water. The volume of water now reads 260.5 mL. From these data calculate the density of silver.
- 1.64** The experiment described in Problem 1.61 is a crude but convenient way to determine the density of some solids. Describe a similar experiment that would enable you to measure the density of ice. Specifically, what would be the requirements for the liquid used in your experiment?
- 1.65** A lead sphere of diameter 48.6 cm has a mass of 6.852×10^5 g. Calculate the density of lead.
- 1.66** Lithium is the least dense metal known (density: 0.53 g/cm^3). What is the volume occupied by 1.20×10^3 g of lithium?
- 1.67** The medicinal thermometer commonly used in homes can be read $\pm 0.1^\circ\text{F}$, whereas those in the doctor's office may be accurate to $\pm 0.1^\circ\text{C}$. In degrees Celsius, express the percent error expected from each of these thermometers in measuring a person's body temperature of 38.9°C .
- 1.68** Vanillin (used to flavor vanilla ice cream and other foods) is the substance whose aroma the human nose detects in the smallest amount. The threshold limit is 2.0×10^{-11} g per liter of air. If the current price of 50 g of vanillin is \$112, determine the cost to supply enough vanillin so that the aroma could be detected in a large aircraft hangar with a volume of $5.0 \times 10^7 \text{ ft}^3$.
- 1.69** At what temperature does the numerical reading on a Celsius thermometer equal that on a Fahrenheit thermometer?
- 1.70** Suppose that a new temperature scale has been devised on which the melting point of ethanol (-117.3°C) and the boiling point of ethanol (78.3°C) are taken as 0°S and 100°S , respectively, where S is the symbol for the new temperature scale. Derive an equation relating a reading on this scale to a reading on the Celsius scale. What would this thermometer read at 25°C ?
- 1.71** A resting adult requires about 240 mL of pure oxygen/min and breathes about 12 times every minute. If inhaled air contains 20 percent oxygen by volume and exhaled air 16 percent, what is the volume of air per breath? (Assume that the volume of inhaled air is equal to that of exhaled air.)
- 1.72** (a) Referring to Problem 1.71, calculate the total volume (in liters) of air an adult breathes in a day. (b) In a city with heavy traffic, the air contains 2.1×10^{-6} L of carbon monoxide (a poisonous gas) per liter. Calculate the average daily intake of carbon monoxide in liters by a person.
- 1.73** Three different 25.0-g samples of solid pellets are added to 20.0 mL of water in three different measuring cylinders. The results are shown here. Given the densities of the three metals used, identify the cylinder

that contains each sample of solid pellets: A (2.9 g/cm^3), B (8.3 g/cm^3), and C (3.3 g/cm^3).



- 1.74** The circumference of an NBA-approved basketball is 29.6 in. Given that the radius of Earth is about 6400 km, how many basketballs would it take to circle around the equator with the basketballs touching one another? Round off your answer to an integer with three significant figures.

- 1.75** A student is given a crucible and asked to prove whether it is made of pure platinum. She first weighs the crucible in air and then weighs it suspended in water (density = 0.9986 g/mL). The readings are 860.2 g and 820.2 g, respectively. Based on these measurements and given that the density of platinum is 21.45 g/cm^3 , what should her conclusion be? (Hint: An object suspended in a fluid is buoyed up by the mass of the fluid displaced by the object. Neglect the buoyance of air.)

- 1.76** The surface area and average depth of the Pacific Ocean are $1.8 \times 10^8 \text{ km}^2$ and $3.9 \times 10^3 \text{ m}$, respectively. Calculate the volume of water in the ocean in liters.

- 1.77** The unit "troy ounce" is often used for precious metals such as gold (Au) and platinum (Pt). (1 troy ounce = 31.103 g.) (a) A gold coin weighs 2.41 troy ounces. Calculate its mass in grams. (b) Is a troy ounce heavier or lighter than an ounce? (1 lb = 16 oz; 1 lb = 453.6 g.)

- 1.78** Osmium (Os) is the densest element known (density = 22.57 g/cm^3). Calculate the mass in pounds and in kilograms of an Os sphere 15 cm in diameter (about the size of a grapefruit). [The volume of a sphere of radius r is $(4/3)\pi r^3$.]

- 1.79** Percent error is often expressed as the absolute value of the difference between the true value and the experimental value, divided by the true value:

$$\text{percent error} = \frac{|\text{true value} - \text{experimental value}|}{|\text{true value}|} \times 100\%$$

The vertical lines indicate absolute value. Calculate the percent error for the following measurements: (a) The density of alcohol (ethanol) is found to be 0.802 g/mL. (True value: 0.798 g/mL.) (b) The mass of gold in an earring is analyzed to be 0.837 g. (True value: 0.864 g.)

- 1.80** The natural abundances of elements in the human body, expressed as percent by mass, are: oxygen (O),

- 65 percent; carbon (C), 18 percent; hydrogen (H), 10 percent; nitrogen (N), 3 percent; calcium (Ca), 1.6 percent; phosphorus (P), 1.2 percent; all other elements, 1.2 percent. Calculate the mass in grams of each element in the body of a 62-kg person.
- 1.81** The men's world record for running a mile outdoors (as of 1999) is 3 min 43.13 s. At this rate, how long would it take to run a 1500-m race? (1 mi = 1609 m.)
- 1.82** Venus, the second closest planet to the sun, has a surface temperature of 7.3×10^2 K. Convert this temperature to °C and °F.
- 1.83** Chalcopyrite, the principal ore of copper (Cu), contains 34.63 percent Cu by mass. How many grams of Cu can be obtained from 5.11×10^3 kg of the ore?
- 1.84** It has been estimated that 8.0×10^4 tons of gold (Au) have been mined. Assume gold costs \$948 per ounce. What is the total worth of this quantity of gold?
- 1.85** A 1.0-mL volume of seawater contains about 4.0×10^{-12} g of gold. The total volume of ocean water is 1.5×10^{21} L. Calculate the total amount of gold (in grams) that is present in seawater, and the worth of the gold in dollars (see Problem 1.84). With so much gold out there, why hasn't someone become rich by mining gold from the ocean?
- 1.86** Measurements show that 1.0 g of iron (Fe) contains 1.1×10^{22} Fe atoms. How many Fe atoms are in 4.9 g of Fe, which is the total amount of iron in the body of an average adult?
- 1.87** The thin outer layer of Earth, called the crust, contains only 0.50 percent of Earth's total mass and yet is the source of almost all the elements (the atmosphere provides elements such as oxygen, nitrogen, and a few other gases). Silicon (Si) is the second most abundant element in Earth's crust (27.2 percent by mass). Calculate the mass of silicon in kilograms in Earth's crust. (The mass of Earth is 5.9×10^{21} tons. 1 ton = 2000 lb; 1 lb = 453.6 g.)
- 1.88** The radius of a copper (Cu) atom is roughly 1.3×10^{-10} m. How many times can you divide evenly a piece of 10-cm copper wire until it is reduced to two separate copper atoms? (Assume there are appropriate tools for this procedure and that copper atoms are lined up in a straight line, in contact with each other. Round off your answer to an integer.)
- 1.89** One gallon of gasoline in an automobile's engine produces on the average 9.5 kg of carbon dioxide, which is a greenhouse gas, that is, it promotes the warming of Earth's atmosphere. Calculate the annual production of carbon dioxide in kilograms if there are 250 million cars in the United States and each car covers a distance of 5000 mi at a consumption rate of 20 miles per gallon.
- 1.90** A sheet of aluminum (Al) foil has a total area of 1.000 ft² and a mass of 3.636 g. What is the thickness of the foil in millimeters? (Density of Al = 2.699 g/cm³.)
- 1.91** Comment on whether each of the following is a homogeneous mixture or a heterogeneous mixture: (a) air in a closed bottle, (b) air over New York City.
- 1.92** Chlorine is used to disinfect swimming pools. The accepted concentration for this purpose is 1 ppm chlorine, or 1 g of chlorine per million grams of water. Calculate the volume of a chlorine solution (in milliliters) a homeowner should add to her swimming pool if the solution contains 6.0 percent chlorine by mass and there are 2.0×10^4 gallons of water in the pool. (1 gallon = 3.79 L; density of liquids = 1.0 g/mL)
- 1.93** An aluminum cylinder is 10.0 cm in length and has a radius of 0.25 cm. If the mass of a single Al atom is 4.48×10^{-23} g, calculate the number of Al atoms present in the cylinder. The density of aluminum is 2.70 g/cm³.
- 1.94** A pycnometer is a device for measuring the density of liquids. It is a glass flask with a close-fitting ground glass stopper having a capillary hole through it. (a) The volume of the pycnometer is determined by using distilled water at 20°C with a known density of 0.99820 g/mL. First, the water is filled to the rim. With the stopper in place, the fine hole allows the excess liquid to escape. The pycnometer is then carefully dried with filter paper. Given that the masses of the empty pycnometer and the same one filled with water are 32.0764 g and 43.1195 g, respectively, calculate the volume of the pycnometer. (b) If the mass of the pycnometer filled with ethanol at 20°C is 40.8051 g, calculate the density of ethanol. (c) Pycnometers can also be used to measure the density of solids. First, small zinc granules weighing 22.8476 g are placed in the pycnometer, which is then filled with water. If the combined mass of the pycnometer plus the zinc granules and water is 62.7728 g, what is the density of zinc?



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- 1.95** In 1849 a gold prospector in California collected a bag of gold nuggets plus sand. Given that the density of gold and sand are 19.3 g/cm^3 and 2.95 g/cm^3 , respectively, and that the density of the mixture is 4.17 g/cm^3 , calculate the percent by mass of gold in the mixture.

- 1.96** The average time it takes for a molecule to diffuse a distance of $x \text{ cm}$ is given by

$$t = \frac{x^2}{2D}$$

where t is the time in seconds and D is the diffusion coefficient. Given that the diffusion coefficient of glucose is $5.7 \times 10^{-7} \text{ cm}^2/\text{s}$, calculate the time it would take for a glucose molecule to diffuse $10 \mu\text{m}$, which is roughly the size of a cell.

- 1.97** A human brain weighs about 1 kg and contains about 10^{11} cells. Assuming that each cell is completely filled with water (density = 1 g/mL), calculate the length of one side of such a cell if it were a cube. If the cells are spread out in a thin layer that is a single cell thick, what is the surface area in square meters?

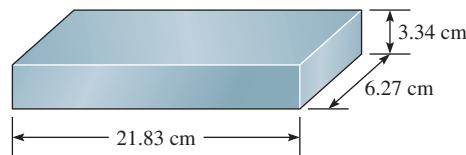
- 1.98** (a) Carbon monoxide (CO) is a poisonous gas because it binds very strongly to the oxygen carrier hemoglobin in blood. A concentration of $8.00 \times 10^2 \text{ ppm}$ by volume of carbon monoxide is considered lethal to humans. Calculate the volume in liters occupied by carbon monoxide in a room that measures 17.6 m long, 8.80 m wide, and 2.64 m high at this concentration. (b) Prolonged exposure to mercury (Hg) vapor can cause neurological disorders and respiratory problems. For safe air quality control, the concentration of mercury vapor must be under 0.050 mg/m^3 . Convert this number to g/L. (c) The general test for type II diabetes is that the blood sugar (glucose) level should be below 120 mg per deciliter (mg/dL). Convert this number to micrograms per milliliter ($\mu\text{g/mL}$).

- 1.99** A bank teller is asked to assemble “one-dollar” sets of coins for his clients. Each set is made of three quarters, one nickel, and two dimes. The masses of the coins are: quarter: 5.645 g; nickel: 4.967 g; dime: 2.316 g. What is the maximum number of sets that can be assembled from 33.871 kg of quarters, 10.432 kg of nickels, and 7.990 kg of dimes? What is the total mass (in g) of the assembled sets of coins?

- 1.100** A graduated cylinder is filled to the 40.00-mL mark with a mineral oil. The masses of the cylinder before and after the addition of the mineral oil are 124.966 g and 159.446 g, respectively. In a separate experiment, a metal ball bearing of mass 18.713 g is placed in the cylinder and the cylinder

is again filled to the 40.00-mL mark with the mineral oil. The combined mass of the ball bearing and mineral oil is 150.952 g. Calculate the density and radius of the ball bearing. [The volume of a sphere of radius r is $(4/3)\pi r^3$.]

- 1.101** A cobalt bar (density = 8.90 g/cm^3) is shown here. What is the mass of this bar to the appropriate number of significant figures?



- 1.102** Bronze is an alloy made of copper (Cu) and tin (Sn) used in applications that require low metal-on-metal friction. Calculate the mass of a bronze cylinder of radius 6.44 cm and length 44.37 cm. The composition of the bronze is 79.42 percent Cu and 20.58 percent Sn and the densities of Cu and Sn are 8.94 g/cm^3 and 7.31 g/cm^3 , respectively. What assumption should you make in this calculation?

- 1.103** You are given a liquid. Briefly describe steps you would take to show whether it is a pure substance or a homogeneous mixture.

- 1.104** A chemist mixes two liquids A and B to form a homogeneous mixture. The densities of the liquids are 2.0514 g/mL for A and 2.6678 g/mL for B. When she drops a small object into the mixture, she finds that the object becomes suspended in the liquid; that is, it neither sinks nor floats. If the mixture is made of 41.37 percent A and 58.63 percent B by volume, what is the density of the metal? Can this procedure be used in general to determine the densities of solids? What assumptions must be made in applying this method?

- 1.105** Tums is a popular remedy for acid indigestion. A typical Tums tablet contains calcium carbonate plus some inert substances. When ingested, it reacts with the gastric juice (hydrochloric acid) in the stomach to give off carbon dioxide gas. When a 1.328-g tablet reacted with 40.00 mL of hydrochloric acid (density: 1.140 g/mL), carbon dioxide gas was given off and the resulting solution weighed 46.699 g. Calculate the number of liters of carbon dioxide gas released if its density is 1.81 g/L.

- 1.106** A 250-mL glass bottle was filled with 242 mL of water at 20°C and tightly capped. It was then left outdoors overnight, where the average temperature was -5°C . Predict what would happen. The density of water at 20°C is 0.998 g/cm^3 and that of ice at -5°C is 0.916 g/cm^3 .

Interpreting, Modeling, & Estimating

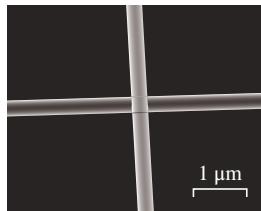
1.107 What is the mass of one mole of ants? (*Useful information:* A mole is the unit used for atomic and subatomic particles. It is approximately 6×10^{23} . A 1-cm-long ant weighs about 3 mg.)

1.108 How much time (in years) does an 80-year-old person spend sleeping during his or her life span?

1.109 Estimate the daily amount of water (in gallons) used indoors by a family of four in the United States.

1.110 Public bowling alleys generally stock bowling balls from 8 to 16 lb, where the mass is given in whole numbers. Given that regulation bowling balls have a diameter of 8.6 in, which (if any) of these bowling balls would you expect to float in water?

1.111 Fusing “nanofibers” with diameters of 100 to 300 nm gives junctions with very small volumes that would potentially allow the study of reactions involving only a few molecules. Estimate the volume in liters of the junction formed between two such fibers with internal diameters of 200 nm. The scale reads 1 μm .



1.112 Estimate the annual consumption of gasoline by passenger cars in the United States.

1.113 Estimate the total amount of ocean water in liters.

1.114 Estimate the volume of blood in an adult in liters.

1.115 How far (in feet) does light travel in one nanosecond?

1.116 Estimate the distance (in miles) covered by an NBA player in a professional basketball game.

1.117 In water conservation, chemists spread a thin film of a certain inert material over the surface of water to cut down on the rate of evaporation of water in reservoirs. This technique was pioneered by Benjamin Franklin three centuries ago. Franklin found that 0.10 mL of oil could spread over the surface of water about 40 m^2 in area. Assuming that the oil forms a *monolayer*, that is, a layer that is only one molecule thick, estimate the length of each oil molecule in nanometers. (1 nm = 1×10^{-9} m.)

Answers to Practice Exercises

1.1 96.5 g. **1.2** 341 g. **1.3** (a) 621.5°F, (b) 78.3°C, (c) -196°C. **1.4** (a) Two, (b) four, (c) three, (d) two, (e) three or two. **1.5** (a) 26.76 L, (b) 4.4 g, (c) $1.6 \times 10^7 \text{ dm}^2$,

(d) 0.0756 g/mL, (e) $6.69 \times 10^4 \text{ m}$. **1.6** 2.36 lb. **1.7** $1.08 \times 10^5 \text{ m}^3$. **1.8** 0.534 g/cm³. **1.9** Roughly 0.03 g.

Answers to Review of Concepts & Facts

1.3.1 c. **1.3.2** Qualitative: b, c. Quantitative: a, d.
1.4.1 Elements: b, d. Compounds: a, c. **1.5.1** a.
1.6.1 Chemical change: b, c. Physical change: d.
1.6.2 Intensive: a, b. Extensive: c. **1.7.1** 0.522 cm³.

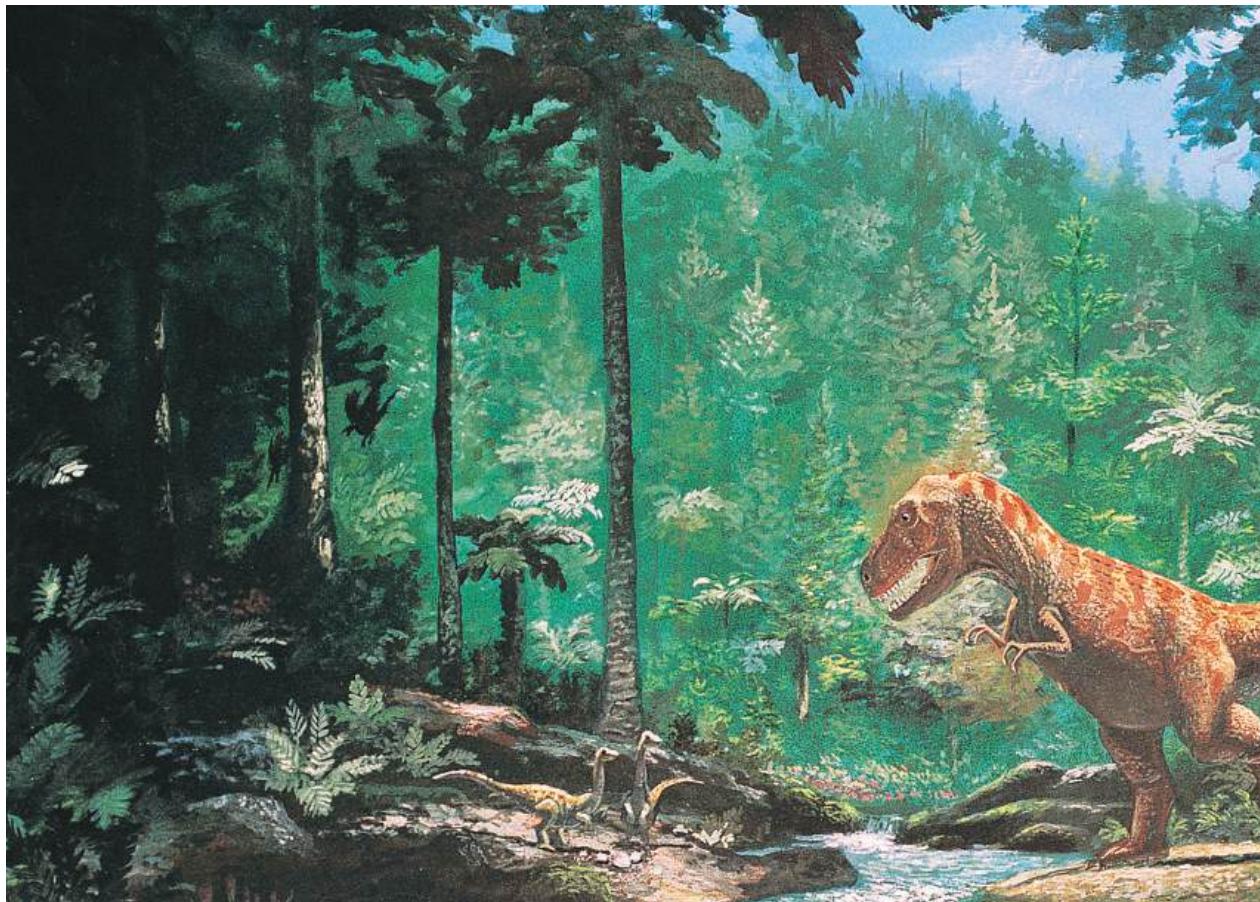
1.7.2 543 K. **1.7.3** a. **1.8.1** Top ruler = 4.6 in. Bottom ruler = 4.57 in. **1.8.2** 10.1 g/cm³. **1.8.3**. Accurate: no. Precise: yes. **1.9.1** 84.6 kcal. **1.9.2** 1.42 L. **1.9.3** $1.45 \times 10^4 \text{ J/g}$.

CHEMICAL *MYSTERY*

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The Disappearance of the Dinosaurs

Dinosaurs dominated life on Earth for millions of years and then disappeared very suddenly. To solve the mystery, paleontologists studied fossils and skeletons found in rocks in various layers of Earth's crust. Their findings enabled them to map out which species existed on Earth during specific geologic periods. They also revealed no dinosaur skeletons in rocks formed immediately after the Cretaceous period, which dates back



©Chris Butler/Science Photo Library/Science Source

some 65 million years. It is therefore assumed that the dinosaurs became extinct about 65 million years ago.

Among the many hypotheses put forward to account for their disappearance were disruptions of the food chain and a dramatic change in climate caused by violent volcanic eruptions. However, there was no convincing evidence for any one hypothesis until 1977. It was then that a group of paleontologists working in Italy obtained some very puzzling data at a site near Gubbio. The chemical analysis of a layer of clay deposited above sediments formed during the Cretaceous period (and therefore a layer that records events occurring *after* the Cretaceous period) showed a surprisingly high content of the element iridium (Ir). Iridium is very rare in Earth's crust but is comparatively abundant in asteroids.

This investigation led to the hypothesis that the extinction of dinosaurs occurred as follows. To account for the quantity of iridium found, scientists suggested that a large asteroid several miles in diameter hit Earth about the time the dinosaurs disappeared. The impact of the asteroid on Earth's surface must have been so tremendous that it literally vaporized a large quantity of surrounding rocks, soils, and other objects. The resulting dust and debris floated through the air and blocked the sunlight for months or perhaps years. Without ample sunlight most plants could not grow, and the fossil record confirms that many types of plants did indeed die out at this time. Consequently, of course, many plant-eating animals perished, and then, in turn, meat-eating animals began to starve. Dwindling food sources would obviously affect large animals needing great amounts of food more quickly and more severely than small animals. Therefore, the huge dinosaurs, the largest of which might have weighed as much as 30 tons, vanished due to lack of food.

Chemical Clues

1. How does the study of dinosaur extinction illustrate the scientific method?
2. Suggest two ways that would enable you to test the asteroid collision hypothesis.
3. In your opinion, is it justifiable to refer to the asteroid explanation as the theory of dinosaur extinction?
4. Available evidence suggests that about 20 percent of the asteroid's mass turned to dust and spread uniformly over Earth after settling out of the upper atmosphere. This dust amounted to about 0.02 g/cm^2 of Earth's surface. The asteroid very likely had a density of about 2 g/cm^3 . Calculate the mass (in kilograms and tons) of the asteroid and its radius in meters, assuming that it was a sphere. (The area of Earth is $5.1 \times 10^{14} \text{ m}^2$; 1 lb = 453.6 g.) (Source: *Consider a Spherical Cow—A Course in Environmental Problem Solving* by J. Harte, University Science Books, Mill Valley, CA 1988. Used with permission.)

Source: *Consider a Spherical Cow—A Course in Environmental Problem Solving* by J. Harte, University Science Books, Mill Valley, CA 1988.

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CHAPTER

2



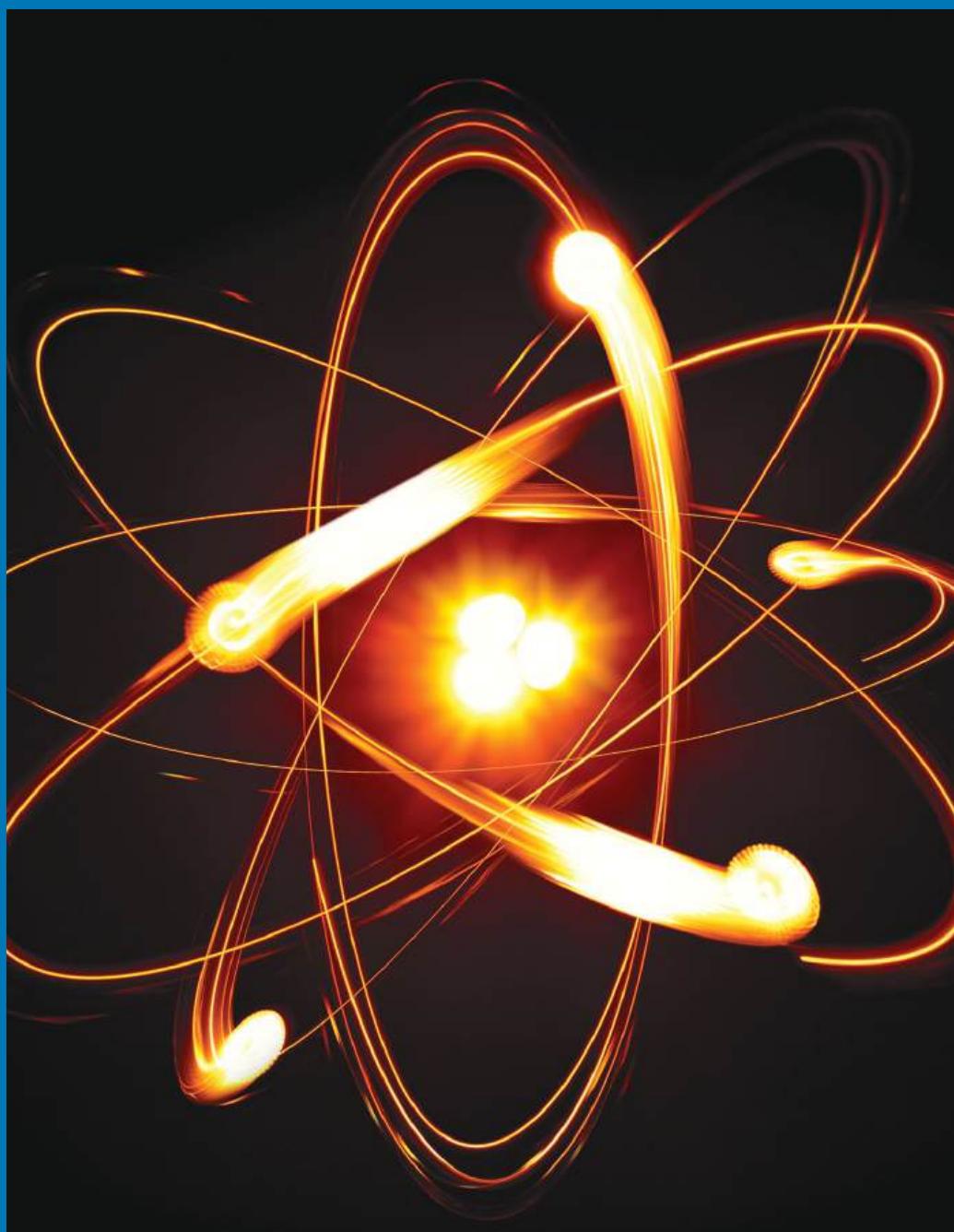
The nuclear model of the atom with a nucleus and orbiting electrons was devised from the work of Ernest Rutherford.

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CHAPTER OUTLINE

- 2.1** The Atomic Theory
- 2.2** The Structure of the Atom
- 2.3** Atomic Number, Mass Number, and Isotopes
- 2.4** The Periodic Table
- 2.5** Molecules and Ions
- 2.6** Chemical Formulas
- 2.7** Naming Compounds
- 2.8** Introduction to Organic Compounds

Atoms, Molecules, and Ions



A LOOK AHEAD

- We begin with a historical perspective of the search for the fundamental units of matter. The modern version of atomic theory was laid by John Dalton in the nineteenth century, who postulated that elements are composed of extremely small particles, called atoms. All atoms of a given element are identical, but they are different from atoms of all other elements. (2.1)
- We note that, through experimentation, scientists have learned that an atom is composed of three elementary particles: proton, electron, and neutron. The proton has a positive charge, the electron has a negative charge, and the neutron has no charge. Protons and neutrons are located in a small region at the center of the atom, called the nucleus, while electrons are spread out about the nucleus at some distance from it. (2.2)
- We will learn the following ways to identify atoms. Atomic number is the number of protons in a nucleus; atoms of different elements have different atomic numbers. Isotopes are atoms of the same element having a different number of neutrons. Mass number is the sum of the number of protons and neutrons in an atom. Because an atom is electrically neutral, the number of protons is equal to the number of electrons in it. (2.3)
- Next we will see how elements can be grouped together according to their chemical and physical properties in a chart called the periodic table. The periodic table enables us to classify elements (as metals, metalloids, and nonmetals) and correlate their properties in a systematic way. (2.4)
- We will see that atoms of most elements interact to form compounds, which are classified as molecules or ionic compounds made of positive (cations) and negative (anions) ions. (2.5)
- We learn to use chemical formulas (molecular and empirical) to represent molecules and ionic compounds and models to represent molecules. (2.6)
- We learn a set of rules that help us name the inorganic compounds. (2.7)
- Finally, we will briefly explore the organic world to which we will return in a later chapter. (2.8)

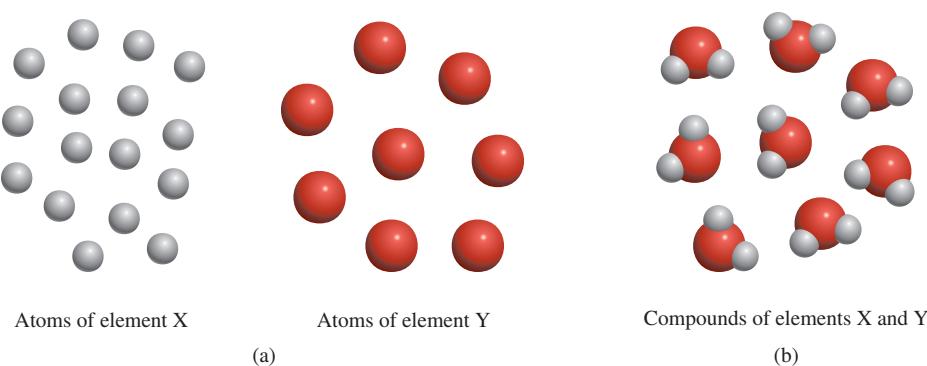
Since ancient times humans have pondered the nature of matter. Our modern ideas of the structure of matter began to take shape in the early nineteenth century with Dalton's atomic theory. We now know that all matter is made of atoms, molecules, and ions. All of chemistry is concerned in one way or another with these species.

2.1 The Atomic Theory

In the fifth century B.C. the Greek philosopher Democritus expressed the belief that all matter consists of very small, indivisible particles, which he named *atomos* (meaning “uncuttable or indivisible”). Although Democritus’ idea was not accepted by many of his contemporaries (notably Plato and Aristotle), somehow it endured. Experimental evidence from early scientific investigations provided support for the notion of “atomism” and gradually gave rise to the modern definitions of elements and compounds. In 1808 an English scientist and schoolteacher, John Dalton,[†] formulated a precise definition of the indivisible building blocks of matter that we call atoms.

[†]John Dalton (1766–1844). English chemist, mathematician, and philosopher. In addition to the atomic theory, he also formulated several gas laws and gave the first detailed description of color blindness, from which he suffered. Dalton was described as an indifferent experimenter, and singularly wanting in the language and power of illustration. His only recreation was lawn bowling on Thursday afternoons. Perhaps it was the sight of those wooden balls that provided him with the idea of the atomic theory.

Figure 2.1 (a) According to Dalton's atomic theory, atoms of the same element are identical, but atoms of one element are different from atoms of other elements. (b) Compound formed from atoms of elements X and Y. In this case, the ratio of the atoms of element X to the atoms of element Y is 2:1. Note that a chemical reaction results only in the rearrangement of atoms, not in their destruction or creation.



Dalton's work marked the beginning of the modern era of chemistry. According to Dalton's atomic theory, the hypotheses about the nature of matter can be summarized as follows:

1. Elements are composed of extremely small particles called atoms.
2. All atoms of a given element are identical, having the same size, mass, and chemical properties. The atoms of one element are different from the atoms of all other elements.
3. Compounds are composed of atoms of more than one element. For any given compound, the atoms present are always in the same ratio.
4. A chemical reaction involves only the separation, combination, or rearrangement of atoms; it does not result in the creation or destruction of atoms.

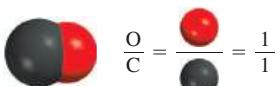
Figure 2.1 is a schematic representation of the last three hypotheses.

Dalton's concept of an atom was far more detailed and specific than Democritus' concept. The second hypothesis states that atoms of one element are different from atoms of all other elements. Dalton made no attempt to describe the structure or composition of atoms—he had no idea what an atom is really like. But he did realize that the different properties shown by elements such as hydrogen and oxygen can be explained by assuming that hydrogen atoms are not the same as oxygen atoms.

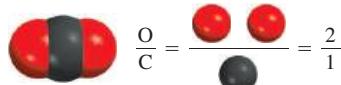
The third hypothesis suggests that, to form a certain compound, we need not only atoms of the right kinds of elements, but specific numbers of these atoms as well. This idea is an extension of a law published in 1799 by Joseph Proust,[†] a French chemist. Proust's **law of definite proportions** states that *different samples of the same compound always contain its constituent elements in the same proportion by mass*. Thus, if we were to analyze samples of carbon dioxide gas obtained from different sources, we would find in each sample the same ratio by mass of carbon to oxygen. It stands to reason, then, that if the ratio of the masses of different elements in a given compound is fixed, the ratio of the atoms of these elements in the compound also must be constant.

Dalton's third hypothesis supports another important law, the **law of multiple proportions**. According to the law, *if two elements can combine to form more than one compound, the masses of one element that combine with a fixed mass of the other element are in ratios of small whole numbers*. Dalton's theory explains the law of multiple proportions quite simply: Different compounds made up of the same elements differ in the number of atoms of each kind that combine. For example, carbon forms two stable compounds with oxygen—namely, carbon monoxide and carbon dioxide. Modern measurement techniques indicate that one atom of carbon combines with one atom of oxygen in carbon monoxide and with two atoms of oxygen in carbon dioxide. Thus, the ratio of oxygen in carbon monoxide to oxygen in carbon dioxide is 1:2. This result is consistent with the law of multiple proportions (Figure 2.2).

Carbon monoxide



Carbon dioxide



Ratio of oxygen in carbon monoxide to oxygen in carbon dioxide: 1:2

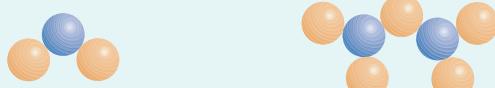
Figure 2.2 An illustration of the law of multiple proportions.

[†]Joseph Louis Proust (1754–1826). French chemist. Proust was the first person to isolate sugar from grapes.

Dalton's fourth hypothesis is another way of stating the *law of conservation of mass*,[‡] which is that *matter can be neither created nor destroyed*. Because matter is made of atoms that are unchanged in a chemical reaction, it follows that mass must be conserved as well. Dalton's brilliant insight into the nature of matter was the main stimulus for the rapid progress of chemistry during the nineteenth century.

Review of Concepts & Facts

- 2.1.1** The atoms of elements A (blue) and B (orange) form two compounds shown here. Do these compounds obey the law of multiple proportions?



2.2 The Structure of the Atom

On the basis of Dalton's atomic theory, we can define an *atom* as *the basic unit of an element that can enter into chemical combination*. Dalton imagined an atom that was both extremely small and indivisible. However, a series of investigations that began in the 1850s and extended into the twentieth century clearly demonstrated that atoms actually possess internal structure; that is, they are made up of even smaller particles, which are called *subatomic particles*. This research led to the discovery of three such particles—electrons, protons, and neutrons.

The Electron

In the 1890s, many scientists became caught up in the study of *radiation, the emission and transmission of energy through space in the form of waves*. Information gained from this research contributed greatly to our understanding of atomic structure. One device used to investigate this phenomenon was a cathode ray tube, the forerunner of the television tube (Figure 2.3). It is a glass tube from which most of the air has been



[‡]According to Albert Einstein, mass and energy are alternate aspects of a single entity called *mass-energy*. Chemical reactions usually involve a gain or loss of heat and other forms of energy. Thus, when energy is lost in a reaction, for example, mass is also lost. Except for nuclear reactions (see Chapter 19), however, changes of mass in chemical reactions are too small to detect. Therefore, for all practical purposes mass is conserved.

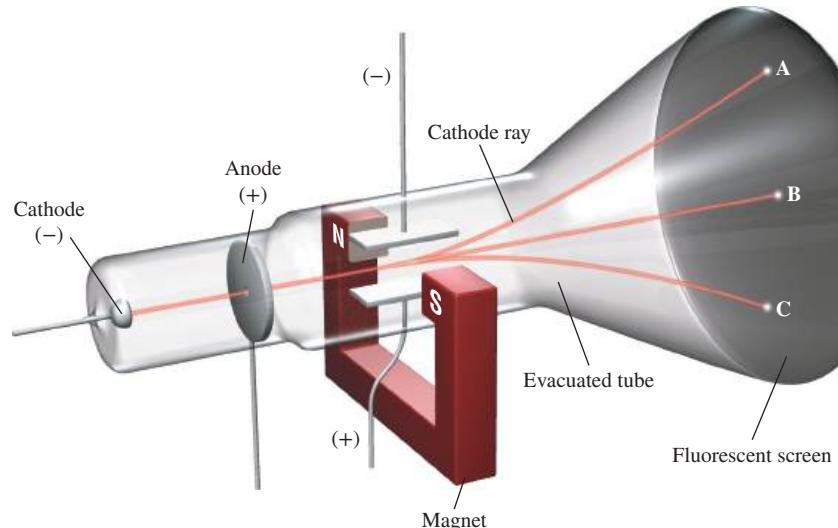


Figure 2.3 A cathode ray tube with an electric field perpendicular to the direction of the cathode rays and an external magnetic field. The symbols N and S denote the north and south poles of the magnet. The cathode rays will strike the end of the tube at A in the presence of a magnetic field, at C in the presence of an electric field, and at B when there are no external fields present or when the effects of the electric field and magnetic field cancel each other.

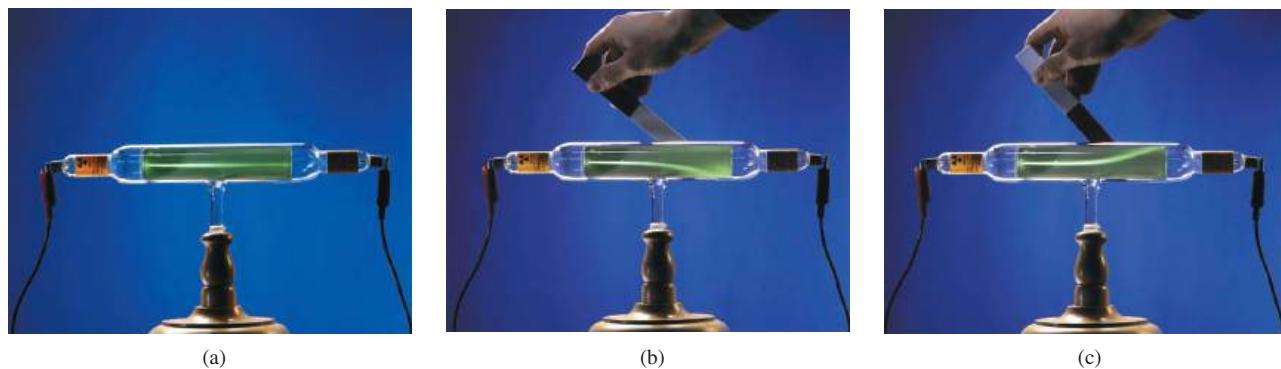


Figure 2.4 (a) A cathode ray produced in a discharge tube traveling from the cathode (left) to the anode (right). The ray itself is invisible, but the fluorescence of a zinc sulfide coating on the glass causes it to appear green. (b) The cathode ray is bent downward when a bar magnet is brought toward it. (c) When the polarity of the magnet is reversed, the ray bends in the opposite direction.

(a, b, c): ©McGraw-Hill Education/Charles D. Winters

evacuated. When the two metal plates are connected to a high-voltage source, the negatively charged plate, called the *cathode*, emits an invisible ray. The cathode ray is drawn to the positively charged plate, called the *anode*, where it passes through a hole and continues traveling to the other end of the tube. When the ray strikes the specially coated surface, it produces a strong fluorescence, or bright light.

In some experiments, two electrically charged plates and a magnet were added to the *outside* of the cathode ray tube (see Figure 2.3). When the magnetic field is on and the electric field is off, the cathode ray strikes point A. When only the electric field is on, the ray strikes point C. When both the magnetic and the electric fields are off or when they are both on but balanced so that they cancel each other's influence, the ray strikes point B. According to electromagnetic theory, a moving charged body behaves like a magnet and can interact with electric and magnetic fields through which it passes. Because the cathode ray is attracted by the plate bearing positive charges and repelled by the plate bearing negative charges, it must consist of negatively charged particles. We know these *negatively charged particles* as **electrons**. Figure 2.4 shows the effect of a bar magnet on the cathode ray.

An English physicist, J. J. Thomson,[†] used a cathode ray tube and his knowledge of electromagnetic theory to determine the ratio of electric charge to the mass of an individual electron. The number he came up with was $-1.76 \times 10^8 \text{ C/g}$, where C stands for *coulomb*, which is the unit of electric charge. Thereafter, in a series of experiments carried out between 1908 and 1917, R. A. Millikan[‡] succeeded in measuring the charge of the electron with great precision. His work proved that the charge on each electron was exactly the same. In his experiment, Millikan examined the motion of single tiny drops of oil that picked up static charge from ions in the air. He suspended the charged drops in air by applying an electric field and followed their motions through a microscope (Figure 2.5). Using his knowledge of electrostatics, Millikan found the charge of an electron to be $-1.6022 \times 10^{-19} \text{ C}$. From these data he calculated the mass of an electron:

$$\begin{aligned}\text{mass of an electron} &= \frac{\text{charge}}{\text{charge/mass}} \\ &= \frac{-1.6022 \times 10^{-19} \text{ C}}{-1.76 \times 10^8 \text{ C/g}} \\ &= 9.10 \times 10^{-28} \text{ g}\end{aligned}$$

This is an exceedingly small mass.

[†]Joseph John Thomson (1856–1940). British physicist who received the Nobel Prize in Physics in 1906 for discovering the electron.

[‡]Robert Andrews Millikan (1868–1953). American physicist who was awarded the Nobel Prize in Physics in 1923 for determining the charge of the electron.

Electrons are normally associated with atoms. However, they can also be studied individually.

Video
Millikan Oil Drop

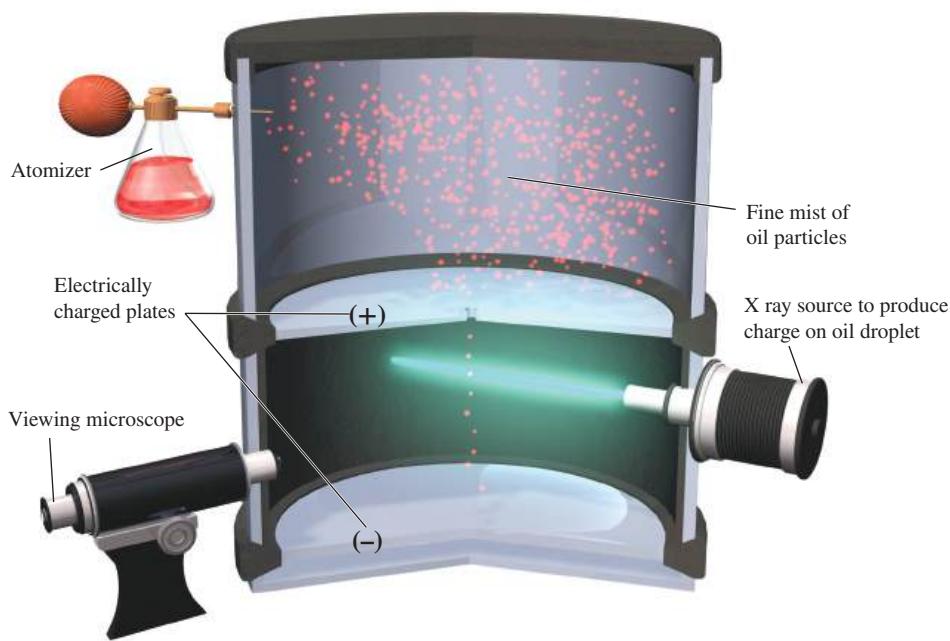


Figure 2.5 Schematic diagram of Millikan's oil drop experiment.

Radioactivity

In 1895 the German physicist Wilhelm Röntgen[§] noticed that cathode rays caused glass and metals to emit very unusual rays. This highly energetic radiation penetrated matter, darkened covered photographic plates, and caused a variety of substances to fluoresce. Because these rays could not be deflected by a magnet, they could not contain charged particles as cathode rays do. Röntgen called them X rays because their nature was not known.

Not long after Röntgen's discovery, Antoine Becquerel,[†] a professor of physics in Paris, began to study the fluorescent properties of substances. Purely by accident, he found that exposing thickly wrapped photographic plates to a certain uranium compound caused them to darken, even without the stimulation of cathode rays. Like X rays, the rays from the uranium compound were highly energetic and could not be deflected by a magnet, but they differed from X rays because they arose spontaneously. One of Becquerel's students, Marie Curie,[‡] suggested the name **radioactivity** to describe this *spontaneous emission of particles and/or radiation*. Since then, any element that spontaneously emits radiation is said to be **radioactive**.

Three types of rays are produced by the *decay*, or breakdown, of radioactive substances such as uranium. Two of the three are deflected by oppositely charged metal plates (Figure 2.6). **Alpha (α) rays** consist of *positively charged particles*, called **α particles**, and therefore are deflected by the positively charged plate. **Beta (β) rays**, or **β particles**, are electrons and are deflected by the negatively charged plate. The third type of radioactive radiation consists of high-energy rays called **gamma (γ) rays**. Like X rays, γ rays have no charge and are not affected by an external field.

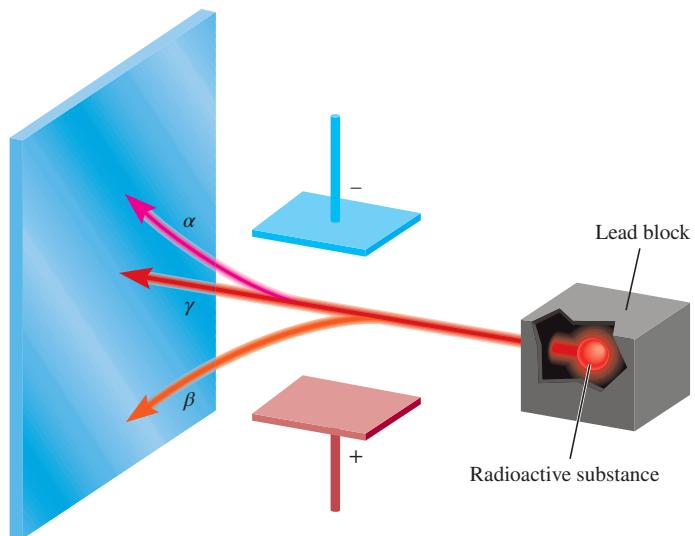
 **Video**
Alpha, Beta, and Gamma Rays

[§]Wilhelm Konrad Röntgen (1845–1923). German physicist who received the Nobel Prize in Physics in 1901 for the discovery of X rays.

[†]Antoine Henri Becquerel (1852–1908). French physicist who was awarded the Nobel Prize in Physics in 1903 for discovering radioactivity in uranium.

[‡]Marie (Marya Skłodowska) Curie (1867–1934). Polish-born chemist and physicist. In 1903 she and her French husband, Pierre Curie, were awarded the Nobel Prize in Physics for their work on radioactivity. In 1911, she again received the Nobel prize, this time in chemistry, for her work on the radioactive elements radium and polonium. She is one of only three people to have received two Nobel prizes in science. Despite her great contribution to science, her nomination to the French Academy of Sciences in 1911 was rejected by one vote because she was a woman! Her daughter Irene, and son-in-law Frederic Joliot-Curie, shared the Nobel Prize in Chemistry in 1935.

Figure 2.6 Three types of rays emitted by radioactive elements. β rays consist of negatively charged particles (electrons) and are therefore attracted by the positively charged plate. The opposite holds true for α rays—they are positively charged and are drawn to the negatively charged plate. Because γ rays have no charges, their path is unaffected by an external electric field.



The Proton and the Nucleus

By the early 1900s, two features of atoms had become clear: They contain electrons, and they are electrically neutral. To maintain electric neutrality, an atom must contain an equal number of positive and negative charges. Therefore, Thomson proposed that an atom could be thought of as a uniform, positive sphere of matter in which electrons are embedded like raisins in a cake (Figure 2.7). This so-called “plum-pudding” model was the accepted theory for a number of years.

[Video](#)
 α -Particle Scattering

[Video](#)
Rutherford's Experiment

In 1910 the New Zealand physicist Ernest Rutherford,[†] who had studied with Thomson at Cambridge University, decided to use α particles to probe the structure of atoms. Together with his associate Hans Geiger[‡] and an undergraduate named Ernest Marsden,[§] Rutherford carried out a series of experiments using very thin foils of gold and other metals as targets for α particles from a radioactive source (Figure 2.8). They observed that the majority of particles penetrated the foil either undeflected or with only a slight deflection. But every now and then an α particle was scattered (or deflected) at a large angle. In some instances, an α particle actually bounced back in the direction from which it had come! This was a most surprising finding, for in Thomson’s model the positive charge of the atom was so diffuse that the positive α particles should have passed through the foil with very little deflection. To quote Rutherford’s initial reaction when told of this discovery: “It was as incredible as if you had fired a 15-inch shell at a piece of tissue paper and it came back and hit you.”

Rutherford explained the results of the α -scattering experiment by introducing a new model for the atom. According to Rutherford, most of the atom must be empty space. This explains why the majority of α particles passed through the gold foil with little or no deflection. The atom’s positive charges, Rutherford proposed, are all concentrated in the **nucleus**, which is *a dense central core within the atom*. Whenever an α particle came close to a nucleus in the scattering experiment, it experienced a large repulsive force and therefore a large deflection. Moreover, an α particle traveling directly toward a nucleus would be completely repelled and its direction would be reversed.

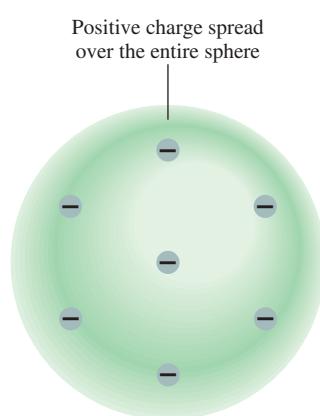
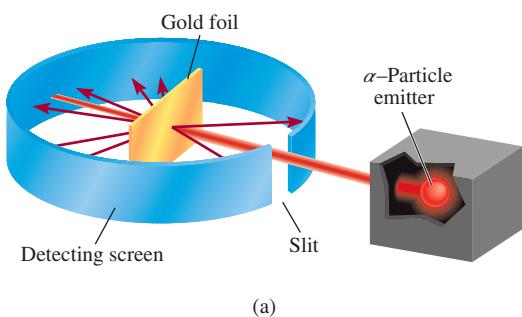


Figure 2.7 Thomson’s model of the atom, sometimes described as the “plum-pudding” model, after a traditional English dessert containing raisins. The electrons are embedded in a uniform, positively charged sphere.

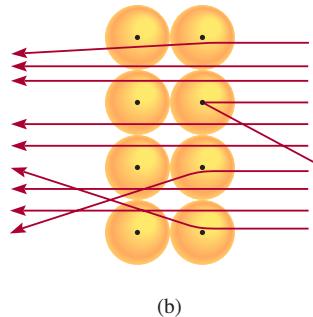
[†]Ernest Rutherford (1871–1937). New Zealand physicist. Rutherford did most of his work in England (Manchester and Cambridge Universities). He received the Nobel Prize in Chemistry in 1908 for his investigations into the structure of the atomic nucleus. His often-quoted comment to his students was that “all science is either physics or stamp-collecting.”

[‡]Johannes Hans Wilhelm Geiger (1882–1945). German physicist. Geiger’s work focused on the structure of the atomic nucleus and on radioactivity. He invented a device for measuring radiation that is now commonly called the Geiger counter.

[§]Ernest Marsden (1889–1970). English physicist. It is gratifying to know that at times an undergraduate can assist in winning a Nobel prize. Marsden went on to contribute significantly to the development of science in New Zealand.



(a)



(b)

Figure 2.8 (a) Rutherford's experimental design for measuring the scattering of α particles by a piece of gold foil. Most of the α particles passed through the gold foil with little or no deflection. A few were deflected at wide angles. Occasionally an α particle was turned back. (b) Magnified view of α particles passing through and being deflected by nuclei.

The positively charged particles in the nucleus are called **protons**. In separate experiments, it was found that each proton carries the same quantity of charge as an electron and has a mass of 1.67262×10^{-24} g—about 1840 times the mass of the oppositely charged electron.

At this stage of investigation, scientists perceived the atom as follows: The mass of a nucleus constitutes most of the mass of the entire atom, but the nucleus occupies only about $1/10^{13}$ of the volume of the atom. We express atomic (and molecular) dimensions in terms of the SI unit called the *picometer* (*pm*), where

$$1 \text{ pm} = 1 \times 10^{-12} \text{ m}$$

A typical atomic radius is about 100 pm, whereas the radius of an atomic nucleus is only about 5×10^{-3} pm. You can appreciate the relative sizes of an atom and its nucleus by imagining that if an atom were the size of a sports stadium, the volume of its nucleus would be comparable to that of a small marble. Although the protons are confined to the nucleus of the atom, the electrons are conceived of as being spread out about the nucleus at some distance from it.

The concept of atomic radius is useful experimentally, but we should not infer that atoms have well-defined boundaries or surfaces. We will learn later that the outer regions of atoms are relatively “fuzzy.”

A common non-SI unit for atomic length is the angstrom (\AA ; $1 \text{\AA} = 100 \text{ pm}$).



If the size of an atom were expanded to that of this sports stadium, the size of the nucleus would be that of a marble.

©The Image Bank/Getty Images

The Neutron

Rutherford's model of atomic structure left one major problem unsolved. It was known that hydrogen, the simplest atom, contains only one proton and that the helium atom contains two protons. Therefore, the ratio of the mass of a helium atom to that of a hydrogen atom should be 2:1. (Because electrons are much lighter than protons, their contribution to atomic mass can be ignored.) In reality, however, the ratio is 4:1. Rutherford and others postulated that there must be another type of subatomic particle in the atomic nucleus; the proof was provided by another English physicist, James Chadwick,[†] in 1932. When Chadwick bombarded a thin sheet of beryllium with α particles, a very high-energy radiation similar to γ rays was emitted by the metal. Later experiments showed that the rays actually consisted of a third type of subatomic particles. Chadwick named these subatomic particles **neutrons**, because they proved to be electrically neutral particles with a mass slightly greater than that of protons. The mystery of the mass ratio could now be explained. In the helium nucleus there are two protons and two neutrons, but in the hydrogen nucleus there is only one proton and no neutrons; therefore, the ratio is 4:1.

Figure 2.9 shows the location of the elementary particles (protons, neutrons, and electrons) in an atom. There are other subatomic particles, but the electron, the proton, and the neutron are the three fundamental components of the atom that are important in chemistry. Table 2.1 shows the masses and charges of these three elementary particles.

[†]James Chadwick (1891–1972). British physicist. In 1935 he received the Nobel Prize in Physics for proving the existence of neutrons.

Figure 2.9 The protons and neutrons of an atom are packed in an extremely small nucleus. Electrons are shown as “clouds” around the nucleus.

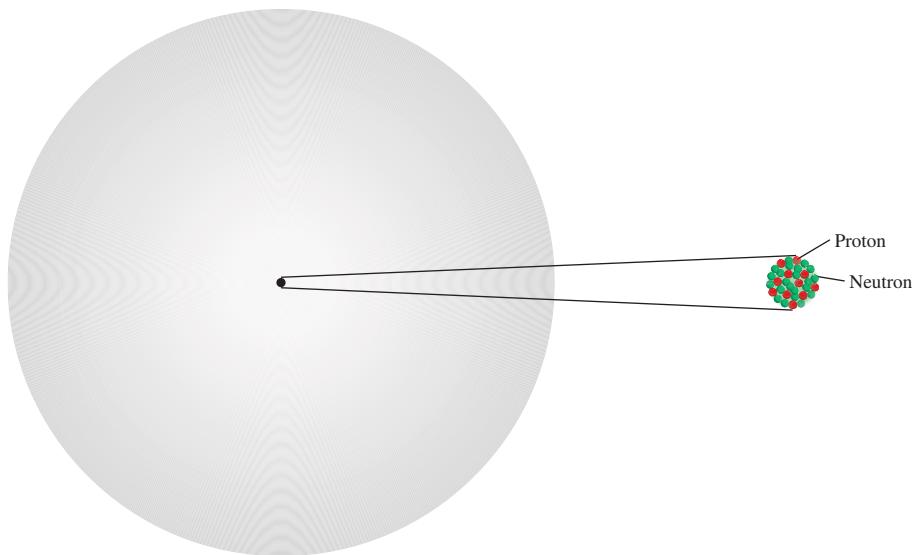


Table 2.1 Mass and Charge of Subatomic Particles

Particle	Mass (g)	Charge	
		Coulomb	Charge Unit
Electron*	9.10938×10^{-28}	-1.6022×10^{-19}	-1
Proton	1.67262×10^{-24}	$+1.6022 \times 10^{-19}$	+1
Neutron	1.67493×10^{-24}	0	0

*More refined measurements have given us a more accurate value of an electron's mass than Millikan's.

2.3 Atomic Number, Mass Number, and Isotopes

All atoms can be identified by the number of protons and neutrons they contain. The **atomic number (Z)** is the number of protons in the nucleus of each atom of an element. In a neutral atom the number of protons is equal to the number of electrons, so the atomic number also indicates the number of electrons present in the atom. The chemical identity of an atom can be determined solely from its atomic number. For example, the atomic number of fluorine is 9. This means that each fluorine atom has 9 protons and 9 electrons. Or, viewed another way, every atom in the universe that contains 9 protons is correctly named “fluorine.”

The **mass number (A)** is the total number of neutrons and protons present in the nucleus of an atom of an element. Except for the most common form of hydrogen, which has one proton and no neutrons, all atomic nuclei contain both protons and neutrons. In general, the mass number is given by

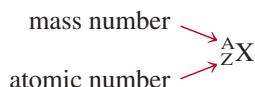
$$\begin{aligned} \text{mass number} &= \text{number of protons} + \text{number of neutrons} \\ &= \text{atomic number} + \text{number of neutrons} \end{aligned} \quad (2.1)$$

The number of neutrons in an atom is equal to the difference between the mass number and the atomic number, or $(A - Z)$. For example, if the mass number of a particular boron atom is 12 and the atomic number is 5 (indicating 5 protons in the nucleus), then the number of neutrons is $12 - 5 = 7$. Note that all three quantities (atomic number, number of neutrons, and mass number) must be positive integers, or whole numbers.

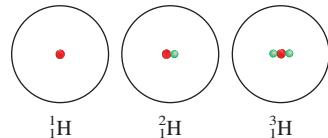
Atoms of a given element do not all have the same mass despite what the first hypothesis of Dalton's atomic theory states. Most elements have two or more **isotopes**, atoms that have the same atomic number (Z) but different mass numbers (A). For

Protons and neutrons are collectively called nucleons.

example, there are three isotopes of hydrogen. One, simply known as hydrogen, has one proton and no neutrons. The *deuterium* isotope contains one proton and one neutron, and *tritium* has one proton and two neutrons. The accepted way to denote the atomic number and mass number of an atom of an element (X) is as follows:



Thus, for the isotopes of hydrogen, we write



As another example, consider two common isotopes of uranium with mass numbers of 235 and 238, respectively:



The first isotope is used in nuclear reactors and atomic bombs, whereas the second isotope lacks the properties necessary for these applications. With the exception of hydrogen, which has different names for each of its isotopes, isotopes of elements are identified by their mass numbers. Thus, the preceding two isotopes are called uranium-235 (pronounced “uranium two thirty-five”) and uranium-238 (pronounced “uranium two thirty-eight”).

The chemical properties of an element are determined primarily by the protons and electrons in its atoms; neutrons do not take part in chemical changes under normal conditions. Therefore, isotopes of the same element have similar chemistries, forming the same types of compounds and displaying similar reactivities.

Example 2.1 shows how to calculate the number of protons, neutrons, and electrons using atomic numbers and mass numbers.

Example 2.1

Give the number of protons, neutrons, and electrons in each of the following species: (a) ${}_{11}^{20} \text{Na}$, (b) ${}_{11}^{22} \text{Na}$, (c) ${}_{8}^{17} \text{O}$, and (d) carbon-14.

Strategy Recall that the superscript denotes the mass number (A) and the subscript denotes the atomic number (Z). Mass number is always greater than atomic number. (The only exception is ${}_1^1 \text{H}$, where the mass number is equal to the atomic number.) In a case where no subscript is shown, as in parts (c) and (d), the atomic number can be deduced from the element symbol or name. To determine the number of electrons, remember that because atoms are electrically neutral, the number of electrons is equal to the number of protons.

Solution

- The atomic number is 11, so there are 11 protons. The mass number is 20, so the number of neutrons is $20 - 11 = 9$. The number of electrons is the same as the number of protons; that is, 11.
- The atomic number is the same as that in (a), or 11. The mass number is 22, so the number of neutrons is $22 - 11 = 11$. The number of electrons is 11. Note that the species in (a) and (b) are chemically similar isotopes of sodium.
- The atomic number of O (oxygen) is 8, so there are 8 protons. The mass number is 17, so there are $17 - 8 = 9$ neutrons. There are 8 electrons.
- Carbon-14 can also be represented as ${}^{14} \text{C}$. The atomic number of carbon is 6, so there are $14 - 6 = 8$ neutrons. The number of electrons is 6.

Practice Exercise

How many protons, neutrons, and electrons are in the following isotope of copper: ${}^{63} \text{Cu}$?

Similar problems: 2.15, 2.16.

Review of Concepts & Facts

- 2.3.1** What is the atomic number of an element if one of its isotopes has 117 neutrons and a mass number of 195?
- 2.3.2** How many neutrons are in an atom of ^{114}Cd ?
- 2.3.3** Which of the following two symbols provides more information: ^{17}O or ${}_8\text{O}$?

2.4 The Periodic Table

More than half of the elements known today were discovered between 1800 and 1900. During this period, chemists noted that many elements show strong similarities to one another. Recognition of periodic regularities in physical and chemical behavior and the need to organize the large volume of available information about the structure and properties of elemental substances led to the development of the *periodic table*, a chart in which elements having similar chemical and physical properties are grouped together. Figure 2.10 shows the modern periodic table in which the elements are arranged by atomic number (Z) (shown above the element symbol) in horizontal rows called *periods* and in vertical columns known as *groups* or *families*, according to similarities in their chemical properties.

The elements can be divided into three categories—metals, nonmetals, and metalloids. A **metal** is a good conductor of heat and electricity, whereas a **nonmetal** is usually a poor conductor of heat and electricity. A **metalloid** has properties that are intermediate between those of metals and nonmetals. Figure 2.10 shows that the majority of

1 1A H	2 2A He											18 8A He					
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg	3 3B	4 4B	5 5B	6 6B	7 7B	8 8B	9	10	11 1B	12 2B	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og
Metals			58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	
Metalloids			90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	
Nonmetals																	

Figure 2.10 The modern periodic table. The elements are arranged according to the atomic numbers above their symbols. With the exception of hydrogen (H), nonmetals appear at the far right of the table. The two rows of metals beneath the main body of the table are conventionally set apart to keep the table from being too wide. Actually, cerium (Ce) should follow lanthanum (La), and thorium (Th) should come right after actinium (Ac). The 1–18 group designation has been recommended by the International Union of Pure and Applied Chemistry (IUPAC) but is not yet in wide use. In this text, we use the standard U.S. notation for group numbers (1A–8A and 1B–8B).

Distribution of Elements on Earth and in Living Systems

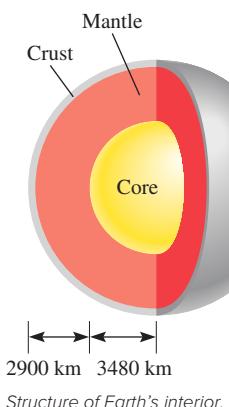
The majority of elements are naturally occurring. How are these elements distributed on Earth, and which are essential to living systems?

Earth's crust extends from the surface to a depth of about 40 km (about 25 mi). Because of technical difficulties, scientists have not been able to study the inner portions of Earth as easily as the crust. Nevertheless, it is believed that there is a solid core consisting mostly of iron at the center of Earth. Surrounding the core is a layer called the *mantle*, which consists of hot fluid containing iron, carbon, silicon, and sulfur.

Of the 83 elements that are found in nature, 12 make up 99.7 percent of Earth's crust by mass. They are, in decreasing order of natural abundance, oxygen (O), silicon (Si), aluminum (Al), iron (Fe), calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), titanium (Ti), hydrogen (H), phosphorus (P), and manganese (Mn). In discussing the natural abundance of

the elements, we should keep in mind that (1) the elements are not evenly distributed throughout Earth's crust, and (2) most elements occur in combined forms. These facts provide the basis for most methods of obtaining pure elements from their compounds, as we will see in later chapters.

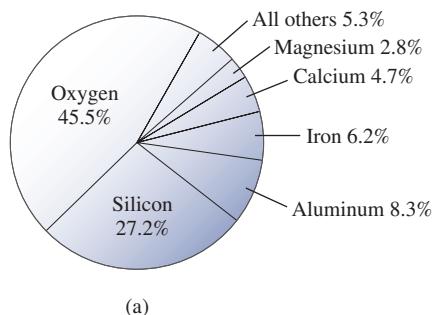
The accompanying table lists the essential elements in the human body. Of special interest are the *trace elements*, such as iron (Fe), copper (Cu), zinc (Zn), iodine (I), and cobalt (Co), which together make up about 0.1 percent of the body's mass. These elements are necessary for biological functions such as growth, transport of oxygen for metabolism, and defense against disease. There is a delicate balance in the amounts of these elements in the human body. Too much or too little over an extended period of time can lead to serious illness, retardation, or even death.



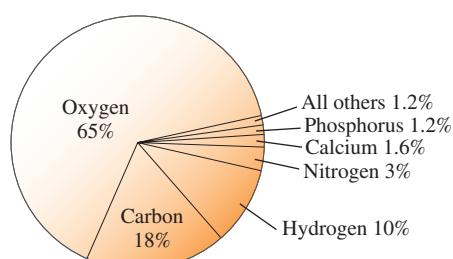
Essential Elements in the Human Body

Element	Percent by Mass*	Element	Percent by Mass*
Oxygen	65	Sodium	0.1
Carbon	18	Magnesium	0.05
Hydrogen	10	Iron	<0.05
Nitrogen	3	Cobalt	<0.05
Calcium	1.6	Copper	<0.05
Phosphorus	1.2	Zinc	<0.05
Potassium	0.2	Iodine	<0.05
Sulfur	0.2	Selenium	<0.01
Chlorine	0.2	Fluorine	<0.01

*Percent by mass gives the mass of the element in grams present in a 100-g sample.



(a) Natural abundance of the elements in percent by mass. For example, oxygen's abundance is 45.5 percent. This means that in a 100-g sample of Earth's crust there are, on the average, 45.5 g of the element oxygen.



(b) Abundance of elements in the human body in percent by mass.

known elements are metals; only 17 elements are nonmetals, and 8 elements are metalloids. From left to right across any period, the physical and chemical properties of the elements change gradually from metallic to nonmetallic.

Elements are often referred to collectively by their periodic table group number (Group 1A, Group 2A, and so on). However, for convenience, some element groups have been given special names. *The Group 1A elements (Li, Na, K, Rb, Cs, and Fr)* are called **alkali metals**, and *the Group 2A elements (Be, Mg, Ca, Sr, Ba, and Ra)* are called **alkaline earth metals**. *Elements in Group 7A (F, Cl, Br, I, and At)* are known as **halogens**, and *elements in Group 8A (He, Ne, Ar, Kr, Xe, and Rn)* are called **noble gases**, or *rare gases*.

The periodic table is a handy tool that correlates the properties of the elements in a systematic way and helps us to make predictions about chemical behavior. We will take a closer look at this keystone of chemistry in Chapter 8.

The Chemistry in Action essay “Distribution of Elements on Earth and in Living Systems” describes the distribution of the elements on Earth and in the human body.

Review of Concepts & Facts

- 2.4.1 In viewing the periodic table, do chemical properties change more markedly across a period or down a group?
- 2.4.2 Identify the following as a metal, metalloid, or nonmetal: (a) K, (b) Se, (c) Sb, (d) W.

2.5 Molecules and Ions

Of all the elements, only the six noble gases in Group 8A of the periodic table (He, Ne, Ar, Kr, Xe, and Rn) exist in nature as single atoms. For this reason, they are called *monatomic* (meaning “one atom”) gases. Most matter is composed of molecules or ions formed by atoms.

Molecules

We will discuss the nature of chemical bonds in Chapters 9 and 10.

Elements that exist as diatomic molecules.

A **molecule** is an aggregate of *at least two atoms in a definite arrangement held together by chemical forces* (also called *chemical bonds*). A molecule may contain atoms of the same element or atoms of two or more elements joined in a fixed ratio, in accordance with the law of definite proportions stated in Section 2.1. Thus, a molecule is not necessarily a compound, which, by definition, is made up of two or more elements (see Section 1.4). Hydrogen gas, for example, is a pure element, but it consists of molecules made up of two H atoms each. Water, on the other hand, is a molecular compound that contains hydrogen and oxygen in a ratio of two H atoms and one O atom. Like atoms, molecules are electrically neutral.

The hydrogen molecule, symbolized as H_2 , is called a **diatomic molecule**, because it *contains only two atoms*. Other elements that normally exist as diatomic molecules are nitrogen (N_2) and oxygen (O_2), as well as the Group 7A elements—fluorine (F_2), chlorine (Cl_2), bromine (Br_2), and iodine (I_2). Of course, a diatomic molecule can contain atoms of different elements. Examples are hydrogen chloride (HCl) and carbon monoxide (CO).

The vast majority of molecules contain more than two atoms. They can be atoms of the same element, as in ozone (O_3), which is made up of three atoms of oxygen, or they can be combinations of two or more different elements. *Molecules containing more than two atoms* are called **polyatomic molecules**. Like ozone, water (H_2O) and ammonia (NH_3) are polyatomic molecules.

Ions

An **ion** is an atom or a group of atoms that has a net positive or negative charge. The number of positively charged protons in the nucleus of an atom remains the same during ordinary chemical changes (called chemical reactions), but negatively

charged electrons may be lost or gained. The loss of one or more electrons from a neutral atom results in a **cation**, *an ion with a net positive charge*. For example, a sodium atom (Na) can readily lose an electron to become a sodium cation, which is represented by Na^+ :

In Chapter 8 we will see why atoms of different elements gain (or lose) a specific number of electrons.

Na Atom	Na⁺ Ion
11 protons	11 protons
11 electrons	10 electrons

On the other hand, an ***anion*** is *an ion whose net charge is negative* due to an increase in the number of electrons. A chlorine atom (Cl), for instance, can gain an electron to become the chloride ion Cl⁻:

Cl Atom	Cl⁻ Ion
17 protons	17 protons
17 electrons	18 electrons

Sodium chloride (NaCl), ordinary table salt, is called an ***ionic compound***, because it is formed from cations and anions.

An atom can lose or gain more than one electron. Examples of ions formed by the loss or gain of more than one electron are Mg^{2+} , Fe^{3+} , S^{2-} , and N^{3-} . These ions, as well as Na^+ and Cl^- , are called ***monatomic ions***, because they *contain only one atom*. Figure 2.11 shows the charges of a number of monatomic ions. With very few exceptions, metals tend to form cations and nonmetals form anions.

In addition, two or more atoms can combine to form an ion that has a net positive or net negative charge. **Polyatomic ions** such as OH^- (hydroxide ion), CN^- (cyanide ion), and NH_4^+ (ammonium ion) are *ions containing more than one atom*.

Review of Concepts & Facts

- 2.5.1** What does S_8 signify? How does it differ from $8S$?

2.5.2 Determine the number of protons and electrons for the following ions:
(a) P^{3-} , (b) Ti^{4+} , (c) Ge^{2+} .

2.5.3 What is the symbol and charge for an ion containing 24 protons and 22 electrons?

Figure 2.11 Common monatomic ions arranged according to their positions in the periodic table. Note that the Hg_2^{2+} ion contains two atoms.

2.6 Chemical Formulas

Chemists use **chemical formulas** to express the composition of molecules and ionic compounds in terms of chemical symbols. By composition we mean not only the elements present but also the ratios in which the atoms are combined. Here we are concerned with two types of formulas: molecular formulas and empirical formulas.

Molecular Formulas

A **molecular formula** shows the exact number of atoms of each element in the smallest unit of a substance. In our discussion of molecules, each example was given with its molecular formula in parentheses. Thus, H_2 is the molecular formula for hydrogen, O_2 is oxygen, O_3 is ozone, and H_2O is water. The subscript numeral indicates the number of atoms of an element present. There is no subscript for O in H_2O because there is only one atom of oxygen in a molecule of water, and so the number “one” is omitted from the formula. Note that oxygen (O_2) and ozone (O_3) are allotropes of oxygen. An **allotrope** is one of two or more distinct forms of an element. Two allotropic forms of the element carbon—diamond and graphite—are dramatically different not only in properties but also in their relative cost.

Molecular Models

See back endpaper for color codes for atoms.

Molecules are too small for us to observe directly. An effective means of visualizing them is by the use of molecular models. Two standard types of molecular models are currently in use: *ball-and-stick* models and *space-filling* models (Figure 2.12). In ball-and-stick model kits, the atoms are wooden or plastic balls with holes in them. Sticks or springs are used to represent chemical bonds. The angles they form between atoms approximate the bond angles in actual molecules. With the exception of the H atom, the balls are all the same size and each type of atom is represented by a specific color. In space-filling models, atoms are represented by truncated balls held together by snap fasteners, so that the bonds are not visible. The balls are proportional in size to atoms.

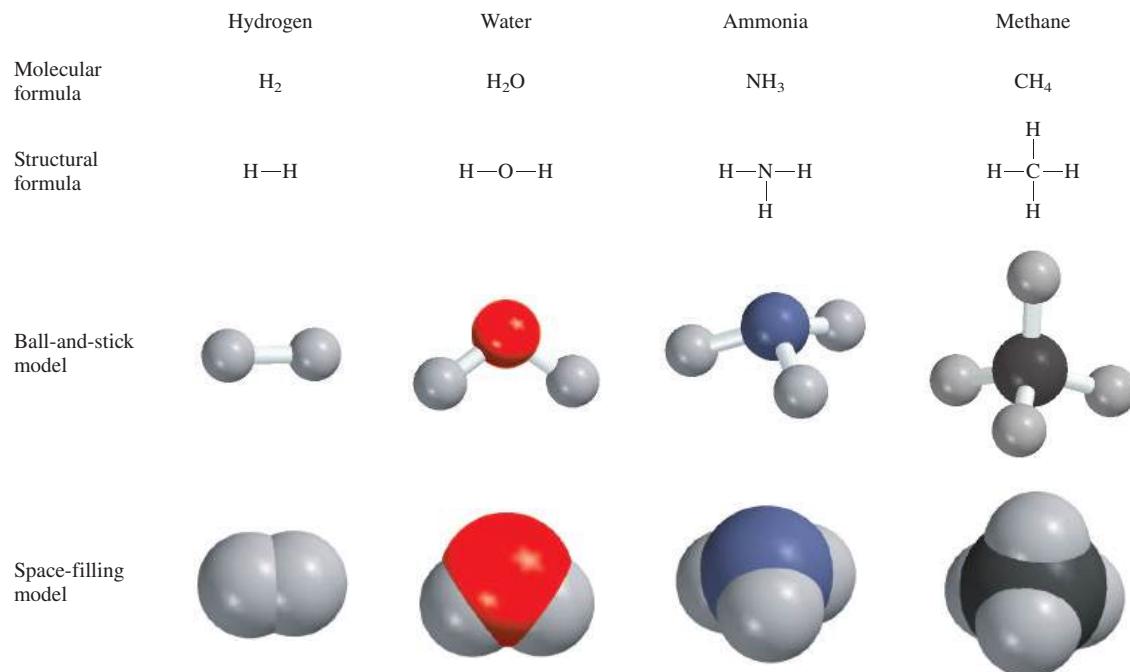


Figure 2.12 Molecular and structural formulas and molecular models of four common molecules.

The first step toward building a molecular model is writing the *structural formula*, which shows how atoms are bonded to one another in a molecule. For example, it is known that each of the two H atoms is bonded to an O atom in the water molecule. Therefore, the structural formula of water is H—O—H. A line connecting the two atomic symbols represents a chemical bond.

Ball-and-stick models show the three-dimensional arrangement of atoms clearly, and they are fairly easy to construct. However, the balls are not proportional to the size of atoms. Furthermore, the sticks greatly exaggerate the space between atoms in a molecule. Space-filling models are more accurate because they show the variation in atomic size. Their drawbacks are that they are time consuming to put together and they do not show the three-dimensional positions of atoms very well. Molecular modeling software can also be used to create ball-and-stick and space-filling models. We will use both models extensively in this text.

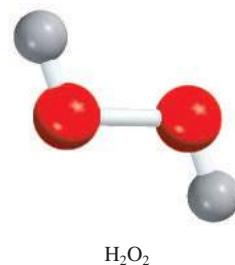
Empirical Formulas

The molecular formula of hydrogen peroxide, a substance used as an antiseptic and as a bleaching agent for textiles and hair, is H_2O_2 . This formula indicates that each hydrogen peroxide molecule consists of two hydrogen atoms and two oxygen atoms. The ratio of hydrogen to oxygen atoms in this molecule is 2:2 or 1:1. The empirical formula of hydrogen peroxide is HO. Thus, the *empirical formula tells us which elements are present and the simplest whole-number ratio of their atoms*. However, empirical formulas do not necessarily tell us the actual number of atoms in a given molecule. As another example, consider the compound hydrazine (N_2H_4), which is used as a rocket fuel. The empirical formula of hydrazine is NH_2 . Although the ratio of nitrogen to hydrogen is 1:2 in both the molecular formula (N_2H_4) and the empirical formula (NH_2), only the molecular formula tells us the actual number of N atoms (two) and H atoms (four) present in a hydrazine molecule.

Empirical formulas are the *simpliest* chemical formulas; they are written by reducing the subscripts in the molecular formulas to the smallest possible whole numbers. Molecular formulas are the *true* formulas of molecules. If we know the molecular formula, we also know the empirical formula, but the reverse is not true. Why, then, do chemists bother with empirical formulas? As we will see in Chapter 3, when chemists analyze an unknown compound, the first step is usually the determination of the compound's empirical formula. With additional information, it is possible to deduce the molecular formula.

For many molecules, the molecular formula and the empirical formula are one and the same. Some examples are water (H_2O), ammonia (NH_3), carbon dioxide (CO_2), and methane (CH_4).

Examples 2.2 and 2.3 deal with writing molecular formulas from molecular models and writing empirical formulas from molecular formulas.



The word *empirical* means "derived from experiment." As we will see in Chapter 3, empirical formulas are determined experimentally.

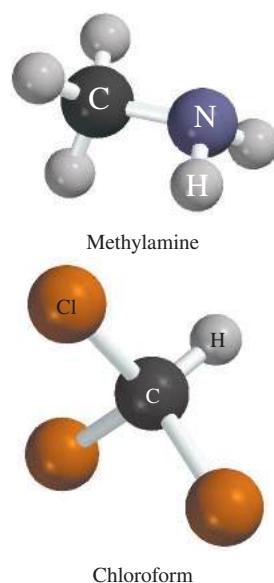
Example 2.2

Write the molecular formula of methylamine, a colorless gas used in the production of pharmaceuticals and pesticides, from its ball-and-stick model, shown here.

Solution Refer to the labels (also see end papers). There are five H atoms, one C atom, and one N atom. Therefore, the molecular formula is CH_5N . However, the standard way of writing the molecular formula for methylamine is CH_3NH_2 because it shows how the atoms are joined in the molecule.

Practice Exercise Write the molecular formula of chloroform, which is used as a solvent and a cleaning agent. The ball-and-stick model of chloroform is shown here.

Similar problems: 2.47, 2.48.



Example 2.3

Write the empirical formulas for the following molecules: (a) diborane (B_2H_6), used in rocket propellants; (b) dimethyl fumarate ($C_8H_{12}O_4$), a substance used to treat psoriasis, a skin disease; and (c) vanillin ($C_8H_8O_3$), a flavoring agent used in foods and beverages.

Strategy Recall that to write the empirical formula, the subscripts in the molecular formula must be converted to the smallest possible whole numbers.

Solution

- There are two boron atoms and six hydrogen atoms in diborane. Dividing the subscripts by 2, we obtain the empirical formula BH_3 .
- In dimethyl fumarate there are 8 carbon atoms, 12 hydrogen atoms, and 4 oxygen atoms. Dividing the subscripts by 4, we obtain the empirical formula C_2H_3O . Note that if we had divided the subscripts by 2, we would have obtained the formula $C_4H_6O_2$. Although the ratio of carbon to hydrogen to oxygen atoms in $C_4H_6O_2$ is the same as that in C_2H_3O (2:3:1), $C_4H_6O_2$ is not the simplest formula because its subscripts are not in the smallest whole-number ratio.
- Because the subscripts in $C_8H_8O_3$ are already the smallest possible whole numbers, the empirical formula for vanillin is the same as its molecular formula.

Practice Exercise

Write the empirical formula for caffeine ($C_8H_{10}N_4O_2$), a stimulant found in tea and coffee.

Similar problems: 2.45, 2.46.

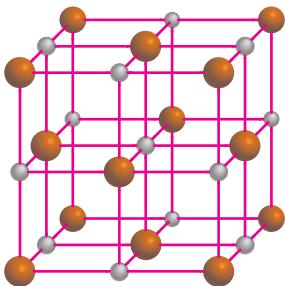


Sodium metal reacting with chlorine gas to form sodium chloride.

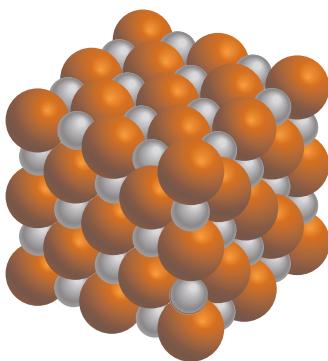
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Formula of Ionic Compounds

The formulas of ionic compounds are usually the same as their empirical formulas, because ionic compounds do not consist of discrete molecular units. For example, a solid sample of sodium chloride ($NaCl$) consists of equal numbers of Na^+ and Cl^- ions arranged in a three-dimensional network called a *lattice* (Figure 2.13). In such a compound there is a 1:1 ratio of cations to anions so that the compound is electrically neutral. As you can see in Figure 2.13, no Na^+ ion in $NaCl$ is associated with just one particular Cl^- ion. In fact, each Na^+ ion is equally held by six surrounding Cl^- ions and vice versa. Thus, $NaCl$ is the empirical formula for sodium chloride. In other ionic compounds, the actual structure may be different, but the arrangement of cations and anions is always such that the compounds are all electrically neutral. Note that the charges on the cation and anion are not shown in the formula for an ionic compound.



(a)



(b)



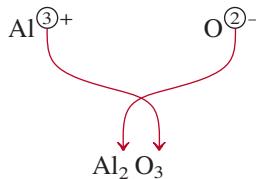
(c)

Figure 2.13 (a) Structure of solid $NaCl$. (b) In reality, the cations are in contact with the anions. In both (a) and (b), the smaller spheres represent Na^+ ions and the larger spheres, Cl^- ions. (c) Crystals of $NaCl$.

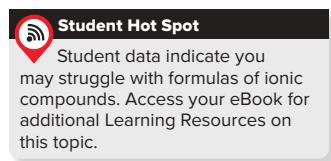
(c): ©Charles D. Winters/Science Source

For ionic compounds to be electrically neutral, the sum of the charges on the cation and anion in each formula unit must be zero. If the charges on the cation and anion are numerically different, we apply the following rule to make the formula electrically neutral: *The subscript of the cation is numerically equal to the charge on the anion, and the subscript of the anion is numerically equal to the charge on the cation.* If the charges are numerically equal, then no subscripts are necessary. This rule follows from the fact that because the formulas of ionic compounds are usually empirical formulas, the subscripts must always be reduced to the smallest ratios. Let us consider some examples.

- **Potassium Bromide.** The potassium cation K^+ and the bromine anion Br^- combine to form the ionic compound potassium bromide. The sum of the charges is $+1 + (-1) = 0$, so no subscripts are necessary. The formula is KBr .
- **Zinc Iodide.** The zinc cation Zn^{2+} and the iodine anion I^- combine to form zinc iodide. The sum of the charges of one Zn^{2+} ion and one I^- ion is $+2 + (-1) = +1$. To make the charges add up to zero we multiply the -1 charge of the anion by 2 and add the subscript “2” to the symbol for iodine. Therefore the formula for zinc iodide is ZnI_2 .
- **Aluminum Oxide.** The cation is Al^{3+} and the oxygen anion is O^{2-} . The following diagram helps us determine the subscripts for the compound formed by the cation and the anion:



Refer to Figure 2.11 for charges of cations and anions.



The sum of the charges is $2(+3) + 3(-2) = 0$. Thus, the formula for aluminum oxide is Al_2O_3 .

Note that in each of the three examples, the subscripts are in the smallest ratios.

Example 2.4

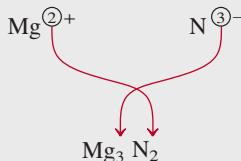
Magnesium nitride is used to prepare Borazon, a very hard compound used in cutting tools and machine parts. Write the formula of magnesium nitride, containing the Mg^{2+} and N^{3-} ions.

Strategy Our guide for writing formulas for ionic compounds is electrical neutrality; that is, the total charge on the cation(s) must be equal to the total charge on the anion(s). Because the charges on the Mg^{2+} and N^{3-} ions are not equal, we know the formula cannot be MgN . Instead, we write the formula as Mg_xN_y , where x and y are subscripts to be determined.

Solution To satisfy electrical neutrality, the following relationship must hold:

$$(2x) + (-3y) = 0$$

Solving, we obtain $x/y = 3/2$. Setting $x = 3$ and $y = 2$, we write



When magnesium burns in air, it forms both magnesium oxide and magnesium nitride.

©Charles D. Winters/Science Source

Check The subscripts are reduced to the smallest whole-number ratio of the atoms because the chemical formula of an ionic compound is usually its empirical formula.

Practice Exercise Write the formulas of the following ionic compounds: (a) chromium sulfate (containing the Cr^{3+} and SO_4^{2-} ions) and (b) titanium oxide (containing the Ti^{4+} and O^{2-} ions).

Similar problems: 2.43, 2.44.

Review of Concepts & Facts

- 2.6.1** Match each of the diagrams shown here with the following ionic compounds: Al_2O_3 , LiH , Na_2S , $\text{Mg}(\text{NO}_3)_2$. (Green spheres represent cations and red spheres represent anions.)



- 2.6.2** Write the formulas for the following ionic compounds: (a) calcium iodide (containing the Ca^{2+} and I^- ions), (b) gallium sulfide (containing the Ga^{3+} and S^{2-} ions).

2.7 Naming Compounds

When chemistry was a young science and the number of known compounds was small, it was possible to memorize their names. Many of the names were derived from their physical appearance, properties, origin, or application—for example, milk of magnesia, laughing gas, limestone, caustic soda, lye, washing soda, and baking soda.

Today the number of known compounds is well over 66 million. Fortunately, it is not necessary to memorize their names. Over the years chemists have devised a clear system for naming chemical substances. The rules are accepted worldwide, facilitating communication among chemists and providing a useful way of labeling an overwhelming variety of substances. Mastering these rules now will prove beneficial almost immediately as we proceed with our study of chemistry.

To begin our discussion of chemical *nomenclature*, the naming of chemical compounds, we must first distinguish between inorganic and organic compounds. **Organic compounds** contain carbon, usually in combination with elements such as hydrogen, oxygen, nitrogen, and sulfur. All other compounds are classified as **inorganic compounds**. For convenience, some carbon-containing compounds, such as carbon monoxide (CO), carbon dioxide (CO_2), carbon disulfide (CS_2), compounds containing the cyanide group (CN^-), and carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) groups are considered to be inorganic compounds. Section 2.8 gives a brief introduction to organic compounds.

To organize and simplify our venture into naming compounds, we can divide inorganic compounds into four categories: ionic compounds, molecular compounds, acids and bases, and hydrates.

Ionic Compounds

In Section 2.5 we learned that ionic compounds are made up of cations (positive ions) and anions (negative ions). With the important exception of the ammonium ion, NH_4^+ , all cations of interest to us are derived from metal atoms. Metal cations take their names from the elements. For example,

1A	2A						8A
Li							N
Na	Mg						O
K	Ca						F
Rb	Sr						Cl
Cs	Ba						Br
							I

The most reactive metals (green) and the most reactive nonmetals (blue) combine to form ionic compounds.

Video
Formation of an Ionic Compound

Element	Name of Cation		
Na	sodium	Na^+	sodium ion (or sodium cation)
K	potassium	K^+	potassium ion (or potassium cation)
Mg	magnesium	Mg^{2+}	magnesium ion (or magnesium cation)
Al	aluminum	Al^{3+}	aluminum ion (or aluminum cation)

Many ionic compounds are **binary compounds**, or compounds formed from just two elements. For binary compounds, the first element named is the metal cation, followed by the nonmetallic anion. Thus, NaCl is sodium chloride. The anion is named by taking the first part of the element name (chlorine) and adding “-ide.” Potassium

Table 2.2**The “-ide” Nomenclature of Some Common Monatomic Anions According to Their Positions in the Periodic Table**

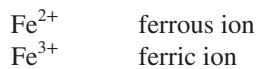
Group 4A	Group 5A	Group 6A	Group 7A
C carbide (C^{4-})*	N nitride (N^{3-})	O oxide (O^{2-})	F fluoride (F^-)
Si silicide (Si^{4-})	P phosphide (P^{3-})	S sulfide (S^{2-})	Cl chloride (Cl^-)
		Se selenide (Se^{2-})	Br bromide (Br^-)
		Te telluride (Te^{2-})	I iodide (I^-)

*The word “carbide” is also used for the anion C_2^{2-} .

bromide (KBr), zinc iodide (ZnI_2), and aluminum oxide (Al_2O_3) are also binary compounds. Table 2.2 shows the “-ide” nomenclature of some common monatomic anions according to their positions in the periodic table.

The “-ide” ending is also used for certain anion groups containing different elements, such as hydroxide (OH^-) and cyanide (CN^-). Thus, the compounds LiOH and KCN are named lithium hydroxide and potassium cyanide, respectively. These and a number of other such ionic substances are called **ternary compounds**, meaning *compounds consisting of three elements*. Table 2.3 lists alphabetically the names of a number of common cations and anions.

Certain metals, especially the *transition metals*, can form more than one type of cation. Take iron as an example. Iron can form two cations: Fe^{2+} and Fe^{3+} . An older nomenclature system that is still in limited use assigns the ending “-ous” to the cation with fewer positive charges and the ending “-ic” to the cation with more positive charges:

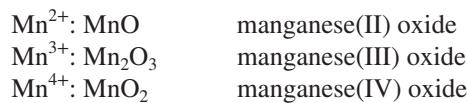


The names of the compounds that these iron ions form with chlorine would thus be

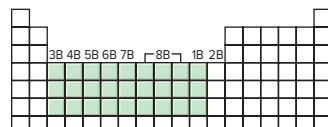


This method of naming ions has some distinct limitations. First, the “-ous” and “-ic” suffixes do not provide information regarding the actual charges of the two cations involved. Thus, the ferric ion is Fe^{3+} , but the cation of copper named cupric has the formula Cu^{2+} . In addition, the “-ous” and “-ic” designations provide names for only two different elemental cations.

Some metals can form three or more ions with different positive charges in compounds. Therefore, it has become increasingly common to designate different cations with Roman numerals. This is called the Stock[†] system. In this system, the Roman numeral I indicates one positive charge on the metal cation, II means two positive charges on the metal cation, and so on. For example, manganese (Mn) atoms can assume several different positive charges:



These names are pronounced “manganese-two oxide,” “manganese-three oxide,” and “manganese-four oxide.” Using the Stock system, we denote the ferrous ion and the ferric ion as iron(II) and iron(III), respectively; ferrous chloride becomes iron(II)



The transition metals are the elements in Groups 1B and 3B–8B (see Figure 2.10).



FeCl_2 (left) and FeCl_3 (right).
©McGraw-Hill Education/Ken Karp

Nontransition metals such as tin (Sn) and lead (Pb) can also form more than one type of cations.

[†]Alfred E. Stock (1876–1946). German chemist. Stock did most of his research in the synthesis and characterization of boron, beryllium, and silicon compounds. He was the first scientist to explore the dangers of mercury poisoning.

Table 2.3**Names and Formulas of Some Common Inorganic Cations and Anions**

Cation	Anion
aluminum (Al^{3+})	bromide (Br^-)
ammonium (NH_4^+)	carbonate (CO_3^{2-})
barium (Ba^{2+})	chlorate (ClO_3^-)
cadmium (Cd^{2+})	chloride (Cl^-)
calcium (Ca^{2+})	chromate (CrO_4^{2-})
cesium (Cs^+)	cyanide (CN^-)
chromium(III) or chromic (Cr^{3+})	dichromate ($\text{Cr}_2\text{O}_7^{2-}$)
cobalt(II) or cobaltous (Co^{2+})	dihydrogen phosphate (H_2PO_4^-)
copper(I) or cuprous (Cu^+)	fluoride (F^-)
copper(II) or cupric (Cu^{2+})	hydride (H^-)
hydrogen (H^+)	hydrogen carbonate or bicarbonate (HCO_3^-)
iron(II) or ferrous (Fe^{2+})	hydrogen phosphate (HPO_4^{2-})
iron(III) or ferric (Fe^{3+})	hydrogen sulfate or bisulfate (HSO_4^-)
lead(II) or plumbous (Pb^{2+})	hydroxide (OH^-)
lithium (Li^+)	iodide (I^-)
magnesium (Mg^{2+})	nitrate (NO_3^-)
manganese(II) or manganous (Mn^{2+})	nitride (N^{3-})
mercury(I) or mercurous (Hg_2^{2+})*	nitrite (NO_2^-)
mercury(II) or mercuric (Hg^{2+})	oxide (O^{2-})
potassium (K^+)	permanganate (MnO_4^-)
rubidium (Rb^+)	peroxide (O_2^{2-})
silver (Ag^+)	phosphate (PO_4^{3-})
sodium (Na^+)	sulfate (SO_4^{2-})
strontium (Sr^{2+})	sulfide (S^{2-})
tin(II) or stannous (Sn^{2+})	sulfite (SO_3^{2-})
zinc (Zn^{2+})	thiocyanate (SCN^-)

*Mercury(I) exists as a pair as shown.


Student Hot Spot

Student data indicate you may struggle with naming an ionic compound from its formula. Access your eBook for additional Learning Resources on this topic.

chloride, and ferric chloride is called iron(III) chloride. In keeping with modern practice, we will favor the Stock system of naming compounds in this textbook.

Examples 2.5 and 2.6 illustrate how to name ionic compounds and write formulas for ionic compounds based on the information given in Figure 2.11 and Tables 2.2 and 2.3.

Example 2.5

Name the following compounds: (a) $\text{Fe}(\text{NO}_3)_2$, (b) Na_2HPO_4 , and (c) $(\text{NH}_4)_2\text{SO}_3$.

Strategy Our reference for the names of cations and anions is Table 2.3. Keep in mind that if a metal can form cations of different charges (see Figure 2.11), we need to use the Stock system.

Solution

- (a) The nitrate ion (NO_3^-) bears one negative charge, so the iron ion must have two positive charges. Because iron forms both Fe^{2+} and Fe^{3+} ions, we need to use the Stock system and call the compound iron(II) nitrate.

(Continued)

- (b) The cation is Na^+ and the anion is HPO_4^{2-} (hydrogen phosphate). Because sodium only forms one type of ion (Na^+), there is no need to use sodium(I) in the name. The compound is sodium hydrogen phosphate.
- (c) The cation is NH_4^+ (ammonium ion) and the anion is SO_3^{2-} (sulfite ion). The compound is ammonium sulfite.

Practice Exercise Name the following compounds: (a) PbO and (b) LiClO_3 .

Similar problems: 2.57(b), (e), (f).

Example 2.6

Write chemical formulas for the following compounds: (a) mercury(I) nitrate, (b) cesium oxide, and (c) strontium nitride.

Strategy We refer to Table 2.3 for the formulas of cations and anions. Recall that the Roman numerals in the Stock system provide useful information about the charges of the cation.

Solution

- (a) The Roman numeral shows that the mercury ion bears a +1 charge. According to Table 2.3, however, the mercury(I) ion is diatomic (that is, Hg_2^{2+}) and the nitrate ion is NO_3^- . Therefore, the formula is $\text{Hg}_2(\text{NO}_3)_2$.
- (b) Each oxide ion bears two negative charges, and each cesium ion bears one positive charge (cesium is in Group 1A, as is sodium). Therefore, the formula is Cs_2O .
- (c) Each strontium ion (Sr^{2+}) bears two positive charges, and each nitride ion (N^{3-}) bears three negative charges. To make the sum of the charges equal zero, we must adjust the numbers of cations and anions:

$$3(+2) + 2(-3) = 0$$

Thus, the formula is Sr_3N_2 .

Practice Exercise Write formulas for the following ionic compounds: (a) rubidium sulfate and (b) barium hydride.

Similar problems: 2.59(a), (b), (d), (h), (i).

Student Hot Spot

Student data indicate you may struggle with naming an ionic compound from its formula. Access your eBook for additional Learning Resources on this topic.

Note that the subscripts of this ionic compound are not reduced to the smallest ratio because the $\text{Hg}(I)$ ion exists as a pair or dimer.

Molecular Compounds

Unlike ionic compounds, molecular compounds contain individual molecular units. They are usually composed of nonmetallic elements (see Figure 2.10). Many molecular compounds are binary compounds. Naming binary molecular compounds is similar to naming binary ionic compounds. We place the name of the first element in the formula first, and the second element is named by adding “-ide” to the root of the element name. Some examples are

HCl	hydrogen chloride
HBr	hydrogen bromide
SiC	silicon carbide

It is quite common for one pair of elements to form several different compounds. In these cases, confusion in naming the compounds is avoided by the use of Greek prefixes

Table 2.4

Greek Prefixes Used in Naming Molecular Compounds	
Prefix	Meaning
mono-	1
di-	2
tri-	3
tetra-	4
penta-	5
hexa-	6
hepta-	7
octa-	8
nona-	9
deca-	10

to denote the number of atoms of each element present (Table 2.4). Consider the following examples:

CO	carbon monoxide
CO ₂	carbon dioxide
SO ₂	sulfur dioxide
SO ₃	sulfur trioxide
NO ₂	nitrogen dioxide
N ₂ O ₄	dinitrogen tetroxide

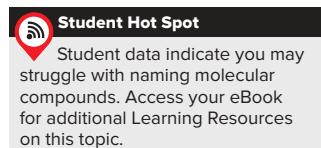
The following guidelines are helpful in naming compounds with prefixes:

- The prefix “mono-” may be omitted for the first element. For example, PCl₃ is named phosphorus trichloride, not monophosphorus trichloride. Thus, the absence of a prefix for the first element usually means there is only one atom of that element present in the molecule.
- For oxides, the ending “a” in the prefix is sometimes omitted. For example, N₂O₄ may be called dinitrogen tetroxide rather than dinitrogen tetraoxide.

Exceptions to the use of Greek prefixes are molecular compounds containing hydrogen. Traditionally, many of these compounds are called either by their common, nonsystematic names or by names that do not specifically indicate the number of H atoms present:

B ₂ H ₆	diborane
CH ₄	methane
SiH ₄	silane
NH ₃	ammonia
PH ₃	phosphine
H ₂ O	water
H ₂ S	hydrogen sulfide

Binary compounds containing carbon and hydrogen are organic compounds; they do not follow the same naming conventions. We will discuss the naming of organic compounds in Chapter 24.



Note that even the order of writing the elements in the formulas for hydrogen compounds is irregular. In water and hydrogen sulfide, H is written first, whereas it appears last in the other compounds.

Writing formulas for molecular compounds is usually straightforward. Thus, the name arsenic trifluoride means that there are three F atoms and one As atom in each molecule, and the molecular formula is AsF₃. Note that the order of elements in the formula is the same as in its name.

Example 2.7

Name the following molecular compounds: (a) PBr₅ and (b) As₂O₅.

Strategy We refer to Table 2.4 for the prefixes used in naming molecular compounds.

Solution

- Because there are five bromine atoms present, the compound is phosphorus pentabromide.
- There are two arsenic atoms and five oxygen atoms present, so the compound is diarsenic pentoxide. Note that the “a” is omitted in “penta.”

Practice Exercise Name the following molecular compounds: (a) NF₃ and (b) Cl₂O₇.

Similar problems: 2.57(c), (i), (j).

Example 2.8

Write chemical formulas for the following molecular compounds: (a) bromine trifluoride and (b) diboron trioxide.

Strategy We refer to Table 2.4 for the prefixes used in naming molecular compounds.

Solution

- (a) Because there are three fluorine atoms and one bromine atom present, the formula is BrF_3 .
- (b) There are two boron atoms and three oxygen atoms present, so the formula is B_2O_3 .

Practice Exercise Write chemical formulas for the following molecular compounds:

- (a) sulfur tetrafluoride and (b) dinitrogen pentoxide.

Similar problems: 2.59(g), (j).

Figure 2.14 summarizes the steps for naming ionic and binary molecular compounds.

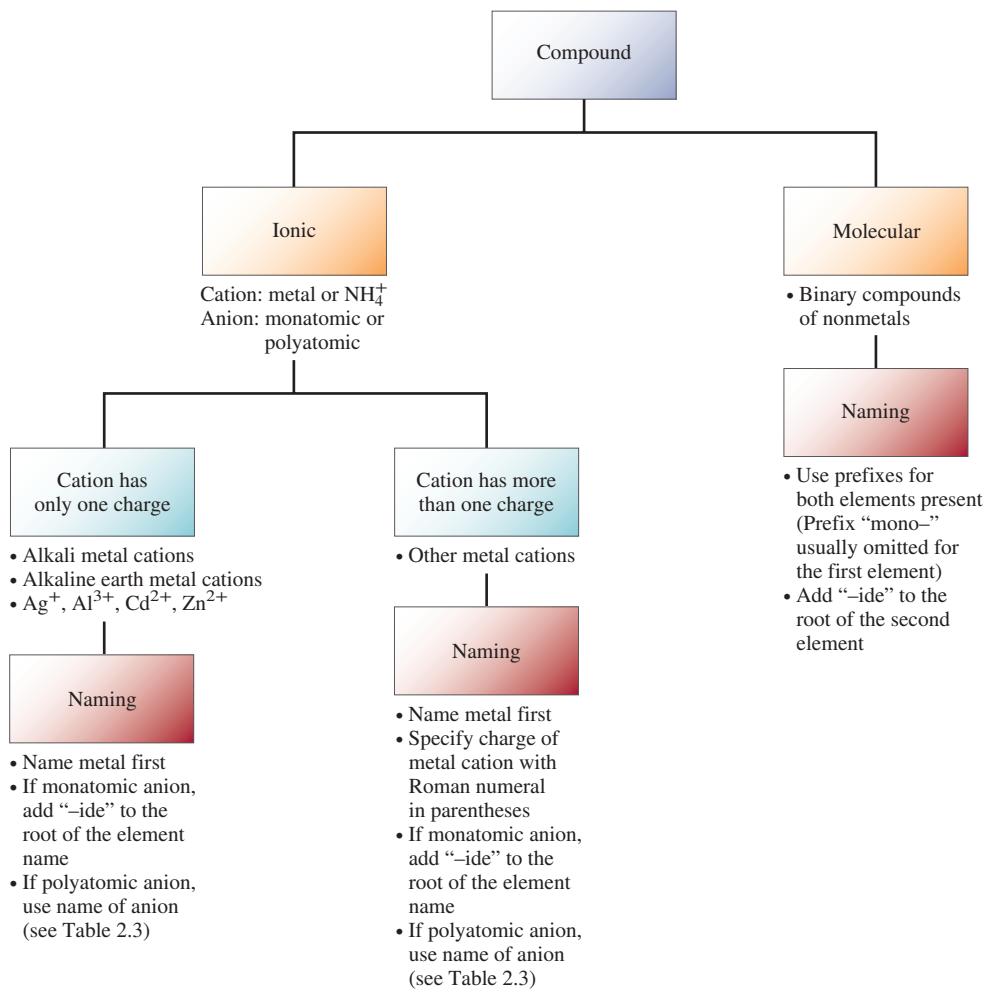


Figure 2.14 Steps for naming ionic and binary molecular compounds.



When dissolved in water, the HCl molecule is converted to the H^+ and Cl^- ions. The H^+ ion is associated with one or more water molecules, and is usually represented as H_3O^+ .

Acids and Bases

Naming Acids

An **acid** can be described as *a substance that yields hydrogen ions (H^+) when dissolved in water.* (H^+ is equivalent to one proton, and is often referred to that way.) Formulas for acids contain one or more hydrogen atoms as well as an anionic group. Anions whose names end in “-ide” form acids with a “hydro-” prefix and an “-ic” ending, as shown in Table 2.5. In some cases two different names seem to be assigned to the same chemical formula.

HCl	hydrogen chloride
HCl	hydrochloric acid

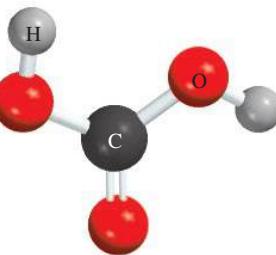
The name assigned to the compound depends on its physical state. In the gaseous or pure liquid state, HCl is a molecular compound called hydrogen chloride. When it is dissolved in water, the molecules break up into H^+ and Cl^- ions; in this state, the substance is called hydrochloric acid.

Oxoacids are acids that *contain hydrogen, oxygen, and another element (the central element).* The formulas of oxoacids are usually written with the H first, followed by the central element and then O. We use the following five common acids as our references in naming oxoacids:

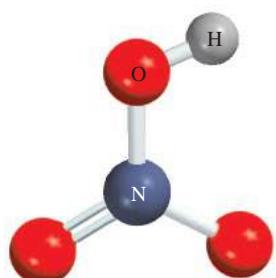
H_2CO_3	carbonic acid
HClO_3	chloric acid
HNO_3	nitric acid
H_3PO_4	phosphoric acid
H_2SO_4	sulfuric acid

Often two or more oxoacids have the same central atom but a different number of O atoms. Starting with our reference oxoacids whose names all end with “-ic,” we use the following rules to name these compounds.

1. Addition of one O atom to the “-ic” acid: The acid is called “per . . . -ic” acid. Thus, adding an O atom to HClO_3 changes chloric acid to perchloric acid, HClO_4 .
2. Removal of one O atom from the “-ic” acid: The acid is called “-ous” acid. Thus, nitric acid, HNO_3 , becomes nitrous acid, HNO_2 .
3. Removal of two O atoms from the “-ic” acid: The acid is called “hypo . . . -ous” acid. Thus, when HBrO_3 is converted to HBrO , the acid is called hypobromous acid.



H_2CO_3



HNO_3

Table 2.5 Some Simple Acids

Molecular Compound	Acid	Corresponding Anion
HF (hydrogen fluoride)	HF (hydrofluoric acid)	F^- (fluoride)
HCl (hydrogen chloride)	HCl (hydrochloric acid)	Cl^- (chloride)
HBr (hydrogen bromide)	HBr (hydrobromic acid)	Br^- (bromide)
HI (hydrogen iodide)	HI (hydroiodic acid)	I^- (iodide)
HCN (hydrogen cyanide)	HCN (hydrocyanic acid)	CN^- (cyanide)
H_2S (hydrogen sulfide)	H_2S (hydrosulfuric acid)	S^{2-} (sulfide)

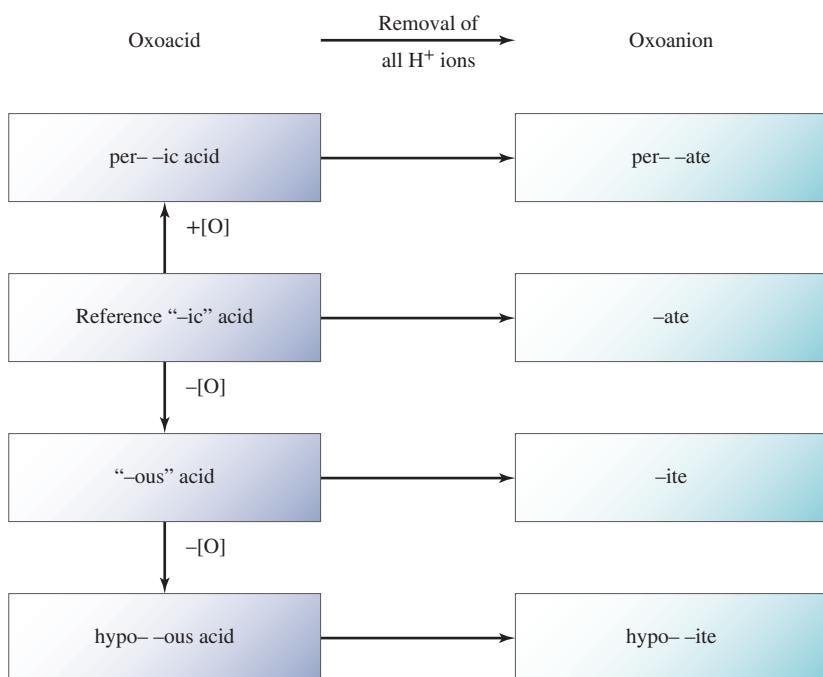


Figure 2.15 Naming oxoacids and oxoanions.

The rules for naming **oxoanions**, *anions of oxoacids*, are as follows:

- When all the H ions are removed from the “-ic” acid, the anion’s name ends with “-ate.” For example, the anion CO_3^{2-} derived from H_2CO_3 is called carbonate.
- When all the H ions are removed from the “-ous” acid, the anion’s name ends with “-ite.” Thus, the anion ClO_2^- derived from HClO_2 is called chlorite.
- The names of anions in which one or more but not all the hydrogen ions have been removed must indicate the number of H ions present. For example, consider the anions derived from phosphoric acid:

H_3PO_4	phosphoric acid
H_2PO_4^-	dihydrogen phosphate
HPO_4^{2-}	hydrogen phosphate
PO_4^{3-}	phosphate

Note that we usually omit the prefix “mono-” when there is only one H in the anion. Figure 2.15 summarizes the nomenclature for the oxoacids and oxoanions, and Table 2.6 gives the names of the oxoacids and oxoanions that contain chlorine.

Example 2.9 deals with the nomenclature for an oxoacid and an oxoanion.

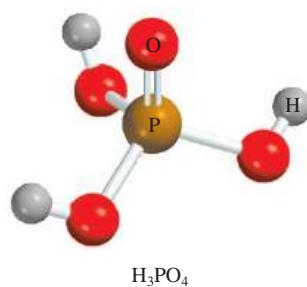


Table 2.6 Names of Oxoacids and Oxoanions That Contain Chlorine

Acid	Corresponding Anion
HClO_4 (perchloric acid)	ClO_4^- (perchlorate)
HClO_3 (chloric acid)	ClO_3^- (chlorate)
HClO_2 (chlorous acid)	ClO_2^- (chlorite)
HClO (hypochlorous acid)	ClO^- (hypochlorite)

**Student Hot Spot**

Student data indicate you may struggle with naming oxoacids and compounds with oxoanions. Access the SmartBook to view additional Learning Resources on this topic.

Example 2.9

Name the following oxoacid and oxoanions: (a) H_2SO_3 , a very unstable acid formed when $\text{SO}_2(g)$ reacts with water, (b) H_2AsO_4^- , once used to control ticks and lice on livestock, and (c) SeO_3^{2-} , used to manufacture colorless glass. H_3AsO_4 is arsenic acid, and H_2SeO_4 is selenic acid.

Strategy We refer to Figure 2.15 and Table 2.6 for the conventions used in naming oxoacids and oxoanions.

Solution

- We start with our reference acid, sulfuric acid (H_2SO_4). Because H_2SO_3 has one fewer O atom, it is called sulfurous acid.
- Because H_3AsO_4 is arsenic acid, the AsO_4^{3-} ion is named arsenate. The H_2AsO_4^- anion is formed by adding two H^+ ions to AsO_4^{3-} , so H_2AsO_4^- is called dihydrogen arsenate.
- The parent acid is H_2SeO_3 . Because the acid has one fewer O atom than selenic acid (H_2SeO_4), it is called selenous acid. Therefore, the SeO_3^{2-} anion derived from H_2SeO_3 is called selenite.

Practice Exercise Name the following oxoacid and oxoanion: (a) HBrO and (b) HSO_4^- .

Similar problems: 2.58(f).

Naming Bases

A **base** can be described as *a substance that yields hydroxide ions (OH^-) when dissolved in water*. Some examples are

NaOH	sodium hydroxide
KOH	potassium hydroxide
$\text{Ba}(\text{OH})_2$	barium hydroxide

Ammonia (NH_3), a molecular compound in the gaseous or pure liquid state, is also classified as a common base. At first glance this may seem to be an exception to the definition of a base. But note that as long as a substance *yields* hydroxide ions when dissolved in water, it need not contain hydroxide ions in its structure to be considered a base. In fact, when ammonia dissolves in water, NH_3 reacts partially with water to yield NH_4^+ and OH^- ions. Thus, it is properly classified as a base.

Hydrates

Hydrates are compounds that have a specific number of water molecules attached to them. For example, in its normal state, each unit of copper(II) sulfate has five water molecules associated with it. The systematic name for this compound is copper(II) sulfate pentahydrate, and its formula is written as $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. The water molecules can be driven off by heating. When this occurs, the resulting compound is CuSO_4 , which is sometimes called *anhydrous* copper(II) sulfate; “anhydrous” means that the compound no longer has water molecules associated with it (Figure 2.16). Some other hydrates are

$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$	barium chloride dihydrate
$\text{LiCl} \cdot \text{H}_2\text{O}$	lithium chloride monohydrate
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	magnesium sulfate heptahydrate
$\text{Sr}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	strontium nitrate tetrahydrate



Figure 2.16 $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (left) is blue; CuSO_4 (right) is white.
©McGraw-Hill Education/Ken Karp

Table 2.7 Common and Systematic Names of Some Compounds

Formula	Common Name	Systematic Name
H_2O	Water	Dihydrogen monoxide
NH_3	Ammonia	Trihydrogen nitride
CO_2	Dry ice	Solid carbon dioxide
NaCl	Table salt	Sodium chloride
N_2O	Laughing gas	Dinitrogen monoxide
CaCO_3	Marble, chalk, limestone	Calcium carbonate
CaO	Quicklime	Calcium oxide
$\text{Ca}(\text{OH})_2$	Slaked lime	Calcium hydroxide
NaHCO_3	Baking soda	Sodium hydrogen carbonate
$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$	Washing soda	Sodium carbonate decahydrate
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	Epsom salt	Magnesium sulfate heptahydrate
$\text{Mg}(\text{OH})_2$	Milk of magnesia	Magnesium hydroxide
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	Gypsum	Calcium sulfate dihydrate

Familiar Inorganic Compounds

Some compounds are better known by their common names than by their systematic chemical names. Familiar examples are listed in Table 2.7.

Review of Concepts & Facts

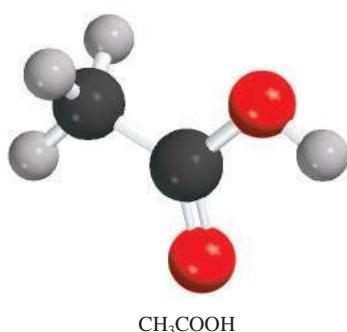
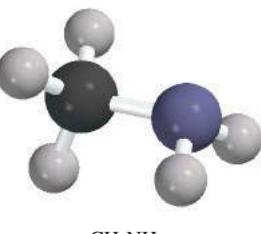
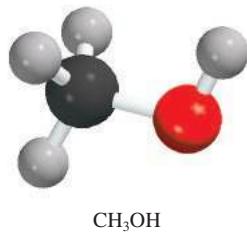
- 2.7.1 Why is it that the name for SeCl_2 , selenium dichloride, contains a prefix, but the name for SrCl_2 , strontium chloride, does not?
- 2.7.2 Why is the following question ambiguous: What is the name of HF? What additional information is needed to answer the question?
- 2.7.3 Name the following compounds: (a) Cs_2SO_3 , (b) $\text{Cu}(\text{NO}_2)_2$.
- 2.7.4 Write formulas for the following compounds: (a) cobalt(II) hydrogen sulfate, (b) chromium(III) cyanide.
- 2.7.5 What are the correct names for the following compounds? (a) BrF_5 , (b) HIO_4 .

2.8 Introduction to Organic Compounds

The simplest type of organic compounds is the *hydrocarbons*, which contain only carbon and hydrogen atoms. The hydrocarbons are used as fuels for domestic and industrial heating, for generating electricity and powering internal combustion engines, and as starting materials for the chemical industry. One class of hydrocarbons is called the *alkanes*. Table 2.8 shows the names, formulas, and molecular models of the first 10 *straight-chain* alkanes, in which the carbon chains have no branches. The name of an

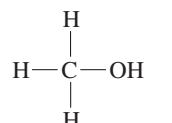
Table 2.8 The First 10 Straight-Chain Alkanes

Name	Formula	Molecular Model
Methane	CH ₄	
Ethane	C ₂ H ₆	
Propane	C ₃ H ₈	
Butane	C ₄ H ₁₀	
Pentane	C ₅ H ₁₂	
Hexane	C ₆ H ₁₄	
Heptane	C ₇ H ₁₆	
Octane	C ₈ H ₁₈	
Nonane	C ₉ H ₂₀	
Decane	C ₁₀ H ₂₂	

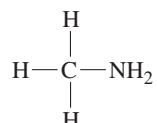


alkane depends on the number of carbon atoms in the molecule and all the names end with “-ane.” Starting with C₅H₁₂, we use the Greek prefixes in Table 2.4 to indicate the number of carbon atoms present.

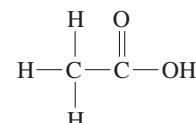
The chemistry of organic compounds is largely determined by the *functional groups*, which consist of one or a few atoms bonded in a specific way. For example, when an H atom in methane is replaced by a hydroxyl group (—OH), an amino group (—NH₂), and a carboxyl group (—COOH), the following molecules are generated:



Methanol



Methylamine



Acetic acid

The chemical properties of these molecules can be predicted based on the reactivity of the functional groups. Although the nomenclature of the major classes of organic compounds and their properties in terms of the functional groups will not be discussed

until Chapter 24, we will frequently use organic compounds as examples to illustrate chemical bonding, acid-base reactions, and other properties throughout the book.

Review of Concepts & Facts

- 2.8.1** How many different molecules can you generate by replacing one H atom with a hydroxyl group ($-\text{OH}$) in butane (see Table 2.8)?

Learning Objectives

- Outline Dalton's hypotheses about the nature of matter. (Section 2.1)
- Understand the concept of the atom and the nature of an element. (Section 2.2)
- Assess the importance of experiments conducted by Thomson, Millikan, Röntgen, and Rutherford, and how they influenced our understanding of the nature and structure of atoms. (Section 2.2)
- Summarize the different types of radiation that radioactive substances can produce. (Section 2.2)
- Describe the location and physical properties of electrons, protons, and neutrons. (Section 2.2)
- Explain the nature and importance of isotopes. (Section 2.3)
- Calculate the mass number of an isotope. (Section 2.3)
- Utilize the mass number of an isotope to solve for the number of electrons, protons, or neutrons, given other relevant information. (Section 2.3)
- Recognize the general organization of the periodic table with respect to metals, metalloids, nonmetals, groups, and periods. (Section 2.4)
- Differentiate between molecules and ions. (Section 2.5)
- Classify chemical formulas as either molecular or empirical. (Section 2.6)
- Determine formulas of ionic compounds. (Section 2.6)
- Utilize the rules of nomenclature to name the different types of compounds including ionic compounds, molecular compounds, acids, bases, oxoacids, hydrates, and simple alkanes. (Section 2.7)
- Identify the common polyatomic ions along with their formulas and charges. (Section 2.7)

Key Equations

$$\begin{aligned}\text{mass number} &= \text{number of protons} + \text{number of neutrons} \\ &= \text{atomic number} + \text{number of neutrons} \quad (2.1)\end{aligned}$$

Summary of Concepts & Facts

1. Modern chemistry began with Dalton's atomic theory, which states that all matter is composed of tiny, indivisible particles called atoms; that all atoms of the same element are identical; that compounds contain atoms of different elements combined in whole-number ratios; and that atoms are neither created nor destroyed in chemical reactions (the law of conservation of mass).
2. Atoms of constituent elements in a particular compound are always combined in the same proportions by mass (law of definite proportions). When two elements can combine to form more than one type of compound,

the masses of one element that combine with a fixed mass of the other element are in a ratio of small whole numbers (law of multiple proportions).

3. An atom consists of a very dense central nucleus containing protons and neutrons, with electrons moving about the nucleus at a relatively large distance from it.
4. Protons are positively charged, neutrons have no charge, and electrons are negatively charged. Protons and neutrons have roughly the same mass, which is about 1840 times greater than the mass of an electron.

5. The atomic number of an element is the number of protons in the nucleus of an atom of the element; it determines the identity of an element. The mass number is the sum of the number of protons and the number of neutrons in the nucleus.
6. Isotopes are atoms of the same element with the same number of protons but different numbers of neutrons.
7. Chemical formulas combine the symbols for the constituent elements with whole-number subscripts to show the type and number of atoms contained in the smallest unit of a compound.
8. The molecular formula conveys the specific number and type of atoms combined in each molecule of a compound. The empirical formula shows the simplest ratios of the atoms combined in a molecule.
9. Chemical compounds are either molecular compounds (in which the smallest units are discrete, individual molecules) or ionic compounds, which are made of cations and anions.
10. The names of many inorganic compounds can be deduced from a set of simple rules. The formulas can be written from the names of the compounds.
11. Organic compounds contain carbon and elements such as hydrogen, oxygen, and nitrogen. Hydrocarbon is the simplest type of organic compound.

Key Words

Acid, p. 64	Chemical formula, p. 54	Law of conservation of mass, p. 43	Nonmetal, p. 50
Alkali metals, p. 52	Diatomeric molecule, p. 52	Law of definite proportions, p. 42	Nucleus, p. 46
Alkaline earth metals, p. 52	Electron, p. 44	Law of multiple proportions, p. 42	Organic compound, p. 58
Allotrope, p. 54	Empirical formula, p. 55	Mass number (<i>A</i>), p. 48	Oxoacid, p. 64
Alpha (α) particles, p. 45	Families, p. 50	Metal, p. 50	Oxoanion, p. 65
Alpha (α) rays, p. 45	Gamma (γ) rays, p. 45	Metalloid, p. 50	Periods, p. 50
Anion, p. 53	Groups, p. 50	Molecular formula, p. 54	Periodic table, p. 50
Atom, p. 43	Halogens, p. 52	Molecule, p. 52	Polyatomic ion, p. 53
Atomic number (<i>Z</i>), p. 48	Hydrate, p. 66	Monatomic ion, p. 53	Polyatomic molecule, p. 52
Base, p. 66	Inorganic compounds, p. 58	Neutron, p. 47	Proton, p. 47
Beta (β) particles, p. 45	Ion, p. 52	Noble gases, p. 52	Radiation, p. 43
Beta (β) rays, p. 45	Ionic compound, p. 53		Radioactivity, p. 45
Binary compound, p. 58	Isotope, p. 48		Structural formula, p. 55
Cation, 2.5, p. 53	Lattice, p. 56		Ternary compound, p. 59

Questions & Problems

Red numbered problems solved in Student Solutions Manual

2.2 The Structure of the Atom

Review Questions

- 2.1 Define the following terms: (a) α particle, (b) β particle, (c) γ ray, (d) X ray.
- 2.2 Name the types of radiation known to be emitted by radioactive elements.
- 2.3 Compare the properties of the following: α particles, cathode rays, protons, neutrons, electrons.
- 2.4 What is meant by the term “fundamental particle”?
- 2.5 Describe the contributions of the following scientists to our knowledge of atomic structure: J. J. Thomson, R. A. Millikan, Ernest Rutherford, James Chadwick.
- 2.6 Describe the experimental basis for believing that the nucleus occupies a very small fraction of the volume of the atom.

Problems

- 2.7 The diameter of a helium atom is about 1×10^2 pm. Suppose that we could line up helium atoms side by side in contact with one another. Approximately how many atoms would it take to make the distance from end to end 1 cm?
- 2.8 Roughly speaking, the radius of an atom is about 10,000 times greater than that of its nucleus. If an atom were magnified so that the radius of its nucleus became 2.0 cm, about the size of a marble, what would be the radius of the atom in miles? (1 mi = 1609 m.)

2.3 Atomic Number, Mass Number, and Isotopes

Review Questions

- 2.9 Use the helium-4 isotope to define atomic number and mass number. Why does a knowledge of atomic number enable us to deduce the number of electrons present in an atom?

- 2.10 Why do all atoms of an element have the same atomic number, although they may have different mass numbers?
- 2.11 What do we call atoms of the same elements with different mass numbers?
- 2.12 Explain the meaning of each term in the symbol ${}_{Z}^{A}X$.

Problems

- 2.13 What is the mass number of an iron atom that has 28 neutrons?
- 2.14** Calculate the number of neutrons in ${}^{239}\text{Pu}$.
- 2.15 For each of the following species, determine the number of protons and the number of neutrons in the nucleus:
 ${}^3\text{He}$, ${}^4\text{He}$, ${}^{24}\text{Mg}$, ${}^{25}\text{Mg}$, ${}^{48}\text{Ti}$, ${}^{79}\text{Br}$, ${}^{195}\text{Pt}$
- 2.16** Indicate the number of protons, neutrons, and electrons in each of the following species:
 ${}^{15}\text{N}$, ${}^{33}\text{S}$, ${}^{63}\text{Cu}$, ${}^{84}\text{Sr}$, ${}^{130}\text{Ba}$, ${}^{186}\text{W}$, ${}^{202}\text{Hg}$
- 2.17 Write the appropriate symbol for each of the following isotopes: (a) $Z = 11$, $A = 23$; (b) $Z = 28$, $A = 64$.
- 2.18** Write the appropriate symbol for each of the following isotopes: (a) $Z = 74$, $A = 186$; (b) $Z = 80$, $A = 201$.

2.4 The Periodic Table

Review Questions

- 2.19 What is the periodic table, and what is its significance in the study of chemistry?
- 2.20 State two differences between a metal and a nonmetal.
- 2.21 Write the names and symbols for four elements in each of the following categories: (a) nonmetal, (b) metal, (c) metalloid.
- 2.22 Define, with two examples, the following terms: (a) alkali metals, (b) alkaline earth metals, (c) halogens, (d) noble gases.

Problems

- 2.23 Elements whose names end with “-ium” are usually metals; sodium is one example. Identify a nonmetal whose name also ends with “-ium”.
- 2.24** Describe the changes in properties (from metals to nonmetals or from nonmetals to metals) as we move (a) down a periodic group and (b) across the periodic table from left to right.
- 2.25 Consult a handbook of chemical and physical data (ask your instructor where you can locate a copy of the handbook) to find (a) two metals less dense than water, (b) two metals more dense than mercury, (c) the densest known solid metallic element, (d) the densest known solid nonmetallic element.
- 2.26** Group the following elements in pairs that you would expect to show similar chemical properties: K, F, P, Na, Cl, and N.

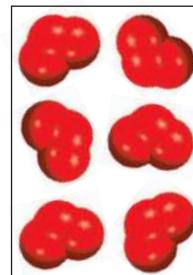
2.5 Molecules and Ions

Review Questions

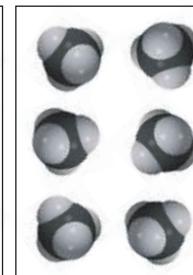
- 2.27 What is the difference between an atom and a molecule?
- 2.28 What are allotropes? Give an example. How are allotropes different from isotopes?
- 2.29 Describe the two commonly used molecular models.
- 2.30 Give an example of each of the following: (a) a monatomic cation, (b) a monatomic anion, (c) a polyatomic cation, (d) a polyatomic anion.

Problems

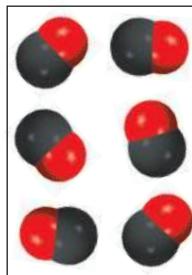
- 2.31** Which of the following diagrams represent diatomic molecules, polyatomic molecules, molecules that are not compounds, molecules that are compounds, or an elemental form of the substance?



(a)

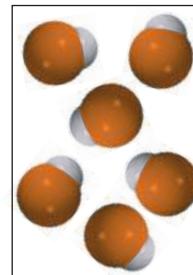


(b)

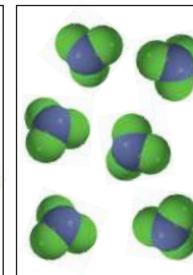


(c)

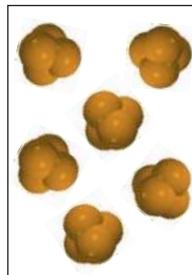
- 2.32** Which of the following diagrams represent diatomic molecules, polyatomic molecules, molecules that are not compounds, molecules that are compounds, or an elemental form of the substance?



(a)



(b)



(c)

- 2.33** Identify the following as elements or compounds: NH_3 , N_2 , S_8 , NO , CO , CO_2 , H_2 , SO_2 .

- 2.34** Give two examples of each of the following: (a) a diatomic molecule containing atoms of the same element, (b) a diatomic molecule containing atoms of different elements, (c) a polyatomic molecule containing atoms of the same element, (d) a polyatomic molecule containing atoms of different elements.

- 2.35** Give the number of protons and electrons in each of the following common ions: Na^+ , Ca^{2+} , Al^{3+} , Fe^{2+} , I^- , F^- , S^{2-} , O^{2-} , and N^{3-} .

- 2.36** Give the number of protons and electrons in each of the following common ions: K^+ , Mg^{2+} , Fe^{3+} , Br^- , Mn^{2+} , C^{4-} , Cu^{2+} .

- 2.37 Pair the following species that contain the same number of electrons: Ar, Sn^{4+} , F^- , Fe^{3+} , P^{3-} , V, Ag^+ , N^{3-} .
- 2.38 Write the correct symbols for the atoms that contain: (a) 25 protons, 25 electrons, and 27 neutrons; (b) 10 protons, 10 electrons, and 12 neutrons; (c) 47 protons, 47 electrons, and 60 neutrons; (d) 53 protons, 53 electrons, and 74 neutrons; (e) 94 protons, 94 electrons, and 145 neutrons.

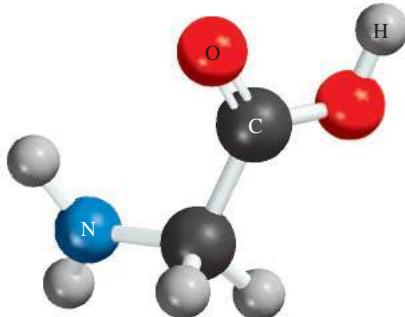
2.6 Chemical Formulas

Review Questions

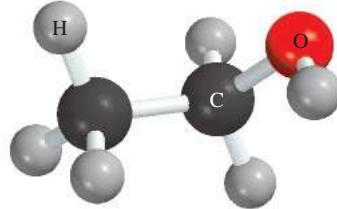
- 2.39 What does a chemical formula represent? What is the ratio of the atoms in the following molecular formulas? (a) NO, (b) NCl_3 , (c) N_2O_4 , (d) P_4O_6
- 2.40 Define molecular formula and empirical formula. What are the similarities and differences between the empirical formula and molecular formula of a compound?
- 2.41 Give an example of a case in which two molecules have different molecular formulas but the same empirical formula.
- 2.42 What does P_4 signify? How does it differ from 4P?
- 2.43 What is an ionic compound? How is electrical neutrality maintained in an ionic compound?
- 2.44** Explain why the chemical formulas of ionic compounds are usually the same as their empirical formulas.

Problems

- 2.45 Write the formulas for the following ionic compounds: (a) sodium oxide, (b) iron sulfide (containing the Fe^{2+} ion), (c) cobalt sulfate (containing the Co^{3+} and SO_4^{2-} ions), and (d) barium fluoride. (*Hint:* See Figure 2.11.)
- 2.46** Write the formulas for the following ionic compounds: (a) copper bromide (containing the Cu^+ ion), (b) manganese oxide (containing the Mn^{3+} ion), (c) mercury iodide (containing the Hg_2^{2+} ion), and (d) magnesium phosphate (containing the PO_4^{3-} ion). (*Hint:* See Figure 2.11.)
- 2.47 What are the empirical formulas of the following compounds? (a) C_2N_2 , (b) C_6H_6 , (c) C_9H_{20} , (d) P_4O_{10} , (e) B_2H_6
- 2.48** What are the empirical formulas of the following compounds? (a) Al_2Br_6 , (b) $\text{Na}_2\text{S}_2\text{O}_4$, (c) N_2O_5 , (d) $\text{K}_2\text{Cr}_2\text{O}_7$
- 2.49 Write the molecular formula of glycine, an amino acid present in proteins. The color codes are: black (carbon), blue (nitrogen), red (oxygen), and gray (hydrogen).



- 2.50** Write the molecular formula of ethanol. The color codes are: black (carbon), red (oxygen), and gray (hydrogen).



- 2.51 Which of the following compounds are likely to be ionic? Which are likely to be molecular? SiCl_4 , LiF , BaCl_2 , B_2H_6 , KCl , C_2H_4
- 2.52 Which of the following compounds are likely to be ionic? Which are likely to be molecular? CH_4 , NaBr , BaF_2 , CCl_4 , ICl , CsCl , NF_3

2.7 Naming Compounds

Review Questions

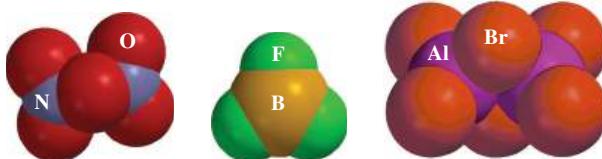
- 2.53 What is the difference between inorganic compounds and organic compounds?
- 2.54 What are the four major categories of inorganic compounds?
- 2.55 Give an example each for a binary compound and a ternary compound.
- 2.56 What is the Stock system? What are its advantages over the older system of naming cations?
- 2.57 Explain why the formula HCl can represent two different chemical systems.
- 2.58** Define the following terms: acids, bases, oxoacids, oxoanions, and hydrates.

Problems

- 2.59 Name these compounds: (a) Na_2CrO_4 , (b) K_2HPO_4 , (c) HBr (gas), (d) HBr (in water), (e) Li_2CO_3 , (f) $\text{K}_2\text{Cr}_2\text{O}_7$, (g) NH_4NO_2 , (h) PF_3 , (i) PF_5 , (j) P_4O_6 , (k) CdI_2 , (l) SrSO_4 , (m) $\text{Al}(\text{OH})_3$, (n) $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$.
- 2.60** Name these compounds: (a) KClO , (b) Ag_2CO_3 , (c) FeCl_2 , (d) KMnO_4 , (e) CsClO_3 , (f) HIO , (g) FeO , (h) Fe_2O_3 , (i) TiCl_4 , (j) NaH , (k) Li_3N , (l) Na_2O , (m) Na_2O_2 , (n) $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$.
- 2.61 Write the formulas for the following compounds: (a) rubidium nitrite, (b) potassium sulfide, (c) sodium hydrogen sulfide, (d) magnesium phosphate, (e) calcium hydrogen phosphate, (f) potassium dihydrogen phosphate, (g) iodine heptafluoride, (h) ammonium sulfate, (i) silver perchlorate, (j) boron trichloride.
- 2.62** Write the formulas for the following compounds: (a) copper(I) cyanide, (b) strontium chlorite, (c) perbromic acid, (d) hydroiodic acid, (e) disodium ammonium phosphate, (f) lead(II) carbonate, (g) tin(II) fluoride, (h) tetraphosphorus decasulfide, (i) mercury(II) oxide, (j) mercury(I) iodide, (k) selenium hexafluoride.
- 2.63 Sulfur (S) and fluorine (F) form several different compounds. One of them, SF_6 , contains 3.55 g of F for every gram of S. Use the law of multiple proportions to determine n , which represents the number

of F atoms in SF_6 , given that it contains 2.37 g of F for every gram of S.

- 2.64** Name the following compounds.



Additional Problems

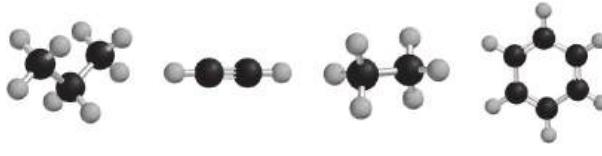
- 2.65** A sample of a uranium compound is found to be losing mass gradually. Explain what is happening to the sample.

- 2.66** In which one of the following pairs do the two species resemble each other most closely in chemical properties? Explain. (a) ${}^1\text{H}$ and ${}^1\text{H}^+$, (b) ${}^{14}\text{N}$ and ${}^{14}\text{N}^{3-}$, (c) ${}^{12}\text{C}$ and ${}^{13}\text{C}$.

- 2.67** One isotope of a metallic element has mass number 65 and 35 neutrons in the nucleus. The cation derived from the isotope has 28 electrons. Write the symbol for this cation.

- 2.68** One isotope of a nonmetallic element has mass number 127 and 74 neutrons in the nucleus. The anion derived from the isotope has 54 electrons. Write the symbol for this anion.

- 2.69** Determine the molecular and empirical formulas of the compounds shown here. (Black spheres are carbon and gray spheres are hydrogen.)



- 2.70** What is wrong with or ambiguous about the phrase “four molecules of NaCl ”?

- 2.71** The following phosphorus sulfides are known: P_4S_3 , P_4S_7 , and P_4S_{10} . Do these compounds obey the law of multiple proportions?

- 2.72** Which of the following are elements, which are molecules but not compounds, which are compounds but not molecules, and which are both compounds and molecules? (a) SO_2 , (b) S_8 , (c) Cs , (d) N_2O_5 , (e) O , (f) O_2 , (g) O_3 , (h) CH_4 , (i) KBr , (j) S , (k) P_4 , (l) LiF

- 2.73** The following table gives numbers of electrons, protons, and neutrons in atoms or ions of a number of elements. Answer the following: (a) Which of the species are neutral? (b) Which are negatively charged? (c) Which are positively charged? (d) What are the conventional symbols for all the species?

Atom or Ion of Element

	A	B	C	D	E	F	G
Number of electrons	5	10	18	28	36	5	9
Number of protons	5	7	19	30	35	5	9
Number of neutrons	5	7	20	36	46	6	10

2.74 Identify the elements represented by the following symbols and give the number of protons and neutrons in each case: (a) ${}^{20}_{10}\text{X}$, (b) ${}^{63}_{29}\text{X}$, (c) ${}^{107}_{47}\text{X}$, (d) ${}^{182}_{74}\text{X}$, (e) ${}^{203}_{84}\text{X}$, (f) ${}^{234}_{94}\text{X}$.

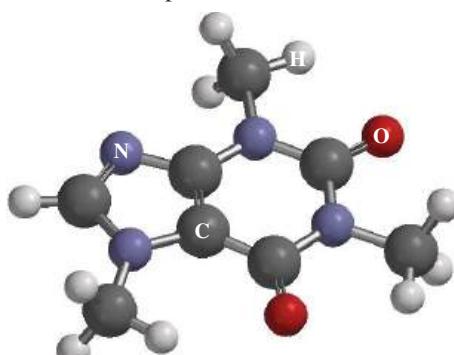
- 2.75** Each of the following pairs of elements will react to form an ionic compound. Write the formulas and name these compounds: (a) barium and oxygen, (b) calcium and phosphorus, (c) aluminum and sulfur, (d) lithium and nitrogen.

- 2.76** Match the descriptions [(a)–(h)] with each of the following elements: P, Cu, Kr, Sb, Cs, Al, Sr, Cl. (a) A transition metal, (b) a nonmetal that forms a -3 ion, (c) a noble gas, (d) an alkali metal, (e) a metal that forms a $+3$ ion, (f) a metalloid, (g) an element that exists as a diatomic gas molecule, (h) an alkaline earth metal.

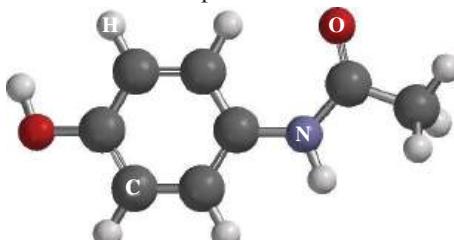
- 2.77** Explain why anions are always larger than the atoms from which they are derived, whereas cations are always smaller than the atoms from which they are derived. (Hint: Consider the electrostatic attraction between protons and electrons.)

- 2.78** (a) Describe Rutherford’s experiment and how it led to the structure of the atom. How was he able to estimate the number of protons in a nucleus from the scattering of the α particles? (b) Consider the ${}^{23}\text{Na}$ atom. Given that the radius and mass of the nucleus are 3.04×10^{-15} m and 3.82×10^{-23} g, respectively, calculate the density of the nucleus in g/cm^3 . The radius of a ${}^{23}\text{Na}$ atom is 186 pm. Calculate the density of the space occupied by the electrons in the sodium atom. Do your results support Rutherford’s model of an atom? [The volume of a sphere of radius r is $(4/3)\pi r^3$.]

- 2.79** Caffeine, shown here, is a psychoactive stimulant drug. Write the molecular formula and empirical formula of the compound.



- 2.80** Acetaminophen, shown here, is the active ingredient in Tylenol. Write the molecular formula and empirical formula of the compound.



- 2.81** What is wrong with the chemical formula for each of the following compounds? (a) magnesium iodate $\text{Mg}(\text{IO}_4)_2$, (b) phosphoric acid H_3PO_3 , (c) barium sulfite BaS , (d) ammonium bicarbonate $(\text{NH}_3\text{HCO}_3)_2$

2.82 What is wrong with the names (in parentheses) for each of the following compounds? SnCl_4 (tin chloride), (b) Cu_2O [copper(II) oxide], (c) $\text{Co}(\text{NO}_3)_2$ (cobalt nitrate), (d) $\text{Na}_2\text{Cr}_2\text{O}_7$ (sodium chromate)

2.83 Fill in the blanks in the following table.

Symbol		$^{54}_{26}\text{Fe}^{2+}$			
Protons	5			79	86
Neutrons	6		16	117	136
Electrons	5		18	79	
Net charge			-3		0

2.84 (a) Which elements are most likely to form ionic compounds? (b) Which metallic elements are most likely to form cations with different charges?

2.85 Write the formula of the common ion derived from each of the following: (a) Li, (b) S, (c) I, (d) N, (e) Al, (f) Cs, (g) Mg.

2.86 Which of the following symbols provides more information about the atom: ^{23}Na or $_{11}\text{Na}$? Explain.

2.87 Write the chemical formulas and names of binary acids and oxoacids that contain Group 7A elements. Do the same for elements in Groups 3A, 4A, 5A, and 6A.

2.88 Of the 118 elements known, only two are liquids at room temperature (25°C). What are they? (*Hint:* One element is a familiar metal and the other element is in Group 7A.)

2.89 For the noble gases (the Group 8A elements), ^4_2He , $^{20}_{10}\text{Ne}$, $^{40}_{18}\text{Ar}$, $^{84}_{36}\text{Kr}$, and $^{132}_{54}\text{Xe}$, (a) determine the number of protons and neutrons in the nucleus of each atom, and (b) determine the ratio of neutrons to protons in the nucleus of each atom. Describe any general trend you discover in the way this ratio changes with increasing atomic number.

2.90 List the elements that exist as gases at room temperature. (*Hint:* Most of these elements can be found in Groups 5A, 6A, 7A, and 8A.)

2.91 The Group 1B metals, Cu, Ag, and Au, are called coinage metals. What chemical properties make them specially suitable for making coins and jewelry?

2.92 The elements in Group 8A of the periodic table are called noble gases. Can you suggest what “noble” means in this context?

2.93 The formula for calcium oxide is CaO . What are the formulas for magnesium oxide and strontium oxide?

2.94 A common mineral of barium is barytes, or barium sulfate (BaSO_4). Because elements in the same periodic group have similar chemical properties, we might expect to find some radium

sulfate (RaSO_4) mixed with barytes since radium is the last member of Group 2A. However, the only source of radium compounds in nature is in uranium minerals. Why?

- 2.95** List five elements each that are (a) named after places, (b) named after people, (c) named after a color. (*Hint:* See an Internet source such as Webelements.com.)

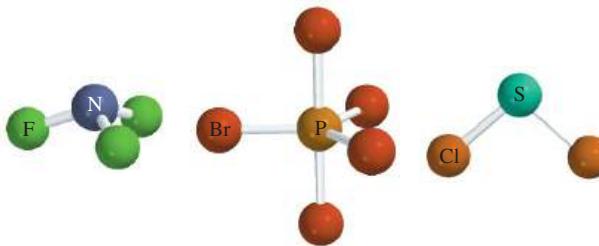
2.96 One isotope of a nonmetallic element has mass number 77 and 43 neutrons in the nucleus. The anion derived from the isotope has 36 electrons. Write the symbol for this anion.

2.97 Fluorine reacts with hydrogen (H) and deuterium (D) to form hydrogen fluoride (HF) and deuterium fluoride (DF), where deuterium (${}^2\text{H}$) is an isotope of hydrogen. Would a given amount of fluorine react with different masses of the two hydrogen isotopes? Does this violate the law of definite proportion? Explain.

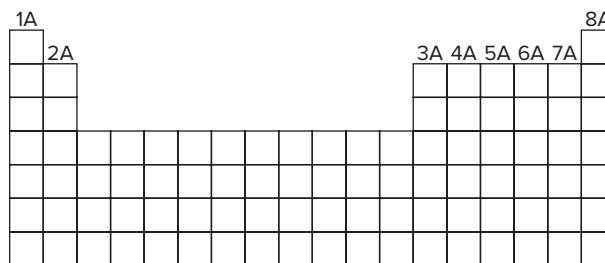
2.98 Predict the formula and name of a binary compound formed from the following elements: (a) Na and H, (b) B and O, (c) Na and S, (d) Al and F, (e) F and O, (f) Sr and Cl.

2.99 Identify each of the following elements: (a) a halogen whose anion contains 36 electrons, (b) a radioactive noble gas with 86 protons, (c) a Group 6A element whose anion contains 36 electrons, (d) an alkali metal cation that contains 36 electrons, (e) a Group 4A cation that contains 80 electrons.

2.100 Write the molecular formulas for and names of the following compounds.



- 2.101 Show the locations of (a) alkali metals, (b) alkaline earth metals, (c) the halogens, and (d) the noble gases in the following outline of a periodic table. Also draw dividing lines between metals and metalloids and between metalloids and nonmetals.



2.102 Fill the blanks in the following table.

Cation	Anion	Formula	Name
			Magnesium bicarbonate
	SrCl ₂		
Fe ³⁺	NO ₂ ⁻		
			Manganese(II) chlorate
	SnBr ₄		
Co ²⁺	PO ₄ ³⁻		
Hg ²⁺	I ⁻		
	Cu ₂ CO ₃		
			Lithium nitride
Al ³⁺	S ²⁻		

- 2.103** Some compounds are better known by their common names than by their systematic chemical names. Give the chemical formulas of the following substances: (a) dry ice, (b) table salt, (c) laughing gas, (d) marble (chalk, limestone), (e) quicklime, (f) slaked lime, (g) baking soda, (h) washing soda, (i) gypsum, (j) milk of magnesia.
- 2.104** In Section 2.1 it was pointed out that mass and energy are alternate aspects of a single entity called *mass-energy*. The relationship between these two physical quantities is Einstein's famous equation, $E = mc^2$, where E is energy, m is mass, and c is the speed of light. In a combustion experiment, it was found that 12.096 g of hydrogen molecules combined with 96.000 g of oxygen molecules to form water and released 1.715×10^3 kJ of heat. Calculate the corresponding mass change in this process and comment on whether the law of conservation of mass holds for ordinary chemical processes. (*Hint:* The Einstein equation can be used to calculate the change in mass as a result of the change in energy. $1\text{ J} = 1\text{ kg m}^2/\text{s}^2$ and $c = 3.00 \times 10^8\text{ m/s}$.)
- 2.105** Draw all possible structural formulas of the following hydrocarbons: CH₄, C₂H₆, C₃H₈, C₄H₁₀, C₅H₁₂.
- 2.106** (a) Assuming nuclei are spherical in shape, show that its radius r is proportional to the cube root of mass number (A). (b) In general, the radius of a nucleus is given by $r = r_0 A^{1/3}$, where r_0 is a proportionality constant given by $1.2 \times 10^{-15}\text{ m}$. Calculate the volume of the ${}^7\text{Li}$ nucleus. (c) Given that the radius of a Li atom is 152 pm, calculate the fraction of the atom's volume occupied by the nucleus. Does your result support Rutherford's model of an atom?
- 2.107** Draw two different structural formulas based on the molecular formula C₂H₆O. Is the fact that you can have more than one compound with the same molecular formula consistent with Dalton's atomic theory?
- 2.108** Ethane and acetylene are two gaseous hydrocarbons. Chemical analyses show that in one sample of ethane, 2.65 g of carbon are combined with 0.665 g

of hydrogen, and in one sample of acetylene, 4.56 g of carbon are combined with 0.383 g of hydrogen. (a) Are these results consistent with the law of multiple proportions? (b) Write reasonable molecular formulas for these compounds.

- 2.109** A cube made of platinum (Pt) has an edge length of 1.0 cm. (a) Calculate the number of Pt atoms in the cube. (b) Atoms are spherical in shape. Therefore, the Pt atoms in the cube cannot fill all of the available space. If only 74 percent of the space inside the cube is taken up by Pt atoms, calculate the radius in picometers of a Pt atom. The density of Pt is 21.45 g/cm^3 and the mass of a single Pt atom is $3.240 \times 10^{-22}\text{ g}$. [The volume of a sphere of radius r is $(4/3)\pi r^3$.]
- 2.110** A monatomic ion has a charge of +2. The nucleus of the parent atom has a mass number of 55. If the number of neutrons in the nucleus is 1.2 times that of the number of protons, what is the name and symbol of the element?
- 2.111** In the following 2×2 crossword, each letter must be correct four ways: horizontally, vertically, diagonally, and by itself. When the puzzle is complete, the four spaces will contain the overlapping symbols of 10 elements. Use capital letters for each square. There is only one correct solution.*

1	2
3	4

Horizontal

- 1–2: Two-letter symbol for a metal used in ancient times
 3–4: Two-letter symbol for a metal that burns in air and is found in Group 5A

Vertical

- 1–3: Two-letter symbol for a metalloid
 2–4: Two-letter symbol for a metal used in U.S. coins

Single Squares

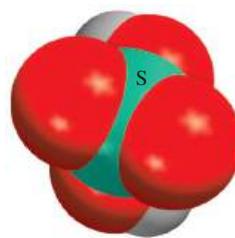
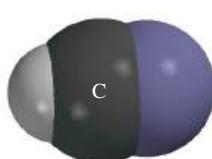
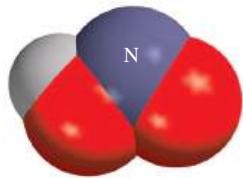
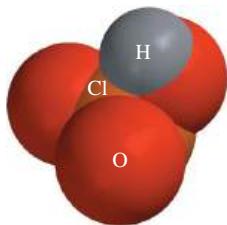
- 1: A colorful nonmetal
 2: A colorless gaseous nonmetal
 3: An element that makes fireworks green
 4: An element that has medicinal uses

Diagonal

- 1–4: Two-letter symbol for an element used in electronics
 2–3: Two-letter symbol for a metal used with Zr to make wires for superconducting magnets

*Reproduced with permission of S. J. Cyvin of the University of Trondheim (Norway). This puzzle appeared in *Chemical & Engineering News*, December 14, 1987 (p. 86) and in *Chem Matters*, October 1988.

- 2.112** Name the following acids.



- 2.113** Calculate the density of the nucleus of a ^{56}Fe atom, given that the nuclear mass is 9.229×10^{-23} g. From your result, comment on the fact that any nucleus containing more than one proton must have neutrons present as well. (*Hint:* See Problem 2.106.)
- 2.114** Element X reacts with element Y to form an ionic compound containing X^{4+} and Y^{2-} ions. Write a formula for the compound and suggest in which periodic groups these elements are likely to be found. Name a representative compound.

- 2.115** Methane, ethane, and propane are shown in Table 2.8. Show that the following data are consistent with the law of multiple proportions.

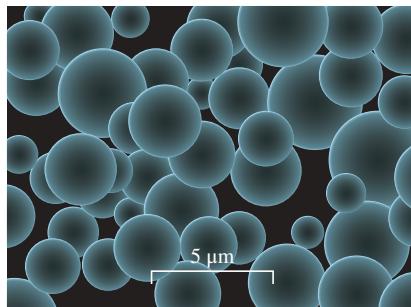
	Mass of Carbon in 1 g Sample	Mass of Hydrogen in 1 g Sample
Methane	0.749 g	0.251 g
Ethane	0.799 g	0.201 g
Propane	0.817 g	0.183 g

Interpreting, Modeling & Estimating

- 2.116** In the Rutherford scattering experiment, an α particle is heading directly toward a gold nucleus. The particle will come to a halt when its kinetic energy is completely converted to electrical potential energy. When this happens, how close will the α particle with a kinetic energy of 6.0×10^{-14} J be from the nucleus? [According to Coulomb's law, the electrical potential energy between two charged particles is $E = kQ_1Q_2/r$, where Q_1 and Q_2 are the charges (in coulombs) of the α particle and the gold nucleus, r is the distance of separation in meters, and k is a constant equal to $9.0 \times 10^9 \text{ kg} \cdot \text{m}^3/\text{s}^2 \cdot \text{C}^2$. Joule (J) is the unit of energy where $1 \text{ J} = 1 \text{ kg} \cdot \text{m}^2/\text{s}^2$.]
- 2.117** Estimate the relative sizes of the following species: Li, Li^+ , Li^- .
- 2.118** Compare the atomic size of the following two magnesium isotopes: ^{24}Mg and ^{26}Mg .
- 2.119** Using visible light, we humans cannot see any object smaller than 2×10^{-5} cm with an unaided eye. Roughly how many silver atoms must be lined up for us to see the atoms?
- 2.120** If the size of the nucleus of an atom were that of a pea, how far would the electrons be (on average) from the nucleus in meters?

- 2.121** Sodium and potassium are roughly equal in natural abundance in Earth's crust and most of their compounds are soluble. However, the composition of seawater is much higher in sodium than potassium. Explain.

- 2.122** One technique proposed for recycling plastic grocery bags is to heat them at 700°C and high pressure to form carbon microspheres that can be used in a number of applications. Electron microscopy shows some representative carbon microspheres obtained in this manner, where the scale is given in the bottom right corner of the figure. Determine the number of carbon atoms in a typical carbon microsphere.



Answers to Practice Exercises

2.1 29 protons, 34 neutrons, and 29 electrons.

2.2 CHCl_3 . **2.3** $\text{C}_4\text{H}_5\text{N}_2\text{O}$. **2.4** (a) $\text{Cr}_2(\text{SO}_4)_3$, (b) TiO_2 .

2.5 (a) Lead(II) oxide, (b) lithium chlorate. **2.6** (a) Rb_2SO_4 ,

(b) BaH_2 . **2.7** (a) Nitrogen trifluoride, (b) dichlorine heptoxide. **2.8** (a) SF_4 , (b) N_2O_5 . **2.9** (a) Hypobromous acid, (b) hydrogen sulfate ion.

Answers to Review of Concepts & Facts

2.1.1 Yes, the ratio of atoms represented by B that combine with A in these two compounds is (2/1):(5/2) or 4:5.

2.3.1 78. **2.3.2** 66. **2.3.3** ^{17}O . **2.4.1** Chemical properties change more markedly across a period. **2.4.2** (a) Metal, (b) nonmetal, (c) metalloid, (d) metal. **2.5.1** S_8 signifies one molecule of sulfur that is composed of 8 S atoms. 8S represents 8 individual atoms of sulfur. **2.5.2** (a) 15 protons, 18 electrons, (b) 22 protons, 18 electrons, (c) 32 protons, 30 electrons. **2.5.3** Cr^{2+} . **2.6.1** (a) $\text{Mg}(\text{NO}_3)_2$, (b) Al_2O_3 ,

(c) LiH , (d) Na_2S . **2.6.2** (a) CaI_2 , (b) Ga_2S_3 . **2.7.1** Se and Cl are both nonmetals, so SeCl_2 is a molecule and prefixes are used when naming the compound. Sr is a metal, so SrCl_2 is an ionic compound and prefixes are not necessary. **2.7.2** HF can be named as a molecule (hydrogen fluoride) or as an acid (hydrofluoric acid). We need to know if the compound is dissolved in water. **2.7.3** (a) Cesium sulfite, (b) copper(II) nitrite. **2.7.4** (a) $\text{Co}(\text{HSO}_4)_2$, (b) $\text{Cr}(\text{CN})_3$. **2.7.5** (a) Bromine pentafluoride, (b) periodic acid. **2.8.1** Two.

Design elements: Student Hot Spot (pointer with web icon): ©LovArt/Shutterstock.com

CHAPTER

3

The reaction between aluminum and ammonium perchlorate fuels the solid rocket boosters to send this rocket into space.

NASA

CHAPTER OUTLINE

- 3.1** Atomic Mass
- 3.2** Avogadro's Number and the Molar Mass of an Element
- 3.3** Molecular Mass
- 3.4** The Mass Spectrometer
- 3.5** Percent Composition of Compounds
- 3.6** Experimental Determination of Empirical Formulas
- 3.7** Chemical Reactions and Chemical Equations
- 3.8** Amounts of Reactants and Products
- 3.9** Limiting Reactants
- 3.10** Reaction Yield

Mass Relationships in Chemical Reactions



A LOOK AHEAD

- We begin by studying the mass of an atom, which is based on the carbon-12 isotope scale. An atom of the carbon-12 isotope is assigned a mass of exactly 12 atomic mass units (amu). To work with the more convenient scale of grams, we use the molar mass. The molar mass of carbon-12 has a mass of exactly 12 grams and contains an Avogadro's number (6.022×10^{23}) of atoms. The molar masses of other elements are also expressed in grams and contain the same number of atoms. (3.1 and 3.2)
- Our discussion of atomic mass leads to molecular mass, which is the sum of the masses of the constituent atoms present. We learn that the most direct way to determine atomic and molecular mass is by the use of a mass spectrometer. (3.3 and 3.4)
- To continue our study of molecules and ionic compounds, we learn how to calculate the percent composition of these species from their chemical formulas. (3.5)
- We will see how the empirical and molecular formulas of a compound are determined by experiment. (3.6)
- Next, we learn how to write a chemical equation to describe the outcome of a chemical reaction. A chemical equation must be balanced so that we have the same number and type of atoms for the reactants, the starting materials, and the products—the substances formed at the end of the reaction. (3.7)
- Building on our knowledge of chemical equations, we then proceed to study the mass relationships of chemical reactions. A chemical equation enables us to use the mole method to predict the amount of product(s) formed, knowing how much of the reactant(s) was used. We will see that the yield of a reaction depends on the amount of limiting reactant present. (A limiting reactant is that species which is used up first.) (3.8 and 3.9)
- We will learn that the actual yield of a reaction is almost always less than that predicted from the equation, called the theoretical yield, because of various complications. (3.10)

In this chapter, we will consider the masses of atoms and molecules and what happens to them when chemical changes occur. Our guide for this discussion will be the law of conservation of mass.

3.1 Atomic Mass

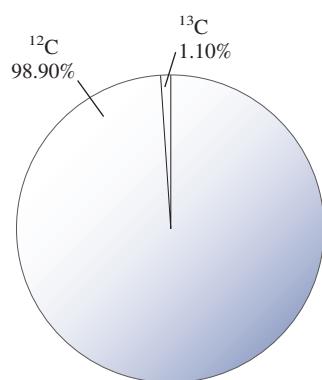
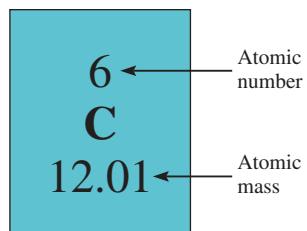
In this chapter, we will use what we have learned about chemical structure and formulas in studying the mass relationships of atoms and molecules. These relationships in turn will help us to explain the composition of compounds and the ways in which composition changes.

The mass of an atom depends on the number of electrons, protons, and neutrons it contains. Knowledge of an atom's mass is important in laboratory work. But atoms are extremely small particles—even the smallest speck of dust that our unaided eyes can detect contains as many as 1×10^{16} atoms! Clearly we cannot weigh a single atom, but it is possible to determine the mass of one atom *relative* to another experimentally. The first step is to assign a value to the mass of one atom of a given element so that it can be used as a standard.

By international agreement, **atomic mass** (sometimes called *atomic weight*) is *the mass of the atom in atomic mass units (amu)*. One **atomic mass unit** is defined as *a mass exactly equal to one-twelfth the mass of one carbon-12 atom*. Carbon-12 is the carbon isotope that has six protons and six neutrons. Setting the atomic mass of carbon-12 at 12 amu provides the standard for measuring the atomic mass of the other elements. For example, experiments have shown that, on average, a hydrogen atom is only 8.400 percent as massive as the carbon-12 atom. Thus, if the mass of one carbon-12 atom is exactly 12 amu, the atomic mass of hydrogen must be 0.08400×12 amu or 1.008 amu. Similar calculations show that the atomic mass of oxygen is 16.00 amu and that of iron is 55.85 amu. Thus, although we do not know just how much an average iron atom's mass is, we know that it is approximately 56 times as massive as a hydrogen atom.

Section 3.4 describes a method for determining atomic mass.

One atomic mass unit is also called one dalton.



Natural abundances of C-12 and C-13 isotopes.

Average Atomic Mass

When you look up the atomic mass of carbon in a periodic table, you will find that its value is not 12.00 amu but 12.01 amu. The reason for the difference is that most naturally occurring elements (including carbon) have more than one isotope. This means that when we measure the atomic mass of an element, we must generally settle for the *average* mass of the naturally occurring mixture of isotopes. For example, the natural abundances of carbon-12 and carbon-13 are 98.90 percent and 1.10 percent, respectively. The atomic mass of carbon-13 has been determined to be 13.00335 amu. Thus, the average atomic mass of carbon can be calculated as follows:

average atomic mass

$$\text{of natural carbon} = (0.9890)(12 \text{ amu}) + (0.0110)(13.00335 \text{ amu}) \\ = 12.01 \text{ amu}$$

Note that in calculations involving percentages, we need to convert percentages to fractions. For example, 98.90 percent becomes 98.90/100, or 0.9890. Because there are many more carbon-12 atoms than carbon-13 atoms in naturally occurring carbon, the average atomic mass is much closer to 12 amu than to 13 amu.

It is important to understand that when we say that the atomic mass of carbon is 12.01 amu, we are referring to the *average* value. If carbon atoms could be examined individually, we would find either an atom of atomic mass exactly 12 amu or one of 13.00335 amu, but never one of 12.01 amu. Example 3.1 shows how to calculate the average atomic mass of an element.

Example 3.1

Boron is used in the manufacture of ceramics and polymers such as fiberglass. The atomic masses of its two stable isotopes, $^{10}_5\text{B}$ (19.80 percent) and $^{11}_5\text{B}$ (80.20 percent), are 10.0129 amu and 11.0093 amu, respectively. The boron-10 isotope is also important as a neutron-capturing agent in nuclear reactors. Calculate the average atomic mass of boron.

Strategy Each isotope contributes to the average atomic mass based on its relative abundance. Multiplying the mass of an isotope by its fractional abundance (not percent) will give the contribution to the average atomic mass of that particular isotope.

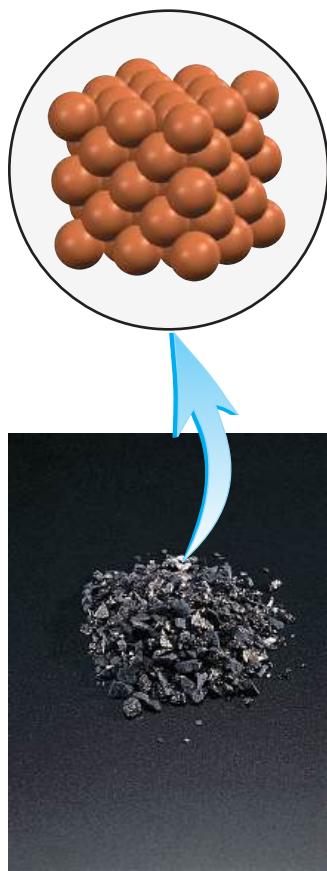
Solution First the percent abundances are converted to fractions: 19.80 percent to 19.80/100 or 0.1980 and 80.20 percent to 80.20/100 or 0.8020. We find the contribution to the average atomic mass for each isotope, and then add the contributions together to obtain the average atomic mass.

$$(0.1980)(10.0129 \text{ amu}) + (0.8020)(11.0093 \text{ amu}) = 10.8129 \text{ amu}$$

Check The average atomic mass should be between the two isotopic masses; therefore, the answer is reasonable. Note that because there are more $^{11}_5\text{B}$ isotopes than $^{10}_5\text{B}$ isotopes, the average atomic mass is closer to 11.0093 amu than to 10.0129 amu.

Practice Exercise The atomic masses of the two stable isotopes of copper, $^{63}_{29}\text{Cu}$ (69.17 percent) and $^{65}_{29}\text{Cu}$ (30.83 percent), are 62.9296 amu and 64.9278 amu, respectively. Calculate the average atomic mass of copper.

Similar problems: 3.5, 3.6.



Boron and the solid-state structure of boron.

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The atomic masses of many elements have been accurately determined to five or six significant figures. However, for our purposes we will normally use atomic masses accurate only to four significant figures (see List of the Elements with Their Symbols and Atomic Masses). For simplicity, we will omit the word “average” when we discuss the atomic masses of the elements.

Review of Concepts & Facts

- 3.1.1** There are two stable isotopes of iridium: ^{191}Ir (190.96 amu) and ^{193}Ir (192.96 amu). If you were to randomly pick an iridium atom from a large collection of iridium atoms, which isotope are you more likely to select?
- 3.1.2** The hypothetical element Q occurs as a mixture of 37.50 percent ^{47}Q (47.054 amu) and 62.50 percent ^{51}Q (50.924 amu). Calculate the average atomic mass of Q.

3.2 Avogadro's Number and the Molar Mass of an Element

Atomic mass units provide a relative scale for the masses of the elements. But because atoms have such small masses, no usable scale can be devised to weigh them in calibrated units of atomic mass units. In any real situation, we deal with macroscopic samples containing enormous numbers of atoms. Therefore, it is convenient to have a special unit to describe a very large number of atoms. The idea of a unit to denote a particular number of objects is not new. For example, the pair (2 items), the dozen (12 items), and the gross (144 items) are all familiar units. Chemists measure atoms and molecules in moles.

In the SI system the **mole (mol)** is *the amount of a substance that contains as many elementary entities (atoms, molecules, or other particles) as there are atoms in exactly 12 g (or 0.012 kg) of the carbon-12 isotope*. The actual number of atoms in 12 g of carbon-12 is determined experimentally. This number is called **Avogadro's number (N_A)**, in honor of the Italian scientist Amedeo Avogadro.[†] The currently accepted value is

$$N_A = 6.0221413 \times 10^{23}$$

Generally, we round Avogadro's number to 6.022×10^{23} . Thus, just as 1 dozen oranges contains 12 oranges, 1 mole of hydrogen atoms contains 6.022×10^{23} H atoms. Figure 3.1 shows samples containing 1 mole each of several common elements.

The adjective formed from the noun "mole" is "molar."



Figure 3.1 One mole each of several common elements. Carbon (black charcoal powder), sulfur (yellow powder), iron (as nails), copper wires, and mercury (shiny liquid metal).

©McGraw-Hill Education/Stephen Frisch

[†]Lorenzo Romano Amedeo Carlo Avogadro di Quarega e di Cerreto (1776–1856). Italian mathematical physicist. He practiced law for many years before he became interested in science. His most famous work, now known as Avogadro's law (see Chapter 5), was largely ignored during his lifetime, although it became the basis for determining atomic masses in the late nineteenth century.

The enormity of Avogadro's number is difficult to imagine. For example, spreading 6.022×10^{23} oranges over the entire surface of Earth would produce a layer 9 mi into space! Because atoms (and molecules) are so tiny, we need a huge number to study them in manageable quantities.

In calculations, the units of molar mass are g/mol or kg/mol.

We have seen that 1 mole of carbon-12 atoms has a mass of exactly 12 g and contains 6.022×10^{23} atoms. This mass of carbon-12 is its **molar mass (\mathcal{M})**, defined as *the mass (in grams or kilograms) of 1 mole of units (such as atoms or molecules) of a substance*. Note that the molar mass of carbon-12 (in grams) is numerically equal to its atomic mass in amu. Likewise, the atomic mass of sodium (Na) is 22.99 amu and its molar mass is 22.99 g; the atomic mass of phosphorus is 30.97 amu and its molar mass is 30.97 g; and so on. If we know the atomic mass of an element, we also know its molar mass.

The molar masses of the elements are given on a periodic table.

Knowing the molar mass and Avogadro's number, we can calculate the mass of a single atom in grams. For example, we know the molar mass of carbon-12 is 12 g and there are 6.022×10^{23} carbon-12 atoms in 1 mole of the substance; therefore, the mass of one carbon-12 atom is given by

$$\frac{12 \text{ g carbon-12 atoms}}{6.022 \times 10^{23} \text{ carbon-12 atoms}} = 1.993 \times 10^{-23} \text{ g}$$

We can use the preceding result to determine the relationship between atomic mass units and grams. Because the mass of every carbon-12 atom is exactly 12 amu, the number of atomic mass units equivalent to 1 gram is

$$\begin{aligned}\frac{\text{amu}}{\text{gram}} &= \frac{12 \text{ amu}}{1 \text{ carbon-12 atom}} \times \frac{1 \text{ carbon-12 atom}}{1.993 \times 10^{-23} \text{ g}} \\ &= 6.022 \times 10^{23} \text{ amu/g}\end{aligned}$$

Thus,

$$1 \text{ g} = 6.022 \times 10^{23} \text{ amu}$$

and

$$1 \text{ amu} = 1.661 \times 10^{-24} \text{ g}$$

This example shows that Avogadro's number can be used to convert from the atomic mass units to mass in grams and vice versa.

The notions of Avogadro's number and molar mass enable us to carry out conversions between mass and moles of atoms and between moles and number of atoms (Figure 3.2). We will employ the following conversion factors in the calculations:

$$\frac{1 \text{ mol X}}{\text{molar mass of X}} \quad \text{and} \quad \frac{1 \text{ mol X}}{6.022 \times 10^{23} \text{ X atoms}}$$

where X represents the symbol of an element. Using the proper conversion factors we can convert one quantity to another, as Examples 3.2–3.4 show.

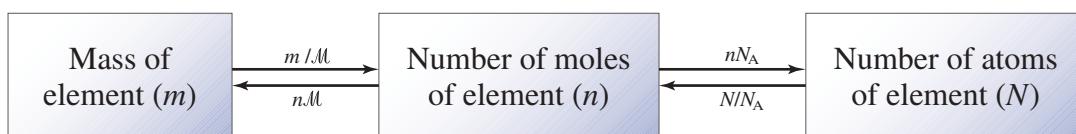


Figure 3.2 The relationships between mass (m in grams) of an element and number of moles of an element (n) and between number of moles of an element and number of atoms (N) of an element. \mathcal{M} is the molar mass (g/mol) of the element and N_A is Avogadro's number.



Student Hot Spot

After some practice, you can use the equations in Figure 3.2 in calculations: $n = m/\mathcal{M}$ and $N = nN_A$.

Student data indicate you may struggle with converting mass of an element into moles and atoms. Access your eBook for additional Learning Resources on this topic.

Example 3.2

Helium (He) is a valuable gas used in industry, low-temperature research, deep-sea diving tanks, and balloons. How many moles of He atoms are in 6.46 g of He?

Strategy We are given grams of helium and asked to solve for moles of helium. What conversion factor do we need to convert between grams and moles? Arrange the appropriate conversion factor so that grams cancel and the unit moles is obtained for your answer.

Solution The conversion factor needed to convert between grams and moles is the molar mass. In the periodic table, we see that the molar mass of He is 4.003 g. This can be expressed as

$$1 \text{ mol He} = 4.003 \text{ g He}$$

From this equality, we can write two conversion factors

$$\frac{1 \text{ mol He}}{4.003 \text{ g He}} \quad \text{and} \quad \frac{4.003 \text{ g He}}{1 \text{ mol He}}$$

The conversion factor on the left is the correct one. Grams will cancel, leaving the unit mol for the answer—that is,

$$6.46 \text{ g He} \times \frac{1 \text{ mol He}}{4.003 \text{ g He}} = 1.61 \text{ mol He}$$

Thus, there are 1.61 moles of He atoms in 6.46 g of He.

Check Because the given mass (6.46 g) is larger than the molar mass of He, we expect to have more than 1 mole of He.

Practice Exercise How many moles of magnesium (Mg) are there in 87.3 g of Mg?

Similar problem: 3.15.



A scientific research helium balloon.

National Scientific Balloon Facility/Palestine, Texas

Example 3.3

Zinc (Zn) is a silvery metal that is used in making brass (with copper) and in plating iron to prevent corrosion. How many grams of Zn are in 0.356 mole of Zn?

Strategy We are trying to solve for grams of zinc. What conversion factor do we need to convert between moles and grams? Arrange the appropriate conversion factor so that moles cancel and the unit grams are obtained for your answer.

Solution The conversion factor needed to convert between moles and grams is the molar mass. In the periodic table, we see the molar mass of Zn is 65.39 g. This can be expressed as

$$1 \text{ mol Zn} = 65.39 \text{ g Zn}$$

From this equality, we can write two conversion factors

$$\frac{1 \text{ mol Zn}}{65.39 \text{ g Zn}} \quad \text{and} \quad \frac{65.39 \text{ g Zn}}{1 \text{ mol Zn}}$$

The conversion factor on the right is the correct one. Moles will cancel, leaving unit of grams for the answer. The number of grams of Zn is

$$0.356 \text{ mol Zn} \times \frac{65.39 \text{ g Zn}}{1 \text{ mol Zn}} = 23.3 \text{ g Zn}$$

Thus, there are 23.3 g of Zn in 0.356 mole of Zn.



Zinc.

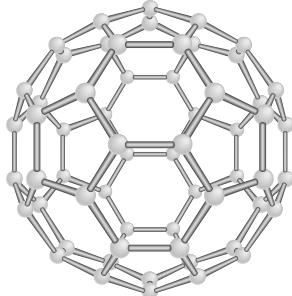
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(Continued)

Check Does a mass of 23.3 g for 0.356 mole of Zn seem reasonable? What is the mass of 1 mole of Zn?

Practice Exercise Calculate the number of grams of lead (Pb) in 12.4 moles of lead.

Similar problem: 3.16.



Buckminsterfullerene (C_{60}) or “buckyball.”

Example 3.4

The C_{60} molecule is called buckminsterfullerene because its shape resembles the geodesic domes designed by the visionary architect R. Buckminster Fuller. What is the mass (in grams) of one C_{60} molecule?

Strategy The question asks for the mass of one C_{60} molecule. Determine the moles of C atoms in one C_{60} molecule, and then use the molar mass of C to calculate the mass of one molecule in grams.

Solution Because one C_{60} molecule contains 60 C atoms, and 1 mole of C contains 6.022×10^{23} C atoms and has a mass of 12.011 g, we can calculate the mass of one C_{60} molecule as follows:

$$1 \text{ } C_{60} \text{ molecule} \times \frac{60 \text{ C atoms}}{1 \text{ } C_{60} \text{ molecule}} \times \frac{1 \text{ mol C}}{6.022 \times 10^{23} \text{ C atoms}} \times \frac{12.01 \text{ g}}{1 \text{ mol C}} = 1.197 \times 10^{-21} \text{ g}$$

Check Because 6.022×10^{23} atoms of C have a mass 12.01 g, a molecule containing only 60 carbon atoms should have a significantly smaller mass.

Practice Exercise Gold atoms form small clusters containing a fixed number of atoms. What is the mass (in grams) of one Au_{31} cluster?

Similar problems: 3.20, 3.21.

Review of Concepts & Facts

3.2.1 Determine which of the following contains the largest number of atoms:
(a) 7.68 g of He, (b) 112 g of Fe, (c) 389 g of Hg.

3.2.2 How many moles of rubidium (Rb) are there in 3.75×10^{24} Rb atoms?

3.2.3 What is the mass in grams of 1.68 moles of vanadium (V)?

3.3 Molecular Mass

If we know the atomic masses of the component atoms, we can calculate the mass of a molecule. The **molecular mass** (sometimes called **molecular weight**) is *the mass (in amu) of one molecule*. It is determined by the sum of the atomic masses of each atom in a molecule. For example, the molecular mass of H_2O is

$$2(\text{atomic mass of H}) + \text{atomic mass of O}$$

$$\text{or} \quad 2(1.008 \text{ amu}) + 16.00 \text{ amu} = 18.02 \text{ amu}$$

In general, we need to multiply the atomic mass of each element by the number of atoms of that element present in the molecule and sum over all the elements. Example 3.5 illustrates this approach.

Example 3.5

Calculate the molecular masses (in amu) of the following compounds: (a) sulfur dioxide (SO_2), a gas that is responsible for acid rain, and (b) caffeine ($\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$), a stimulant present in tea, coffee, and cola beverages.

Strategy How do atomic masses of different elements combine to give the molecular mass of a compound?

Solution To calculate molecular mass, we need to sum all the atomic masses in the molecule. For each element, we multiply the atomic mass of the element by the number of atoms of that element in the molecule. We find atomic masses in the periodic table.

(a) There are two O atoms and one S atom in SO_2 , so that

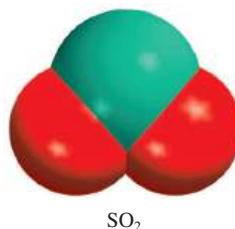
$$\begin{aligned}\text{molecular mass of } \text{SO}_2 &= 32.07 \text{ amu} + 2(16.00 \text{ amu}) \\ &= 64.07 \text{ amu}\end{aligned}$$

(b) There are eight C atoms, ten H atoms, four N atoms, and two O atoms in caffeine, so the molecular mass of $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$ is given by

$$8(12.01 \text{ amu}) + 10(1.008 \text{ amu}) + 4(14.01 \text{ amu}) + 2(16.00 \text{ amu}) = 194.20 \text{ amu}$$

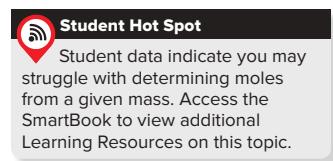
Practice Exercise What is the molecular mass of methanol (CH_4O)?

Similar problems: 3.23, 3.24.



From the molecular mass we can determine the molar mass of a molecule or compound. The molar mass of a compound (in grams) is numerically equal to its molecular mass (in amu). For example, the molecular mass of water is 18.02 amu, so its molar mass is 18.02 g. Note that 1 mole of water weighs 18.02 g and contains 6.022×10^{23} H_2O molecules, just as 1 mole of elemental carbon contains 6.022×10^{23} carbon atoms.

As Examples 3.6 and 3.7 show, a knowledge of the molar mass enables us to calculate the numbers of moles and individual atoms in a given quantity of a compound.



Example 3.6

Methane (CH_4) is the principal component of natural gas. How many moles of CH_4 are present in 6.07 g of CH_4 ?

Strategy We are given grams of CH_4 and asked to solve for moles of CH_4 . What conversion factor do we need to convert between grams and moles? Arrange the appropriate conversion factor so that grams cancel and the unit moles are obtained for your answer.

Solution The conversion factor needed to convert between grams and moles is the molar mass. First we need to calculate the molar mass of CH_4 , following the procedure in Example 3.5:

$$\begin{aligned}\text{molar mass of } \text{CH}_4 &= 12.01 \text{ g} + 4(1.008 \text{ g}) \\ &= 16.04 \text{ g}\end{aligned}$$

Because

$$1 \text{ mol } \text{CH}_4 = 16.04 \text{ g } \text{CH}_4$$

the conversion factor we need should have grams in the denominator so that the unit g will cancel, leaving the unit mol in the numerator:

$$\frac{1 \text{ mol } \text{CH}_4}{16.04 \text{ g } \text{CH}_4}$$

(Continued)



Methane gas burning on a cooking range.

©Steve Allen/Getty Images

We now write

$$6.07 \text{ g CH}_4 \times \frac{1 \text{ mol CH}_4}{16.04 \text{ g CH}_4} = 0.378 \text{ mol CH}_4$$

Thus, there is 0.378 mole of CH₄ in 6.07 g of CH₄.

Check Should 6.07 g of CH₄ equal less than 1 mole of CH₄? What is the mass of 1 mole of CH₄?

Practice Exercise Calculate the number of moles of chloroform (CHCl₃) in 198 g of chloroform.

Similar problem: 3.26.



Urea.

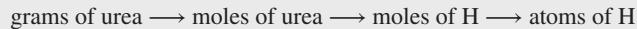
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Example 3.7

How many hydrogen atoms are present in 25.6 g of urea [(NH₂)₂CO], which is used as a fertilizer, in animal feed, and in the manufacture of polymers? The molar mass of urea is 60.06 g.

Strategy We are asked to solve for atoms of hydrogen in 25.6 g of urea. We cannot convert directly from grams of urea to atoms of hydrogen. How should molar mass and Avogadro's number be used in this calculation? How many moles of H are in 1 mole of urea?

Solution To calculate the number of H atoms, we first must convert grams of urea to moles of urea using the molar mass of urea. This part is similar to Example 3.2. The molecular formula of urea shows there are four moles of H atoms in one mole of urea molecule, so the mole ratio is 4:1. Finally, knowing the number of moles of H atoms, we can calculate the number of H atoms using Avogadro's number. We need two conversion factors: molar mass and Avogadro's number. We can combine these conversions



into one step:

$$25.6 \text{ g } (\text{NH}_2)_2\text{CO} \times \frac{1 \text{ mol } (\text{NH}_2)_2\text{CO}}{60.06 \text{ g } (\text{NH}_2)_2\text{CO}} \times \frac{4 \text{ mol H}}{1 \text{ mol } (\text{NH}_2)_2\text{CO}} \times \frac{6.022 \times 10^{23} \text{ H atoms}}{1 \text{ mol H}} = 1.03 \times 10^{24} \text{ H atoms}$$

Check Does the answer look reasonable? How many atoms of H would 60.06 g of urea contain?

Practice Exercise How many H atoms are in 72.5 g of isopropanol (rubbing alcohol), C₃H₈O?

Similar problems: 3.27, 3.28.

Note that the combined mass of a Na⁺ ion and a Cl⁻ ion is equal to the combined mass of a Na atom and a Cl atom.

Finally, note that for ionic compounds like NaCl and MgO that do not contain discrete molecular units, we use the term *formula mass* instead. The formula unit of NaCl consists of one Na⁺ ion and one Cl⁻ ion. Thus, the formula mass of NaCl is the mass of one formula unit:

$$\begin{aligned} \text{formula mass of NaCl} &= 22.99 \text{ amu} + 35.45 \text{ amu} \\ &= 58.44 \text{ amu} \end{aligned}$$

and its molar mass is 58.44 g.

Review of Concepts & Facts

- 3.3.1 Determine the molecular mass and the molar mass of citric acid, $\text{H}_3\text{C}_6\text{H}_5\text{O}_7$.
- 3.3.2 What is the mass in grams of 0.382 moles of caffeine, $\text{C}_8\text{H}_{10}\text{O}_2\text{N}_4$?
- 3.3.3 How many oxygen atoms are in 124 g of calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$ (molar mass = 310.2 g)?

3.4 The Mass Spectrometer

The most direct and accurate method for determining atomic and molecular masses is mass spectrometry, depicted in Figure 3.3. In one type of a *mass spectrometer*, a gaseous sample is bombarded by a stream of high-energy electrons. Collisions between the electrons and the gaseous atoms (or molecules) produce positive ions by dislodging an electron from each atom or molecule. These positive ions (of mass m and charge e) are accelerated by two oppositely charged plates as they pass through the plates. The emerging ions are deflected into a circular path by a magnet. The radius of the path depends on the charge-to-mass ratio (that is, e/m). Ions of smaller e/m ratio trace a wider curve than those having a larger e/m ratio, so that ions with equal charges but different masses are separated from one another. The mass of each ion (and hence its parent atom or molecule) is determined from the magnitude of its deflection. Eventually the ions arrive at the detector, which registers a current for each type of ion. The amount of current generated is directly proportional to the number of ions, so it enables us to determine the relative abundance of isotopes.

The first mass spectrometer, developed in the 1920s by the English physicist F. W. Aston,[†] was crude by today's standards. Nevertheless, it provided indisputable evidence of the existence of isotopes—neon-20 (atomic mass 19.9924 amu and natural abundance 90.92 percent) and neon-22 (atomic mass 21.9914 amu and natural abundance 8.82 percent). When more sophisticated and sensitive mass spectrometers became available, scientists were surprised to discover that neon has a third stable isotope with an atomic mass of 20.9940 amu and natural abundance 0.257 percent (Figure 3.4). This

Note that it is possible to determine the molar mass of a compound without knowing its chemical formula.

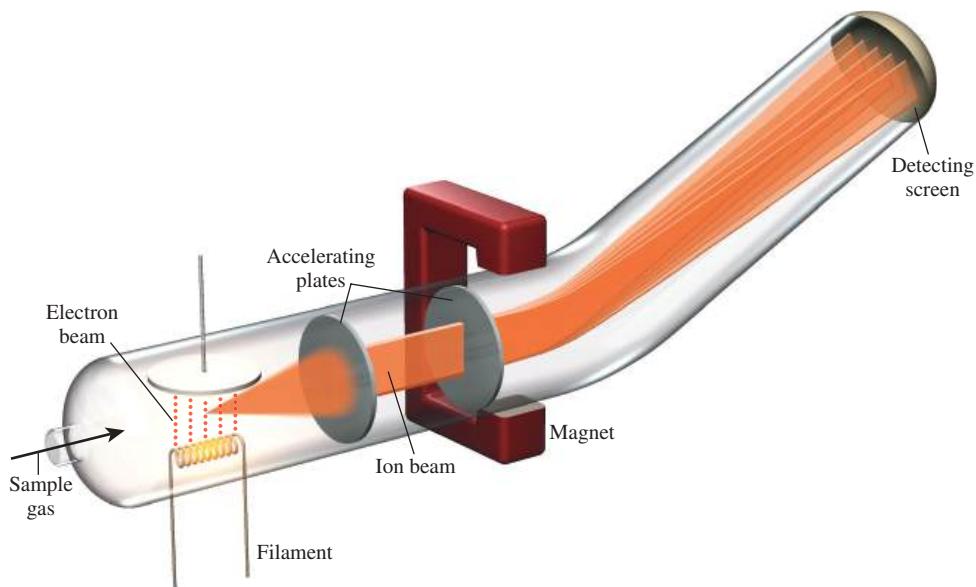


Figure 3.3 Schematic diagram of one type of mass spectrometer.

[†]Francis William Aston (1877–1945). English chemist and physicist. He was awarded the Nobel Prize in Chemistry in 1922 for developing the mass spectrometer.

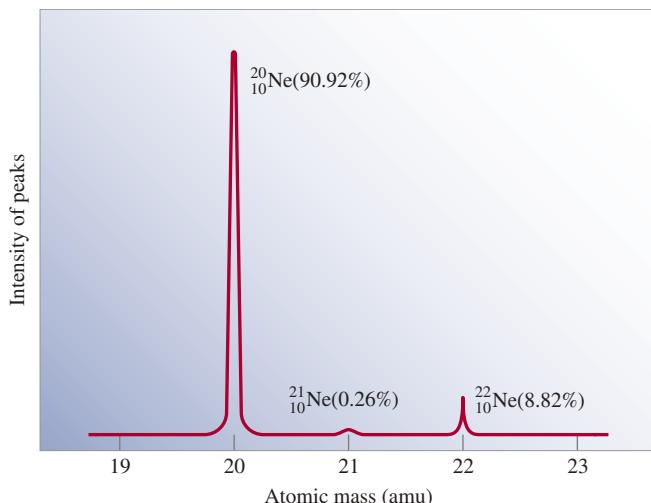


Figure 3.4 The mass spectrum of the three isotopes of neon.

example illustrates how very important experimental accuracy is to a quantitative science like chemistry. Early experiments failed to detect neon-21 because its natural abundance is just 0.257 percent. In other words, only 26 in 10,000 Ne atoms are neon-21. The masses of molecules can be determined in a similar manner by the mass spectrometer.

Review of Concepts & Facts

- 3.4.1** Explain how the mass spectrometer enables chemists to determine the average atomic mass of chlorine, which has two stable isotopes (^{35}Cl and ^{37}Cl).

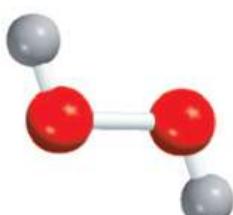
3.5 Percent Composition of Compounds

As we have seen, the formula of a compound tells us the numbers of atoms of each element in a unit of the compound. However, suppose we needed to verify the purity of a compound for use in a laboratory experiment. From the formula we could calculate what percent of the total mass of the compound is contributed by each element. Then, by comparing the result to the percent composition obtained experimentally for our sample, we could determine the purity of the sample.

The **percent composition by mass** is the *percent by mass of each element in a compound*. Percent composition is obtained by dividing the mass of each element in 1 mole of the compound by the molar mass of the compound and multiplying by 100 percent. Mathematically, the percent composition of an element in a compound is expressed as

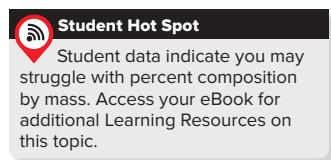
$$\text{percent composition of an element} = \frac{n \times \text{molar mass of element}}{\text{molar mass of compound}} \times 100\% \quad (3.1)$$

where n is the number of moles of the element in 1 mole of the compound. For example, in 1 mole of hydrogen peroxide (H_2O_2) there are 2 moles of H atoms and 2 moles of O atoms. The molar masses of H_2O_2 , H, and O are 34.02 g, 1.008 g, and 16.00 g, respectively. Therefore, the percent composition of H_2O_2 is calculated as follows:



$$\begin{aligned} \% \text{H} &= \frac{2 \times 1.008 \text{ g H}}{34.02 \text{ g H}_2\text{O}_2} \times 100\% = 5.926\% \\ \% \text{O} &= \frac{2 \times 16.00 \text{ g O}}{34.02 \text{ g H}_2\text{O}_2} \times 100\% = 94.06\% \end{aligned}$$

The sum of the percentages is $5.926\% + 94.06\% = 99.99\%$. The small discrepancy from 100 percent is due to the way we rounded off the molar masses of the elements. If we had used the empirical formula HO for the calculation, we would have obtained the same percentages. This is so because both the molecular formula and empirical formula tell us the percent composition by mass of the compound.



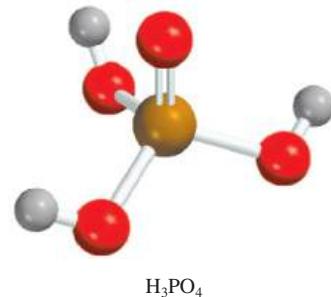
Example 3.8

Phosphoric acid (H_3PO_4) is a colorless, syrupy liquid used in detergents, fertilizers, toothpastes, and in carbonated beverages for a “tangy” flavor. Calculate the percent composition by mass of H, P, and O in this compound.

Strategy Recall the procedure for calculating a percentage. Assume that we have 1 mole of H_3PO_4 . The percent by mass of each element (H, P, and O) is given by the combined molar mass of the atoms of the element in 1 mole of H_3PO_4 divided by the molar mass of H_3PO_4 , then multiplied by 100 percent.

Solution The molar mass of H_3PO_4 is 97.99 g. The percent by mass of each of the elements in H_3PO_4 is calculated as follows:

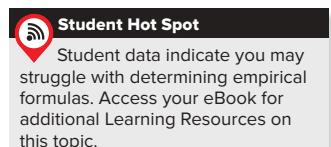
$$\begin{aligned}\% \text{H} &= \frac{3(1.008 \text{ g}) \text{ H}}{97.99 \text{ g } \text{H}_3\text{PO}_4} \times 100\% = 3.086\% \\ \% \text{P} &= \frac{30.97 \text{ g P}}{97.99 \text{ g } \text{H}_3\text{PO}_4} \times 100\% = 31.61\% \\ \% \text{O} &= \frac{4(16.00 \text{ g}) \text{ O}}{97.99 \text{ g } \text{H}_3\text{PO}_4} \times 100\% = 65.31\%\end{aligned}$$



Check Do the percentages add to 100 percent? The sum of the percentages is $(3.086\% + 31.61\% + 65.31\%) = 100.01\%$. The small discrepancy from 100 percent is due to the way we rounded off.

Practice Exercise Calculate the percent composition by mass of each of the elements in sulfuric acid (H_2SO_4).

Similar problem: 3.38.



The procedure used in the example can be reversed if necessary. Given the percent composition by mass of a compound, we can determine the empirical formula of the compound (Figure 3.5). Because we are dealing with percentages and the sum of all the percentages is 100 percent, it is convenient to assume that we started with 100 g of a compound, as Example 3.9 shows.

Example 3.9

Ascorbic acid (vitamin C) cures scurvy. It is composed of 40.92 percent carbon (C), 4.58 percent hydrogen (H), and 54.50 percent oxygen (O) by mass. Determine its empirical formula.

Strategy In a chemical formula, the subscripts represent the ratio of the number of moles of each element that combine to form one mole of the compound. How can we convert from mass percent to moles? If we assume an exactly 100-g sample of the compound, do we know the mass of each element in the compound? How do we then convert from grams to moles?

(Continued)

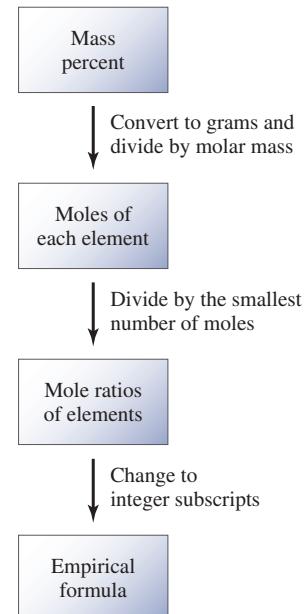


Figure 3.5 Procedure for calculating the empirical formula of a compound from its percent compositions.



The molecular formula of ascorbic acid is $C_6H_8O_6$.

Solution If we have 100 g of ascorbic acid, then each percentage can be converted directly to grams. In this sample, there will be 40.92 g of C, 4.58 g of H, and 54.50 g of O. Because the subscripts in the formula represent a mole ratio, we need to convert the grams of each element to moles. The conversion factor needed is the molar mass of each element. Let n represent the number of moles of each element so that

$$\begin{aligned} n_C &= 40.92 \text{ g } C \times \frac{1 \text{ mol } C}{12.01 \text{ g } C} = 3.407 \text{ mol } C \\ n_H &= 4.58 \text{ g } H \times \frac{1 \text{ mol } H}{1.008 \text{ g } H} = 4.54 \text{ mol } H \\ n_O &= 54.50 \text{ g } O \times \frac{1 \text{ mol } O}{16.00 \text{ g } O} = 3.406 \text{ mol } O \end{aligned}$$

Thus, we arrive at the formula $C_{3.407}H_{4.54}O_{3.406}$, which gives the identity and the mole ratios of atoms present. However, chemical formulas are written with whole numbers. Try to convert to whole numbers by dividing all the subscripts by the smallest subscript (3.406):

$$C: \frac{3.407}{3.406} \approx 1 \quad H: \frac{4.54}{3.406} = 1.33 \quad O: \frac{3.406}{3.406} = 1$$

where the \approx sign means “approximately equal to.” This gives $CH_{1.33}O$ as the formula for ascorbic acid. Next, we need to convert 1.33, the subscript for H, into an integer. This can be done by a trial-and-error procedure:

$$\begin{aligned} 1.33 \times 1 &= 1.33 \\ 1.33 \times 2 &= 2.66 \\ 1.33 \times 3 &= 3.99 \approx 4 \end{aligned}$$

Because 1.33×3 gives us an integer (4), we multiply all the subscripts by 3 and obtain $C_3H_4O_3$ as the empirical formula for ascorbic acid.

Check Are the subscripts in $C_3H_4O_3$ reduced to the smallest whole numbers?

Practice Exercise Determine the empirical formula of a compound having the following percent composition by mass: K: 24.75 percent; Mn: 34.77 percent; O: 40.51 percent.

Similar problems: 3.43, 3.44.

Chemists often want to know the actual mass of an element in a certain mass of a compound. For example, in the mining industry, this information will tell the scientists about the quality of the ore. Because the percent composition by mass of the elements in the substance can be readily calculated, such a problem can be solved in a rather direct way.



Chalcopyrite.
©The Natural History Museum/Alamy Stock Photo

Example 3.10

Chalcopyrite ($CuFeS_2$) is a principal mineral of copper. Calculate the number of kilograms of Cu in 3.71×10^3 kg of chalcopyrite.

Strategy Chalcopyrite is composed of Cu, Fe, and S. The mass due to Cu is based on its percentage by mass in the compound. How do we calculate mass percent of an element?

Solution The molar masses of Cu and $CuFeS_2$ are 63.55 g and 183.5 g, respectively. The mass percent of Cu is therefore

$$\begin{aligned} \%Cu &= \frac{\text{molar mass of Cu}}{\text{molar mass of } CuFeS_2} \times 100\% \\ &= \frac{63.55 \text{ g}}{183.5 \text{ g}} \times 100\% = 34.63\% \end{aligned}$$

(Continued)

To calculate the mass of Cu in a 3.71×10^3 kg sample of CuFeS₂, we need to convert the percentage to a fraction (that is, convert 34.63 percent to 34.63/100, or 0.3463) and write

$$\text{mass of Cu in CuFeS}_2 = 0.3463 \times (3.71 \times 10^3 \text{ kg}) = 1.28 \times 10^3 \text{ kg}$$

Check As a ball-park estimate, note that the mass percent of Cu is roughly 33 percent, so that a third of the mass should be Cu—that is, $\frac{1}{3} \times 3.71 \times 10^3 \text{ kg} \approx 1.24 \times 10^3 \text{ kg}$. This quantity is quite close to the answer.

Practice Exercise Calculate the number of grams of Al in 371 g of Al₂O₃.

Similar problem: 3.41.

Review of Concepts & Facts

- 3.5.1 Without doing detailed calculations, estimate whether the percent composition by mass of Sr is greater than or smaller than that of O in strontium nitrate [Sr(NO₃)₂].
- 3.5.2 What is the percent composition by mass of each of the elements present in fumaric acid, C₄H₄O₄?
- 3.5.3 Determine the empirical formula of a compound having the following percent composition by mass: P: 43.64 percent; O: 56.36 percent.

3.6 Experimental Determination of Empirical Formulas

The fact that we can determine the empirical formula of a compound if we know the percent composition enables us to identify compounds experimentally. The procedure is as follows. First, chemical analysis tells us the number of grams of each element present in a given amount of a compound. Then, we convert the quantities in grams to number of moles of each element. Finally, using the method given in Example 3.9, we find the empirical formula of the compound.

As a specific example, let us consider the compound ethanol. When ethanol is burned in an apparatus such as that shown in Figure 3.6, carbon dioxide (CO₂) and water (H₂O) are given off. Because neither carbon nor hydrogen was in the inlet gas, we can conclude that both carbon (C) and hydrogen (H) were present in ethanol and that oxygen (O) may also be present. (Molecular oxygen was added in the combustion process, but some of the oxygen may also have come from the original ethanol sample.)

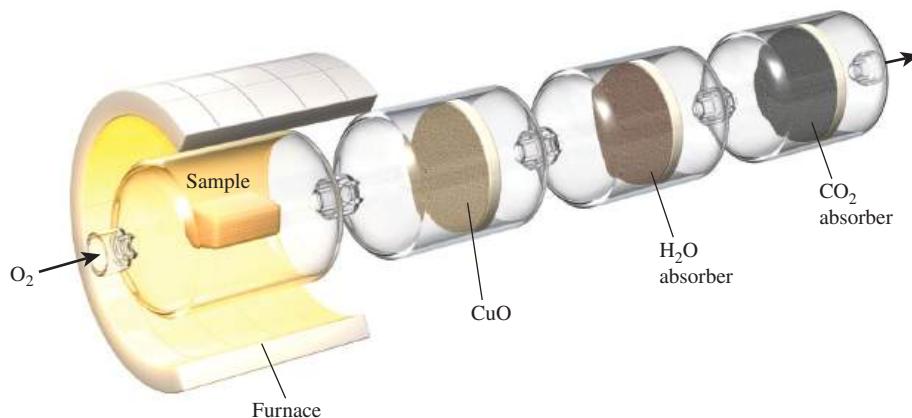


Figure 3.6 Apparatus for determining the empirical formula of ethanol. The absorbers are substances that can retain water and carbon dioxide, respectively. CuO is used to ensure complete combustion of all carbon to CO₂.

The masses of CO₂ and of H₂O produced can be determined by measuring the increase in mass of the CO₂ and H₂O absorbers, respectively. Suppose that in one experiment the combustion of 11.5 g of ethanol produced 22.0 g of CO₂ and 13.5 g of H₂O. We can calculate the mass of carbon and hydrogen in the original 11.5-g sample of ethanol as follows:

$$\text{mass of C} = 22.0 \text{ g CO}_2 \times \frac{1 \text{ mol CO}_2}{44.01 \text{ g CO}_2} \times \frac{1 \text{ mol C}}{1 \text{ mol CO}_2} \times \frac{12.01 \text{ g C}}{1 \text{ mol C}}$$

$$= 6.00 \text{ g C}$$

$$\text{mass of H} = 13.5 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} \times \frac{2 \text{ mol H}}{1 \text{ mol H}_2\text{O}} \times \frac{1.008 \text{ g H}}{1 \text{ mol H}}$$

$$= 1.51 \text{ g H}$$

Thus, 11.5 g of ethanol contains 6.00 g of carbon and 1.51 g of hydrogen. The remainder must be oxygen, whose mass is

$$\text{mass of O} = \text{mass of sample} - (\text{mass of C} + \text{mass of H})$$

$$= 11.5 \text{ g} - (6.00 \text{ g} + 1.51 \text{ g})$$

$$= 4.0 \text{ g}$$

The number of moles of each element present in 11.5 g of ethanol is

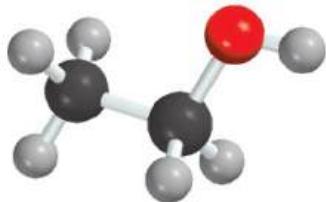
$$\text{moles of C} = 6.00 \text{ g C} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 0.500 \text{ mol C}$$

$$\text{moles of H} = 1.51 \text{ g H} \times \frac{1 \text{ mol H}}{1.008 \text{ g H}} = 1.50 \text{ mol H}$$

$$\text{moles of O} = 4.00 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 0.25 \text{ mol O}$$

The formula of ethanol is therefore C_{0.50}H_{1.5}O_{0.25} (we round off the number of moles to two significant figures). Because the number of atoms must be an integer, we divide the subscripts by 0.25, the smallest subscript, and obtain for the empirical formula C₂H₆O.

Now we can better understand the word “empirical,” which literally means “based only on observation and measurement.” The empirical formula of ethanol is determined from analysis of the compound in terms of its component elements. No knowledge of how the atoms are linked together in the compound is required.



It happens that the molecular formula of ethanol is the same as its empirical formula.

 **Student Hot Spot**
Student data indicate you may struggle with combustion analysis and determining molecular formulas. Access your eBook for additional Learning Resources on this topic.

Determination of Molecular Formulas

The formula calculated from percent composition by mass is always the empirical formula, because the subscripts in the formula are always reduced to the smallest whole numbers. To calculate the actual, molecular formula we must know the *approximate* molar mass of the compound in addition to its empirical formula. Knowing that the molar mass of a compound must be an integral multiple of the molar mass of its empirical formula, we can use the molar mass to find the molecular formula, as Example 3.11 demonstrates.

Example 3.11

A sample of a compound contains 30.46 percent nitrogen and 69.54 percent oxygen by mass, as determined by a mass spectrometer. In a separate experiment, the molar mass of the compound is found to be between 90 g and 95 g. Determine the molecular formula and the accurate molar mass of the compound.

(Continued)

Strategy To determine the molecular formula, we first need to determine the empirical formula. Comparing the empirical molar mass to the experimentally determined molar mass will reveal the relationship between the empirical formula and molecular formula.

Solution We start by assuming that there are 100 g of the compound. Then each percentage can be converted directly to grams—that is, 30.46 g of N and 69.54 g of O. Let n represent the number of moles of each element so that

$$n_N = 30.46 \text{ g N} \times \frac{1 \text{ mol N}}{14.01 \text{ g N}} = 2.174 \text{ mol N}$$

$$n_O = 69.54 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 4.346 \text{ mol O}$$

Thus, we arrive at the formula $\text{N}_{2.174}\text{O}_{4.346}$, which gives the identity and the ratios of atoms present. However, chemical formulas are written with whole numbers. Try to convert to whole numbers by dividing the subscripts by the smaller subscript (2.174). After rounding off, we obtain NO_2 as the empirical formula.

The molecular formula might be the same as the empirical formula or some integral multiple of it (for example, two, three, four, or more times the empirical formula). Comparing the ratio of the molar mass to the molar mass of the empirical formula will show the integral relationship between the empirical and molecular formulas. The molar mass of the empirical formula NO_2 is

$$\text{empirical molar mass} = 14.01 \text{ g} + 2(16.0 \text{ g}) = 46.01 \text{ g}$$

Next, we determine the ratio between the molar mass and the empirical molar mass

$$\frac{\text{molar mass}}{\text{empirical molar mass}} = \frac{90 \text{ g}}{46.01 \text{ g}} \approx 2$$

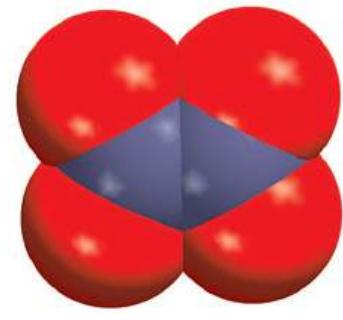
The molar mass is twice the empirical molar mass. This means that there are two NO_2 units in each molecule of the compound, and the molecular formula is $(\text{NO}_2)_2$ or N_2O_4 .

The actual molar mass of the compound is two times the empirical molar mass—that is, $2(46.01 \text{ g})$ or 92.02 g —which is between 90 g and 95 g.

Check Note that in determining the molecular formula from the empirical formula, we need only know the *approximate* molar mass of the compound. The reason is that the true molar mass is an integral multiple ($1\times$, $2\times$, $3\times$, ...) of the empirical molar mass. Therefore, the ratio (molar mass/empirical molar mass) will always be close to an integer.

Practice Exercise A sample of a compound containing boron (B) and hydrogen (H) contains 6.444 g of B and 1.803 g of H. The molar mass of the compound is about 30 g. What is its molecular formula?

Similar problems: 3.48, 3.49, 3.52.



N_2O_4

Review of Concepts & Facts

- 3.6.1** What is the molecular formula of a compound containing only carbon and hydrogen if combustion of 1.05 g of the compound produces 3.30 g CO_2 and 1.35 g H_2O and its molar mass is about 70 g?

3.7 Chemical Reactions and Chemical Equations

Having discussed the masses of atoms and molecules, we turn next to what happens to atoms and molecules in a **chemical reaction**, *a process in which a substance (or substances) is changed into one or more new substances*. To communicate with one another about chemical reactions, chemists have devised a standard way to represent them

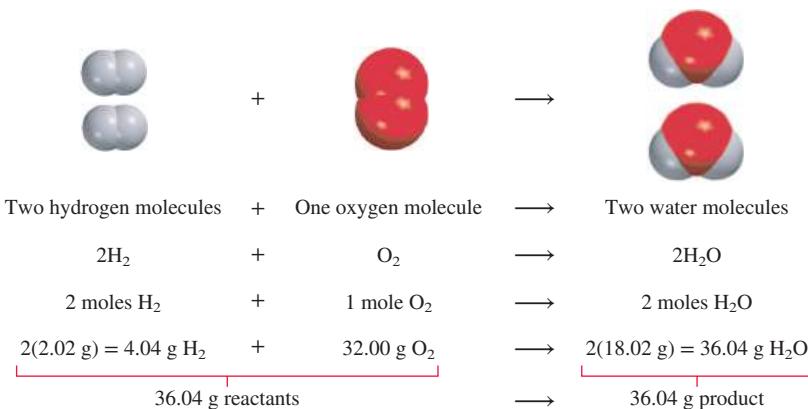


Figure 3.7 Three ways of representing the combustion of hydrogen. In accordance with the law of conservation of mass, the number of each type of atom must be the same on both sides of the equation.

using chemical equations. A **chemical equation** uses chemical symbols to show what happens during a chemical reaction. In this section, we will learn how to write chemical equations and balance them.

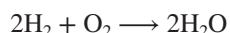
Writing Chemical Equations

Consider what happens when hydrogen gas (H_2) burns in air (which contains oxygen, O_2) to form water (H_2O). This reaction can be represented by the chemical equation



where the “plus” sign means “reacts with” and the arrow means “to yield.” Thus, this symbolic expression can be read: “Molecular hydrogen reacts with molecular oxygen to yield water.” The reaction is assumed to proceed from left to right as the arrow indicates.

Equation (3.2) is not complete, however, because there are twice as many oxygen atoms on the left side of the arrow (two) as on the right side (one). To conform with the law of conservation of mass, there must be the same number of each type of atom on both sides of the arrow—that is, we must have as many atoms after the reaction ends as we did before it started. We can *balance* Equation (3.2) by placing the appropriate coefficient (2 in this case) in front of H_2 and H_2O :

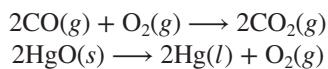


This *balanced chemical equation* shows that “two hydrogen molecules can combine or react with one oxygen molecule to form two water molecules” (Figure 3.7). Because the ratio of the number of molecules is equal to the ratio of the number of moles, the equation can also be read as “2 moles of hydrogen molecules react with 1 mole of oxygen molecules to produce 2 moles of water molecules.” We know the mass of a mole of each of these substances, so we can also interpret the equation as “4.04 g of H_2 react with 32.00 g of O_2 to give 36.04 g of H_2O .” These three ways of reading the equation are summarized in Figure 3.7.

We refer to H_2 and O_2 in Equation (3.2) as **reactants**, which are *the starting materials in a chemical reaction*. Water is the **product**, which is *the substance formed as a result of a chemical reaction*. A chemical equation, then, is just the chemist’s shorthand description of a reaction. In a chemical equation, the reactants are conventionally written on the left and the products on the right of the arrow:



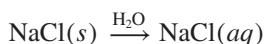
To provide additional information, chemists often indicate the physical states of the reactants and products by using the letters *g*, *l*, and *s* to denote gas, liquid, and solid, respectively. For example,



We use the law of conservation of mass as our guide in balancing chemical equations.

When the coefficient is 1, as in the case of O_2 , it is not shown.

To represent what happens when sodium chloride (NaCl) is added to water, we write

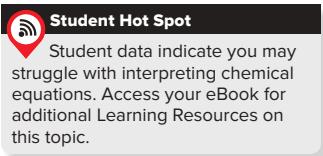


where *aq* denotes the aqueous (that is, water) environment. Writing H₂O above the arrow symbolizes the physical process of dissolving a substance in water, although it is sometimes left out for simplicity.

Knowing the states of the reactants and products is especially useful in the laboratory. For example, when potassium bromide (KBr) and silver nitrate (AgNO₃) react in an aqueous environment, a solid, silver bromide (AgBr), is formed. This reaction can be represented by the equation



If the physical states of reactants and products are not given, an uninformed person might try to bring about the reaction by mixing solid KBr with solid AgNO₃. These solids would react very slowly or not at all. Imagining the process on the microscopic level, we can understand that for a product like silver bromide to form, the Ag⁺ and Br⁻ ions would have to come in contact with each other. However, these ions are locked in place in their solid compounds and have little mobility. (Here is an example of how we explain a phenomenon by thinking about what happens at the molecular level, as discussed in Section 1.2.)



Balancing Chemical Equations

Suppose we want to write an equation to describe a chemical reaction that we have just carried out in the laboratory. How should we go about doing it? Because we know the identities of the reactants, we can write their chemical formulas. The identities of products are more difficult to establish. For simple reactions it is often possible to guess the product(s). For more complicated reactions involving three or more products, chemists may need to perform further tests to establish the presence of specific compounds.

Once we have identified all the reactants and products and have written the correct formulas for them, we assemble them in the conventional sequence—reactants on the left separated by an arrow from products on the right. The equation written at this point is likely to be *unbalanced*; that is, the number of each type of atom on one side of the arrow differs from the number on the other side. In general, we can balance a chemical equation by the following steps:

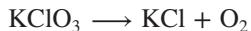
1. Identify all reactants and products and write their correct formulas on the left side and right side of the equation, respectively.
2. Begin balancing the equation by trying different coefficients to make the number of atoms of each element the same on both sides of the equation. We can change the coefficients (the numbers preceding the formulas) but not the subscripts (the numbers within formulas). Changing the subscripts would change the identity of the substance. For example, 2NO₂ means “two molecules of nitrogen dioxide,” but if we double the subscripts, we have N₂O₄, which is the formula of dinitrogen tetroxide, a completely different compound.
3. First, look for elements that appear only once on each side of the equation with the same number of atoms on each side: The formulas containing these elements must have the same coefficient. Therefore, there is no need to adjust the coefficients of these elements at this point. Next, look for elements that appear only once on each side of the equation but in unequal numbers of atoms. Balance these elements. Finally, balance elements that appear in two or more formulas on the same side of the equation.
4. Check your balanced equation to be sure that you have the same total number of each type of atoms on both sides of the equation arrow.



Heating potassium chlorate produces oxygen, which supports the combustion of a wood splint.

©McGraw-Hill Education/Ken Karp

Let's consider a specific example. In the laboratory, small amounts of oxygen gas can be prepared by heating potassium chlorate (KClO_3). The products are oxygen gas (O_2) and potassium chloride (KCl). From this information, we write



(For simplicity, we omit the physical states of reactants and products.) All three elements (K, Cl, and O) appear only once on each side of the equation, but only for K and Cl do we have equal numbers of atoms on both sides. Thus, KClO_3 and KCl must have the same coefficient. The next step is to make the number of O atoms the same on both sides of the equation. Because there are three O atoms on the left and two O atoms on the right of the equation, we can balance the O atoms by placing a 2 in front of KClO_3 and a 3 in front of O_2 .



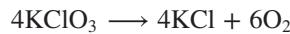
Finally, we balance the K and Cl atoms by placing a 2 in front of KCl:



As a final check, we can draw up a balance sheet for the reactants and products where the number in parentheses indicates the number of atoms of each element:

Reactants	Products
K (2)	K (2)
Cl (2)	Cl (2)
O (6)	O (6)

Note that this equation could also be balanced with coefficients that are multiples of 2 (for KClO_3), 2 (for KCl), and 3 (for O_2); for example,

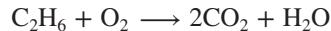


However, it is common practice to use the *simplest* possible set of whole-number coefficients to balance the equation. Equation (3.3) conforms to this convention.

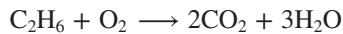
Now let us consider the combustion (that is, burning) of the natural gas component ethane (C_2H_6) in oxygen or air, which yields carbon dioxide (CO_2) and water. The unbalanced equation is



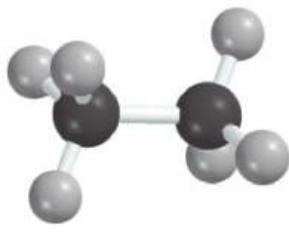
We see that the number of atoms is not the same on both sides of the equation for any of the elements (C, H, and O). In addition, C and H appear only once on each side of the equation; O appears in two compounds on the right side (CO_2 and H_2O). To balance the C atoms, we place a 2 in front of CO_2 :



To balance the H atoms, we place a 3 in front of H_2O :

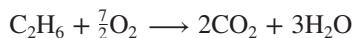


At this stage, the C and H atoms are balanced, but the O atoms are not because there are seven O atoms on the right-hand side and only two O atoms on the left-hand side of the



C_2H_6

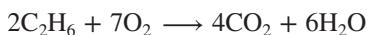
equation. This inequality of O atoms can be eliminated by writing $\frac{7}{2}$ in front of the O₂ on the left-hand side:



The “logic” for using $\frac{7}{2}$ as a coefficient is that there were seven oxygen atoms on the right-hand side of the equation, but only a pair of oxygen atoms (O₂) on the left. To balance them we ask how many *pairs* of oxygen atoms are needed to equal seven oxygen atoms. Just as 3.5 pairs of shoes equal seven shoes, $\frac{7}{2}$ O₂ molecules equal seven O atoms. As the following tally shows, the equation is now balanced.

Reactants	Products
C (2)	C (2)
H (6)	H (6)
O (7)	O (7)

However, we normally prefer to express the coefficients as whole numbers rather than as fractions. Therefore, we multiply the entire equation by 2 to convert $\frac{7}{2}$ to 7:



The final tally is

Reactants	Products
C (4)	C (4)
H (12)	H (12)
O (14)	O (14)

Note that the coefficients used in balancing the last equation are the smallest possible set of whole numbers.

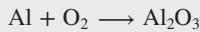
In Example 3.12 we will continue to practice our equation-balancing skills.

Example 3.12

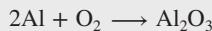
When aluminum metal is exposed to air, a protective layer of aluminum oxide (Al₂O₃) forms on its surface. This layer prevents further reaction between aluminum and oxygen, and it is the reason that aluminum beverage cans do not corrode. [In the case of iron, the rust, or iron(III) oxide, that forms is too porous to protect the iron metal underneath, so rusting continues.] Write a balanced equation for the formation of Al₂O₃.

Strategy Remember that the formula of an element or compound cannot be changed when balancing a chemical equation. The equation is balanced by placing the appropriate coefficients in front of the formulas. Follow the procedure for balancing equations described earlier.

Solution The unbalanced equation is

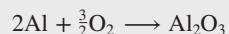


In a balanced equation, the number and types of atoms on each side of the equation must be the same. We see that there is one Al atom on the reactants side and there are two Al atoms on the product side. We can balance the Al atoms by placing a coefficient of 2 in front of Al on the reactants side.



(Continued)

There are two O atoms on the reactants side, and three O atoms on the product side of the equation. We can balance the O atoms by placing a coefficient of $\frac{3}{2}$ in front of O₂ on the reactants side.



This is a balanced equation. However, equations are normally balanced with the smallest set of *whole-number* coefficients. Multiplying both sides of the equation by 2 gives whole-number coefficients.



or



Check For an equation to be balanced, the number and types of atoms on each side of the equation must be the same. The final tally is

Reactants	Products
Al (4)	Al (4)
O (6)	O (6)

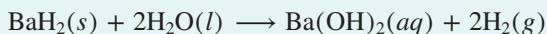
The equation is balanced. Also, the coefficients are reduced to the simplest set of whole numbers.

Practice Exercise Balance the equation representing the reaction between iron(III) oxide (Fe₂O₃) and carbon monoxide (CO) to yield iron (Fe) and carbon dioxide (CO₂).

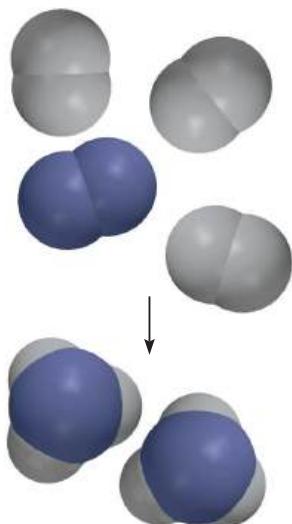
Similar problems: 3.55, 3.56.

Review of Concepts & Facts

- 3.7.1** Which parts of the equation shown here are essential for a balanced equation and which parts are helpful if we want to carry out the reaction in the laboratory?



- 3.7.2** What is the balanced equation representing the reaction between potassium thiosulfate (K₂S₂O₃) and iodine (I₂) to produce potassium tetrathionate (K₂S₄O₆) and potassium iodide (KI)?

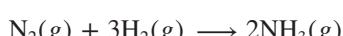


The synthesis of NH₃ from H₂ and N₂.

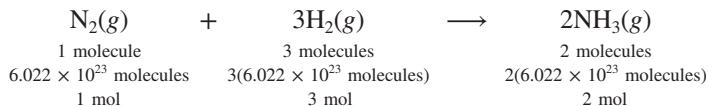
3.8 Amounts of Reactants and Products

A basic question raised in the chemical laboratory is, “How much product will be formed from specific amounts of starting materials (reactants)?” Or in some cases, we might ask the reverse question, “How much starting material must be used to obtain a specific amount of product?” To interpret a reaction quantitatively, we need to apply our knowledge of molar masses and the mole concept. **Stoichiometry** is the quantitative study of reactants and products in a chemical reaction.

Whether the units given for reactants (or products) are moles, grams, liters (for gases), or some other units, we use moles to calculate the amount of product formed in a reaction. This approach is called the **mole method**, which means simply that *the stoichiometric coefficients in a chemical equation can be interpreted as the number of moles of each substance*. For example, industrially ammonia is synthesized from hydrogen and nitrogen as follows:



The stoichiometric coefficients show that one molecule of N₂ reacts with three molecules of H₂ to form two molecules of NH₃. It follows that the relative numbers of moles are the same as the relative number of molecules:



Thus, this equation can also be read as “1 mole of N₂ gas combines with 3 moles of H₂ gas to form 2 moles of NH₃ gas.” In stoichiometric calculations, we say that three moles of H₂ are equivalent to two moles of NH₃, that is,

$$3 \text{ mol H}_2 \simeq 2 \text{ mol NH}_3$$

where the symbol \simeq means “stoichiometrically equivalent to” or simply “equivalent to.” This relationship enables us to write the conversion factors

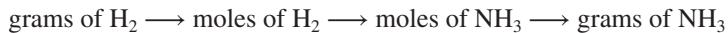
$$\frac{3 \text{ mol H}_2}{2 \text{ mol NH}_3} \quad \text{and} \quad \frac{2 \text{ mol NH}_3}{3 \text{ mol H}_2}$$

Similarly, we have 1 mol N₂ \simeq 2 mol NH₃ and 1 mol N₂ \simeq 3 mol H₂.

Let’s consider a simple example in which 6.0 moles of H₂ react completely with N₂ to form NH₃. To calculate the amount of NH₃ produced in moles, we use the conversion factor that has H₂ in the denominator and write

$$\begin{aligned} \text{moles of NH}_3 \text{ produced} &= 6.0 \cancel{\text{mol H}_2} \times \frac{2 \text{ mol NH}_3}{3 \cancel{\text{mol H}_2}} \\ &= 4.0 \text{ mol NH}_3 \end{aligned}$$

Now suppose 16.0 g of H₂ react completely with N₂ to form NH₃. How many grams of NH₃ will be formed? To do this calculation, we note that the link between H₂ and NH₃ is the mole ratio from the balanced equation. So we need to first convert grams of H₂ to moles of H₂, then to moles of NH₃, and finally to grams of NH₃. The conversion steps are



First, we convert 16.0 g of H₂ to number of moles of H₂, using the molar mass of H₂ as the conversion factor.

$$\begin{aligned} \text{moles of H}_2 &= 16.0 \cancel{\text{g H}_2} \times \frac{1 \text{ mol H}_2}{2.016 \cancel{\text{g H}_2}} \\ &= 7.94 \text{ mol H}_2 \end{aligned}$$

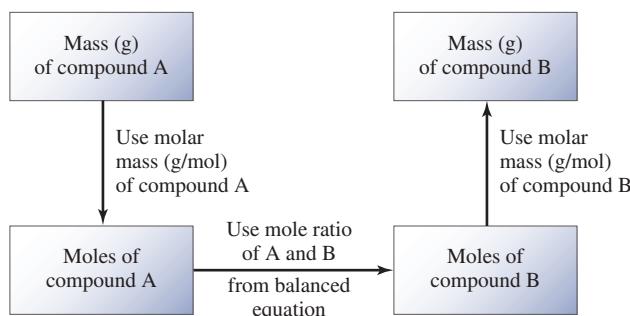
Next, we calculate the number of moles of NH₃ produced.

$$\begin{aligned} \text{moles of NH}_3 &= 7.94 \cancel{\text{mol H}_2} \times \frac{2 \text{ mol NH}_3}{3 \cancel{\text{mol H}_2}} \\ &= 5.29 \text{ mol NH}_3 \end{aligned}$$

Finally, we calculate the mass of NH₃ produced in grams using the molar mass of NH₃ as the conversion factor.

$$\begin{aligned} \text{grams of NH}_3 &= 5.29 \cancel{\text{mol NH}_3} \times \frac{17.03 \text{ g NH}_3}{1 \cancel{\text{mol NH}_3}} \\ &= 90.1 \text{ g NH}_3 \end{aligned}$$

Figure 3.8 The procedure for calculating the amounts of reactants or products in a reaction using the mole method.



These three separate calculations can be combined in a single step as follows:

$$\text{grams of NH}_3 = 16.0 \text{ g H}_2 \times \frac{1 \text{ mol H}_2}{2.016 \text{ g H}_2} \times \frac{2 \text{ mol NH}_3}{3 \text{ mol H}_2} \times \frac{17.03 \text{ g NH}_3}{1 \text{ mol NH}_3} \\ = 90.1 \text{ g NH}_3$$

Similarly, we can calculate the mass in grams of N₂ consumed in this reaction. The conversion steps are



By using the relationship 1 mol N₂ ≈ 3 mol H₂, we write

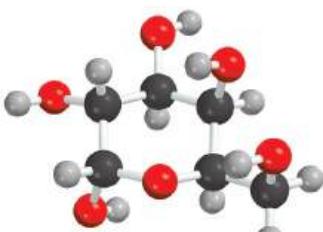
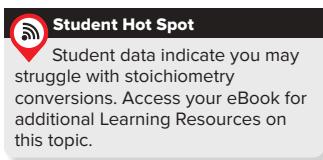
$$\text{grams of N}_2 = 16.0 \text{ g H}_2 \times \frac{1 \text{ mol H}_2}{2.016 \text{ g H}_2} \times \frac{1 \text{ mol N}_2}{3 \text{ mol H}_2} \times \frac{28.02 \text{ g N}_2}{1 \text{ mol N}_2} \\ = 74.1 \text{ g N}_2$$

The general approach for solving stoichiometry problems is summarized next.

1. Write a balanced equation for the reaction.
2. Convert the given amount of the reactant (in grams or other units) to number of moles.
3. Use the mole ratio from the balanced equation to calculate the number of moles of product formed.
4. Convert the moles of product to grams (or other units) of product.

Figure 3.8 shows these steps. Sometimes we may be asked to calculate the amount of a reactant needed to form a specific amount of product. In those cases, we can reverse the steps shown in Figure 3.8.

Examples 3.13 and 3.14 illustrate the application of this approach.



Example 3.13

The food we eat is degraded, or broken down, in our bodies to provide energy for growth and function. A general overall equation for this very complex process represents the degradation of glucose (C₆H₁₂O₆) to carbon dioxide (CO₂) and water (H₂O):



If 856 g of C₆H₁₂O₆ is consumed by a person over a certain period, what is the mass of CO₂ produced?

(Continued)

Strategy Looking at the balanced equation, how do we compare the amounts of C₆H₁₂O₆ and CO₂? We can compare them based on the *mole ratio* from the balanced equation. Starting with grams of C₆H₁₂O₆, how do we convert to moles of C₆H₁₂O₆? Once moles of CO₂ are determined using the mole ratio from the balanced equation, how do we convert to grams of CO₂?

Solution We follow the preceding steps and Figure 3.8.

Step 1: The balanced equation is given in the problem.

Step 2: To convert grams of C₆H₁₂O₆ to moles of C₆H₁₂O₆, we write

$$856 \text{ g } \cancel{\text{C}_6\text{H}_{12}\text{O}_6} \times \frac{1 \text{ mol C}_6\text{H}_{12}\text{O}_6}{180.2 \text{ g } \cancel{\text{C}_6\text{H}_{12}\text{O}_6}} = 4.750 \text{ mol C}_6\text{H}_{12}\text{O}_6$$

Step 3: From the mole ratio, we see that 1 mol C₆H₁₂O₆ \approx 6 mol CO₂. Therefore, the number of moles of CO₂ formed is

$$4.750 \text{ mol } \cancel{\text{C}_6\text{H}_{12}\text{O}_6} \times \frac{6 \text{ mol CO}_2}{1 \text{ mol } \cancel{\text{C}_6\text{H}_{12}\text{O}_6}} = 28.50 \text{ mol CO}_2$$

Step 4: Finally, the number of grams of CO₂ formed is given by

$$28.50 \text{ mol } \cancel{\text{CO}_2} \times \frac{44.01 \text{ g CO}_2}{1 \text{ mol } \cancel{\text{CO}_2}} = 1.25 \times 10^3 \text{ g CO}_2$$

After some practice, we can combine the conversion steps



into one equation:

$$\begin{aligned} \text{mass of CO}_2 &= 856 \text{ g } \cancel{\text{C}_6\text{H}_{12}\text{O}_6} \times \frac{1 \text{ mol } \cancel{\text{C}_6\text{H}_{12}\text{O}_6}}{180.2 \text{ g } \cancel{\text{C}_6\text{H}_{12}\text{O}_6}} \times \frac{6 \text{ mol CO}_2}{1 \text{ mol } \cancel{\text{C}_6\text{H}_{12}\text{O}_6}} \times \frac{44.01 \text{ g CO}_2}{1 \text{ mol } \cancel{\text{CO}_2}} \\ &= 1.25 \times 10^3 \text{ g CO}_2 \end{aligned}$$

Check Does the answer seem reasonable? Should the mass of CO₂ produced be larger than the mass of C₆H₁₂O₆ reacted, even though the molar mass of CO₂ is considerably less than the molar mass of C₆H₁₂O₆? What is the mole ratio between CO₂ and C₆H₁₂O₆?

Practice Exercise Methanol (CH₃OH) burns in air according to the equation



If 209 g of methanol are used up in a combustion process, what is the mass of H₂O produced?

Similar problem: 3.72.

Example 3.14

All alkali metals react with water to produce hydrogen gas and the corresponding alkali metal hydroxide. A typical reaction is that between lithium and water:



How many grams of Li are needed to produce 9.89 g of H₂?

(Continued)



Lithium reacting with water to produce hydrogen gas.

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Strategy The question asks for number of grams of reactant (Li) to form a specific amount of product (H_2). Therefore, we need to reverse the steps shown in Figure 3.8. From the equation we see that $2 \text{ mol Li} \approx 1 \text{ mol } H_2$.

Solution The conversion steps are



Combining these steps into one equation, we write

$$9.89 \text{ g } H_2 \times \frac{1 \text{ mol } H_2}{2.016 \text{ g } H_2} \times \frac{2 \text{ mol Li}}{1 \text{ mol } H_2} \times \frac{6.941 \text{ g Li}}{1 \text{ mol Li}} = 68.1 \text{ g Li}$$

Check There are roughly 5 moles of H_2 in 9.89 g H_2 , so we need 10 moles of Li. From the approximate molar mass of Li (7 g), does the answer seem reasonable?

Practice Exercise The reaction between nitric oxide (NO) and oxygen to form nitrogen dioxide (NO_2) is a key step in photochemical smog formation:



How many grams of O_2 are needed to produce 2.21 g of NO_2 ?

Similar problem: 3.64.

Review of Concepts & Facts

3.8.1 Which of the following statements is correct for the equation shown here?



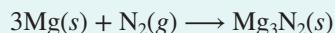
- (a) 6 g of $H_2\text{O}$ are produced for every 4 g of NH_3 reacted.
- (b) 1 mole of NO is produced per mole of NH_3 reacted.
- (c) 2 moles of NO are produced for every 3 moles of O_2 reacted.

3.8.2 Silicon reacts with chromium(III) oxide according to the equation



If 59.4 g of silicon is consumed in the reaction, what is the mass of SiO_2 produced?

3.8.3 At high temperatures, magnesium reacts with nitrogen gas according to the equation



How many grams of magnesium are needed to produce 25.0 g of Mg_3N_2 ?

3.9 Limiting Reactants



Video

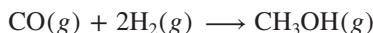
Limiting Reagent

When a chemist carries out a reaction, the reactants are usually not present in exact **stoichiometric amounts**, that is, *in the proportions indicated by the balanced equation*. Because the goal of a reaction is to produce the maximum quantity of a useful compound from the starting materials, frequently a large excess of one reactant is supplied to ensure that the more expensive reactant is completely converted to the desired product. Consequently, some reactant will be left over at the end of the reaction. *The reactant used up first in a reaction is called the **limiting reactant***, because the maximum

amount of product formed depends on how much of this reactant was originally present. When this reactant is used up, no more product can be formed. **Excess reactants** are the reactants present in quantities greater than necessary to react with the quantity of the limiting reagent.

The concept of the limiting reactant is analogous to the relationship between men and women in a dance contest at a club. If there are 14 men and only 9 women, then only 9 female/male pairs can compete. Five men will be left without partners. The number of women thus *limits* the number of men that can dance in the contest, and there is an *excess* of men.

Consider the industrial synthesis of methanol (CH_3OH) from carbon monoxide and hydrogen at high temperatures:



Suppose initially we have 4 moles of CO and 6 moles of H_2 (Figure 3.9). One way to determine which of two reactants is the limiting reagent is to calculate the number of moles of CH_3OH obtained based on the initial quantities of CO and H_2 . From the preceding definition, we see that only the limiting reactant will yield the *smaller* amount of the product. Starting with 4 moles of CO, we find the number of moles of CH_3OH produced is

$$4 \cancel{\text{mol CO}} \times \frac{1 \text{ mol CH}_3\text{OH}}{1 \cancel{\text{mol CO}}} = 4 \text{ mol CH}_3\text{OH}$$

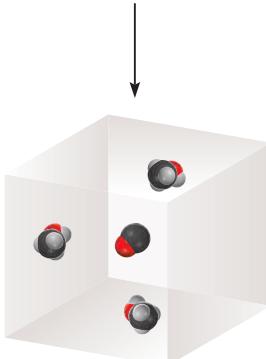
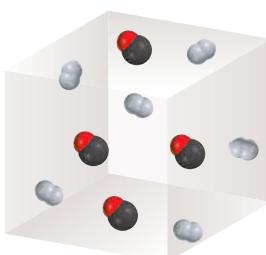
and starting with 6 moles of H_2 , the number of moles of CH_3OH formed is

$$6 \cancel{\text{mol H}_2} \times \frac{1 \text{ mol CH}_3\text{OH}}{2 \cancel{\text{mol H}_2}} = 3 \text{ mol CH}_3\text{OH}$$

Because H_2 results in a smaller amount of CH_3OH , it must be the limiting reagent. Therefore, CO is the excess reagent.

In stoichiometric calculations involving limiting reactants, the first step is to decide which reactant is the limiting reactant. After the limiting reactant has been identified, the rest of the problem can be solved as outlined in Section 3.8. Example 3.15 illustrates this approach.

Before reaction has started



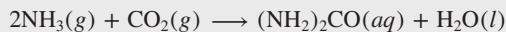
After reaction is complete



Figure 3.9 At the start of the reaction, there were six H_2 molecules and four CO molecules. At the end, all the H_2 molecules are gone and only one CO molecule is left. Therefore, H_2 molecule is the limiting reactant and CO is the excess reagent. Each molecule can also be treated as one mole of the substance in this reaction.

Example 3.15

The synthesis of urea, $(\text{NH}_2)_2\text{CO}$, is considered to be the first recognized example of preparing a biological compound from nonbiological reactants, challenging the notion that biological processes involved a “vital force” present only in living systems. Today urea is produced industrially by reacting ammonia with carbon dioxide:



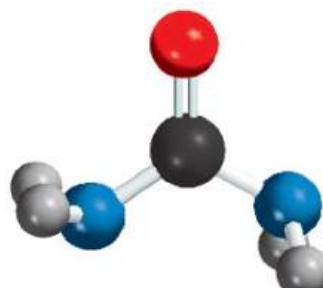
In one process, 637.2 g of NH_3 are treated with 1142 g of CO_2 . (a) Which of the two reactants is the limiting reactant? (b) Calculate the mass of $(\text{NH}_2)_2\text{CO}$ formed. (c) How much excess reagent (in grams) is left at the end of the reaction?

(a) Strategy The reactant that produces fewer moles of product is the limiting reactant because it limits the amount of product that can be formed. How do we convert from the amount of reactant to the amount of product? Perform this calculation for each reactant, then compare the moles of product, $(\text{NH}_2)_2\text{CO}$, formed by the given amounts of NH_3 and CO_2 to determine which reactant is the limiting reagent.

(Continued)

Student Hot Spot

Student data indicate you may struggle with finding the limiting reactant. Access your eBook for additional Learning Resources on this topic.



Solution We carry out two separate calculations. First, starting with 637.2 g of NH₃, we calculate the number of moles of (NH₂)₂CO that could be produced if all the NH₃ reacted according to the following conversions.



Combining these conversions in one step, we write

$$\begin{aligned}\text{moles of (NH}_2\text{)}_2\text{CO} &= 637.2 \cancel{\text{g NH}_3} \times \frac{1 \text{ mol NH}_3}{17.03 \cancel{\text{g NH}_3}} \times \frac{1 \text{ mol (NH}_2\text{)}_2\text{CO}}{2 \cancel{\text{mol NH}_3}} \\ &= 18.71 \text{ mol (NH}_2\text{)}_2\text{CO}\end{aligned}$$

Second, for 1142 g of CO₂, the conversions are



The number of moles of (NH₂)₂CO that could be produced if all the CO₂ reacted is

$$\begin{aligned}\text{moles of (NH}_2\text{)}_2\text{CO} &= 1142 \cancel{\text{g CO}_2} \times \frac{1 \text{ mol CO}_2}{44.01 \cancel{\text{g CO}_2}} \times \frac{1 \text{ mol (NH}_2\text{)}_2\text{CO}}{1 \cancel{\text{mol CO}_2}} \\ &= 25.95 \text{ mol (NH}_2\text{)}_2\text{CO}\end{aligned}$$

It follows, therefore, that NH₃ must be the limiting reactant because it produces a smaller amount of (NH₂)₂CO.

(b) Strategy We determined the moles of (NH₂)₂CO produced in part (a), using NH₃ as the limiting reactant. How do we convert from moles to grams?

Solution The molar mass of (NH₂)₂CO is 60.06 g. We use this as a conversion factor to convert from moles of (NH₂)₂CO to grams of (NH₂)₂CO:

$$\begin{aligned}\text{mass of (NH}_2\text{)}_2\text{CO} &= 18.71 \cancel{\text{mol (NH}_2\text{)}_2\text{CO}} \times \frac{60.06 \text{ g (NH}_2\text{)}_2\text{CO}}{1 \cancel{\text{mol (NH}_2\text{)}_2\text{CO}}} \\ &= 1124 \text{ g (NH}_2\text{)}_2\text{CO}\end{aligned}$$

Check Does your answer seem reasonable? Note that 18.71 moles of product are formed. What is the mass of 1 mole of (NH₂)₂CO?

(c) Strategy Working backward, we can determine the amount of CO₂ that reacted to produce 18.71 moles of (NH₂)₂CO. The amount of CO₂ left over is the difference between the initial amount and the amount reacted.

Solution Starting with 18.71 moles of (NH₂)₂CO, we can determine the mass of CO₂ that reacted using the mole ratio from the balanced equation and the molar mass of CO₂. The conversion steps are



so that

$$\begin{aligned}\text{mass of CO}_2 \text{ reacted} &= 18.71 \cancel{\text{mol (NH}_2\text{)}_2\text{CO}} \times \frac{1 \text{ mol CO}_2}{1 \cancel{\text{mol (NH}_2\text{)}_2\text{CO}}} \times \frac{44.01 \text{ g CO}_2}{1 \text{ mol CO}_2} \\ &= 823.4 \text{ g CO}_2\end{aligned}$$

The amount of CO₂ remaining (in excess) is the difference between the initial amount (1142 g) and the amount reacted (823.4 g):

$$\text{mass of CO}_2 \text{ remaining} = 1142 \text{ g} - 823.4 \text{ g} = 319 \text{ g}$$

(Continued)

Practice Exercise The reaction between aluminum and iron(III) oxide can generate temperatures approaching 3000°C and is used in welding metals:



In one process, 124 g of Al are reacted with 601 g of Fe_2O_3 . (a) Calculate the mass (in grams) of Al_2O_3 formed. (b) How much of the excess reactant is left at the end of the reaction?

Similar problem: 3.86.

Example 3.15 brings out an important point. In practice, chemists usually choose the more expensive chemical as the limiting reactant so that all or most of it will be converted to products in the reaction. In the synthesis of urea, NH_3 is invariably the limiting reactant because it is more expensive than CO_2 . At other times, an excess of one reactant is used to help drive the reaction to completion, or to compensate for a side reaction that consumes that reactant. Synthetic chemists often have to calculate the amount of reactant to use based on this need to have one or more components in excess, as Example 3.16 shows.

Example 3.16

The reaction between alcohols and halogen compounds to form ethers is important in organic chemistry, as illustrated here for the reaction between methanol (CH_3OH) and methyl bromide (CH_3Br) to form dimethylether (CH_3OCH_3), which is a useful precursor to other organic compounds and an aerosol propellant.



This reaction is carried out in a dry (water-free) organic solvent, and the butyl lithium (LiC_4H_9) serves to remove a hydrogen ion from CH_3OH . Butyl lithium will also react with any residual water in the solvent, so the reaction is typically carried out with 2.5 molar equivalents of that reagent. How many grams of CH_3Br and LiC_4H_9 will be needed to carry out the preceding reaction with 10.0 g of CH_3OH ?

Solution We start with the knowledge that CH_3OH and CH_3Br are present in stoichiometric amounts and that LiC_4H_9 is the excess reactant. To calculate the quantities of CH_3Br and LiC_4H_9 needed, we proceed as shown in Example 3.14.

$$\begin{aligned}\text{grams of CH}_3\text{Br} &= 10.0 \cancel{\text{g CH}_3\text{OH}} \times \frac{1 \text{ mol CH}_3\text{OH}}{32.04 \cancel{\text{g CH}_3\text{OH}}} \times \frac{1 \text{ mol CH}_3\text{Br}}{1 \cancel{\text{mol CH}_3\text{OH}}} \times \frac{94.93 \text{ g CH}_3\text{Br}}{1 \cancel{\text{mol CH}_3\text{Br}}} \\ &= 29.6 \text{ g CH}_3\text{Br}\end{aligned}$$

$$\begin{aligned}\text{grams of LiC}_4\text{H}_9 &= 10.0 \cancel{\text{g CH}_3\text{OH}} \times \frac{1 \text{ mol CH}_3\text{OH}}{32.04 \cancel{\text{g CH}_3\text{OH}}} \times \frac{2.5 \text{ mol LiC}_4\text{H}_9}{1 \cancel{\text{mol CH}_3\text{OH}}} \times \frac{64.05 \text{ g LiC}_4\text{H}_9}{1 \cancel{\text{mol LiC}_4\text{H}_9}} \\ &= 50.0 \text{ g LiC}_4\text{H}_9\end{aligned}$$

Practice Exercise The reaction between benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$) and octanol ($\text{C}_8\text{H}_{17}\text{OH}$) to yield octyl benzoate ($\text{C}_6\text{H}_5\text{COOC}_8\text{H}_{17}$) and water

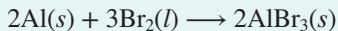


is carried out with an excess of $\text{C}_8\text{H}_{17}\text{OH}$ to help drive the reaction to completion and maximize the yield of product. If an organic chemist wants to use 1.5 molar equivalents of $\text{C}_8\text{H}_{17}\text{OH}$, how many grams of $\text{C}_8\text{H}_{17}\text{OH}$ would be required to carry out the reaction with 15.7 g of $\text{C}_6\text{H}_5\text{COOH}$?

Similar problems: 3.137, 3.138.

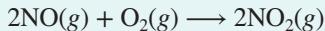
Review of Concepts & Facts

3.9.1 Aluminum and bromine vigorously react according to the equation

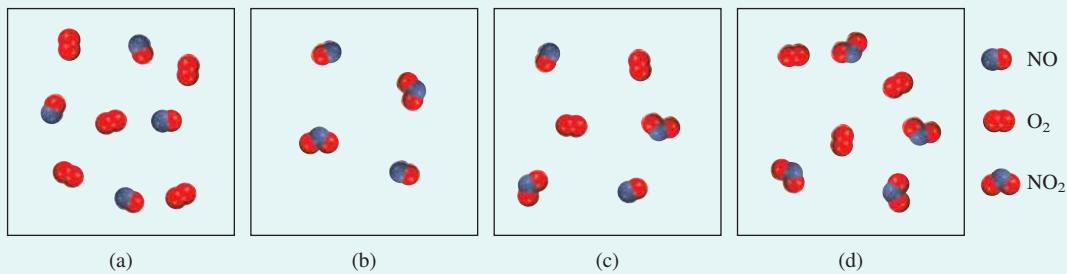


(a) If 5.00 g of aluminum and 22.2 g of bromine react, what mass of AlBr_3 is produced? (b) What mass of the excess reactant remains at the end of the reaction?

3.9.2 Consider the following reaction:



Starting with the reactants shown in (a), which of the diagrams shown in (b)–(d) best represents the situation in which the limiting reactant has completely reacted?



3.10 Reaction Yield

Keep in mind that the theoretical yield is the yield that you calculate using the balanced equation. The actual yield is the yield obtained by carrying out the reaction.

The amount of limiting reactant present at the start of a reaction determines the **theoretical yield** of the reaction—that is, *the amount of product that would result if all the limiting reactant reacted*. The theoretical yield, then, is the *maximum obtainable yield*, predicted by the balanced equation. In practice, the **actual yield**, or *the amount of product actually obtained from a reaction*, is almost always less than the theoretical yield. There are many reasons for the difference between actual and theoretical yields. For instance, many reactions are reversible, and so they do not proceed 100 percent from left to right. Even when a reaction is 100 percent complete, it may be difficult to recover all of the product from the reaction medium (say, from an aqueous solution). Some reactions are complex in the sense that the products formed may react further among themselves or with the reactants to form still other products. These additional reactions will reduce the yield of the first reaction.

To determine how efficient a given reaction is, chemists often figure the **percent yield**, which describes *the proportion of the actual yield to the theoretical yield*. It is calculated as follows:

$$\% \text{yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\% \quad (3.4)$$

Percent yields may range from a fraction of 1 percent to 100 percent. Chemists strive to maximize the percent yield in a reaction. Factors that can affect the percent yield include temperature and pressure. We will study these effects later.

In Example 3.17 we will calculate the yield of an industrial process.

Example 3.17

Titanium is a strong, lightweight, corrosion-resistant metal that is used in rockets, aircraft, jet engines, and bicycle frames. It is prepared by the reaction of titanium(IV) chloride with molten magnesium between 950°C and 1150°C:



(Continued)

In a certain industrial operation 3.54×10^7 g of TiCl_4 are reacted with 1.13×10^7 g of Mg.

(a) Calculate the theoretical yield of Ti in grams. (b) Calculate the percent yield if 7.91×10^6 g of Ti are actually obtained.

(a) Strategy Because there are two reactants, this is likely to be a limiting reactant problem. The reactant that produces fewer moles of product is the limiting reactant. How do we convert from amount of reactant to amount of product? Perform this calculation for each reactant, then compare the moles of product, Ti, formed.

Solution Carry out two separate calculations to see which of the two reactants is the limiting reactant. First, starting with 3.54×10^7 g of TiCl_4 , calculate the number of moles of Ti that could be produced if all the TiCl_4 reacted. The conversions are



so that

$$\begin{aligned} \text{moles of Ti} &= 3.54 \times 10^7 \text{ g } \cancel{\text{TiCl}_4} \times \frac{1 \text{ mol } \text{TiCl}_4}{189.7 \text{ g } \cancel{\text{TiCl}_4}} \times \frac{1 \text{ mol Ti}}{1 \text{ mol } \cancel{\text{TiCl}_4}} \\ &= 1.87 \times 10^5 \text{ mol Ti} \end{aligned}$$

Next, we calculate the number of moles of Ti formed from 1.13×10^7 g of Mg. The conversion steps are



and we write

$$\begin{aligned} \text{moles of Ti} &= 1.13 \times 10^7 \text{ g } \cancel{\text{Mg}} \times \frac{1 \text{ mol Mg}}{24.31 \text{ g } \cancel{\text{Mg}}} \times \frac{1 \text{ mol Ti}}{2 \text{ mol } \cancel{\text{Mg}}} \\ &= 2.32 \times 10^5 \text{ mol Ti} \end{aligned}$$

Therefore, TiCl_4 is the limiting reactant because it produces a smaller amount of Ti. The mass of Ti formed is

$$1.87 \times 10^5 \text{ mol Ti} \times \frac{47.88 \text{ g Ti}}{1 \text{ mol Ti}} = 8.95 \times 10^6 \text{ g Ti}$$

(b) Strategy The mass of Ti determined in part (a) is the theoretical yield. The amount given in part (b) is the actual yield of the reaction.

Solution The percent yield is given by

$$\begin{aligned} \% \text{ yield} &= \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\% \\ &= \frac{7.91 \times 10^6 \text{ g}}{8.95 \times 10^6 \text{ g}} \times 100\% \\ &= 88.4\% \end{aligned}$$

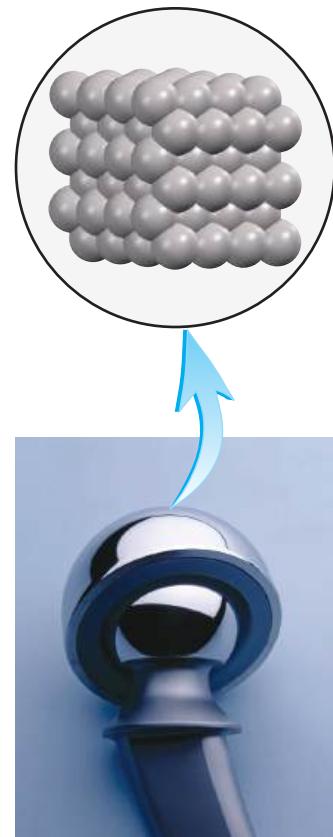
Check Should the percent yield be less than 100 percent?

Practice Exercise Industrially, vanadium metal, which is used in steel alloys, can be obtained by reacting vanadium(V) oxide with calcium at high temperatures:



In one process, 1.54×10^3 g of V_2O_5 react with 1.96×10^3 g of Ca. (a) Calculate the theoretical yield of V. (b) Calculate the percent yield if 803 g of V are obtained.

Similar problems: 3.89, 3.90.



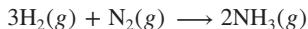
An artificial hip joint made of titanium and the structure of solid titanium.

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Chemical Fertilizers

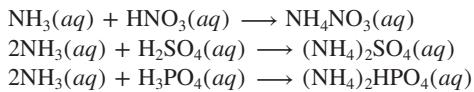
Feeding the world's rapidly increasing population requires that farmers produce ever-larger and healthier crops. Every year they add hundreds of millions of tons of chemical fertilizers to the soil to increase crop quality and yield. In addition to carbon dioxide and water, plants need at least six elements for satisfactory growth. They are N, P, K, Ca, S, and Mg. The preparation and properties of several nitrogen- and phosphorus-containing fertilizers illustrate some of the principles introduced in this chapter.

Nitrogen fertilizers contain nitrate (NO_3^-) salts, ammonium (NH_4^+) salts, and other compounds. Plants can absorb nitrogen in the form of nitrate directly, but ammonium salts and ammonia (NH_3) must first be converted to nitrates by the action of soil bacteria. The principal raw material of nitrogen fertilizers is ammonia, prepared by the reaction between hydrogen and nitrogen:



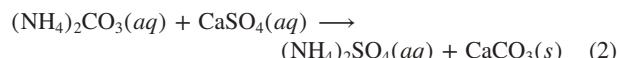
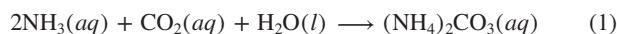
(This reaction will be discussed in detail in Chapters 13 and 14.) In its liquid form, ammonia can be injected directly into the soil.

Alternatively, ammonia can be converted to ammonium nitrate (NH_4NO_3), ammonium sulfate [$(\text{NH}_4)_2\text{SO}_4$], or ammonium hydrogen phosphate [$(\text{NH}_4)_2\text{HPO}_4$] in the following acid-base reactions:



Liquid ammonia being applied to the soil before planting.
©Glyn Thomas/Alamy Stock Photo

Another method of preparing ammonium sulfate requires two steps:



This approach is desirable because the starting materials—carbon dioxide and calcium sulfate—are less costly than sulfuric acid. To increase the yield, ammonia is made the limiting reagent in Reaction (1) and ammonium carbonate is made the limiting reagent in Reaction (2).

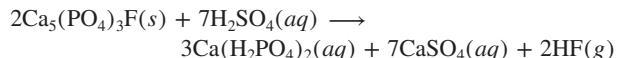
The table lists the percent composition by mass of nitrogen in some common fertilizers. The preparation of urea was discussed in Example 3.15.

Percent Composition by Mass of Nitrogen in Five Common Fertilizers

Fertilizer	% N by Mass
NH_3	82.4
NH_4NO_3	35.0
$(\text{NH}_4)_2\text{SO}_4$	21.2
$(\text{NH}_4)_2\text{HPO}_4$	21.2
$(\text{NH}_2)_2\text{CO}$	46.7

Several factors influence the choice of one fertilizer over another: (1) cost of the raw materials needed to prepare the fertilizer; (2) ease of storage, transportation, and utilization; (3) percent composition by mass of the desired element; and (4) suitability of the compound, that is, whether the compound is soluble in water and whether it can be readily taken up by plants. Considering all these factors together, we find that NH_4NO_3 is the most important nitrogen-containing fertilizer in the world, even though ammonia has the highest percentage by mass of nitrogen.

Phosphorus fertilizers are derived from phosphate rock, called *fluorapatite*, $\text{Ca}_5(\text{PO}_4)_3\text{F}$. Fluorapatite is insoluble in water, so it must first be converted to water-soluble calcium dihydrogen phosphate [$\text{Ca}(\text{H}_2\text{PO}_4)_2$]:



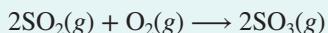
For maximum yield, fluorapatite is made the limiting reagent in this reaction.

The reactions we have discussed for the preparation of fertilizers all appear relatively simple, yet much effort has been expended to improve the yields by changing conditions such as temperature, pressure, and so on. Industrial chemists usually run promising reactions first in the laboratory and then test them in a pilot facility before putting them into mass production.

Industrial processes usually involve huge quantities (thousands to millions of tons) of products. Thus, even a slight improvement in the yield can significantly reduce the cost of production. A case in point is the manufacture of chemical fertilizers, discussed in the Chemistry in Action essay “Chemical Fertilizers.”

Review of Concepts & Facts

- 3.10.1** Can the percent yield ever exceed the theoretical yield of a reaction?
3.10.2 Sulfur trioxide (SO_3) is prepared from the oxidation of sulfur dioxide (SO_2) according to the equation



If 16.4 g of SO_2 produces 18.1 g of SO_3 , what is the percent yield of the reaction?

Learning Objectives

- Discuss the nature of the atomic mass scale. (Section 3.1)
- Determine the average atomic mass of an element from isotopic mass and relative abundance information. (Section 3.1)
- Describe and apply the concept of a mole. (Section 3.2)
- Calculate the molecular and molar mass of compounds. (Section 3.3)
- Interconvert between mass, moles, and number of atoms or molecules. (Section 3.3)
- Deduce the percent composition by mass for elements in a compound. (Section 3.4)
- Solve for the empirical formula of a compound from percent composition or from combustion analysis. (Section 3.6)
- Predict the molecular formula of a compound from the empirical formula and molar mass. (Section 3.6)
- Balance chemical equations using stoichiometric coefficients. (Section 3.7)
- Determine amounts of reactant required or product formed using stoichiometry. (Section 3.8)
- Identify limiting reactants in a chemical reaction. (Section 3.9)
- Calculate theoretical yield, actual yield, and percent yield of a reaction. (Section 3.10)

Key Equations

percent composition of an element in a compound =

$$\frac{n \times \text{molar mass of element}}{\text{molar mass of compound}} \times 100\% \quad (3.1)$$

$$\% \text{yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\% \quad (3.4)$$

Summary of Concepts & Facts

1. Atomic masses are measured in atomic mass units (amu), a relative unit based on a value of exactly 12 for the C-12 isotope. The atomic mass given for the atoms of a particular element is the average of the naturally occurring

isotope distribution of that element. The molecular mass of a molecule is the sum of the atomic masses of the atoms in the molecule. Both atomic mass and molecular mass can be accurately determined with a mass spectrometer.

- A mole is Avogadro's number (6.022×10^{23}) of atoms, molecules, or other particles. The molar mass (in grams) of an element or a compound is numerically equal to its mass in atomic mass units (amu) and contains Avogadro's number of atoms (in the case of elements), molecules (in the case of molecular substances), or simplest formula units (in the case of ionic compounds).
- The percent composition by mass of a compound is the percent by mass of each element present. If we know the percent composition by mass of a compound, we can deduce the empirical formula of the compound and also the molecular formula of the compound if the approximate molar mass is known.
- Chemical changes, called chemical reactions, are represented by chemical equations. Substances that undergo change—the reactants—are written on the left and the

substances formed—the products—appear to the right of the arrow. Chemical equations must be balanced, in accordance with the law of conservation of mass. The number of atoms of each element in the reactants must equal the number in the products.

- Stoichiometry is the quantitative study of products and reactants in chemical reactions. Stoichiometric calculations are best done by expressing both the known and unknown quantities in terms of moles and then converting to other units if necessary. A limiting reactant is the reactant that is present in the smallest stoichiometric amount. It limits the amount of product that can be formed. The amount of product obtained in a reaction (the actual yield) may be less than the maximum possible amount (the theoretical yield). The ratio of the two multiplied by 100 percent is expressed as the percent yield.

Key Words

Actual yield, p. 106	Chemical reaction, p. 93	Mole method, p. 98	Product, p. 94
Atomic mass, p. 79	Excess reactant, p. 103	Molecular mass, p. 84	Reactant, p. 94
Atomic mass unit (amu), p. 79	Limiting reactant, p. 102	Percent composition	Stoichiometric amounts, p. 102
Avogadro's number (N_A), p. 81	Molar mass (\mathcal{M}), p. 82	by mass, p. 88	Stoichiometry, p. 98
Chemical equation, p. 94	Mole (mol), p. 81	Percent yield, p. 106	Theoretical yield, p. 106

Questions & Problems

Red numbered problems solved in *Student Solutions Manual*

3.1 Atomic Mass

Review Questions

- What is an atomic mass unit? Why is it necessary to introduce such a unit?
- What is the mass (in amu) of a carbon-12 atom? Why is the atomic mass of carbon listed as 12.01 amu in the List of the Elements with Their Symbols and Atomic Masses?
- Explain clearly what is meant by the statement, "The atomic mass of gold is 197.0 amu."
- What information would you need to calculate the average atomic mass of an element?

Problems

- The atomic masses of $^{35}_{17}\text{Cl}$ (75.53 percent) and $^{37}_{17}\text{Cl}$ (24.47 percent) are 34.968 amu and 36.956 amu, respectively. Calculate the average atomic mass of chlorine. The percentages in parentheses denote the relative abundances.
- The atomic masses of $^6_{3}\text{Li}$ and $^7_{3}\text{Li}$ are 6.0151 amu and 7.0160 amu, respectively. Calculate the natural abundances of these two isotopes. The average atomic mass of Li is 6.941 amu.

- What is the mass in grams of 13.2 amu?

- How many amu are there in 8.4 g?

3.2 Avogadro's Number and the Molar Mass of an Element

Review Questions

- Define the term "mole." What is the unit for mole in calculations? What does the mole have in common with the pair, the dozen, and the gross? What does Avogadro's number represent?
- What is the molar mass of an atom? What are the commonly used units for molar mass?

Problems

- Earth's population is about 7.2 billion. Suppose that every person on Earth participates in a process of counting identical particles at the rate of two particles per second. How many years would it take to count 6.0×10^{23} particles? Assume that there are 365 days in a year.
- The thickness of a piece of paper is 0.0036 in. Suppose a certain book has an Avogadro's number of pages; calculate the thickness of the book in light-years. (Hint: See Problem 1.51 for the definition of light-year.)

- 3.13 How many atoms are there in 5.10 moles of sulfur (S)?
- 3.14** How many moles of cobalt (Co) atoms are there in 6.00×10^9 (6 billion) Co atoms?
- 3.15 How many moles of calcium (Ca) atoms are in 77.4 g of Ca?
- 3.16** How many grams of gold (Au) are there in 15.3 moles of Au?
- 3.17 What is the mass in grams of a single atom of each of the following elements? (a) Hg, (b) Ne.
- 3.18** What is the mass in grams of a single atom of each of the following elements? (a) As, (b) Ni.
- 3.19 What is the mass in grams of 1.00×10^{12} lead (Pb) atoms?
- 3.20** A modern penny weighs 2.5 g but contains only 0.063 g of copper (Cu). How many copper atoms are present in a modern penny?
- 3.21 Which of the following has more atoms: 1.10 g of hydrogen atoms or 14.7 g of chromium atoms?
- 3.22** Which of the following has a greater mass: 2 atoms of lead or 5.1×10^{-23} mole of helium.

3.3 Molecular Mass

Problems

- 3.23 Calculate the molecular mass or formula mass (in amu) of each of the following substances: (a) CH₄, (b) NO₂, (c) SO₃, (d) C₆H₆, (e) NaI, (f) K₂SO₄, (g) Ca₃(PO₄)₂.
- 3.24** Calculate the molar mass of the following substances: (a) Li₂CO₃, (b) CS₂, (c) CHCl₃ (chloroform), (d) C₆H₈O₆ (ascorbic acid, or vitamin C), (e) KNO₃, (f) Mg₃N₂.
- 3.25 Calculate the molar mass of a compound if 0.372 mole of it has a mass of 152 g.
- 3.26** How many molecules of ethane (C₂H₆) are present in 0.334 g of C₂H₆?
- 3.27 Calculate the number of C, H, and O atoms in 1.50 g of glucose (C₆H₁₂O₆), a sugar.
- 3.28** Dimethyl sulfoxide [(CH₃)₂SO], also called DMSO, is an important solvent that penetrates the skin, enabling it to be used as a topical drug-delivery agent. Calculate the number of C, S, H, and O atoms in 7.14×10^3 g of dimethyl sulfoxide.
- 3.29 Pheromones are a special type of compound secreted by the females of many insect species to attract the males for mating. One pheromone has the molecular formula C₁₉H₃₈O. Normally, the amount of this pheromone secreted by a female insect is about 1.0×10^{-12} g. How many molecules are there in this quantity?
- 3.30** The density of water is 1.00 g/mL at 4°C. How many water molecules are present in 2.56 mL of water at this temperature?

3.4 The Mass Spectrometer

Review Questions

- 3.31 Describe the operation of a mass spectrometer.

- 3.32 Describe how you would determine the isotopic abundance of an element from its mass spectrum.

Problems

- 3.33 Carbon has two stable isotopes, ¹²C and ¹³C, and fluorine has only one stable isotope, ¹⁹F. How many peaks would you observe in the mass spectrum of the positive ion of CF₄⁺? Assume that the ion does not break up into smaller fragments.
- 3.34** Hydrogen has two stable isotopes, ¹H and ²H, and sulfur has four stable isotopes, ³²S, ³³S, ³⁴S, and ³⁶S. How many peaks would you observe in the mass spectrum of the positive ion of hydrogen sulfide, H₂S⁺? Assume no decomposition of the ion into smaller fragments.

3.5 Percent Composition of Compounds

Review Questions

- 3.35 Use ammonia (NH₃) to explain what is meant by the percent composition by mass of a compound.
- 3.36 Describe how the knowledge of the percent composition by mass of an unknown compound can help us identify the compound.

Problems

- 3.37 Tin (Sn) exists in Earth's crust as SnO₂. Calculate the percent composition by mass of Sn and O in SnO₂.
- 3.38** For many years chloroform (CHCl₃) was used as an inhalation anesthetic in spite of the fact that it is also a toxic substance that may cause severe liver, kidney, and heart damage. Calculate the percent composition by mass of this compound.
- 3.39 Cinnamic alcohol is used mainly in perfumery, particularly in soaps and cosmetics. Its molecular formula is C₉H₁₀O. (a) Calculate the percent composition by mass of C, H, and O in cinnamic alcohol. (b) How many molecules of cinnamic alcohol are contained in a sample of mass 0.469 g?
- 3.40** All of the substances listed here are fertilizers that contribute nitrogen to the soil. Which of these is the richest source of nitrogen on a mass percentage basis?
 (a) Urea, (NH₂)₂CO
 (b) Ammonium nitrate, NH₄NO₃
 (c) Guanidine, HNC(NH₂)₂
 (d) Ammonia, NH₃
- 3.41 The formula for rust can be represented by Fe₂O₃. How many moles of Fe are present in 24.6 g of the compound?
- 3.42** Tin(II) fluoride (SnF₂) is often added to toothpaste as an ingredient to prevent tooth decay. What is the mass of F in grams in 24.6 g of the compound?
- 3.43 What are the empirical formulas of the compounds with the following compositions? (a) 2.1 percent H, 65.3 percent O, 32.6 percent S; (b) 20.2 percent Al, 79.8 percent Cl.

- 3.44** What are the empirical formulas of the compounds with the following compositions? (a) 40.1 percent C, 6.6 percent H, 53.3 percent O; (b) 18.4 percent C, 21.5 percent N, 60.1 percent K.
- 3.45** The anticaking agent added to Morton salt is calcium silicate, CaSiO_3 . This compound can absorb up to 2.5 times its mass of water and still remain a free-flowing powder. Calculate the percent composition of CaSiO_3 .

3.6 Experimental Determination of Empirical Formulas

Review Questions

- 3.46** What does the word “empirical” in empirical formula mean?
- 3.47** If we know the empirical formula of a compound, what additional information do we need to determine its molecular formula?

Problems

- 3.48** The empirical formula of a compound is CH. If the molar mass of this compound is about 78 g, what is its molecular formula?
- 3.49** The molar mass of caffeine is 194.19 g. Is the molecular formula of caffeine $\text{C}_4\text{H}_5\text{N}_2\text{O}$ or $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$?
- 3.50** Peroxyacetyl nitrate (PAN) is one of the components of smog. It is a compound of C, H, N, and O. Determine the percent composition of oxygen and the empirical formula from the following percent composition by mass: 19.8 percent C, 2.50 percent H, 11.6 percent N. What is its molecular formula given that its molar mass is about 120 g?
- 3.51** Allicin is the compound responsible for the characteristic smell of garlic. An analysis of the compound gives the following percent composition by mass: C: 44.4 percent, H: 6.21 percent, S: 39.5 percent, O: 9.86 percent. Calculate its empirical formula. What is its molecular formula given that its molar mass is about 162 g?
- 3.52** Monosodium glutamate (MSG), a food-flavor enhancer, has been blamed for “Chinese restaurant syndrome,” the symptoms of which are headaches and chest pains. MSG has the following composition by mass: 35.51 percent C, 4.77 percent H, 37.85 percent O, 8.29 percent N, and 13.60 percent Na. What is its molecular formula if its molar mass is about 169 g?

3.7 Chemical Reactions and Chemical Equations

Review Questions

- 3.53** Use the formation of water from hydrogen and oxygen to explain the following terms: chemical reaction, reactant, product.
- 3.54** What is the difference between a chemical reaction and a chemical equation?
- 3.55** Why must a chemical equation be balanced? What law is obeyed by a balanced chemical equation?

- 3.56** Write the symbols used to represent gas, liquid, solid, and the aqueous phase in chemical equations.

Problems

- 3.57** Balance the following equations using the method outlined in Section 3.7.
- $\text{C} + \text{O}_2 \longrightarrow \text{CO}$
 - $\text{CO} + \text{O}_2 \longrightarrow \text{CO}_2$
 - $\text{H}_2 + \text{Br}_2 \longrightarrow \text{HBr}$
 - $\text{K} + \text{H}_2\text{O} \longrightarrow \text{KOH} + \text{H}_2$
 - $\text{Mg} + \text{O}_2 \longrightarrow \text{MgO}$
 - $\text{O}_3 \longrightarrow \text{O}_2$
 - $\text{H}_2\text{O}_2 \longrightarrow \text{H}_2\text{O} + \text{O}_2$
 - $\text{N}_2 + \text{H}_2 \longrightarrow \text{NH}_3$
 - $\text{Zn} + \text{AgCl} \longrightarrow \text{ZnCl}_2 + \text{Ag}$
 - $\text{S}_8 + \text{O}_2 \longrightarrow \text{SO}_2$
 - $\text{NaOH} + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$
 - $\text{Cl}_2 + \text{NaI} \longrightarrow \text{NaCl} + \text{I}_2$
 - $\text{KOH} + \text{H}_3\text{PO}_4 \longrightarrow \text{K}_3\text{PO}_4 + \text{H}_2\text{O}$
 - $\text{CH}_4 + \text{Br}_2 \longrightarrow \text{CBr}_4 + \text{HBr}$
- 3.58** Balance the following equations using the method outlined in Section 3.7.
- $\text{N}_2\text{O}_5 \longrightarrow \text{N}_2\text{O}_4 + \text{O}_2$
 - $\text{KNO}_3 \longrightarrow \text{KNO}_2 + \text{O}_2$
 - $\text{NH}_4\text{NO}_3 \longrightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$
 - $\text{NH}_4\text{NO}_2 \longrightarrow \text{N}_2 + \text{H}_2\text{O}$
 - $\text{NaHCO}_3 \longrightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2$
 - $\text{P}_4\text{O}_{10} + \text{H}_2\text{O} \longrightarrow \text{H}_3\text{PO}_4$
 - $\text{HCl} + \text{CaCO}_3 \longrightarrow \text{CaCl}_2 + \text{H}_2\text{O} + \text{CO}_2$
 - $\text{Al} + \text{H}_2\text{SO}_4 \longrightarrow \text{Al}_2(\text{SO}_4)_3 + \text{H}_2$
 - $\text{CO}_2 + \text{KOH} \longrightarrow \text{K}_2\text{CO}_3 + \text{H}_2\text{O}$
 - $\text{CH}_4 + \text{O}_2 \longrightarrow \text{CO}_2 + \text{H}_2\text{O}$
 - $\text{Be}_2\text{C} + \text{H}_2\text{O} \longrightarrow \text{Be}(\text{OH})_2 + \text{CH}_4$
 - $\text{Cu} + \text{HNO}_3 \longrightarrow \text{Cu}(\text{NO}_3)_2 + \text{NO} + \text{H}_2\text{O}$
 - $\text{S} + \text{HNO}_3 \longrightarrow \text{H}_2\text{SO}_4 + \text{NO}_2 + \text{H}_2\text{O}$
 - $\text{NH}_3 + \text{CuO} \longrightarrow \text{Cu} + \text{N}_2 + \text{H}_2\text{O}$

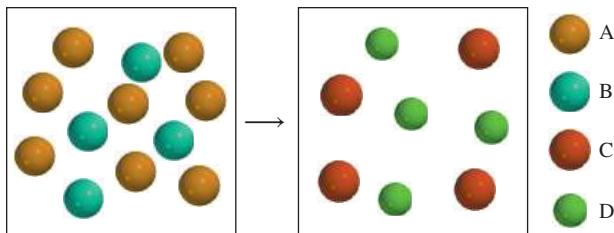
3.8 Amounts of Reactants and Products

Review Questions

- 3.59** On what law is stoichiometry based? Why is it essential to use balanced equations in solving stoichiometric problems?
- 3.60** Describe the steps involved in the mole method.

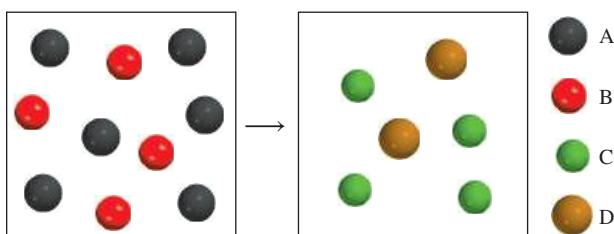
Problems

- 3.61** Which of the following equations best represents the reaction shown in the diagram?
- $8\text{A} + 4\text{B} \longrightarrow \text{C} + \text{D}$
 - $4\text{A} + 8\text{B} \longrightarrow 4\text{C} + 4\text{D}$
 - $2\text{A} + \text{B} \longrightarrow \text{C} + \text{D}$
 - $4\text{A} + 2\text{B} \longrightarrow 4\text{C} + 4\text{D}$
 - $2\text{A} + 4\text{B} \longrightarrow \text{C} + \text{D}$

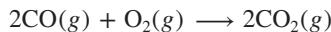


- 3.62** Which of the following equations best represents the reaction shown in the diagram?

- $A + B \rightarrow C + D$
- $6A + 4B \rightarrow C + D$
- $A + 2B \rightarrow 2C + D$
- $3A + 2B \rightarrow 2C + D$
- $3A + 2B \rightarrow 4C + 2D$

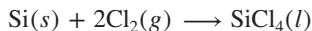


- 3.63** Consider the combustion of carbon monoxide (CO) in oxygen gas:



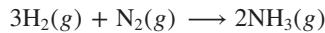
Starting with 3.60 moles of CO , calculate the number of moles of CO_2 produced if there is enough oxygen gas to react with all of the CO .

- 3.64** Silicon tetrachloride (SiCl_4) can be prepared by heating Si in chlorine gas:



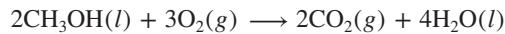
In one reaction, 0.507 mole of SiCl_4 is produced. How many moles of molecular chlorine were used in the reaction?

- 3.65** Ammonia is a principal nitrogen fertilizer. It is prepared by the reaction between hydrogen and nitrogen.



In a particular reaction, 6.0 moles of NH_3 were produced. How many moles of H_2 and how many moles of N_2 were reacted to produce this amount of NH_3 ?

- 3.66** Certain race cars use methanol (CH_3OH , also called wood alcohol) as a fuel. The combustion of methanol occurs according to the following equation:

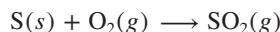


In a particular reaction, 9.8 moles of CH_3OH are reacted with an excess of O_2 . Calculate the number of moles of H_2O formed.

- 3.67** Calculate the mass in grams of iodine (I_2) that will react completely with 20.4 g of aluminum (Al) to form aluminum iodide (AlI_3).

- 3.68** How many grams of sulfur (S) are needed to react completely with 246 g of mercury (Hg) to form HgS ?

- 3.69** The annual production of sulfur dioxide from burning coal and fossil fuels, auto exhaust, and other sources is about 26 million tons. The equation for the reaction is



How much sulfur (in tons), present in the original materials, would result in that quantity of SO_2 ?

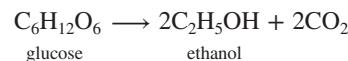
- 3.70** When baking soda (sodium bicarbonate or sodium hydrogen carbonate, NaHCO_3) is heated, it releases carbon dioxide gas, which is responsible for the rising of cookies, donuts, and bread. (a) Write a balanced equation for the decomposition of the compound (one of the products is Na_2CO_3). (b) Calculate the mass of NaHCO_3 required to produce 20.5 g of CO_2 .

- 3.71** If chlorine bleach is mixed with other cleaning products containing ammonia, the toxic gas $\text{NCl}_3(g)$ can form according to the equation



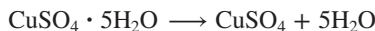
When 2.94 g of NH_3 reacts with an excess of NaClO according to the preceding reaction, how many grams of NCl_3 are formed?

- 3.72** Fermentation is a complex chemical process of wine making in which glucose is converted into ethanol and carbon dioxide:



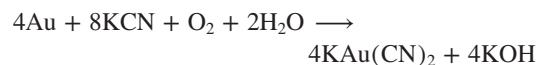
Starting with 500.4 g of glucose, what is the maximum amount of ethanol in grams and in liters that can be obtained by this process? (Density of ethanol = 0.789 g/mL.)

- 3.73** Each copper(II) sulfate unit is associated with five water molecules in crystalline copper(II) sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$). When this compound is heated in air above 100°C, it loses the water molecules and also its blue color:



If 9.60 g of CuSO_4 are left after heating 15.01 g of the blue compound, calculate the number of moles of H_2O originally present in the compound.

- 3.74** For many years the recovery of gold—that is, the separation of gold from other materials—involved the use of potassium cyanide:

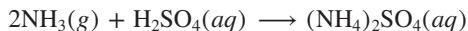


What is the minimum amount of KCN in moles needed to extract 29.0 g (about an ounce) of gold?

- 3.75** Limestone (CaCO_3) is decomposed by heating to quicklime (CaO) and carbon dioxide. Calculate how many grams of quicklime can be produced from 1.0 kg of limestone.

- 3.76** Nitrous oxide (N_2O) is also called “laughing gas.” It can be prepared by the thermal decomposition of ammonium nitrate (NH_4NO_3). The other product is H_2O . (a) Write a balanced equation for this reaction. (b) How many grams of N_2O are formed if 0.46 mole of NH_4NO_3 is used in the reaction?

- 3.77** The fertilizer ammonium sulfate [$(\text{NH}_4)_2\text{SO}_4$] is prepared by the reaction between ammonia (NH_3) and sulfuric acid:



How many kilograms of NH_3 are needed to produce 1.00×10^5 kg of $(\text{NH}_4)_2\text{SO}_4$?

- 3.78** A common laboratory preparation of oxygen gas is the thermal decomposition of potassium chlorate (KClO_3). Assuming complete decomposition, calculate the number of grams of O_2 gas that can be obtained from 46.0 g of KClO_3 . (The products are KCl and O_2 .)

3.9 Limiting Reactants

Review Questions

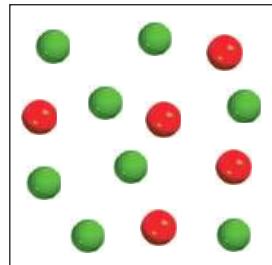
- 3.79** Define limiting reactant and excess reactant. What is the significance of the limiting reactant in predicting the amount of the product obtained in a reaction? Can there be a limiting reactant if only one reactant is present?
- 3.80** Give an everyday example that illustrates the limiting reactant concept.

Problems

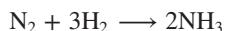
- 3.81** Consider the reaction



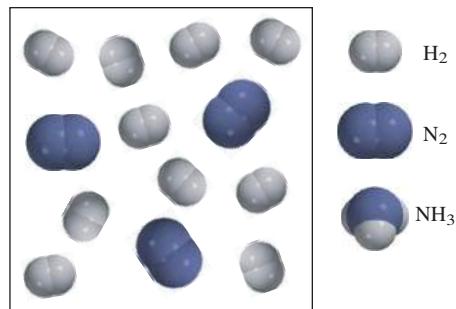
- (a) In the diagram here that represents the reaction, which reactant, A or B, is the limiting reactant?
 (b) Assuming complete reaction, draw a molecular-model representation of the amounts of reactants and products left after the reaction. The atomic arrangement in C is ABA.



- 3.82** Consider the reaction



Assuming each model represents 1 mole of the substance, show the number of moles of the product and the excess reactant left after the complete reaction.



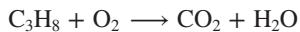
- 3.83** Nitric oxide (NO) reacts with oxygen gas to form nitrogen dioxide (NO_2), a dark-brown gas:



In one experiment 0.886 mole of NO is mixed with 0.503 mole of O_2 . Calculate which of the two reactants is the limiting reactant. Calculate also the number of moles of NO_2 produced.

- 3.84** Ammonia and sulfuric acid react to form ammonium sulfate. (a) Write an equation for the reaction. (b) Determine the starting mass (in grams) of each reactant if 20.3 g of ammonium sulfate is produced and 5.89 g of sulfuric acid remains unreacted.

- 3.85** Propane (C_3H_8) is a component of natural gas and is used in domestic cooking and heating. (a) Balance the following equation representing the combustion of propane in air.



(b) How many grams of carbon dioxide can be produced by burning 3.65 moles of propane? Assume that oxygen is the excess reactant in this reaction.

- 3.86** Consider the reaction



If 0.86 mole of MnO_2 and 48.2 g of HCl react, which reactant will be used up first? How many grams of Cl_2 will be produced?

3.10 Reaction Yield

Review Questions

- 3.87** Why is the theoretical yield of a reaction determined only by the amount of the limiting reactant?
3.88 Why is the actual yield of a reaction almost always smaller than the theoretical yield?

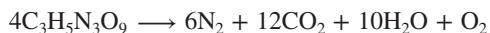
Problems

- 3.89** Hydrogen fluoride is used in the manufacture of Freons (which destroy ozone in the stratosphere) and in the production of aluminum metal. It is prepared by the reaction



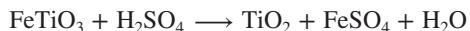
In one process, 6.00 kg of CaF_2 are treated with an excess of H_2SO_4 and yield 2.86 kg of HF. Calculate the percent yield of HF.

- 3.90** Nitroglycerin ($\text{C}_3\text{H}_5\text{N}_3\text{O}_9$) is a powerful explosive. Its decomposition may be represented by



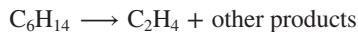
This reaction generates a large amount of heat and many gaseous products. It is the sudden formation of these gases, together with their rapid expansion, that produces the explosion. (a) What is the maximum amount of O_2 in grams that can be obtained from 2.00×10^2 g of nitroglycerin? (b) Calculate the percent yield in this reaction if the amount of O_2 generated is found to be 6.55 g.

- 3.91** Titanium(IV) oxide (TiO_2) is a white substance produced by the action of sulfuric acid on the mineral ilmenite (FeTiO_3):



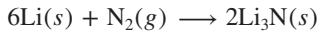
Its opaque and nontoxic properties make it suitable as a pigment in plastics and paints. In one process, 8.00×10^3 kg of FeTiO_3 yielded 3.67×10^3 kg of TiO_2 . What is the percent yield of the reaction?

- 3.92** Ethylene (C_2H_4), an important industrial organic chemical, can be prepared by heating hexane (C_6H_{14}) at 800°C :



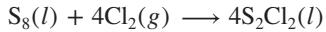
If the yield of ethylene production is 42.5 percent, what mass of hexane must be reacted to produce 481 g of ethylene?

- 3.93** When heated, lithium reacts with nitrogen to form lithium nitride:



What is the theoretical yield of Li_3N in grams when 12.3 g of Li are heated with 33.6 g of N_2 ? If the actual yield of Li_3N is 5.89 g, what is the percent yield of the reaction?

- 3.94** Disulfide dichloride (S_2Cl_2) is used in the vulcanization of rubber, a process that prevents the slippage of rubber molecules past one another when stretched. It is prepared by heating sulfur in an atmosphere of chlorine:



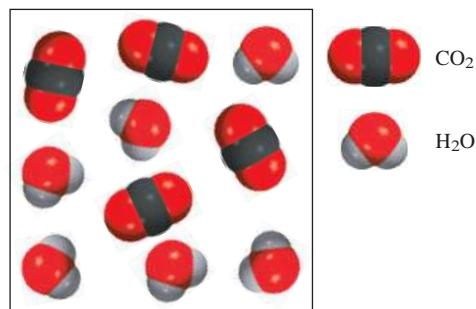
What is the theoretical yield of S_2Cl_2 in grams when 4.06 g of S_8 are heated with 6.24 g of Cl_2 ? If the actual yield of S_2Cl_2 is 6.55 g, what is the percent yield?

Additional Problems

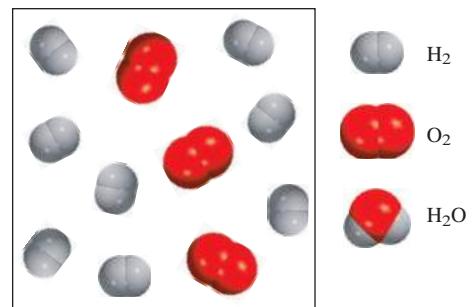
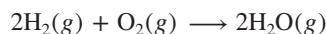
- 3.95** Gallium is an important element in the production of semiconductors. The average atomic mass of ^{69}Ga (68.9256 amu) and ^{71}Ga (70.9247 amu) is 69.72 amu. Calculate the natural abundances of the gallium isotopes.

Rubidium is used in “atomic clocks” and other precise electronic equipment. The average atomic mass of ^{85}Rb (84.912 amu) and ^{87}Rb (86.909 amu) is 85.47 amu. Calculate the natural abundances of the rubidium isotopes.

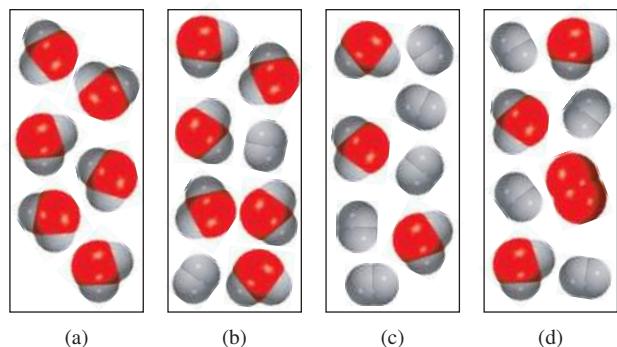
- 3.97** This diagram represents the products (CO_2 and H_2O) formed after the combustion of a hydrocarbon (a compound containing only C and H atoms). Write an equation for the reaction. (Hint: The molar mass of the hydrocarbon is about 30 g.)



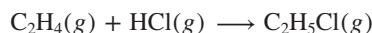
- 3.98** Consider the reaction of hydrogen gas with oxygen gas:



Assuming complete reaction, which of the diagrams (a)–(d) represents the amounts of reactants and products left after the reaction?



- 3.99** Ethylene reacts with hydrogen chloride to form ethyl chloride:



Calculate the mass of ethyl chloride formed if 4.66 g of ethylene reacts with an 89.4 percent yield.

- 3.100** Write balanced equations for the following reactions described in words.
- Pentane burns in oxygen to form carbon dioxide and water.
 - Sodium bicarbonate reacts with hydrochloric acid to form carbon dioxide, sodium chloride, and water.
 - When heated in an atmosphere of nitrogen, lithium forms lithium nitride.
 - Phosphorus trichloride reacts with water to form phosphorus acid and hydrogen chloride.
 - Copper(II) oxide heated with ammonia will form copper, nitrogen gas, and water.
- 3.101 Industrially, nitric acid is produced by the Ostwald process represented by the following equations:
- $$\begin{aligned} 4\text{NH}_3(g) + 5\text{O}_2(g) &\longrightarrow 4\text{NO}(g) + 6\text{H}_2\text{O}(l) \\ 2\text{NO}(g) + \text{O}_2(g) &\longrightarrow 2\text{NO}_2(g) \\ 2\text{NO}_2(g) + \text{H}_2\text{O}(l) &\longrightarrow \text{HNO}_3(aq) + \text{HNO}_2(aq) \end{aligned}$$
- What mass of NH_3 (in grams) must be used to produce 1.00 ton of HNO_3 by the above procedure, assuming an 80 percent yield in each step? (1 ton = 2000 lb; 1 lb = 453.6 g.)
- 3.102** A sample of a compound of Cl and O reacts with an excess of H_2 to give 0.233 g of HCl and 0.403 g of H_2O . Determine the empirical formula of the compound.
- 3.103 How many grams of H_2O will be produced from the complete combustion of 26.7 g of butane (C_4H_{10})?
- 3.104** A 26.2-g sample of oxalic acid hydrate ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) is heated in an oven until all the water is driven off. How much of the anhydrous acid is left?
- 3.105 The atomic mass of element X is 33.42 amu. A 27.22-g sample of X combines with 84.10 g of another element Y to form a compound XY. Calculate the atomic mass of Y.
- 3.106** How many moles of O are needed to combine with 0.212 mole of C to form (a) CO and (b) CO_2 ?
- 3.107 A research chemist used a mass spectrometer to study the two isotopes of an element. Over time, she recorded a number of mass spectra of these isotopes. On analysis, she noticed that the ratio of the taller peak (the more abundant isotope) to the shorter peak (the less abundant isotope) gradually increased with time. Assuming that the mass spectrometer was functioning normally, what do you think was causing this change?
- 3.108** The aluminum sulfate hydrate $[\text{Al}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}]$ contains 8.10 percent Al by mass. Calculate x —that is, the number of water molecules associated with each $\text{Al}_2(\text{SO}_4)_3$ unit.
- 3.109 The explosive nitroglycerin ($\text{C}_3\text{H}_5\text{N}_3\text{O}_9$) has also been used as a drug to treat heart patients to relieve pain (angina pectoris). We now know that nitroglycerin produces nitric oxide (NO), which causes muscles to relax and allows the arteries to dilate. If each nitroglycerin molecule releases one NO per atom of N, calculate the mass percent of NO available from nitroglycerin.
- 3.110** The carat is the unit of mass used by jewelers. One carat is exactly 200 mg. How many carbon atoms are present in a 24-carat diamond?
- 3.111 An iron bar weighed 664 g. After the bar had been standing in moist air for a month, exactly one-eighth of the iron turned to rust (Fe_2O_3). Calculate the final mass of the iron bar and rust.
- 3.112** A certain metal oxide has the formula MO, where M denotes the metal. A 39.46-g sample of the compound is strongly heated in an atmosphere of hydrogen to remove oxygen as water molecules. At the end, 31.70 g of the metal is left over. If O has an atomic mass of 16.00 amu, calculate the atomic mass of M and identify the element.
- 3.113 An impure sample of zinc (Zn) is treated with an excess of sulfuric acid (H_2SO_4) to form zinc sulfate (ZnSO_4) and molecular hydrogen (H_2). (a) Write a balanced equation for the reaction. (b) If 0.0764 g of H_2 is obtained from 3.86 g of the sample, calculate the percent purity of the sample. (c) What assumptions must you make in (b)?
- 3.114** One of the reactions that occurs in a blast furnace, where iron ore is converted to cast iron, is
- $$\text{Fe}_2\text{O}_3 + 3\text{CO} \longrightarrow 2\text{Fe} + 3\text{CO}_2$$
- Suppose that 1.64×10^3 kg of Fe are obtained from a 2.62×10^3 kg sample of Fe_2O_3 . Assuming that the reaction goes to completion, what is the percent purity of Fe_2O_3 in the original sample?
- 3.115 Carbon dioxide (CO_2) is the gas that is mainly responsible for global warming (the greenhouse effect). The burning of fossil fuels is a major cause of the increased concentration of CO_2 in the atmosphere. Carbon dioxide is also the end product of metabolism (see Example 3.13). Using glucose as an example of food, calculate the annual human production of CO_2 in grams, assuming that each person consumes 5.0×10^2 g of glucose per day. The world's population is 7.2 billion, and there are 365 days in a year.
- 3.116** Carbohydrates are compounds containing carbon, hydrogen, and oxygen in which the hydrogen to oxygen ratio is 2:1. A certain carbohydrate contains 40.0 percent carbon by mass. Calculate the empirical and molecular formulas of the compound if the approximate molar mass is 178 g.
- 3.117 Which of the following has the greater mass: 0.72 g of O_2 or 0.0011 mole of chlorophyll ($\text{C}_{55}\text{H}_{72}\text{MgN}_4\text{O}_5$)?
- 3.118** Analysis of a metal chloride XCl_3 shows that it contains 67.2 percent Cl by mass. Calculate the molar mass of X and identify the element.
- 3.119 Hemoglobin ($\text{C}_{2952}\text{H}_{4664}\text{N}_{812}\text{O}_{832}\text{S}_8\text{Fe}_4$) is the oxygen carrier in blood. (a) Calculate its molar mass. (b) An average adult has about 5.0 L of blood. Every milliliter of blood has approximately 5.0×10^9 erythrocytes, or red blood cells, and every red blood cell has about 2.8×10^8 hemoglobin molecules. Calculate the mass of hemoglobin molecules in grams in an average adult.

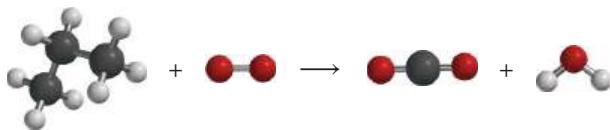
3.120 Myoglobin stores oxygen for metabolic processes in muscle. Chemical analysis shows that it contains 0.34 percent Fe by mass. What is the molar mass of myoglobin? (There is one Fe atom per molecule.)

3.121 Calculate the number of cations and anions in each of the following compounds: (a) 0.764 g of CsI, (b) 72.8 g of $K_2Cr_2O_7$, (c) 6.54 g of $Hg_2(NO_3)_2$.

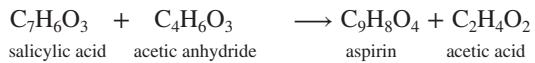
3.122 A mixture of NaBr and Na_2SO_4 contains 29.96 percent Na by mass. Calculate the percent by mass of each compound in the mixture.

3.123 Consider the reaction $3A + 2B \rightarrow 3C$. A student mixed 4.0 moles of A with 4.0 moles of B and obtained 2.8 moles of C. What is the percent yield of the reaction?

3.124 Balance the equation shown here in molecular models.



3.125 Aspirin or acetyl salicylic acid is synthesized by reacting salicylic acid with acetic anhydride:



(a) How much salicylic acid is required to produce 0.400 g of aspirin (about the content in a tablet), assuming acetic anhydride is present in excess? (b) Calculate the amount of salicylic acid needed if only 74.9 percent of salicylic acid is converted to aspirin. (c) In one experiment, 9.26 g of salicylic acid is reacted with 8.54 g of acetic anhydride. Calculate the theoretical yield of aspirin and the percent yield if only 10.9 g of aspirin is produced.

3.126 Calculate the percent composition by mass of all the elements in calcium phosphate $[Ca_3(PO_4)_2]$, a major component of bone.

3.127 Lysine, an essential amino acid in the human body, contains C, H, O, and N. In one experiment, the complete combustion of 2.175 g of lysine gave 3.94 g CO_2 and 1.89 g H_2O . In a separate experiment, 1.873 g of lysine gave 0.436 g NH_3 . (a) Calculate the empirical formula of lysine. (b) The approximate molar mass of lysine is 150 g. What is the molecular formula of the compound?

3.128 Does 1 g of hydrogen molecules contain as many H atoms as 1 g of hydrogen atoms?

3.129 Avogadro's number has sometimes been described as a conversion factor between atomic mass units and grams. Use the fluorine atom (19.00 amu) as an example to show the relation between the atomic mass unit and the gram.

3.130 The natural abundances of the two stable isotopes of hydrogen (hydrogen and deuterium) are 1H : 99.985 percent and 2H : 0.015 percent. Assume that water exists as either H_2O or D_2O . Calculate the number of D_2O molecules in exactly 400 mL of water. (Density = 1.00 g/mL.)

3.131 A compound containing only C, H, and Cl was examined in a mass spectrometer. The highest mass peak seen corresponds to an ion mass of 52 amu. The most abundant mass peak seen corresponds to an ion mass of 50 amu and is about three times as intense as the peak at 52 amu. Deduce a reasonable molecular formula for the compound and explain the positions and intensities of the mass peaks mentioned. (*Hint:* Chlorine is the only element that has isotopes in comparable abundances: ^{35}Cl : 75.5 percent; ^{37}Cl : 24.5 percent. For H, use 1H ; for C, use ^{12}C .)

3.132 In the formation of carbon monoxide, CO, it is found that 2.445 g of carbon combine with 3.257 g of oxygen. What is the atomic mass of oxygen if the atomic mass of carbon is 12.01 amu?

3.133 What mole ratio of molecular chlorine (Cl_2) to molecular oxygen (O_2) would result from the breakup of the compound Cl_2O_7 into its constituent elements?

3.134 Which of the following substances contains the greatest mass of chlorine? (a) 5.0 g Cl_2 , (b) 60.0 g $NaClO_3$, (c) 0.10 mol KCl , (d) 30.0 g $MgCl_2$, (e) 0.50 mol Cl_2 .

3.135 A compound made up of C, H, and Cl contains 55.0 percent Cl by mass. If 9.00 g of the compound contain 4.19×10^{23} H atoms, what is the empirical formula of the compound?

3.136 Platinum forms two different compounds with chlorine. One contains 26.7 percent Cl by mass, and the other contains 42.1 percent Cl by mass. Determine the empirical formulas of the two compounds.

3.137 The following reaction is stoichiometric as written
 $C_4H_9Cl + NaOC_2H_5 \longrightarrow C_4H_8 + C_2H_5OH + NaCl$
 but it is often carried out with an excess of $NaOC_2H_5$ to react with any water present in the reaction mixture that might reduce the yield. If the reaction shown was carried out with 6.83 g of C_4H_9Cl , how many grams of $NaOC_2H_5$ would be needed to have a 50 percent molar excess of that reactant?

3.138 Compounds containing ruthenium(II) and bipyridine, $C_{10}H_8N_2$, have received considerable interest because of their role in systems that convert solar energy to electricity. The compound $[Ru(C_{10}H_8N_2)_3]Cl_2$ is synthesized by reacting $RuCl_3 \cdot 3H_2O(s)$ with three molar equivalents of $C_{10}H_8N_2(s)$, along with an excess of triethylamine, $N(C_2H_5)_3(l)$, to convert ruthenium(III) to ruthenium(II). The density of triethylamine is 0.73 g/mL, and typically eight molar equivalents are used in the synthesis. (a) Assuming that you start with 6.5 g of $RuCl_3 \cdot 3H_2O$, how many grams of $C_{10}H_8N_2$ and what volume of $N(C_2H_5)_3$ should be used in the reaction? (b) Given that the yield of this reaction is 91 percent, how many grams of $[Ru(C_{10}H_8N_2)_3]Cl_2$ will be obtained?

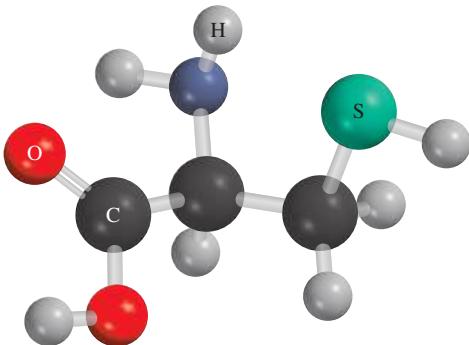
3.139 Heating 2.40 g of the oxide of metal X (molar mass of X = 55.9 g/mol) in carbon monoxide (CO) yields the pure metal and carbon dioxide. The mass of the metal product is 1.68 g. From the data given, show that the simplest formula of the oxide is X_2O_3 and write a balanced equation for the reaction.

3.140 A compound X contains 63.3 percent manganese (Mn) and 36.7 percent O by mass. When X is heated, oxygen gas is evolved and a new compound Y containing 72.0 percent Mn and 28.0 percent O is formed. (a) Determine the empirical formulas of X and Y. (b) Write a balanced equation for the conversion of X to Y.

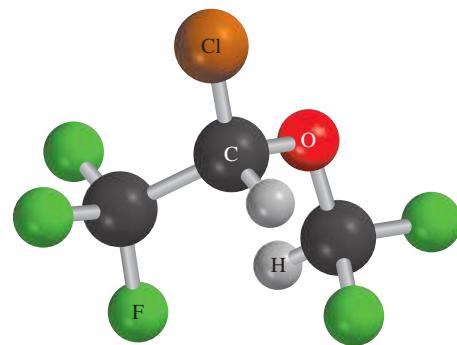
3.141 The formula of a hydrate of barium chloride is $\text{BaCl}_2 \cdot x\text{H}_2\text{O}$. If 1.936 g of the compound gives 1.864 g of anhydrous BaSO_4 upon treatment with sulfuric acid, calculate the value of x .

3.142 It is estimated that the day Mt. St. Helens erupted (May 18, 1980), about 4.0×10^5 tons of SO_2 were released into the atmosphere. If all the SO_2 were eventually converted to sulfuric acid, how many tons of H_2SO_4 were produced?

3.143 Cysteine, shown here, is one of the 20 amino acids found in proteins in humans. Write the molecular formula and calculate its percent composition by mass.



3.144 Isoflurane, shown here, is a common inhalation anesthetic. Write its molecular formula and calculate its percent composition by mass.



3.145 A mixture of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ is heated until all the water is lost. If 5.020 g of the mixture gives 2.988 g of the anhydrous salts, what is the percent by mass of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in the mixture?

3.146 When 0.273 g of Mg is heated strongly in a nitrogen (N_2) atmosphere, a chemical reaction occurs. The product of the reaction weighs 0.378 g. Calculate the empirical formula of the compound containing Mg and N. Name the compound.

3.147 A mixture of methane (CH_4) and ethane (C_2H_6) of mass 13.43 g is completely burned in oxygen. If the total mass of CO_2 and H_2O produced is 64.84 g, calculate the fraction of CH_4 in the mixture.

3.148 Leaded gasoline contains an additive to prevent engine “knocking.” On analysis, the additive compound is found to contain carbon, hydrogen, and lead (Pb) (hence, “leaded gasoline”). When 51.36 g of this compound are burned in an apparatus such as that shown in Figure 3.6, 55.90 g of CO_2 and 28.61 g of H_2O are produced. Determine the empirical formula of the gasoline additive.

3.149 Because of its detrimental effect on the environment, the lead compound described in Problem 3.148 has been replaced by methyl *tert*-butyl ether (a compound of C, H, and O) to enhance the performance of gasoline. (This compound is also being phased out because of its contamination of drinking water.) When 12.1 g of the compound are burned in an apparatus like the one shown in Figure 3.6, 30.2 g of CO_2 and 14.8 g of H_2O are formed. What is the empirical formula of the compound?

3.150 Suppose you are given a cube made of magnesium (Mg) metal of edge length 1.0 cm. (a) Calculate the number of Mg atoms in the cube. (b) Atoms are spherical in shape. Therefore, the Mg atoms in the cube cannot fill all of the available space. If only 74 percent of the space inside the cube is taken up by Mg atoms, calculate the radius in picometers of a Mg atom. (The density of Mg is 1.74 g/cm³ and the volume of a sphere of radius r is $\frac{4}{3}\pi r^3$.)

3.151 A certain sample of coal contains 1.6 percent sulfur by mass. When the coal is burned, the sulfur is converted to sulfur dioxide. To prevent air pollution, this sulfur dioxide is treated with calcium oxide (CaO) to form calcium sulfite (CaSO_3). Calculate the daily mass (in kilograms) of CaO needed by a power plant that uses 6.60×10^6 kg of coal per day.

3.152 Air is a mixture of many gases. However, in calculating its “molar mass” we need consider only the three major components: nitrogen, oxygen, and argon. Given that one mole of air at sea level is made up of 78.08 percent nitrogen, 20.95 percent oxygen, and 0.97 percent argon, what is the molar mass of air?

3.153 (a) Determine the mass of calcium metal that contains the same number of moles as 89.6 g of zinc metal. (b) Calculate the number of moles of molecular fluorine that has the same mass as 36.9 moles of argon. (c) What is the mass of sulfuric acid that contains 0.56 mole of oxygen atoms? (d) Determine the number of moles of phosphoric acid that contains 2.12 g of hydrogen atoms.

3.154 A major industrial use of hydrochloric acid is in metal pickling. This process involves the removal of metal oxide layers from metal surfaces to prepare them for coating. (a) Write an equation between iron(III) oxide, which represents the rust

- layer over iron, and HCl to form iron(III) chloride and water. (b) If 1.22 moles of Fe_2O_3 and 289.2 g of HCl react, how many grams of FeCl_3 will be produced?
- 3.155** Octane (C_8H_{18}) is a component of gasoline. Complete combustion of octane yields H_2O and CO_2 . Incomplete combustion produces H_2O and CO, which not only reduces the efficiency of the engine using the fuel but is also toxic. In a certain test run, 1.000 gal of octane is burned in an engine. The total mass of CO, CO_2 , and H_2O produced is 11.53 kg. Calculate the efficiency of the process; that is, calculate the fraction of octane converted to CO_2 . The density of octane is 2.650 kg/gal.
- 3.156** Industrially, hydrogen gas can be prepared by reacting propane gas (C_3H_8) with steam at about 400°C . The products are carbon monoxide (CO) and hydrogen gas (H_2). (a) Write a balanced equation for the reaction. (b) How many kilograms of H_2 can be obtained from 2.84×10^3 kg of propane?
- 3.157** In a natural product synthesis, a chemist prepares a complex biological molecule entirely from nonbiological starting materials. The target molecules are often known to have some promise as therapeutic agents, and the organic reactions that are developed along the way benefit all chemists. The overall synthesis, however, requires many steps, so it is important to have the best possible percent yields at each step. What is the overall percent yield for such a synthesis that has 24 steps with an 80 percent yield at each step?
- 3.158** What is wrong or ambiguous with each of the statements here?
- NH_4NO_2 is the limiting reactant in the reaction
- $$\text{NH}_4\text{NO}_2(s) \longrightarrow \text{N}_2(g) + 2\text{H}_2\text{O}(l)$$
- The limiting reactants for the reaction shown here are NH_3 and NaCl.
- $$\text{NH}_3(aq) + \text{NaCl}(aq) + \text{H}_2\text{CO}_3(aq) \longrightarrow \text{NaHCO}_3(aq) + \text{NH}_4\text{Cl}(aq)$$
- 3.159** (a) For molecules having small molecular masses, mass spectrometry can be used to identify their formulas. To illustrate this point, identify the molecule that most likely accounts for the observation of a peak in a mass spectrum at 16 amu, 17 amu, 18 amu, and 64 amu. (b) Note that there are (among others) two likely molecules that would give rise to a peak at 44 amu, namely, C_3H_8 and CO_2 . In such cases, a chemist might try to look for other peaks generated when some of the molecules break apart in the spectrometer. For example, if a chemist sees a peak at 44 amu and also one at 15 amu, which molecule is producing the 44-amu peak? Why? (c) Using the following precise atomic masses— ${}^1\text{H}$ (1.00797 amu), ${}^{12}\text{C}$ (12.00000 amu), and ${}^{16}\text{O}$ (15.99491 amu)—how precisely must the masses of C_3H_8 and CO_2 be measured to distinguish between them?
- 3.160** Potash is any potassium mineral that is used for its potassium content. Most of the potash produced in the United States goes into fertilizer. The major sources of potash are potassium chloride (KCl) and potassium sulfate (K_2SO_4). Potash production is often reported as the potassium oxide (K_2O) equivalent or the amount of K_2O that could be made from a given mineral. (a) If KCl costs \$0.55 per kg, for what price (dollar per kg) must K_2SO_4 be sold to supply the same amount of potassium on a per dollar basis? (b) What mass (in kg) of K_2O contains the same number of moles of K atoms as 1.00 kg of KCl?
- 3.161** A 21.496-g sample of magnesium is burned in air to form magnesium oxide and magnesium nitride. When the products are treated with water, 2.813 g of gaseous ammonia are generated. Calculate the amounts of magnesium nitride and magnesium oxide formed.
- 3.162** A certain metal M forms a bromide containing 53.79 percent Br by mass. What is the chemical formula of the compound?
- 3.163** A sample of iron weighing 15.0 g was heated with potassium chlorate (KClO_3) in an evacuated container. The oxygen generated from the decomposition of KClO_3 converted some of the Fe to Fe_2O_3 . If the combined mass of Fe and Fe_2O_3 was 17.9 g, calculate the mass of Fe_2O_3 formed and the mass of KClO_3 decomposed.
- 3.164** A sample containing NaCl, Na_2SO_4 , and NaNO_3 gives the following elemental analysis: Na: 32.08 percent; O: 36.01 percent; Cl: 19.51 percent. Calculate the mass percent of each compound in the sample.
- 3.165** A sample of 10.00 g of sodium reacts with oxygen to form 13.83 g of sodium oxide (Na_2O) and sodium peroxide (Na_2O_2). Calculate the percent composition of the mixture.

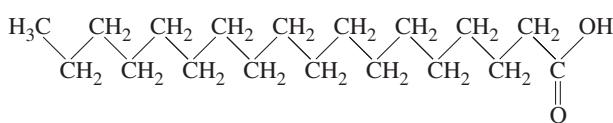
Interpreting, Modeling & Estimating

- 3.166** While most isotopes of light elements such as oxygen and phosphorus contain relatively equal numbers of protons and neutrons, recent results indicate that a new class of isotopes called neutron-rich isotopes can be prepared. These neutron-rich isotopes push the limits of nuclear stability as the large

number of neutrons approach the “neutron drip line.” They may play a critical role in the nuclear reactions of stars. An unusually heavy isotope of aluminum (${}^{43}\text{Al}$) has been reported. How many more neutrons does this atom contain compared to an average aluminum atom?

- 3.167 Without doing any detailed calculations, arrange the following substances in the increasing order of number of moles: 20.0 g Cl, 35.0 g Br, and 94.0 g I.
- 3.168 Without doing any detailed calculations, estimate which element has the highest percent composition by mass in each of the following compounds:
- $\text{Hg}(\text{NO}_3)_2$
 - NF_3
 - $\text{K}_2\text{Cr}_2\text{O}_7$
 - $\text{C}_{2952}\text{H}_{4664}\text{N}_{812}\text{O}_{832}\text{S}_8\text{Fe}_4$
- 3.169 Consider the reaction
- $$6\text{Li}(s) + \text{N}_2(g) \longrightarrow 2\text{Li}_3\text{N}(s)$$
- Without doing any detailed calculations, choose one of the following combinations in which nitrogen is the limiting reactant:
- 44 g Li and 38 g N_2
 - 1380 g Li and 842 g N_2
 - 1.1 g Li and 0.81 g N_2

- 3.170 Estimate how high in miles you can stack up an Avogadro's number of oranges covering the entire Earth.
- 3.171 The following is a crude but effective method for estimating the *order of magnitude* of Avogadro's number using stearic acid ($\text{C}_{18}\text{H}_{36}\text{O}_2$) shown here. When stearic acid is added to water, its molecules collect at the surface and form a monolayer; that is, the layer is only one molecule thick. The cross-sectional area of each stearic acid molecule has been measured to be 0.21 nm^2 . In one experiment it is found that $1.4 \times 10^{-4} \text{ g}$ of stearic acid is needed to form a monolayer over water in a dish of diameter 20 cm. Based on these measurements, what is Avogadro's number?



Answers to Practice Exercises

3.1 63.55 amu. **3.2** 3.59 moles. **3.3** $2.57 \times 10^3 \text{ g}$. **3.4** $1.0 \times 10^{-20} \text{ g}$. **3.5** 32.04 amu. **3.6** 1.66 moles. **3.7** $5.81 \times 10^{24} \text{ H}$ atoms. **3.8** H: 2.055%; S: 32.69%; O: 65.25%. **3.9** KMnO_4

(potassium permanganate). **3.10** 196 g. **3.11** B_2H_6 . **3.12** $\text{Fe}_2\text{O}_3 + 3\text{CO} \rightarrow 2\text{Fe} + 3\text{CO}_2$. **3.13** 235 g. **3.14** 0.769 g. **3.15** (a) 234 g, (b) 234 g. **3.16** 25.1 g. **3.17** (a) 863 g, (b) 93.0%.

Answers to Review of Concepts & Facts

3.1.1 ^{193}Ir . **3.1.2** 49.473 amu. **3.2.1** (b). **3.2.2** 6.23 moles. **3.2.3** 85.6 g. **3.3.1** Molecular mass = 192.12 amu, molar mass = 192.12 g. **3.3.2** 74.2 g. **3.3.3** $1.93 \times 10^{24} \text{ O}$ atoms. **3.4.1** When isotopes of the two chlorine atoms arrive at the detector of a mass spectrometer, a current is registered for each type of ion. The amount of current generated is directly proportional to the number of ions, so it enables us to determine the relative abundance of each isotope. A weighted average of the masses of the two isotopes based on relative abundance gives the average

mass of chlorine. **3.5.1** The percent composition by mass of Sr is smaller than that of O. You need only to compare the relative masses of one Sr atom and six O atoms. **3.5.2** C: 41.39%; H: 3.47%; O: 55.14%. **3.5.3** P_2O_5 . **3.6.1** C_5H_{10} . **3.7.1** Essential part: The number of each type of atom on both sides of the reaction arrow. Helpful part: The physical states of the reactants and products. **3.7.2** $2\text{K}_2\text{S}_2\text{O}_3 + \text{I}_2 \rightarrow \text{K}_2\text{S}_4\text{O}_6 + 2\text{KI}$. **3.8.1** (b). **3.8.2** 127 g. **3.8.3** 18.1 g. **3.9.1** (a) 24.7 g, (b) 2.50 g Al. **3.9.2** Diagram (d) shows that NO is the limiting reactant. **3.10.1** No. **3.10.2** 88.3%.

CHAPTER

4

Reactions in Aqueous Solutions

By varying the size and concentration of quantum dots in solution, chemists can tune the emission of different colors of light.

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CHAPTER OUTLINE

- 4.1** General Properties of Aqueous Solutions
- 4.2** Precipitation Reactions
- 4.3** Acid-Base Reactions
- 4.4** Oxidation-Reduction Reactions
- 4.5** Concentration of Solutions
- 4.6** Gravimetric Analysis
- 4.7** Acid-Base Titrations
- 4.8** Redox Titrations



A LOOK AHEAD

- ▶ We begin by studying the properties of solutions prepared by dissolving substances in water, called aqueous solutions. Aqueous solutions can be classified as nonelectrolyte or electrolyte, depending on their ability to conduct electricity. (4.1)
- ▶ We will see that precipitation reactions are those in which the product is an insoluble compound. We learn to represent these reactions using ionic equations and net ionic equations. (4.2)
- ▶ Next, we learn acid-base reactions, which involve the transfer of protons (H^+) from an acid to a base. (4.3)
- ▶ We then learn oxidation-reduction (redox) reactions in which electrons are transferred between reactants. We will see that there are several types of redox reactions. (4.4)
- ▶ To carry out quantitative studies of solutions, we learn how to express the concentration of a solution in molarity. (4.5)
- ▶ Lastly, we apply our knowledge of the mole method from Chapter 3 to the three types of reactions studied here. We will see how gravimetric analysis is used to study precipitation reactions, and how the titration technique is used to study acid-base and redox reactions. (4.6, 4.7, and 4.8)

Many chemical reactions and virtually all biological processes take place in water. In this chapter, we will discuss three major categories of reactions that occur in aqueous solutions: precipitation reactions, acid-base reactions, and redox reactions. In later chapters, we will study the structural characteristics and properties of water—the so-called *universal solvent*—and its solutions.

4.1 General Properties of Aqueous Solutions

A **solution** is a *homogeneous mixture of two or more substances*. The **solute** is the substance present in a smaller amount, and the **solvent** is the substance present in a larger amount. A solution may be gaseous (such as air), solid (such as an alloy), or liquid (seawater, for example). In this section we will discuss only **aqueous solutions**, in which the solute initially is a liquid or a solid and the solvent is water.

Electrolytic Properties

All solutes that dissolve in water fit into one of two categories: electrolytes and non-electrolytes. An **electrolyte** is a substance that, when dissolved in water, results in a solution that can conduct electricity. A **nonelectrolyte** does not conduct electricity when dissolved in water. Figure 4.1 shows an easy and straightforward method of distinguishing between electrolytes and nonelectrolytes. A pair of inert electrodes (copper or platinum) is immersed in a beaker of water. To light the bulb, electric current must flow from one electrode to the other, thus completing the circuit. Pure water is a very poor conductor of electricity. However, if we add a small amount of sodium chloride (NaCl), the bulb will glow as soon as the salt dissolves in the water. Solid NaCl, an ionic compound, breaks up into Na^+ and Cl^- ions when it dissolves in water. The Na^+ ions are attracted to the negative electrode, and the Cl^- ions to the positive electrode. The movement of these ions allows the solution to conduct electricity. Because the NaCl solution conducts electricity, we say that NaCl is an electrolyte. Pure water contains very few ions, so it cannot conduct electricity.

Tap water does conduct electricity because it contains many dissolved ions.

 Video
Strong Electrolytes, Weak Electrolytes, and Nonelectrolytes

Comparing the lightbulb's brightness for the same molar amounts of dissolved substances helps us distinguish between strong and weak electrolytes. A characteristic of strong electrolytes is that the solute is assumed to be 100 percent dissociated into ions in solution. (By *dissociation* we mean the breaking up of the

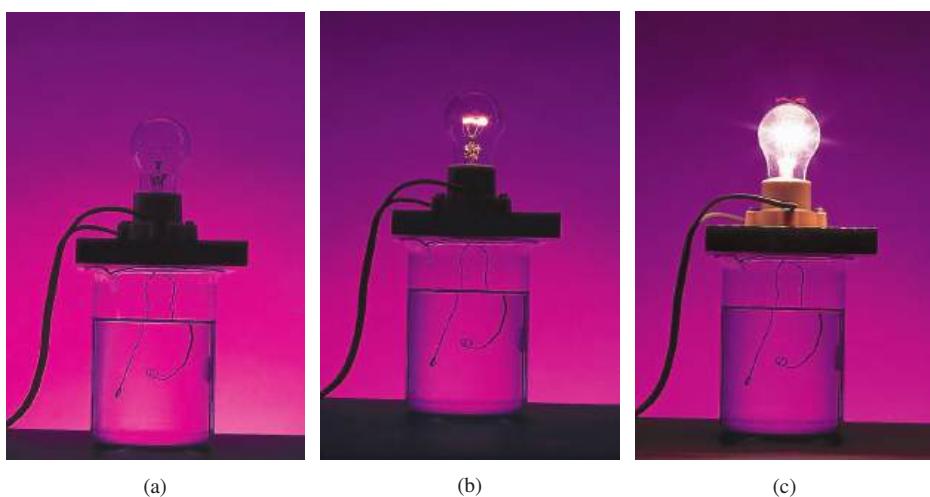
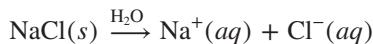


Figure 4.1 An arrangement for distinguishing between electrolytes and nonelectrolytes. A solution's ability to conduct electricity depends on the number of ions it contains. (a) A nonelectrolyte solution does not contain ions, and the lightbulb is not lit. (b) A weak electrolyte solution contains a small number of ions, and the lightbulb is dimly lit. (c) A strong electrolyte solution contains a large number of ions, and the lightbulb is brightly lit. The molar amounts of the dissolved solutes are equal in all three cases.

(a, b, c): ©McGraw-Hill Education/Ken Karp

compound into cations and anions.) Thus, we can represent sodium chloride dissolving in water as



This equation says that all sodium chloride that enters the solution ends up as Na^+ and Cl^- ions; there are no undissociated NaCl units in solution.

Table 4.1 lists examples of strong electrolytes, weak electrolytes, and nonelectrolytes. Ionic compounds, such as sodium chloride, potassium iodide (KI), and calcium nitrate $[\text{Ca}(\text{NO}_3)_2]$, are strong electrolytes. It is interesting to note that human body fluids contain many strong and weak electrolytes.

Water is a very effective solvent for ionic compounds. Although water is an electrically neutral molecule, it has a positive region (the H atoms) and a negative region (the O atom), or positive and negative “poles”; for this reason it is a *polar* solvent. When an ionic compound such as sodium chloride dissolves in water, the three-dimensional lattice of ions in the solid is broken apart. The Na^+ and Cl^- ions are separated from each other and undergo **hydration**, *the process in which an ion is surrounded by water molecules*. Each Na^+ ion is surrounded by a number of water molecules orienting their negative poles toward the cation. Similarly, each Cl^- ion is surrounded by water molecules with their positive poles oriented toward the anion (Figure 4.2). Hydration helps to stabilize ions in solution and prevents cations from recombining with anions.

Acids and bases are also electrolytes. Some acids, including hydrochloric acid (HCl) and nitric acid (HNO_3), are strong electrolytes. These acids are assumed to ionize



Table 4.1 Classification of Solutes in Aqueous Solution

Strong Electrolyte	Weak Electrolyte	Nonelectrolyte
HCl	CH_3COOH	$(\text{NH}_2)_2\text{CO}$ (urea)
HNO_3	HF	CH_3OH (methanol)
HClO_4	HNO_2	$\text{C}_2\text{H}_5\text{OH}$ (ethanol)
H_2SO_4^*	NH_3	$\text{C}_6\text{H}_{12}\text{O}_6$ (glucose)
NaOH	$\text{H}_2\text{O}^\dagger$	$\text{C}_{12}\text{H}_{22}\text{O}_{11}$ (sucrose)
$\text{Ba}(\text{OH})_2$		
Ionic compounds		

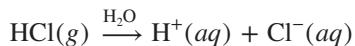
* H_2SO_4 has two ionizable H^+ ions, but only one of the H^+ ions is totally ionized.

[†]Pure water is an extremely weak electrolyte.

Figure 4.2 Hydration of Na^+ and Cl^- ions.



completely in water; for example, when hydrogen chloride gas dissolves in water, it produces hydrated H^+ and Cl^- ions:



In other words, *all* the dissolved HCl molecules separate into hydrated H⁺ and Cl⁻ ions. Thus, when we write HCl(*aq*), it is understood that it is a solution of only H⁺(*aq*) and Cl⁻(*aq*) ions and that there are no hydrated HCl molecules present.

On the other hand, certain acids, such as acetic acid (CH_3COOH), which gives vinegar its tart flavor, do not ionize completely and are weak electrolytes. We represent the ionization of acetic acid as

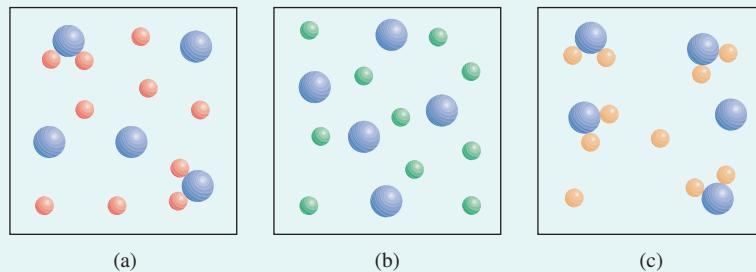


where CH_3COO^- is called the acetate ion. We use the term *ionization* to describe the separation of acids and bases into ions. By writing the formula of acetic acid as CH_3COOH , we indicate that the ionizable proton is in the COOH group.

The ionization of acetic acid is written with a double arrow to show that it is a ***reversible reaction***, meaning *the reaction can occur in both directions*. Initially, a number of CH_3COOH molecules break up into CH_3COO^- and H^+ ions. As time goes on, some of the CH_3COO^- and H^+ ions recombine into CH_3COOH molecules. Eventually, a state is reached in which the acid molecules ionize as fast as the ions recombine. Such a chemical state, in which no net change can be observed (although activity is continuous on the molecular level), is called *chemical equilibrium*. Acetic acid, then, is a weak electrolyte because its ionization in water is incomplete. By contrast, in a hydrochloric acid solution the H^+ and Cl^- ions have no tendency to recombine and form molecular HCl. We use a single arrow to represent complete ionizations.

Review of Concepts & Facts

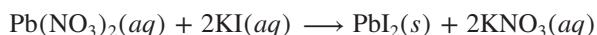
- 4.1.1** The diagrams here show three compounds, (a) AB_2 , (b) AC_2 , and (c) AD_2 , dissolved in water. Which is the strongest electrolyte and which is the weakest? (For simplicity, water molecules are not shown.)



- 4.1.2** Predict whether the following compounds are a strong electrolyte, weak electrolyte, or nonelectrolyte: (a) KBr, (b) NaI, (c) $\text{C}_3\text{H}_7\text{OH}$.

4.2 Precipitation Reactions

One common type of reaction that occurs in aqueous solution is the ***precipitation reaction***, which results in the formation of an insoluble product, known as a ***precipitate***. A ***precipitate*** is an insoluble solid that separates from the solution. Precipitation reactions usually involve ionic compounds. For example, when an aqueous solution of lead(II) nitrate $\text{[Pb}(\text{NO}_3)_2]$ is added to an aqueous solution of potassium iodide (KI), a yellow precipitate of lead(II) iodide (PbI_2) is formed:



Potassium nitrate remains in solution. Figure 4.3 shows this reaction in progress.

The preceding reaction is an example of a ***metathesis reaction*** (also called a double-displacement reaction), a reaction that involves the exchange of parts between the two compounds. (In this case, the cations in the two compounds exchange anions, so Pb^{2+} ends up with I^- as PbI_2 and K^+ ends up with NO_3^- as KNO_3 .) As we will see, the precipitation reactions discussed in this chapter are examples of metathesis reactions.

Solubility

How can we predict whether a precipitate will form when a compound is added to a solution or when two solutions are mixed? It depends on the ***solubility*** of the solute, which is defined as *the maximum amount of solute that will dissolve in a given quantity of solvent at a specific temperature*. Chemists refer to substances as soluble, slightly soluble, or insoluble in a qualitative sense. A substance is said to be soluble if a fair amount of it visibly dissolves when added to water. If not, the substance is described as slightly soluble or insoluble. All ionic compounds are strong electrolytes, but they are not equally soluble.

Table 4.2 classifies a number of common ionic compounds as soluble or insoluble. Keep in mind, however, that even insoluble compounds dissolve to a certain extent. Figure 4.4 shows several precipitates.

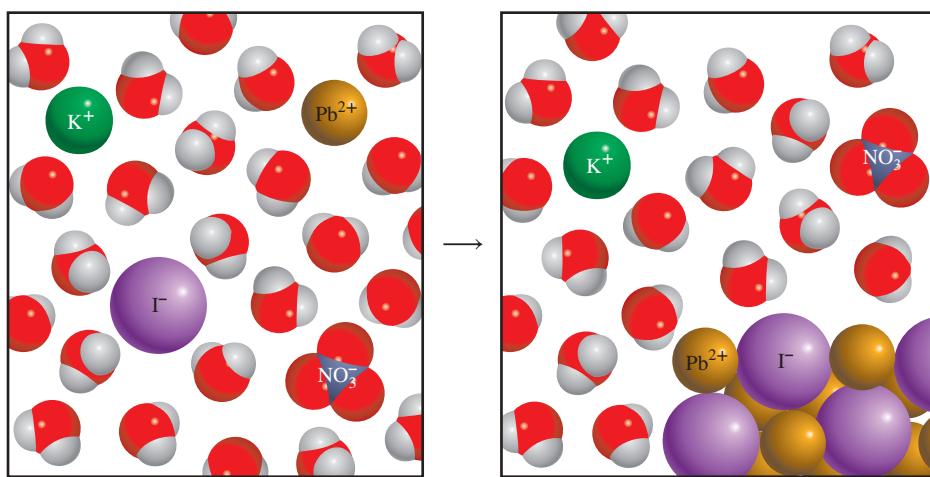


Figure 4.3 Formation of yellow PbI_2 precipitate as a solution of $\text{Pb}(\text{NO}_3)_2$ is added to a solution of KI .
(left): ©McGraw-Hill Education/Charles D. Winters

Table 4.2 Solubility Rules for Common Ionic Compounds in Water at 25°C

Soluble Compounds	Insoluble Exceptions
Compounds containing alkali metal ions (Li^+ , Na^+ , K^+ , Rb^+ , Cs^+) and the ammonium ion (NH_4^+)	
Nitrates (NO_3^-), acetates (CH_3COO^-), bicarbonates (HCO_3^-), chlorates (ClO_3^-), and perchlorates (ClO_4^-)	
Halides (Cl^- , Br^- , I^-)	Halides of Ag^+ , Hg_2^{2+} , and Pb^{2+}
Sulfates (SO_4^{2-})	Sulfates of Ag^+ , Ca^{2+} , Sr^{2+} , Ba^{2+} , Hg_2^{2+} , and Pb^{2+}
Insoluble Compounds	Soluble Exceptions
Carbonates (CO_3^{2-}), phosphates (PO_4^{3-}), chromates (CrO_4^{2-}), sulfides (S^{2-})	Compounds containing alkali metal ions and the ammonium ion
Hydroxides (OH^-)	Compounds containing alkali metal ions and the Ba^{2+} ion

Figure 4.4 Appearance of several precipitates. From left to right: CdS , PbS , Ni(OH)_2 , and Al(OH)_3 .

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Example 4.1 applies the solubility rules from Table 4.2.

Example 4.1

Classify the following ionic compounds as soluble or insoluble: (a) silver sulfate (Ag_2SO_4), (b) calcium carbonate (CaCO_3), (c) sodium phosphate (Na_3PO_4).

Strategy Although it is not necessary to memorize the solubilities of compounds, you should keep in mind the following useful rules: All ionic compounds containing alkali metal cations; the ammonium ion; and the nitrate, bicarbonate, and chloride ions are soluble. For other compounds, we need to refer to Table 4.2.

(Continued)

Solution

- (a) According to Table 4.2, Ag_2SO_4 is insoluble.
 (b) This is a carbonate and Ca is a Group 2A metal. Therefore, CaCO_3 is insoluble.
 (c) Sodium is an alkali metal (Group 1A) so Na_3PO_4 is soluble.

Practice Exercise Classify the following ionic compounds as soluble or insoluble:

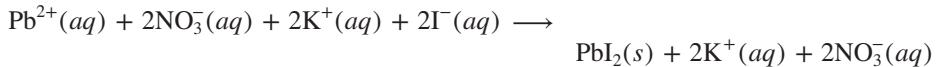
- (a) CuS , (b) $\text{Ca}(\text{OH})_2$, (c) $\text{Zn}(\text{NO}_3)_2$.

Similar problems: 4.19, 4.20.

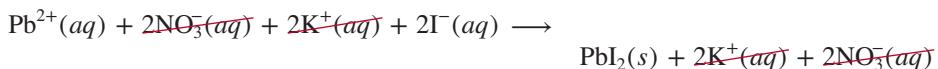
Molecular Equations, Ionic Equations, and Net Ionic Equations

The earlier equation describing the precipitation of lead(II) iodide is called a **molecular equation**, because *the formulas of the compounds are written as though all species existed as molecules or whole units*. A molecular equation is useful because it identifies the reagents [that is, lead(II) nitrate and potassium iodide]. If we wanted to bring about this reaction in the laboratory, we would use the molecular equation. However, a molecular equation does not describe in detail what actually is happening in solution.

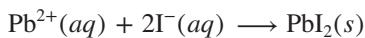
As pointed out earlier, when ionic compounds dissolve in water, they break apart into their component cations and anions. To be more realistic, the equations should show the dissociation of dissolved ionic compounds into ions. Therefore, returning to the reaction between potassium iodide and lead(II) nitrate, we would write



The preceding equation is an example of an **ionic equation**, which *shows dissolved species as free, hydrated ions*. To see whether a precipitate might form from this solution, we first combine the cation and anion from different compounds; that is, PbI_2 and KNO_3 . Referring to Table 4.2, we see that PbI_2 is an insoluble compound and KNO_3 is soluble. Therefore, the dissolved KNO_3 remains in solution as separate K^+ and NO_3^- ions, which are called **spectator ions**, or *ions that are not involved in the overall reaction*. Because spectator ions appear on both sides of an equation, they can be eliminated from the ionic equation



Finally, we end up with the **net ionic equation**, which *shows only the species that actually take part in the reaction*:



Looking at another example, we find that when an aqueous solution of barium chloride (BaCl_2) is added to an aqueous solution of sodium sulfate (Na_2SO_4), a white precipitate is formed (Figure 4.5). Treating this as a metathesis reaction, the products are BaSO_4 and NaCl . From Table 4.2 we see that only BaSO_4 is insoluble. Therefore, we write the molecular equation as



The ionic equation for the reaction is

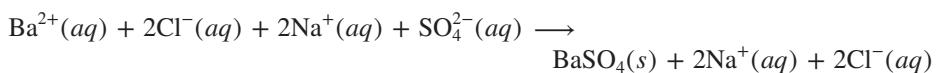
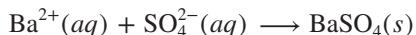


Figure 4.5 Formation of BaSO_4 precipitate.

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Cancelling the spectator ions (Na^+ and Cl^-) on both sides of the equation gives us the net ionic equation



The following four steps summarize the procedure for writing ionic and net ionic equations.

1. Write a balanced molecular equation for the reaction, using the correct formulas for the reactant and product ionic compounds. Refer to Table 4.2 to decide which of the products is insoluble and therefore will appear as a precipitate.
2. Write the ionic equation for the reaction. The compound that does not appear as the precipitate should be shown as free ions.
3. Identify and cancel the spectator ions on both sides of the equation. Write the net ionic equation for the reaction.
4. Check that the charges and number of atoms balance in the net ionic equation.

These steps are applied in Example 4.2.



Precipitate formed by the reaction between $\text{K}_3\text{PO}_4(aq)$ and $\text{Ca}(\text{NO}_3)_2(aq)$.

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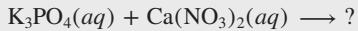
Student Hot Spot

Student data indicate you may struggle with precipitation reactions. Access your eBook for additional Learning Resources on this topic.

Example 4.2

Predict what happens when a potassium phosphate (K_3PO_4) solution is mixed with a calcium nitrate [$\text{Ca}(\text{NO}_3)_2$] solution. Write a net ionic equation for the reaction.

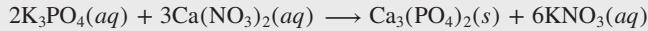
Strategy From the given information, it is useful to first write the unbalanced equation



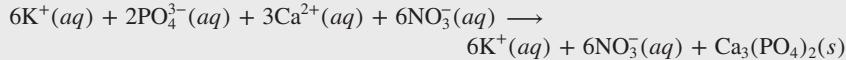
What happens when ionic compounds dissolve in water? What ions are formed from the dissociation of K_3PO_4 and $\text{Ca}(\text{NO}_3)_2$? What happens when the cations encounter the anions in solution?

Solution In solution, K_3PO_4 dissociates into K^+ and PO_4^{3-} ions and $\text{Ca}(\text{NO}_3)_2$ dissociates into Ca^{2+} and NO_3^- ions. According to Table 4.2, calcium ions (Ca^{2+}) and phosphate ions (PO_4^{3-}) will form an insoluble compound, calcium phosphate [$\text{Ca}_3(\text{PO}_4)_2$], while the other product, KNO_3 , is soluble and remains in solution. Therefore, this is a precipitation reaction. We follow the stepwise procedure just outlined.

Step 1: The balanced molecular equation for this reaction is



Step 2: To write the ionic equation, the soluble compounds are shown as dissociated ions:



Step 3: Cancelling the spectator ions (K^+ and NO_3^-) on each side of the equation, we obtain the net ionic equation:



Step 4: Note that because we balanced the molecular equation first, the net ionic equation is balanced as to the number of atoms on each side, and the number of positive (+6) and negative (-6) charges on the left-hand side is the same.

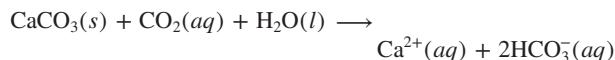
Practice Exercise Predict the precipitate produced by mixing an $\text{Al}(\text{NO}_3)_3$ solution with a NaOH solution. Write the net ionic equation for the reaction.

Similar problems: 4.21, 4.22.

The Chemistry in Action essay, “An Undesirable Precipitation Reaction,” discusses some practical problems associated with precipitation reactions.

An Undesirable Precipitation Reaction

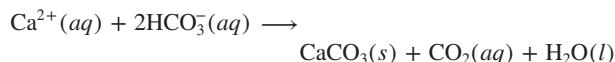
Limestone (CaCO_3) and dolomite ($\text{CaCO}_3 \cdot \text{MgCO}_3$), which are widespread on Earth's surface, often enter the water supply. According to Table 4.2, calcium carbonate is insoluble in water. However, in the presence of dissolved carbon dioxide (from the atmosphere), calcium carbonate is converted to soluble calcium bicarbonate [$\text{Ca}(\text{HCO}_3)_2$]:



where HCO_3^- is the bicarbonate ion.

Water containing Ca^{2+} and/or Mg^{2+} ions is called *hard water*, and water that is mostly free of these ions is called *soft water*. Hard water is unsuitable for some household and industrial uses.

When water containing Ca^{2+} and HCO_3^- ions is heated or boiled, the solution reaction is reversed to produce the CaCO_3 precipitate



and gaseous carbon dioxide is driven off:



Solid calcium carbonate formed in this way is the main component of the scale that accumulates in boilers, water heaters, pipes, and tea kettles. A thick layer of scale reduces heat transfer and decreases the efficiency and durability of boilers, pipes,



Boiler scale almost fills this hot-water pipe. The deposits consist mostly of CaCO_3 with some MgCO_3 .

©Sheila Terry/Science Source

and appliances. In household hot-water pipes it can restrict or totally block the flow of water. A simple method used by plumbers to remove scale deposits is to introduce a small amount of hydrochloric acid, which reacts with (and therefore dissolves) CaCO_3 :



In this way, CaCO_3 is converted to soluble CaCl_2 .

Review of Concepts & Facts

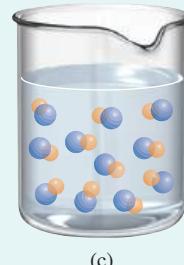
- 4.2.1** Which of the diagrams (a)–(c) accurately describes the reaction between $\text{Ca}(\text{NO}_3)_2(aq)$ and $\text{Na}_2\text{CO}_3(aq)$? For simplicity, only the Ca^{2+} (yellow) and CO_3^{2-} (blue) ions are shown.



(a)



(b)



(c)

- 4.2.2** Classify each of the following compounds as soluble or insoluble in water:
 (a) $\text{Fe}(\text{NO}_3)_3$, (b) AgBr , (c) NH_4Cl .
- 4.2.3** Write the net ionic equation for the precipitation reaction between $\text{Cu}(\text{NO}_3)_2$ and $(\text{NH}_4)_2\text{S}$.

4.3 Acid-Base Reactions

Acids and bases are as familiar as aspirin and milk of magnesia although many people do not know their chemical names—acetylsalicylic acid (aspirin) and magnesium hydroxide (milk of magnesia). In addition to being the basis of many medicinal and household products, acid-base chemistry is important in industrial processes and essential in sustaining biological systems. Before we can discuss acid-base reactions, we need to know more about acids and bases themselves.

General Properties of Acids and Bases

In Section 2.7 we defined acids as substances that ionize in water to produce H^+ ions and bases as substances that ionize in water to produce OH^- ions. These definitions were formulated in the late nineteenth century by the Swedish chemist Svante Arrhenius[†] to classify substances whose properties in aqueous solutions were well known.

Acids

- Acids have a sour taste; for example, vinegar owes its sourness to acetic acid, and lemons and other citrus fruits contain citric acid.
- Acids cause color changes in plant dyes; for example, they change the color of litmus from blue to red.
- Acids react with certain metals, such as zinc, magnesium, and iron, to produce hydrogen gas. A typical reaction is that between hydrochloric acid and magnesium:

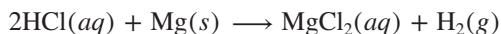
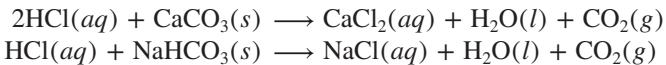


Figure 4.6 A piece of blackboard chalk, which is mostly CaCO_3 , reacts with hydrochloric acid.

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- Acids react with carbonates and bicarbonates, such as Na_2CO_3 , CaCO_3 , and NaHCO_3 , to produce carbon dioxide gas (Figure 4.6). For example,



- Aqueous acid solutions conduct electricity.

Bases

- Bases have a bitter taste.
- Bases feel slippery; for example, soaps, which contain bases, exhibit this property.
- Bases cause color changes in plant dyes; for example, they change the color of litmus from red to blue.
- Aqueous base solutions conduct electricity.

Brønsted Acids and Bases

Arrhenius's definitions of acids and bases are limited in that they apply only to aqueous solutions. Broader definitions were proposed by the Danish chemist Johannes Brønsted[‡] in 1932; a **Brønsted acid** is a proton donor, and a **Brønsted base** is a proton acceptor. Note that Brønsted's definitions do not require acids and bases to be in aqueous solution.

[†]Svante August Arrhenius (1859–1927). Swedish chemist. Arrhenius made important contributions in the study of chemical kinetics and electrolyte solutions. He also speculated that life had come to Earth from other planets, a theory now known as *panspermia*. Arrhenius was awarded the Nobel Prize in Chemistry in 1903.

[‡]Johannes Nicolaus Brønsted (1879–1947). Danish chemist. In addition to his theory of acids and bases, Brønsted worked on thermodynamics and the separation of mercury isotopes. In some texts, Brønsted acids and bases are called Brønsted-Lowry acids and bases. Thomas Martin Lowry (1874–1936). English chemist. Brønsted and Lowry developed essentially the same acid-base theory independently in 1923.

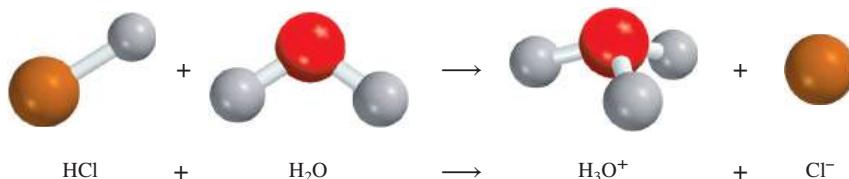
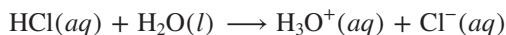


Figure 4.7 Ionization of HCl in water to form the hydronium ion and the chloride ion.

Hydrochloric acid is a Brønsted acid because it donates a proton, symbolized by $\text{H}^+(aq)$, in water:



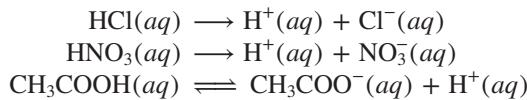
Note that the H^+ ion is a hydrogen atom that has lost its electron; that is, it is just a bare proton. The size of a proton is about 10^{-15} m, compared to a diameter of 10^{-10} m for an average atom or ion. Such an exceedingly small charged particle cannot exist as a separate entity in aqueous solution owing to its strong attraction for the negative pole (the O atom) in H_2O . Consequently, the proton exists in the hydrated form, as shown in Figure 4.7. Therefore, the ionization of hydrochloric acid should be written as



The *hydrated proton*, $\text{H}_3\text{O}^+(aq)$, is called the **hydronium ion**. This equation shows a reaction in which a Brønsted acid (HCl) donates a proton to a Brønsted base (H_2O).

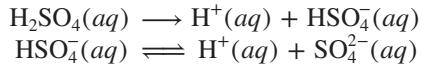
Experiments show that the hydronium ion is further hydrated so that the proton may have several water molecules associated with it. Because the acidic properties of the proton are unaffected by the degree of hydration, in this text we will generally use $\text{H}^+(aq)$ to represent the hydrated proton. This notation is for convenience, but H_3O^+ is closer to reality. Keep in mind that both notations represent the same species in aqueous solution.

Acids commonly used in the laboratory include hydrochloric acid (HCl), nitric acid (HNO_3), acetic acid (CH_3COOH), sulfuric acid (H_2SO_4), and phosphoric acid (H_3PO_4). The first three are **monoprotic acids**; that is, *each unit of the acid yields one hydrogen ion upon ionization*:



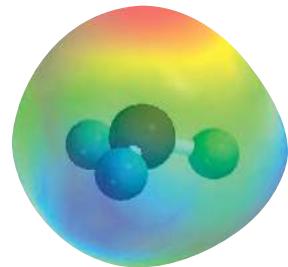
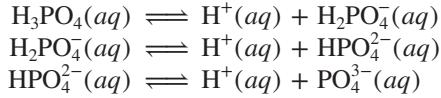
As mentioned earlier, because the ionization of acetic acid is incomplete (note the double arrows), it is a weak electrolyte. For this reason it is called a weak acid (see Table 4.1). On the other hand, HCl and HNO_3 are strong acids because they are strong electrolytes, so they are completely ionized in solution (note the use of single arrows).

Sulfuric acid (H_2SO_4) is a **diprotic acid**, because *each unit of the acid gives up two H^+ ions*, in two separate steps:



H_2SO_4 is a strong electrolyte or strong acid (the first step of ionization is complete), but HSO_4^- is a weak acid or weak electrolyte, and we need a double arrow to represent its incomplete ionization.

Triprotic acids, which yield three H^+ ions, are relatively few in number. The best known triprotic acid is phosphoric acid, whose ionizations are



Electrostatic potential map of the H_3O^+ ion. In the rainbow color spectrum representation, the most electron-rich region is red and the most electron-poor region is blue.

In most cases, acids start with H in the formula or have a COOH group.

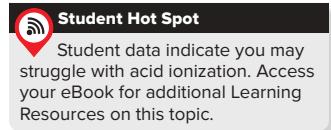


Table 4.3

Some Common Strong and Weak Acids	
Strong Acids	
Hydrochloric acid	HCl
Hydrobromic acid	HBr
Hydroiodic acid	HI
Nitric acid	HNO ₃
Sulfuric acid	H ₂ SO ₄
Perchloric acid	HClO ₄
Weak Acids	
Hydrofluoric acid	HF
Nitrous acid	HNO ₂
Phosphoric acid	H ₃ PO ₄
Acetic acid	CH ₃ COOH

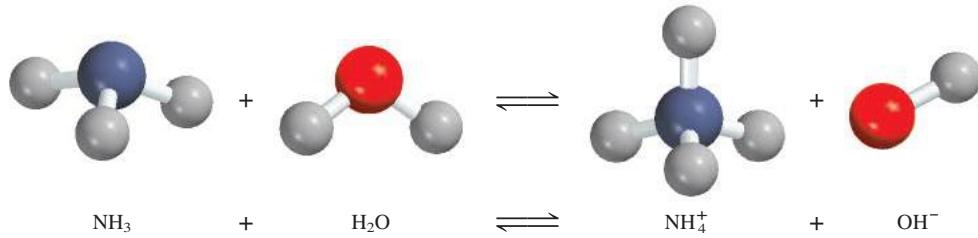
**Student Hot Spot**

Student data indicate you may struggle with base ionization. Access your eBook for additional Learning Resources on this topic.



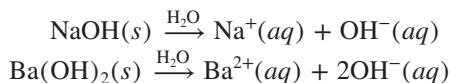
Note that this bottle of aqueous ammonia is erroneously labeled.

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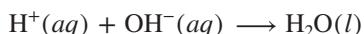
**Figure 4.8** Ionization of ammonia in water to form the ammonium ion and the hydroxide ion.

All three species (H_3PO_4 , H_2PO_4^- , and HPO_4^{2-}) in this case are weak acids, and we use the double arrows to represent each ionization step. Anions such as H_2PO_4^- and HPO_4^{2-} are found in aqueous solutions of phosphates such as NaH_2PO_4 and Na_2HPO_4 . Table 4.3 lists several common strong and weak acids.

Table 4.1 shows that sodium hydroxide (NaOH) and barium hydroxide [$\text{Ba}(\text{OH})_2$] are strong electrolytes. This means that they are completely ionized in solution:



The OH^- ion can accept a proton as follows:



Thus, OH^- is a Brønsted base.

Ammonia (NH_3) is classified as a Brønsted base because it can accept a H^+ ion (Figure 4.8):



Ammonia is a weak electrolyte (and therefore a weak base) because only a small fraction of dissolved NH_3 molecules react with water to form NH_4^+ and OH^- ions.

The most commonly used strong base in the laboratory is sodium hydroxide. It is cheap and soluble. (In fact, all of the alkali metal hydroxides are soluble.) The most commonly used weak base is aqueous ammonia solution, which is sometimes erroneously called ammonium hydroxide. There is no evidence that the species NH_4OH actually exists, other than the NH_4^+ and OH^- ions in solution. All of the Group 2A elements form hydroxides of the type $\text{M}(\text{OH})_2$, where M denotes an alkaline earth metal. Of these hydroxides, only $\text{Ba}(\text{OH})_2$ is soluble. Magnesium and calcium hydroxides are used in medicine and industry. Hydroxides of other metals, such as $\text{Al}(\text{OH})_3$ and $\text{Zn}(\text{OH})_2$, are insoluble and are not used as bases.

Example 4.3 classifies substances as Brønsted acids or Brønsted bases.

Example 4.3

Classify each of the following species in aqueous solution as a Brønsted acid or base:

- (a) HBr , (b) NO_2^- , (c) HCO_3^- .

Strategy What are the characteristics of a Brønsted acid? Does it contain at least an H atom? With the exception of ammonia, most Brønsted bases that you will encounter at this stage are anions.

(Continued)

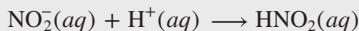
Solution

- (a) We know that HCl is an acid. Because Br and Cl are both halogens (Group 7A), we expect HBr, like HCl, to ionize in water as follows:



Therefore HBr is a Brønsted acid.

- (b) In solution the nitrite ion can accept a proton from water to form nitrous acid:

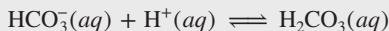


This property makes NO_2^- a Brønsted base.

- (c) The bicarbonate ion is a Brønsted acid because it ionizes in solution as follows:



It is also a Brønsted base because it can accept a proton to form carbonic acid:



Comment The HCO_3^- species is said to be *amphoteric* because it possesses both acidic and basic properties. The double arrows show that this is a reversible reaction.

Practice Exercise Classify each of the following species as a Brønsted acid or base:

- (a) SO_4^{2-} , (b) HI.

Similar problems: 4.31, 4.32.

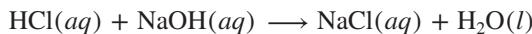
Acid-Base Neutralization

A **neutralization reaction** is a reaction between an acid and a base. Generally, aqueous acid-base reactions produce water and a **salt**, which is an ionic compound made up of a cation from the base and an anion from the acid:

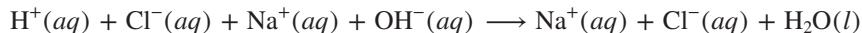


The substance we know as table salt, NaCl, is a product of the acid-base reaction

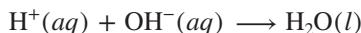
Acid-base reactions generally go to completion.



However, because both the acid and the base are strong electrolytes, they are completely ionized in solution. The ionic equation is



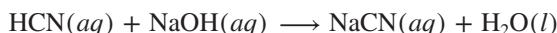
Therefore, the reaction can be represented by the net ionic equation



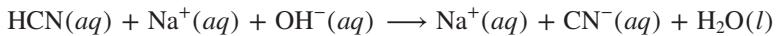
Both Na^+ and Cl^- are spectator ions.

If we had started the preceding reaction with equal molar amounts of the acid and the base, at the end of the reaction we would have only a salt and no leftover acid or base. This is a characteristic of acid-base neutralization reactions.

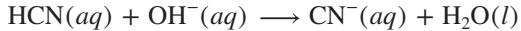
A reaction between a weak acid such as hydrocyanic acid (HCN) and a strong base is



Because HCN is a weak acid, it does not ionize appreciably in solution. Thus, the ionic equation is written as

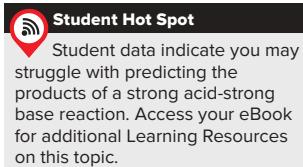
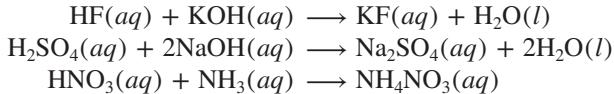


and the net ionic equation is

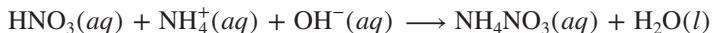


Note that only Na^+ is a spectator ion; OH^- and CN^- are not.

The following are also examples of acid-base neutralization reactions, represented by molecular equations:



The last equation looks different because it does not show water as a product. However, if we express $\text{NH}_3(aq)$ as $\text{NH}_4^+(aq)$ and $\text{OH}^-(aq)$, as discussed earlier, then the equation becomes



Example 4.4

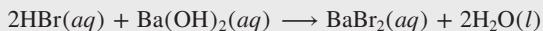
Write molecular, ionic, and net ionic equations for each of the following acid-base reactions:

- hydrobromic acid(*aq*) + barium hydroxide(*aq*) →
- sulfuric acid(*aq*) + potassium hydroxide(*aq*) →

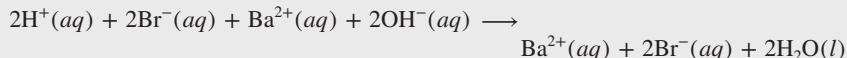
Strategy The first step is to identify the acids and bases as strong or weak. We see that HBr is a strong acid and H_2SO_4 is a strong acid for the first step ionization and a weak acid for the second step ionization. Both $\text{Ba}(\text{OH})_2$ and KOH are strong bases.

Solution

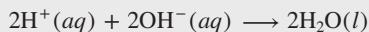
- (a) Molecular equation:



Ionic equation:



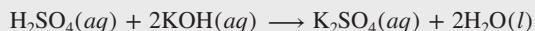
Net ionic equation:



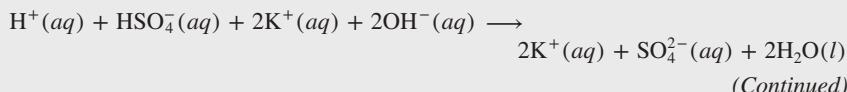
or $\text{H}^+(aq) + \text{OH}^-(aq) \longrightarrow \text{H}_2\text{O}(l)$

Both Ba^{2+} and Br^- are spectator ions.

- (b) Molecular equation:

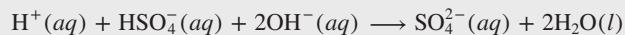


Ionic equation:



(Continued)

Net ionic equation:



Note that because HSO_4^- is a weak acid and does not ionize appreciably in water, the only spectator ion is K^+ .

Practice Exercise Write a molecular equation, an ionic equation, and a net ionic equation for the reaction between aqueous solutions of phosphoric acid and sodium hydroxide.

Similar problem: 4.33(b).

Acid-Base Reactions Leading to Gas Formation

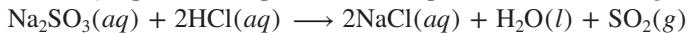
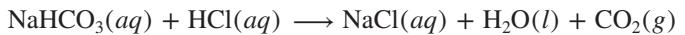
Certain salts like carbonates (containing the CO_3^{2-} ion), bicarbonates (containing the HCO_3^- ion), sulfites (containing the SO_3^{2-} ion), and sulfides (containing the S^{2-} ion) react with acids to form gaseous products. For example, the molecular equation for the reaction between sodium carbonate (Na_2CO_3) and $\text{HCl}(aq)$ is (see Figure 4.6)



Carbonic acid is unstable and if present in solution in sufficient concentrations decomposes as follows:

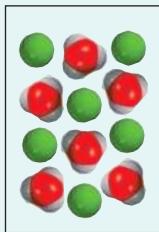


Similar reactions involving other mentioned salts are

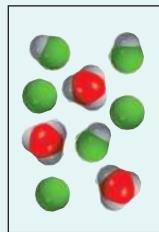


Review of Concepts & Facts

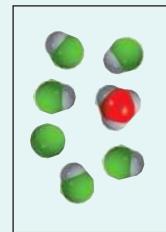
- 4.3.1** Which of the diagrams (a)–(c) best represents a weak acid? Which represents a very weak acid? Which represents a strong acid? The proton exists in water as the hydronium ion. All acids are monoprotic. (For simplicity, water molecules are not shown.)



(a)



(b)



(c)

- 4.3.2** Identify the Brønsted acid and Brønsted base in the following equation:



- 4.3.3** Write the net ionic equation for the following acid-base reaction:

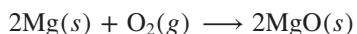


4.4 Oxidation-Reduction Reactions

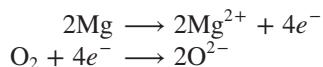
 Video
Oxidation-Reduction Reactions

Whereas acid-base reactions can be characterized as proton-transfer processes, the class of reactions called **oxidation-reduction**, or **redox, reactions** are considered *electron-transfer reactions*. Oxidation-reduction reactions are very much a part of the world around us. They range from the burning of fossil fuels to the action of household bleach. Additionally, most metallic and nonmetallic elements are obtained from their ores by the process of oxidation or reduction.

Many important redox reactions take place in water, but not all redox reactions occur in aqueous solution. We begin our discussion with a reaction in which two elements combine to form a compound. Consider the formation of magnesium oxide (MgO) from magnesium and oxygen (Figure 4.9):

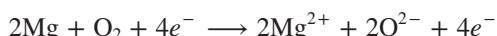


Magnesium oxide (MgO) is an ionic compound made up of Mg^{2+} and O^{2-} ions. In this reaction, two Mg atoms give up or transfer four electrons to two O atoms (in O_2). For convenience, we can think of this process as two separate steps, one involving the loss of four electrons by the two Mg atoms and the other being the gain of four electrons by an O_2 molecule:

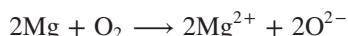


Note that in an oxidation half-reaction, electrons appear as the product; in a reduction half-reaction, electrons appear as the reactant.

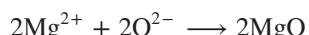
Each of these steps is called a **half-reaction**, which *explicitly shows the electrons involved in a redox reaction*. The sum of the half-reactions gives the overall reaction:



or, if we cancel the electrons that appear on both sides of the equation,



Finally, the Mg^{2+} and O^{2-} ions combine to form MgO :



A useful mnemonic for redox is OIL RIG:
Oxidation Is Loss (of electrons) and
Reduction Is Gain (of electrons).

The term **oxidation reaction** refers to the *half-reaction that involves loss of electrons*. Chemists originally used “oxidation” to denote the combination of elements with oxygen. However, it now has a broader meaning that includes reactions not

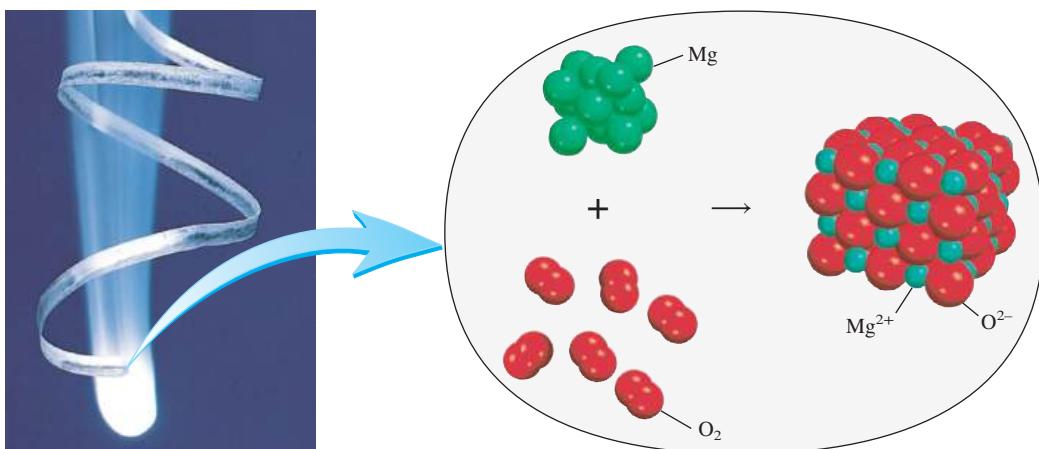


Figure 4.9 Magnesium burns in oxygen to form magnesium oxide.

(left): ©McGraw-Hill Education/Ken Karp

involving oxygen. A **reduction reaction** is a half-reaction that involves gain of electrons. In the formation of magnesium oxide, magnesium is oxidized. It is said to act as a **reducing agent**, because it *donates electrons* to oxygen and causes oxygen to be reduced. Oxygen is reduced and acts as an **oxidizing agent**, because it *accepts electrons* from magnesium, causing magnesium to be oxidized. Note that the extent of oxidation in a redox reaction must be equal to the extent of reduction; that is, the number of electrons lost by a reducing agent must be equal to the number of electrons gained by an oxidizing agent.

The occurrence of electron transfer is more apparent in some redox reactions than others. When metallic zinc is added to a solution containing copper(II) sulfate (CuSO_4), zinc reduces Cu^{2+} by donating two electrons to it:



In the process, the solution loses the blue color that characterizes the presence of hydrated Cu^{2+} ions (Figure 4.10):



Oxidizing agents are always reduced and reducing agents are always oxidized.
This statement may be somewhat confusing, but it is simply a consequence of the definitions of the two processes.

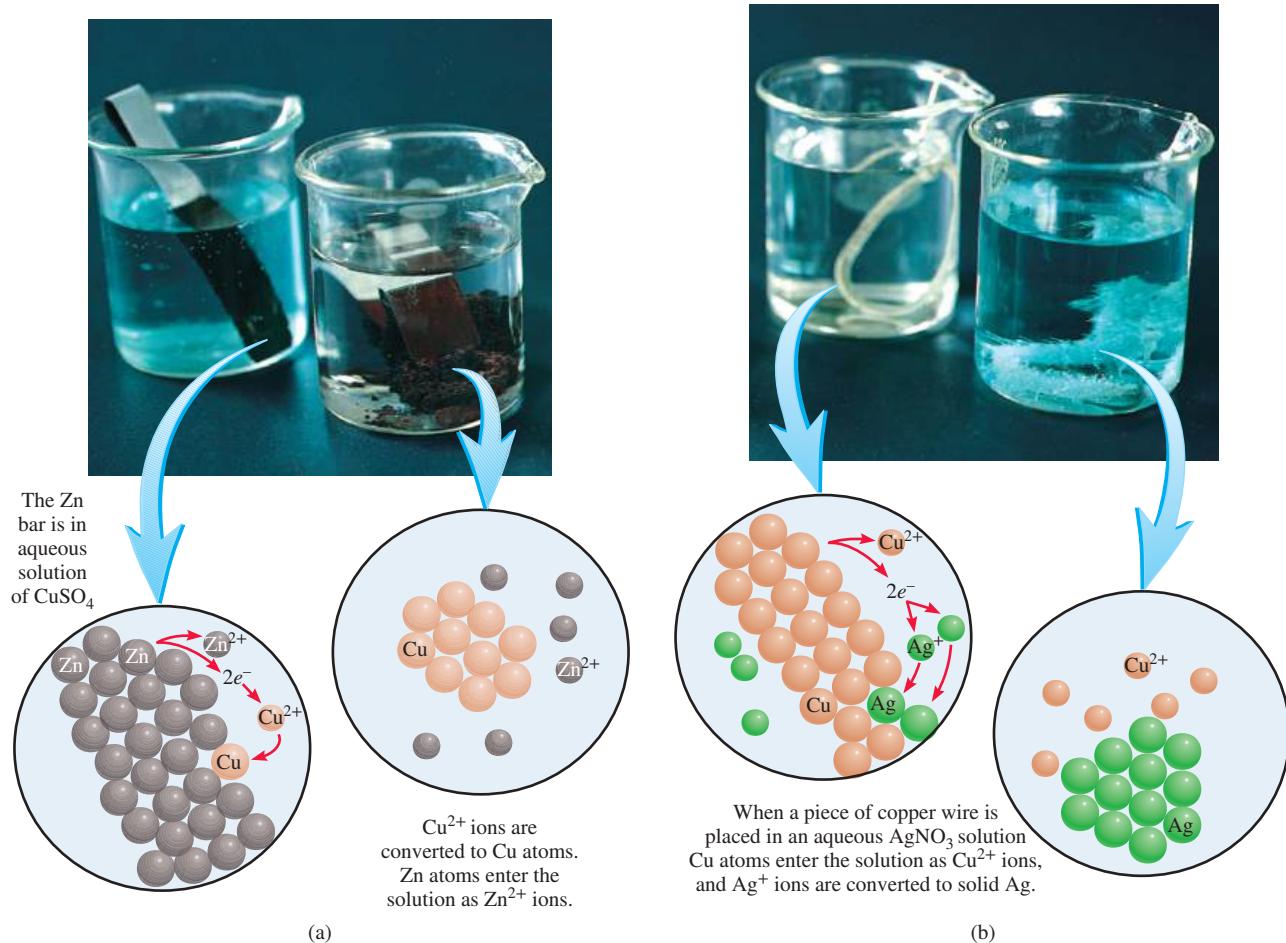
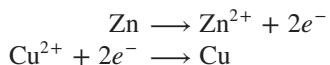


Figure 4.10 Metal displacement reactions in solution. (a) First beaker: A zinc strip is placed in a blue CuSO_4 solution. Immediately Cu^{2+} ions are reduced to metallic Cu in the form of a dark layer. Second beaker: In time, most of the Cu^{2+} ions are reduced and the solution becomes colorless. (b) First beaker: A piece of Cu wire is placed in a colorless AgNO_3 solution. Ag^+ ions are reduced to metallic Ag. Second beaker: As time progresses, most of the Ag^+ ions are reduced and the solution acquires the characteristic blue color due to the presence of hydrated Cu^{2+} ions.

(a and b): ©McGraw-Hill Education/Ken Karp

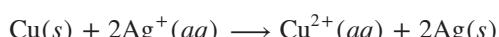
The oxidation and reduction half-reactions are



Similarly, metallic copper reduces silver ions in a solution of silver nitrate (AgNO₃):

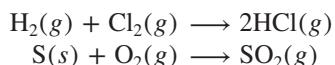


or



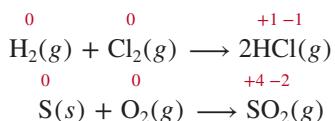
Oxidation Number

The definitions of oxidation and reduction in terms of loss and gain of electrons apply to the formation of ionic compounds such as MgO and the reduction of Cu²⁺ ions by Zn. However, these definitions do not accurately characterize the formation of hydrogen chloride (HCl) and sulfur dioxide (SO₂):



Because HCl and SO₂ are not ionic but molecular compounds, no electrons are actually transferred in the formation of these compounds, as they are in the case of MgO. Nevertheless, chemists find it convenient to treat these reactions as redox reactions, because experimental measurements show that there is a partial transfer of electrons (from H to Cl in HCl and from S to O in SO₂).

To keep track of electrons in redox reactions, it is useful to assign oxidation numbers to the reactants and products. An atom's **oxidation number**, also called **oxidation state**, signifies the *number of charges the atom would have in a molecule (or an ionic compound) if electrons were transferred completely*. For example, we can rewrite the previous equations for the formation of HCl and SO₂ as follows:



The numbers above the element symbols are the oxidation numbers. In both of the reactions shown, there is no charge on the atoms in the reactant molecules. Thus, their oxidation number is zero. For the product molecules, however, it is assumed that complete electron transfer has taken place and that atoms have gained or lost electrons. The oxidation numbers reflect the number of electrons “transferred.”

Oxidation numbers enable us to identify elements that are oxidized and reduced at a glance. The elements that show an increase in oxidation number—hydrogen and sulfur in the preceding examples—are oxidized. Chlorine and oxygen are reduced, so their oxidation numbers show a decrease from their initial values. Note that the sum of the oxidation numbers of H and Cl in HCl (+1 and -1) is zero. Likewise, if we add the oxidation numbers of S (+4) and two atoms of O [2 × (-2)], the total is zero. The reason is that the HCl and SO₂ molecules are neutral, so the charges must cancel.

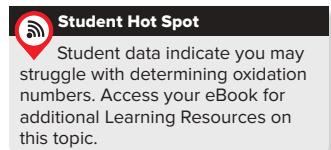
We use the following rules to assign oxidation numbers.

1. In free elements (that is, in the uncombined state), each atom has an oxidation number of zero. Thus, each atom in H₂, Br₂, Na, Be, K, O₂, and P₄ has the same oxidation number: zero.
2. For ions composed of only one atom (that is, monatomic ions), the oxidation number is equal to the charge on the ion. Thus, Li⁺ ion has an oxidation number of +1;

Ba^{2+} ion, +2; Fe^{3+} ion, +3; I^- ion, -1; O^{2-} ion, -2; and so on. All alkali metals have an oxidation number of +1 and all alkaline earth metals have an oxidation number of +2 in their compounds. Aluminum has an oxidation number of +3 in all its compounds.

3. The oxidation number of oxygen in most compounds (for example, MgO and H_2O) is -2, but in hydrogen peroxide (H_2O_2) and peroxide ion (O_2^{2-}), it is -1.
4. The oxidation number of hydrogen is +1, except when it is bonded to metals in binary compounds. In these cases (for example, LiH , NaH , CaH_2), its oxidation number is -1.
5. Fluorine has an oxidation number of -1 in *all* its compounds. Other halogens (Cl, Br, and I) have negative oxidation numbers when they occur as halide ions in their compounds. When combined with oxygen—for example in oxoacids and oxoanions (see Section 2.7)—they have positive oxidation numbers.
6. In a neutral molecule, the sum of the oxidation numbers of all the atoms must be zero. In a polyatomic ion, the sum of oxidation numbers of all the elements in the ion must be equal to the net charge of the ion. For example, in the ammonium ion, NH_4^+ , the oxidation number of N is -3 and that of H is +1. Thus, the sum of the oxidation numbers is $-3 + 4(+1) = +1$, which is equal to the net charge of the ion.
7. Oxidation numbers do not have to be integers. For example, the oxidation number of O in the superoxide ion, O_2^- , is $-\frac{1}{2}$.

We apply the preceding rules to assign oxidation numbers in Example 4.5.



Example 4.5

Assign oxidation numbers to all the elements in the following compounds and ion:

- (a) Li_2O , (b) HNO_3 , (c) $\text{Cr}_2\text{O}_7^{2-}$.

Strategy In general, we follow the rules just listed for assigning oxidation numbers. Remember that all alkali metals have an oxidation number of +1, and in most cases hydrogen has an oxidation number of +1 and oxygen has an oxidation number of -2 in their compounds.

Solution

- (a) By rule 2 we see that lithium has an oxidation number of +1 (Li^+) and oxygen's oxidation number is -2 (O^{2-}).
- (b) This is the formula for nitric acid, which yields a H^+ ion and a NO_3^- ion in solution. From rule 4 we see that H has an oxidation number of +1. Thus the other group (the nitrate ion) must have a net oxidation number of -1. Oxygen has an oxidation number of -2, and if we use x to represent the oxidation number of nitrogen, then the nitrate ion can be written as



or

$$x = +5$$

- (c) From rule 6 we see that the sum of the oxidation numbers in the dichromate ion $\text{Cr}_2\text{O}_7^{2-}$ must be -2. We know that the oxidation number of O is -2, so all that remains is to determine the oxidation number of Cr, which we call y . The dichromate ion can be written as



or

$$y = +6$$

(Continued)

Check In each case, does the sum of the oxidation numbers of all the atoms equal the net charge on the species?

Practice Exercise Assign oxidation numbers to all the elements in the following compound and ion: (a) PF_3 , (b) MnO_4^- .

Similar problems: 4.47, 4.49.

Figure 4.11 shows the known oxidation numbers of the familiar elements, arranged according to their positions in the periodic table. We can summarize the content of this figure as follows:

- Metallic elements have only positive oxidation numbers, whereas nonmetallic elements may have either positive or negative oxidation numbers.
 - The highest oxidation number an element in Groups 1A–7A can have is its group number. For example, the halogens are in Group 7A, so their highest possible oxidation number is +7.
 - The transition metals (Groups 1B, 3B–8B) usually have several possible oxidation numbers.

Figure 4.11 The oxidation numbers of elements in their compounds. The more common oxidation numbers are in color.

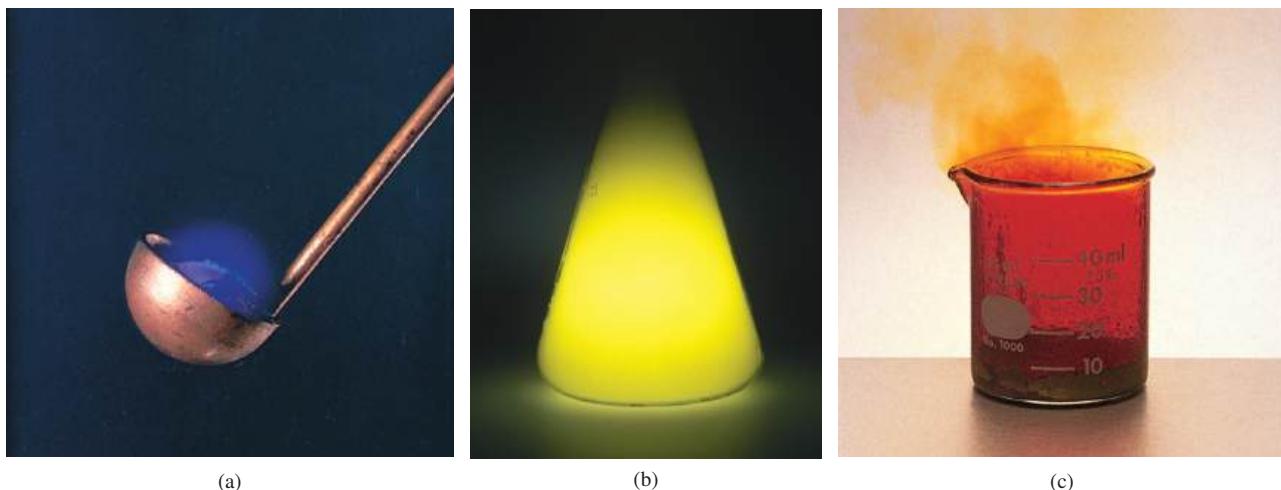


Figure 4.12 Some simple combination redox reactions. (a) Sulfur burning in air to form sulfur dioxide. (b) Sodium burning in chlorine to form sodium chloride. (c) Aluminum reacting with bromine to form aluminum bromide.

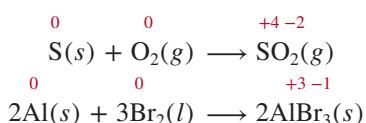
(a): ©McGraw-Hill Education/Ken Karp; (b): ©Charles D. Winters/Science Source; (c): ©McGraw-Hill Education/Ken Karp

Types of Redox Reactions

Among the most common oxidation-reduction reactions are combination, decomposition, combustion, and displacement reactions. A more involved type is called disproportionation reactions, which will also be discussed in this section.

Combination Reactions

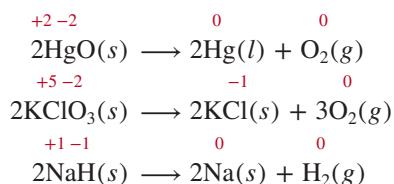
A **combination reaction** is a reaction in which two or more substances combine to form a single product. Figure 4.12 shows some combination reactions. For example,



Not all combination reactions are redox in nature. The same holds for decomposition reactions.

Decomposition Reactions

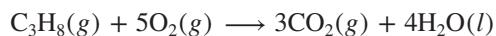
Decomposition reactions are the opposite of combination reactions. Specifically, a **decomposition reaction** is the breakdown of a compound into two or more components (Figure 4.13). For example,



We show oxidation numbers only for elements that are oxidized or reduced.

Combustion Reactions

A **combustion reaction** is a reaction in which a substance reacts with oxygen, usually with the release of heat and light to produce a flame. The reactions between magnesium and sulfur with oxygen described earlier are combustion reactions. Another example is the burning of propane (C_3H_8), a component of natural gas that is used for domestic heating and cooking:



All combustion reactions are redox processes.

Assigning an oxidation number to C atoms in organic compounds is more involved. Here, we focus only on the oxidation number of O atoms, which changes from 0 to -2 .

Figure 4.13 (a) On heating, mercury(II) oxide (HgO) decomposes to form mercury and oxygen. (b) Heating potassium chlorate (KClO_3) produces oxygen, which supports the combustion of the wood splint.

(a): ©McGraw-Hill Education/Charles D. Winters; (b): ©McGraw-Hill Education/Ken Karp

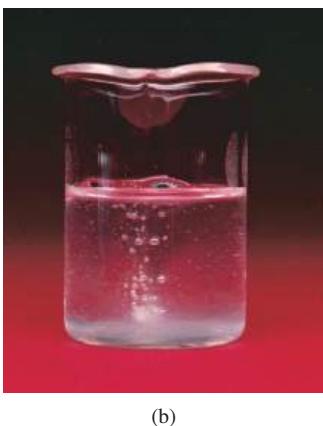
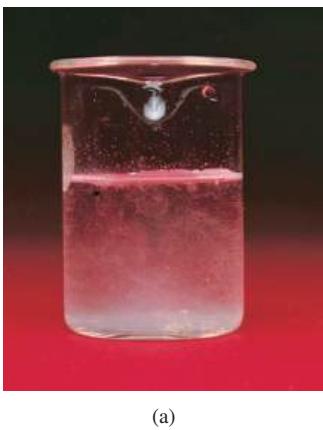
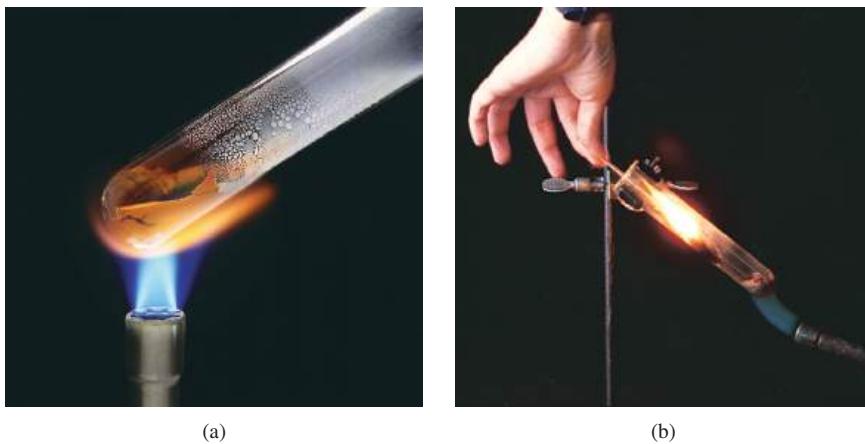


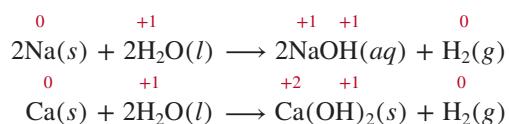
Figure 4.14 Reactions of (a) sodium (Na) and (b) calcium (Ca) with cold water. Note that the reaction is more vigorous with Na than with Ca .

(a and b): ©McGraw-Hill Education/Ken Karp

Displacement Reactions

In a **displacement reaction**, an ion (or atom) in a compound is replaced by an ion (or atom) of another element: Most displacement reactions fit into one of three subcategories: hydrogen displacement, metal displacement, or halogen displacement.

1. Hydrogen Displacement. All alkali metals and some alkaline earth metals (Ca, Sr, and Ba), which are the most reactive of the metallic elements, will displace hydrogen from cold water (Figure 4.14):



Many metals, including those that do not react with water, are capable of displacing hydrogen from acids. For example, zinc (Zn) and magnesium (Mg) do not react with cold water but do react with hydrochloric acid, as follows:

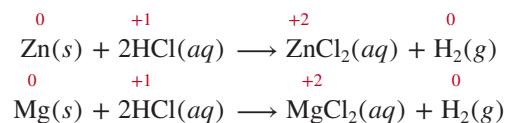


Figure 4.15 shows the reactions between hydrochloric acid (HCl) and iron (Fe), zinc (Zn), and magnesium (Mg). These reactions are used to prepare hydrogen gas in the laboratory.

2. Metal Displacement. A metal in a compound can be displaced by another metal in the elemental state. We have already seen examples of zinc replacing copper ions and copper replacing silver ions (see Figure 4.10). Reversing the roles of the metals would result in no reaction. Thus, copper metal will not displace zinc ions from zinc sulfate, and silver metal will not displace copper ions from copper nitrate.

An easy way to predict whether a metal or hydrogen displacement reaction will actually occur is to refer to an **activity series** (sometimes called the *electrochemical series*), shown in Figure 4.16. An activity series is a convenient summary of the results of many possible displacement reactions similar to the ones already discussed. According to this series, any metal above hydrogen will displace it from water or from an acid, but metals below hydrogen will not react with either water or an acid. In fact, any metal listed in the series will react with any metal (in a compound) below it. For example, Zn is above Cu, so zinc metal will displace copper ions from copper sulfate.

Metal displacement reactions find many applications in metallurgical processes, the goal of which is to separate pure metals from their ores. For example, vanadium is obtained by treating vanadium(V) oxide with metallic calcium:



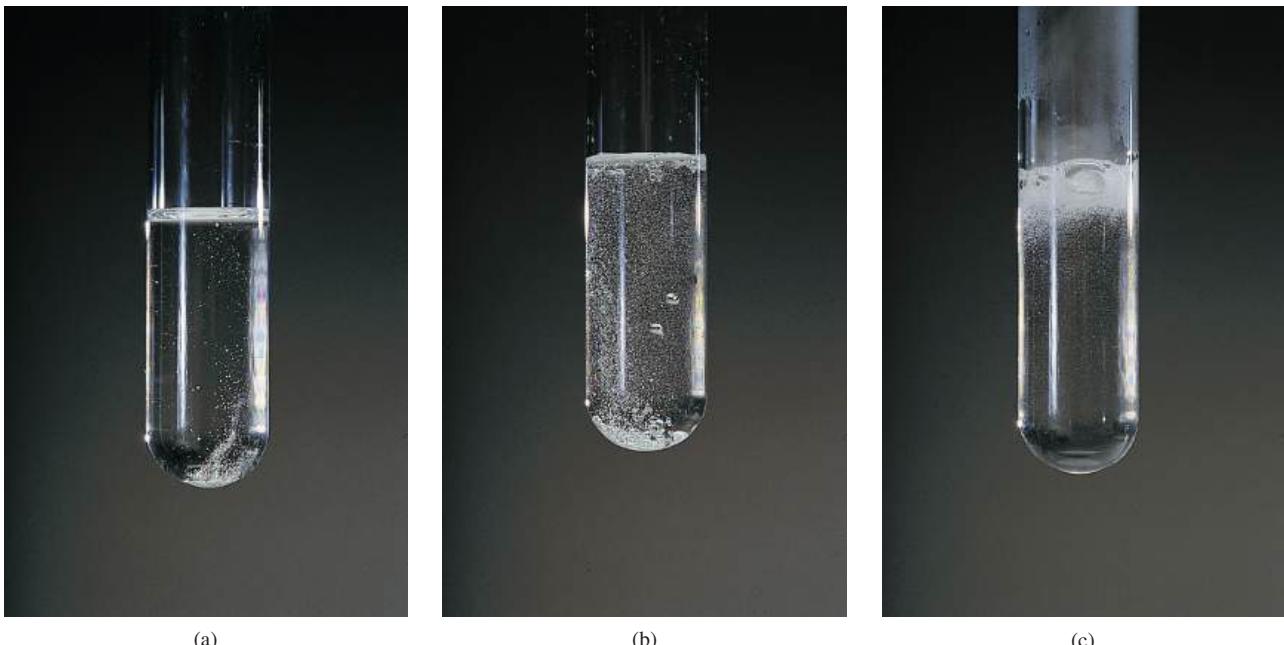


Figure 4.15 Reactions of (a) iron (Fe), (b) zinc (Zn), and (c) magnesium (Mg) with hydrochloric acid to form hydrogen gas and the metal chlorides (FeCl_2 , ZnCl_2 , MgCl_2). The reactivity of these metals is reflected in the rate of hydrogen gas evolution, which is slowest for the least reactive metal, Fe, and fastest for the most reactive metal, Mg.

(a, b, c) ©McGraw-Hill Education/Stephen Frisch

<p>Reducing strength increases</p>	<table border="1"> <tbody> <tr><td>$\text{Li} \rightarrow \text{Li}^+ + e^-$</td><td></td></tr> <tr><td>$\text{K} \rightarrow \text{K}^+ + e^-$</td><td>React with cold water to produce H_2</td></tr> <tr><td>$\text{Ba} \rightarrow \text{Ba}^{2+} + 2e^-$</td><td></td></tr> <tr><td>$\text{Ca} \rightarrow \text{Ca}^{2+} + 2e^-$</td><td></td></tr> <tr><td>$\text{Na} \rightarrow \text{Na}^+ + e^-$</td><td></td></tr> <tr><td>$\text{Mg} \rightarrow \text{Mg}^{2+} + 2e^-$</td><td></td></tr> <tr><td>$\text{Al} \rightarrow \text{Al}^{3+} + 3e^-$</td><td></td></tr> <tr><td>$\text{Zn} \rightarrow \text{Zn}^{2+} + 2e^-$</td><td>React with steam to produce H_2</td></tr> <tr><td>$\text{Cr} \rightarrow \text{Cr}^{3+} + 3e^-$</td><td></td></tr> <tr><td>$\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^-$</td><td></td></tr> <tr><td>$\text{Cd} \rightarrow \text{Cd}^{2+} + 2e^-$</td><td></td></tr> <tr><td>$\text{Co} \rightarrow \text{Co}^{2+} + 2e^-$</td><td></td></tr> <tr><td>$\text{Ni} \rightarrow \text{Ni}^{2+} + 2e^-$</td><td>React with acids to produce H_2</td></tr> <tr><td>$\text{Sn} \rightarrow \text{Sn}^{2+} + 2e^-$</td><td></td></tr> <tr><td>$\text{Pb} \rightarrow \text{Pb}^{2+} + 2e^-$</td><td></td></tr> <tr><td>$\text{H}_2 \rightarrow 2\text{H}^+ + 2e^-$</td><td></td></tr> <tr><td>$\text{Cu} \rightarrow \text{Cu}^{2+} + 2e^-$</td><td></td></tr> <tr><td>$\text{Ag} \rightarrow \text{Ag}^+ + e^-$</td><td></td></tr> <tr><td>$\text{Hg} \rightarrow \text{Hg}^{2+} + 2e^-$</td><td></td></tr> <tr><td>$\text{Pt} \rightarrow \text{Pt}^{2+} + 2e^-$</td><td>Do not react with water or acids to produce H_2</td></tr> <tr><td>$\text{Au} \rightarrow \text{Au}^{3+} + 3e^-$</td><td></td></tr> </tbody> </table>	$\text{Li} \rightarrow \text{Li}^+ + e^-$		$\text{K} \rightarrow \text{K}^+ + e^-$	React with cold water to produce H_2	$\text{Ba} \rightarrow \text{Ba}^{2+} + 2e^-$		$\text{Ca} \rightarrow \text{Ca}^{2+} + 2e^-$		$\text{Na} \rightarrow \text{Na}^+ + e^-$		$\text{Mg} \rightarrow \text{Mg}^{2+} + 2e^-$		$\text{Al} \rightarrow \text{Al}^{3+} + 3e^-$		$\text{Zn} \rightarrow \text{Zn}^{2+} + 2e^-$	React with steam to produce H_2	$\text{Cr} \rightarrow \text{Cr}^{3+} + 3e^-$		$\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^-$		$\text{Cd} \rightarrow \text{Cd}^{2+} + 2e^-$		$\text{Co} \rightarrow \text{Co}^{2+} + 2e^-$		$\text{Ni} \rightarrow \text{Ni}^{2+} + 2e^-$	React with acids to produce H_2	$\text{Sn} \rightarrow \text{Sn}^{2+} + 2e^-$		$\text{Pb} \rightarrow \text{Pb}^{2+} + 2e^-$		$\text{H}_2 \rightarrow 2\text{H}^+ + 2e^-$		$\text{Cu} \rightarrow \text{Cu}^{2+} + 2e^-$		$\text{Ag} \rightarrow \text{Ag}^+ + e^-$		$\text{Hg} \rightarrow \text{Hg}^{2+} + 2e^-$		$\text{Pt} \rightarrow \text{Pt}^{2+} + 2e^-$	Do not react with water or acids to produce H_2	$\text{Au} \rightarrow \text{Au}^{3+} + 3e^-$	
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$\text{Au} \rightarrow \text{Au}^{3+} + 3e^-$																																											

Figure 4.16 The activity series for metals. The metals are arranged according to their ability to displace hydrogen from an acid or water. Li (lithium) is the most reactive metal, and Au (gold) is the least reactive.

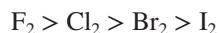
Similarly, titanium is obtained from titanium(IV) chloride according to the reaction



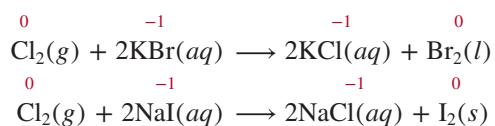
In each case, the metal that acts as the reducing agent lies above the metal that is reduced (that is, Ca is above V and Mg is above Ti) in the activity series. We will see more examples of this type of reaction in Chapter 18.

The halogens

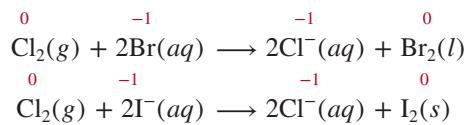
3. Halogen Displacement. Another activity series summarizes the halogens' behavior in halogen displacement reactions:



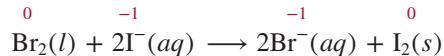
The power of these elements as oxidizing agents decreases as we move down Group 7A from fluorine to iodine, so molecular fluorine can replace chloride, bromide, and iodide ions in solution. In fact, molecular fluorine is so reactive that it also attacks water; thus these reactions cannot be carried out in aqueous solutions. On the other hand, molecular chlorine can displace bromide and iodide ions in aqueous solution. The displacement equations are



The ionic equations are



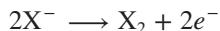
Molecular bromine, in turn, can displace iodide ion in solution:



Reversing the roles of the halogens produces no reaction. Thus, bromine cannot displace chloride ions, and iodine cannot displace bromide and chloride ions.

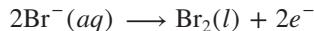
The halogen displacement reactions have a direct industrial application. The halogens as a group are the most reactive of the nonmetallic elements. They are all strong oxidizing agents. As a result, they are found in nature in the combined state (with metals) as halides and never as free elements. Of these four elements, chlorine is by far the most important industrial chemical. In 2010 the amount of chlorine produced in the United States was about 25 billion pounds, making chlorine the tenth-ranking industrial chemical. The annual production of bromine is only one-hundredth that of chlorine, while the amounts of fluorine and iodine produced are even less.

Recovering the halogens from their halides requires an oxidation process, which is represented by



where X denotes a halogen element. Seawater and natural brine (for example, underground water in contact with salt deposits) are rich sources of Cl^- , Br^- , and I^- ions. Minerals such as fluorite (CaF_2) and cryolite (Na_3AlF_6) are used to prepare fluorine. Because fluorine is the strongest oxidizing agent known, there is no way to convert F^- ions to F_2 by chemical means. The only way to carry out the oxidation is by electrolytic means, the details of which will be discussed in Chapter 18. Industrially, chlorine, like fluorine, is produced electrolytically.

Bromine is prepared industrially by oxidizing Br^- ions with chlorine, which is a strong enough oxidizing agent to oxidize Br^- ions but not water:



One of the richest sources of Br⁻ ions is the Dead Sea—about 4000 parts per million (ppm) by mass of all dissolved substances in the Dead Sea is Br. Following the oxidation of Br⁻ ions, bromine is removed from the solution by blowing air over the solution, and the air-bromine mixture is then cooled to condense the bromine (Figure 4.17).

Iodine is also prepared from seawater and natural brine by the oxidation of I^- ions with chlorine. Because Br^- and I^- ions are invariably present in the same source, they are both oxidized by chlorine. However, it is relatively easy to separate Br_2 from I_2 ,



Figure 4.17 The condensation of liquid bromine

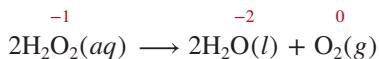
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Bromine is a fuming red liquid.

because iodine is a solid that is sparingly soluble in water. The air-blowing procedure will remove most of the bromine formed but will not affect the iodine present.

Disproportionation Reaction

In this special type of redox reaction, called a ***disproportionation reaction***, an element in one oxidation state is simultaneously oxidized and reduced. One reactant in a disproportionation reaction always contains an element that can have at least three oxidation states. The element itself is in an intermediate oxidation state; that is, both higher and lower oxidation states exist for that element in the products. The decomposition of hydrogen peroxide is an example of a disproportionation reaction:



Here the oxidation number of oxygen in the reactant (-1) both increases to zero in O_2 and decreases to -2 in H_2O . Another example is the reaction between molecular chlorine and $NaOH$ solution:



This reaction describes the formation of household bleaching agents, for it is the hypochlorite ion (ClO^-) that oxidizes the color-bearing substances in stains, converting them to colorless compounds.

Finally, it is interesting to compare redox reactions and acid-base reactions. They are analogous in that acid-base reactions involve the transfer of protons while redox reactions involve the transfer of electrons. However, while acid-base reactions are quite easy to recognize (because they always involve an acid and a base), there is no simple procedure for identifying a redox process. The only sure way is to compare the oxidation numbers of all the elements in the reactants and products. Any change in oxidation number guarantees that the reaction is redox in nature.

The classification of different types of redox reactions is illustrated in Example 4.6.

Example 4.6

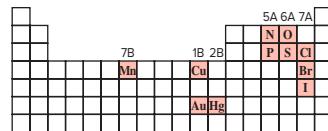
Classify the following redox reactions and indicate changes in the oxidation numbers of the elements:

- (a) $2\text{N}_2\text{O}(g) \longrightarrow 2\text{N}_2(g) + \text{O}_2(g)$
 (b) $6\text{Li}(s) + \text{N}_2(g) \longrightarrow 2\text{Li}_3\text{N}(s)$
 (c) $\text{Ni}(s) + \text{Pb}(\text{NO}_3)_2(aq) \longrightarrow \text{Pb}(s) + \text{Ni}(\text{NO}_3)_2(aq)$
 (d) $2\text{NO}_2(g) + \text{H}_2\text{O}(l) \longrightarrow \text{HNO}_2(aq) + \text{HNO}_3(aq)$

Strategy Review the definitions of combination reactions, decomposition reactions, displacement reactions, and disproportionation reactions.

Solution

- (a) This is a decomposition reaction because one reactant is converted to two different products. The oxidation number of N changes from +1 to 0, while that of O changes from -2 to 0.
 - (b) This is a combination reaction (two reactants form a single product). The oxidation number of Li changes from 0 to +1 while that of N changes from 0 to -3.
 - (c) This is a metal displacement reaction. The Ni metal replaces (reduces) the Pb^{2+} ion. The oxidation number of Ni increases from 0 to +2 while that of Pb decreases from +2 to 0.
 - (d) The oxidation number of N is +4 in NO_2 and it is +3 in HNO_2 and +5 in HNO_3 . Because the oxidation number of the *same* element both increases and decreases, this is a disproportionation reaction.



Elements that are most likely to undergo disproportionation reactions.

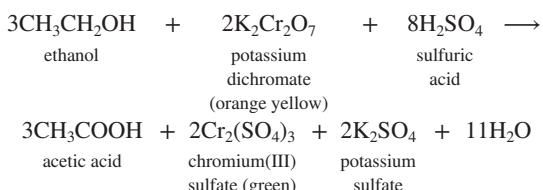
Note that the oxidation number of H remains unchanged at +1.

CHEMISTRY *in Action*

Breathalyzer

Every year in the United States about 25,000 people are killed and 500,000 more are injured as a result of drunk driving. In spite of efforts to educate the public about the dangers of driving while intoxicated and stiffer penalties for drunk driving offenses, law enforcement agencies still have to devote a great deal of work to removing drunk drivers from America's roads.

The police often use a device called a breathalyzer to test drivers suspected of being drunk. The chemical basis of this device is a redox reaction. A sample of the driver's breath is drawn into the breathalyzer, where it is treated with an acidic solution of potassium dichromate. The alcohol (ethanol) in the breath is converted to acetic acid as shown in the following equation:

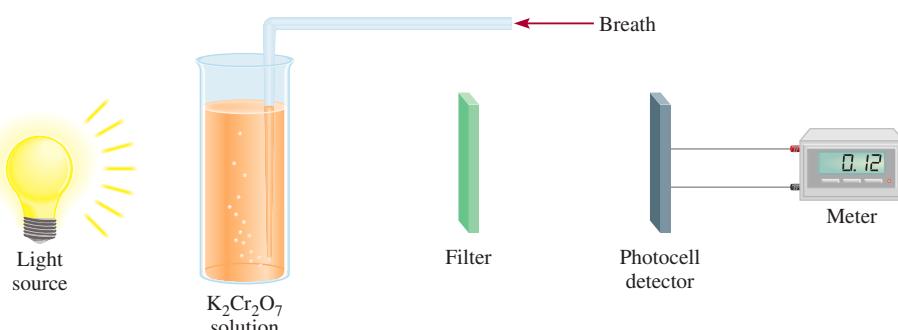


In this reaction, the ethanol is oxidized to acetic acid and the chromium(VI) in the orange-yellow dichromate ion is reduced



A driver being tested for blood alcohol content with a handheld breathalyzer.
©Jim Varney/Science Source

to the green chromium(III) ion (see Figure 4.22). The driver's blood alcohol level can be determined readily by measuring the degree of this color change (read from a calibrated meter on the instrument). The current legal limit of blood alcohol content is 0.08 percent by mass. Anything higher constitutes intoxication.



Schematic diagram of a breathalyzer. The alcohol in the driver's breath is reacted with a potassium dichromate solution. The change in the absorption of light due to the formation of chromium(III) sulfate is registered by the detector and shown on a meter, which directly displays the alcohol content in blood. The filter selects only one wavelength of light for measurement.

Practice Exercise

Identify the following redox reactions by type:

- (a) $\text{Fe} + \text{H}_2\text{SO}_4 \longrightarrow \text{FeSO}_4 + \text{H}_2$
- (b) $\text{S} + 3\text{F}_2 \longrightarrow \text{SF}_6$
- (c) $2\text{CuCl} \longrightarrow \text{Cu} + \text{CuCl}_2$
- (d) $2\text{Ag} + \text{PtCl}_2 \longrightarrow 2\text{AgCl} + \text{Pt}$

Similar problems: 4.55, 4.56.

The Chemistry in Action essay, "Breathalyzer," describes how law enforcement makes use of a redox reaction to apprehend drunk drivers.

Review of Concepts & Facts

- 4.4.1** Which of the following combination reactions is not a redox reaction?
- $2\text{Mg}(s) + \text{O}_2(g) \longrightarrow 2\text{MgO}(s)$
 - $\text{H}_2(g) + \text{F}_2(g) \longrightarrow 2\text{HF}(g)$
 - $\text{NH}_3(g) + \text{HCl}(g) \longrightarrow \text{NH}_4\text{Cl}(s)$
 - $2\text{Na}(s) + \text{S}(s) \longrightarrow \text{Na}_2\text{S}(s)$
- 4.4.2** Determine the oxidation number of the underlined atoms in the following compounds and ions: (a) MnO₂, (b) N₂F₄, (c) CrO₂⁻.

4.5 Concentration of Solutions

To study solution stoichiometry, we must know how much of the reactants are present in a solution and also how to control the amounts of reactants used to bring about a reaction in aqueous solution.

The **concentration of a solution** is *the amount of solute present in a given amount of solvent, or a given amount of solution*. (For this discussion, we will assume the solute is a liquid or a solid and the solvent is a liquid.) The concentration of a solution can be expressed in many different ways, as we will see in Chapter 12. Here we will consider one of the most commonly used units in chemistry, **molarity (M)**, or **molar concentration**, which is *the number of moles of solute per liter of solution*. Molarity is defined as

$$\text{molarity} = \frac{\text{moles of solute}}{\text{liters of solution}} \quad (4.1)$$

Equation (4.1) can also be expressed algebraically as

$$M = \frac{n}{V} \quad (4.2)$$

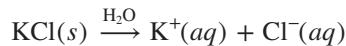
where n denotes the number of moles of solute and V is the volume of the solution in liters.

A 1.46 molar glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) solution, written as $1.46\text{ M C}_6\text{H}_{12}\text{O}_6$, contains 1.46 moles of the solute ($\text{C}_6\text{H}_{12}\text{O}_6$) in 1 L of the solution. Of course, we do not always work with solution volumes of 1 L. Thus, a 500-mL solution containing 0.730 mole of $\text{C}_6\text{H}_{12}\text{O}_6$ also has a concentration of 1.46 M:

$$\text{molarity} = \frac{0.730 \text{ mol C}_6\text{H}_{12}\text{O}_6}{500 \text{ mL soln}} \times \frac{1000 \text{ mL soln}}{1 \text{ L soln}} = 1.46 \text{ M C}_6\text{H}_{12}\text{O}_6$$

Note that concentration, like density, is an intensive property, so its value does not depend on how much of the solution is present.

It is important to keep in mind that molarity refers only to the amount of solute originally dissolved in water and does not take into account any subsequent processes, such as the dissociation of a salt or the ionization of an acid. Consider what happens when a sample of potassium chloride (KCl) is dissolved in enough water to make a 1 M solution:



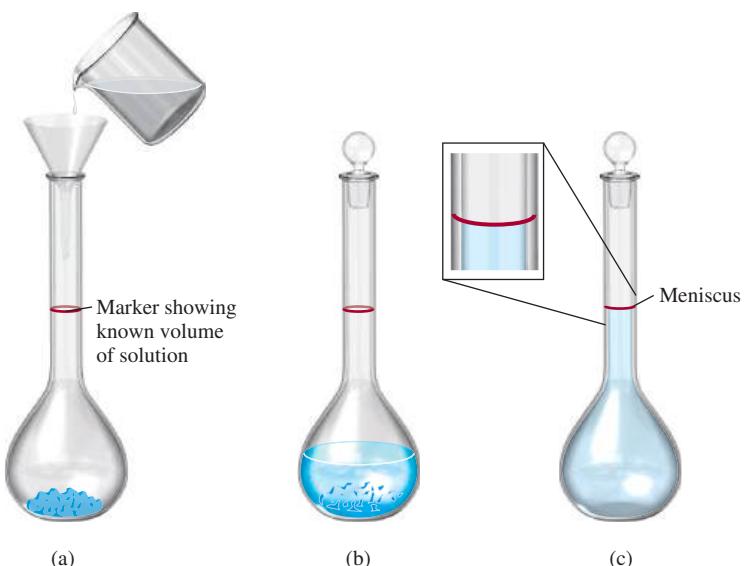
Because KCl is a strong electrolyte, it undergoes complete dissociation in solution. Thus, a 1 M KCl solution contains 1 mole of K^+ ions and 1 mole of Cl^- ions, and no KCl units are present. The concentrations of the ions can be expressed as $[\text{K}^+] = 1\text{ M}$ and $[\text{Cl}^-] = 1\text{ M}$, where the square brackets [] indicate that the concentration is expressed in molarity. Similarly, in a 1 M barium nitrate $[\text{Ba}(\text{NO}_3)_2]$ solution



we have $[\text{Ba}^{2+}] = 1\text{ M}$ and $[\text{NO}_3^-] = 2\text{ M}$ and no $\text{Ba}(\text{NO}_3)_2$ units at all.

Keep in mind that volume (V) is liters of solution, not liters of solvent. Also, the molarity of a solution depends on temperature.

Figure 4.18 Preparing a solution of known molarity. (a) A known amount of a solid solute is transferred into the volumetric flask; then water is added through a funnel. (b) The solid is slowly dissolved by gently swirling the flask. (c) After the solid has completely dissolved, more water is added to bring the level of solution to the mark. Knowing the volume of the solution and the amount of solute dissolved in it, we can calculate the molarity of the prepared solution.



The procedure for preparing a solution of known molarity is as follows. First, the solute is accurately weighed and transferred to a volumetric flask through a funnel (Figure 4.18). Next, water is added to the flask, which is carefully swirled to dissolve the solid. After *all* the solid has dissolved, more water is added slowly to bring the level of solution exactly to the volume mark. Knowing the volume of the solution in the flask and the quantity of compound (the number of moles) dissolved, we can calculate the molarity of the solution using Equation (4.1). Note that this procedure does not require knowing the amount of water added, as long as the volume of the final solution is known.

Examples 4.7 and 4.8 illustrate the applications of Equations (4.1) and (4.2).



A $\text{K}_2\text{Cr}_2\text{O}_7$ solution.
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Example 4.7

How many grams of potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) are required to prepare a 250-mL solution whose concentration is 2.16 M?

Strategy How many moles of $\text{K}_2\text{Cr}_2\text{O}_7$ does a 1-L (or 1000 mL) 2.16 M $\text{K}_2\text{Cr}_2\text{O}_7$ solution contain? A 250-mL solution? How would you convert moles to grams?

Solution The first step is to determine the number of moles of $\text{K}_2\text{Cr}_2\text{O}_7$ in 250 mL or 0.250 L of a 2.16 M solution. Rearranging Equation (4.1) gives

$$\text{moles of solute} = \text{molarity} \times \text{L soln}$$

Thus,

$$\begin{aligned}\text{moles of } \text{K}_2\text{Cr}_2\text{O}_7 &= \frac{2.16 \text{ mol } \text{K}_2\text{Cr}_2\text{O}_7}{1 \text{ L soln}} \times 0.25 \text{ L soln} \\ &= 0.540 \text{ mol } \text{K}_2\text{Cr}_2\text{O}_7\end{aligned}$$

The molar mass of $\text{K}_2\text{Cr}_2\text{O}_7$ is 294.2 g, so we write

$$\begin{aligned}\text{grams of } \text{K}_2\text{Cr}_2\text{O}_7 \text{ needed} &= 0.540 \text{ mol } \text{K}_2\text{Cr}_2\text{O}_7 \times \frac{294.2 \text{ g } \text{K}_2\text{Cr}_2\text{O}_7}{1 \text{ mol } \text{K}_2\text{Cr}_2\text{O}_7} \\ &= 159 \text{ g } \text{K}_2\text{Cr}_2\text{O}_7\end{aligned}$$

(Continued)

Check As a ball-park estimate, the mass should be given by [molarity (mol/L) \times volume (L) \times molar mass (g/mol)] or [2 mol/L \times 0.25 L \times 300 g/mol] = 150 g. So the answer is reasonable.

Practice Exercise What is the molarity of an 85.0-mL ethanol (C_2H_5OH) solution containing 1.77 g of ethanol?

Similar problems: 4.65, 4.68.

Example 4.8

A chemist needs to add 3.81 g of glucose to a reaction mixture. Calculate the volume in milliliters of a 2.53 M glucose solution she should use for the addition.

Strategy We must first determine the number of moles contained in 3.81 g of glucose and then use Equation (4.2) to calculate the volume.

Solution From the molar mass of glucose, we write

$$3.81 \text{ g } C_6H_{12}O_6 \times \frac{1 \text{ mol } C_6H_{12}O_6}{180.2 \text{ g } C_6H_{12}O_6} = 2.114 \times 10^{-2} \text{ mol } C_6H_{12}O_6$$

Next, we calculate the volume of the solution that contains 2.114×10^{-2} mole of the solute. Rearranging Equation (4.2) gives

$$\begin{aligned} V &= \frac{n}{M} \\ &= \frac{2.114 \times 10^{-2} \text{ mol } C_6H_{12}O_6}{2.53 \text{ mol } C_6H_{12}O_6/\text{L soln}} \times \frac{1000 \text{ mL soln}}{1 \text{ L soln}} \\ &= 8.36 \text{ mL soln} \end{aligned}$$

Note that we have carried an additional digit past the number of significant figures for the intermediate step.

Check One liter of the solution contains 2.53 moles of $C_6H_{12}O_6$. Therefore, the number of moles in 8.36 mL or 8.36×10^{-3} L is $(2.53 \text{ mol} \times 8.36 \times 10^{-3})$ or 2.12×10^{-2} mol. The small difference is due to the different ways of rounding off.

Practice Exercise What volume (in milliliters) of a 0.315 M NaOH solution contains 6.22 g of NaOH?

Similar problem: 4.67.

Dilution of Solutions

Concentrated solutions are often stored in the laboratory stockroom for use as needed. Frequently we dilute these “stock” solutions before working with them. **Dilution** is the procedure for preparing a less concentrated solution from a more concentrated one.

Suppose that we want to prepare 1 L of a 0.400 M $KMnO_4$ solution from a solution of 1.00 M $KMnO_4$. For this purpose we need 0.400 mole of $KMnO_4$. Because there is 1.00 mole of $KMnO_4$ in 1 L of a 1.00 M $KMnO_4$ solution, there is 0.400 mole of $KMnO_4$ in 0.400 L of the same solution:

$$\frac{1.00 \text{ mol}}{1 \text{ L soln}} = \frac{0.400 \text{ mol}}{0.400 \text{ L soln}}$$

Therefore, we must withdraw 400 mL from the 1.00 M $KMnO_4$ solution and dilute it to 1000 mL by adding water (in a 1-L volumetric flask). This method gives us 1 L of the desired solution of 0.400 M $KMnO_4$.

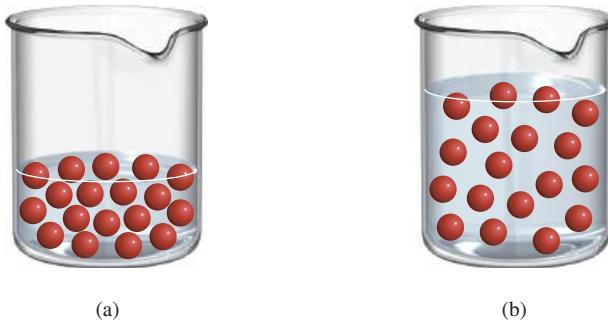
In carrying out a dilution process, it is useful to remember that adding more solvent to a given amount of the stock solution changes (decreases) the concentration of the



Two $KMnO_4$ solutions of different concentrations.

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Figure 4.19 The dilution of a more concentrated solution (a) to a less concentrated one (b) does not change the total number of solute particles (18).



solution without changing the number of moles of solute present in the solution (Figure 4.19). In other words,

$$\text{moles of solute before dilution} = \text{moles of solute after dilution}$$

Molarity is defined as moles of solute in 1 liter of solution, so the number of moles of solute is given by [see Equation (4.2)]

$$\underbrace{\frac{\text{moles of solute}}{\text{liters of soln}}}_{M} \times \underbrace{\text{volume of soln (in liters)}}_V = \underbrace{\text{moles of solute}}_n$$

or

$$MV = n$$

Because all the solute comes from the original stock solution, we can conclude that n remains the same; that is,

$$\frac{M_i V_i}{\text{moles of solute before dilution}} = \frac{M_f V_f}{\text{moles of solute after dilution}} \quad (4.3)$$

Student Hot Spot

Student data indicate you may struggle with dilution calculations. Access your eBook for additional Learning Resources on this topic.

where M_i and M_f are the initial and final concentrations of the solution in molarity and V_i and V_f are the initial and final volumes of the solution, respectively. Of course, the units of V_i and V_f must be the same (mL or L) for the calculation to work. To check the reasonableness of your results, be sure that $M_i > M_f$ and $V_f > V_i$.

We apply Equation (4.3) in Example 4.9.

Example 4.9

Describe how you would prepare 5.00×10^2 mL of a 1.75 M H_2SO_4 solution, starting with an 8.61 M stock solution of H_2SO_4 .

Strategy Because the concentration of the final solution is less than that of the original one, this is a dilution process. Keep in mind that in dilution, the concentration of the solution decreases but the number of moles of the solute remains the same.

Solution We prepare for the calculation by tabulating our data:

$$\begin{array}{ll} M_i = 8.61\text{ M} & M_f = 1.75\text{ M} \\ V_i = ? & V_f = 5.00 \times 10^2\text{ mL} \end{array}$$

Substituting in Equation (4.3),

$$\begin{aligned} (8.61\text{ M})(V_i) &= (1.75\text{ M})(5.00 \times 10^2\text{ mL}) \\ V_i &= \frac{(1.75\text{ M})(5.00 \times 10^2\text{ mL})}{8.61\text{ M}} \\ &= 102\text{ mL} \end{aligned}$$

(Continued)

Thus, we must dilute 102 mL of the 8.61 M H₂SO₄ solution with sufficient water to give a final volume of 5.00 × 10² mL in a 500-mL volumetric flask to obtain the desired concentration.

Check The initial volume is less than the final volume, so the answer is reasonable.

Practice Exercise How would you prepare 2.00 × 10² mL of a 0.866 M NaOH solution, starting with a 5.07 M stock solution?

Similar problems: 4.75, 4.76.

Now that we have discussed the concentration and dilution of solutions, we can examine the quantitative aspects of reactions in aqueous solution, or *solution stoichiometry*. Sections 4.6, 4.7, and 4.8 focus on two techniques for studying solution stoichiometry: gravimetric analysis and titration. These techniques are important tools of **quantitative analysis**, which is *the determination of the amount or concentration of a substance in a sample*.

Review of Concepts & Facts

- 4.5.1 What is the final concentration of a 0.6 M NaCl solution if its volume is doubled and the number of moles of solute is tripled?
- 4.5.2 How many moles of LiOH are present in 27.5 mL of 0.250 M LiOH solution?
- 4.5.3 What mass of Ca(NO₃)₂ in grams is needed to prepare 375 mL of a 1.25 M solution?

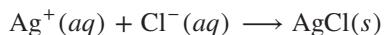
4.6 Gravimetric Analysis

Gravimetric analysis is an analytical technique based on the measurement of mass. One type of gravimetric analysis experiment involves the formation, isolation, and mass determination of a precipitate. Generally, this procedure is applied to ionic compounds. First, a sample substance of unknown composition is dissolved in water and allowed to react with another substance to form a precipitate. Then the precipitate is filtered off, dried, and weighed. Knowing the mass and chemical formula of the precipitate formed, we can calculate the mass of a particular chemical component (that is, the anion or cation) of the original sample. Finally, from the mass of the component and the mass of the original sample, we can determine the percent composition by mass of the component in the original compound.

A reaction that is often studied in gravimetric analysis, because the reactants can be obtained in pure form, is



The net ionic equation is



The precipitate is silver chloride (see Table 4.2). As an example, let us say that we wanted to determine *experimentally* the percent by mass of Cl in NaCl. First, we would accurately weigh out a sample of NaCl and dissolve it in water. Next, we would add enough AgNO₃ solution to the NaCl solution to cause the precipitation of all the Cl⁻ ions present in solution as AgCl. In this procedure, NaCl is the limiting reactant and AgNO₃ the excess reactant. The AgCl precipitate is separated from the solution by filtration, dried, and weighed. From the measured mass of AgCl, we can calculate the mass of Cl using the percent by mass of Cl in AgCl. Because this same amount of Cl was present in the original NaCl sample, we can calculate the percent by mass of Cl in NaCl. Figure 4.20 shows how this procedure is performed.

This procedure would enable us to determine the purity of the NaCl sample.

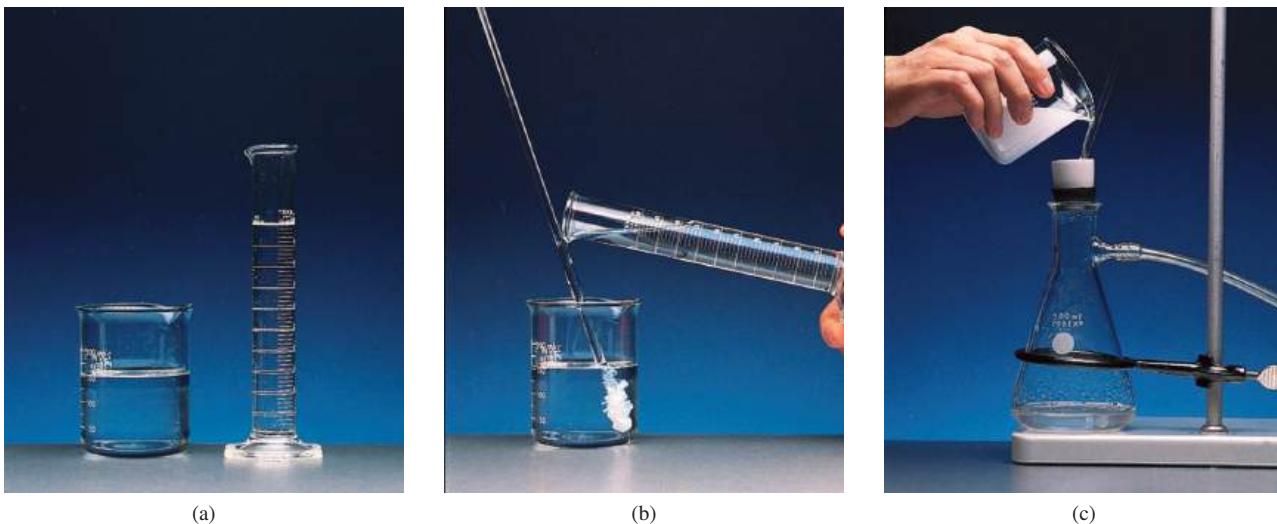


Figure 4.20 Basic steps for gravimetric analysis. (a) A solution containing a known amount of NaCl in a beaker. (b) The precipitation of AgCl upon the addition of AgNO₃ solution from a measuring cylinder. In this reaction, AgNO₃ is the excess reactant and NaCl is the limiting reactant. (c) The solution containing the AgCl precipitate is filtered through a preweighed sintered-disk crucible, which allows the liquid (but not the precipitate) to pass through. The crucible is then removed from the apparatus, dried in an oven, and weighed again. The difference between this mass and that of the empty crucible gives the mass of the AgCl precipitate.

(a, b, c): ©McGraw-Hill Education/Ken Karp

Gravimetric analysis is a highly accurate technique, because the mass of a sample can be measured accurately. However, this procedure is applicable only to reactions that go to completion, or have nearly 100 percent yield. Thus, if AgCl were slightly soluble instead of being insoluble, it would not be possible to remove all the Cl⁻ ions from the NaCl solution and the subsequent calculation would be in error.

Example 4.10 shows the calculations involved in a gravimetric experiment.

Example 4.10

A 0.5662-g sample of an ionic compound containing chloride ions and an unknown metal is dissolved in water and treated with an excess of AgNO₃. If 1.0882 g of AgCl precipitate forms, what is the percent by mass of Cl in the original compound?

Strategy We are asked to calculate the percent by mass of Cl in the unknown sample, which is

$$\% \text{Cl} = \frac{\text{mass of Cl}}{0.5662 \text{ g sample}} \times 100\%$$

The only source of Cl⁻ ions is the original compound. These chloride ions eventually end up in the AgCl precipitate. Can we calculate the mass of the Cl⁻ ions if we know the percent by mass of Cl in AgCl?

Solution The molar masses of Cl and AgCl are 35.45 g and 143.4 g, respectively. Therefore, the percent by mass of Cl in AgCl is given by

$$\begin{aligned}\% \text{Cl} &= \frac{35.45 \text{ g Cl}}{143.4 \text{ g AgCl}} \times 100\% \\ &= 24.72\%\end{aligned}$$

Next, we calculate the mass of Cl in 1.0882 g of AgCl. To do so we convert 24.72 percent to 0.2472 and write

$$\begin{aligned}\text{mass of Cl} &= 0.2472 \times 1.0882 \text{ g} \\ &= 0.2690 \text{ g}\end{aligned}$$

(Continued)

Because the original compound also contained this amount of Cl^- ions, the percent by mass of Cl in the compound is

$$\begin{aligned}\% \text{Cl} &= \frac{0.2690 \text{ g}}{0.5662 \text{ g}} \times 100\% \\ &= 47.51\%\end{aligned}$$

Check AgCl is about 25 percent chloride by mass, so the roughly 1 g of AgCl precipitate that formed corresponds to about 0.25 g of chloride, which is a little less than half of the mass of the original sample. Therefore, the calculated percent chloride of 47.51 percent is reasonable.

Practice Exercise A sample of 0.3220 g of an ionic compound containing the bromide ion (Br^-) is dissolved in water and treated with an excess of AgNO_3 . If the mass of the AgBr precipitate that forms is 0.6964 g, what is the percent by mass of Br in the original compound?

Similar problem: 4.82.

Note that gravimetric analysis does not establish the whole identity of the unknown. Thus, in Example 4.10 we still do not know what the cation is. However, knowing the percent by mass of Cl greatly helps us to narrow the possibilities. Because no two compounds containing the same anion (or cation) have the same percent composition by mass, comparison of the percent by mass obtained from gravimetric analysis with that calculated from a series of known compounds would reveal the identity of the unknown.

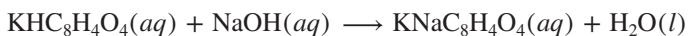
Review of Concepts & Facts

- 4.6.1** Calculate the mass of AgBr formed if a solution containing 6.00 g of KBr is treated with an excess of AgNO_3 .

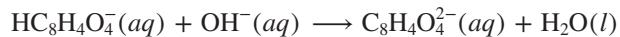
4.7 Acid-Base Titrations

Quantitative studies of acid-base neutralization reactions are most conveniently carried out using a technique known as titration. In *titration*, a solution of accurately known concentration, called a **standard solution**, is added gradually to another solution of unknown concentration, until the chemical reaction between the two solutions is complete. If we know the volumes of the standard and unknown solutions used in the titration, along with the concentration of the standard solution, we can calculate the concentration of the unknown solution.

Sodium hydroxide is one of the bases commonly used in the laboratory. However, it is difficult to obtain solid sodium hydroxide in a pure form because it has a tendency to absorb water from air, and its solution reacts with carbon dioxide. For these reasons, a solution of sodium hydroxide must be *standardized* before it can be used in accurate analytical work. We can standardize the sodium hydroxide solution by titrating it against an acid solution of accurately known concentration. The acid often chosen for this task is a monoprotic, weak acid called potassium hydrogen phthalate (KHP), for which the molecular formula is $\text{KHC}_8\text{H}_4\text{O}_4$ (molar mass = 204.2 g). KHP is a white, soluble solid that is commercially available in highly pure form. The reaction between KHP and sodium hydroxide is



and the net ionic equation is



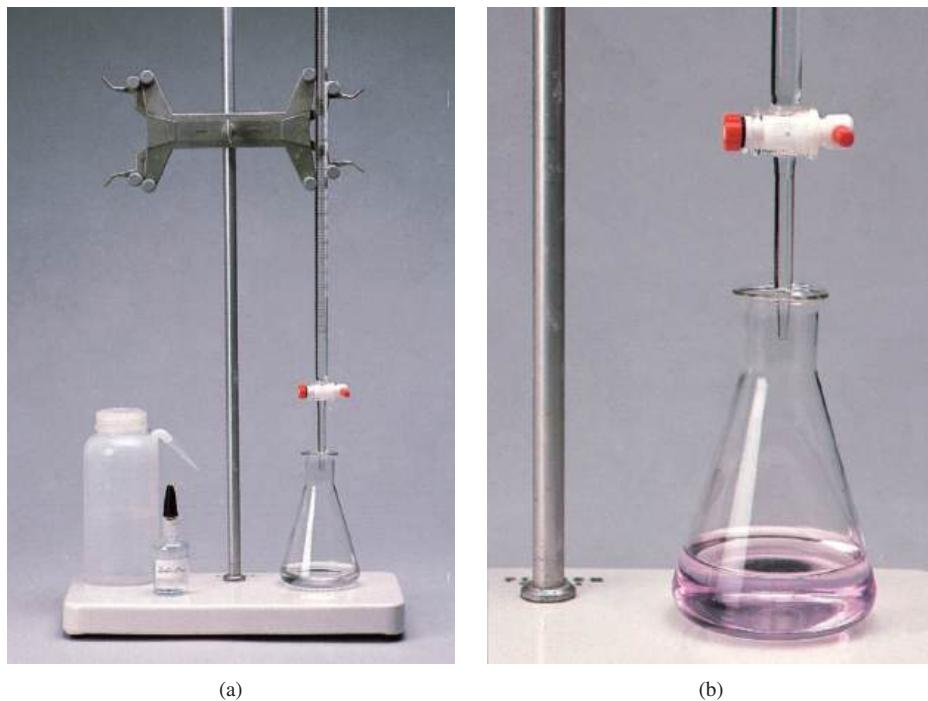
The procedure for the titration is shown in Figure 4.21. First, a known amount of KHP is transferred to an Erlenmeyer flask and some distilled water is added to make up a solution. Next, NaOH solution is carefully added to the KHP solution from a buret



Potassium hydrogen phthalate (KHP).
©McGraw-Hill Education/Ken Karp

Figure 4.21 (a) Apparatus for acid-base titration. A NaOH solution is added from the buret to a KHP solution in an Erlenmeyer flask. (b) A reddish-pink color appears when the equivalence point is reached. The color here has been intensified for visual display.

(a and b): ©McGraw-Hill Education/Ken Karp



until we reach the **equivalence point**, that is, *the point at which the acid has completely reacted with or been neutralized by the base*. The equivalence point is usually signaled by a sharp change in the color of an indicator in the acid solution. In acid-base titrations, **indicators** are substances that have distinctly different colors in acidic and basic media. One commonly used indicator is phenolphthalein, which is colorless in acidic and neutral solutions but reddish pink in basic solutions. At the equivalence point, all the KHP present has been neutralized by the added NaOH and the solution is still colorless. However, if we add just one more drop of NaOH solution from the buret, the solution will immediately turn pink because the solution is now basic. Example 4.11 illustrates such a titration.

Example 4.11

In a titration experiment, a student finds that 23.48 mL of a NaOH solution are needed to neutralize 0.5468 g of KHP. What is the concentration (in molarity) of the NaOH solution?

Strategy We want to determine the molarity of the NaOH solution. What is the definition of molarity?

$$\text{molarity of NaOH} = \frac{\text{mol NaOH}}{\text{L soln}}$$

want to calculate

need to find

given

The volume of NaOH solution is given in the problem. Therefore, we need to find the number of moles of NaOH to solve for molarity. From the preceding equation for the reaction between KHP and NaOH shown in the text we see that 1 mole of KHP neutralizes 1 mole of NaOH. How many moles of KHP are contained in 0.5468 g of KHP?

Solution First we calculate the number of moles of KHP consumed in the titration:

$$\begin{aligned}\text{moles of KHP} &= 0.5468 \cancel{\text{g KHP}} \times \frac{1 \text{ mol KHP}}{204.2 \cancel{\text{g KHP}}} \\ &= 2.678 \times 10^{-3} \text{ mol KHP}\end{aligned}$$

(Continued)

Recall that KHP is $\text{KHC}_8\text{H}_4\text{O}_4$.

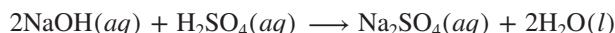
Because $1 \text{ mol KHP} \approx 1 \text{ mol NaOH}$, there must be 2.678×10^{-3} mole of NaOH in 23.48 mL of NaOH solution. Finally, we calculate the number of moles of NaOH in 1 L of the solution or the molarity as follows:

$$\begin{aligned}\text{molarity of NaOH soln} &= \frac{2.678 \times 10^{-3} \text{ mol NaOH}}{23.48 \text{ mL soln}} \times \frac{1000 \text{ mL soln}}{1 \text{ L soln}} \\ &= 0.1141 \text{ mol NaOH/L soln} = 0.1141 \text{ M}\end{aligned}$$

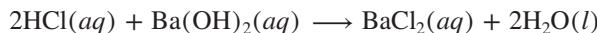
Practice Exercise How many grams of KHP are needed to neutralize 18.64 mL of a 0.1004 M NaOH solution?

Similar problems: 4.89, 4.90.

The neutralization reaction between NaOH and KHP is one of the simplest types of acid-base neutralization known. Suppose, though, that instead of KHP, we wanted to use a diprotic acid such as H_2SO_4 for the titration. The reaction is represented by

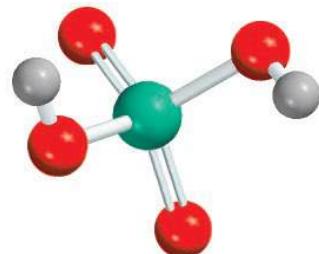


Because 2 mol NaOH \approx 1 mol H_2SO_4 , we need twice as much NaOH to react completely with a H_2SO_4 solution of the *same* molar concentration and volume as a monoprotic acid like HCl. On the other hand, we would need twice the amount of HCl to neutralize a $\text{Ba}(\text{OH})_2$ solution compared to a NaOH solution having the same concentration and volume because 1 mole of $\text{Ba}(\text{OH})_2$ yields 2 moles of OH^- ions:



In calculations involving acid-base titrations, regardless of the acid or base that takes place in the reaction, keep in mind that the total number of moles of H^+ ions that have reacted at the equivalence point must be equal to the total number of OH^- ions that have reacted.

Example 4.12 shows the titration of a NaOH solution with a diprotic acid.



H_2SO_4 has two ionizable protons.

Student Hot Spot

Student data indicate you may struggle with titration calculations. Access your eBook for additional Learning Resources on this topic.

Example 4.12

The sodium hydroxide solution standardized in Example 4.11 is used to titrate 25.00 mL of a sulfuric acid solution. The titration requires 43.79 mL of the 0.1172 M NaOH solution to completely neutralize the acid. What is the concentration of the H_2SO_4 solution?

Strategy We want to calculate the concentration of the H_2SO_4 solution. Starting with the volume of NaOH solution required to neutralize the acid, we calculate the moles of NaOH.

$$\text{L soln} \times \frac{\text{mol NaOH}}{\text{L soln}} = \text{mol NaOH}$$

want to find
 ↑
 given
 ↑
 measured

From the equation for the neutralization reaction just shown, we see that 2 moles of NaOH neutralize 1 mole of H_2SO_4 . How many moles of NaOH are contained in 43.79 mL of a 0.1172 M NaOH solution? How many moles of H_2SO_4 would this quantity of NaOH neutralize? What would be the concentration of the H_2SO_4 solution?

Solution First, we calculate the number of moles of NaOH contained in 43.79 mL of solution:

$$43.79 \text{ mL} \times \frac{1 \text{ L soln}}{1000 \text{ mL soln}} \times \frac{0.1172 \text{ mol NaOH}}{1 \text{ L soln}} = 5.132 \times 10^{-3} \text{ mol NaOH}$$

(Continued)

From the stoichiometry we see that 1 mol H₂SO₄ ≈ 2 mol NaOH. Therefore, the number of moles of H₂SO₄ reacted must be

$$5.132 \times 10^{-3} \text{ mol NaOH} \times \frac{1 \text{ mol H}_2\text{SO}_4}{2 \text{ mol NaOH}} = 2.566 \times 10^{-3} \text{ mol H}_2\text{SO}_4$$

From the definition of molarity [see Equation (4.1)], we have

$$\text{molarity} = \frac{\text{moles of solute}}{\text{liters of soln}}$$

So the molarity of the H₂SO₄ solution is

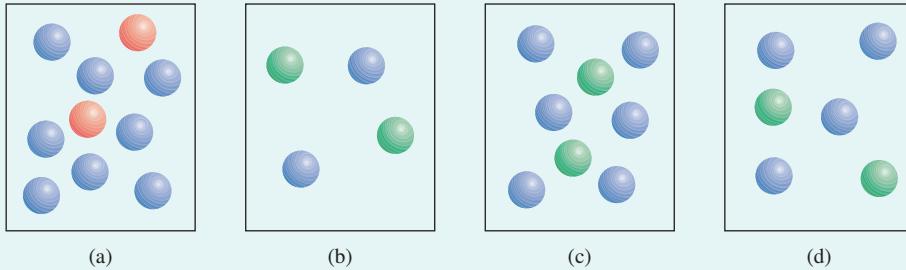
$$\frac{2.566 \times 10^{-3} \text{ mol H}_2\text{SO}_4}{25 \text{ mL} \times (1 \text{ L}/1000 \text{ mL})} = 0.1026 \text{ M H}_2\text{SO}_4$$

Practice Exercise If 60.2 mL of 0.427 M KOH solution are required to neutralize 10.1 mL of H₂SO₄ solution, what is the concentration of the H₂SO₄ solution in molarity?

Similar problem: 4.91(b), (c).

Review of Concepts & Facts

- 4.7.1** A NaOH solution is initially mixed with an acid solution shown in (a). Which of the diagrams (b)–(d) corresponds to one of the following acids: HCl, H₂SO₄, H₃PO₄? Color codes: blue spheres (OH⁻ ions); red spheres (acid molecules); green spheres (anions of the acids). Assume all the acid-base neutralization reactions go to completion.



- 4.7.2** What volume of a 0.215 M HNO₃ solution is required to neutralize 25.0 mL of 0.370 M NaOH?

4.8 Redox Titrations

As mentioned earlier, redox reactions involve the transfer of electrons, and acid-base reactions involve the transfer of protons. Just as an acid can be titrated against a base, we can titrate an oxidizing agent against a reducing agent, using a similar procedure. We can, for example, carefully add a solution containing an oxidizing agent to a solution containing a reducing agent. The *equivalence point* is reached when the reducing agent is completely oxidized by the oxidizing agent.

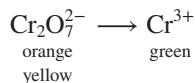
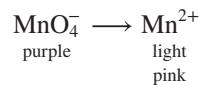
Like acid-base titrations, redox titrations normally require an indicator that clearly changes color. In the presence of large amounts of reducing agent, the color of the indicator is characteristic of its reduced form. The indicator assumes the color of its oxidized form when it is present in an oxidizing medium. At or near the equivalence point, a sharp change in the indicator's color will occur as it changes from one form to the other, so the equivalence point can be readily identified.

There are not as many redox indicators as there are acid-base indicators.



Figure 4.22 Left to right:
Solutions containing the MnO_4^- ,
 Mn^{2+} , $Cr_2O_7^{2-}$, and Cr^{3+} ions.
©McGraw-Hill Education/Ken Karp

Two common oxidizing agents are potassium permanganate (KMnO_4) and potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$). As Figure 4.22 shows, the colors of the permanganate and dichromate anions are distinctly different from those of the reduced species:



Thus, these oxidizing agents can themselves be used as an *internal* indicator in a redox titration because they have distinctly different colors in the oxidized and reduced forms.

Redox titrations require the same type of calculations (based on the mole method) as acid-base neutralizations. The difference is that the equations and the stoichiometry tend to be more complex for redox reactions. Example 4.13 describes a redox titration.

Example 4.13

A 16.42-mL volume of 0.1327 M KMnO_4 solution is needed to oxidize 25.00 mL of a FeSO_4 solution in an acidic medium. What is the concentration of the FeSO_4 solution in molarity? The net ionic equation is



Strategy We want to calculate the molarity of the FeSO_4 solution. From the definition of molarity

$$\text{molarity of FeSO}_4 = \frac{\text{mol FeSO}_4}{\text{L soln}}$$

want to calculate

need to find

given

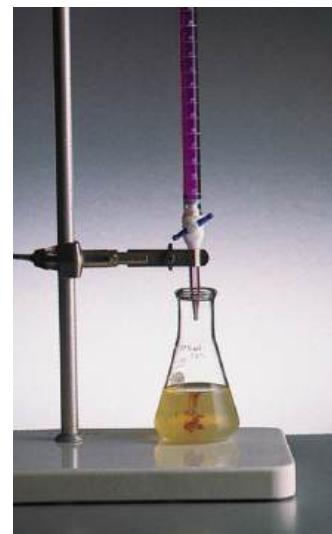
The volume of the FeSO_4 solution is given in the problem. Therefore, we need to find the number of moles of FeSO_4 to solve for the molarity. From the net ionic equation, what is the stoichiometric equivalence between Fe^{2+} and MnO_4^- ? How many moles of KMnO_4 are contained in 16.42 mL of 0.1327 M KMnO_4 solution?

Solution The number of moles of KMnO_4 in 16.42 mL of the solution is

$$\text{moles of KMnO}_4 = \frac{0.1327 \text{ mol KMnO}_4}{1000 \text{ mL soln}} \times 16.42 \text{ mL}$$

$$= 2.179 \times 10^{-3} \text{ mol KMnO}_4$$

(Continued)



Addition of a $KMnO_4$ solution from a buret to a $FeSO_4$ solution.

CHEMISTRY *in Action*

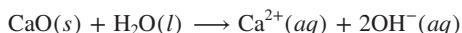
Metal from the Sea

Magnesium is a valuable, lightweight metal used as a structural material as well as in alloys, in batteries, and in chemical synthesis. Although magnesium is plentiful in Earth's crust, it is cheaper to "mine" the metal from seawater. Magnesium forms the second most abundant cation in the sea (after sodium); there are about 1.3 g of magnesium in a kilogram of seawater. The process for obtaining magnesium from seawater employs all three types of reactions discussed in this chapter: precipitation, acid-base, and redox reactions.

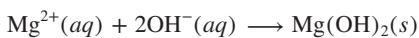
In the first stage in the recovery of magnesium, limestone (CaCO_3) is heated at high temperatures to produce quicklime, or calcium oxide (CaO):



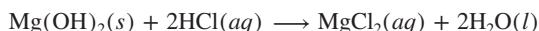
When calcium oxide is treated with seawater, it forms calcium hydroxide [$\text{Ca}(\text{OH})_2$], which is slightly soluble and ionizes to give Ca^{2+} and OH^- ions:



The surplus hydroxide ions cause the much less soluble magnesium hydroxide to precipitate:



The solid magnesium hydroxide is filtered and reacted with hydrochloric acid to form magnesium chloride (MgCl_2):

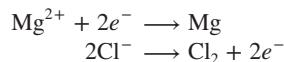


After the water is evaporated, the solid magnesium chloride is melted in a steel cell. The molten magnesium chloride contains both Mg^{2+} and Cl^- ions. In a process called *electrolysis*, an

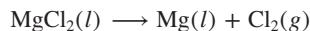


Magnesium hydroxide was precipitated from processed seawater in settling ponds at the Dow Chemical Company once operated in Freeport, Texas.
Courtesy of The Dow Chemical Company

electric current is passed through the cell to reduce the Mg^{2+} ions and oxidize the Cl^- ions. The half-reactions are



The overall reaction is



This is how magnesium metal is produced. The chlorine gas generated can be converted to hydrochloric acid and recycled through the process.

From the net ionic equation we see that $5 \text{ mol Fe}^{2+} \approx 1 \text{ mol MnO}_4^-$. Therefore, the number of moles of FeSO_4 oxidized is

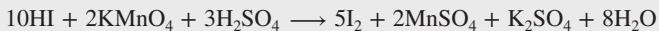
$$\begin{aligned}\text{moles FeSO}_4 &= 2.179 \times 10^{-3} \text{ mol KMnO}_4 \times \frac{5 \text{ mol FeSO}_4}{1 \text{ mol KMnO}_4} \\ &= 1.090 \times 10^{-2} \text{ mol FeSO}_4\end{aligned}$$

The concentration of the FeSO_4 solution in moles of FeSO_4 per liter of solution is

$$\begin{aligned}\text{molarity of FeSO}_4 &= \frac{\text{mol FeSO}_4}{\text{L soln}} \\ &= \frac{1.090 \times 10^{-2} \text{ mol FeSO}_4}{25.00 \text{ mL soln}} \times \frac{1000 \text{ mL soln}}{1 \text{ L soln}} \\ &= 0.4360 \text{ M}\end{aligned}$$

(Continued)

Practice Exercise How many milliliters of a 0.206 M HI solution are needed to reduce 22.5 mL of a 0.374 M KMnO₄ solution according to the following equation?

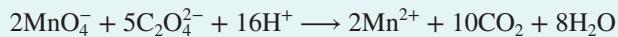


Similar problems: 4.95, 4.96.

The Chemistry in Action essay, “Metal from the Sea,” describes an industrial process that involves the types of reactions discussed in this chapter.

Review of Concepts & Facts

- 4.8.1** If a solution of a reducing agent is titrated with a solution of an oxidizing agent, and the initial concentrations of the two solutions are the same, does that mean that the equivalence point will be reached when an equal volume of oxidizing has been added? Explain.
- 4.8.2** The concentration of a KMnO₄ solution can be determined by redox titration with oxalate ion, C₂O₄²⁻, according to the net ionic equation



What is the concentration of a KMnO₄ solution if 20.24 mL of 0.2558 M C₂O₄²⁻ solution is needed to reduce 25.00 mL of KMnO₄ solution?

Learning Objectives

- Evaluate substances in aqueous solutions as nonelectrolytes, weak electrolytes, or strong electrolytes. (Section 4.1)
- Apply solubility guidelines toward determining whether a reaction will produce a precipitate. (Section 4.2)
- Compose the molecular, ionic, and net ionic equations for a reaction. (Section 4.2)
- Identify the spectator ions in a reaction. (Section 4.2)
- Compare the definitions of Brønsted acids and bases. (Section 4.3)
- Classify acids and bases as weak or strong. (Section 4.3)
- Categorize an acid as monoprotic, diprotic, or tripotic. (Section 4.3)
- Summarize a neutralization reaction between an acid and a base. (Section 4.3)
- Identify the various components of an oxidation-reduction reaction including reducing/oxidizing agents and half-reactions. (Section 4.4)
- Apply oxidation number rules toward determining the oxidation number of each element in a compound or polyatomic ion. (Section 4.4)
- Differentiate the types of reactions that may be oxidation-reduction reactions, including combustion, decomposition, displacement, and disproportionation. (Section 4.4)
- Utilize the activity series to determine whether a metal displacement reaction occurs. (Section 4.4)
- Calculate the molarity of a solution. (Section 4.5)
- Determine the concentration of a solution that has been diluted. (Section 4.5)
- Solve stoichiometry problems for reactions in solution, including gravimetric analysis, acid-base titration, and redox titrations. (Sections 4.6, 4.7, 4.8)

Key Equations

$$\text{molarity} = \frac{\text{moles of solute}}{\text{liters of solution}} \quad (4.1)$$

$$M = \frac{n}{V} \quad (4.2)$$

$$M_i V_i = M_f V_f \quad (4.3)$$

Calculating molarity

Calculating molarity

Dilution of solution

Summary of Concepts & Facts

- Aqueous solutions are electrically conducting if the solutes are electrolytes. If the solutes are nonelectrolytes, the solutions do not conduct electricity.
- Three major categories of chemical reactions that take place in aqueous solution are precipitation reactions, acid-base reactions, and oxidation-reduction reactions.
- From general rules about solubilities of ionic compounds, we can predict whether a precipitate will form in a reaction.
- Arrhenius acids ionize in water to give H^+ ions, and Arrhenius bases ionize in water to give OH^- ions. Brønsted acids donate protons, and Brønsted bases accept protons.
- The reaction of an acid and a base is called neutralization.
- In redox reactions, oxidation and reduction always occur simultaneously. Oxidation is characterized by the loss of electrons, reduction by the gain of electrons.
- Oxidation numbers help us keep track of charge distribution and are assigned to all atoms in a compound or ion according to specific rules. Oxidation can be defined as an increase in oxidation number; reduction can be defined as a decrease in oxidation number.
- Many redox reactions can be subclassified as combination, decomposition, combustion, displacement, or disproportionation reactions.
- The concentration of a solution is the amount of solute present in a given amount of solution. Molarity expresses concentration as the number of moles of solute in 1 L of solution.
- Adding a solvent to a solution, a process known as dilution, decreases the concentration (molarity) of the solution without changing the total number of moles of solute present in the solution.
- Gravimetric analysis is a technique for determining the identity of a compound and/or the concentration of a solution by measuring mass. Gravimetric experiments often involve precipitation reactions.
- In acid-base titration, a solution of known concentration (say, a base) is added gradually to a solution of unknown concentration (say, an acid) with the goal of determining the unknown concentration. The point at which the reaction in the titration is complete, as shown by the change in the indicator's color, is called the equivalence point.
- Redox titrations are similar to acid-base titrations. The point at which the oxidation-reduction reaction is complete is called the equivalence point.

Key Words

Activity series, p. 142
 Aqueous solution, p. 122
 Brønsted acid, p. 130
 Brønsted base, p. 130
 Combination reaction, p. 141
 Combustion reaction, p. 141
 Concentration of a solution, p. 147
 Decomposition reaction, p. 141
 Dilution, p. 149
 Diprotic acid, p. 131
 Displacement reaction, p. 142
 Disproportionation reaction, p. 145

Electrolyte, p. 122
 Equivalence point, p. 154
 Gravimetric analysis, p. 151
 Half-reaction, p. 136
 Hydration, p. 123
 Hydronium ion, p. 131
 Indicators, p. 154
 Ionic equation, p. 127
 Metathesis reaction, p. 125
 Molar concentration, p. 147
 Molarity (M), p. 147
 Molecular equation, p. 127
 Monoprotic acid, p. 131

Net ionic equation, p. 127
 Neutralization reaction, p. 133
 Nonelectrolyte, p. 122
 Oxidation number, p. 138
 Oxidation reaction, p. 136
 Oxidation-reduction reaction, p. 136
 Oxidation state, p. 138
 Oxidizing agent, p. 137
 Precipitate, p. 125
 Precipitation reaction, p. 125
 Quantitative analysis, p. 151
 Redox reaction, p. 136

Reducing agent, p. 137
 Reduction reaction, p. 137
 Reversible reaction, p. 124
 Salt, p. 133
 Solubility, p. 125
 Solute, p. 122
 Solution, p. 122
 Solvent, p. 122
 Spectator ion, p. 127
 Standard solution, p. 153
 Titration, p. 153
 Triprotic acid, p. 131

Questions & Problems

Red numbered problems solved in Student Solutions Manual

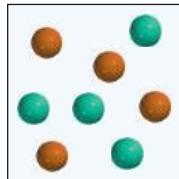
4.1 General Properties of Aqueous Solutions

Review Questions

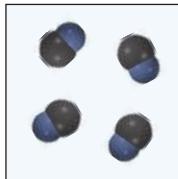
- 4.1 Define *solute*, *solvent*, and *solution* by describing the process of dissolving a solid in a liquid.
- 4.2 What is the difference between a nonelectrolyte and an electrolyte? Between a weak electrolyte and a strong electrolyte?
- 4.3 Describe hydration. What properties of water enable its molecules to interact with ions in solution?
- 4.4 What is the difference between the following symbols in chemical equations: \longrightarrow and \equiv ?
- 4.5 Water is an extremely weak electrolyte and therefore cannot conduct electricity. Why are we often cautioned not to operate electrical appliances when our hands are wet?
- 4.6 Sodium sulfate (Na_2SO_4) is a strong electrolyte. What species are present in $\text{Na}_2\text{SO}_4(aq)$?

Problems

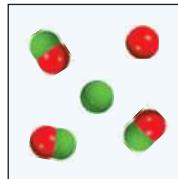
- 4.7 The aqueous solutions of three compounds are shown. Identify each compound as a nonelectrolyte, a weak electrolyte, and a strong electrolyte.



(a)

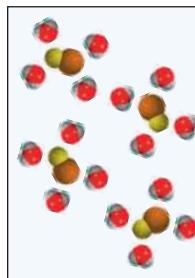


(b)

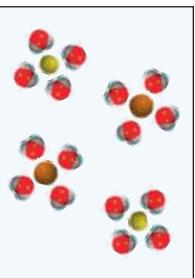


(c)

- 4.8 Which diagram (a)–(c) best represents the hydration of NaCl when dissolved in water? The Cl^- ion is larger in size than the Na^+ ion.



(a)



(b)



(c)

- 4.9 Identify each of the following substances as a strong electrolyte, weak electrolyte, or nonelectrolyte: (a) H_2O , (b) KCl , (c) HNO_3 , (d) CH_3COOH , (e) $\text{C}_{12}\text{H}_{22}\text{O}_{11}$.

- 4.10** Identify each of the following substances as a strong electrolyte, weak electrolyte, or nonelectrolyte: (a) $\text{Ba}(\text{NO}_3)_2$, (b) Ne , (c) NH_3 , (d) NaOH .

- 4.11** The passage of electricity through an electrolyte solution is caused by the movement of (a) electrons only, (b) cations only, (c) anions only, (d) both cations and anions.

- 4.12** Predict and explain which of the following systems are electrically conducting: (a) solid NaCl , (b) molten NaCl , (c) an aqueous solution of NaCl .

- 4.13** You are given a water-soluble compound X. Describe how you would determine whether it is an electrolyte or a nonelectrolyte. If it is an electrolyte, how would you determine whether it is strong or weak?

- 4.14** Explain why a solution of HCl in benzene does not conduct electricity but in water it does.

4.2 Precipitation Reactions

Review Questions

- 4.15 What is the difference between an ionic equation and a molecular equation?
- 4.16 What is the advantage of writing net ionic equations?

Problems

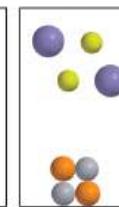
- 4.17** Two aqueous solutions of AgNO_3 and NaCl are mixed. Which of the diagrams (a)–(d) best represents the mixture? For simplicity, water molecules are not shown. (Color codes: Ag^+ = gray, Cl^- = orange, Na^+ = green, NO_3^- = blue)



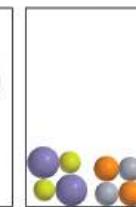
(a)



(b)

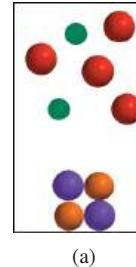


(c)

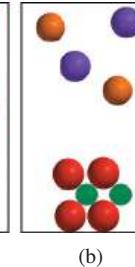


(d)

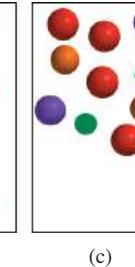
- 4.18** Two aqueous solutions of KOH and MgCl_2 are mixed. Which of the diagrams (a)–(d) best represents the mixture? For simplicity, water molecules are not shown. (Color codes: K^+ = purple, OH^- = red, Mg^{2+} = green, Cl^- = orange)



(a)



(b)



(c)



(d)

- 4.19 Characterize the following compounds as soluble or insoluble in water: (a) $\text{Ca}_3(\text{PO}_4)_2$, (b) $\text{Mn}(\text{OH})_2$, (c) AgClO_3 , (d) K_2S .
- 4.20** Characterize the following compounds as soluble or insoluble in water: (a) CaCO_3 , (b) ZnSO_4 , (c) $\text{Hg}(\text{NO}_3)_2$, (d) HgSO_4 , (e) NH_4ClO_4 .
- 4.21 Write ionic and net ionic equations for the following reactions.
- $\text{AgNO}_3(aq) + \text{Na}_2\text{SO}_4(aq) \longrightarrow$
 - $\text{BaCl}_2(aq) + \text{ZnSO}_4(aq) \longrightarrow$
 - $(\text{NH}_4)_2\text{CO}_3(aq) + \text{CaCl}_2(aq) \longrightarrow$
- 4.22** Write ionic and net ionic equations for the following reactions.
- $\text{Na}_2\text{S}(aq) + \text{ZnCl}_2(aq) \longrightarrow$
 - $\text{K}_3\text{PO}_4(aq) + 3\text{Sr}(\text{NO}_3)_2(aq) \longrightarrow$
 - $\text{Mg}(\text{NO}_3)_2(aq) + 2\text{NaOH}(aq) \longrightarrow$
- 4.23 Which of the following processes will likely result in a precipitation reaction: (a) mixing a NaNO_3 solution with a CuSO_4 solution, or (b) mixing a BaCl_2 solution with a K_2SO_4 solution? Write a net ionic equation for the precipitation reaction.
- 4.24** With reference to Table 4.2, suggest one method by which you might separate (a) K^+ from Ag^+ , (b) Ba^{2+} from Pb^{2+} , (c) NH_4^+ from Ca^{2+} , (d) Ba^{2+} from Cu^{2+} . All cations are assumed to be in aqueous solution, and the common anion is the nitrate ion.

4.3 Acid-Base Reactions

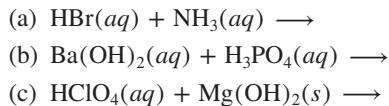
Review Questions

- 4.25 List the general properties of acids and bases.
- 4.26 Give Arrhenius's and Brønsted's definitions of an acid and a base. Why are Brønsted's definitions more useful in describing acid-base properties?
- 4.27 Give an example of a monoprotic acid, a diprotic acid, and a triprotic acid.
- 4.28 What are the characteristics of an acid-base neutralization reaction?
- 4.29 What factors qualify a compound as a salt? Specify which of the following compounds are salts: CH_4 , NaF , NaOH , CaO , BaSO_4 , HNO_3 , NH_3 , KBr .
- 4.30 Identify the following as a weak or strong acid or base: (a) NH_3 , (b) H_3PO_4 , (c) LiOH , (d) HCOOH (formic acid), (e) H_2SO_4 , (f) HF , (g) $\text{Ba}(\text{OH})_2$.

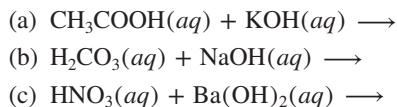
Problems

- 4.31 Identify each of the following species as a Brønsted acid, base, or both: (a) HI , (b) CH_3COO^- , (c) H_2PO_4^- , (d) HSO_4^- .
- 4.32** Identify each of the following species as a Brønsted acid, base, or both: (a) PO_4^{3-} , (b) ClO_2^- , (c) NH_4^+ , (d) HCO_3^- .

- 4.33 Balance the following equations and write the corresponding ionic and net ionic equations (if appropriate).



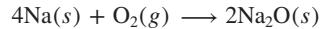
- 4.34** Balance the following equations and write the corresponding ionic and net ionic equations (if appropriate).



4.4 Oxidation-Reduction Reactions

Review Questions

- 4.35 Give an example of a combination redox reaction, a decomposition redox reaction, and a displacement redox reaction.
- 4.36 True or false: All combustion reactions are redox reactions. Explain your answer.
- 4.37 What is an oxidation number? How is it used to identify redox reactions? Explain why, except for ionic compounds, oxidation number does not have any physical significance.
- 4.38 (a) Without referring to Figure 4.11, give the oxidation numbers of the alkali and alkaline earth metals in their compounds. (b) Give the highest oxidation numbers that the Groups 3A–7A elements can have.
- 4.39 How is the activity series organized? How is it used in the study of redox reactions?
- 4.40 Use the following reaction to define *redox reaction*, *half-reaction*, *oxidizing agent*, and *reducing agent*.



- 4.41 Is it possible to have a reaction in which oxidation occurs and reduction does not? Explain.
- 4.42 What is the requirement for an element to undergo disproportionation reactions? Name five common elements that are likely to take part in such reactions.

Problems

- 4.43 For the complete redox reactions given here, (i) break down each reaction into its half-reactions; (ii) identify the oxidizing agent; (iii) identify the reducing agent.
- $2\text{Sr} + \text{O}_2 \longrightarrow 2\text{SrO}$
 - $2\text{Li} + \text{H}_2 \longrightarrow 2\text{LiH}$
 - $2\text{Cs} + \text{Br}_2 \longrightarrow 2\text{CsBr}$
 - $3\text{Mg} + \text{N}_2 \longrightarrow \text{Mg}_3\text{N}_2$

- 4.44** For the complete redox reactions given here, write the half-reactions and identify the oxidizing and reducing agents.
- $4\text{Fe} + 3\text{O}_2 \longrightarrow 2\text{Fe}_2\text{O}_3$
 - $\text{Cl}_2 + 2\text{NaBr} \longrightarrow 2\text{NaCl} + \text{Br}_2$
 - $\text{Si} + 2\text{F}_2 \longrightarrow \text{SiF}_4$
 - $\text{H}_2 + \text{Cl}_2 \longrightarrow 2\text{HCl}$
- 4.45** Arrange the following species in order of increasing oxidation number of the sulfur atom: (a) H_2S , (b) S_8 , (c) H_2SO_4 , (d) S^{2-} , (e) HS^- , (f) SO_2 , (g) SO_3 .
- 4.46** Phosphorus forms many oxoacids. Indicate the oxidation number of phosphorus in each of the following acids: (a) HPO_3 , (b) H_3PO_2 , (c) H_3PO_3 , (d) H_3PO_4 , (e) $\text{H}_4\text{P}_2\text{O}_7$, (f) $\text{H}_5\text{P}_3\text{O}_{10}$.
- 4.47** Give the oxidation number of the underlined atoms in the following molecules and ions: (a) $\underline{\text{C}}\text{IF}$, (b) $\underline{\text{I}}\text{F}_7$, (c) $\underline{\text{C}}\text{H}_4$, (d) $\underline{\text{C}}_2\text{H}_2$, (e) $\underline{\text{C}}_2\text{H}_4$, (f) $\text{K}_2\underline{\text{Cr}}\text{O}_4$, (g) $\text{K}_2\underline{\text{Cr}}_2\text{O}_7$, (h) $\text{KMn}\underline{\text{O}}_4$, (i) $\text{NaH}\underline{\text{C}}\text{O}_3$, (j) $\underline{\text{Li}}_2$, (k) $\text{Na}\underline{\text{I}}\text{O}_3$, (l) $\text{KO}\underline{\text{O}}_2$, (m) $\underline{\text{P}}\text{F}_6^-$, (n) $\text{KAu}\underline{\text{Cl}}_4$.
- 4.48** Give the oxidation number for the following species: H_2 , Se_8 , P_4 , O , U , As_4 , B_{12} .
- 4.49** Give oxidation number for the underlined atoms in the following molecules and ions: (a) $\underline{\text{Cs}}_2\text{O}$, (b) $\text{Ca}\underline{\text{I}}_2$, (c) $\underline{\text{Al}}_2\text{O}_3$, (d) $\text{H}_3\underline{\text{As}}\text{O}_3$, (e) $\text{Ti}\underline{\text{O}}_2$, (f) $\underline{\text{Mo}}\text{O}_4^{2-}$, (g) $\underline{\text{Pt}}\text{Cl}_4^{2-}$, (h) $\underline{\text{Pt}}\text{Cl}_6^{2-}$, (i) $\underline{\text{Sn}}\text{F}_2$, (j) $\underline{\text{Cl}}\text{F}_3$, (k) $\underline{\text{Sb}}\text{F}_6^-$.
- 4.50** Give the oxidation number of the underlined atoms in the following molecules and ions: (a) $\text{Mg}_3\underline{\text{N}}_2$, (b) $\text{Cs}\underline{\text{O}}_2$, (c) $\text{Ca}\underline{\text{C}}_2$, (d) $\underline{\text{C}}\text{O}_3^{2-}$, (e) $\underline{\text{C}}_2\text{O}_4^{2-}$, (f) $\text{Zn}\underline{\text{O}}_2^{2-}$, (g) $\text{Na}\underline{\text{B}}\text{H}_4$, (h) $\underline{\text{W}}\text{O}_4^{2-}$.
- 4.51** Nitric acid is a strong oxidizing agent. State which of the following species is *least* likely to be produced when nitric acid reacts with a strong reducing agent such as zinc metal, and explain why: N_2O , NO , NO_2 , N_2O_4 , N_2O_5 , NH_4^+ .
- 4.52** Which of the following metals can react with water? (a) Au, (b) Li, (c) Hg, (d) Ca, (e) Pt.
- 4.53** On the basis of oxidation number considerations, one of the following oxides would not react with molecular oxygen: NO , N_2O , SO_2 , SO_3 , P_4O_6 . Which one is it? Why?
- 4.54** Predict the outcome of the reactions represented by the following equations by using the activity series, and balance the equations.
- $\text{Cu}(s) + \text{HCl}(aq) \longrightarrow$
 - $\text{I}_2(s) + \text{NaBr}(aq) \longrightarrow$
 - $\text{Mg}(s) + \text{CuSO}_4(aq) \longrightarrow$
 - $\text{Cl}_2(g) + \text{KBr}(aq) \longrightarrow$
- 4.55** Classify the following redox reactions.
- $2\text{H}_2\text{O}_2 \longrightarrow 2\text{H}_2\text{O} + \text{O}_2$
 - $\text{Mg} + 2\text{AgNO}_3 \longrightarrow \text{Mg}(\text{NO}_3)_2 + 2\text{Ag}$
 - $\text{NH}_4\text{NO}_2 \longrightarrow \text{N}_2 + 2\text{H}_2\text{O}$
 - $\text{H}_2 + \text{Br}_2 \longrightarrow 2\text{HBr}$
- 4.56** Classify the following redox reactions.
- $\text{P}_4 + 10\text{Cl}_2 \longrightarrow 4\text{PCl}_5$
 - $2\text{NO} \longrightarrow \text{N}_2 + \text{O}_2$
 - $\text{Cl}_2 + 2\text{KI} \longrightarrow 2\text{KCl} + \text{I}_2$
 - $3\text{HNO}_2 \longrightarrow \text{HNO}_3 + \text{H}_2\text{O} + 2\text{NO}$
- 4.57** Which of the following are redox processes?
- $\text{CO}_2 \longrightarrow \text{CO}_3^{2-}$
 - $\text{VO}_3 \longrightarrow \text{VO}_2$
 - $\text{SO}_3 \longrightarrow \text{SO}_4^{2-}$
 - $\text{NO}_2^- \longrightarrow \text{NO}_3^-$
 - $\text{Cr}^{3+} \longrightarrow \text{CrO}_4^{2-}$
- 4.58** Of the following, which is most likely to be the strongest oxidizing agent: O_2 , O_2^+ , O_2^- , O_2^{2-} ?

4.5 Concentration of Solutions

Review Questions

- 4.59** Write the equation for calculating molarity. Why is molarity a convenient concentration unit in chemistry?
- 4.60** Describe the steps involved in preparing a solution of known molar concentration using a volumetric flask.
- 4.61** Describe the basic steps involved in diluting a solution of known concentration.
- 4.62** Write the equation that enables us to calculate the concentration of a diluted solution. Give units for all the terms.

Problems

- 4.63** Calculate the mass of KI in grams required to prepare 5.00×10^2 mL of a 2.80 M solution.
- 4.64** Describe how you would prepare 250 mL of a 0.707 M NaNO_3 solution.
- 4.65** How many moles of MgCl_2 are present in 60.0 mL of 0.100 M MgCl_2 solution?
- 4.66** How many grams of KOH are present in 35.0 mL of a 5.50 M solution?
- 4.67** Calculate the molarity of each of the following solutions: (a) 29.0 g of ethanol ($\text{C}_2\text{H}_5\text{OH}$) in 545 mL of solution, (b) 15.4 g of sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) in 74.0 mL of solution, (c) 9.00 g of sodium chloride (NaCl) in 86.4 mL of solution.
- 4.68** Calculate the molarity of each of the following solutions: (a) 6.57 g of methanol (CH_3OH) in 1.50×10^2 mL of solution, (b) 10.4 g of calcium chloride (CaCl_2) in 2.20×10^2 mL of solution, (c) 7.82 g of naphthalene (C_{10}H_8) in 85.2 mL of benzene solution.
- 4.69** Calculate the volume in milliliters of a solution required to provide the following: (a) 2.14 g of sodium chloride from a 0.270 M solution, (b) 4.30 g of ethanol from a 1.50 M solution, (c) 0.85 g of acetic acid (CH_3COOH) from a 0.30 M solution.

- 4.70** Determine how many grams of each of the following solutes would be needed to make 2.50×10^2 mL of a 0.100 M solution: (a) cesium iodide (CsI), (b) sulfuric acid (H_2SO_4), (c) sodium carbonate (Na_2CO_3), (d) potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), (e) potassium permanganate (KMnO_4).
- 4.71** What volume of 0.416 M $\text{Mg}(\text{NO}_3)_2$ should be added to 255 mL of 0.102 M KNO_3 to produce a solution with a concentration of 0.278 M NO_3^- ions? Assume volumes are additive.
- 4.72** Barium hydroxide, often used to titrate weak organic acids, is obtained as the octahydrate, $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$. What mass of $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ would be required to make 500.0 mL of a solution that is 0.1500 M in hydroxide ions?
- 4.73** Describe how to prepare 1.00 L of 0.646 M HCl solution, starting with a 2.00 M HCl solution.
- 4.74** Water is added to 25.0 mL of a 0.866 M KNO_3 solution until the volume of the solution is exactly 500 mL. What is the concentration of the final solution?
- 4.75** How would you prepare 60.0 mL of 0.200 M HNO_3 from a stock solution of 4.00 M HNO_3 ?
- 4.76** You have 505 mL of a 0.125 M HCl solution and you want to dilute it to exactly 0.100 M . How much water should you add? Assume volumes are additive.
- 4.77** A 35.2-mL, 1.66 M KMnO_4 solution is mixed with 16.7 mL of 0.892 M KMnO_4 solution. Calculate the concentration of the final solution.
- 4.78** A 46.2-mL, 0.568 M calcium nitrate [$\text{Ca}(\text{NO}_3)_2$] solution is mixed with 80.5 mL of 1.396 M calcium nitrate solution. Calculate the concentration of the final solution.

4.6 Gravimetric Analysis

Review Questions

- 4.79** Describe the basic steps involved in gravimetric analysis. How does this procedure help us determine the identity of a compound or the purity of a compound if its formula is known?
- 4.80** Distilled water must be used in the gravimetric analysis of chlorides. Why?

Problems

- 4.81** If 30.0 mL of 0.150 M CaCl_2 is added to 15.0 mL of 0.100 M AgNO_3 , what is the mass in grams of AgCl precipitate?
- 4.82** A sample of 0.6760 g of an unknown compound containing barium ions (Ba^{2+}) is dissolved in water and treated with an excess of Na_2SO_4 . If the mass of the BaSO_4 precipitate formed is 0.4105 g, what is the percent by mass of Ba in the original unknown compound?
- 4.83** How many grams of NaCl are required to precipitate most of the Ag^+ ions from 2.50×10^2 mL of 0.0113 M AgNO_3 solution? Write the net ionic equation for the reaction.

- 4.84** The concentration of sulfate in water can be determined by adding a solution of barium chloride to precipitate the sulfate ion. Write the net ionic equation for this reaction. Treating a 145-mL sample of water with excess $\text{BaCl}_2(aq)$ precipitated 0.330 g of BaSO_4 . Determine the concentration of sulfate in the original water sample.

4.7 Acid-Base Titrations

Review Questions

- 4.85** Describe the basic steps involved in an acid-base titration. Why is this technique of great practical value?
- 4.86** How does an acid-base indicator work?
- 4.87** A student carried out two titrations using a NaOH solution of unknown concentration in the buret. In one titration she weighed out 0.2458 g of KHP (see Section 4.7) and transferred it to an Erlenmeyer flask. She then added 20.00 mL of distilled water to dissolve the acid. In the other titration she weighed out 0.2507 g of KHP but added 40.00 mL of distilled water to dissolve the acid. Assuming no experimental error, would she obtain the same result for the concentration of the NaOH solution?
- 4.88** Would the volume of a 0.10 M NaOH solution needed to titrate 25.0 mL of a 0.10 M HNO_2 (a weak acid) solution be different from that needed to titrate 25.0 mL of a 0.10 M HCl (a strong acid) solution?

Problems

- 4.89** A quantity of 18.68 mL of a KOH solution is needed to neutralize 0.4218 g of KHP. What is the concentration (in molarity) of the KOH solution?
- 4.90** Calculate the concentration (in molarity) of a NaOH solution if 25.0 mL of the solution are needed to neutralize 17.4 mL of a 0.312 M HCl solution.
- 4.91** Calculate the volume in milliliters of a 1.420 M NaOH solution required to titrate the following solutions.
- 25.00 mL of a 2.430 M HCl solution
 - 25.00 mL of a 4.500 M H_2SO_4 solution
 - 25.00 mL of a 1.500 M H_3PO_4 solution
- 4.92** What volume of a 0.500 M HCl solution is needed to neutralize each of the following?
- 10.0 mL of a 0.300 M NaOH solution
 - 10.0 mL of a 0.200 M $\text{Ba}(\text{OH})_2$ solution

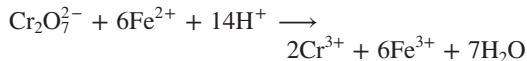
4.8 Redox Titrations

Review Questions

- 4.93** What are the similarities and differences between acid-base titrations and redox titrations?
- 4.94** Explain why potassium permanganate (KMnO_4) and potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) can serve as internal indicators in redox titrations.

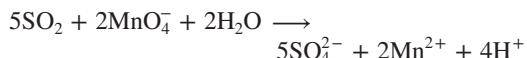
Problems

- 4.95 Iron(II) can be oxidized by an acidic $\text{K}_2\text{Cr}_2\text{O}_7$ solution according to the net ionic equation



If it takes 26.0 mL of 0.0250 M $\text{K}_2\text{Cr}_2\text{O}_7$ to titrate 25.0 mL of a solution containing Fe^{2+} , what is the molar concentration of Fe^{2+} ?

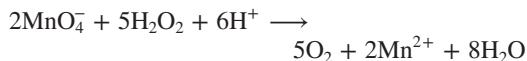
- 4.96 The SO_2 present in air is mainly responsible for the acid rain phenomenon. Its concentration can be determined by titrating against a standard permanganate solution as follows:



Calculate the number of grams of SO_2 in a sample of air if 7.37 mL of 0.00800 M KMnO_4 solution are required for the titration.

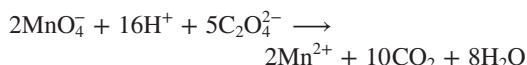
- 4.97 A sample of iron ore (containing only Fe^{2+} ions) weighing 0.2792 g was dissolved in dilute acid solution, and all the Fe(II) was converted to Fe(III) ions. The solution required 23.30 mL of 0.0194 M $\text{K}_2\text{Cr}_2\text{O}_7$ for titration. Calculate the percent by mass of iron in the ore. (*Hint:* See Problem 4.95 for the balanced equation.)

- 4.98 The concentration of a hydrogen peroxide solution can be conveniently determined by titration against a standardized potassium permanganate solution in an acidic medium according to the equation



If 36.44 mL of a 0.01652 M KMnO_4 solution are required to oxidize 25.00 mL of a H_2O_2 solution, calculate the molarity of the H_2O_2 solution.

- 4.99 Oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) is present in many plants and vegetables. If 24.0 mL of 0.0100 M KMnO_4 solution is needed to titrate 1.00 g of a sample of $\text{H}_2\text{C}_2\text{O}_4$ to the equivalence point, what is the percent by mass of $\text{H}_2\text{C}_2\text{O}_4$ in the sample? The net ionic equation is



- 4.100 A 15.0-mL sample of an oxalic acid solution requires 25.2 mL of 0.149 M NaOH for neutralization. Calculate the volume of a 0.122 M KMnO_4 solution needed to react with a second 15.0-mL sample of the oxalic acid solution. (*Hint:* Oxalic acid is a diprotic acid. See Problem 4.99 for redox equation.)

- 4.101 Iodate ion, IO_3^- , oxidizes SO_3^{2-} in acidic solution. The half-reaction for the oxidation is



A 100.0-mL sample of solution containing 1.390 g of KIO_3 reacts with 32.5 mL of 0.500 M Na_2SO_3 . What is the final oxidation state of the iodine after the reaction has occurred?

- 4.102 Calcium oxalate (CaC_2O_4), the main component of kidney stones, is insoluble in water. For this reason it can be used to determine the amount of Ca^{2+} ions in fluids such as blood. The calcium oxalate isolated from blood is dissolved in acid and titrated against a standardized KMnO_4 solution, as shown in Problem 4.99. In one test it is found that the calcium oxalate isolated from a 10.0-mL sample of blood requires 24.2 mL of 9.56×10^{-4} M KMnO_4 for titration. Calculate the number of milligrams of calcium per milliliter of blood.

Additional Problems

- 4.103 Classify the following reactions according to the types discussed in the chapter.

- (a) $\text{Cl}_2 + 2\text{OH}^- \longrightarrow \text{Cl}^- + \text{ClO}^- + \text{H}_2\text{O}$
- (b) $\text{Ca}^{2+} + \text{CO}_3^{2-} \longrightarrow \text{CaCO}_3$
- (c) $\text{NH}_3 + \text{H}^+ \longrightarrow \text{NH}_4^+$
- (d) $2\text{CCl}_4 + \text{CrO}_4^{2-} \longrightarrow 2\text{COCl}_2 + \text{CrO}_2\text{Cl}_2 + 2\text{Cl}^-$
- (e) $\text{Ca} + \text{F}_2 \longrightarrow \text{CaF}_2$
- (f) $2\text{Li} + \text{H}_2 \longrightarrow 2\text{LiH}$
- (g) $\text{Ba}(\text{NO}_3)_2 + \text{Na}_2\text{SO}_4 \longrightarrow 2\text{NaNO}_3 + \text{BaSO}_4$
- (h) $\text{CuO} + \text{H}_2 \longrightarrow \text{Cu} + \text{H}_2\text{O}$
- (i) $\text{Zn} + 2\text{HCl} \longrightarrow \text{ZnCl}_2 + \text{H}_2$
- (j) $2\text{FeCl}_2 + \text{Cl}_2 \longrightarrow 2\text{FeCl}_3$
- (k) $\text{LiOH} + \text{HNO}_3 \longrightarrow \text{LiNO}_3 + \text{H}_2\text{O}$

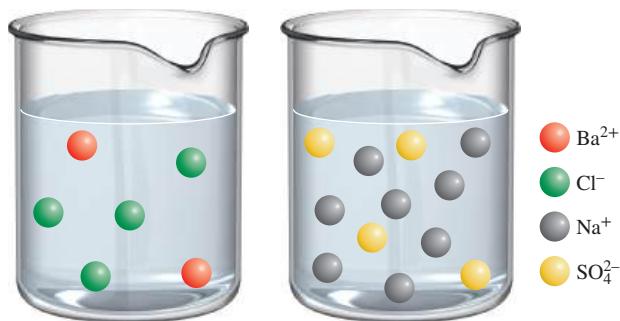
- 4.104 Oxygen (O_2) and carbon dioxide (CO_2) are colorless and odorless gases. Suggest two chemical tests that would enable you to distinguish between these two gases.

- 4.105 Which of the following aqueous solutions would you expect to be the best conductor of electricity at 25°C? Explain your answer.

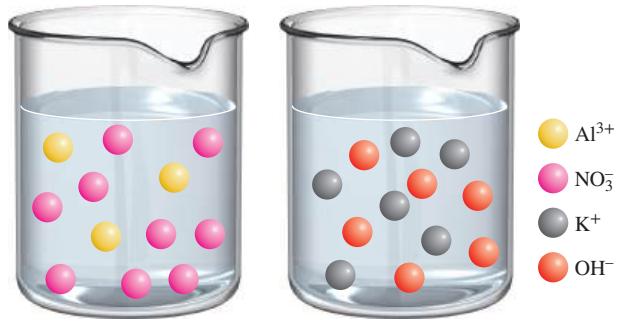
- (a) 0.20 M NaCl
- (b) 0.60 M CH_3COOH
- (c) 0.25 M HCl
- (d) 0.20 M $\text{Mg}(\text{NO}_3)_2$

- 4.106 A 5.00×10^2 mL sample of 2.00 M HCl solution is treated with 4.47 g of magnesium. Calculate the concentration of the acid solution after all the metal has reacted. Assume that the volume remains unchanged.

- 4.107 Shown are two aqueous solutions containing various ions. The volume of each solution is 200 mL.
 (a) Calculate the mass of the precipitate (in grams) after the solutions are mixed.
 (b) What are the concentrations (in M) of the ions in the final solution? Treat each sphere as 0.100 mol. Assume the volumes are additive.

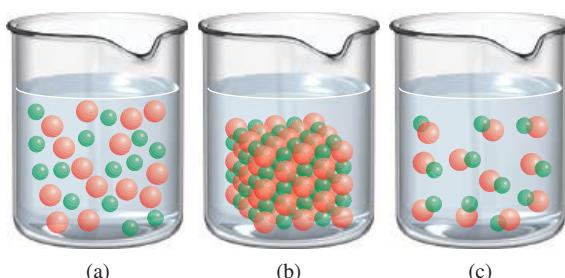


- 4.108** Shown are two aqueous solutions containing various ions. The volume of each solution is 200 mL. (a) Calculate the mass of the precipitate (in grams) after the solutions are mixed. (b) What are the concentrations (in *M*) of the ions in the final solution? Treat each sphere as 0.100 mol. Assume the volumes are additive.



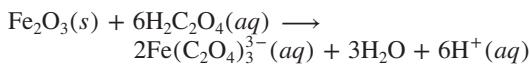
- 4.109** Calculate the volume of a 0.156 *M* CuSO₄ solution that would react with 7.89 g of zinc.
- 4.110** Sodium carbonate (Na₂CO₃) is available in very pure form and can be used to standardize acid solutions. What is the molarity of a HCl solution if 28.3 mL of the solution are required to react with 0.256 g of Na₂CO₃?
- 4.111** A 3.664-g sample of a monoprotic acid was dissolved in water. It took 20.27 mL of a 0.1578 *M* NaOH solution to neutralize the acid. Calculate the molar mass of the acid.
- 4.112** Acetic acid (CH₃COOH) is an important ingredient of vinegar. A sample of 50.0 mL of a commercial vinegar is titrated against a 1.00 *M* NaOH solution. What is the concentration (in *M*) of acetic acid present in the vinegar if 5.75 mL of the base are needed for the titration?
- 4.113** A 15.00-mL solution of potassium nitrate (KNO₃) was diluted to 125.0 mL, and 25.00 mL of this solution were then diluted to 1.000 × 10³ mL. The concentration of the final solution is 0.00383 *M*. Calculate the concentration of the original solution.
- 4.114** When a 2.50-g zinc strip was placed in a AgNO₃ solution, silver metal formed on the surface of the strip. After some time had passed, the strip was removed from the solution, dried, and weighed. If the mass of the strip was 3.37 g, calculate the mass of Ag and Zn metals present.
- 4.115** Calculate the mass of the precipitate formed when 2.27 L of 0.0820 *M* Ba(OH)₂ are mixed with 3.06 L of 0.0664 *M* Na₂SO₄.
- 4.116** Calculate the concentration of the acid (or base) remaining in solution when 10.7 mL of 0.211 *M* HNO₃ are added to 16.3 mL of 0.258 *M* NaOH.
- 4.117** (a) Describe a preparation for magnesium hydroxide [Mg(OH)₂] and predict its solubility. (b) Milk of magnesia contains mostly Mg(OH)₂ and is effective in treating acid (mostly hydrochloric acid) indigestion. Calculate the volume of a 0.035 *M* HCl solution (a typical acid concentration in an upset stomach) needed to react with two spoonfuls (approximately 10 mL) of milk of magnesia [at 0.080 g Mg(OH)₂/mL].
- 4.118** A 1.00-g sample of a metal X (that is known to form X²⁺ ions) was added to 0.100 L of 0.500 *M* H₂SO₄. After all the metal had reacted, the remaining acid required 0.0334 L of 0.500 *M* NaOH solution for neutralization. Calculate the molar mass of the metal and identify the element.
- 4.119** Carbon dioxide in air can be removed by an aqueous metal hydroxide solution such as LiOH and Ba(OH)₂. (a) Write equations for the reactions. (Carbon dioxide reacts with water to form carbonic acid.) (b) Calculate the mass of CO₂ that can be removed by 5.00 × 10² mL of a 0.800 *M* LiOH and a 0.800 *M* Ba(OH)₂ solution. (c) Which solution would you choose for use in a space capsule and which for use in a submarine?
- 4.120** The molecular formula of malonic acid is C₃H₄O₄. If a solution containing 0.762 g of the acid requires 12.44 mL of 1.174 *M* NaOH for neutralization, how many ionizable H atoms are present in the molecule?
- 4.121** A quantitative definition of solubility is the maximum number of grams of a solute that will dissolve in a given volume of water at a particular temperature. Describe an experiment that would enable you to determine the solubility of a soluble compound.
- 4.122** A 60.0-mL 0.513 *M* glucose (C₆H₁₂O₆) solution is mixed with 120.0 mL of 2.33 *M* glucose solution. What is the concentration of the final solution? Assume the volumes are additive.
- 4.123** An ionic compound X is only slightly soluble in water. What test would you employ to show that the compound does indeed dissolve in water to a certain extent?
- 4.124** A student is given an unknown that is either iron(II) sulfate or iron(III) sulfate. Suggest a chemical procedure for determining its identity. (Both iron compounds are water soluble.)
- 4.125** You are given a colorless liquid. Describe three chemical tests you would perform on the liquid to show that it is water.

- 4.126** Using the apparatus shown in Figure 4.1, a student found that a sulfuric acid solution caused the lightbulb to glow brightly. However, after the addition of a certain amount of a barium hydroxide $[\text{Ba}(\text{OH})_2]$ solution, the light began to dim even though $\text{Ba}(\text{OH})_2$ is also a strong electrolyte. Explain.
- 4.127** The molar mass of a certain metal carbonate, MCO_3 , can be determined by adding an excess of HCl acid to react with all the carbonate and then “back titrating” the remaining acid with a NaOH solution. (a) Write an equation for these reactions. (b) In a certain experiment, 20.00 mL of 0.0800 M HCl were added to a 0.1022-g sample of MCO_3 . The excess HCl required 5.64 mL of 0.1000 M NaOH for neutralization. Calculate the molar mass of the carbonate and identify M.
- 4.128** A 5.012-g sample of an iron chloride hydrate was dried in an oven. The mass of the anhydrous compound was 3.195 g. The compound was then dissolved in water and reacted with an excess of AgNO_3 . The AgCl precipitate formed weighed 7.225 g. What is the formula of the original compound?
- 4.129** You are given a soluble compound of unknown molecular formula. (a) Describe three tests that would show that the compound is an acid. (b) Once you have established that the compound is an acid, describe how you would determine its molar mass using a NaOH solution of known concentration. (Assume the acid is monoprotic.) (c) How would you find out whether the acid is weak or strong? You are provided with a sample of NaCl and an apparatus like that shown in Figure 4.1 for comparison.
- 4.130** You are given two colorless solutions, one containing NaCl and the other sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$). Suggest a chemical and a physical test that would allow you to distinguish between these two solutions.
- 4.131** The concentration of lead ions (Pb^{2+}) in a sample of polluted water that also contains nitrate ions (NO_3^-) is determined by adding solid sodium sulfate (Na_2SO_4) to exactly 500 mL of the water. (a) Write the molecular and net ionic equations for the reaction. (b) Calculate the molar concentration of Pb^{2+} if 0.00450 g of Na_2SO_4 was needed for the complete precipitation of Pb^{2+} ions as PbSO_4 .
- 4.132** Hydrochloric acid is not an oxidizing agent in the sense that sulfuric acid and nitric acid are. Explain why the chloride ion is not a strong oxidizing agent like SO_4^{2-} and NO_3^- .
- 4.133** Explain how you would prepare potassium iodide (KI) by means of (a) an acid-base reaction and (b) a reaction between an acid and a carbonate compound.
- 4.134** Sodium reacts with water to yield hydrogen gas. Why is this reaction not used in the laboratory preparation of hydrogen?
- 4.135** Describe how you would prepare the following compounds: (a) $\text{Mg}(\text{OH})_2$, (b) AgI , (c) $\text{Ba}_3(\text{PO}_4)_2$.
- 4.136** Someone spilled concentrated sulfuric acid on the floor of a chemistry laboratory. To neutralize the acid, would it be preferable to pour concentrated sodium hydroxide solution or spray solid sodium bicarbonate over the acid? Explain your choice and the chemical basis for the action.
- 4.137** Describe in each case how you would separate the cations or anions in an aqueous solution of: (a) NaNO_3 and $\text{Ba}(\text{NO}_3)_2$, (b) $\text{Mg}(\text{NO}_3)_2$ and KNO_3 , (c) KBr and KNO_3 , (d) K_3PO_4 and KNO_3 , (e) Na_2CO_3 and NaNO_3 .
- 4.138** The following are common household compounds: table salt (NaCl), table sugar (sucrose), vinegar (contains acetic acid), baking soda (NaHCO_3), washing soda ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$), boric acid (H_3BO_3 , used in eyewash), epsom salt ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), sodium hydroxide (used in drain openers), ammonia, milk of magnesia [$\text{Mg}(\text{OH})_2$], and calcium carbonate. Based on what you have learned in this chapter, describe test(s) that would enable you to identify each of these compounds.
- 4.139** Sulfites (compounds containing the SO_3^{2-} ions) are used as preservatives in dried fruit and vegetables and in wine making. In an experiment to test the presence of sulfite in fruit, a student first soaked several dried apricots in water overnight and then filtered the solution to remove all solid particles. She then treated the solution with hydrogen peroxide (H_2O_2) to oxidize the sulfite ions to sulfate ions. Finally, the sulfate ions were precipitated by treating the solution with a few drops of a barium chloride (BaCl_2) solution. Write a balanced equation for each of the preceding steps.
- 4.140** A 0.8870-g sample of a mixture of NaCl and KCl is dissolved in water, and the solution is then treated with an excess of AgNO_3 to yield 1.913 g of AgCl . Calculate the percent by mass of each compound in the mixture.
- 4.141** Based on oxidation number consideration, explain why carbon monoxide (CO) is flammable but carbon dioxide (CO_2) is not.
- 4.142** Which of the diagrams (a)–(c) corresponds to the reaction between $\text{AgOH}(s)$ and $\text{HNO}_3(aq)$? Write a balanced equation for the reaction. The green spheres represent the Ag^+ ions and the red spheres represent the NO_3^- ions.



- 4.143 Chlorine forms a number of oxides with the following oxidation numbers: +1, +3, +4, +6, and +7. Write a formula for each of these compounds.

- 4.144** A useful application of oxalic acid is the removal of rust (Fe_2O_3) from, say, bathtub rings according to the reaction



Calculate the number of grams of rust that can be removed by 5.00×10^2 mL of a 0.100 M solution of oxalic acid.

- 4.145 Acetylsalicylic acid ($\text{C}_9\text{H}_8\text{O}_4$) is a monoprotic acid commonly known as “aspirin.” A typical aspirin tablet, however, contains only a small amount of the acid. In an experiment to determine its composition, an aspirin tablet was crushed and dissolved in water. It took 12.25 mL of 0.1466 M NaOH to neutralize the solution. Calculate the number of grains of aspirin in the tablet. (One grain = 0.0648 g.)

- 4.146** A 0.9157-g mixture of CaBr_2 and NaBr is dissolved in water, and AgNO_3 is added to the solution to form AgBr precipitate. If the mass of the precipitate is 1.6930 g, what is the percent by mass of NaBr in the original mixture?

- 4.147 Hydrogen halides (HF , HCl , HBr , HI) are highly reactive compounds that have many industrial and laboratory uses. (a) In the laboratory, HF and HCl can be generated by reacting CaF_2 and NaCl with concentrated sulfuric acid. Write appropriate equations for the reactions. (Hint: These are not redox reactions.) (b) Why is it that HBr and HI cannot be prepared similarly—that is, by reacting NaBr and NaI with concentrated sulfuric acid? (Hint: H_2SO_4 is a stronger oxidizing agent than both Br_2 and I_2 .) (c) HBr can be prepared by reacting phosphorus tribromide (PBr_3) with water. Write an equation for this reaction.

- 4.148** A 325-mL sample of solution contains 25.3 g of CaCl_2 . (a) Calculate the molar concentration of Cl^- in this solution. (b) How many grams of Cl^- are in 0.100 L of this solution?

- 4.149 Phosphoric acid (H_3PO_4) is an important industrial chemical used in fertilizers, in detergents, and in the food industry. It is produced by two different methods. In the *electric furnace method*, elemental phosphorus (P_4) is burned in air to form P_4O_{10} , which is then reacted with water to give H_3PO_4 . In the *wet process*, the mineral phosphate rock fluorapatite [$\text{Ca}_5(\text{PO}_4)_3\text{F}$] is reacted with sulfuric acid to give H_3PO_4 (and HF and CaSO_4). Write equations for these processes and classify each step as precipitation, acid-base, or redox reaction.

- 4.150** Ammonium nitrate (NH_4NO_3) is one of the most important nitrogen-containing fertilizers. Its purity can be analyzed by titrating a solution of NH_4NO_3 with a standard NaOH solution. In one experiment

a 0.2041-g sample of industrially prepared NH_4NO_3 required 24.42 mL of 0.1023 M NaOH for neutralization.

- (a) Write a net ionic equation for the reaction.

- (b) What is the percent purity of the sample?

- 4.151 Is the following reaction a redox reaction? Explain.



- 4.152** What is the oxidation number of O in HFO ?

- 4.153 Use molecular models like those in Figures 4.7 and 4.8 to represent the following acid-base reactions.



Identify the Brønsted acid and base in each case.

- 4.154** The alcohol content in a 10.0-g sample of blood from a driver required 4.23 mL of 0.07654 M $\text{K}_2\text{Cr}_2\text{O}_7$ for titration. Should the police prosecute the individual for drunken driving? (Hint: See the Chemistry in Action essay in Section 4.8.)

- 4.155 On standing, a concentrated nitric acid gradually turns yellow. Explain. (Hint: Nitric acid slowly decomposes. Nitrogen dioxide is a colored gas.)

- 4.156** Describe the laboratory preparation for the following gases: (a) hydrogen, (b) oxygen, (c) carbon dioxide, (d) nitrogen. Indicate the physical states of the reactants and products in each case. [Hint: Nitrogen can be obtained by heating ammonium nitrite (NH_4NO_2].

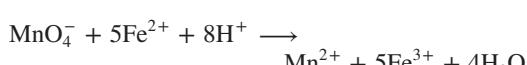
- 4.157 Referring to Figure 4.18, explain why one must first dissolve the solid completely before making up the solution to the correct volume.

- 4.158** Can the following decomposition reaction be characterized as an acid-base reaction? Explain.

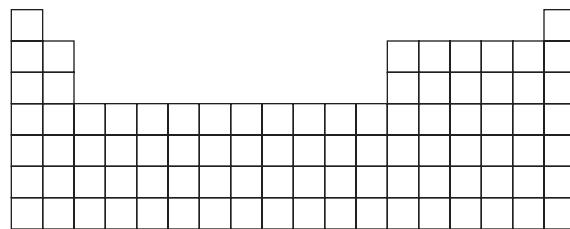


- 4.159 Give a chemical explanation for each of the following: (a) When calcium metal is added to a sulfuric acid solution, hydrogen gas is generated. After a few minutes, the reaction slows down and eventually stops even though none of the reactants is used up. (b) In the activity series, aluminum is above hydrogen, yet the metal appears to be unreactive toward steam and hydrochloric acid. (c) Sodium and potassium lie above copper in the activity series. In your explanation, discuss why Cu^{2+} ions in a CuSO_4 solution are not converted to metallic copper upon the addition of these metals. (d) A metal M reacts slowly with steam. There is no visible change when it is placed in a pale green iron(II) sulfate solution. Where should we place M in the activity series? (e) Before aluminum metal was obtained by electrolysis, it was produced by reducing its chloride (AlCl_3) with an active metal. What metals would you use to produce aluminum in that way?

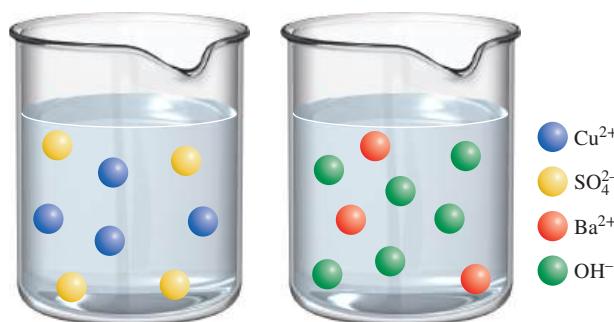
- 4.160** The recommended procedure for preparing a very dilute solution is not to weigh out a very small mass or measure a very small volume of a stock solution. Instead, it is done by a series of dilutions. A sample of 0.8214 g of KMnO_4 was dissolved in water and made up to the volume in a 500-mL volumetric flask. A 2.000-mL sample of this solution was transferred to a 1000-mL volumetric flask and diluted to the mark with water. Next, 10.00 mL of the diluted solution were transferred to a 250-mL flask and diluted to the mark with water. (a) Calculate the concentration (in molarity) of the final solution. (b) Calculate the mass of KMnO_4 needed to directly prepare the final solution.
- 4.161** The following “cycle of copper” experiment is performed in some general chemistry laboratories. The series of reactions starts with copper and ends with metallic copper. The steps are as follows: (1) A piece of copper wire of known mass is allowed to react with concentrated nitric acid [the products are copper(II) nitrate, nitrogen dioxide, and water]. (2) The copper(II) nitrate is treated with a sodium hydroxide solution to form copper(II) hydroxide precipitate. (3) On heating, copper(II) hydroxide decomposes to yield copper(II) oxide. (4) The copper(II) oxide is reacted with concentrated sulfuric acid to yield copper(II) sulfate. (5) Copper(II) sulfate is treated with an excess of zinc metal to form metallic copper. (6) The remaining zinc metal is removed by treatment with hydrochloric acid, and metallic copper is filtered, dried, and weighed. (a) Write a balanced equation for each step and classify the reactions. (b) Assuming that a student started with 65.6 g of copper, calculate the theoretical yield at each step. (c) Considering the nature of the steps, comment on why it is possible to recover most of the copper used at the start.
- 4.162** A quantity of 25.0 mL of a solution containing both Fe^{2+} and Fe^{3+} ions is titrated with 23.0 mL of 0.0200 M KMnO_4 (in dilute sulfuric acid). As a result, all of the Fe^{2+} ions are oxidized to Fe^{3+} ions. Next, the solution is treated with Zn metal to convert all of the Fe^{3+} ions to Fe^{2+} ions. Finally, the solution containing only the Fe^{2+} ions requires 40.0 mL of the same KMnO_4 solution for oxidation to Fe^{3+} . Calculate the molar concentrations of Fe^{2+} and Fe^{3+} in the original solution. The net ionic equation is



- 4.163** Use the periodic table framework provided to show the names and positions of two metals that can displace hydrogen from (a) cold water, (b) steam, and (c) acid. Also show two metals that can react neither with water nor acid.



- 4.164** Referring to the Chemistry in Action essay in Section 4.8, answer the following questions: (a) Identify the precipitation, acid-base, and redox processes. (b) Instead of calcium oxide, why don't we simply add sodium hydroxide to seawater to precipitate magnesium hydroxide? (c) Sometimes a mineral called dolomite (a mixture of CaCO_3 and MgCO_3) is substituted for limestone to bring about the precipitation of magnesium hydroxide. What is the advantage of using dolomite?
- 4.165** A 22.02-mL solution containing 1.615 g $\text{Mg}(\text{NO}_3)_2$ is mixed with a 28.64-mL solution containing 1.073 g NaOH. Calculate the concentrations of the ions remaining in solution after the reaction is complete. Assume volumes are additive.
- 4.166** Chemical tests of four metals A, B, C, and D show the following results. (a) Only B and C react with 0.5 M HCl to give H_2 gas. (b) When B is added to a solution containing the ions of the other metals, metallic A, C, and D are formed. (c) A reacts with 6 M HNO_3 but D does not. Arrange the metals in the increasing order as reducing agents. Suggest four metals that fit these descriptions.
- 4.167** The antibiotic gramicidin A can transport Na^+ ions into a certain cell at the rate of $5.0 \times 10^7 \text{ Na}^+$ ions s^{-1} . Calculate the time in seconds to transport enough Na^+ ions to increase its concentration by 8.0×10^{-3} M in a cell whose intracellular volume is 2.0×10^{-10} mL.
- 4.168** Shown are two aqueous solutions containing various ions. The volume of each solution is 600 mL. (a) Write a net ionic equation for the reaction after the solutions are mixed. (b) Calculate the mass of the precipitates formed and the concentrations of the ions in the mixed solution. Treat each sphere as 0.0500 mol.



Interpreting, Modeling & Estimating

- 4.169 Many proteins contain metal ions for structural and/or redox functions. Which of the following metals fit into one or both categories: Ca, Cu, Fe, Mg, Mn, Ni, Zn?
- 4.170 The fastest way to introduce therapeutic agents into the bloodstream is by direct delivery into a vein [intravenous (IV) therapy]. A clinical researcher wishes to establish an initial concentration of 6×10^{-4} mmol/L in the bloodstream of an adult male participating in a trial study of a new drug. The drug serum is prepared in the hospital's pharmacy at a concentration of 1.2×10^{-3} mol/L. How much of the serum should be introduced intravenously in order to achieve the desired initial blood concentration of the drug?
- 4.171 Public water supplies are often "fluoridated" by the addition of compounds such as NaF, H₂SiF₆, and Na₂SiF₆. It is well established that fluoride helps prevent tooth decay; however, care must be taken not to exceed safe levels of fluoride, which can stain or etch tooth enamel (dental fluorosis). A safe and effective concentration of fluoride in drinking water is generally considered to be around 1 mg/L. How much fluoride would a person consume by drinking fluoridated water in 1 year? What would be the equivalent mass as sodium fluoride?
- 4.172 Potassium superoxide (KO₂), a useful source of oxygen employed in breathing equipment, reacts with water to form potassium hydroxide, hydrogen peroxide, and oxygen. Furthermore, potassium superoxide also reacts with carbon dioxide to form potassium carbonate and oxygen. (a) Write equations for these two reactions and comment on the effectiveness of potassium superoxide in this application. (b) Focusing only on the reaction between KO₂ and CO₂, estimate the amount of KO₂ needed to sustain a worker in a polluted environment for 30 minutes. See Problem 1.71 for useful information.

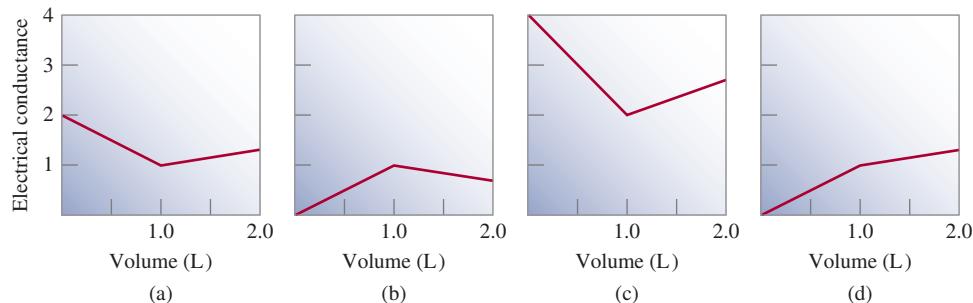


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- 4.173 Muriatic acid, a commercial-grade hydrochloric acid used for cleaning masonry surfaces, is typically around 10 percent HCl by mass and has a density of 1.2 g/cm³. A 0.5-in layer of boiler scale has accumulated on a 6.0-ft section of hot water pipe with an internal diameter of 2.0 in (see the Chemistry in Action essay in Section 4.8). What is the minimum volume of muriatic acid in gallons that would be needed to remove the boiler scale?
- 4.174 Because acid-base and precipitation reactions discussed in this chapter all involve ionic species, their progress can be monitored by measuring the electrical conductance of the solution. Match the following reactions with diagrams (a)–(d). The electrical conductance is shown in arbitrary units.
- (1) A 1.0 M KOH solution is added to 1.0 L of 1.0 M CH₃COOH.

- (2) A 1.0 M NaOH solution is added to 1.0 L of 1.0 M HCl.
 (3) A 1.0 M BaCl₂ solution is added to 1.0 L of 1.0 M K₂SO₄.

- (4) A 1.0 M NaCl solution is added to 1.0 L of 1.0 M AgNO₃.
 (5) A 1.0 M CH₃COOH solution is added to 1.0 L of 1.0 M NH₃.



Answers to Practice Exercises

4.1 (a) Insoluble, (b) insoluble, (c) soluble. **4.2** Al³⁺(aq) + 3OH⁻(aq) → Al(OH)₃(s). **4.3** (a) Brønsted base, (b) Brønsted acid. **4.4** Molecular equation: H₃PO₄(aq) + 3NaOH(aq) → Na₃PO₄(aq) + 3H₂O(l); ionic equation: H₃PO₄(aq) + 3Na⁺(aq) + 3OH⁻(aq) → 3Na⁺(aq) + PO₄³⁻(aq) + 3H₂O(l); net ionic equation: H₃PO₄(aq) +

3OH⁻(aq) → PO₄³⁻(aq) + 3H₂O(l). **4.5** (a) P: +3, F: -1; (b) Mn: +7, O: -2. **4.6** (a) Hydrogen displacement reaction, (b) combination reaction, (c) disproportionation reaction, (d) metal displacement reaction. **4.7** 0.452 M. **4.8** 494 mL. **4.9** Dilute 34.2 mL of the stock solution to 200 mL. **4.10** 92.02%. **4.11** 0.3822 g. **4.12** 1.27 M. **4.13** 204 mL.

Answers to Review of Concepts & Facts

4.1.1 Strongest (b), weakest (c). **4.1.2** (a) Strong electrolyte, (b) strong electrolyte, (c) nonelectrolyte. **4.2.1** (a). **4.2.2** (a) Soluble, (b) insoluble, (c) soluble. **4.2.3** Cu²⁺(aq) + S²⁻(aq) → CuS(s). **4.3.1** Weak acid (b), very weak acid (c), strong acid (a). **4.3.2** Brønsted acid: HBr, Brønsted base: NH₃. **4.3.3** H⁺(aq) + OH⁻(aq) → H₂O(l). **4.4.1** (c). **4.4.2** (a) +4, (b) +2, (c) +3. **4.5.1** 0.9 M.

4.5.2 6.88 × 10⁻³ mol. **4.5.3** 76.9 g. **4.6.1** 9.47 g. **4.7.1** HCl (c), H₂SO₄ (d), H₃PO₄ (b). **4.7.2** 43.0 mL. **4.8.1** Not necessarily. The equivalence point will be reached when an equal volume of oxidizing agent is added only if the reducing agent and the oxidizing agent have the same coefficients in the balanced chemical equation for the redox reaction. **4.8.2** 0.1264 M.

CHEMICAL MYSTERY

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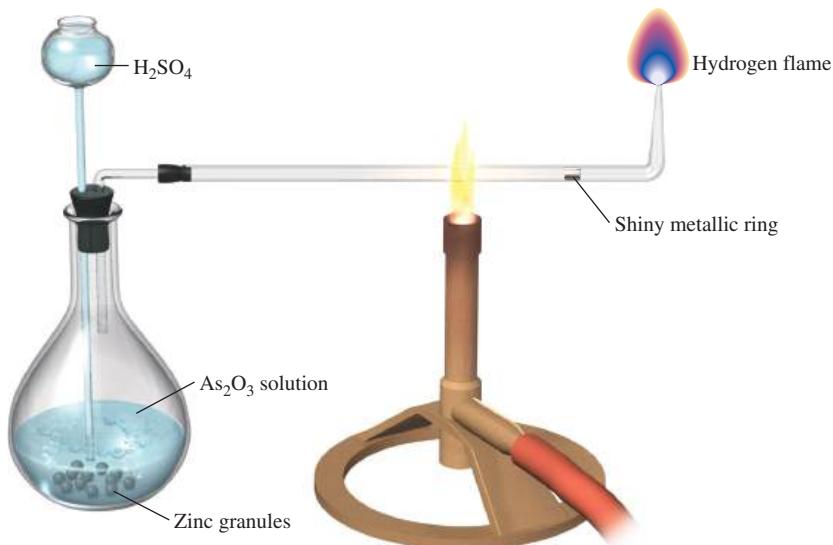
Who Killed Napoleon?

After his defeat at Waterloo in 1815, Napoleon was exiled to St. Helena, a small island in the Atlantic Ocean, where he spent the last six years of his life. In the 1960s, samples of his hair were analyzed and found to contain a high level of arsenic, suggesting that he might have been poisoned. The prime suspects are the governor of St. Helena, with whom Napoleon did not get along, and the French royal family, who wanted to prevent his return to France.

Elemental arsenic is not that harmful. The commonly used poison is actually arsenic(III) oxide, As_2O_3 , a white compound that dissolves in water, is tasteless, and, if administered over a period of time, is hard to detect. It was once known as the “inheritance powder,” because it could be added to grandfather’s wine to hasten his demise so that his grandson could inherit the estate!

In 1832 the English chemist James Marsh devised a procedure for detecting arsenic. This test, which now bears Marsh’s name, combines hydrogen formed by the reaction between zinc and sulfuric acid with a sample of the suspected poison. If As_2O_3 is present, it reacts with hydrogen to form a toxic gas, arsine (AsH_3). When arsine gas is heated, it decomposes to form arsenic, which is recognized by its metallic luster. The Marsh test is an effective deterrent to murder by As_2O_3 , but it was invented too late to do Napoleon any good, if, in fact, he was a victim of deliberate arsenic poisoning.

Apparatus for Marsh’s test. Sulfuric acid is added to zinc metal and a solution containing arsenic(III) oxide. The hydrogen produced reacts with As_2O_3 to yield arsine (AsH_3). On heating, arsine decomposes to elemental arsenic, which has a metallic appearance, and hydrogen gas.



Doubts about the conspiracy theory of Napoleon's death developed in the early 1990s, when a sample of the wallpaper from his drawing room was found to contain copper arsenite (CuHAsO_4), a green pigment that was commonly used at the time Napoleon lived. It has been suggested that the damp climate on St. Helena promoted the growth of molds on the wallpaper. To rid themselves of arsenic, the molds could have converted it to trimethyl arsenine [$(\text{CH}_3)_3\text{As}$], which is a volatile and highly poisonous compound. Prolonged exposure to these vapors would have ruined Napoleon's health and would also account for the presence of arsenic in his body, though it may not have been the primary cause of his death. This provocative theory is supported by the fact that Napoleon's regular guests suffered from gastrointestinal disturbances and other symptoms of arsenic poisoning and that their health all seemed to improve whenever they spent hours working outdoors in the garden, their main hobby on the island.

We will probably never know whether Napoleon died from arsenic poisoning, intentional or accidental, but this exercise in historical sleuthing provides a fascinating example of the use of chemical analysis. Not only is chemical analysis used in forensic science, but it also plays an essential part in endeavors ranging from pure research to practical applications, such as quality control of commercial products and medical diagnosis.

Chemical Clues

1. The arsenic in Napoleon's hair was detected using a technique called *neutron activation*. When As-75 is bombarded with high-energy neutrons, it is converted to the radioactive As-76 isotope. The energy of the γ rays emitted by the radioactive isotope is characteristic of arsenic, and the intensity of the rays establishes how much arsenic is present in a sample. With this technique, as little as 5 ng (5×10^{-9} g) of arsenic can be detected in 1 g of material. (a) Write symbols for the two isotopes of As, showing mass number and atomic number. (b) Name two advantages of analyzing the arsenic content by neutron activation instead of a chemical analysis.
2. Arsenic is not an essential element for the human body. (a) Based on its position in the periodic table, suggest a reason for its toxicity. (b) In addition to hair, where else might one look for the accumulation of the element if arsenic poisoning is suspected?
3. The Marsh test for arsenic involves the following steps: (a) the generation of hydrogen gas when sulfuric acid is added to zinc, (b) the reaction of hydrogen with As(III) oxide to produce arsine, and (c) the conversion of arsine to arsenic by heating. Write equations representing these steps and identify the type of the reaction in each step.



A lock of Napoleon's hair.
©Dirck Halstead

CHAPTER

5



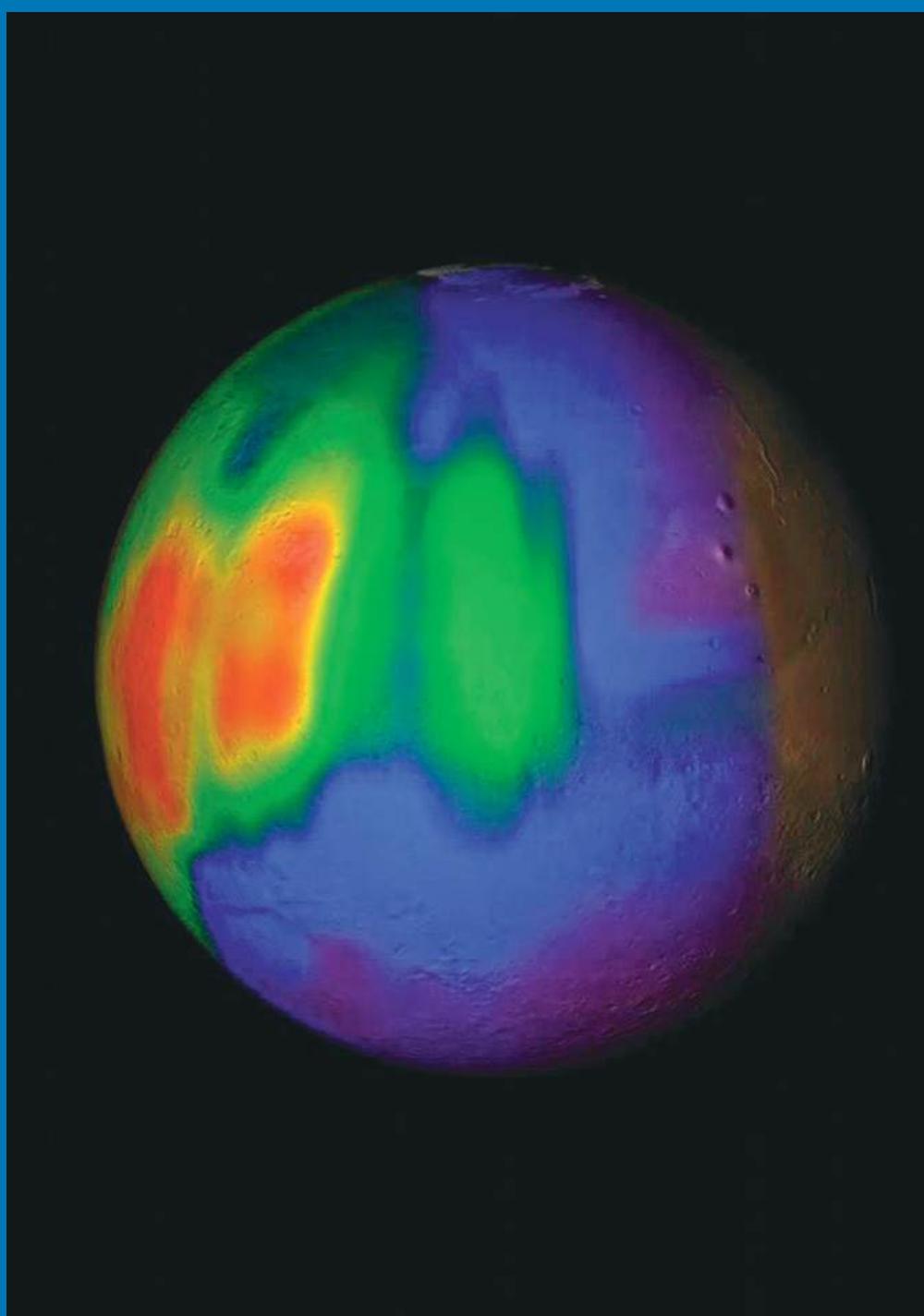
Water vapor and methane have recently been detected in significant amounts in the Martian atmosphere. (The concentration increases from purple to red.) The methane could be released by geothermal activity, or it could be produced by bacteria, fueling speculation that there may be life on Mars.

Source: NASA

CHAPTER OUTLINE

- 5.1** Substances That Exist as Gases
- 5.2** Pressure of a Gas
- 5.3** The Gas Laws
- 5.4** The Ideal Gas Equation
- 5.5** Gas Stoichiometry
- 5.6** Dalton's Law of Partial Pressures
- 5.7** The Kinetic Molecular Theory of Gases
- 5.8** Deviation from Ideal Behavior

Gases



A LOOK AHEAD

- ▶ We begin by examining the substances that exist as gases and their general properties. (5.1)
- ▶ We learn units for expressing gas pressure and the characteristics of atmospheric pressure. (5.2)
- ▶ Next, we study the relationship among pressure, volume, temperature, and amount of a gas in terms of various gas laws. We will see that these laws can be summarized by the ideal gas equation, which can be used to calculate the density or molar mass of a gas. (5.3 and 5.4)
- ▶ We will see that the ideal gas equation can be used to study the stoichiometry involving gases. (5.5)
- ▶ We learn that the behavior of a mixture of gases can be understood by Dalton's law of partial pressures, which is an extension of the ideal gas equation. (5.6)
- ▶ We will see how the kinetic molecular theory of gases, which is based on the properties of individual molecules, can be used to describe macroscopic properties such as the pressure and temperature of a gas. We learn that this theory enables us to obtain an expression for the speed of molecules at a given temperature, and understand phenomena such as gas diffusion and effusion. (5.7)
- ▶ Lastly, we will study the correction for the nonideal behavior of gases using the van der Waals equation. (5.8)

Under certain conditions of pressure and temperature, most substances can exist in any one of three states of matter: solid, liquid, or gas. Water, for example, can be solid ice, liquid water, steam, or water vapor. The physical properties of a substance often depend on its state.

Gases, the subject of this chapter, are simpler than liquids and solids in many ways. Molecular motion in gases is totally random, and the forces of attraction between gas molecules are so small that each molecule moves freely and essentially independently of other molecules. Subjected to changes in temperature and pressure, it is easier to predict the behavior of gases. The laws that govern this behavior have played an important role in the development of the atomic theory of matter and the kinetic molecular theory of gases.

5.1 Substances That Exist as Gases

We live at the bottom of an ocean of air whose composition by volume is roughly 78 percent N₂, 21 percent O₂, and 1 percent other gases, including CO₂. Today, the chemistry of this vital mixture of gases has become a source of great interest because of the detrimental effects of environmental pollution. The chemistry of the atmosphere and polluting gases is discussed in Chapter 20. Here we will focus generally on the behavior of substances that exist as gases under normal atmospheric conditions, which are defined as 25°C and 1 atmosphere (atm) pressure.

Figure 5.1 shows the elements that are gases under normal atmospheric conditions. Note that hydrogen, nitrogen, oxygen, fluorine, and chlorine exist as gaseous diatomic molecules: H₂, N₂, O₂, F₂, and Cl₂. An allotrope of oxygen, ozone (O₃), is also a gas at room temperature. All the elements in Group 8A, the noble gases, are monatomic gases: He, Ne, Ar, Kr, Xe, and Rn.

Ionic compounds do not exist as gases at 25°C and 1 atm, because cations and anions in an ionic solid are held together by very strong electrostatic forces—that is, forces between positive and negative charges. To overcome these attractions we must apply a large amount of energy, which in practice means strongly heating the solid. Under normal conditions, all we can do is melt the solid; for example, NaCl melts at the rather high temperature of 801°C. To boil it, we would have to raise the temperature to well above 1000°C.

1A																8A	
H		2A															He
Li	Be																F
Na	Mg															Ar	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og

Figure 5.1 Elements that exist as gases at 25°C and 1 atm. The noble gases (the Group 8A elements) are monatomic species; the other elements exist as diatomic molecules. Ozone (O_3) is also a gas.

Although “gas” and “vapor” are often used interchangeably, there is a difference. A gas is a substance that is normally in the gaseous state at ordinary temperatures and pressures; a vapor is the gaseous form of any substance that is a liquid or a solid at normal temperatures and pressures. Thus, at 25°C and 1 atm pressure, we speak of water vapor and oxygen gas.

The behavior of molecular compounds is more varied. Some—for example, CO, CO_2 , HCl, NH_3 , and CH_4 (methane)—are gases, but the majority of molecular compounds are liquids or solids at room temperature. However, on heating they are converted to gases much more easily than ionic compounds. In other words, molecular compounds usually boil at much lower temperatures than ionic compounds do. There is no simple rule to help us determine whether a certain molecular compound is a gas under normal atmospheric conditions. To make such a determination we need to understand the nature and magnitude of the attractive forces among the molecules, called *intermolecular forces* (discussed in Chapter 11). In general, the stronger these attractions, the less likely a compound can exist as a gas at ordinary temperatures.

Of the gases listed in Table 5.1, only O_2 is essential for our survival. Hydrogen sulfide (H_2S) and hydrogen cyanide (HCN) are deadly poisons. Several others, such as

Table 5.1 Some Substances Found as Gases at 1 atm and 25°C

Elements

H_2 (molecular hydrogen)	N_2 (molecular nitrogen)
O_2 (molecular oxygen)	O_3 (ozone)
F_2 (molecular fluorine)	Cl_2 (molecular chlorine)
He (helium)	Ne (neon)
Ar (argon)	Kr (krypton)
Xe (xenon)	Rn (radon)

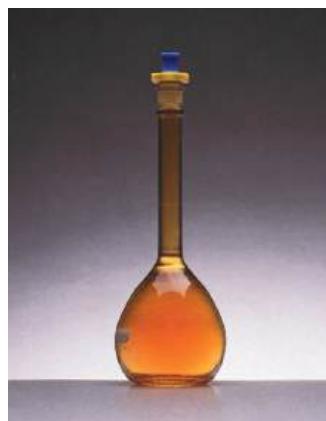
Compounds

HF (hydrogen fluoride)	HCl (hydrogen chloride)
HBr (hydrogen bromide)	HI (hydrogen iodide)
CO (carbon monoxide)	CO_2 (carbon dioxide)
CH_4 (methane)	C_2H_2 (acetylene)
NH_3 (ammonia)	NO (nitric oxide)
NO_2 (nitrogen dioxide)	N_2O (nitrous oxide)
SO_2 (sulfur dioxide)	SF_6 (sulfur hexafluoride)
H_2S (hydrogen sulfide)	HCN (hydrogen cyanide)*

*The boiling point of HCN is 26°C, but it is close enough to qualify as a gas at ordinary atmospheric conditions.

CO, NO₂, O₃, and SO₂, are somewhat less toxic. The gases He, Ne, and Ar are chemically inert; that is, they do not react with any other substance. Most gases are colorless. Exceptions are F₂, Cl₂, and NO₂. The dark brown color of NO₂ is sometimes visible in polluted air. All gases have the following physical characteristics:

- Gases assume the volume and shape of their containers.
- Gases are the most compressible of the states of matter.
- Gases will mix evenly and completely when confined to the same container.
- Gases have much lower densities than liquids and solids.



NO₂ gas.
©McGraw-Hill Education/Ken Karp

5.2 Pressure of a Gas

Gases exert pressure on any surface or container with which they come in contact, because gas particles are constantly in motion. We humans have adapted so well physiologically to the pressure of the air around us that we are usually unaware of it, perhaps as fish are not conscious of the water's pressure on them.

It is easy to demonstrate atmospheric pressure. One everyday example is the ability to drink a liquid through a straw. Sucking air out of the straw reduces the pressure inside the straw. The greater atmospheric pressure on the liquid pushes it up into the straw to replace the air that has been sucked out.

SI Units of Pressure

Pressure is one of the most readily measurable properties of a gas. In order to understand how we measure the pressure of a gas, it is helpful to know how the units of measurement are derived. We begin with velocity and acceleration.

Velocity is defined as the change in distance with elapsed time; that is,

$$\text{velocity} = \frac{\text{distance moved}}{\text{elapsed time}}$$

The SI unit for velocity is m/s, although we also use cm/s.

Acceleration is the change in velocity with time, or

$$\text{acceleration} = \frac{\text{change in velocity}}{\text{elapsed time}}$$

Acceleration is measured in m/s² (or cm/s²).

The second law of motion, formulated by Sir Isaac Newton[†] in the late seventeenth century, defines another *force*, from which the units of pressure are derived. According to this law,

$$\text{force} = \text{mass} \times \text{acceleration}$$

In this context, the *SI unit of force* is the **newton (N)**, where

$$1 \text{ N} = 1 \text{ kg m/s}^2$$

1 N is roughly equivalent to the force exerted by Earth's gravity on an apple.

Finally, we define **pressure** as *force applied per unit area*.

$$\text{pressure} = \frac{\text{force}}{\text{area}}$$

[†]Sir Isaac Newton (1642–1726). English mathematician, physicist, and astronomer. Newton is regarded by many as one of the two greatest physicists the world has known (the other is Albert Einstein). There was hardly a branch of physics to which Newton did not make a significant contribution. His book *Principia*, published in 1687, marks a milestone in the history of science.

The SI unit of pressure is the **pascal (Pa)**,[‡] defined as *one newton per square meter*.

$$1 \text{ Pa} = 1 \text{ N/m}^2$$

Atmospheric Pressure

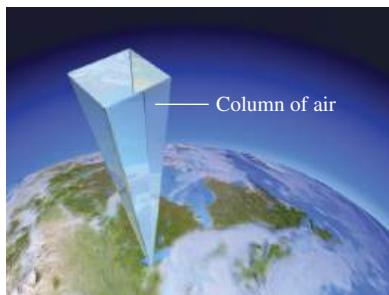


Figure 5.2 A column of air extending from sea level to the upper atmosphere.

The atoms and molecules of the gases in the atmosphere, like those of all other matter, are subject to Earth's gravitational pull. As a consequence, the atmosphere is much denser near the surface of Earth than at high altitudes. (The air outside the pressurized cabin of an airplane at 9 km is too thin to breathe.) In fact, the density of air decreases very rapidly with increasing distance from Earth. Measurements show that about 50 percent of the atmosphere lies within 6.4 km of Earth's surface, 90 percent within 16 km, and 99 percent within 32 km. Not surprisingly, the denser the air is, the greater the pressure it exerts. The force experienced by any area exposed to Earth's atmosphere is equal to *the weight of the column of air above it*. **Atmospheric pressure** is the pressure exerted by Earth's atmosphere (Figure 5.2). The actual value of atmospheric pressure depends on location, temperature, and weather conditions.

Does atmospheric pressure act only downward, as you might infer from its definition? Imagine what would happen, then, if you were to hold a piece of paper tight (with both hands) above your head. You might expect the paper to bend due to the pressure of air acting on it, but this does not happen. The reason is that air, like water, is a fluid. The pressure exerted on an object in a fluid comes from all directions—downward and upward, as well as from the left and from the right. At the molecular level, air pressure results from collisions between the air molecules and any surface with which they come in contact. The magnitude of pressure depends on how often and how strongly the molecules impact the surface. It turns out that there are just as many molecules hitting the paper from the top as there are from underneath, so the paper stays flat.

How is atmospheric pressure measured? The **barometer** is probably the most familiar instrument for measuring atmospheric pressure. A simple barometer consists of a long glass tube, closed at one end and filled with mercury. If the tube is carefully inverted in a dish of mercury so that no air enters the tube, some mercury will flow out of the tube into the dish, creating a vacuum at the top (Figure 5.3). The weight of the mercury remaining in the tube is supported by atmospheric pressure acting on the surface of the mercury in the dish.

Standard atmospheric pressure (1 atm) is equal to *the pressure that supports a column of mercury exactly 760 mm (or 76 cm) high at 0°C at sea level*. In other words, the standard atmosphere equals a pressure of 760 mmHg, where mmHg represents the pressure exerted by a column of mercury 1 mm high. The mmHg unit is also called the **torr**, after the Italian scientist Evangelista Torricelli,[†] who invented the barometer. Thus,

$$1 \text{ torr} = 1 \text{ mmHg}$$

and

$$1 \text{ atm} = 760 \text{ mmHg} \text{ (exactly)}$$

The relation between atmospheres and pascals (see Appendix 1) is

$$\begin{aligned} 1 \text{ atm} &= 101,325 \text{ Pa} \\ &= 1.01325 \times 10^5 \text{ Pa} \end{aligned}$$

and because $1000 \text{ Pa} = 1 \text{ kPa}$ (kilopascal)

$$1 \text{ atm} = 1.01325 \times 10^2 \text{ kPa}$$

Examples 5.1 and 5.2 show the conversion from mmHg to atm and kPa.

[‡]Blaise Pascal (1623–1662). French mathematician and physicist. Pascal's work ranged widely in mathematics and physics, but his specialty was in the area of hydrodynamics (the study of the motion of fluids). He also invented a calculating machine.

[†]Evangelista Torricelli (1608–1674). Italian mathematician. Torricelli was supposedly the first person to recognize the existence of atmospheric pressure.

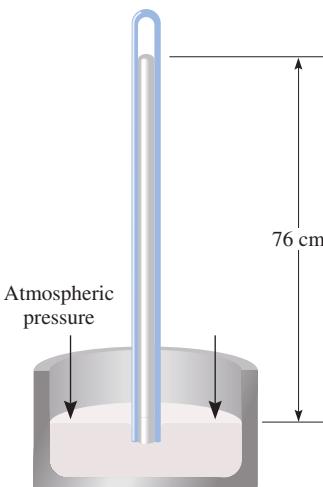


Figure 5.3 A barometer for measuring atmospheric pressure. Above the mercury in the tube is a vacuum. The column of mercury is supported by the atmospheric pressure.

Example 5.1

The pressure outside a jet plane flying at high altitude falls considerably below standard atmospheric pressure. Therefore, the air inside the cabin must be pressurized to protect the passengers. What is the pressure in atmospheres in the cabin if the barometer reading is 688 mmHg?

Strategy Because 1 atm = 760 mmHg, the following conversion factor is needed to obtain the pressure in atmospheres:

$$\frac{1 \text{ atm}}{760 \text{ mmHg}}$$

Solution The pressure in the cabin is given by

$$\begin{aligned} \text{pressure} &= 688 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} \\ &= 0.905 \text{ atm} \end{aligned}$$

Practice Exercise Convert 749 mmHg to atmospheres.

Similar problem: 5.13.

Example 5.2

Hurricane Sandy (“Superstorm Sandy”) was one of the most destructive hurricanes in recent years, affecting the Caribbean, Cuba, the Bahamas, and 24 states along the U.S. east coast. The lowest pressure recorded for Hurricane Sandy was 705 mmHg. What was the pressure in kPa?

Strategy Here we are asked to convert mmHg to kPa. Because

$$1 \text{ atm} = 1.01325 \times 10^5 \text{ Pa} = 760 \text{ mmHg}$$

the conversion factor we need is

$$\frac{1.01325 \times 10^5 \text{ Pa}}{760 \text{ mmHg}}$$

Solution The pressure in kPa is

$$\begin{aligned} \text{pressure} &= 705 \text{ mmHg} \times \frac{1.01325 \times 10^5 \text{ Pa}}{760 \text{ mmHg}} \\ &= 9.40 \times 10^4 \text{ Pa} \\ &= 94.0 \text{ kPa} \end{aligned}$$

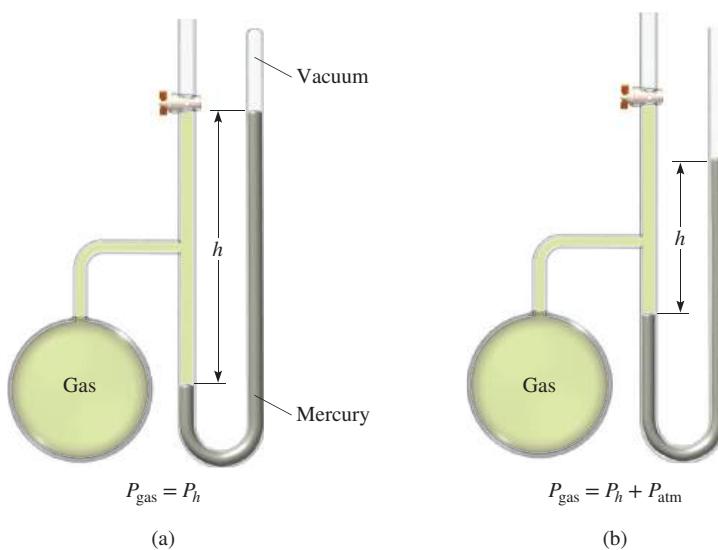
Practice Exercise Convert 295 mmHg to kilopascals.

Similar problem: 5.14.

A **manometer** is a device used to measure the pressure of gases other than the atmosphere. The principle of operation of a manometer is similar to that of a barometer. There are two types of manometers, shown in Figure 5.4. The *closed-tube manometer* is normally used to measure pressures below atmospheric pressure [Figure 5.4(a)], whereas the *open-tube manometer* is better suited for measuring pressures equal to or greater than atmospheric pressure [Figure 5.4(b)].

Nearly all barometers and many manometers use mercury as the working fluid, despite the fact that it is a toxic substance with a harmful vapor. The reason is that mercury has a very high density (13.6 g/mL) compared with most other liquids. Because the

Figure 5.4 Two types of manometers used to measure gas pressures. (a) Gas pressure may be less or greater than atmospheric pressure. (b) Gas pressure is greater than atmospheric pressure.



height of the liquid in a column is inversely proportional to the liquid's density, this property enables the construction of manageable small barometers and manometers.

Review of Concepts & Facts

- 5.2.1 Express 1184 torr in units of mmHg, atm, and kPa.
- 5.2.2 Rank the following pressures from lowest to highest: (a) 736 mmHg, (b) 0.928 atm, (c) 728 torr, (d) 1.12×10^5 Pa.
- 5.2.3 Would it be easier to drink water with a straw on top or at the foot of Mt. Everest?

5.3 The Gas Laws

The gas laws we will study in this chapter are the product of countless experiments on the physical properties of gases that were carried out over several centuries. Each of these generalizations regarding the macroscopic behavior of gaseous substances represents a milestone in the history of science. Together they have played a major role in the development of many ideas in chemistry.

The Pressure-Volume Relationship: Boyle's Law

Video
The Gas Laws

In the seventeenth century, Robert Boyle[†] studied the behavior of gases systematically and quantitatively. In one series of studies, Boyle investigated the pressure-volume relationship of a gas sample. Typical data collected by Boyle are shown in Table 5.2. Note that as the pressure (P) is increased at constant temperature, the volume (V) occupied by a given amount of gas decreases. Compare the first data point with a pressure of 724 mmHg and a volume of 1.50 (in arbitrary unit) to the last data point with a pressure of 2250 mmHg and a volume of 0.58. Clearly there is an inverse relationship between pressure and volume of a gas at constant temperature. As the pressure is increased, the volume occupied by the gas decreases. Conversely, if the applied pressure is decreased, the volume the gas occupies increases. This relationship is now known as **Boyle's law**, which states that *the pressure of a fixed amount of gas at a constant temperature is inversely proportional to the volume of the gas*.

[†]Robert Boyle (1627–1691). British chemist and natural philosopher. Although Boyle is commonly associated with the gas law that bears his name, he made many other significant contributions in chemistry and physics. Despite the fact that Boyle was often at odds with scientists of his generation, his book *The Skeptical Chymist* (1661) influenced generations of chemists.

Table 5.2 Typical Pressure-Volume Relationship Obtained by Boyle

P (mmHg)	724	869	951	998	1230	1893	2250
V (arbitrary units)	1.50	1.33	1.22	1.18	0.94	0.61	0.58
PV	1.09×10^3	1.16×10^3	1.16×10^3	1.18×10^3	1.2×10^3	1.2×10^3	1.3×10^3

The apparatus used by Boyle in this experiment was very simple (Figure 5.5). In Figure 5.5(a), the pressure exerted on the gas is equal to atmospheric pressure and the volume of the gas is 100 mL. (Note that the tube is open at the top and is therefore exposed to atmospheric pressure.) In Figure 5.5(b), more mercury has been added to double the pressure on the gas, and the gas volume decreases to 50 mL. Tripling the pressure on the gas decreases its volume to a third of the original value [Figure 5.5(c)].

We can write a mathematical expression showing the inverse relationship between pressure and volume:

$$P \propto \frac{1}{V}$$

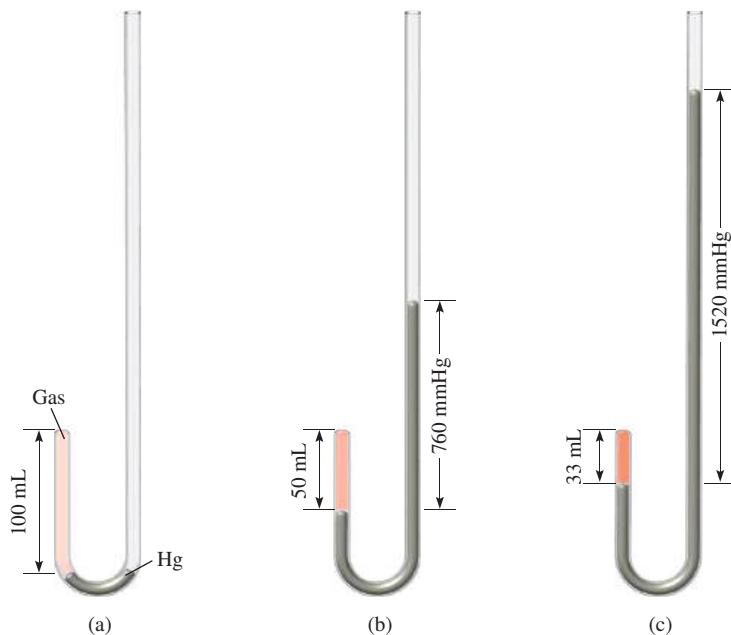
where the symbol \propto means *proportional to*. We can change \propto to an equals sign and write

$$P = k_1 \times \frac{1}{V} \quad (5.1a)$$

where k_1 is a constant called the *proportionality constant*. Equation (5.1a) is the mathematical expression of Boyle's law. We can rearrange Equation (5.1a) and obtain

$$PV = k_1 \quad (5.1b)$$

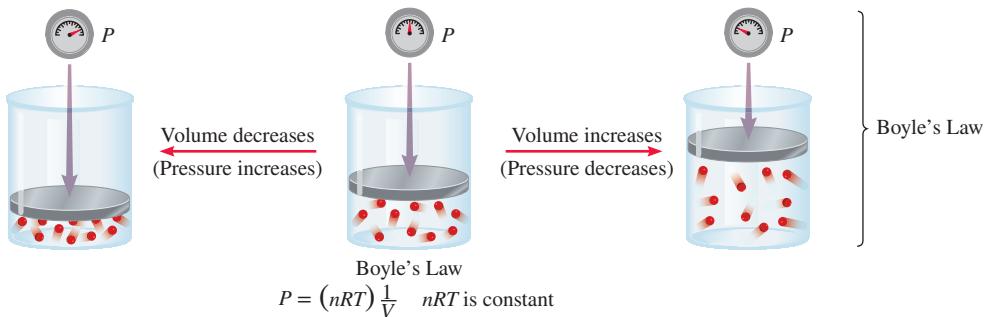
This form of Boyle's law says that the product of the pressure and volume of a gas at constant temperature and amount of gas is a constant. The top diagram in Figure 5.6 is a schematic representation of Boyle's law. The quantity n is the number of moles of the gas and R is a constant, to be defined in Section 5.4. We will see there that the proportionality constant k_1 in Equation (5.1) is equal to nRT .



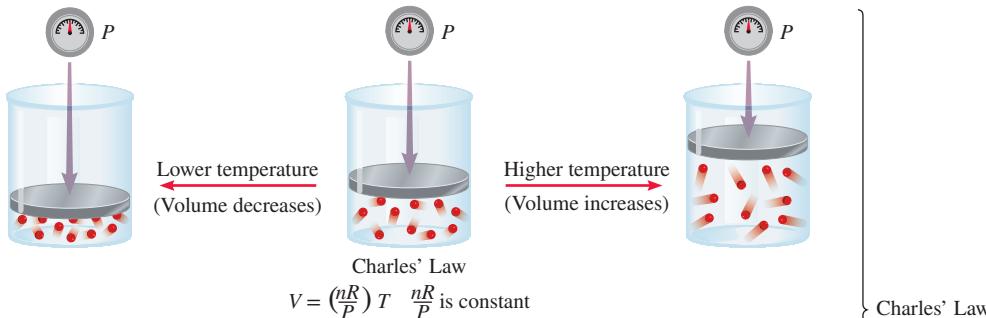
The pressure applied to a gas is equal to the gas pressure.

Figure 5.5 Apparatus for studying the relationship between pressure and volume of a gas. (a) The levels of mercury are equal and the pressure of the gas is equal to the atmospheric pressure (760 mmHg). The gas volume is 100 mL. (b) Doubling the pressure by adding more mercury reduces the gas volume to 50 mL. (c) Tripling the pressure decreases the gas volume to one-third of the original value. The temperature and amount of gas are kept constant.

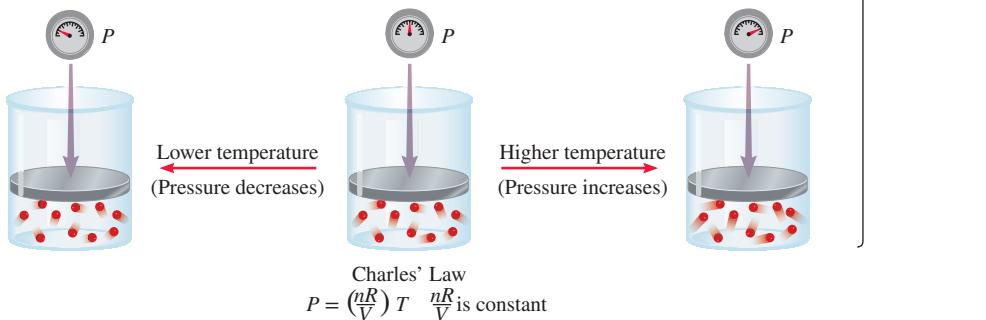
Increasing or decreasing the volume of a gas at a constant temperature



Heating or cooling a gas at constant pressure



Heating or cooling a gas at constant volume



Dependence of volume on amount of gas at constant temperature and pressure

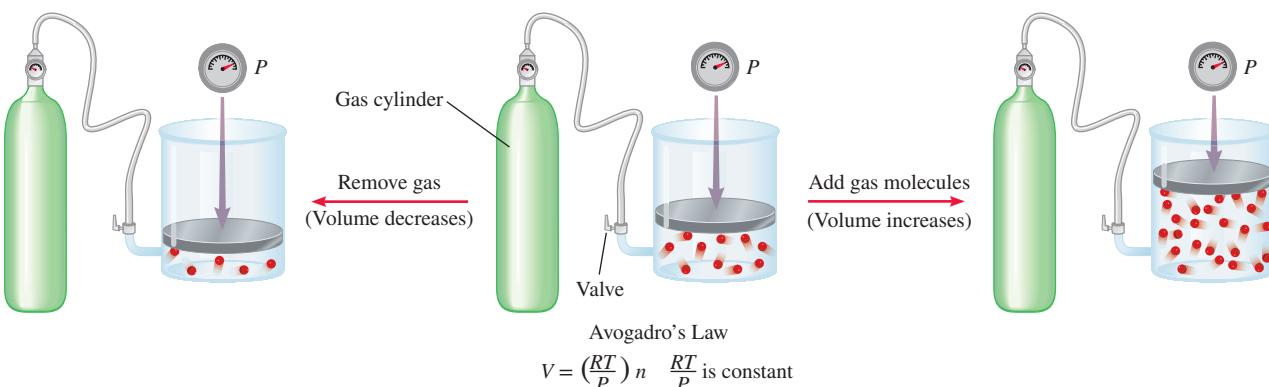


Figure 5.6 Schematic illustrations of Boyle's law, Charles' law, and Avogadro's law.

The concept of one quantity being proportional to another and the use of a proportionality constant can be clarified through the following analogy. The daily income of a movie theater depends on both the price of the tickets (in dollars per ticket) and the number of tickets sold. Assuming that the theater charges one price for all tickets, we write

$$\text{income} = (\text{dollar/ticket}) \times \text{number of tickets sold}$$

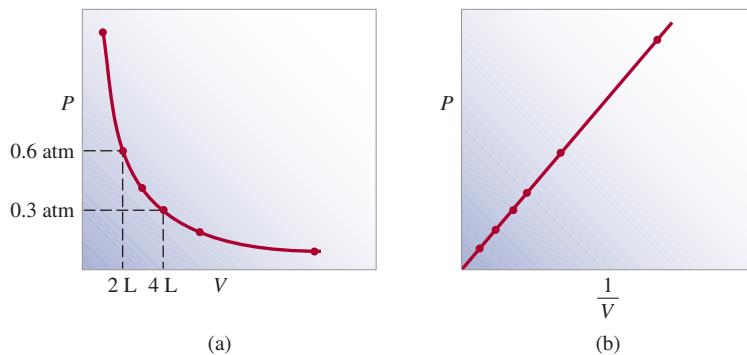


Figure 5.7 Graphs showing variation of the volume of a gas with the pressure exerted on the gas, at constant temperature. (a) P versus V . Note that the volume of the gas doubles as the pressure is halved. (b) P versus $1/V$. The slope of the line is equal to k_1 .

Because the number of tickets sold varies from day to day, the income on a given day is said to be proportional to the number of tickets sold; that is

$$\begin{aligned} \text{income} &\propto \text{number of tickets sold} \\ &= C \times \text{number of tickets sold} \end{aligned}$$

where C , the proportionality constant, is the price per ticket.

Figure 5.7 shows two conventional ways of expressing Boyle's findings graphically. Figure 5.7(a) is a graph of the equation $PV = k_1$; Figure 5.7(b) is a graph of the equivalent equation $P = k_1 \times 1/V$. Note that the latter is a linear equation of the form $y = mx + b$, where $b = 0$ and $m = k_1$.

Although the individual values of pressure and volume can vary greatly for a given sample of gas, as long as the temperature is held constant and the amount of the gas does not change, P times V is always equal to the same constant. Therefore, for a given sample of gas under two different sets of conditions at constant temperature, we have

$$\begin{aligned} P_1V_1 &= k_1 = P_2V_2 \\ \text{or} \quad P_1V_1 &= P_2V_2 \end{aligned} \tag{5.2}$$

where V_1 and V_2 are the volumes at pressures P_1 and P_2 , respectively.

The Temperature-Volume Relationship: Charles' and Gay-Lussac's Law

Boyle's law depends on the temperature of the system remaining constant. But suppose the temperature changes: How does a change in temperature affect the volume and pressure of a gas? Let us first look at the effect of temperature on the volume of a gas. The earliest investigators of this relationship were French scientists, Jacques Charles[†] and Joseph Gay-Lussac.[‡] Their studies showed that, at constant pressure, the volume of a gas sample increases when heated and decreases when cooled (Figure 5.8). The quantitative relations involved in changes in gas temperature and volume turn out to be remarkably consistent. For example, we observe an interesting phenomenon when we study the temperature-volume relationship at various pressures. At any given pressure, the plot of volume versus temperature yields a straight line. By extending the line to zero volume, we find the intercept on the temperature axis to be -273.15°C . At any other pressure, we obtain a different straight line for the volume-temperature plot, but we get the same zero-volume temperature intercept at -273.15°C (Figure 5.9). (In practice, we can measure the volume of a gas over only a limited temperature range, because all gases condense at low temperatures to form liquids.)

[†]Jacques Alexandre Cesar Charles (1746–1823). French physicist. He was a gifted lecturer, an inventor of scientific apparatus, and the first person to use hydrogen to inflate balloons.

[‡]Joseph Louis Gay-Lussac (1778–1850). French chemist and physicist. Like Charles, Gay-Lussac was a balloon enthusiast. Once he ascended to an altitude of 20,000 ft to collect air samples for analysis.

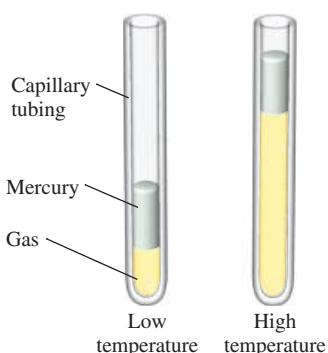
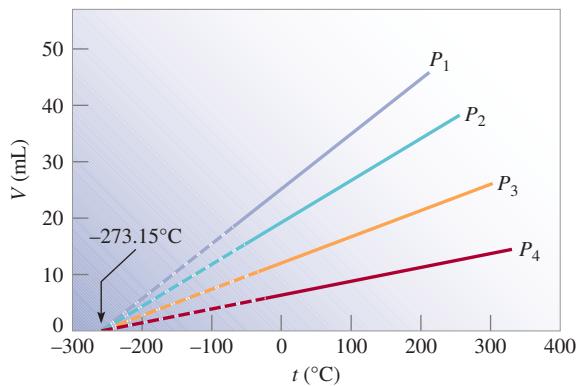


Figure 5.8 Variation of the volume of a gas sample with temperature, at constant pressure. The pressure exerted on the gas is the sum of the atmospheric pressure and the pressure due to the weight of the mercury.

Figure 5.9 Variation of the volume of a gas sample with temperature, at constant pressure. Each line represents the variation at a certain pressure. The pressures increase from P_1 to P_4 . All gases ultimately condense (become liquids) if they are cooled to sufficiently low temperatures; the solid portions of the lines represent the temperature region above the condensation point. When these lines are extrapolated, or extended (the dashed portions), they all intersect at the point representing zero volume and a temperature of -273.15°C .



In 1848 Lord Kelvin[†] realized the significance of this phenomenon. He identified -273.15°C as **absolute zero**, *theoretically the lowest attainable temperature*. Then he set up an **absolute temperature scale**, now called the **Kelvin temperature scale**, with **absolute zero as the starting point** (see Section 1.7). On the Kelvin scale, one kelvin (K) is equal in magnitude to one degree Celsius. The only difference between the absolute temperature scale and the Celsius scale is that the zero position is shifted. Important points on the two scales match up as follows:

	Kelvin Scale	Celsius Scale
Absolute zero	0 K	-273.15°C
Freezing point of water	273.15 K	0°C
Boiling point of water	373.15 K	100°C

Under special experimental conditions, scientists have succeeded in approaching absolute zero to within a small fraction of a kelvin.

The conversion between $^{\circ}\text{C}$ and K is given in Section 1.7. In most calculations we will use 273 instead of 273.15 as the term relating K and $^{\circ}\text{C}$. By convention, we use T to denote absolute (kelvin) temperature and t to indicate temperature on the Celsius scale.

The dependence of the volume of a gas on temperature is given by

$$\begin{aligned}V &\propto T \\V &= k_2 T \\ \text{or} \quad \frac{V}{T} &= k_2\end{aligned}\tag{5.3}$$

Remember that temperature must be in kelvins in gas law calculations.

where k_2 is the proportionality constant. Equation (5.3) is known as **Charles' and Gay-Lussac's law**, or simply **Charles' law**, which states that *the volume of a fixed amount of gas maintained at constant pressure is directly proportional to the absolute temperature of the gas*. Charles' law is also illustrated in Figure 5.6. We see that the proportionality constant k_2 in Equation (5.3) is equal to nR/P .

Just as we did for pressure-volume relationships at constant temperature, we can compare two sets of volume-temperature conditions for a given sample of gas at constant pressure. From Equation (5.3) we can write

$$\frac{V_1}{T_1} = k_2 = \frac{V_2}{T_2}$$

$$\text{or} \quad \frac{V_1}{T_1} = \frac{V_2}{T_2}\tag{5.4}$$

where V_1 and V_2 are the volumes of the gas at temperatures T_1 and T_2 (both in kelvins), respectively.

[†]William Thomson, Lord Kelvin (1824–1907). Scottish mathematician and physicist. Kelvin did important work in many branches of physics.

Another form of Charles' law shows that at constant amount of gas and volume, the pressure of a gas is proportional to temperature; that is

$$\begin{aligned} P &\propto T \\ P &= k_3 T \end{aligned}$$

or

$$\frac{P}{T} = k_3 \quad (5.5)$$

From Figure 5.6 we see that $k_3 = nR/V$. Starting with Equation (5.5), we have

$$\frac{P_1}{T_1} = k_3 = \frac{P_2}{T_2}$$

or

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \quad (5.6)$$

where P_1 and P_2 are the pressures of the gas at temperatures T_1 and T_2 , respectively.

The Volume-Amount Relationship: Avogadro's Law

The work of the Italian scientist Amedeo Avogadro complemented the studies of Boyle, Charles, and Gay-Lussac. In 1811 he published a hypothesis stating that at the same temperature and pressure, equal volumes of different gases contain the same number of molecules (or atoms if the gas is monatomic). It follows that the volume of any given gas must be proportional to the number of moles of molecules present; that is,

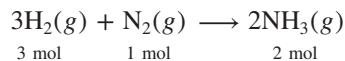
$$V \propto n$$

$$V = k_4 n \quad (5.7)$$

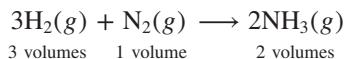
where n represents the number of moles and k_4 is the proportionality constant. Equation (5.7) is the mathematical expression of **Avogadro's law**, which states that *at constant pressure and temperature, the volume of a gas is directly proportional to the number of moles of the gas present*. From Figure 5.6 we see that $k_4 = RT/P$.

Avogadro's name first appeared in Section 3.2.

According to Avogadro's law we see that when two gases react with each other, their reacting volumes have a simple ratio to each other. If the product is a gas, its volume is related to the volume of the reactants by a simple ratio (a fact demonstrated earlier by Gay-Lussac). For example, consider the synthesis of ammonia from molecular hydrogen and molecular nitrogen:

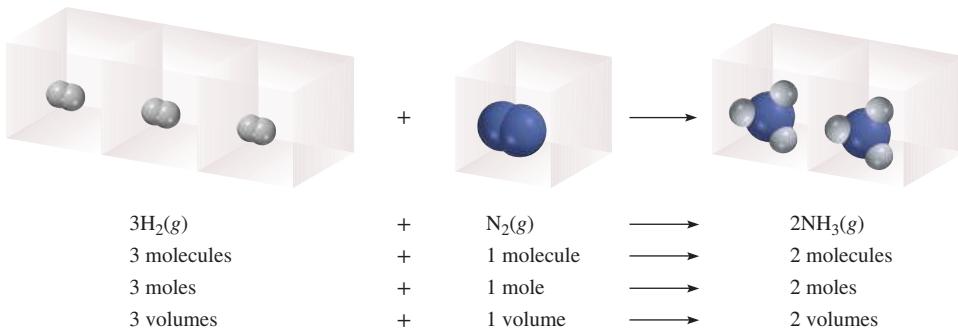


Because, at the same temperature and pressure, the volumes of gases are directly proportional to the number of moles of the gases present, we can now write



The volume ratio of molecular hydrogen to molecular nitrogen is 3:1, and that of ammonia (the product) to the sum of the volumes of molecular hydrogen and molecular nitrogen (the reactants) is 2:4 or 1:2 (Figure 5.10).

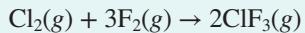
Figure 5.10 Volume relationship of gases in a chemical reaction. The ratio of the volumes of molecular hydrogen to molecular nitrogen is 3:1, and that of ammonia (the product) to molecular hydrogen and molecular nitrogen combined (the reactants) is 2:4, or 1:2.



Worked examples illustrating the gas laws are presented in Section 5.4.

Review of Concepts & Facts

- 5.3.1 A gas occupies a volume of 2.50 L at 375 mmHg. What is the volume of the gas if the pressure is increased to 725 mmHg at constant temperature?
- 5.3.2 Compare the changes in volume when the temperature of a gas is increased at constant pressure from (a) 200 K to 400 K, (b) 200°C to 400°C.
- 5.3.3 What volume of ClF_3 will be produced when 75.0 mL of F_2 reacts with 25.0 mL of Cl_2 according to the following balanced equation?



Assume the pressure and temperature are held constant.

5.4 The Ideal Gas Equation

Let us summarize the gas laws we have discussed so far:

$$\text{Boyle's law: } V \propto \frac{1}{P} \quad (\text{at constant } n \text{ and } T)$$

$$\text{Charles' law: } V \propto T \quad (\text{at constant } n \text{ and } P)$$

$$\text{Avogadro's law: } V \propto n \quad (\text{at constant } P \text{ and } T)$$

We can combine all three expressions to form a single master equation for the behavior of gases:

$$V \propto \frac{nT}{P}$$

$$V = R \frac{nT}{P}$$

or

$$PV = nRT \quad (5.8)$$

Keep in mind that the ideal gas equation, unlike the gas laws discussed in Section 5.3, applies to systems that do not undergo changes in pressure, volume, temperature, and amount of a gas.

where R , the proportionality constant, is called the **gas constant**. Equation (5.8), which is called the **ideal gas equation**, describes the relationship among the four variables P , V , T , and n . An **ideal gas** is a hypothetical gas whose pressure-volume-temperature behavior can be completely accounted for by the ideal gas equation. The molecules of an ideal gas do not attract or repel one another, and their volume is negligible compared with the volume of the container. Although there is no such thing in nature as an ideal gas, the ideal gas approximation works rather well for most reasonable temperature and pressure ranges. Thus, we can safely use the ideal gas equation to solve many gas problems.

Before we can apply the ideal gas equation to a real system, we must evaluate the gas constant R . At 0°C (273.15 K) and 1 atm pressure, many real gases behave like an ideal gas. Experiments show that under these conditions, 1 mole of an ideal gas occupies

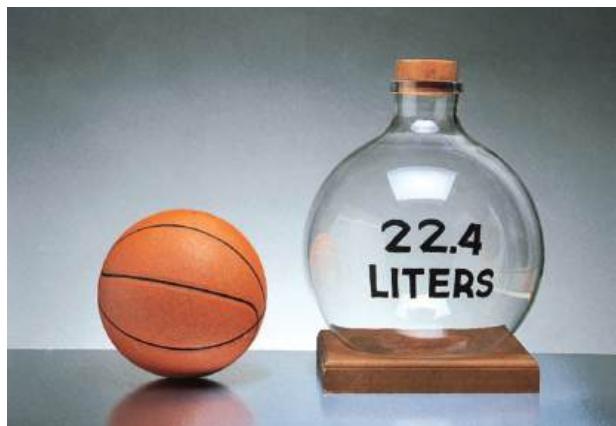


Figure 5.11 A comparison of the molar volume at STP (which is approximately 22.4 L) with a basketball.

©McGraw-Hill Education/Ken Karp

22.414 L, which is somewhat greater than the volume of a basketball, as shown in Figure 5.11. The conditions 0°C and 1 atm are called **standard temperature and pressure**, often abbreviated **STP**. From Equation (5.8) we can write

$$\begin{aligned} R &= \frac{PV}{nT} \\ &= \frac{(1 \text{ atm})(22.414 \text{ L})}{(1 \text{ mol})(273.15 \text{ K})} \\ &= 0.082057 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} \\ &= 0.082057 \text{ L} \cdot \text{atm/K} \cdot \text{mol} \end{aligned}$$

The gas constant can be expressed in different units (see Appendix 1).

The dots between L and atm and between K and mol remind us that both L and atm are in the numerator and both K and mol are in the denominator. For most calculations, we will round off the value of R to three significant figures (0.0821 L · atm/K · mol) and use 22.41 L for the molar volume of a gas at STP.

Example 5.3 shows that if we know the quantity, volume, and temperature of a gas, we can calculate its pressure using the ideal gas equation. Unless otherwise stated, we assume that the temperatures given in °C in calculations are exact so that they do not affect the number of significant figures.

Student Hot Spot
Student data indicate you may struggle with the ideal gas law. Access your eBook for additional Learning Resources on this topic.

Example 5.3

Sulfur hexafluoride (SF_6) is a colorless and odorless gas. Due to its lack of chemical reactivity, it is used as an insulator in electronic equipment. Calculate the pressure (in atm) exerted by 1.82 moles of the gas in a steel vessel of volume 5.43 L at 69.5°C.

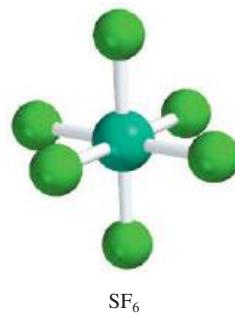
Strategy The problem gives the amount of the gas and its volume and temperature. Is the gas undergoing a change in any of its properties? What equation should we use to solve for the pressure? What temperature unit should we use?

Solution Because no changes in gas properties occur, we can use the ideal gas equation to calculate the pressure. Rearranging Equation (5.8), we write

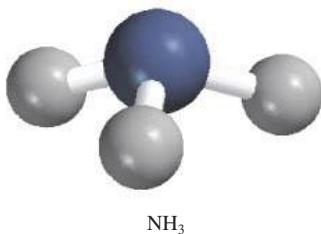
$$\begin{aligned} P &= \frac{nRT}{V} \\ &= \frac{(1.82 \text{ mol})(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(69.5 + 273) \text{ K}}{5.43 \text{ L}} \\ &= 9.42 \text{ atm} \end{aligned}$$

Practice Exercise Calculate the volume (in liters) occupied by 2.12 moles of nitric oxide (NO) at 6.54 atm and 76°C.

Similar problem: 5.32.



By using the fact that the molar volume of a gas occupies 22.41 L at STP, we can calculate the volume of a gas at STP without using the ideal gas equation, as shown in Example 5.4.



Industrial ammonia refrigeration system.

Courtesy of Industrial Refrigeration Service, Inc. & MTC Logistics

Example 5.4

Ammonia gas is used as a refrigerant in food processing and storage industries. Calculate the volume (in liters) occupied by 7.40 g of NH₃ at STP.

Strategy What is the volume of 1 mole of an ideal gas at STP? How many moles are there in 7.40 g of NH₃?

Solution Recognizing that 1 mole of an ideal gas occupies 22.41 L at STP and using the molar mass of NH₃ (17.03 g), we write the sequence of conversions as

$$\text{grams of NH}_3 \longrightarrow \text{moles of NH}_3 \longrightarrow \text{liters of NH}_3 \text{ at STP}$$

so the volume of NH₃ is given by

$$V = 7.40 \text{ g NH}_3 \times \frac{1 \text{ mol NH}_3}{17.03 \text{ g NH}_3} \times \frac{22.41 \text{ L}}{1 \text{ mol NH}_3} \\ = 9.74 \text{ L}$$

It is often true in chemistry, particularly in gas law calculations, that a problem can be solved in more than one way. Here the problem can also be solved by first converting 7.40 g of NH₃ to number of moles of NH₃, and then applying the ideal gas equation ($V = nRT/P$). Try it.

Check Because 7.40 g of NH₃ is smaller than its molar mass, its volume at STP should be smaller than 22.41 L. Therefore, the answer is reasonable.

Practice Exercise What is the volume (in liters) occupied by 49.8 g of HCl at STP?

Similar problem: 5.40.

The ideal gas equation is useful for problems that do not involve changes in P , V , T , and n for a gas sample. Thus, if we know any three of the variables we can calculate the fourth one using the equation. At times, however, we need to deal with changes in pressure, volume, and temperature, or even in the amount of gas. When conditions change, we must employ a modified form of the ideal gas equation that takes into account the initial and final conditions. We derive the modified equation as follows. From Equation (5.8),

$$R = \frac{P_1 V_1}{n_1 T_1} \text{ (before change)} \quad \text{and} \quad R = \frac{P_2 V_2}{n_2 T_2} \text{ (after change)}$$

Therefore,

$$\frac{P_1 V_1}{n_1 T_1} = \frac{P_2 V_2}{n_2 T_2} \tag{5.9}$$

It is interesting to note that all the gas laws discussed in Section 5.3 can be derived from Equation (5.9). If $n_1 = n_2$, as is usually the case because the amount of gas normally does not change, the equation then becomes

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \tag{5.10}$$

Applications of Equation (5.9) are shown in Examples 5.5 through 5.7.

The subscripts 1 and 2 denote the initial and final states of the gas, respectively.

Example 5.5

An inflated helium balloon with a volume of 0.55 L at sea level (1.0 atm) is allowed to rise to a height of 6.5 km, where the pressure is about 0.40 atm. Assuming that the temperature remains constant, what is the final volume of the balloon?

Strategy The amount of gas inside the balloon and its temperature remain constant, but both the pressure and the volume change. What gas law do you need?

Solution We start with Equation (5.9)

$$\frac{P_1 V_1}{n_1 T_1} = \frac{P_2 V_2}{n_2 T_2}$$

Because $n_1 = n_2$ and $T_1 = T_2$,

$$P_1 V_1 = P_2 V_2$$

which is Boyle's law [see Equation (5.2)]. The given information is tabulated:

Initial Conditions	Final Conditions
$P_1 = 1.0 \text{ atm}$	$P_2 = 0.40 \text{ atm}$
$V_1 = 0.55 \text{ L}$	$V_2 = ?$

Therefore,

$$\begin{aligned} V_2 &= V_1 \times \frac{P_1}{P_2} \\ &= 0.55 \text{ L} \times \frac{1.0 \text{ atm}}{0.40 \text{ atm}} \\ &= 1.4 \text{ L} \end{aligned}$$

Check When pressure applied on the balloon is reduced (at constant temperature), the helium gas expands and the balloon's volume increases. The final volume is greater than the initial volume, so the answer is reasonable.

Practice Exercise A sample of chlorine gas occupies a volume of 946 mL at a pressure of 726 mmHg. Calculate the pressure of the gas (in mmHg) if the volume is reduced at constant temperature to 154 mL.

Similar problem: 5.19.



A scientific research helium balloon.
Source: National Scientific Balloon Facility/
Palestine, Texas

Example 5.6

Argon is an inert gas used in lightbulbs to retard the vaporization of the tungsten filament. A certain lightbulb containing argon at 1.20 atm and 18°C is heated to 85°C at constant volume. Calculate its final pressure (in atm).

Strategy The temperature and pressure of argon change but the amount and volume of gas remain the same. What equation would you use to solve for the final pressure? What temperature unit should you use?

Solution Because $n_1 = n_2$ and $V_1 = V_2$, Equation (5.9) becomes

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$



Electric lightbulbs are usually filled with argon.
©Ingram Publishing

(Continued)

Remember to convert °C to K when solving gas law problems.

One practical consequence of this relationship is that automobile tire pressures should be checked only when the tires are at normal temperatures. After a long drive (especially in the summer), tires become quite hot, and the air pressure inside them rises.

which is Charles' law [see Equation (5.6)]. Next we write

Initial Conditions	Final Conditions
$P_1 = 1.20 \text{ atm}$	$P_2 = ?$
$T_1 = (18 + 273) \text{ K} = 291 \text{ K}$	$T_2 = (85 + 273) \text{ K} = 358 \text{ K}$

The final pressure is given by

$$\begin{aligned} P_2 &= P_1 \times \frac{T_2}{T_1} \\ &= 1.20 \text{ atm} \times \frac{358 \text{ K}}{291 \text{ K}} \\ &= 1.48 \text{ atm} \end{aligned}$$

Check At constant volume, the pressure of a given amount of gas is directly proportional to its absolute temperature. Therefore the increase in pressure is reasonable.

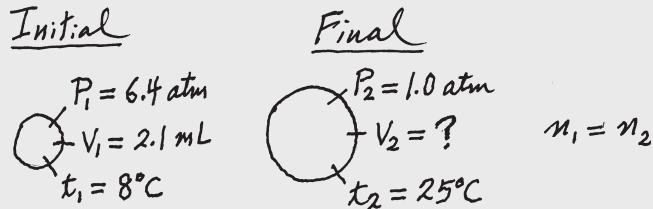
Practice Exercise A sample of oxygen gas initially at 0.97 atm is cooled from 21°C to –68°C at constant volume. What is its final pressure (in atm)?

Similar problem: 5.36.

Example 5.7

A small bubble rises from the bottom of a lake, where the temperature and pressure are 8°C and 6.4 atm, to the water's surface, where the temperature is 25°C and the pressure is 1.0 atm. Calculate the final volume (in mL) of the bubble if its initial volume was 2.1 mL.

Strategy In solving this kind of problem, where a lot of information is given, it is sometimes helpful to make a sketch of the situation, as shown here:



What temperature unit should be used in the calculation?

Solution According to Equation (5.9)

$$\frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}$$

We assume that the amount of air in the bubble remains constant, that is, $n_1 = n_2$ so that

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

which is Equation (5.10). The given information is summarized:

Initial Conditions	Final Conditions
$P_1 = 6.4 \text{ atm}$	$P_2 = 1.0 \text{ atm}$
$V_1 = 2.1 \text{ mL}$	$V_2 = ?$
$T_1 = (8 + 273) \text{ K} = 281 \text{ K}$	$T_2 = (25 + 273) \text{ K} = 298 \text{ K}$

(Continued)

We can use any appropriate units for volume (or pressure) as long as we use the same units on both sides of the equation.

Rearranging Equation (5.10) gives

$$\begin{aligned} V_2 &= V_1 \times \frac{P_1}{P_2} \times \frac{T_2}{T_1} \\ &= 2.1 \text{ mL} \times \frac{6.4 \text{ atm}}{1.0 \text{ atm}} \times \frac{298 \text{ K}}{281 \text{ K}} \\ &= 14 \text{ mL} \end{aligned}$$

Check We see that the final volume involves multiplying the initial volume by a ratio of pressures (P_1/P_2) and a ratio of temperatures (T_2/T_1). Recall that volume is inversely proportional to pressure, and volume is directly proportional to temperature. Because the pressure decreases and temperature increases as the bubble rises, we expect the bubble's volume to increase. In fact, here the change in pressure plays a greater role in the volume change.

Practice Exercise A gas initially at 4.0 L, 1.2 atm, and 66°C undergoes a change so that its final volume and temperature are 1.7 L and 42°C. What is its final pressure? Assume the number of moles remains unchanged.

Similar problem: 5.35.

Density Calculations

If we rearrange the ideal gas equation, we can calculate the density of a gas as

$$\frac{n}{V} = \frac{P}{RT}$$

The number of moles of the gas, n , is given by

$$n = \frac{m}{\mathcal{M}}$$

where m is the mass of the gas in grams and \mathcal{M} is its molar mass. Therefore

$$\frac{m}{\mathcal{M}V} = \frac{P}{RT}$$

Because density, d , is mass per unit volume, we can write

$$d = \frac{m}{V} = \frac{P\mathcal{M}}{RT} \quad (5.11)$$

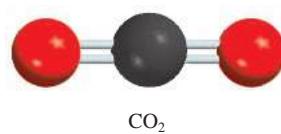
Unlike molecules in condensed matter (that is, in liquids and solids), gaseous molecules are separated by distances that are large compared with their size. Consequently, the density of gases is very low under atmospheric conditions. For this reason, gas densities are usually expressed in grams per liter (g/L) rather than grams per milliliter (g/mL), as Example 5.8 shows.

Example 5.8

Calculate the density of carbon dioxide (CO_2) in grams per liter (g/L) at 0.990 atm and 55°C.

Strategy We need Equation (5.11) to calculate gas density. Is sufficient information provided in the problem? What temperature unit should be used?

(Continued)



Solution To use Equation (5.11), we convert temperature to kelvins ($T = 273 + 55 = 328 \text{ K}$) and use 44.01 g for the molar mass of CO_2 ; that is,

$$\begin{aligned} d &= \frac{P\mathcal{M}}{RT} \\ &= \frac{(0.990 \text{ atm})(44.01 \text{ g/mol})}{(0.0821 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol})(328 \text{ K})} = 1.62 \text{ g/L} \end{aligned}$$

Alternatively, we can solve for the density by writing

$$\text{density} = \frac{\text{mass}}{\text{volume}}$$

Being an intensive property, density is independent of the amount of substance. Therefore, we can use any convenient amount to help us solve the problem.

Assuming that we have 1 mole of CO_2 , the mass is 44.01 g. The volume of the gas can be obtained from the ideal gas equation

$$\begin{aligned} V &= \frac{nRT}{P} \\ &= \frac{(1 \text{ mol})(0.0821 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol})(328 \text{ K})}{0.990 \text{ atm}} \\ &= 27.2 \text{ L} \end{aligned}$$

Therefore, the density of CO_2 is given by

$$d = \frac{44.01 \text{ g}}{27.2 \text{ L}} = 1.62 \text{ g/L}$$

Comment In units of grams per milliliter, the gas density is $1.62 \times 10^{-3} \text{ g/mL}$, which is a very small number. In comparison, the density of water is 1.0 g/mL and that of gold is 19.3 g/cm³.

Practice Exercise What is the density (in g/L) of uranium hexafluoride (UF_6) at 779 mmHg and 62°C?

Similar problem: 5.48.



Figure 5.12 An apparatus for measuring the density of a gas. A bulb of known volume is filled with the gas under study at a certain temperature and pressure. First the bulb is weighed, and then it is emptied (evacuated) and weighed again. The difference in masses gives the mass of the gas. Knowing the volume of the bulb, we can calculate the density of the gas. Under atmospheric conditions, 100 mL of air weigh about 0.12 g, an easily measured quantity.

The Molar Mass of a Gaseous Substance

From what we have seen so far, you may have the impression that the molar mass of a substance is found by examining its formula and summing the molar masses of its component atoms. However, this procedure works only if the actual formula of the substance is known. In practice, chemists often deal with substances of unknown or only partially defined composition. If the unknown substance is gaseous, its molar mass can nevertheless be found thanks to the ideal gas equation. All that is needed is an experimentally determined density value (or mass and volume data) for the gas at a known temperature and pressure. By rearranging Equation (5.11) we get

$$\mathcal{M} = \frac{dRT}{P} \quad (5.12)$$

In a typical experiment, a bulb of known volume is filled with the gaseous substance under study. The temperature and pressure of the gas sample are recorded, and the total mass of the bulb plus gas sample is determined (Figure 5.12). The bulb is then evacuated (emptied) and weighed again. The difference in mass is the mass of the gas. The density of the gas is equal to its mass divided by the volume of the bulb. Once we know the density of a gas, we can calculate the molar mass of the substance using Equation (5.12).

The mass spectrometer has become the dominant instrument for determining molar mass, but the determination of molar mass by the density method is still useful, as illustrated by Example 5.9.

Example 5.9

A chemist has synthesized a greenish-yellow gaseous compound of chlorine and oxygen and finds that its density is 7.71 g/L at 36°C and 2.88 atm. Calculate the molar mass of the compound and determine its molecular formula.

Strategy Because Equations (5.11) and (5.12) are rearrangements of each other, we can calculate the molar mass of a gas if we know its density, temperature, and pressure. The molecular formula of the compound must be consistent with its molar mass. What temperature unit should we use?

Solution From Equation (5.12)

$$\begin{aligned}\mathcal{M} &= \frac{dRT}{P} \\ &= \frac{(7.71 \text{ g/L})(0.0821 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol})(36 + 273) \text{ K}}{2.88 \text{ atm}} \\ &= 67.9 \text{ g/mol}\end{aligned}$$

Alternatively, we can solve for the molar mass by writing

$$\text{molar mass of compound} = \frac{\text{mass of compound}}{\text{moles of compound}}$$

Note that we can determine the molar mass of a gaseous compound by this procedure without knowing its chemical formula.

From the given density we know there are 7.71 g of the gas in 1 L. The number of moles of the gas in this volume can be obtained from the ideal gas equation

$$\begin{aligned}n &= \frac{PV}{RT} \\ &= \frac{(2.88 \text{ atm})(1.00 \text{ L})}{(0.0821 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol})(309 \text{ K})} \\ &= 0.1135 \text{ mol}\end{aligned}$$

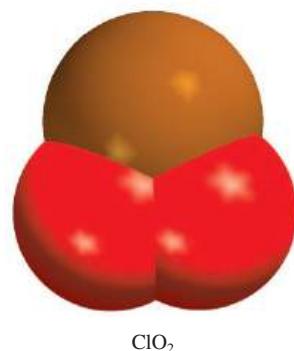
Therefore, the molar mass is given by

$$\mathcal{M} = \frac{\text{mass}}{\text{number of moles}} = \frac{7.71 \text{ g}}{0.1135 \text{ mol}} = 67.9 \text{ g/mol}$$

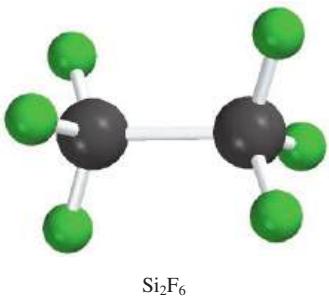
We can determine the molecular formula of the compound by trial and error, using only the knowledge of the molar masses of chlorine (35.45 g) and oxygen (16.00 g). We know that a compound containing one Cl atom and one O atom would have a molar mass of 51.45 g, which is too low, while the molar mass of a compound made up of two Cl atoms and one O atom is 86.90 g, which is too high. Thus, the compound must contain one Cl atom and two O atoms and have the formula ClO_2 , which has a molar mass of 67.45 g.

Practice Exercise The density of a gaseous organic compound is 3.38 g/L at 40°C and 1.97 atm. What is its molar mass?

Similar problems: 5.43, 5.47.



Because Equation (5.12) is derived from the ideal gas equation, we can also calculate the molar mass of a gaseous substance using the ideal gas equation, as shown in Example 5.10.



Example 5.10

Chemical analysis of a gaseous compound showed that it contained 33.0 percent silicon (Si) and 67.0 percent fluorine (F) by mass. At 35°C, 0.210 L of the compound exerted a pressure of 1.70 atm. If the mass of 0.210 L of the compound was 2.38 g, calculate the molecular formula of the compound.

Strategy This problem can be divided into two parts. First, it asks for the empirical formula of the compound from the percent by mass of Si and F. Second, the information provided enables us to calculate the molar mass of the compound and hence determine its molecular formula. What is the relationship between empirical molar mass and molar mass calculated from the molecular formula?

Solution We follow the procedure in Example 3.9 (Section 3.5) to calculate the empirical formula by assuming that we have 100 g of the compound, so the percentages are converted to grams. The number of moles of Si and F are given by

$$n_{\text{Si}} = 33.0 \frac{\text{g Si}}{28.09 \frac{\text{g Si}}{\text{mol}}} = 1.17 \text{ mol Si}$$

$$n_{\text{F}} = 67.0 \frac{\text{g F}}{19.00 \frac{\text{g F}}{\text{mol}}} = 3.53 \text{ mol F}$$

Therefore, the empirical formula is $\text{Si}_{1.17}\text{F}_{3.53}$, or, dividing by the smaller subscript (1.17), we obtain SiF_3 .

To calculate the molar mass of the compound, we need first to calculate the number of moles contained in 2.38 g of the compound. From the ideal gas equation

$$n = \frac{PV}{RT}$$

$$= \frac{(1.70 \text{ atm})(0.210 \text{ L})}{(0.0821 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol})(308 \text{ K})} = 0.0141 \text{ mol}$$

Because there are 2.38 g in 0.0141 mole of the compound, the mass in 1 mole, or the molar mass, is given by

$$\mathcal{M} = \frac{2.38 \text{ g}}{0.0141 \text{ mol}} = 169 \text{ g/mol}$$

The molar mass of the empirical formula SiF_3 is 85.09 g. Recall that the ratio (molar mass/empirical molar mass) is always an integer ($169/85.09 \approx 2$). Therefore, the molecular formula of the compound must be $(\text{SiF}_3)_2$ or Si_2F_6 .

Practice Exercise A gaseous compound is 78.14 percent boron and 21.86 percent hydrogen. At 27°C, 74.3 mL of the gas exerted a pressure of 1.12 atm. If the mass of the gas was 0.0934 g, what is its molecular formula?

Similar problem: 5.49.

Review of Concepts & Facts

- 5.4.1 The volume of a gas is 52.0 mL at 15.0°C and 2.75 atm. At what temperature will the gas have a pressure of 3.50 atm and a volume of 65.0 mL?
- 5.4.2 Assuming ideal behavior, which of the following gases will have the greatest volume at STP: (a) 0.82 mole of He, (b) 24 g of N₂, or (c) 5.0×10^{23} molecules of Cl₂? Which gas will have the greatest density?
- 5.4.3 What is the molar mass of an unknown compound if a 194-mL sample has a mass of 0.477 g at 0.976 atm and 100°C?

5.5 Gas Stoichiometry

In Chapter 3 we used relationships between amounts (in moles) and masses (in grams) of reactants and products to solve stoichiometry problems. When the reactants and/or products are gases, we can also use the relationships between amounts (moles, n) and volume (V) to solve such problems (Figure 5.13). Examples 5.11, 5.12, and 5.13 show how the gas laws are used in these calculations.

The key to solving stoichiometry problems is mole ratio, regardless of the physical state of the reactants and products.

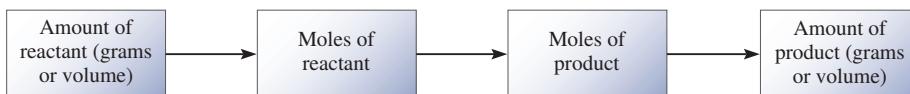


Figure 5.13 Stoichiometric calculations involving gases.

Example 5.11

The combustion of acetylene with pure oxygen produces a very high-temperature flame used for welding and cutting metals. Calculate the volume of O_2 (in liters) required for the complete combustion of 7.64 L of acetylene (C_2H_2) measured at the same temperature and pressure.



Strategy Note that the temperature and pressure of O_2 and C_2H_2 are the same. Which gas law do we need to relate the volume of the gases to the moles of gases?

Solution According to Avogadro's law, at the same temperature and pressure, the number of moles of gases are directly related to their volumes. From the equation, we have 5 mol $\text{O}_2 \approx 2$ mol C_2H_2 ; therefore, we can also write 5 L $\text{O}_2 \approx 2$ L C_2H_2 . The volume of O_2 that will react with 7.64 L C_2H_2 is given by

$$\begin{aligned} \text{volume of } \text{O}_2 &= 7.64 \text{ L } \cancel{\text{C}_2\text{H}_2} \times \frac{5 \text{ L } \text{O}_2}{2 \text{ L } \cancel{\text{C}_2\text{H}_2}} \\ &= 19.1 \text{ L} \end{aligned}$$

Practice Exercise Assuming no change in temperature and pressure, calculate the volume of O_2 (in liters) required for the complete combustion of 14.9 L of butane (C_4H_{10}).



Similar problem: 5.26.



The reaction of calcium carbide (CaC_2) with water produces acetylene (C_2H_2), a flammable gas.

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Example 5.12

Sodium azide (NaN_3) is used in some automobile air bags. The impact of a collision triggers the decomposition of NaN_3 as follows:



The nitrogen gas produced quickly inflates the bag between the driver and the windshield and dashboard. Calculate the volume of N_2 generated at 80°C and 823 mmHg by the decomposition of 60.0 g of NaN_3 .

Strategy From the balanced equation we see that 2 mol $\text{NaN}_3 \approx 3$ mol N_2 so the conversion factor between NaN_3 and N_2 is

$$\frac{3 \text{ mol N}_2}{2 \text{ mol NaN}_3}$$

(Continued)



An air bag can protect the driver in an automobile collision.

©Caspar Benson/fStop Images/Getty Images

Because the mass of NaN_3 is given, we can calculate the number of moles of NaN_3 and hence the number of moles of N_2 produced. Finally, we can calculate the volume of N_2 using the ideal gas equation.

Solution First we calculate number of moles of N_2 produced by 60.0 g NaN_3 using the following sequence of conversions



so that

$$\begin{aligned} \text{moles of } \text{N}_2 &= 60.0 \text{ g } \cancel{\text{NaN}_3} \times \frac{1 \text{ mol } \cancel{\text{NaN}_3}}{65.02 \text{ g } \cancel{\text{NaN}_3}} \times \frac{3 \text{ mol } \text{N}_2}{2 \text{ mol } \cancel{\text{NaN}_3}} \\ &= 1.38 \text{ mol } \text{N}_2 \end{aligned}$$

The volume of 1.38 moles of N_2 can be obtained by using the ideal gas equation

$$\begin{aligned} V &= \frac{nRT}{P} = \frac{(1.38 \text{ mol})(0.0821 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol})(80 + 273 \text{ K})}{(823/760) \text{ atm}} \\ &= 36.9 \text{ L} \end{aligned}$$

Practice Exercise The equation for the metabolic breakdown of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) is the same as the equation for the combustion of glucose in air; that is



Calculate the volume of CO_2 produced at 37°C and 1.00 atm when 5.60 g of glucose is used up in the reaction.

Similar problem: 5.62.



The air in submerged submarines and space vehicles needs to be purified continuously.

©StockTrek/SuperStock

Example 5.13

Aqueous lithium hydroxide solution is used to purify air in spacecrafts and submarines because it absorbs carbon dioxide, which is an end product of metabolism, according to the equation



The pressure of carbon dioxide inside the cabin of a submarine having a volume of $2.4 \times 10^5 \text{ L}$ is $7.9 \times 10^{-3} \text{ atm}$ at 312 K. A solution of lithium hydroxide (LiOH) of negligible volume is introduced into the cabin. Eventually the pressure of CO_2 falls to $1.2 \times 10^{-4} \text{ atm}$. How many grams of lithium carbonate are formed by this process?

Strategy How do we calculate the number of moles of CO_2 reacted from the drop in CO_2 pressure? From the ideal gas equation we write

$$n = P \times \left(\frac{V}{RT} \right)$$

At constant T and V , the change in pressure of CO_2 , ΔP , corresponds to the change in the number of moles of CO_2 , Δn . Thus,

$$\Delta n = \Delta P \times \left(\frac{V}{RT} \right)$$

What is the conversion factor between CO_2 and Li_2CO_3 ?

(Continued)

Solution The drop in CO_2 pressure is $(7.9 \times 10^{-3} \text{ atm}) - (1.2 \times 10^{-4} \text{ atm})$ or $7.8 \times 10^{-3} \text{ atm}$. Therefore, the number of moles of CO_2 reacted is given by

$$\begin{aligned}\Delta n &= 7.8 \times 10^{-3} \text{ atm} \times \frac{2.4 \times 10^5 \text{ L}}{(0.0821 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol})(312 \text{ K})} \\ &= 73 \text{ mol}\end{aligned}$$

From the chemical equation we see that 1 mol $\text{CO}_2 \approx 1$ mol Li_2CO_3 , so the amount of Li_2CO_3 formed is also 73 moles. Then, with the molar mass of Li_2CO_3 (73.89 g), we calculate its mass.

$$\begin{aligned}\text{mass of Li}_2\text{CO}_3 \text{ formed} &= 73 \text{ mol Li}_2\text{CO}_3 \times \frac{73.89 \text{ g Li}_2\text{CO}_3}{1 \text{ mol Li}_2\text{CO}_3} \\ &= 5.4 \times 10^3 \text{ g Li}_2\text{CO}_3\end{aligned}$$

Practice Exercise A 2.14-L sample of hydrogen chloride (HCl) gas at 2.61 atm and 28°C is completely dissolved in 668 mL of water to form hydrochloric acid solution. Calculate the molarity of the acid solution. Assume no change in volume.

Similar problem: 5.100.

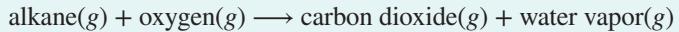
Review of Concepts & Facts

5.5.1 Zinc metal reacts with hydrochloric acid according to the following equation:



What volume of hydrogen gas is produced at STP when 16.4 g of zinc is used in the reaction?

5.5.2 Alkanes ($\text{C}_n\text{H}_{2n+2}$) are discussed in Section 2.8. For which alkanes, if any, does the number of moles of gas remain constant as the gas-phase combustion reaction



proceeds from reactants to products?

5.6 Dalton's Law of Partial Pressures

Thus far we have concentrated on the behavior of pure gaseous substances, but experimental studies very often involve mixtures of gases. For example, for a study of air pollution, we may be interested in the pressure-volume-temperature relationship of a sample of air, which contains several gases. In this case, and all cases involving mixtures of gases, the total gas pressure is related to **partial pressures**, that is, *the pressures of individual gas components in the mixture*. In 1801 Dalton formulated a law, now known as **Dalton's law of partial pressures**, which states that *the total pressure of a mixture of gases is just the sum of the pressures that each gas would exert if it were present alone*. Figure 5.14 illustrates Dalton's law.

Consider a case in which two gases, A and B, are in a container of volume V . The pressure exerted by gas A, according to the ideal gas equation, is

$$P_A = \frac{n_A RT}{V}$$

where n_A is the number of moles of A present. Similarly, the pressure exerted by gas B is

$$P_B = \frac{n_B RT}{V}$$

Volume and temperature are constant

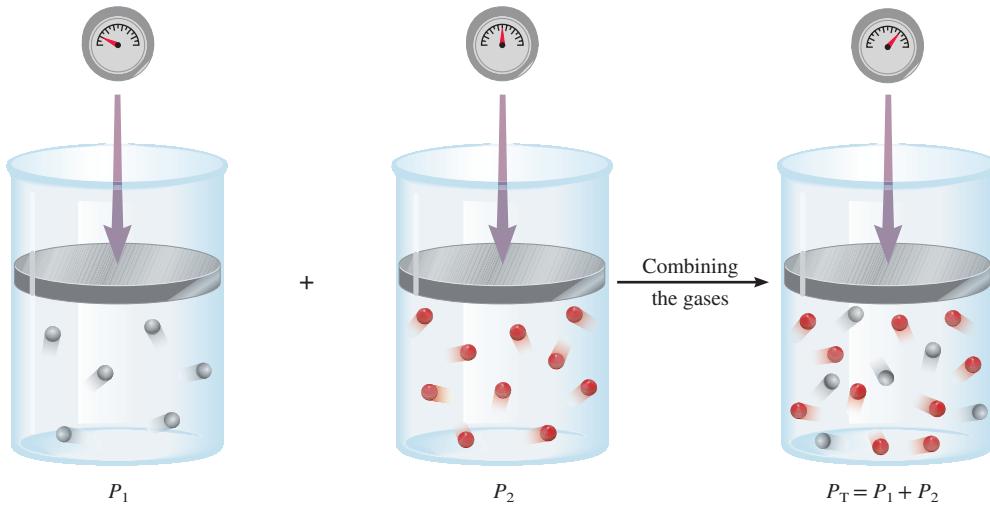


Figure 5.14 Schematic illustration of Dalton's law of partial pressures.

In a mixture of gases A and B, the total pressure P_T is the result of the collisions of both types of molecules, A and B, with the walls of the container. Thus, according to Dalton's law,

$$\begin{aligned} P_T &= P_A + P_B \\ &= \frac{n_A RT}{V} + \frac{n_B RT}{V} \\ &= \frac{RT}{V} (n_A + n_B) \\ &= \frac{n_T RT}{V} \end{aligned}$$

where n_T , the total number of moles of gases present, is given by $n = n_A + n_B$, and P_A and P_B are the partial pressures of gases A and B, respectively. For a mixture of gases, then, P_T depends only on the total number of moles of gas present, not on the nature of the gas molecules.

In general, the total pressure of a mixture of gases is given by

$$P_T = P_1 + P_2 + P_3 + \dots$$

where P_1, P_2, P_3, \dots are the partial pressures of components 1, 2, 3, \dots . To see how each partial pressure is related to the total pressure, consider again the case of a mixture of two gases, A and B. Dividing P_A by P_T , we obtain

$$\begin{aligned} \frac{P_A}{P_T} &= \frac{n_A RT/V}{(n_A + n_B)RT/V} \\ &= \frac{n_A}{n_A + n_B} \\ &= X_A \end{aligned}$$

where X_A is called the mole fraction of A. The **mole fraction** is the ratio of the number of moles of one component to the number of moles of all components present. In general, the mole fraction of component i in a mixture is given by

$$X_i = \frac{n_i}{n_T} \quad (5.13)$$

where n_i and n_T are the number of moles of component i and the total number of moles present, respectively. The mole fraction is a dimensionless quantity and is always less than 1. We can now express the partial pressure of A as

$$P_A = X_A P_T$$

Similarly,

$$P_B = X_B P_T$$

Note that the sum of the mole fractions for a mixture of gases must equal 1. If only two components are present, then

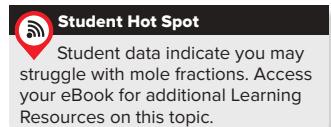
$$X_A + X_B = \frac{n_A}{n_A + n_B} + \frac{n_B}{n_A + n_B} = 1$$

If a system contains more than two gases, then the partial pressure of the i th component is related to the total pressure by

$$P_i = X_i P_T \quad (5.14)$$

How are partial pressures determined? A manometer can measure only the total pressure of a gaseous mixture. To obtain the partial pressures, we need to know the mole fractions of the components, which would involve elaborate chemical analyses. The most direct method of measuring partial pressures is using a mass spectrometer. The relative intensities of the peaks in a mass spectrum are directly proportional to the amounts, and hence to the mole fractions, of the gases present.

From mole fractions and total pressure, we can calculate the partial pressures of individual components, as Example 5.14 shows. A direct application of Dalton's law of partial pressures to scuba diving is discussed in this section's Chemistry in Action essay, "Scuba Diving and the Gas Laws."



Example 5.14

A mixture of gases contains 4.46 moles of neon (Ne), 0.74 mole of argon (Ar), and 2.15 moles of xenon (Xe). Calculate the partial pressures of the gases if the total pressure is 2.00 atm at a certain temperature.

Strategy What is the relationship between the partial pressure of a gas and the total gas pressure? How do we calculate the mole fraction of a gas?

Solution According to Equation (5.14), the partial pressure of Ne (P_{Ne}) is equal to the product of its mole fraction (X_{Ne}) and the total pressure (P_T).

$$P_{\text{Ne}} = X_{\text{Ne}} P_T$$

want to calculate need to find
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Using Equation (5.13), we calculate the mole fraction of Ne as follows:

$$X_{\text{Ne}} = \frac{n_{\text{Ne}}}{n_{\text{Ne}} + n_{\text{Ar}} + n_{\text{Xe}}} = \frac{4.46 \text{ mol}}{4.46 \text{ mol} + 0.74 \text{ mol} + 2.15 \text{ mol}} = 0.607$$

Therefore,

$$\begin{aligned} P_{\text{Ne}} &= X_{\text{Ne}} P_T \\ &= 0.607 \times 2.00 \text{ atm} \\ &= 1.21 \text{ atm} \end{aligned}$$

(Continued)

Similarly,

$$\begin{aligned}P_{\text{Ar}} &= X_{\text{Ar}} P_{\text{T}} \\&= 0.10 \times 2.00 \text{ atm} \\&= 0.20 \text{ atm}\end{aligned}$$

and

$$\begin{aligned}P_{\text{Xe}} &= X_{\text{Xe}} P_{\text{T}} \\&= 0.293 \times 2.00 \text{ atm} \\&= 0.586 \text{ atm}\end{aligned}$$

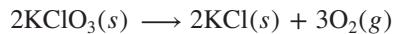
Check Make sure that the sum of the partial pressures is equal to the given total pressure; that is, $(1.21 + 0.20 + 0.586) \text{ atm} = 2.00 \text{ atm}$.

Practice Exercise A sample of natural gas contains 8.24 moles of methane (CH_4), 0.421 mole of ethane (C_2H_6), and 0.116 mole of propane (C_3H_8). If the total pressure of the gases is 1.37 atm, what are the partial pressures of the gases?

Similar problem: 5.67.

 **Video**
Collecting a Gas over Water

An important application of Dalton's law of partial pressures involves calculating the amount of a gas collected over water. Gases that are commonly used in the laboratory are generally obtained from pressurized gas cylinders, but if there is an occasional need for a small amount of a certain gas, it may be more convenient to prepare it chemically. For example, when potassium chlorate (KClO_3) is heated, it decomposes to KCl and O_2 ; that is,



The oxygen gas can be collected over water, as shown in Figure 5.15. Initially, the inverted bottle is completely filled with water. As oxygen gas is generated, the gas

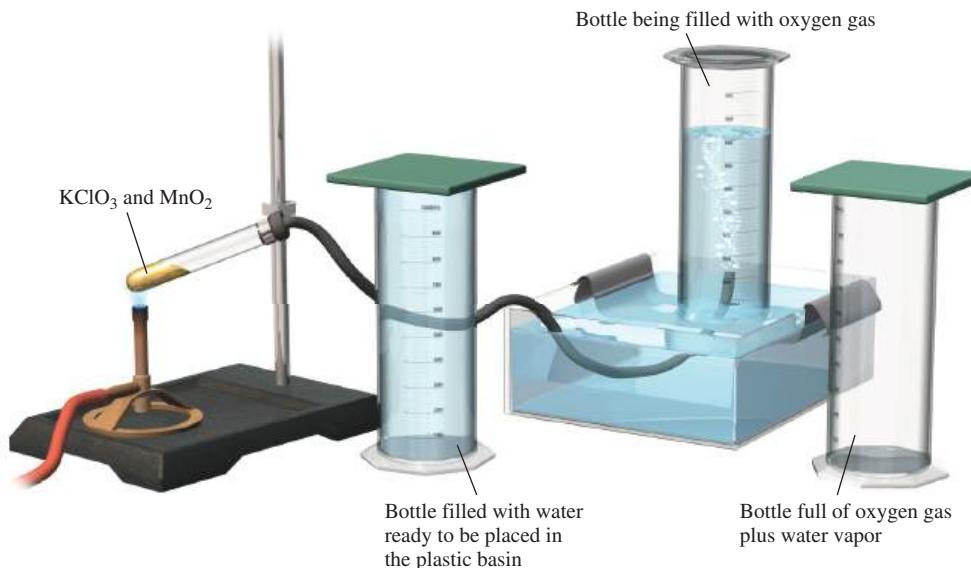


Figure 5.15 An apparatus for collecting gas over water. The oxygen generated by heating potassium chlorate (KClO_3) in the presence of a small amount of manganese dioxide (MnO_2), which speeds up the reaction, is bubbled through water and collected in a bottle as shown. Water originally present in the bottle is pushed into the trough by the oxygen gas.

bubbles rise to the top and displace water from the bottle. This method of collecting a gas is based on the assumptions that the gas does not react with water and that it is not appreciably soluble in it. These assumptions are valid for oxygen gas, but not for gases such as NH_3 , which dissolves readily in water. The oxygen gas collected in this way is not pure, however, because water vapor is also present in the bottle. The total gas pressure is equal to the sum of the pressures exerted by the oxygen gas and the water vapor:

$$P_T = P_{\text{O}_2} + P_{\text{H}_2\text{O}}$$

Consequently, we must allow for the pressure caused by the presence of water vapor when we calculate the amount of O_2 generated. Table 5.3 shows the pressure of water vapor at various temperatures. These data are plotted in Figure 5.16.

Example 5.15 shows how to use Dalton's law to calculate the amount of a gas collected over water.

Example 5.15

Oxygen gas generated by the decomposition of potassium chlorate is collected as shown in Figure 5.15. The volume of oxygen collected at 24°C and atmospheric pressure of 762 mmHg is 128 mL. Calculate the mass (in grams) of oxygen gas obtained. The pressure of the water vapor at 24°C is 22.4 mmHg.

Strategy To solve for the mass of O_2 generated, we must first calculate the partial pressure of O_2 in the mixture. What gas law do we need? How do we convert pressure of O_2 gas to mass of O_2 in grams?

Solution From Dalton's law of partial pressures we know that

$$P_T = P_{\text{O}_2} + P_{\text{H}_2\text{O}}$$

Therefore,

$$\begin{aligned} P_{\text{O}_2} &= P_T - P_{\text{H}_2\text{O}} \\ &= 762 \text{ mmHg} - 22.4 \text{ mmHg} \\ &= 740 \text{ mmHg} \end{aligned}$$

From the ideal gas equation we write

$$PV = mRT = \frac{n}{M}RT$$

where m and M are the mass of O_2 collected and the molar mass of O_2 , respectively. Rearranging the equation we obtain

$$\begin{aligned} m &= \frac{PV\cancel{M}}{RT} = \frac{(740/760)\text{atm}(0.128 \text{ L})(32.00 \text{ g/mol})}{(0.0821 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol})(273 + 24) \text{ K}} \\ &= 0.164 \text{ g} \end{aligned}$$

Check The density of the oxygen gas is $(0.164 \text{ g}/0.128 \text{ L})$, or 1.28 g/L, which is a reasonable value for gases under atmospheric conditions (see Example 5.8 in Section 5.4).

Practice Exercise Hydrogen gas generated when calcium metal reacts with water is collected as shown in Figure 5.15. The volume of gas collected at 30°C and pressure of 988 mmHg is 641 mL. What is the mass (in grams) of the hydrogen gas obtained? The pressure of water vapor at 30°C is 31.82 mmHg.

Similar problem: 5.72.

Table 5.3

Temperature (°C)	Water Vapor Pressure (mmHg)
0	4.58
5	6.54
10	9.21
15	12.79
20	17.54
25	23.76
30	31.82
35	42.18
40	55.32
45	71.88
50	92.51
55	118.04
60	149.38
65	187.54
70	233.7
75	289.1
80	355.1
85	433.6
90	525.76
95	633.90
100	760.00

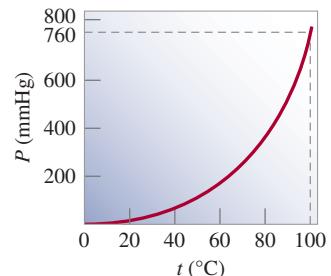


Figure 5.16 The pressure of water vapor as a function of temperature. Note that at the boiling point of water (100°C) the pressure is 760 mmHg, which is exactly equal to 1 atm.

Scuba Diving and the Gas Laws

Scuba diving is an exhilarating sport, and, thanks in part to the gas laws, it is also a safe activity for trained individuals who are in good health. (“Scuba” is an acronym for self-contained underwater breathing apparatus.) Two applications of the gas laws to this popular pastime are the development of guidelines for returning safely to the surface after a dive and the determination of the proper mix of gases to prevent a potentially fatal condition during a dive.

A typical dive might be 40 to 65 ft, but dives to 90 ft are not uncommon. Because seawater has a slightly higher density than fresh water—about 1.03 g/mL, compared with 1.00 g/mL—the pressure exerted by a column of 33 ft of seawater is equivalent to 1 atm pressure. Pressure increases with increasing depth, so at a depth of 66 ft the pressure of the water will be 2 atm, and so on.

What would happen if a diver rose to the surface from a depth of, say, 20 ft rather quickly without breathing? The total decrease in pressure for this change in depth would be $(20 \text{ ft}/33 \text{ ft}) \times 1 \text{ atm}$, or 0.6 atm. When the diver reached the surface, the volume of air trapped in the lungs would have increased by a factor of $(1 + 0.6) \text{ atm}/1 \text{ atm}$, or 1.6 times. This sudden expansion of air can fatally rupture the membranes of the lungs. Another serious possibility is that an *air embolism* might develop. As air expands in the lungs, it is forced into tiny blood vessels called capillaries. The presence of air bubbles in these vessels can

block normal blood flow to the brain. As a result, the diver might lose consciousness before reaching the surface. The only cure for an air embolism is recompression. For this painful process, the victim is placed in a chamber filled with compressed air. Here bubbles in the blood are slowly squeezed down to harmless size over the course of several hours to a day. To avoid these unpleasant complications, divers know they must ascend slowly, pausing at certain points to give their body time to adjust to the falling pressure.

Our second example is a direct application of Dalton’s law. Oxygen gas is essential for our survival, so it is hard to believe that an excess of oxygen could be harmful. Nevertheless, the toxicity of too much oxygen is well established. For example, newborn infants placed in oxygen tents often sustain damage to the retinal tissue, which can cause partial or total blindness.

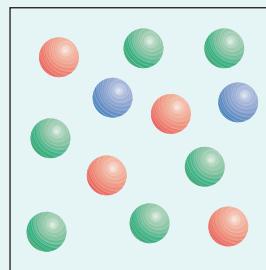
Our bodies function best when oxygen gas has a partial pressure of about 0.20 atm, as it does in the air we breathe. The oxygen partial pressure is given by

$$P_{\text{O}_2} = X_{\text{O}_2} P_{\text{T}} = \frac{n_{\text{O}_2}}{n_{\text{O}_2} + n_{\text{N}_2}} P_{\text{T}}$$

where P_{T} is the total pressure. However, because volume is directly proportional to the number of moles of gas

Review of Concepts & Facts

- 5.6.1** Each of the color spheres represents a different gas molecule. Calculate the partial pressures of the gases if the total pressure is 2.6 atm.



- 5.6.2** What is the mole fraction of Xe in a mixture of 0.234 mole of Ar, 0.176 mole of Ne, and 0.209 mole of Xe?
- 5.6.3** Calculate the partial pressure of fluorine in a gas mixture containing 1.45 moles of chlorine, 1.38 moles of fluorine, and 4.23 moles of He. The total pressure of the mixture is 3.59 atm.

present (at constant temperature and pressure), we can now write

$$P_{O_2} = \frac{V_{O_2}}{V_{O_2} + V_{N_2}} P_T$$

Thus, the composition of air is 20 percent oxygen gas and 80 percent nitrogen gas by volume. When a diver is submerged, the pressure of the water on the diver is greater than atmospheric pressure. The air pressure inside the body cavities (for example, lungs, sinuses) must be the same as the pressure of the surrounding water; otherwise they would collapse. A special valve automatically adjusts the pressure of the air breathed from a scuba tank to ensure that the air pressure equals the water pressure at all times. For example, at a depth where the total pressure is 2.0 atm, the oxygen content in air should be reduced to 10 percent by volume to maintain the same partial pressure of 0.20 atm; that is,

$$P_{O_2} = 0.20 \text{ atm} = \frac{V_{O_2}}{V_{O_2} + V_{N_2}} \times 2.0 \text{ atm}$$
$$\frac{V_{O_2}}{V_{O_2} + V_{N_2}} = \frac{0.20 \text{ atm}}{2.0 \text{ atm}} = 0.10 \text{ or } 10\%$$

Although nitrogen gas may seem to be the obvious choice to mix with oxygen gas, there is a serious problem with it. When the partial pressure of nitrogen gas exceeds 1 atm, enough of the gas dissolves in the blood to cause a condition known as *nitrogen narcosis*. The effects on the diver resemble



Scuba divers.
©Comstock/Getty Images

those associated with alcohol intoxication. Divers suffering from nitrogen narcosis have been known to do strange things, such as dancing on the seafloor and chasing sharks. For this reason, helium is often used to dilute oxygen gas. An inert gas, helium is much less soluble in blood than nitrogen and produces no narcotic effects.

5.7 The Kinetic Molecular Theory of Gases

The gas laws help us to predict the behavior of gases, but they do not explain what happens at the molecular level to cause the changes we observe in the macroscopic world. For example, why does a gas expand on heating?

In the nineteenth century, a number of physicists, notably Ludwig Boltzmann[†] and James Clerk Maxwell[‡], found that the physical properties of gases can be explained in terms of the motion of individual molecules. This molecular movement is a form of *energy*, which we define as the capacity to do work or to produce change. In mechanics, *work* is defined as force times distance. Because energy can be measured as work, we can write

$$\begin{aligned} \text{energy} &= \text{work done} \\ &= \text{force} \times \text{distance} \end{aligned}$$

[†]Ludwig Eduard Boltzmann (1844–1906). Austrian physicist. Although Boltzmann was one of the greatest theoretical physicists of all time, his work was not recognized by other scientists in his own lifetime. Suffering from poor health and great depression, he committed suicide in 1906.

[‡]James Clerk Maxwell (1831–1879). Scottish physicist. Maxwell was one of the great theoretical physicists of the nineteenth century; his work covered many areas in physics, including kinetic theory of gases, thermodynamics, and electricity and magnetism.

The **joule (J)**[§] is the SI unit of energy.

$$\begin{aligned} 1 \text{ J} &= 1 \text{ kg} \cdot \text{m}^2/\text{s}^2 \\ &= 1 \text{ N m} \end{aligned}$$

Alternatively, energy can be expressed in kilojoules (kJ).

$$1 \text{ kJ} = 1000 \text{ J}$$

As we will see in Chapter 6, there are many different kinds of energy. **Kinetic energy (KE)** is the type of energy expended by a moving object, or *energy of motion*.

The findings of Maxwell, Boltzmann, and others resulted in *a number of generalizations about gas behavior* that have since been known as the **kinetic molecular theory of gases**, or simply the **kinetic theory of gases**. Central to the kinetic theory are the following assumptions:

The kinetic theory of gases treats molecules as hard spheres without internal structure.

1. A gas is composed of molecules that are separated from each other by distances far greater than their own dimensions. The molecules can be considered to be “points”; that is, they possess mass but have negligible volume.
2. Gas molecules are in constant motion in random directions, and they frequently collide with one another. Collisions among molecules are perfectly elastic. In other words, energy can be transferred from one molecule to another as a result of a collision. Nevertheless, the total energy of all the molecules in a system remains the same.
3. Gas molecules exert neither attractive nor repulsive forces on one another.
4. The average kinetic energy of the molecules is proportional to the temperature of the gas in kelvins. Any two gases at the same temperature will have the same average kinetic energy. The average kinetic energy of a molecule is given by

$$\overline{\text{KE}} = \frac{1}{2}mu^2$$

where m is the mass of the molecule and u is its speed. The horizontal bar denotes an average value. The quantity $\overline{u^2}$ is called mean square speed; it is the average of the square of the speeds of all the molecules:

$$\overline{u^2} = \frac{u_1^2 + u_2^2 + \dots + u_N^2}{N}$$

where N is the number of molecules.

Assumption 4 enables us to write

$$\begin{aligned} \overline{\text{KE}} &\propto T \\ \frac{1}{2}mu^2 &\propto T \end{aligned}$$

Hence,

$$\overline{\text{KE}} = \frac{1}{2}mu^2 = CT \quad (5.15)$$

where C is the proportionality constant and T is the absolute temperature.

According to the kinetic molecular theory, gas pressure is the result of collisions between molecules and the walls of their container. It depends on the frequency of collision per unit area and on how “hard” the molecules strike the wall. The theory also provides a molecular interpretation of temperature. According to Equation (5.15), the absolute temperature of a gas is a measure of the average kinetic energy of the molecules. In other words, the absolute temperature is an indication of the random motion of the molecules—the higher the temperature, the more energetic the molecules. Because it is related to the temperature of the gas sample, random molecular motion is sometimes referred to as thermal motion.

[§]James Prescott Joule (1818–1889). English physicist. As a young man, Joule was tutored by John Dalton. He is most famous for determining the mechanical equivalent of heat, the conversion between mechanical energy and thermal energy.

Application to the Gas Laws

Although the kinetic theory of gases is based on a rather simple model, the mathematical details involved are very complex. However, on a qualitative basis, it is possible to use the theory to account for the general properties of substances in the gaseous state. The following examples illustrate the range of its utility.

- **Compressibility of Gases.** Because molecules in the gas phase are separated by large distances (assumption 1), gases can be compressed easily to occupy less volume.
- **Boyle's Law.** The pressure exerted by a gas results from the impact of its molecules on the walls of the container. The collision rate, or the number of molecular collisions with the walls per second, is proportional to the number density (that is, number of molecules per unit volume) of the gas. Decreasing the volume of a given amount of gas increases its number density and hence its collision rate. For this reason, the pressure of a gas is inversely proportional to the volume it occupies; as volume decreases, pressure increases and vice versa.
- **Charles' Law.** Because the average kinetic energy of gas molecules is proportional to the sample's absolute temperature (assumption 4), raising the temperature increases the average kinetic energy. Consequently, molecules will collide with the walls of the container more frequently and with greater impact if the gas is heated, and thus the pressure increases. The volume of gas will expand until the gas pressure is balanced by the constant external pressure (see Figure 5.8).
- **Avogadro's Law.** We have shown that the pressure of a gas is directly proportional to both the density and the temperature of the gas. Because the mass of the gas is directly proportional to the number of moles (n) of the gas, we can represent density by n/V . Therefore

$$P \propto \frac{n}{V} T$$

For two gases, 1 and 2, we write

$$\begin{aligned} P_1 &\propto \frac{n_1 T_1}{V_1} = C \frac{n_1 T_1}{V_1} \\ P_2 &\propto \frac{n_2 T_2}{V_2} = C \frac{n_2 T_2}{V_2} \end{aligned}$$

where C is the proportionality constant. Thus, for two gases under the same conditions of pressure, volume, and temperature (that is, when $P_1 = P_2$, $T_1 = T_2$, and $V_1 = V_2$), it follows that $n_1 = n_2$, which is a mathematical expression of Avogadro's law.

- **Dalton's Law of Partial Pressures.** If molecules do not attract or repel one another (assumption 3), then the pressure exerted by one type of molecule is unaffected by the presence of another gas. Consequently, the total pressure is given by the sum of individual gas pressures.

Another way of stating Avogadro's law is that at the same pressure and temperature, equal volumes of gases, whether they are the same or different gases, contain equal numbers of molecules.

Distribution of Molecular Speeds

The kinetic theory of gases enables us to investigate molecular motion in more detail. Suppose we have a large number of gas molecules, say, 1 mole, in a container. As long as we hold the temperature constant, the average kinetic energy and the mean-square speed will remain unchanged as time passes. As you might expect, the motion of the molecules is totally random and unpredictable. At a given instant, how many molecules are moving at a particular speed? To answer this question Maxwell analyzed the behavior of gas molecules at different temperatures.

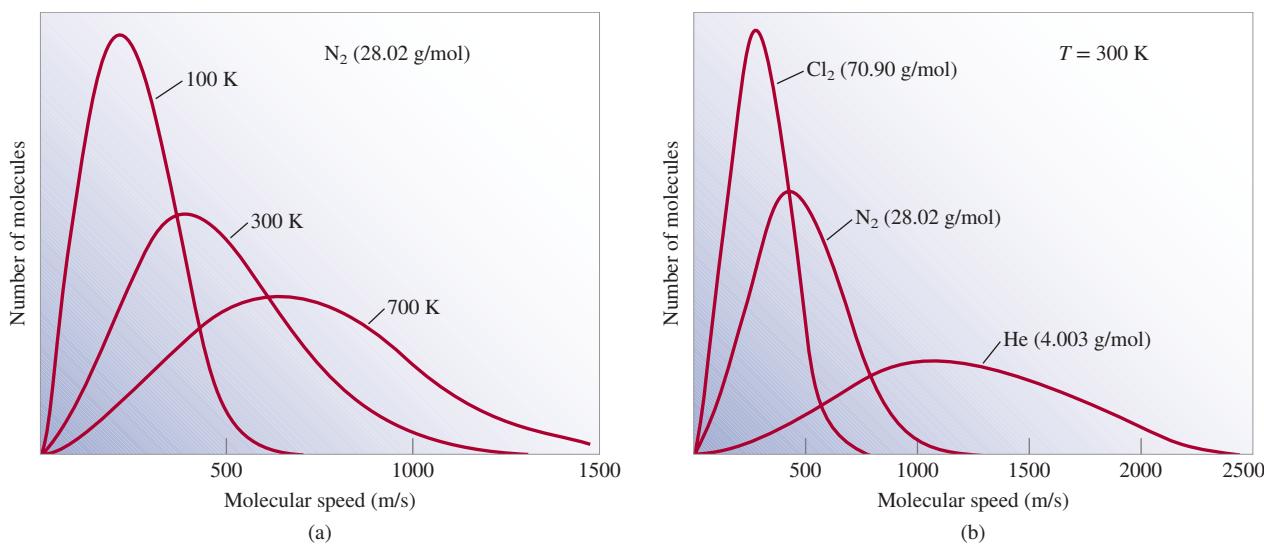
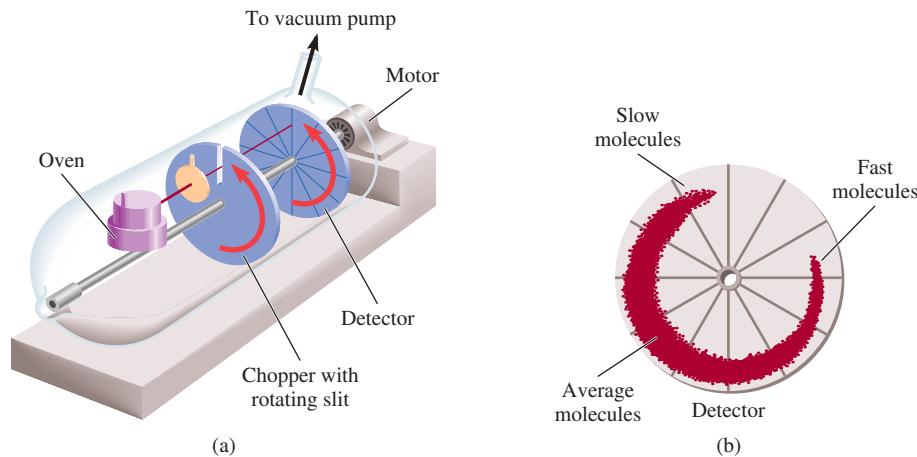


Figure 5.17 (a) The distribution of speeds for nitrogen gas at three different temperatures. At the higher temperatures, more molecules are moving at faster speeds. (b) The distribution of speeds for three gases at 300 K. At a given temperature, the lighter molecules are moving faster, on the average.

Figure 5.17(a) shows typical *Maxwell speed distribution curves* for nitrogen gas at three different temperatures. At a given temperature, the distribution curve tells us the number of molecules moving at a certain speed. The peak of each curve represents the *most probable speed*, that is, the speed of the largest number of molecules. Note that the most probable speed increases as temperature increases (the peak shifts toward the right). Furthermore, the curve also begins to flatten out with increasing temperature, indicating that larger numbers of molecules are moving at greater speed. Figure 5.17(b) shows the speed distributions of three gases at the *same* temperature. The difference in the curves can be explained by noting that lighter molecules move faster, on average, than heavier ones.

The distribution of molecular speeds can be demonstrated with the apparatus shown in Figure 5.18. A beam of atoms (or molecules) exits from an oven at a known temperature and passes through a pinhole (to collimate the beam). Two circular plates mounted on the same shaft are rotated by a motor. The first plate is called the “chopper” and the second is the detector. The purpose of the chopper is to allow small bursts of atoms (or molecules) to pass through it whenever the slit is aligned with the beam. Within each burst, the faster-moving molecules will reach the detector earlier than the slower-moving ones. Eventually, a layer of deposit will accumulate on the detector.

Figure 5.18 (a) Apparatus for studying molecular speed distribution at a certain temperature. The vacuum pump causes the molecules to travel from left to right as shown. (b) The spread of the deposit on the detector gives the range of molecular speeds, and the density of the deposit is proportional to the fraction of molecules moving at different speeds.



Because the two plates are rotating at the same speed, molecules in the next burst will hit the detector plate at approximately the same place as molecules from the previous burst having the same speed. In time, the molecular deposition will become visible. The density of the deposition indicates the distribution of molecular speeds at that particular temperature.

Root-Mean-Square Speed

How fast does a molecule move, on the average, at any temperature T ? One way to estimate molecular speed is to calculate the **root-mean-square (rms) speed** (u_{rms}), which is *an average molecular speed*. One of the results of the kinetic theory of gases is that the total kinetic energy of a mole of any gas equals $\frac{3}{2}RT$. Earlier we saw that the average kinetic energy of one molecule is $\frac{1}{2}mu^2$ and so we can write

$$\overline{\text{KE}} = \frac{3}{2}RT$$

$$N_A(\frac{1}{2}mu^2) = \frac{3}{2}RT$$

There are comparable ways to estimate the “average” speed of molecules, of which root-mean-square speed is one.

where N_A is Avogadro’s number and m is the mass of a single molecule. Because $N_A m = M$, the above equation can be rearranged to give

$$\overline{u^2} = \frac{3RT}{M}$$

Taking the square root of both sides gives

$$\sqrt{\overline{u^2}} = u_{\text{rms}} = \sqrt{\frac{3RT}{M}} \quad (5.16)$$

Equation (5.16) shows that the root-mean-square speed of a gas increases with the square root of its temperature (in kelvins). Because M appears in the denominator, it follows that the heavier the gas, the more slowly its molecules move. If we substitute 8.314 J/K · mol for R (see Appendix 1) and convert the molar mass to kg/mol, then u_{rms} will be calculated in meters per second (m/s). This procedure is illustrated in Example 5.16.

Example 5.16

Calculate the root-mean-square speeds of helium atoms and nitrogen molecules in m/s at 25°C.

Strategy To calculate the root-mean-square speed we need Equation (5.16). What units should we use for R and M so that u_{rms} will be expressed in m/s?

Solution To calculate u_{rms} , the units of R should be 8.314 J/K · mol and, because 1 J = 1 kg · m²/s², the molar mass must be in kg/mol. The molar mass of He is 4.003 g/mol, or 4.003×10^{-3} kg/mol. From Equation (5.16),

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

$$= \sqrt{\frac{3(8.314 \text{ J/K} \cdot \text{mol})(298 \text{ K})}{4.003 \times 10^{-3} \text{ kg/mol}}}$$

$$= \sqrt{1.86 \times 10^6 \text{ J/kg}}$$

(Continued)

Using the conversion factor $1 \text{ J} = 1 \text{ kg m}^2/\text{s}^2$ we get

$$\begin{aligned} u_{\text{rms}} &= \sqrt{1.86 \times 10^6 \text{ kg m}^2/\text{kg} \cdot \text{s}^2} \\ &= \sqrt{1.86 \times 10^6 \text{ m}^2/\text{s}^2} \\ &= 1.36 \times 10^3 \text{ m/s} \end{aligned}$$

The procedure is the same for N_2 , the molar mass of which is 28.02 g/mol, or 2.802×10^{-2} kg/mol so that we write

$$\begin{aligned} u_{\text{rms}} &= \sqrt{\frac{3(8.314 \text{ J/K} \cdot \text{mole})(298 \text{ K})}{2.802 \times 10^{-2} \text{ kg/mol}}} \\ &= \sqrt{2.65 \times 10^5 \text{ m}^2/\text{s}^2} \\ &= 515 \text{ m/s} \end{aligned}$$

Check Because He is a lighter gas, we expect it to move faster, on average, than N_2 . A quick way to check the answers is to note that the ratio of the two u_{rms} values ($1.36 \times 10^3/515 \approx 2.6$) should be equal to the square root of the ratios of the molar masses of N_2 to He, that is, $\sqrt{28/4} \approx 2.6$.

Practice Exercise Calculate the root-mean-square speed of molecular chlorine in m/s at 20°C.

Similar problems: 5.81, 5.82.



Jupiter. The interior of this massive planet consists mainly of hydrogen.

Source: NASA-JPL

The calculation in Example 5.16 has an interesting relationship to the composition of Earth's atmosphere. Unlike Jupiter, Earth does not have appreciable amounts of hydrogen or helium in its atmosphere. Why is this the case? A smaller planet than Jupiter, Earth has a weaker gravitational attraction for these lighter molecules. A fairly straightforward calculation shows that to escape Earth's gravitational field, a molecule must possess an escape velocity equal to or greater than 1.1×10^4 m/s. Because the average speed of helium is considerably greater than that of molecular nitrogen or molecular oxygen, more helium atoms escape from Earth's atmosphere into outer space. Consequently, only a trace amount of helium is present in our atmosphere. On the other hand, Jupiter, with a mass about 320 times greater than that of Earth, retains both heavy and light gases in its atmosphere.

The Chemistry in Action essay "Super Cold Atoms" describes a fascinating phenomenon involving gases at extremely low temperatures.

Gas Diffusion and Effusion

We will now discuss two phenomena based on gaseous motion.

Gas Diffusion

A direct demonstration of gaseous random motion is provided by *diffusion*, the gradual mixing of molecules of one gas with molecules of another by virtue of their kinetic properties. Despite the fact that molecular speeds are very great, the diffusion process takes a relatively long time to complete. For example, when a bottle of concentrated ammonia solution is opened at one end of a lab bench, it takes some time before a person at the other end of the bench can smell it. The reason is that a molecule experiences numerous collisions while moving from one end of the bench to the other, as shown in Figure 5.19. Thus, diffusion of gases always happens gradually, and not instantly as molecular speeds seem to suggest. Furthermore, because the root-mean-square speed of a light gas is greater than that of a heavier gas (see Example 5.16 earlier in this section), a lighter gas will diffuse

Diffusion always proceeds from a region of higher concentration to one where the concentration is lower.

Video
Diffusion of Gases

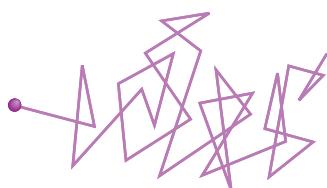


Figure 5.19 The path traveled by a single gas molecule. Each change in direction represents a collision with another molecule.

CHEMISTRY *in Action*

Super Cold Atoms

What happens to a gas when cooled to nearly absolute zero? More than 85 years ago, Albert Einstein, extending work by the Indian physicist Satyendra Nath Bose, predicted that at extremely low temperatures gaseous atoms of certain elements would “merge” or “condense” to form a single entity and a new form of matter. Unlike ordinary gases, liquids, and solids, this supercooled substance, which was named the *Bose-Einstein condensate (BEC)*, would contain no individual atoms because the original atoms would overlap one another, leaving no space in between.

Einstein’s hypothesis inspired an international effort to produce the BEC. But, as sometimes happens in science, the necessary technology was not available until fairly recently, and so early investigations were fruitless. Lasers, which use a process based on another of Einstein’s ideas, were not designed specifically for BEC research, but they became a critical tool for this work.

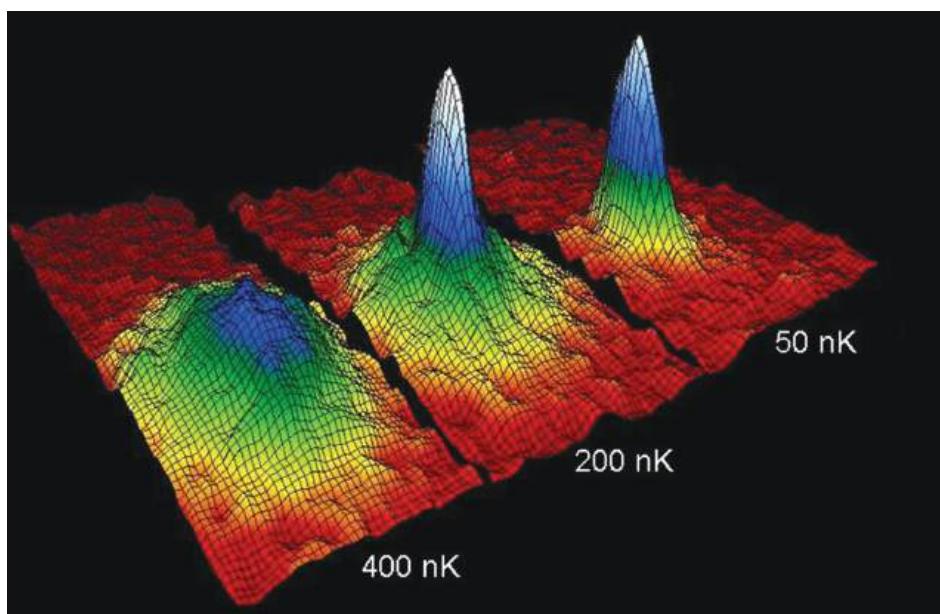
Finally, in 1995, physicists found the evidence they had sought for so long. A team at the University of Colorado was the first to report success. They created a BEC by cooling a sample of gaseous rubidium (Rb) atoms to about 5.0×10^{-3} K using a technique called “laser cooling,” a process in which a laser light is directed at a beam of atoms, hitting them head on and dramatically slowing them down. The Rb atoms were further cooled in an “optical molasses” produced by the intersection of six lasers. The slowest, coolest atoms were trapped in a magnetic field while the faster-moving, “hotter” atoms escaped, thereby removing more energy from the gas. Under these conditions, the kinetic energy of the trapped atoms was virtually zero, which accounts for the extremely low temperature of the gas. At this point the Rb atoms formed the condensate, just as Einstein had

predicted. Although this BEC was invisible to the naked eye (it measured only 5×10^{-3} cm across), the scientists were able to capture its image on a computer screen by focusing another laser beam on it. The laser caused the BEC to break up after about 15 seconds, but that was long enough to record its existence.

The figure shows the Maxwell velocity distribution[†] of the Rb atoms at this temperature. The colors indicate the number of atoms having velocity specified by the two horizontal axes. The blue and white portions represent atoms that have merged to form the BEC.

Within weeks of the Colorado team’s discovery, a group of scientists at Rice University, using similar techniques, succeeded in producing a BEC with lithium atoms and in 1998 scientists at the Massachusetts Institute of Technology were able to produce a BEC with hydrogen atoms. Since then, many advances have been made in understanding the properties of the BEC in general and experiments are being extended to molecular systems. It is expected that studies of the BEC will shed light on atomic properties that are still not fully understood (see Chapter 7) and on the mechanism of superconductivity (see the Chemistry in Action essay High-Temperature Superconductors in Chapter 11). An additional benefit might be the development of better lasers. Other applications will depend on further study of the BEC itself. Nevertheless, the discovery of a new form of matter has to be one of the foremost scientific achievements of the twentieth century.

[†]Velocity distribution differs from speed distribution in that velocity has both magnitude and direction. Thus, velocity can have both positive and negative values but speed can have only zero or positive values.



Maxwell velocity distribution of Rb atoms at three different temperatures during the formation of Bose-Einstein condensate. In each case, the velocity increases from the center (zero) outward along the two axes. The red color represents the lower number of Rb atoms and the white color the highest.

©Mike Matthews, JILA

Figure 5.20 A demonstration of gas diffusion. NH_3 gas (from a bottle containing aqueous ammonia) combines with HCl gas (from a bottle containing hydrochloric acid) to form solid NH_4Cl . Because NH_3 is lighter and therefore diffuses faster, solid NH_4Cl first appears nearer the HCl bottle (on the right).

©McGraw-Hill Education/Ken Karp



through a certain space more quickly than will a heavier gas. Figure 5.20 illustrates gaseous diffusion.

In 1832 the Scottish chemist Thomas Graham[†] found that *under the same conditions of temperature and pressure, rates of diffusion for gases are inversely proportional to the square roots of their molar masses*. This statement, now known as **Graham's law of diffusion**, is expressed mathematically as

$$\frac{r_1}{r_2} = \sqrt{\frac{\mathcal{M}_2}{\mathcal{M}_1}} \quad (5.17)$$

where r_1 and r_2 are the diffusion rates of gases 1 and 2, and \mathcal{M}_1 and \mathcal{M}_2 are their molar masses, respectively.



Student Hot Spot

Student data indicate you may struggle with rates of diffusion and molar masses. Access your eBook for additional Learning Resources on this topic.

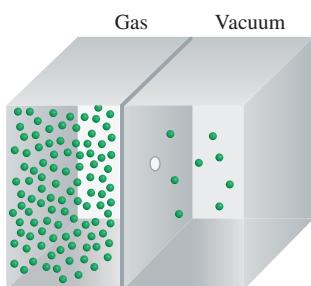


Figure 5.21 Gas effusion. Gas molecules move from a high-pressure region (left) to a low-pressure one through a pinhole.

Gas Effusion

Whereas diffusion is a process by which one gas gradually mixes with another, **effusion** is the process by which a gas under pressure escapes from one compartment of a container to another by passing through a small opening. Figure 5.21 shows the effusion of a gas into a vacuum. Although effusion differs from diffusion in nature, the rate of effusion of a gas has the same form as Graham's law of diffusion [see Equation (5.17)]. A helium-filled rubber balloon deflates faster than an air-filled one because the rate of effusion through the pores of the rubber is faster for the lighter helium atoms than for the air molecules. Industrially, gas effusion is used to separate uranium isotopes in the forms of gaseous $^{235}\text{UF}_6$ and $^{238}\text{UF}_6$. By subjecting the gases to many stages of effusion, scientists were able to obtain highly enriched ^{235}U isotope, which was used in the construction of atomic bombs during World War II.

Example 5.17 shows an application of Graham's law.

Example 5.17

A flammable gas made up only of carbon and hydrogen is found to effuse through a porous barrier in 1.50 min. Under the same conditions of temperature and pressure, it takes an equal volume of bromine vapor 4.73 min to effuse through the same barrier. Calculate the molar mass of the unknown gas, and suggest what this gas might be.

(Continued)

[†]Thomas Graham (1805–1869). Scottish chemist. Graham did important work on osmosis and characterized a number of phosphoric acids.

Strategy The rate of effusion is the number of molecules passing through a porous barrier in a given time. The longer the time it takes, the slower is the rate. Therefore, the rate is *inversely proportional to the time required for effusion*. Equation (5.17) can now be written as $r_1/r_2 = t_2/t_1 = \sqrt{\mathcal{M}_2/\mathcal{M}_1}$, where t_1 and t_2 are the times for effusion for gases 1 and 2, respectively.

Solution From the molar mass of Br_2 , we write

$$\frac{1.50 \text{ min}}{4.73 \text{ min}} = \sqrt{\frac{\mathcal{M}}{159.8 \text{ g/mol}}}$$

where \mathcal{M} is the molar mass of the unknown gas. Solving for \mathcal{M} , we obtain

$$\begin{aligned}\mathcal{M} &= \left(\frac{1.50 \text{ min}}{4.73 \text{ min}}\right)^2 \times 159.8 \text{ g/mol} \\ &= 16.1 \text{ g/mol}\end{aligned}$$

Because the molar mass of carbon is 12.01 g and that of hydrogen is 1.008 g, the gas is methane (CH_4).

Practice Exercise It takes 192 s for an unknown gas to effuse through a porous wall and 84 s for the same volume of N_2 gas to effuse at the same temperature and pressure. What is the molar mass of the unknown gas?

Similar problems: 5.87, 5.88.

Review of Concepts & Facts

- 5.7.1 If one mole each of He and Cl_2 gases are compared at STP, which of the following quantities will be equal to each other? (a) Root-mean-square speed, (b) effusion rate, (c) average kinetic energy, (d) volume.
- 5.7.2 Which gas effuses faster, Ne or Xe, and how much faster does it effuse?

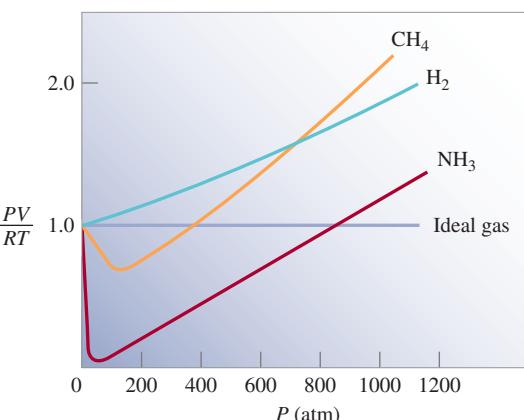
5.8 Deviation from Ideal Behavior

The gas laws and the kinetic molecular theory assume that molecules in the gaseous state do not exert any force, either attractive or repulsive, on one another. The other assumption is that the volume of the molecules is negligibly small compared with that of the container. A gas that satisfies these two conditions is said to exhibit *ideal behavior*.

Although we can assume that real gases behave like an ideal gas, we cannot expect them to do so under all conditions. For example, without intermolecular forces, gases could not condense to form liquids. The important question is: Under what conditions will gases most likely exhibit nonideal behavior?

Figure 5.22 shows PV/RT plotted against P for three real gases and an ideal gas at a given temperature. This graph provides a test of ideal gas behavior. According to the ideal gas equation (for 1 mole of gas), PV/RT equals 1, regardless of the actual gas pressure. (When $n = 1$, $PV = nRT$ becomes $PV = RT$, or $PV/RT = 1$.) For real gases, this is true only at moderately low pressures (≤ 5 atm); significant deviations occur as pressure increases. Attractive forces operate among molecules at relatively short distances. At atmospheric pressure, the molecules in a gas are far apart and the attractive forces are negligible. At high pressures, the density of the gas increases; the molecules are much closer to one another. Intermolecular forces can then be significant enough to affect the motion of the molecules, and the gas will not behave ideally.

Figure 5.22 Plot of PV/RT versus P of 1 mole of a gas at 0°C. For 1 mole of an ideal gas, PV/RT is equal to 1, no matter what the pressure of the gas is. For real gases, we observe various deviations from ideality at high pressures. At very low pressures, all gases exhibit ideal behavior; that is, their PV/RT values all converge to 1 as P approaches zero.



Another way to observe the nonideal behavior of gases is to lower the temperature. Cooling a gas decreases the molecules' average kinetic energy, which in a sense deprives molecules of the drive they need to break from their mutual attraction.

To study real gases accurately, then, we need to modify the ideal gas equation, taking into account intermolecular forces and finite molecular volumes. Such an analysis was first made by the Dutch physicist J. D. van der Waals[†] in 1873. Besides being mathematically simple, his treatment provides us with an interpretation of real gas behavior at the molecular level.

Consider the approach of a particular molecule toward the wall of a container (Figure 5.23). The intermolecular attractions exerted by its neighbors tend to soften the impact made by this molecule against the wall. The overall effect is a lower gas pressure than we would expect for an ideal gas. Van der Waals suggested that the pressure exerted by an ideal gas, P_{ideal} , is related to the experimentally measured pressure, P_{real} , by the equation

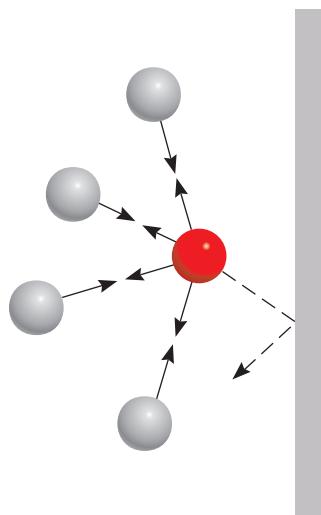


Figure 5.23 Effect of intermolecular forces on the pressure exerted by a gas. The speed of a molecule that is moving toward the container wall (red sphere) is reduced by the attractive forces exerted by its neighbors (gray spheres). Consequently, the impact this molecule makes with the wall is not as great as it would be if no intermolecular forces were present. In general, the measured gas pressure is lower than the pressure the gas would exert if it behaved ideally.

$$P_{\text{ideal}} = P_{\text{real}} + \frac{an^2}{V^2}$$

↑ ↑
observed pressure correction term

where a is a constant and n and V are the number of moles and volume of the container, respectively. The correction term for pressure (an^2/V^2) can be understood as follows: The intermolecular interaction that gives rise to nonideal behavior depends on how frequently any two molecules approach each other closely. The frequency of such “encounters” increases with the square of the number of molecules per unit volume (n^2/V^2), because the probability of finding each of the two molecules in a particular region is proportional to n/V . Thus, a is just a proportionality constant.

Another correction concerns the volume occupied by the gas molecules. In the ideal gas equation, V represents the volume of the container. However, each molecule does occupy a finite, although small, intrinsic volume, so the effective volume of the gas becomes $(V - nb)$, where n is the number of moles of the gas and b is a constant. The term nb represents the volume occupied by n moles of the gas.

[†]Johannes Diderck van der Waals (1837–1923). Dutch physicist. Van der Waals received the Nobel Prize in Physics in 1910 for his work on the properties of gases and liquids.

Having taken into account the corrections for pressure and volume, we can rewrite the ideal gas equation as follows:

$$\underbrace{\left(P + \frac{an^2}{V^2} \right)}_{\text{corrected pressure}} \underbrace{(V - nb)}_{\text{corrected volume}} = nRT \quad (5.18)$$

Keep in mind that in Equation (5.18), P is the experimentally measured gas pressure and V is the volume of the gas container.

Equation (5.18), relating P , V , T , and n for a nonideal gas, is known as the **van der Waals equation**. The van der Waals constants a and b are selected to give the best possible agreement between Equation (5.18) and observed behavior of a particular gas.

Table 5.4 lists the values of a and b for a number of gases. The value of a indicates how strongly molecules of a given type of gas attract one another. We see that helium atoms have the weakest attraction for one another, because helium has the smallest a value. There is also a rough correlation between molecular size and b . Generally, the larger the molecule (or atom), the greater b is, but the relationship between b and molecular (or atomic) size is not a simple one.

Example 5.18 compares the pressure of a gas calculated using the ideal gas equation and the van der Waals equation.

Example 5.18

Given that 3.50 moles of NH_3 occupy 5.20 L at 47°C, calculate the pressure of the gas (in atm) using (a) the ideal gas equation and (b) the van der Waals equation.

Strategy To calculate the pressure of NH_3 using the ideal gas equation, we proceed as in Example 5.3 (Section 5.4). What corrections are made to the pressure and volume terms in the van der Waals equation?

Solution (a) We have the following data:

$$\begin{aligned} V &= 5.20 \text{ L} \\ T &= (47 + 273) \text{ K} = 320 \text{ K} \\ n &= 3.50 \text{ mol} \\ R &= 0.0821 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol} \end{aligned}$$

Substituting these values in the ideal gas equation, we write

$$\begin{aligned} P &= \frac{nRT}{V} \\ &= \frac{(3.50 \text{ mol})(0.0821 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol})(320 \text{ K})}{5.20 \text{ L}} \\ &= 17.7 \text{ atm} \end{aligned}$$

(b) We need Equation (5.18). It is convenient to first calculate the correction terms in Equation (5.18) separately. From Table 5.4, we have

$$\begin{aligned} a &= 4.17 \text{ atm} \cdot \text{L}^2/\text{mol}^2 \\ b &= 0.0371 \text{ L/mol} \end{aligned}$$

so that the correction terms for pressure and volume are

$$\begin{aligned} \frac{an^2}{V^2} &= \frac{(4.17 \text{ atm} \cdot \text{L}^2/\text{mol}^2)(3.50 \text{ mol})^2}{(5.20 \text{ L})^2} = 1.89 \text{ atm} \\ nb &= (3.50 \text{ mol})(0.0371 \text{ L/mol}) = 0.130 \text{ L} \end{aligned}$$

(Continued)

Student Hot Spot

Student data indicate you may struggle with the van der Waals equation. Access your eBook for additional Learning Resources on this topic.

Table 5.4

van der Waals Constants of Some Common Gases

Gas	a $\left(\frac{\text{atm} \cdot \text{L}^2}{\text{mol}^2} \right)$	b $\left(\frac{\text{L}}{\text{mol}} \right)$
He	0.034	0.0237
Ne	0.211	0.0171
Ar	1.34	0.0322
Kr	2.32	0.0398
Xe	4.19	0.0266
H_2	0.244	0.0266
N_2	1.39	0.0391
O_2	1.36	0.0318
Cl_2	6.49	0.0562
CO_2	3.59	0.0427
CH_4	2.25	0.0428
CCl_4	20.4	0.138
NH_3	4.17	0.0371
H_2O	5.46	0.0305

Finally, substituting these values in the van der Waals equation, we have

$$(P + 1.89 \text{ atm})(5.20 \text{ L} - 0.130 \text{ L}) = (3.50 \text{ mol})(0.0821 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol})(320 \text{ K})$$

$$P = 16.2 \text{ atm}$$

Check Based on your understanding of nonideal gas behavior, is it reasonable that the pressure calculated using the van der Waals equation should be smaller than that using the ideal gas equation? Why?

Practice Exercise Using the data shown in Table 5.4, calculate the pressure exerted by 4.37 moles of molecular chlorine confined in a volume of 2.45 L at 38°C. Compare the pressure with that calculated using the ideal gas equation.

Similar problem: 5.93.

Review of Concepts & Facts

- 5.8.1 What pressure and temperature conditions cause the most deviation from ideal gas behavior?
- 5.8.2 Using the van der Waals equation, determine the pressure exerted by 2.25 moles of CH₄ in a 5.25-L vessel at 25°C.

Learning Objectives

- Summarize the characteristics of gases that differentiate them from solids and liquids. (Section 5.1)
- Understand the definition and the common units of pressure. (Section 5.2)
- Interconvert units of pressure. (Section 5.2)
- Appraise Boyle's, Charles', and Avogadro's laws and how they may be combined to interconvert measurements of pressure, volume, and temperature. (Section 5.3)
- Apply the ideal gas equation to determine the pressure, volume, moles, or temperature of a gas given all of the other values. (Section 5.4)
- Identify the conditions of standard temperature and pressures for gases. (Section 5.4)
- Employ the ideal gas equation to determine the density and molar mass of a gas. (Section 5.4)
- Manipulate the ideal gas equation to calculate stoichiometric quantities. (Section 5.5)
- Determine mole fractions and partial pressures for gases in a mixture. (Section 5.6)
- Interpret the basic assumptions of the kinetic molecular theory. (Section 5.7)
- Compare effusion and diffusion. (Section 5.7)
- Explain the factors that cause gases to deviate from ideal gas behavior. (Section 5.8)
- Demonstrate the use of the van der Waals equation to determine the pressure of a real gas. (Section 5.8)

Key Equations

$$P_1V_1 = P_2V_2 \quad (5.2)$$

Boyle's law. For calculating pressure or volume changes.

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad (5.4)$$

Charles' law. For calculating temperature or volume changes.

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \quad (5.6)$$

Charles' law. For calculating temperature or pressure changes.

$$V = k_4 n \quad (5.7)$$

$$PV = nRT \quad (5.8)$$

$$\frac{P_1 V_1}{n_1 T_1} = \frac{P_2 V_2}{n_2 T_2} \quad (5.9)$$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad (5.10)$$

$$d = \frac{m}{V} = \frac{P\mathcal{M}}{RT} \quad (5.11)$$

$$X_i = \frac{n_i}{n_T} \quad (5.13)$$

$$P_i = X_i P_T \quad (5.14)$$

$$\overline{\text{KE}} = \frac{1}{2} m \overline{u^2} = CT \quad (5.15)$$

$$u_{\text{rms}} = \sqrt{\frac{3RT}{\mathcal{M}}} \quad (5.16)$$

$$\frac{r_1}{r_2} = \sqrt{\frac{\mathcal{M}_2}{\mathcal{M}_1}} \quad (5.17)$$

$$\left(P + \frac{an^2}{V^2} \right) (V - nb) = nRT \quad (5.18)$$

Avogadro's law. Constant P and T .

Ideal gas equation.

For calculating changes in pressure, temperature, volume, or amount of gas.

For calculating changes in pressure, temperature, or volume when n is constant.

For calculating density or molar mass.

Definition of mole fraction.

Dalton's law of partial pressures. For calculating partial pressures.

Relating the average kinetic energy of a gas to its absolute temperature.

For calculating the root-mean-square speed of gas molecules.

Graham's law of diffusion and effusion.

Van der Waals equation. For calculating the pressure of a nonideal gas.

Summary of Concepts & Facts

- At 25°C and 1 atm, a number of elements and molecular compounds exist as gases. Ionic compounds are solids rather than gases under atmospheric conditions.
- Gases exert pressure because their molecules move freely and collide with any surface with which they make contact. Units of gas pressure include millimeters of mercury (mmHg), torr, pascals, and atmospheres. One atmosphere equals 760 mmHg, or 760 torr.
- The pressure-volume relationships of ideal gases are governed by Boyle's law: Volume is inversely proportional to pressure (at constant T and n).
- The temperature-volume relationships of ideal gases are described by Charles' and Gay-Lussac's law: Volume is directly proportional to temperature (at constant P and n).
- Absolute zero (-273.15°C) is the lowest theoretically attainable temperature. The Kelvin temperature scale takes 0 K as absolute zero. In all gas law calculations, temperature must be expressed in kelvins.
- The amount-volume relationships of ideal gases are described by Avogadro's law: Equal volumes of gases contain equal numbers of molecules (at the same T and P).
- The ideal gas equation, $PV = nRT$, combines the laws of Boyle, Charles, and Avogadro. This equation describes the behavior of an ideal gas.
- Dalton's law of partial pressures states that each gas in a mixture of gases exerts the same pressure as it would if it were alone and occupied the same volume.
- The kinetic molecular theory, a mathematical way of describing the behavior of gas molecules, is based on the following assumptions: Gas molecules are separated by distances far greater than their own dimensions, they possess mass but have negligible volume, they are in constant motion, and they frequently collide with one another. The molecules neither attract nor repel one another.
- A Maxwell speed distribution curve shows how many gas molecules are moving at various speeds at a given temperature. As temperature increases, more molecules move at greater speeds.
- In diffusion, two gases gradually mix with each other. In effusion, gas molecules move through a small opening under pressure. Both processes are governed by the same mathematical law—Graham's law of diffusion and effusion.
- The van der Waals equation is a modification of the ideal gas equation that takes into account the nonideal behavior of real gases. It corrects for the fact that real gas molecules do exert forces on each other and that they do have volume. The van der Waals constants are determined experimentally for each gas.

Key Words

Absolute temperature scale, p. 184	Dalton's law of partial pressures, p. 197	Kelvin temperature scale, p. 184	Pressure, p. 177
Absolute zero, p. 184	Diffusion, p. 208	Kinetic energy (KE), p. 204	Root-mean-square (rms) speed (u_{rms}), p. 207
Atmospheric pressure, p. 178	Effusion, p. 210	Kinetic molecular theory of gases, p. 204	Standard atmospheric pressure (1 atm), p. 178
Avogadro's law, p. 185	Gas constant (R), p. 186	Manometer, p. 179	Standard temperature and pressure (STP), p. 187
Barometer, p. 178	Graham's law of diffusion, p. 210	Mole fraction, p. 198	van der Waals equation, p. 213
Boyle's law, p. 180	Ideal gas, p. 186	Newton (N), p. 177	
Charles' and Gay-Lussac's law, p. 184	Ideal gas equation, p. 186	Partial pressure, p. 197	
Charles' law, p. 184	Joule (J), p. 204	Pascal (Pa), p. 178	

Questions & Problems

Red numbered problems solved in *Student Solutions Manual*

5.1 Substances That Exist as Gases

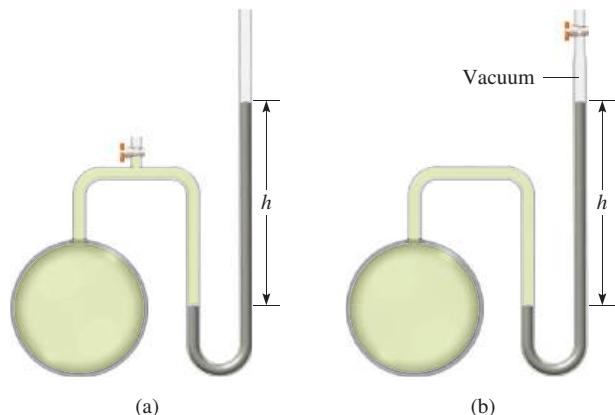
Review Questions

- 5.1 Name five elements and five compounds that exist as gases at room temperature.
 5.2 List the physical characteristics of gases.

5.2 Pressure of a Gas

Review Questions

- 5.3 Define pressure and give the common units for pressure.
 5.4 When you are in a plane flying at high altitudes, your ears often experience pain. This discomfort can be temporarily relieved by yawning or swallowing some water. Explain.
 5.5 Why is mercury a more suitable substance to use in a barometer than water?
 5.6 Explain why the height of mercury in a barometer is independent of the cross-sectional area of the tube. Would the barometer still work if the tubing were tilted at an angle, say 15 degrees (see Figure 5.3)?
 5.7 Explain how a unit of length (mmHg) can be used as a unit for pressure.
 5.8 Describe what would happen to the column of mercury in these manometers when the stopcock is opened.



- 5.9 What is the difference between a gas and a vapor? At 25°C, which of the following substances in the gas phase should be properly called a gas and which should be called a vapor: molecular nitrogen (N_2), mercury?
 5.10 If the maximum distance that water may be brought up a well by a suction pump is 34 ft (10.3 m), how is it possible to obtain water and oil from hundreds of feet below the surface of Earth?
 5.11 Why is it that if the barometer reading falls in one part of the world, it must rise somewhere else?
 5.12 Why do astronauts have to wear protective suits when they are on the surface of the moon?

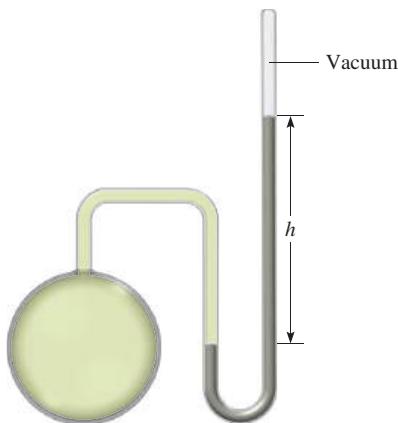
Problems

- 5.13 Convert 562 mmHg to atm.
5.14 The atmospheric pressure at the summit of Denali (formerly known as Mt. McKinley) is 606 mmHg on a certain day. What is the pressure in atm and in kPa?

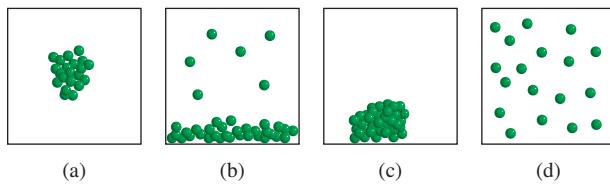
5.3 The Gas Laws

Review Questions

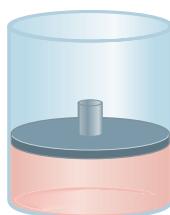
- 5.15 State the following gas laws in words and also in the form of an equation: Boyle's law, Charles' law, Avogadro's law. In each case, indicate the conditions under which the law is applicable, and give the units for each quantity in the equation.
 5.16 A certain amount of gas is contained in a closed mercury manometer as shown here. Assuming no other parameters change, would h increase, decrease, or remain the same if (a) the amount of the gas were increased; (b) the molar mass of the gas were doubled; (c) the temperature of the gas was increased; (d) the atmospheric pressure in the room was increased; (e) the mercury in the tube were replaced with a less dense fluid; (f) some gas was added to the vacuum at the top of the right-side tube; (g) a hole was drilled in the top of the right-side tube?

**Problems**

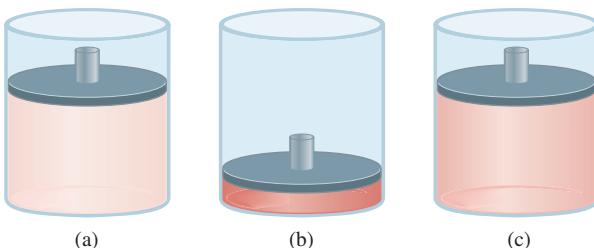
- 5.17** A gaseous sample of a substance is cooled at constant pressure. Which of the diagrams (a)–(d) best represents the situation if the final temperature is (i) above the boiling point of the substance, and (ii) below the boiling point but above the freezing point of the substance?



- 5.18** Consider the following gaseous sample in a cylinder fitted with a movable piston. Initially there are n moles of the gas at temperature T , pressure P , and volume V .



Choose the cylinder that correctly represents the gas after each of the following changes. (1) The pressure on the piston is tripled at constant n and T . (2) The temperature is doubled at constant n and P . (3) n moles of another gas are added at constant T and P . (4) T is halved and pressure on the piston is reduced to a quarter of its original value.



- 5.19** A gas occupying a volume of 725 mL at a pressure of 0.970 atm is allowed to expand at constant temperature until its pressure reaches 0.541 atm. What is its final volume?

- 5.20** At 46°C a sample of ammonia gas exerts a pressure of 5.3 atm. What is the pressure when the volume of the gas is reduced to one-tenth (0.10) of the original value at the same temperature?

- 5.21** The volume of a gas is 5.80 L, measured at 1.00 atm. What is the pressure of the gas in mmHg if the volume is changed to 9.65 L? (The temperature remains constant.)

- 5.22** A sample of air occupies 3.8 L when the pressure is 1.2 atm. (a) What volume does it occupy at 6.6 atm? (b) What pressure is required in order to compress it to 0.075 L? (The temperature is kept constant.)

- 5.23** A 36.4-L volume of methane gas is heated from 25°C to 88°C at constant pressure. What is the final volume of the gas?

- 5.24** Under constant-pressure conditions a sample of hydrogen gas initially at 88°C and 9.6 L is cooled until its final volume is 3.4 L. What is its final temperature?

- 5.25** Ammonia burns in oxygen gas to form nitric oxide (NO) and water vapor. How many volumes of NO are obtained from one volume of ammonia at the same temperature and pressure?

- 5.26** Molecular chlorine and molecular fluorine combine to form a gaseous product. Under the same conditions of temperature and pressure it is found that one volume of Cl_2 reacts with three volumes of F_2 to yield two volumes of the product. What is the formula of the product?

5.4 The Ideal Gas Equation**Review Questions**

- 5.27** List the characteristics of an ideal gas. Write the ideal gas equation and also state it in words. Give the units for each term in the equation.

- 5.28** Use Equation (5.9) to derive all the gas laws.

- 5.29** What are standard temperature and pressure (STP)? What is the significance of STP in relation to the volume of 1 mole of an ideal gas?

- 5.30** Why is the density of a gas much lower than that of a liquid or solid under atmospheric conditions? What units are normally used to express the density of gases?

Problems

- 5.31** A sample of nitrogen gas kept in a container of volume 2.3 L and at a temperature of 32°C exerts a pressure of 4.7 atm. Calculate the number of moles of gas present.

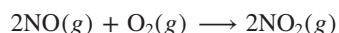
- 5.32** Given that 6.9 moles of carbon monoxide gas are present in a container of volume 30.4 L, what is the pressure of the gas (in atm) if the temperature is 62°C?

- 5.33 What volume will 5.6 moles of sulfur hexafluoride (SF_6) gas occupy if the temperature and pressure of the gas are 128°C and 9.4 atm?
- 5.34** A certain amount of gas at 25°C and at a pressure of 0.800 atm is contained in a glass vessel. Suppose that the vessel can withstand a pressure of 2.00 atm. How high can you raise the temperature of the gas without bursting the vessel?
- 5.35 A gas-filled balloon having a volume of 2.50 L at 1.2 atm and 25°C is allowed to rise to the stratosphere (about 30 km above the surface of Earth), where the temperature and pressure are -23°C and 3.00×10^{-3} atm, respectively. Calculate the final volume of the balloon.
- 5.36** The temperature of 2.5 L of a gas initially at STP is raised to 250°C at constant volume. Calculate the final pressure of the gas in atm.
- 5.37 The pressure of 6.0 L of an ideal gas in a flexible container is decreased to one-third of its original pressure, and its absolute temperature is decreased by one-half. What is the final volume of the gas?
- 5.38** A gas evolved during the fermentation of glucose (wine making) has a volume of 0.78 L at 20.1°C and 1.00 atm. What was the volume of this gas at the fermentation temperature of 36.5°C and 1.00 atm pressure?
- 5.39 An ideal gas originally at 0.85 atm and 66°C was allowed to expand until its final volume, pressure, and temperature were 94 mL, 0.60 atm, and 45°C , respectively. What was its initial volume?
- 5.40** Calculate its volume (in liters) of 88.4 g of CO_2 at STP.
- 5.41 A gas at 772 mmHg and 35.0°C occupies a volume of 6.85 L. Calculate its volume at STP.
- 5.42** Dry ice is solid carbon dioxide. A 0.050-g sample of dry ice is placed in an evacuated 4.6-L vessel at 30°C . Calculate the pressure inside the vessel after all the dry ice has been converted to CO_2 gas.
- 5.43 At STP, 0.280 L of a gas weighs 0.400 g. Calculate the molar mass of the gas.
- 5.44** At 741 torr and 44°C , 7.10 g of a gas occupy a volume of 5.40 L. What is the molar mass of the gas?
- 5.45 Ozone molecules in the stratosphere absorb much of the harmful radiation from the sun. Typically, the temperature and pressure of ozone in the stratosphere are 250 K and 1.0×10^{-3} atm, respectively. How many ozone molecules are present in 1.0 L of air under these conditions?
- 5.46** Assuming that air contains 78 percent N_2 , 21 percent O_2 , and 1 percent Ar, all by volume, how many molecules of each type of gas are present in 1.0 L of air at STP?
- 5.47 A 2.10-L vessel contains 4.65 g of a gas at 1.00 atm and 27.0°C . (a) Calculate the density of the gas in grams per liter. (b) What is the molar mass of the gas?
- 5.48** Calculate the density of hydrogen bromide (HBr) gas in grams per liter at 733 mmHg and 46°C .
- 5.49 A certain anesthetic contains 64.9 percent C, 13.5 percent H, and 21.6 percent O by mass. At 120°C and 750 mmHg, 1.00 L of the gaseous compound weighs 2.30 g. What is the molecular formula of the compound?
- 5.50** A compound has the empirical formula SF_4 . At 20°C , 0.100 g of the gaseous compound occupies a volume of 22.1 mL and exerts a pressure of 1.02 atm. What is the molecular formula of the gas?
- 5.51 What pressure will be required for neon at 30°C to have the same density as nitrogen at 20°C and 1.0 atm?
- 5.52** The density of a mixture of fluorine and chlorine gases is 1.77 g/L at 14°C and 0.893 atm. Calculate the mass percent of the gases.

5.5 Gas Stoichiometry

Problems

- 5.53 Consider the formation of nitrogen dioxide from nitric oxide and oxygen:



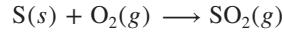
If 9.0 L of NO are reacted with excess O_2 at STP, what is the volume in liters of the NO_2 produced?

- 5.54** Methane, the principal component of natural gas, is used for heating and cooking. The combustion process is



If 15.0 moles of CH_4 are reacted, what is the volume of CO_2 (in liters) produced at 23.0°C and 0.985 atm?

- 5.55 When coal is burned, the sulfur present in coal is converted to sulfur dioxide (SO_2), which is responsible for the acid rain phenomenon.



If 2.54 kg of S are reacted with oxygen, calculate the volume of SO_2 gas (in mL) formed at 30.5°C and 1.12 atm.

- 5.56** In alcohol fermentation, yeast converts glucose to ethanol and carbon dioxide:



If 5.97 g of glucose are reacted and 1.44 L of CO_2 gas are collected at 293 K and 0.984 atm, what is the percent yield of the reaction?

- 5.57 A compound of P and F was analyzed as follows: Heating 0.2324 g of the compound in a 378-cm³ container turned all of it to gas, which had a pressure of 97.3 mmHg at 77°C . Then the gas was mixed with calcium chloride solution, which turned all of the F to 0.2631 g of CaF_2 . Determine the molecular formula of the compound.

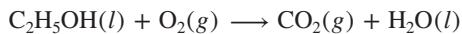
- 5.58** A quantity of 0.225 g of a metal M (molar mass = 27.0 g/mol) liberated 0.303 L of molecular hydrogen (measured at 17°C and 741 mmHg) from an excess of hydrochloric acid. Deduce from these data the corresponding equation and write formulas for the oxide and sulfate of M.

5.59 What is the mass of the solid NH₄Cl formed when 73.0 g of NH₃ are mixed with an equal mass of HCl? What is the volume of the gas remaining, measured at 14.0°C and 752 mmHg? What gas is it?

5.60 Dissolving 3.00 g of an impure sample of calcium carbonate in hydrochloric acid produced 0.656 L of carbon dioxide (measured at 20.0°C and 792 mmHg). Calculate the percent by mass of calcium carbonate in the sample. State any assumptions.

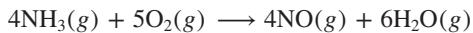
5.61 Calculate the mass in grams of hydrogen chloride produced when 5.6 L of molecular hydrogen measured at STP react with an excess of molecular chlorine gas.

5.62 Ethanol (C₂H₅OH) burns in air:

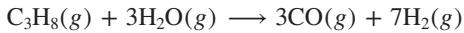


Balance the equation and determine the volume of air in liters at 35.0°C and 790 mmHg required to burn 227 g of ethanol. Assume that air is 21.0 percent O₂ by volume.

5.63 (a) What volumes (in liters) of ammonia and oxygen must react to form 12.8 L of nitric oxide according to the equation at the same temperature and pressure?



(b) What volumes (in liters) of propane and water vapor must react to form 8.96 L of hydrogen according to the equation at the same temperature and pressure?



5.64 A 4.00-g sample of FeS containing nonsulfide impurities reacted with HCl to give 896 mL of H₂S at 14°C and 782 mmHg. Calculate mass percent purity of the sample.

5.6 Dalton's Law of Partial Pressures

Review Questions

5.65 State Dalton's law of partial pressures and explain what mole fraction is. Does mole fraction have units?

5.66 A sample of air contains only nitrogen and oxygen gases whose partial pressures are 0.80 atm and 0.20 atm, respectively. Calculate the total pressure and the mole fractions of the gases.

Problems

5.67 A mixture of gases contains 0.31 mol CH₄, 0.25 mol C₂H₆, and 0.29 mol C₃H₈. The total pressure is 1.50 atm. Calculate the partial pressures of the gases.

5.68 A 2.5-L flask at 15°C contains a mixture of N₂, He, and Ne at partial pressures of 0.32 atm for N₂, 0.15 atm for He, and 0.42 atm for Ne. (a) Calculate the total pressure of the mixture. (b) Calculate the volume in liters at STP occupied by He and Ne if the N₂ is removed selectively.

5.69 Dry air near sea level has the following composition by volume: N₂, 78.08 percent; O₂, 20.94 percent; Ar, 0.93 percent; CO₂, 0.05 percent. The atmospheric

pressure is 1.00 atm. Calculate (a) the partial pressure of each gas in atm and (b) the concentration of each gas in moles per liter at 0°C. (*Hint:* Because volume is proportional to the number of moles present, mole fractions of gases can be expressed as ratios of volumes at the same temperature and pressure.)

5.70 A mixture of helium and neon gases is collected over water at 28.0°C and 745 mmHg. If the partial pressure of helium is 368 mmHg, what is the partial pressure of neon? (Vapor pressure of water at 28°C = 28.3 mmHg.)

5.71 A piece of sodium metal reacts completely with water as follows:



The hydrogen gas generated is collected over water at 25.0°C. The volume of the gas is 246 mL measured at 1.00 atm. Calculate the number of grams of sodium used in the reaction. (Vapor pressure of water at 25°C = 0.0313 atm.)

5.72 A sample of zinc metal reacts completely with an excess of hydrochloric acid:

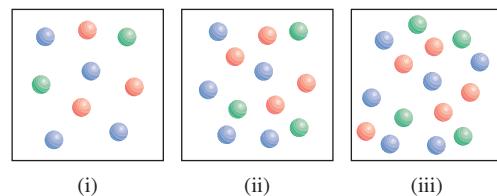


The hydrogen gas produced is collected over water at 25.0°C using an arrangement similar to that shown in Figure 5.15. The volume of the gas is 7.80 L, and the pressure is 0.980 atm. Calculate the amount of zinc metal in grams consumed in the reaction. (Vapor pressure of water at 25°C = 23.8 mmHg.)

5.73 Helium is mixed with oxygen gas for deep-sea divers. Calculate the percent by volume of oxygen gas in the mixture if the diver has to submerge to a depth where the total pressure is 4.2 atm. The partial pressure of oxygen is maintained at 0.20 atm at this depth.

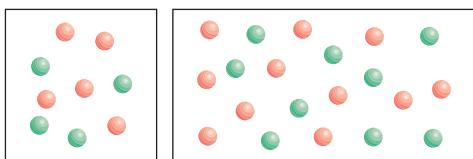
5.74 A sample of ammonia (NH₃) gas is completely decomposed to nitrogen and hydrogen gases over heated iron wool. If the total pressure is 866 mmHg, calculate the partial pressures of N₂ and H₂.

5.75 Consider the three gas containers (i)–(iii). All of them have the same volume and are at the same temperature. (a) Which container has the smallest mole fraction of gas A (blue sphere)? (b) Which container has the highest partial pressure of gas B (green sphere)?



5.76 The volume of the box on the right is twice that of the box on the left. The boxes contain helium atoms (red) and hydrogen molecules (green) at the same temperature. (a) Which box has a higher total

pressure? (b) Which box has a lower partial pressure of helium?



5.7 The Kinetic Molecular Theory of Gases

Review Questions

- 5.77 What are the basic assumptions of the kinetic molecular theory of gases? How does the kinetic molecular theory explain Boyle's law, Charles' law, Avogadro's law, and Dalton's law of partial pressures?
- 5.78 What does the Maxwell speed distribution curve tell us? Does Maxwell's theory work for a sample of 200 molecules? Explain.
- 5.79 Which of the following statements is correct? (a) Heat is produced by the collision of gas molecules against one another. (b) When a gas is heated, the molecules collide with one another more often.
- 5.80 What is the difference between gas diffusion and effusion? State Graham's law and define the terms in Equation (5.17).

Problems

- 5.81 Compare the root-mean-square speeds of O₂ and UF₆ at 65°C.
- 5.82** The temperature in the stratosphere is -23°C. Calculate the root-mean-square speeds of N₂, O₂, and O₃ molecules in this region.
- 5.83 The average distance traveled by a molecule between successive collisions is called *mean free path*. For a given amount of a gas, how does the mean free path of a gas depend on (a) density, (b) temperature at constant volume, (c) pressure at constant temperature, (d) volume at constant temperature, and (e) size of the atoms?
- 5.84** At a certain temperature the speeds of six gaseous molecules in a container are 2.0 m/s, 2.2 m/s, 2.6 m/s, 2.7 m/s, 3.3 m/s, and 3.5 m/s. Calculate the root-mean-square speed and the average speed of the molecules. These two average values are close to each other, but the root-mean-square value is always the larger of the two. Why?
- 5.85 Based on your knowledge of the kinetic theory of gases, derive Graham's law [Equation (5.17)].
- 5.86** The ²³⁵U isotope undergoes fission when bombarded with neutrons. However, its natural abundance is only 0.72 percent. To separate it from the more abundant ²³⁸U isotope, uranium is first converted to UF₆, which is easily vaporized above room temperature. The mixture of the ²³⁵UF₆ and ²³⁸UF₆ gases is then subjected to many stages of effusion. Calculate the separation factor, that is, the enrichment of ²³⁵U relative to ²³⁸U after one stage of effusion.

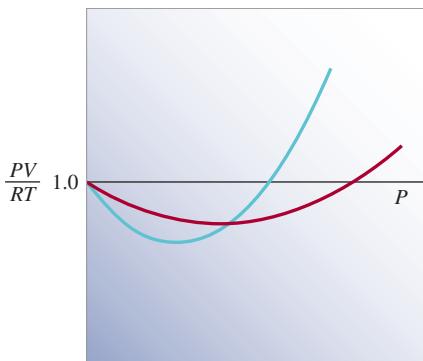
5.87 A gas evolved from the fermentation of glucose is found to effuse through a porous barrier in 15.0 min. Under the same conditions of temperature and pressure, it takes an equal volume of N₂ 12.0 min to effuse through the same barrier. Calculate the molar mass of the gas and suggest what the gas might be.

5.88 Nickel forms a gaseous compound of the formula Ni(CO)_x. What is the value of *x* given the fact that under the same conditions of temperature and pressure, methane (CH₄) effuses 3.3 times faster than the compound?

5.8 Deviation from Ideal Behavior

Review Questions

- 5.89 Cite two pieces of evidence to show that gases do not behave ideally under all conditions.
- 5.90 Under what set of conditions would a gas be expected to behave most ideally: (a) high temperature and low pressure, (b) high temperature and high pressure, (c) low temperature and high pressure, or (d) low temperature and low pressure?
- 5.91 Shown are plots of PV/RT against P for one mole of a nonideal gas at two different temperatures. Which curve is at the higher temperature?



- 5.92 (a) A real gas is introduced into a flask of volume V. Is the corrected volume of the gas greater or less than V? (b) Ammonia has a larger *a* value than neon does (see Table 5.4). What can you conclude about the relative strength of the attractive forces between molecules of ammonia and between atoms of neon?

Problems

- 5.93 Using the data shown in Table 5.4, calculate the pressure exerted by 2.50 moles of CO₂ confined in a volume of 5.00 L at 450 K. Compare the pressure with that predicted by the ideal gas equation.
- 5.94** At 27°C, 10.0 moles of a gas in a 1.50-L container exert a pressure of 130 atm. Is this an ideal gas?

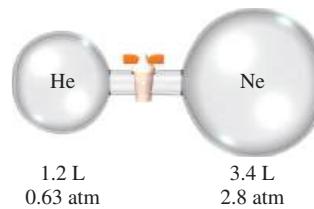
Additional Problems

- 5.95 Discuss the following phenomena in terms of the gas laws: (a) the pressure increase in an automobile tire on a hot day; (b) the "popping" of a paper

- bag; (c) the expansion of a weather balloon as it rises in the air; (d) the loud noise heard when a lightbulb shatters.
- 5.96** Under the same conditions of temperature and pressure, which of the following gases would behave most ideally: Ne, N₂, or CH₄? Explain.
- 5.97 Nitroglycerin, an explosive compound, decomposes according to the equation
- $$4\text{C}_3\text{H}_5(\text{NO}_3)_3(s) \longrightarrow 12\text{CO}_2(g) + 10\text{H}_2\text{O}(g) + 6\text{N}_2(g) + \text{O}_2(g)$$
- Calculate the total volume of gases when collected at 1.2 atm and 25°C from 2.6 × 10² g of nitroglycerin. What are the partial pressures of the gases under these conditions?
- 5.98** The empirical formula of a compound is CH. At 200°C, 0.145 g of this compound occupies 97.2 mL at a pressure of 0.74 atm. What is the molecular formula of the compound?
- 5.99 When ammonium nitrite (NH₄NO₂) is heated, it decomposes to give nitrogen gas. This property is used to inflate some tennis balls. (a) Write a balanced equation for the reaction. (b) Calculate the quantity (in grams) of NH₄NO₂ needed to inflate a tennis ball to a volume of 86.2 mL at 1.20 atm and 22°C.
- 5.100** The percent by mass of bicarbonate (HCO₃⁻) in a certain Alka-Seltzer product is 32.5 percent. Calculate the volume of CO₂ generated (in mL) at 37°C and 1.00 atm when a person ingests a 3.29-g tablet. (*Hint:* The reaction is between HCO₃⁻ and HCl acid in the stomach.)
- 5.101 The boiling point of liquid nitrogen is -196°C. On the basis of this information alone, do you think nitrogen is an ideal gas?
- 5.102** In the metallurgical process of refining nickel, the metal is first combined with carbon monoxide to form tetracarbonylnickel, which is a gas at 43°C:
- $$\text{Ni}(s) + 4\text{CO}(g) \longrightarrow \text{Ni}(\text{CO})_4(g)$$
- This reaction separates nickel from other solid impurities. (a) Starting with 86.4 g of Ni, calculate the pressure of Ni(CO)₄ in a container of volume 4.00 L. (Assume the above reaction goes to completion.) (b) At temperatures above 43°C, the pressure of the gas is observed to increase much more rapidly than predicted by the ideal gas equation. Explain.
- 5.103 The partial pressure of carbon dioxide varies with seasons. Would you expect the partial pressure in the Northern Hemisphere to be higher in the summer or winter? Explain.
- 5.104** A healthy adult exhales about 5.0 × 10² mL of a gaseous mixture with each breath. Calculate the number of molecules present in this volume at 37°C and 1.1 atm. List the major components of this gaseous mixture.
- 5.105 Sodium bicarbonate (NaHCO₃) is called baking soda because when heated, it releases carbon dioxide gas, which is responsible for the rising of

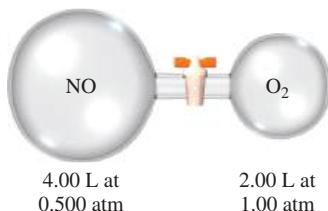
cookies, doughnuts, and bread. (a) Calculate the volume (in liters) of CO₂ produced by heating 5.0 g of NaHCO₃ at 180°C and 1.3 atm. (b) Ammonium bicarbonate (NH₄HCO₃) has also been used for the same purpose. Suggest one advantage and one disadvantage of using NH₄HCO₃ instead of NaHCO₃ for baking.

- 5.106** A barometer having a cross-sectional area of 1.00 cm² at sea level measures a pressure of 76.0 cm of mercury. The pressure exerted by this column of mercury is equal to the pressure exerted by all the air on 1 cm² of Earth's surface. Given that the density of mercury is 13.6 g/mL and the average radius of Earth is 6371 km, calculate the total mass of Earth's atmosphere in kilograms. (*Hint:* The surface area of a sphere is $4\pi r^2$, where r is the radius of the sphere.)
- 5.107 Some commercial drain cleaners contain a mixture of sodium hydroxide and aluminum powder. When the mixture is poured down a clogged drain, the following reaction occurs:
- $$2\text{NaOH}(aq) + 2\text{Al}(s) + 6\text{H}_2\text{O}(l) \longrightarrow 2\text{NaAl(OH)}_4(aq) + 3\text{H}_2(g)$$
- The heat generated in this reaction helps melt away obstructions such as grease, and the hydrogen gas released stirs up the solids clogging the drain. Calculate the volume of H₂ formed at 23°C and 1.00 atm if 3.12 g of Al are treated with an excess of NaOH.
- 5.108** The volume of a sample of pure HCl gas was 189 mL at 25°C and 108 mmHg. It was completely dissolved in about 60 mL of water and titrated with an NaOH solution; 15.7 mL of the NaOH solution were required to neutralize the HCl. Calculate the molarity of the NaOH solution.
- 5.109 Propane (C₃H₈) burns in oxygen to produce carbon dioxide gas and water vapor. (a) Write a balanced equation for this reaction. (b) Calculate the number of liters of carbon dioxide measured at STP that could be produced from 7.45 g of propane.
- 5.110** Consider this apparatus. Calculate the partial pressures of helium and neon after the stopcock is open. The temperature remains constant at 16°C.

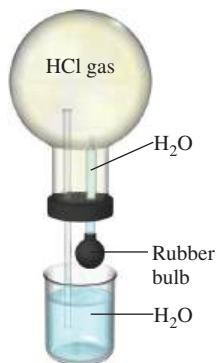


- 5.111 Nitric oxide (NO) reacts with molecular oxygen as follows:
- $$\text{C}_2\text{H}_5\text{OH}(l) + \text{O}_2(g) \longrightarrow \text{CO}_2(g) + \text{H}_2\text{O}(l)$$
- Initially NO and O₂ are separated as shown here. When the valve is opened, the reaction quickly goes

to completion. Determine what gases remain at the end and calculate their partial pressures. Assume that the temperature remains constant at 25°C.



- 5.112** Consider this apparatus. When a small amount of water is introduced into the flask by squeezing the bulb of the medicine dropper, water is squirted upward out of the long glass tubing. Explain this observation. (*Hint:* Hydrogen chloride gas is soluble in water.)



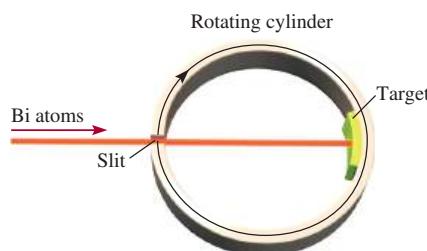
- 5.113** Describe how you would measure, by either chemical or physical means, the partial pressures of a mixture of gases of the following composition: (a) CO₂ and H₂, (b) He and N₂.

- 5.114** A certain hydrate has the formula MgSO₄ · xH₂O. A quantity of 54.2 g of the compound is heated in an oven to drive off the water. If the steam generated exerts a pressure of 24.8 atm in a 2.00-L container at 120°C, calculate *x*.

- 5.115** A mixture of Na₂CO₃ and MgCO₃ of mass 7.63 g is reacted with an excess of hydrochloric acid. The CO₂ gas generated occupies a volume of 1.67 L at 1.24 atm and 26°C. From these data, calculate the percent composition by mass of Na₂CO₃ in the mixture.

- 5.116** The following apparatus can be used to measure atomic and molecular speed. Suppose that a beam of metal atoms is directed at a rotating cylinder in a vacuum. A small opening in the cylinder allows the atoms to strike a target area. Because the cylinder is rotating, atoms traveling at different speeds will strike the target at different positions. In time, a layer of the metal will deposit on the target area, and the variation in its thickness is found to correspond to Maxwell's speed distribution. In one experiment it is found that at 850°C some bismuth (Bi) atoms struck the target at a point 2.80 cm from the spot

directly opposite the slit. The diameter of the cylinder is 15.0 cm and it is rotating at 130 revolutions per second. (a) Calculate the speed (m/s) at which the target is moving. (*Hint:* The circumference of a circle is given by $2\pi r$, where *r* is the radius.) (b) Calculate the time (in seconds) it takes for the target to travel 2.80 cm. (c) Determine the speed of the Bi atoms. Compare your result in (c) with the *u*_{rms} of Bi at 850°C. Comment on the difference.



- 5.117** If 10.00 g of water are introduced into an evacuated flask of volume 2.500 L at 65°C, calculate the mass of water vaporized. (*Hint:* Assume that the volume of the remaining liquid water is negligible; the vapor pressure of water at 65°C is 187.5 mmHg.)

- 5.118** Commercially, compressed oxygen is sold in metal cylinders. If a 120-L cylinder is filled with oxygen to a pressure of 132 atm at 22°C, what is the mass (in grams) of O₂ present? How many liters of O₂ gas at 1.00 atm and 22°C could the cylinder produce? (Assume ideal behavior.)

- 5.119** The shells of hard-boiled eggs sometimes crack due to the rapid thermal expansion of the shells at high temperatures. Suggest another reason why the shells may crack.

- 5.120** Ethylene gas (C₂H₄) is emitted by fruits and is known to be responsible for their ripening. Based on this information, explain why a bunch of bananas ripens faster in a closed paper bag than in a bowl.

- 5.121** About 8.0×10^6 tons of urea [(NH₂)₂CO] are used annually as a fertilizer. The urea is prepared at 200°C and under high-pressure conditions from carbon dioxide and ammonia (the products are urea and steam). Calculate the volume of ammonia (in liters) measured at 150 atm needed to prepare 1.0 ton of urea.

- 5.122** Some ballpoint pens have a small hole in the main body of the pen. What is the purpose of this hole?

- 5.123** The gas laws are vitally important to scuba divers. The pressure exerted by 33 ft of seawater is equivalent to 1 atm pressure. (a) A diver ascends quickly to the surface of the water from a depth of 36 ft without exhaling gas from his lungs. By what factor will the volume of his lungs increase by the time he reaches the surface? Assume that the temperature is constant. (b) The partial pressure of oxygen in air is about 0.20 atm. (Air is 20 percent oxygen by volume.) In deep-sea diving, the composition of air the diver breathes must be changed to maintain this partial pressure. What must the oxygen content (in percent by volume) be when the total pressure exerted

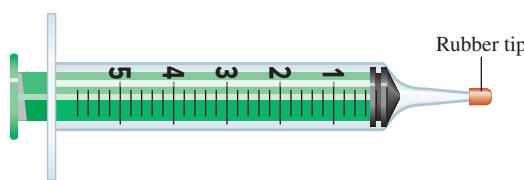
on the diver is 4.0 atm? (At constant temperature and pressure, the volume of a gas is directly proportional to the number of moles of gases.) (*Hint:* See the Chemistry in Action essay “Scuba Diving and the Gas Laws” in Section 5.6.)

- 5.124** Nitrous oxide (N_2O) can be obtained by the thermal decomposition of ammonium nitrate (NH_4NO_3). (a) Write a balanced equation for the reaction. (b) In a certain experiment, a student obtains 0.340 L of the gas at 718 mmHg and 24°C. If the gas weighs 0.580 g, calculate the value of the gas constant.

- 5.125** Two vessels are labeled A and B. Vessel A contains NH_3 gas at 70°C, and vessel B contains Ne gas at the same temperature. If the average kinetic energy of NH_3 is 7.1×10^{-21} J/molecule, calculate the root-mean-square speed of Ne atoms.

- 5.126** Which of the following molecules has the largest a value: CH_4 , F_2 , C_6H_6 , Ne ?

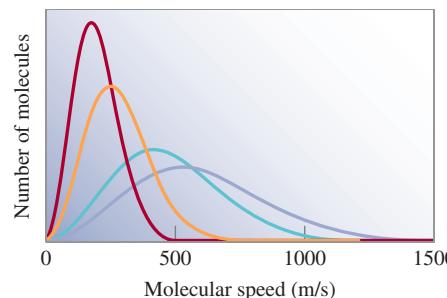
- 5.127** The following procedure is a simple though somewhat crude way to measure the molar mass of a gas. A liquid of mass 0.0184 g is introduced into a syringe like the one shown here by injection through the rubber tip using a hypodermic needle. The syringe is then transferred to a temperature bath heated to 45°C, and the liquid vaporizes. The final volume of the vapor (measured by the outward movement of the plunger) is 5.58 mL and the atmospheric pressure is 760 mmHg. Given that the compound's empirical formula is CH_2 , determine the molar mass of the compound.



- 5.128** In 1995 a man suffocated as he walked by an abandoned mine in England. At that moment there was a sharp drop in atmospheric pressure due to a change in the weather. Suggest what might have caused the man's death.

- 5.129** Acidic oxides such as carbon dioxide react with basic oxides like calcium oxide (CaO) and barium oxide (BaO) to form salts (metal carbonates). (a) Write equations representing these two reactions. (b) A student placed a mixture of BaO and CaO of combined mass 4.88 g in a 1.46-L flask containing carbon dioxide gas at 35°C and 746 mmHg. After the reactions were complete, she found that the CO_2 pressure had dropped to 252 mmHg. Calculate the percent composition by mass of the mixture. Assume volumes of the solids are negligible.

- 5.130** Identify the Maxwell speed distribution curves shown here with the following gases: Br_2 , CH_4 , N_2 , SO_3 .



- 5.131** The running engine of an automobile produces carbon monoxide (CO), a toxic gas, at the rate of about 188 g CO per hour. A car is left idling in a poorly ventilated garage that is 6.0 m long, 4.0 m wide, and 2.2 m high at 20°C. (a) Calculate the rate of CO production in moles per minute. (b) How long would it take to build up a lethal concentration of CO of 1000 ppmv (parts per million by volume)?

- 5.132** Interstellar space contains mostly hydrogen atoms at a concentration of about 1 atom/cm³. (a) Calculate the pressure of the H atoms. (b) Calculate the volume (in liters) that contains 1.0 g of H atoms. The temperature is 3 K.

- 5.133** Atop Mt. Everest, the atmospheric pressure is 210 mmHg and the air density is 0.426 kg/m³. (a) Calculate the air temperature, given that the molar mass of air is 29.0 g/mol. (b) Assuming no change in air composition, calculate the percent decrease in oxygen gas from sea level to the top of Mt. Everest.

- 5.134** Relative humidity is defined as the ratio (expressed as a percentage) of the partial pressure of water vapor in the air to the equilibrium vapor pressure (see Table 5.3) at a given temperature. On a certain summer day in North Carolina the partial pressure of water vapor in the air is 3.9×10^3 Pa at 30°C. Calculate the relative humidity.

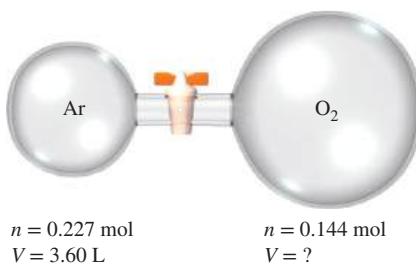
- 5.135** Under the same conditions of temperature and pressure, why does 1 L of moist air weigh less than 1 L of dry air? In weather forecasts, an oncoming low-pressure front usually means imminent rainfall. Explain.

- 5.136** Air entering the lungs ends up in tiny sacs called alveoli. It is from the alveoli that oxygen diffuses into the blood. The average radius of the alveoli is 0.0050 cm and the air inside contains 14 percent oxygen. Assuming that the pressure in the alveoli is 1.0 atm and the temperature is 37°C, calculate the number of oxygen molecules in one of the alveoli. (*Hint:* The volume of a sphere of radius r is $\frac{4}{3}\pi r^3$.)

- 5.137** A student breaks a thermometer and spills most of the mercury (Hg) onto the floor of a laboratory that measures 15.2 m long, 6.6 m wide, and 2.4 m high. (a) Calculate the mass of mercury vapor (in grams) in the room at 20°C. The vapor pressure of mercury at 20°C is 1.7×10^{-6} atm. (b) Does the concentration of mercury vapor exceed the air quality regulation of 0.050 mg Hg/m³ of air? (c) One way to treat

small quantities of spilled mercury is to spray sulfur powder over the metal. Suggest a physical and a chemical reason for this action.

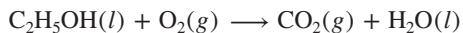
- 5.138** Consider two bulbs containing argon (left) and oxygen (right) gases. After the stopcock is opened, the pressure of the combined gases is 1.08 atm. Calculate the volume of the right bulb. The temperature is kept at 20°C. Assume ideal behavior.



- 5.139** Nitrogen dioxide (NO_2) cannot be obtained in a pure form in the gas phase because it exists as a mixture of NO_2 and N_2O_4 . At 25°C and 0.98 atm, the density of this gas mixture is 2.7 g/L. What is the partial pressure of each gas?

- 5.140** The Chemistry in Action essay “Super Cold Atoms” in Section 5.7. describes the cooling of rubidium vapor to 5.0×10^{-8} K. Calculate the root-mean-square speed and average kinetic energy of a Rb atom at this temperature.

- 5.141** Lithium hydride reacts with water as follows:



During World War II, U.S. pilots carried LiH tablets. In the event of a crash landing at sea, the LiH would react with the seawater and fill their life belts and lifeboats with hydrogen gas. How many grams of LiH are needed to fill a 4.1-L life belt at 0.97 atm and 12°C?

- 5.142** The atmosphere on Mars is composed mainly of carbon dioxide. The surface temperature is 220 K and the atmospheric pressure is about 6.0 mmHg. Taking these values as Martian “STP,” calculate the molar volume in liters of an ideal gas on Mars.

- 5.143** The atmosphere on Venus is composed of 96.5 percent CO_2 , 3.5 percent N_2 , and 0.015 percent SO_2 by volume. Its standard atmospheric pressure is 9.0×10^6 Pa. Calculate the partial pressures of the gases in pascals.

- 5.144** A student tries to determine the volume of a bulb like the one shown in Figure 5.12. These are her results: Mass of the bulb filled with dry air at 23°C and 744 mmHg = 91.6843 g; mass of evacuated bulb = 91.4715 g. Assume the composition of air is 78 percent N_2 , 21 percent O_2 , and 1 percent argon. What is the volume (in milliliters) of the bulb? (Hint: First calculate the average molar mass of air, as shown in Problem 3.152.)

- 5.145** Apply your knowledge of the kinetic theory of gases to the following situations. (a) Two flasks of

volumes V_1 and V_2 ($V_2 > V_1$) contain the same number of helium atoms at the same temperature. (i) Compare the root-mean-square (rms) speeds and average kinetic energies of the helium (He) atoms in the flasks. (ii) Compare the frequency and the force with which the He atoms collide with the walls of their containers. (b) Equal numbers of He atoms are placed in two flasks of the same volume at temperatures T_1 and T_2 ($T_2 > T_1$). (i) Compare the rms speeds of the atoms in the two flasks. (ii) Compare the frequency and the force with which the He atoms collide with the walls of their containers. (c) Equal numbers of He and neon (Ne) atoms are placed in two flasks of the same volume, and the temperature of both gases is 74°C. Comment on the validity of the following statements: (i) The rms speed of He is equal to that of Ne. (ii) The average kinetic energies of the two gases are equal. (iii) The rms speed of each He atom is 1.47×10^3 m/s.

- 5.146** It has been said that every breath we take, on average, contains molecules that were once exhaled by Wolfgang Amadeus Mozart (1756–1791). The following calculations demonstrate the validity of this statement. (a) Calculate the total number of molecules in the atmosphere. (Hint: Use the result in Problem 5.106 and 29.0 g/mol as the molar mass of air.) (b) Assuming the volume of every breath (inhale or exhale) is 500 mL, calculate the number of molecules exhaled in each breath at 37°C, which is the body temperature. (c) If Mozart’s life span was exactly 35 years, what is the number of molecules he exhaled in that period? (Given that an average person breathes 12 times per minute.) (d) Calculate the fraction of molecules in the atmosphere that was exhaled by Mozart. How many of Mozart’s molecules do we breathe in with every inhalation of air? Round off your answer to one significant figure. (e) List three important assumptions in these calculations.

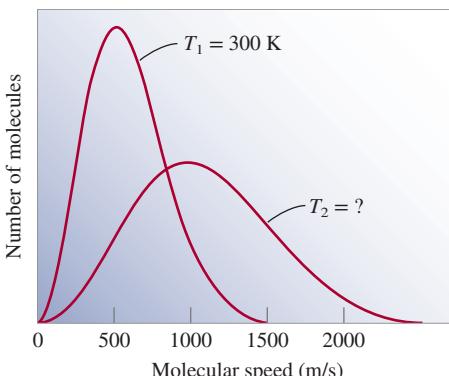
- 5.147** At what temperature will He atoms have the same u_{rms} value as N_2 molecules at 25°C?

- 5.148** Estimate the distance (in nanometers) between molecules of water vapor at 100°C and 1.0 atm. Assume ideal behavior. Repeat the calculation for liquid water at 100°C, given that the density of water is 0.96 g/cm³ at that temperature. Comment on your results. (Assume water molecule to be a sphere with a diameter of 0.3 nm.) (Hint: First calculate the number density of water molecules. Next, convert the number density to linear density, that is, number of molecules in one direction.)

- 5.149** Which of the noble gases would not behave ideally under any circumstance? Why?

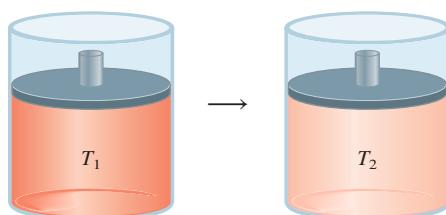
- 5.150** A relation known as the barometric formula is useful for estimating the change in atmospheric pressure with altitude. The formula is given by $P = P_0 e^{-g \mathcal{M} h / RT}$, where P and P_0 are the pressures at height h and sea level, respectively; g is the acceleration due to gravity (9.8 m/s²); \mathcal{M} is the average molar mass of air (29.0 g/mol); and R is the gas

- constant. Calculate the atmospheric pressure in atm at a height of 5.0 km, assuming the temperature is constant at 5°C and $P_0 = 1.0$ atm.
- 5.151** A 5.72-g sample of graphite was heated with 68.4 g of O₂ in a 8.00-L flask. The reaction that took place was
- $$\text{C(graphite)} + \text{O}_2(g) \longrightarrow \text{CO}_2(g)$$
- After the reaction was complete, the temperature in the flask was 182°C. What was the total pressure inside the flask?
- 5.152** An equimolar mixture of H₂ and D₂ effuses through an orifice (small hole) at a certain temperature. Calculate the composition (in mole fractions) of the gases that pass through the orifice. The molar mass of D₂ is 2.014 g/mol.
- 5.153** A mixture of calcium carbonate (CaCO₃) and magnesium carbonate (MgCO₃) of mass 6.26 g reacts completely with hydrochloric acid (HCl) to generate 1.73 L of CO₂ at 48°C and 1.12 atm. Calculate the mass percentages of CaCO₃ and MgCO₃ in the mixture.
- 5.154** A 6.11-g sample of a Cu-Zn alloy reacts with HCl acid to produce hydrogen gas. If the hydrogen gas has a volume of 1.26 L at 22°C and 728 mmHg, what is the percent of Zn in the alloy? (*Hint:* Cu does not react with HCl.)
- 5.155** A stockroom supervisor measured the contents of a partially filled 25.0-gallon acetone drum on a day when the temperature was 18.0°C and atmospheric pressure was 750 mmHg, and found that 15.4 gallons of the solvent remained. After tightly sealing the drum, an assistant dropped the drum while carrying it upstairs to the organic laboratory. The drum was dented and its internal volume was decreased to 20.4 gallons. What is the total pressure inside the drum after the accident? The vapor pressure of acetone at 18.0°C is 400 mmHg. (*Hint:* At the time the drum was sealed, the pressure inside the drum, which is equal to the sum of the pressures of air and acetone, was equal to the atmospheric pressure.)
- 5.156** In 2.00 min, 29.7 mL of He effuse through a small hole. Under the same conditions of pressure and temperature, 10.0 mL of a mixture of CO and CO₂ effuse through the hole in the same amount of time. Calculate the percent composition by volume of the mixture.
- 5.157** Referring to Figure 5.22, explain the following: (a) Why do the curves dip below the horizontal line labeled ideal gas at low pressures and then why do they arise above the horizontal line at high pressures? (b) Why do the curves all converge to 1 at very low pressures? (c) Each curve intercepts the horizontal line labeled ideal gas. Does it mean that at that point the gas behaves ideally?
- 5.158** A mixture of methane (CH₄) and ethane (C₂H₆) is stored in a container at 294 mmHg. The gases are burned in air to form CO₂ and H₂O. If the pressure of CO₂ is 356 mmHg measured at the same temperature and volume as the original mixture, calculate the mole fractions of the gases.
- 5.159** Use the kinetic theory of gases to explain why hot air rises.
- 5.160** One way to gain a physical understanding of b in the van der Waals equation is to calculate the “excluded volume.” Assume that the distance of closest approach between two similar atoms is the sum of their radii (2r). (a) Calculate the volume around each atom into which the center of another atom cannot penetrate. (b) From your result in (a), calculate the excluded volume for 1 mole of the atoms, which is the constant b . How does this volume compare with the sum of the volumes of 1 mole of the atoms?
- 5.161** Use the van der Waals constants in Table 5.4 to estimate the radius of argon in picometers. (*Hint:* See Problem 5.160.)
- 5.162** Identify the gas whose root-mean-square speed is 2.82 times that of hydrogen iodide (HI) at the same temperature.
- 5.163** A 5.00-mole sample of NH₃ gas is kept in a 1.92-L container at 300 K. If the van der Waals equation is assumed to give the correct answer for the pressure of the gas, calculate the percent error made in using the ideal gas equation to calculate the pressure.
- 5.164** The root-mean-square speed of a certain gaseous oxide is 493 m/s at 20°C. What is the molecular formula of the compound?
- 5.165** Referring to Figure 5.17, we see that the maximum of each speed distribution plot is called the most probable speed (u_{mp}) because it is the speed possessed by the largest number of molecules. It is given by $u_{mp} = \sqrt{2RT/\bar{M}}$. (a) Compare u_{mp} with u_{rms} for nitrogen at 25°C. (b) The following diagram shows the Maxwell speed distribution curves for an ideal gas at two different temperatures T_1 and T_2 . Calculate the value of T_2 .

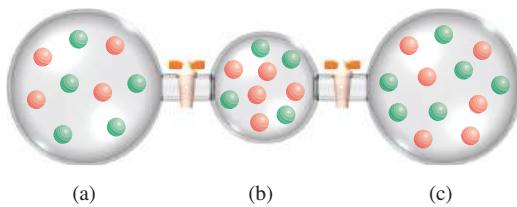


- 5.166** A gaseous reaction takes place at constant volume and constant pressure in this cylinder. Which of the following equations best describes the reaction? The initial temperature (T_1) is twice that of the final temperature (T_2).
 (a) A + B → C
 (b) AB → C + D

- (c) $A + B \longrightarrow C + D$
 (d) $A + B \longrightarrow 2C + D$



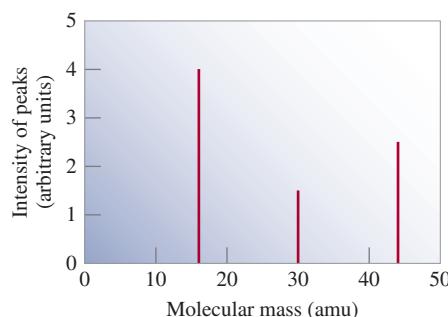
- 5.167 A gaseous hydrocarbon (containing C and H atoms) in a container of volume 20.2 L at 350 K and 6.63 atm reacts with an excess of oxygen to form 205.1 g of CO_2 and 168.0 g of H_2O . What is the molecular formula of the hydrocarbon?
- 5.168 Three flasks (a)–(c) contain gases A (red) and B (green). (i) If the pressure in (a) is 4.0 atm, what are the pressures in (b) and (c)? (ii) Calculate the total pressure and partial pressure of each gas after the valves are opened. The volumes of (a) and (c) are 4.0 L each and that of (b) is 2.0 L. The temperature is the same throughout.



- 5.169 (a) Show that the pressure exerted by a fluid P (in pascals) is given by $P = h \rho g$, where h is the column of the fluid in meters, ρ is the density in kg/m^3 , and g is the acceleration due to gravity (9.81 m/s^2). (Hint: See Appendix 1.) (b) The volume of an air bubble that starts at the bottom of a lake at 5.24°C increases by a factor of 6 as it rises to the surface of

water where the temperature is 18.73°C and the air pressure is 0.973 atm. The density of the lake water is 1.02 g/cm^3 . Use the equation in (a) to determine the depth of the lake in meters.

- 5.170 A student first measured the total pressure of a mixture of gases methane (CH_4), ethane (C_2H_6), and propane (C_3H_8) at a certain temperature, which turned out to be 4.50 atm. She then recorded the mass spectra of the gases shown here. Calculate the partial pressure of the gases.



- 5.171 In 2012, Felix Baumgartner jumped from a balloon roughly 24 mi above Earth, breaking the record for the highest skydive. He reached speeds of more than 700 miles per hour and became the first skydiver to exceed the speed of sound during free fall. The helium-filled plastic balloon used to carry Baumgartner to the edge of space was designed to expand to $8.5 \times 10^8 \text{ L}$ in order to accommodate the low pressures at the altitude required to break the record. (a) Calculate the mass of helium in the balloon from the conditions at the time of the jump ($8.5 \times 10^8 \text{ L}$, -67.8°C , 0.027 mmHg). (b) Determine the volume of the helium in the balloon just before it was released, assuming a pressure of 1.0 atm and a temperature of 23°C .

Interpreting, Modeling & Estimating

- 5.172 Which of the following has a greater mass: a sample of air of volume V at a certain temperature T and pressure P or a sample of air plus water vapor having the same volume and at the same temperature and pressure?
- 5.173 A flask with a volume of 14.5 L contains 1.25 moles of helium gas. Estimate the average distance between He atoms in nanometers.
- 5.174 Hyperbaric oxygen therapy (HBOT) is very effective in treating burns, crush injuries that impede blood flow, and tissue-damaging infections, as well as carbon monoxide poisoning. However, it has generated some controversy in its application to other maladies (for example, autism, multiple sclerosis). A typical oxygen hyperbaric chamber is shown here. HBOT can be administered using pressure up to 6 atmospheres, but lower pressures are more common. (a) If this chamber was pressurized

to 3.0 atm with pure oxygen, how many moles of O_2 would be contained in an empty chamber? (b) Given that a full tank of oxygen contains about 2500 moles of the gas, how many times could the chamber be filled with a single tank of oxygen?

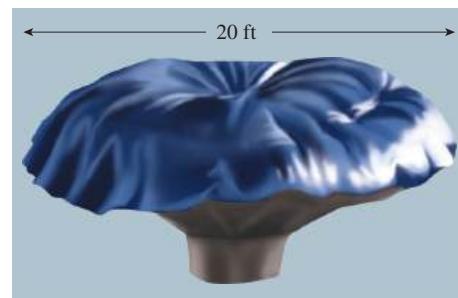


Courtesy of Sechrist Industries, Inc.

5.175 (a) Fluorescent lightbulbs contain a small amount of mercury, giving a mercury vapor pressure of around 1×10^{-5} atm. When excited electrically, the Hg atoms emit UV light, which excites the phosphor coating of the inner tube, which then emits visible (white) light. Estimate the mass of Hg vapor present in the type of long, thin fluorescent tubes used in offices. (b) Ordinary tungsten incandescent lightbulbs used in households are filled with argon gas at about 0.5 atm to retard the sublimation of the tungsten filament. Estimate the number of moles of Ar in a typical lightbulb.

5.176 (a) Estimate the volume of air at 1.0 atm and 22°C needed to fill a bicycle tire to a pressure of 5.0 atm at the same temperature. (Note that the 5.0 atm is the gauge pressure, which is the difference between the pressure in the tire and atmospheric pressure.) (b) The tire is pumped by filling the cylinder of a hand pump with air at 1.0 atm and then, by compressing the gas in the cylinder, adding all the air in the pump to the air in the tire. If the volume of the pump is 33 percent of the tire's volume, what is the gauge pressure in the tire after three full strokes of the pump?

5.177 On October 15, 2009, a homemade helium balloon was released, and for a while authorities were led to believe that a 6-year-old boy had been carried away in the balloon. (The incident was later revealed to be a hoax.) The balloon traveled more than 50 mi and reached a height of 7000 ft. The shape and span of the balloon are shown in the figure. How much weight could this balloon lift? (A helium balloon can lift a mass equal to the difference in the mass of air and the mass of helium that would be contained in the balloon.) Could it actually lift a 6-year-old boy?



Answers to Practice Exercises

5.1 0.986 atm. **5.2** 39.3 kPa. **5.3** 9.29 L. **5.4** 30.6 L. **5.5** 4.46×10^3 mmHg. **5.6** 0.68 atm. **5.7** 2.6 atm. **5.8** 13.1 g/L. **5.9** 44.1 g/mol. **5.10** B₂H₆. **5.11** 96.9 L. **5.12** 4.75 L.

5.13 0.338 M. **5.14** CH₄: 1.29 atm; C₂H₆: 0.0657 atm; C₃H₈: 0.0181 atm. **5.15** 0.0653 g. **5.16** 321 m/s. **5.17** 146 g/mol. **5.18** 30.0 atm; 45.5 atm using the ideal gas equation.

Answers to Review of Concepts & Facts

5.2.1 1184 mmHg, 1.558 atm, 157.9 kPa. **5.2.2** (b) < (c) < (a) < (d). **5.2.3** It would be easier to drink water with a straw at the foot of Mt. Everest because the atmospheric pressure is greater there, which helps to push the water up the straw. **5.3.1** 1.29 L. **5.3.2** (a) Volume doubles; (b) volume increases 1.4 times. **5.3.3** 50.0 mL. **5.4.1** 458 K or 185°C. **5.4.2** Greatest volume, (b); greatest density, (c).

5.4.3 77.1 g/mol. **5.5.1** 11.3 L. **5.5.2** Only for the combustion of methane, $\text{CH}_4(g) + 2\text{O}_2(g) \longrightarrow \text{CO}_2(l) + 2\text{H}_2\text{O}(g)$. **5.6.1** Blue sphere: 0.43 atm; green sphere: 1.3 atm; red sphere: 0.87 atm. **5.6.2** $X_{\text{Ne}} = 0.338$. **5.6.3** 0.702 atm. **5.7.1** (c) and (d). **5.7.2** Ne effuses faster. It effuses 2.551 times faster. **5.8.1** High pressure and low temperature. **5.8.2** 10.3 atm.

CHEMICAL MYSTERY

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Out of Oxygen[†]

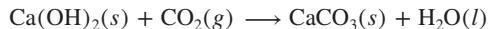
In September 1991 four men and four women entered the world's largest glass bubble, known as Biosphere II, to test the idea that humans could design and build a totally self-contained ecosystem, a model for some future colony on another planet. Biosphere II (Earth is considered Biosphere I) was a 3-acre mini-world, complete with a tropical rain forest, savanna, marsh, desert, and working farm that was intended to be fully self-sufficient. This unique experiment was to continue for 2 to 3 years, but almost immediately there were signs that the project could be in jeopardy.

Soon after the bubble had been sealed, sensors inside the facility showed that the concentration of oxygen in Biosphere II's atmosphere had fallen from its initial level of 21 percent (by volume), while the amount of carbon dioxide had risen from a level of 0.035 percent (by volume), or 350 ppm (parts per million). Alarmingly, the oxygen level continued to fall at a rate of about 0.5 percent a month and the level of carbon dioxide kept rising, forcing the crew to turn on electrically powered chemical scrubbers, similar to those on submarines, to remove some of the excess CO₂. Gradually the CO₂ level stabilized around 4000 ppm, which is high but not dangerous. The loss of oxygen did not stop, though. By January 1993—16 months into the experiment—the oxygen concentration had dropped to 14 percent, which is equivalent to the O₂ concentration in air at an elevation of 4360 m (14,300 ft). The crew began having trouble performing normal tasks. For their safety it was necessary to pump pure oxygen into Biosphere II.

With all the plants present in Biosphere II, the production of oxygen should have been greater as a consequence of photosynthesis. Why had the oxygen concentration declined to such a low level? A small part of the loss was blamed on unusually cloudy weather, which had slowed plant growth. The possibility that iron in the soil was reacting with oxygen to form iron(III) oxide or rust was ruled out, along with several other explanations, for lack of evidence. The most plausible hypothesis was that microbes (microorganisms) were using oxygen to metabolize the excess organic matter that had been added to the soils to promote plant growth. This turned out to be the case.

Identifying the cause of oxygen depletion raised another question. Metabolism produces carbon dioxide. Based on the amount of oxygen consumed by the microbes, the CO₂ level should have been at 40,000 ppm, 10 times what was measured. What happened to the excess gas? After ruling out leakage to the outside world and reactions between CO₂ with compounds in the soils and in water, scientists found that the concrete inside Biosphere II was consuming large amounts of CO₂!

Concrete is a mixture of sand and gravel held together by a binding agent that is a mixture of calcium silicate hydrates and calcium hydroxide. The calcium hydroxide is the key ingredient in the CO₂ mystery. Carbon dioxide diffuses into the porous structure of concrete, then reacts with calcium hydroxide to form calcium carbonate and water:



Under normal conditions, this reaction goes on slowly. But CO₂ concentrations in Biosphere II were much higher than normal, so the reaction proceeded much faster. In fact, in just over

Adapted with permission from "Biosphere II: Out of Oxygen," by Joe Alper, CHEM MATTERS, February, 1995, p. 8. Copyright 1995 American Chemical Society.



Vegetations in Biosphere II.

(left): ©Camerique/ClassicStock/Getty Images;

(right): ©Corbis Documentary/Getty Images

2 years, CaCO_3 had accumulated to a depth of more than 2 cm in Biosphere II's concrete. Some $10,000 \text{ m}^2$ of exposed concrete was hiding 500,000 to 1,500,000 moles of CO_2 .

The water produced in the reaction between Ca(OH)_2 and CO_2 created another problem: CO_2 also reacts with water to form carbonic acid (H_2CO_3), and hydrogen ions produced by the acid promote the corrosion of the reinforcing iron bars in the concrete, thereby weakening its structure. This situation was dealt with effectively by painting all concrete surfaces with an impermeable coating.

In the meantime, the decline in oxygen (and hence also the rise in carbon dioxide) slowed, perhaps because there was now less organic matter in the soils and because new lights in the agricultural areas may have boosted photosynthesis. The project was terminated prematurely; and in 1996, the facility was transformed into a science education and research center. As of 2011, the Biosphere is under the management of the University of Arizona.

The Biosphere II experiment is an interesting project from which we can learn a lot about Earth and its inhabitants. If nothing else, it has shown us how complex Earth's ecosystems are and how difficult it is to mimic nature, even on a small scale.

Chemical Clues

1. What solution would you use in a chemical scrubber to remove carbon dioxide?
2. Photosynthesis converts carbon dioxide and water to carbohydrates and oxygen gas, while metabolism is the process by which carbohydrates react with oxygen to form carbon dioxide and water. Using glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) to represent carbohydrates, write equations for these two processes.
3. Why was diffusion of O_2 from Biosphere II to the outside world not considered a possible cause for the depletion in oxygen?
4. Carbonic acid is a diprotic acid. Write equations for the stepwise ionization of the acid in water.
5. What are the factors to consider in choosing a planet on which to build a structure like Biosphere II?

CHAPTER

6

Thermochemistry

Powerful explosives decompose violently when detonated and release tremendous amounts of heat in exothermic reactions.

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CHAPTER OUTLINE

- 6.1** The Nature of Energy and Types of Energy
- 6.2** Energy Changes in Chemical Reactions
- 6.3** Introduction to Thermodynamics
- 6.4** Enthalpy of Chemical Reactions
- 6.5** Calorimetry
- 6.6** Standard Enthalpy of Formation and Reaction
- 6.7** Heat of Solution and Dilution



A LOOK AHEAD

- ▶ We begin by studying the nature and different types of energy, which, in principle, are interconvertible. (6.1)
- ▶ Next, we build up our vocabulary in learning thermochemistry, which is the study of heat change in chemical reactions. We see that the vast majority of reactions are either endothermic (absorbing heat) or exothermic (releasing heat). (6.2)
- ▶ We learn that thermochemistry is part of a broader subject called the first law of thermodynamics, which is based on the law of conservation of energy. We see that the change in internal energy can be expressed in terms of the changes in heat and work done of a system. (6.3)
- ▶ We then become acquainted with a new term for energy, called enthalpy, whose change applies to processes carried out under constant-pressure conditions. (6.4)
- ▶ We learn ways to measure the heats of reaction or calorimetry, and the meaning of specific heat and heat capacity, quantities used in experimental work. (6.5)
- ▶ Knowing the standard enthalpies of formation of reactants and products enables us to calculate the enthalpy of a reaction. We will discuss ways to determine these quantities either by the direct method from the elements or by the indirect method, which is based on Hess's law of heat summation. (6.6)
- ▶ Finally, we will study the heat changes when a solute dissolves in a solvent (heat of solution) and when a solution is diluted (heat of dilution). (6.7)

Every chemical reaction obeys two fundamental laws: the law of conservation of mass and the law of conservation of energy. We discussed the mass relationship between reactants and products in Chapter 3; here we will look at the energy changes that accompany chemical reactions.

6.1 The Nature of Energy and Types of Energy

“Energy” is a much-used term that represents a rather abstract concept. For instance, when we feel tired, we might say we haven’t any *energy*; and we read about the need to find alternatives to nonrenewable *energy* sources. Unlike matter, energy is known and recognized by its effects. It cannot be seen, touched, smelled, or weighed.

Energy is usually defined as *the capacity to do work*. In Chapter 5 we defined work as “force × distance,” but we will soon see that there are other kinds of work. All forms of energy are capable of doing work (that is, of exerting a force over a distance), but not all of them are equally relevant to chemistry. The energy contained in tidal waves, for example, can be harnessed to perform useful work, but the relationship between tidal waves and chemistry is minimal. Chemists define **work** as *directed energy change resulting from a process*. Kinetic energy—the energy produced by a moving object—is one form of energy that is of particular interest to chemists. Others include radiant energy, thermal energy, chemical energy, and potential energy.

Kinetic energy was introduced in Section 5.7.

Radiant energy, or *solar energy*, comes from the sun and is Earth’s primary energy source. Solar energy heats the atmosphere and Earth’s surface, stimulates the growth of vegetation through the process known as photosynthesis, and influences global climate patterns.

Thermal energy is the energy associated with the random motion of atoms and molecules. In general, thermal energy can be calculated from temperature measurements. The more vigorous the motion of the atoms and molecules in a sample of matter, the hotter the sample is and the greater its thermal energy. However, we need to distinguish carefully between thermal energy and temperature. A cup of coffee at 70°C has a higher temperature than a bathtub filled with warm water at 40°C, but much more thermal energy is stored in the bathtub water because it has a much larger volume and greater mass than the coffee and therefore more water molecules and more molecular motion.



As the water falls over the dam, its potential energy is converted to kinetic energy. Use of this energy to generate electricity is called hydroelectric power.

©Jacques Jangoux/Science Source

Chemical energy is stored within the structural units of chemical substances; its quantity is determined by the type and arrangement of constituent atoms. When substances participate in chemical reactions, chemical energy is released, stored, or converted to other forms of energy.

Potential energy is energy available by virtue of an object's position. For instance, because of its altitude, a rock at the top of a cliff has more potential energy and will make a bigger splash if it falls into the water below than a similar rock located partway down the cliff. Chemical energy can be considered a form of potential energy because it is associated with the relative positions and arrangements of atoms within a given substance.

All forms of energy can be converted (at least in principle) from one form to another. We feel warm when we stand in sunlight because radiant energy is converted to thermal energy on our skin. When we exercise, chemical energy stored in our bodies is used to produce kinetic energy. When a ball starts to roll downhill, its potential energy is converted to kinetic energy. You can undoubtedly think of many other examples. Although energy can assume many different forms that are interconvertible, scientists have concluded that energy can be neither destroyed nor created. When one form of energy disappears, some other form of energy (of equal magnitude) must appear, and vice versa. This principle is summarized by the **law of conservation of energy**: *The total quantity of energy in the universe is assumed constant.*



This infrared photo shows where energy (heat) leaks through the house. The more red the color, the more energy is lost to the outside.

©Edward Kinsman/Science Source

▶ Video Heat Flow

When heat is absorbed or released during a process, energy is conserved, but it is transferred between system and surroundings.

6.2 Energy Changes in Chemical Reactions

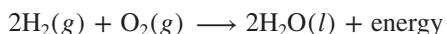
Often the energy changes that take place during chemical reactions are of as much practical interest as the mass relationships we discussed in Chapter 3. For example, combustion reactions involving fuels such as natural gas and oil are carried out in daily life more for the thermal energy they release than for their products, which are water and carbon dioxide.

Almost all chemical reactions absorb or produce (release) energy, generally in the form of heat. It is important to understand the distinction between thermal energy and heat. **Heat** is the transfer of thermal energy between two bodies that are at different temperatures. Thus, we often speak of the “heat flow” from a hot object to a cold one. Although the term “heat” by itself implies the transfer of energy, we customarily talk of “heat absorbed” or “heat released” when describing the energy changes that occur during a process. **Thermochemistry** is the study of heat change in chemical reactions.

To analyze energy changes associated with chemical reactions we must first define the **system**, or the specific part of the universe that is of interest to us. For chemists, systems usually include substances involved in chemical and physical changes. For example, in an acid-base neutralization experiment, the system may be a beaker containing 50 mL of HCl to which 50 mL of NaOH is added. The **surroundings** are the rest of the universe outside the system.

There are three types of systems. An **open system** can exchange mass and energy, usually in the form of heat with its surroundings. For example, an open system may consist of a quantity of water in an open container, as shown in Figure 6.1(a). If we close the flask, as in Figure 6.1(b), so that no water vapor can escape from or condense into the container, we create a **closed system**, which allows the transfer of energy (heat) but not mass. By placing the water in a totally insulated container, we can construct an **isolated system**, which does not allow the transfer of either mass or energy, as shown in Figure 6.1(c).

The combustion of hydrogen gas in oxygen is one of many chemical reactions that release considerable quantities of energy (Figure 6.2):



In this case, we label the reacting mixture (hydrogen, oxygen, and water molecules) the **system** and the rest of the universe the **surroundings**. Because energy cannot be created

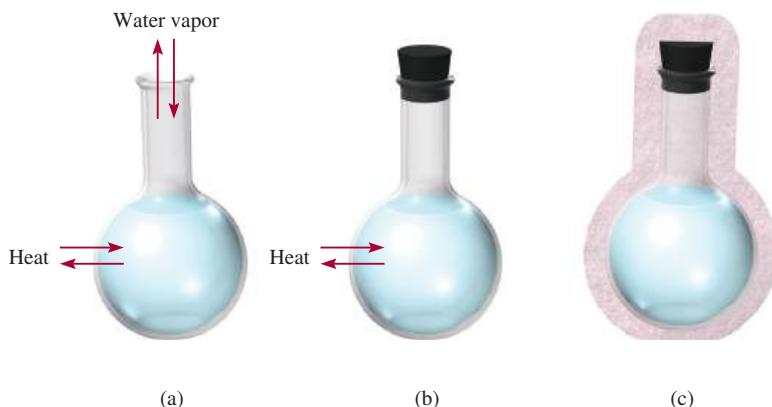


Figure 6.1 Three systems represented by water in a flask: (a) an open system, which allows the exchange of both energy and mass with surroundings; (b) a closed system, which allows the exchange of energy but not mass; and (c) an isolated system, which allows neither energy nor mass to be exchanged (here the flask is enclosed by a vacuum jacket).



Figure 6.2 The Hindenburg disaster. The Hindenburg, a German airship filled with hydrogen gas, was destroyed in a spectacular fire at Lakehurst, New Jersey, in 1937.

©akg-images/Newscom

or destroyed, any energy lost by the system must be gained by the surroundings. Thus, the heat generated by the combustion process is transferred from the system to its surroundings. This reaction is an example of an **exothermic process**, which is *any process that gives off heat*—that is, *transfers thermal energy to the surroundings*. Figure 6.3(a) shows the energy change for the combustion of hydrogen gas.

Exo- comes from the Greek word meaning “outside”; **endo-** means “within.”

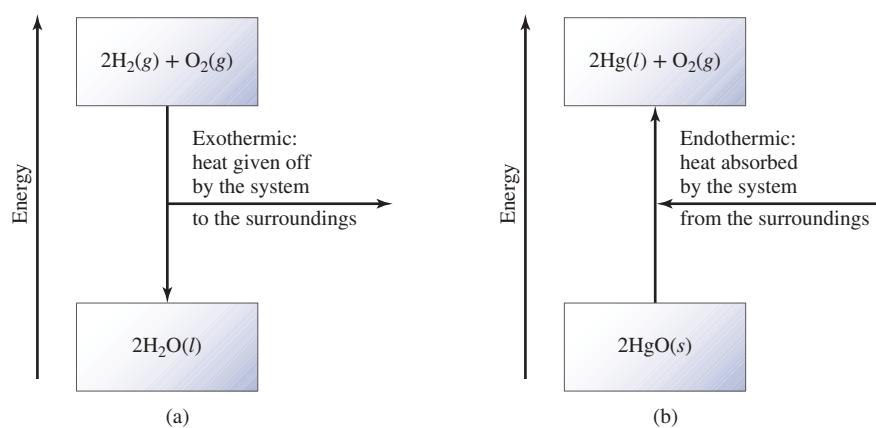


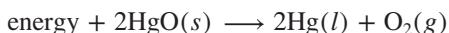
Figure 6.3 (a) An exothermic process. (b) An endothermic process. Parts (a) and (b) are not drawn to the same scale; that is, the heat released in the formation of H_2O from H_2 and O_2 is not equal to the heat absorbed in the decomposition of HgO .



On heating, HgO decomposes to give Hg and O₂.

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Now consider another reaction, the decomposition of mercury(II) oxide (HgO) at high temperatures:



This reaction is an *endothermic process*, in which heat has to be supplied to the system (that is, to HgO) by the surroundings [Figure 6.3(b)].

From Figure 6.3 you can see that in exothermic reactions, the total energy of the products is less than the total energy of the reactants. The difference is the heat supplied by the system to the surroundings. Just the opposite happens in endothermic reactions. Here, the difference between the energy of the products and the energy of the reactants is equal to the heat supplied to the system by the surroundings.

Review of Concepts & Facts

- 6.2.1** Classify each of the following as an open system, a closed system, or an isolated system.
- Milk kept in a closed thermo flask
 - A student reading in her dorm room
 - Air inside a tennis ball
- 6.2.2** Determine if the following processes are endothermic or exothermic.
- ZnS(s) decomposes to Zn(s) and S(s).
 - Propane gas burns in the presence of oxygen in a grill.
 - Ice cubes melt in a glass.

6.3 Introduction to Thermodynamics

Thermochemistry is part of a broader subject called *thermodynamics*, which is *the scientific study of the interconversion of heat and other kinds of energy*. The laws of thermodynamics provide useful guidelines for understanding the energetics and directions of processes. In this section we will concentrate on the first law of thermodynamics, which is particularly relevant to the study of thermochemistry. We will continue our discussion of thermodynamics in Chapter 17.

In thermodynamics, we study changes in the *state of a system*, which is defined by *the values of all relevant macroscopic properties, for example, composition, energy, temperature, pressure, and volume*. Energy, pressure, volume, and temperature are said to be *state functions—properties that are determined by the state of the system, regardless of how that condition was achieved*. In other words, when the state of a system changes, the magnitude of change in any state function depends only on the initial and final states of the system and not on how the change is accomplished or the pathway taken during the change.

The state of a given amount of a gas is specified by its volume, pressure, and temperature. Consider a gas at 2 atm, 300 K, and 1 L (the initial state). Suppose a process is carried out at constant temperature such that the gas pressure decreases to 1 atm. According to Boyle's law, its volume must increase to 2 L. The final state then corresponds to 1 atm, 300 K, and 2 L. The change in volume (ΔV) is

$$\begin{aligned}\Delta V &= V_f - V_i \\ &= 2 \text{ L} - 1 \text{ L} \\ &= 1 \text{ L}\end{aligned}$$

The Greek letter *delta*, Δ , symbolizes change. We use Δ in this text to mean final – initial; that is, final “minus” initial.

where V_i and V_f denote the initial and final volume, respectively. No matter how we arrive at the final state (for example, the pressure of the gas can be increased first and then decreased to 1 atm), the change in volume is always 1 L. Thus, the volume of a gas is a state function. In a similar manner, we can show that pressure and temperature are also state functions.



Figure 6.4 The gain in gravitational potential energy that occurs when a person climbs from the base to the top of a mountain is independent of the path taken.
©Uwe Steffens/Ullstein bild via Getty Images

Energy is another state function. Using potential energy as an example, we find that the net increase in gravitational potential energy when we go from the same starting point to the top of a mountain is always the same, regardless of how we get there (Figure 6.4).

Recall that an object possesses potential energy by virtue of its position or chemical composition.

The First Law of Thermodynamics

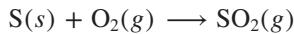
The *first law of thermodynamics*, which is based on the law of conservation of energy, states that *energy can be converted from one form to another, but cannot be created or destroyed.*[†] How do we know this is so? It would be impossible to prove the validity of the first law of thermodynamics if we had to determine the total energy content of the universe. Even determining the total energy content of 1 g of iron, say, would be extremely difficult. Fortunately, we can test the validity of the first law by measuring only the *change* in the internal energy of a system between its *initial state* and its *final state* in a process. The change in internal energy ΔU is given by

$$\Delta U = U_f - U_i$$

where U_i and U_f are the internal energies of the system in the initial and final states, respectively.

The internal energy of a system has two components: kinetic energy and potential energy. The kinetic energy component consists of various types of molecular motion and the movement of electrons within molecules. Potential energy is determined by the attractive interactions between electrons and nuclei and by repulsive interactions between electrons and between nuclei in individual molecules, as well as by interaction between molecules. It is impossible to measure all these contributions accurately, so we cannot calculate the total energy of a system with any certainty. Changes in energy, on the other hand, can be determined experimentally.

Consider the reaction between 1 mole of sulfur and 1 mole of oxygen gas to produce 1 mole of sulfur dioxide:



In this case, our system is composed of the reactant molecules S and O_2 (the initial state) and the product molecules SO_2 (the final state). We do not know the internal energy content of either the reactant molecules or the product molecules, but we can accurately measure the *change* in energy content, ΔU , given by

$$\begin{aligned}\Delta U &= U(\text{product}) - U(\text{reactants}) \\ &= \text{energy content of 1 mol } SO_2(g) - \text{energy content of [1 mol } S(s) + 1 \text{ mol } O_2(g)\text{]}\end{aligned}$$

We find that this reaction gives off heat. Therefore, the energy of the product is less than that of the reactants, and ΔU is negative.

Interpreting the release of heat in this reaction to mean that some of the chemical energy contained in the molecules has been converted to thermal energy, we conclude

Student Hot Spot

Student data indicate you may struggle with state functions. Access your eBook for additional Learning Resources on this topic.



Sulfur burning in air to form SO_2 .
©Andrew Lambert Photography/SPL/Science Source

[†]See footnote in Section 2.1 for a discussion of mass and energy relationship in chemical reactions.

that the transfer of energy from the system to the surroundings does not change the total energy of the universe. That is, the sum of the energy changes must be zero:

$$\Delta U_{\text{sys}} + \Delta U_{\text{surr}} = 0$$

or

$$\Delta U_{\text{sys}} = -\Delta U_{\text{surr}}$$

where the subscripts “sys” and “surr” denote system and surroundings, respectively. Thus, if one system undergoes an energy change ΔU_{sys} , the rest of the universe, or the surroundings, must undergo a change in energy that is equal in magnitude but opposite in sign ($-\Delta U_{\text{surr}}$); energy gained in one place must have been lost somewhere else. Furthermore, because energy can be changed from one form to another, the energy lost by one system can be gained by another system in a different form. For example, the energy lost by burning oil in a power plant may ultimately turn up in our homes as electrical energy, heat, light, and so on.

In chemistry, we are normally interested in the energy changes associated with the system (which may be a flask containing reactants and products), not with its surroundings. Therefore, a more useful form of the first law is

$$\Delta U = q + w \quad (6.1)$$

We use lowercase letters (such as w and q) to represent thermodynamic quantities that are not state functions.

For convenience, we sometimes omit the word “internal” when discussing the energy of a system.

(We drop the subscript “sys” for simplicity.) Equation (6.1) says that the change in the internal energy, ΔU , of a system is the sum of the heat exchange q between the system and the surroundings and the work done w on (or by) the system. The sign conventions for q and w are as follows: q is positive for an endothermic process and negative for an exothermic process and w is positive for work done on the system by the surroundings and negative for work done by the system on the surroundings. We can think of the first law of thermodynamics as an energy balance sheet, much like a money balance sheet kept in a bank that does currency exchange. You can withdraw or deposit money in either of two different currencies (like energy change due to heat exchange and work done). However, the value of your bank account depends only on the net amount of money left in it after these transactions, not on which currency you used.

Equation (6.1) may seem abstract, but it is actually quite logical. If a system loses heat to the surroundings or does work on the surroundings, we would expect its internal energy to decrease because those are energy-depleting processes. For this reason, both q and w are negative. Conversely, if heat is added to the system or if work is done on the system, then the internal energy of the system would increase. In this case, both q and w are positive. Table 6.1 summarizes the sign conventions for q and w .

Work and Heat

We will now look at the nature of work and heat in more detail.

Work

We have seen that work can be defined as force F multiplied by distance d :

$$w = F \times d \quad (6.2)$$

Table 6.1 Sign Conventions for Work and Heat

Process	Sign
Work done by the system on the surroundings	–
Work done on the system by the surroundings	+
Heat absorbed by the system from the surroundings (endothermic process)	+
Heat absorbed by the surroundings from the system (exothermic process)	–

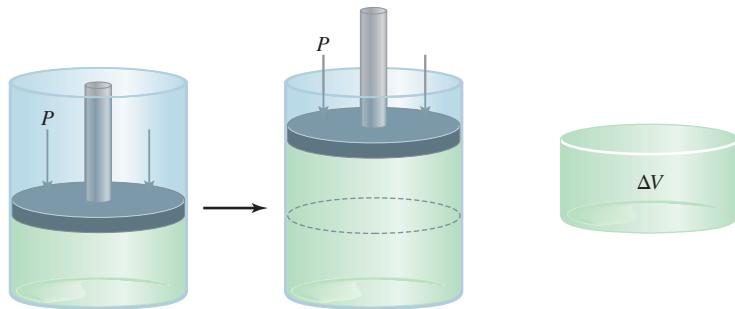


Figure 6.5 The expansion of a gas against a constant external pressure (such as atmospheric pressure). The gas is in a cylinder fitted with a weightless movable piston. The work done is given by $-P\Delta V$. Because $\Delta V > 0$, the work done is a negative quantity.

In thermodynamics, work has a broader meaning that includes mechanical work (for example, a crane lifting a steel beam), electrical work (a battery supplying electrons to light the bulb of a flashlight), and surface work (blowing up a soap bubble). In this section we will concentrate on mechanical work; in Chapter 18 we will discuss the nature of electrical work.

One way to illustrate mechanical work is to study the expansion or compression of a gas. Many chemical and biological processes involve gas volume changes. Breathing and exhaling air involves the expansion and contraction of the tiny sacs called alveoli in the lungs. Another example is the internal combustion engine of the automobile. The successive expansion and compression of the cylinders due to the combustion of the gasoline-air mixture provide power to the vehicle. Figure 6.5 shows a gas in a cylinder fitted with a weightless, frictionless movable piston at a certain temperature, pressure, and volume. As it expands, the gas pushes the piston upward against a constant opposing external atmospheric pressure P . The work done by the gas on the surroundings is

$$w = -P\Delta V \quad (6.3)$$

where ΔV , the change in volume, is given by $V_f - V_i$. The minus sign in Equation (6.3) takes care of the sign convention for w . For gas expansion (work done *by* the system), $\Delta V > 0$, so $-P\Delta V$ is a negative quantity. For gas compression (work done *on* the system), $\Delta V < 0$, and $-P\Delta V$ is a positive quantity.

Equation (6.3) derives from the fact that pressure \times volume can be expressed as (force/area) \times volume; that is,

$$\begin{array}{c} P \times V = \frac{F}{d^2} \times d^3 \\ \text{pressure} \qquad \qquad \text{volume} \end{array} = F \times d = w$$

where F is the opposing force and d has the dimension of length, d^2 has the dimensions of area, and d^3 has the dimensions of volume. Thus, the product of pressure and volume is equal to force times distance, or work. You can see that for a given increase in volume (that is, for a certain value of ΔV), the work done depends on the magnitude of the external, opposing pressure P . If P is zero (that is, if the gas is expanding against a vacuum), the work done must also be zero. If P is some positive, nonzero value, then the work done is given by $-P\Delta V$.

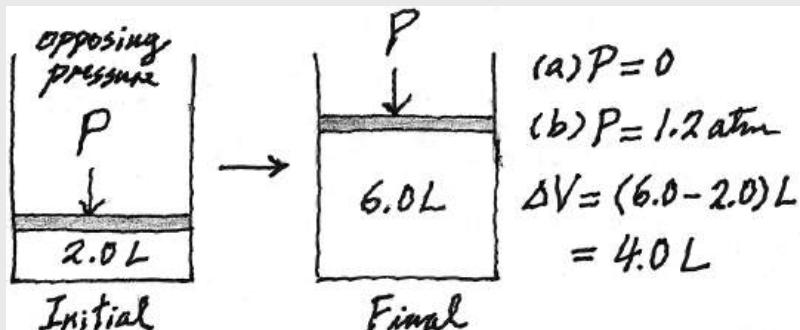
According to Equation (6.3), the units for work done by or on a gas are liter atmospheres. To express the work done in the more familiar unit of joules, we use the conversion factor (see Appendix 1).

$$1 \text{ L} \cdot \text{atm} = 101.3 \text{ J}$$

Example 6.1

A certain gas expands in volume from 2.0 L to 6.0 L at constant temperature. Calculate the work done by the gas if it expands (a) against a vacuum and (b) against a constant pressure of 1.2 atm.

Strategy A simple sketch of the situation is helpful here:



The work done in gas expansion is equal to the product of the external, opposing pressure and the change in volume. What is the conversion factor between L · atm and J?

Solution

(a) Because the external pressure is zero, no work is done in the expansion.

$$\begin{aligned} w &= -P\Delta V \\ &= -(0)(6.0 - 2.0) \text{ L} \\ &= 0 \end{aligned}$$

(b) The external, opposing pressure is 1.2 atm, so

$$\begin{aligned} w &= -P\Delta V \\ &= -(1.2 \text{ atm})(6.0 - 2.0) \text{ L} \\ &= -4.8 \text{ L} \cdot \text{atm} \end{aligned}$$

To convert the answer to joules, we write

$$\begin{aligned} w &= -4.8 \text{ L} \cdot \text{atm} \times \frac{101.3 \text{ J}}{1 \text{ L} \cdot \text{atm}} \\ &= -4.9 \times 10^2 \text{ J} \end{aligned}$$

Check Because this is gas expansion (work is done by the system on the surroundings), the work done has a negative sign.

Practice Exercise A gas expands from 264 mL to 971 mL at constant temperature. Calculate the work done (in joules) by the gas if it expands (a) against a vacuum and (b) against a constant pressure of 4.00 atm.

Similar problems: 6.15, 6.16.

Because temperature is kept constant, you can use Boyle's law to show that the final pressure is the same in (a) and (b).

Example 6.1 shows that work is not a state function. Although the initial and final states are the same in (a) and (b), the amount of work done is different because the external, opposing pressures are different. We *cannot* write $\Delta w = w_f - w_i$ for a change. Work done depends not only on the initial state and final state, but also on how the process is carried out—that is, on the path.

Heat

The other component of internal energy is heat, q . Like work, heat is not a state function. For example, it takes 4184 J of energy to raise the temperature of 100 g of water

from 20°C to 30°C. This energy can be gained (a) directly as heat energy from a Bunsen burner, without doing any work on the water; (b) by doing work on the water without adding heat energy (for example, by stirring the water with a magnetic stir bar); or (c) by some combination of the procedures described in (a) and (b). This simple illustration shows that heat associated with a given process, like work, depends on how the process is carried out. It is important to note that regardless of which procedure is taken, the change in internal energy of the system, ΔU , depends on the sum of $(q + w)$. If changing the path from the initial state to the final state increases the value of q , then it will decrease the value of w by the same amount and vice versa, so that ΔU remains unchanged.

In summary, heat and work are not state functions because they are not properties of a system. They manifest themselves only during a process (during a change). Thus, their values depend on the path of the process and vary accordingly.

Example 6.2

The work done when a gas is compressed in a cylinder like that shown in Figure 6.5 is 462 J. During this process, there is a heat transfer of 128 J from the gas to the surroundings. Calculate the energy change for this process.

Strategy Compression is work done on the gas, so what is the sign for w ? Heat is released by the gas to the surroundings. Is this an endothermic or exothermic process? What is the sign for q ?

Solution To calculate the energy change of the gas, we need Equation (6.1). Work of compression is positive and because heat is released by the gas, q is negative. Therefore, we have

$$\begin{aligned}\Delta U &= q + w \\ &= -128 \text{ J} + 462 \text{ J} \\ &= 334 \text{ J}\end{aligned}$$

As a result, the energy of the gas increases by 334 J.

Practice Exercise A gas expands and does $P\text{-}V$ work on the surroundings equal to 279 J. At the same time, it absorbs 216 J of heat from the surroundings. What is the change in energy of the system?

Similar problems: 6.17, 6.18.

Review of Concepts & Facts

- 6.3.1 Two ideal gases at the same temperature and pressure are placed in two equal-volume containers. One container has a fixed volume, while the other is a cylinder fitted with a weightless movable piston like that shown in Figure 6.5. Initially, the gas pressures are equal to the external atmospheric pressure. The gases are then heated with a Bunsen burner. What are the signs of q and w for the gases under these conditions?
- 6.3.2 Calculate the work done when a gas at a pressure of 2.4 atm and constant temperature expands in volume from 1.0 L to 2.2 L.
- 6.3.3 What is the change in internal energy of a gas when the work done to compress the gas is 58 J, and 79 J of heat is released to the surroundings?

Making Snow and Inflating a Bicycle Tire

Many phenomena in everyday life can be explained by the first law of thermodynamics. Here we will discuss two examples of interest to lovers of the outdoors.

Making Snow

If you are an avid downhill skier, you have probably skied on artificial snow. How is this stuff made in quantities large enough to meet the needs of skiers on snowless days? The secret of snowmaking is in the equation $\Delta U = q + w$. A snowmaking machine contains a mixture of compressed air and water vapor at about 20 atm. Because of the large difference in pressure between the tank and the outside atmosphere, when the mixture is sprayed into the atmosphere it expands so rapidly that, as a good approximation, no heat exchange occurs between the system (air and water) and its surroundings; that is, $q = 0$. (In thermodynamics, such a process is called an *adiabatic process*.) Thus, we write

$$\Delta U = q + w = w$$

Because the system does work on the surroundings, w is a negative quantity, and there is a decrease in the system's energy.

Kinetic energy is part of the total energy of the system. In Section 5.7 we saw that the average kinetic energy of a gas is directly proportional to the absolute temperature [Equation (5.15)]. It follows, therefore, that the change in energy ΔU is given by

$$\Delta U = C\Delta T$$

where C is the proportionality constant. Because ΔU is negative, ΔT must also be negative, and it is this cooling effect (or the decrease in the kinetic energy of the water molecules) that is responsible for the formation of snow. Although we need only water to form snow, the presence of air, which

also cools on expansion, helps to lower the temperature of the water vapor.

Inflating a Bicycle Tire

If you have ever pumped air into a bicycle tire, you probably noticed a warming effect at the valve stem. This phenomenon, too, can be explained by the first law of thermodynamics. The action of the pump compresses the air inside the pump and the tire. The process is rapid enough to be treated as approximately adiabatic, so that $q = 0$ and $\Delta U = w$. Because work is done on the gas in this case (it is being compressed), w is positive, and there is an increase in energy. Hence, the temperature of the system increases also, accordinging to the equation

$$\Delta U = C\Delta T$$



A snowmaking machine in operation.
©Sergey Podkolzin/Alamy Stock Photo

6.4 Enthalpy of Chemical Reactions

Our next step is to see how the first law of thermodynamics can be applied to processes carried out under different conditions. Specifically, we will consider two situations most commonly encountered in the laboratory: one in which the volume of the system is kept constant and one in which the pressure applied on the system is kept constant.

If a chemical reaction is run at constant volume, then $\Delta V = 0$ and no $P\text{-}V$ work will result from this change. From Equation (6.1) it follows that

$$\begin{aligned}\Delta U &= q - P\Delta V \\ &= q_v\end{aligned}\tag{6.4}$$

Recall that $w = -P\Delta V$.

We add the subscript “*v*” to remind us that this is a constant-volume process. This equality may seem strange at first, for we showed earlier that *q* is not a state function. The process is carried out under constant-volume conditions, however, so that the heat change can have only a specific value, which is equal to ΔU .

Enthalpy

Constant-volume conditions are often inconvenient and sometimes impossible to achieve. Most reactions occur under conditions of constant pressure (usually atmospheric pressure). If such a reaction results in a net increase in the number of moles of a gas, then the system does work on the surroundings (expansion). This result follows from the fact that for the gas formed to enter the atmosphere, it must push the surrounding air back. Conversely, if more gas molecules are consumed than are produced, work is done on the system by the surroundings (compression). Finally, no work is done if there is no net change in the number of moles of gases from reactants to products.

In general, for a constant-pressure process we write

$$\begin{aligned}\Delta U &= q + w \\ &= q_p - P\Delta V \\ \text{or} \quad q_p &= \Delta U + P\Delta V\end{aligned}\tag{6.5}$$

where the subscript “*p*” denotes constant-pressure condition.

We now introduce a new thermodynamic function of a system called **enthalpy (H)**, which is defined by the equation

$$H = U + PV\tag{6.6}$$

where *U* is the internal energy of the system and *P* and *V* are the pressure and volume of the system, respectively. Because *U* and *PV* have energy units, enthalpy also has energy units. Furthermore, *U*, *P*, and *V* are all state functions; that is, the changes in (*U* + *PV*) depend only on the initial and final states. It follows, therefore, that the change in *H*, or ΔH , also depends only on the initial and final states. Thus, *H* is a state function.

For any process, the change in enthalpy according to Equation (6.6) is given by

$$\Delta H = \Delta U + \Delta(PV)\tag{6.7}$$

If the pressure is held constant, then

$$\Delta H = \Delta U + P\Delta V\tag{6.8}$$

Comparing Equation (6.8) with Equation (6.5), we see that for a constant-pressure process, $q_p = \Delta H$. Again, although *q* is not a state function, the heat change at constant pressure is equal to ΔH because the “path” is defined and therefore it can have only a specific value.

In Section 6.5 we will discuss ways to measure heat changes at constant volume and constant pressure.

We now have two quantities— ΔU and ΔH —that can be associated with a reaction. If the reaction occurs under constant-volume conditions, then the heat change, q_v , is equal to ΔU . On the other hand, when the reaction is carried out at constant pressure, the heat change, q_p , is equal to ΔH .

Enthalpy of Reactions

Because most reactions are constant-pressure processes, we can equate the heat change in these cases to the change in enthalpy. For any reaction of the type



we define the change in enthalpy, called the **enthalpy of reaction**, ΔH_{rxn} , as the difference between the enthalpies of the products and the enthalpies of the reactants:

We often omit the subscript "rxn" and simply write ΔH for enthalpy changes of reactions.

This analogy assumes that you will not overdraw your bank account. The enthalpy of a substance cannot be negative.

$$\Delta H = H(\text{products}) - H(\text{reactants}) \quad (6.9)$$

The enthalpy of reaction can be positive or negative, depending on the process. For an endothermic process (heat absorbed by the system from the surroundings), ΔH is positive (that is, $\Delta H > 0$). For an exothermic process (heat released by the system to the surroundings), ΔH is negative (that is, $\Delta H < 0$).

An analogy for enthalpy change is a change in the balance in your bank account. Suppose your initial balance is \$100. After a transaction (deposit or withdrawal), the change in your bank balance, ΔX , is given by

$$\Delta X = X_{\text{final}} - X_{\text{initial}}$$

where X represents the bank balance. If you deposit \$80 into your account, then $\Delta X = \$180 - \$100 = \$80$. This corresponds to an endothermic reaction. (The balance increases and so does the enthalpy of the system.) On the other hand, a withdrawal of \$60 means $\Delta X = \$40 - \$100 = -\$60$. The negative sign of ΔX means your balance has decreased. Similarly, a negative value of ΔH reflects a decrease in enthalpy of the system as a result of an exothermic process. The difference between this analogy and Equation (6.9) is that while you always know your exact bank balance, there is no way to know the enthalpies of individual products and reactants. In practice, we can only measure the *difference* in their values.

Now let us apply the idea of enthalpy changes to two common processes, the first involving a physical change, the second a chemical change.

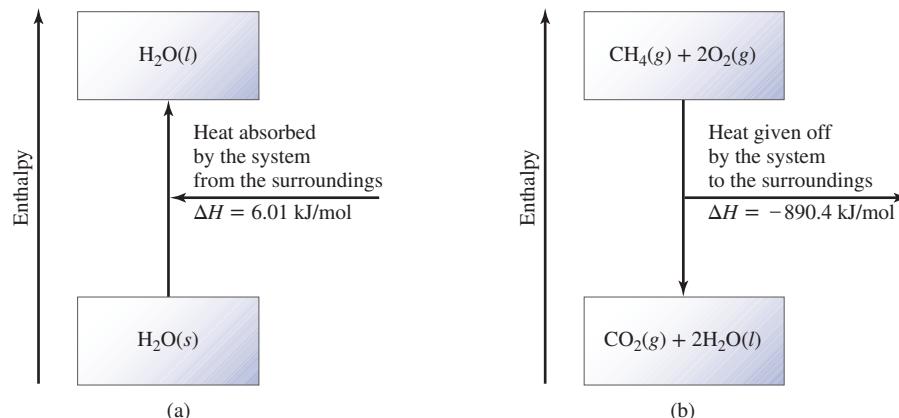
Thermochemical Equations

At 0°C and a pressure of 1 atm, ice melts to form liquid water. Measurements show that for every mole of ice converted to liquid water under these conditions, 6.01 kilojoules (kJ) of heat energy are absorbed by the system (ice). Because the pressure is constant, the heat change is equal to the enthalpy change, ΔH . Furthermore, this is an endothermic process, as expected for the energy-absorbing change of melting ice [Figure 6.6(a)]. Therefore, ΔH is a positive quantity. The equation for this physical change is

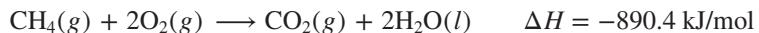


For simplicity, we use "per mole" rather than "per mole of reaction" for ΔH in thermochemical equations.

Figure 6.6 (a) Melting 1 mole of ice at 0°C (an endothermic process) results in an enthalpy increase in the system of 6.01 kJ. (b) Burning 1 mole of methane in oxygen gas (an exothermic process) results in an enthalpy decrease in the system of 890.4 kJ. Parts (a) and (b) are not drawn to the same scale.



As another example, consider the combustion of methane (CH_4), the principal component of natural gas:



From experience we know that burning natural gas releases heat to the surroundings, so it is an exothermic process. Under constant-pressure condition this heat change is equal to enthalpy change and ΔH must have a negative sign [Figure 6.6(b)]. Again, the per mole of reaction unit for ΔH means that when 1 mole of CH_4 reacts with 2 moles of O_2 to produce 1 mole of CO_2 and 2 moles of liquid H_2O , 890.4 kJ of heat energy are released to the surroundings. It is important to keep in mind that the ΔH value does not refer to a particular reactant or product. It simply means that the quoted ΔH value refers to all the reacting species in molar quantities. Thus, the following conversion factors can be created:

$$\frac{-890.4 \text{ kJ}}{1 \text{ mol CH}_4} \quad \frac{-890.4 \text{ kJ}}{2 \text{ mol O}_2} \quad \frac{-890.4 \text{ kJ}}{1 \text{ mol CO}_2} \quad \frac{-890.4 \text{ kJ}}{2 \text{ mol H}_2\text{O}}$$

Expressing ΔH in units of kJ/mol (rather than just kJ) conforms to the standard convention; its merit will become apparent when we continue our study of thermodynamics in Chapter 17.

The equations for the melting of ice and the combustion of methane are examples of **thermochemical equations**, which *show the enthalpy changes as well as the mass relationships*. It is essential to specify a balanced equation when quoting the enthalpy change of a reaction. The following guidelines are helpful in writing and interpreting thermochemical equations.

- When writing thermochemical equations, we must always specify the physical states of all reactants and products, because they help determine the actual enthalpy changes. For example, in the equation for the combustion of methane, if we show water vapor rather than liquid water as a product,



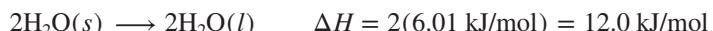
the enthalpy change is -802.4 kJ rather than -890.4 kJ because 88.0 kJ are needed to convert 2 moles of liquid water to water vapor; that is,



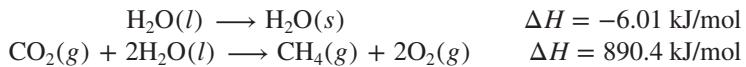
- If we multiply both sides of a thermochemical equation by a factor n , then ΔH must also change by the same factor. Returning to the melting of ice



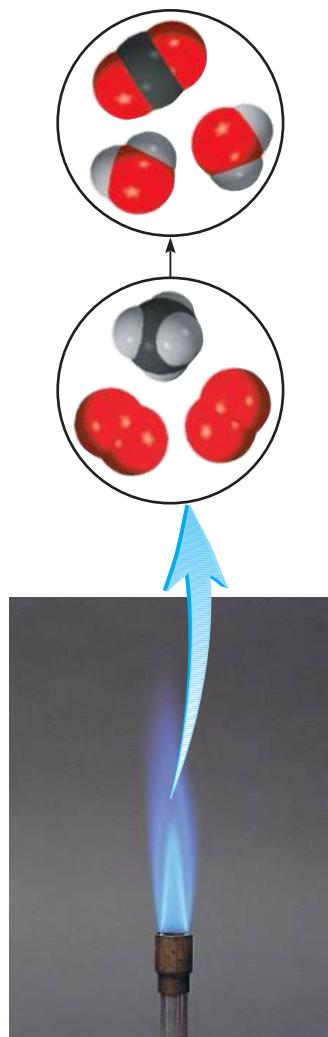
If we multiply the equation throughout by 2; that is, if we set $n = 2$, then



- When we reverse an equation, we change the roles of reactants and products. Consequently, the magnitude of ΔH for the equation remains the same, but its sign changes. For example, if a reaction consumes thermal energy from its surroundings (that is, if it is endothermic), then the reverse reaction must release thermal energy back to its surroundings (that is, it must be exothermic) and the enthalpy change expression must also change its sign. Thus, reversing the melting of ice and the combustion of methane, the thermochemical equations become



and what was an endothermic process becomes exothermic, and vice versa.

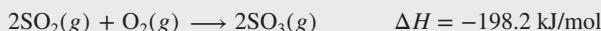


Methane gas burning from a Bunsen burner.

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Example 6.3

Given the thermochemical equation



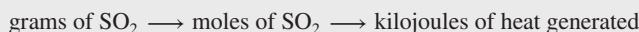
calculate the heat evolved when 87.9 g of SO_2 (molar mass = 64.07 g/mol) is converted to SO_3 .

Strategy The thermochemical equation shows that for every 2 moles of SO_2 reacted, 198.2 kJ of heat are given off (note the negative sign). Therefore, the conversion factor is

$$\frac{-198.2 \text{ kJ}}{2 \text{ mol SO}_2}$$

How many moles of SO_2 are in 87.9 g of SO_2 ? What is the conversion factor between grams and moles?

Solution We need to first calculate the number of moles of SO_2 in 87.9 g of the compound and then find the number of kilojoules produced from the exothermic reaction. The sequence of conversions is as follows:



Therefore, the enthalpy change for this reaction is given by

$$\Delta H = 87.9 \text{ g } \cancel{\text{SO}_2} \times \frac{1 \text{ mol } \cancel{\text{SO}_2}}{64.07 \text{ g } \cancel{\text{SO}_2}} \times \frac{-198.2 \text{ kJ}}{2 \text{ mol } \cancel{\text{SO}_2}} = -136 \text{ kJ}$$

and the heat released to the surroundings is 136 kJ.

Check Because 87.9 g is less than twice the molar mass of SO_2 ($2 \times 64.07 \text{ g}$) as shown in the preceding thermochemical equation, we expect the heat released to be smaller than 198.2 kJ.

Practice Exercise Calculate the heat evolved when 266 g of white phosphorus (P_4) burns in air according to the equation



Similar problem: 6.26.



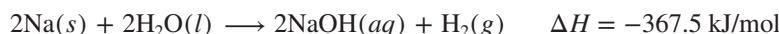
Sodium reacting with water to form hydrogen gas.

©Charles D. Winters/Science Source

Recall that $1 \text{ L} \cdot \text{atm} = 101.3 \text{ J}$.

A Comparison of ΔH and ΔU

What is the relationship between ΔH and ΔU for a process? To find out, let us consider the reaction between sodium metal and water:



This thermochemical equation says that when two moles of sodium react with an excess of water, 367.5 kJ of heat are given off. Note that one of the products is hydrogen gas, which must push back air to enter the atmosphere. Consequently, some of the energy produced by the reaction is used to do work of pushing back a volume of air (ΔV) against atmospheric pressure (P) (Figure 6.7). To calculate the change in internal energy, we rearrange Equation (6.8) as follows:

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

If we assume the temperature to be 25°C and ignore the small change in the volume of the solution, we can show that the volume of 1 mole of H_2 gas at 1.0 atm and 298 K is 24.5 L, so that $-P\Delta V = -24.5 \text{ L} \cdot \text{atm}$ or -2.5 kJ . Finally,

$$\begin{aligned} \Delta U &= -367.5 \text{ kJ/mol} - 2.5 \text{ kJ/mol} \\ &= -370.0 \text{ kJ/mol} \end{aligned}$$

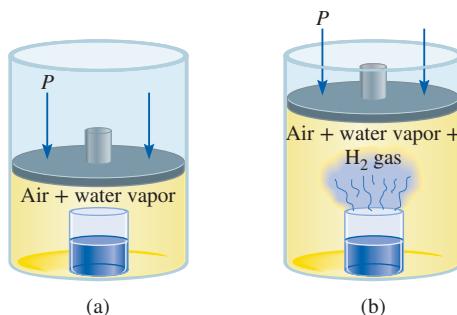


Figure 6.7 (a) A beaker of water inside a cylinder fitted with a movable piston. The pressure inside is equal to the atmospheric pressure. (b) As the sodium metal reacts with water, the hydrogen gas generated pushes the piston upward (doing work on the surroundings) until the pressure inside is again equal to that of outside.

This calculation shows that ΔU and ΔH are approximately the same. The reason ΔH is smaller than ΔU in magnitude is that some of the internal energy released is used to do gas expansion work, so less heat is evolved. For reactions that do not involve gases, ΔV is usually very small and so ΔU is practically the same as ΔH .

Another way to calculate the internal energy change of a gaseous reaction is to assume ideal gas behavior and constant temperature. In this case,

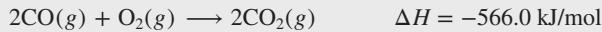
$$\begin{aligned}\Delta U &= \Delta H - \Delta(PV) \\ &= \Delta H - \Delta(nRT) \\ &= \Delta H - RT\Delta n\end{aligned}\quad (6.10)$$

where Δn is defined as

$$\Delta n = \text{number of moles of product gases} - \text{number of moles of reactant gases}$$

Example 6.4

Calculate the change in internal energy when 2 moles of CO are converted to 2 moles of CO₂ at 1 atm and 25°C:



Strategy We are given the enthalpy change, ΔH , for the reaction and are asked to calculate the change in internal energy, ΔU . Therefore, we need Equation (6.10). What is the change in the number of moles of gases? ΔH is given in kilojoules, so what units should we use for R ?

Solution From the chemical equation we see that 3 moles of gases are converted to 2 moles of gases so that

$$\begin{aligned}\Delta n &= \text{number of moles of product gas} - \text{number of moles of reactant gases} \\ &= 2 - 3 \\ &= -1\end{aligned}$$

Using 8.314 J/K · mol for R and $T = 298$ K in Equation (6.10), we write

$$\begin{aligned}\Delta U &= \Delta H - RT\Delta n \\ &= -566.0 \text{ kJ/mol} - (8.314 \text{ J/K} \cdot \text{mol}) \left(\frac{1 \text{ kJ}}{1000 \text{ J}} \right) (298 \text{ K})(-1) \\ &= -563.5 \text{ kJ/mol}\end{aligned}$$

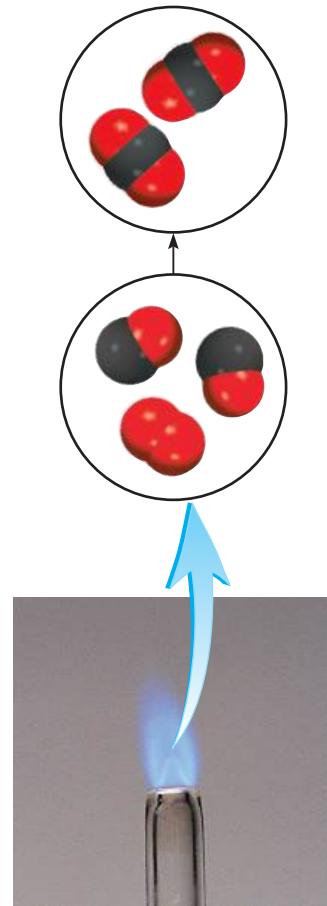
Check Knowing that the reacting gaseous system undergoes a compression (3 moles to 2 moles), is it reasonable to have $\Delta H > \Delta U$ in magnitude?

Practice Exercise What is ΔU for the formation of 1 mole of CO at 1 atm and 25°C?



Similar problem: 6.27.

For reactions that do not result in a change in the number of moles of gases from reactants to products [for example, H₂(g) + F₂(g) → 2HF(g)], $\Delta U = \Delta H$.



Carbon monoxide burns in air to form carbon dioxide.

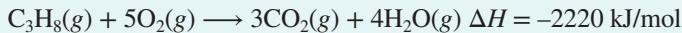
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Review of Concepts & Facts

6.4.1 Which of the constant-pressure processes shown here has the smallest difference between ΔU and ΔH ?

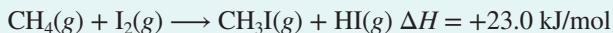
- (a) water \longrightarrow water vapor
- (b) water \longrightarrow ice
- (c) ice \longrightarrow water vapor

6.4.2 Given the thermochemical equation



calculate the heat evolved when 53.2 g of C_3H_8 (molar mass = 44.10 g/mol) is burned in excess oxygen.

6.4.3 Calculate ΔU for the following reaction at 1 atm and 25°C:



6.5 Calorimetry

In the laboratory, heat changes in physical and chemical processes are measured with a *calorimeter*, a closed container designed specifically for this purpose. Our discussion of *calorimetry, the measurement of heat changes*, will depend on an understanding of specific heat and heat capacity, so let us consider them first.

Specific Heat and Heat Capacity

The *specific heat (s)* of a substance is *the amount of heat required to raise the temperature of one gram of the substance by one degree Celsius*. It has the units $\text{J/g} \cdot ^\circ\text{C}$. The *heat capacity (C)* of a substance is *the amount of heat required to raise the temperature of a given quantity of the substance by one degree Celsius*. Its units are $\text{J}/^\circ\text{C}$. Specific heat is an intensive property, whereas heat capacity is an extensive property. The relationship between the heat capacity and specific heat of a substance is

$$C = ms \quad (6.11)$$

where m is the mass of the substance in grams. For example, the specific heat of water is $4.184 \text{ J/g} \cdot ^\circ\text{C}$, and the heat capacity of 60.0 g of water is

$$(60.0 \text{ g})(4.184 \text{ J/g} \cdot ^\circ\text{C}) = 251 \text{ J}/^\circ\text{C}$$

Table 6.2 shows the specific heat of some common substances.

If we know the specific heat and the amount of a substance, then the change in the sample's temperature (Δt) will tell us the amount of heat (q) that has been absorbed or released in a particular process. The equations for calculating the heat change are given by

$$q = ms\Delta t \quad (6.12)$$

$$q = C\Delta t \quad (6.13)$$

where Δt is the temperature change:

$$\Delta t = t_{\text{final}} - t_{\text{initial}}$$

The sign convention for q is the same as that for enthalpy change; q is positive for endothermic processes and negative for exothermic processes.

Table 6.2

The Specific Heats of Some Common Substances

Substance	Specific Heat (J/g · °C)
Al	0.900
Au	0.129
C (graphite)	0.720
C (diamond)	0.502
Cu	0.385
Fe	0.444
Hg	0.139
Pb	0.158
H_2O	4.184
$\text{C}_2\text{H}_5\text{OH}$ (ethanol)	2.46



Student Hot Spot

Student data indicate you may struggle with specific heat. Access your eBook for additional Learning Resources on this topic.

Example 6.5

A 466-g sample of water is heated from 8.50°C to 74.60°C. Calculate the amount of heat absorbed (in kilojoules) by the water.

Strategy We know the quantity of water and the specific heat of water. With this information and the temperature rise, we can calculate the amount of heat absorbed (q).

Solution Using Equation (6.12), we write

$$\begin{aligned} q &= ms\Delta t \\ &= (466 \text{ g})(4.184 \text{ J/g} \cdot ^\circ\text{C})(74.60^\circ\text{C} - 8.50^\circ\text{C}) \\ &= 1.29 \times 10^5 \text{ J} \times \frac{1 \text{ kJ}}{1000 \text{ J}} \\ &= 129 \text{ kJ} \end{aligned}$$

Check The units g and °C cancel, and we are left with the desired unit kJ. Because heat is absorbed by the water from the surroundings, it has a positive sign.

Practice Exercise An iron bar of mass 869 g cools from 94°C to 5°C. Calculate the heat released (in kilojoules) by the metal.

Similar problem: 6.33.

Constant-Volume Calorimetry

Heat of combustion is usually measured by placing a known mass of a compound in a steel container called a *constant-volume bomb calorimeter*, which is filled with oxygen at about 30 atm of pressure. The closed bomb is immersed in a known amount of water, as shown in Figure 6.8. The sample is ignited electrically, and the heat produced by the combustion reaction can be calculated accurately by recording the rise in temperature of the water. The heat given off by the sample is absorbed by the water and the bomb. The special design of the calorimeter enables us to assume that no heat (or mass) is lost to the surroundings during the time it takes to make measurements. Therefore, we can call the

"Constant volume" refers to the volume of the container, which does not change during the reaction. Note that the container remains intact after the measurement. The term "bomb calorimeter" connotes the explosive nature of the reaction (on a small scale) in the presence of excess oxygen gas.

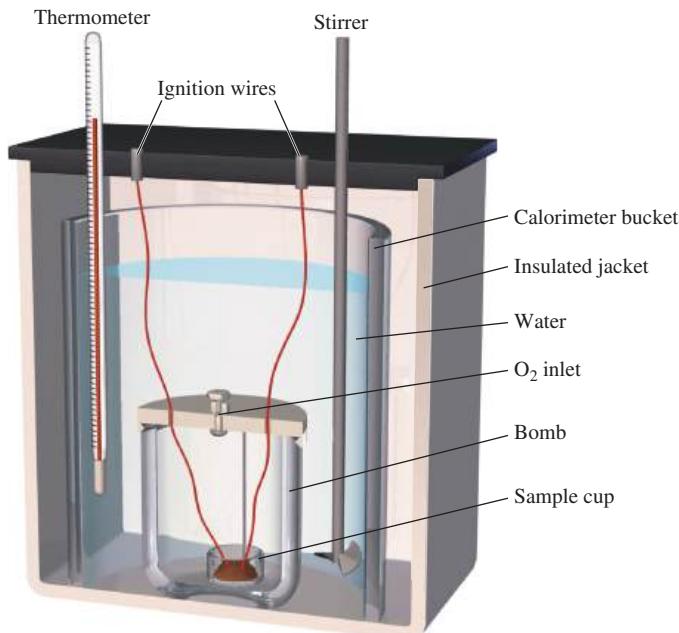


Figure 6.8 A constant-volume bomb calorimeter. The calorimeter is filled with oxygen gas before it is placed in the bucket. The sample is ignited electrically, and the heat produced by the reaction can be accurately determined by measuring the temperature increase in the known amount of surrounding water.

bomb and the water in which it is submerged an isolated system. Because no heat enters or leaves the system throughout the process, the heat change of the system (q_{system}) must be zero and we can write

$$\begin{aligned} q_{\text{system}} &= q_{\text{cal}} + q_{\text{rxn}} \\ &= 0 \end{aligned} \quad (6.14)$$

where q_{cal} and q_{rxn} are the heat changes for the calorimeter and the reaction, respectively. Thus,

$$q_{\text{rxn}} = -q_{\text{cal}} \quad (6.15)$$

Note that C_{cal} comprises both the bomb and the surrounding water.

To calculate q_{cal} , we need to know the heat capacity of the calorimeter (C_{cal}) and the temperature rise, that is,

$$q_{\text{cal}} = C_{\text{cal}}\Delta t \quad (6.16)$$

Note that although the combustion reaction is exothermic, q_{cal} is a positive quantity because it represents the heat absorbed by the calorimeter.

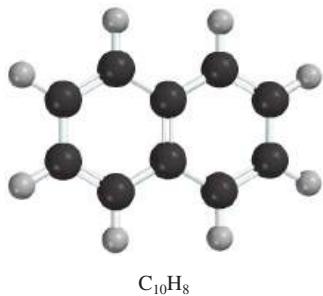
The quantity C_{cal} is calibrated by burning a substance with an accurately known heat of combustion. For example, it is known that the combustion of 1 g of benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$) releases 26.42 kJ of heat. If the temperature rise is 4.673°C , then the heat capacity of the calorimeter is given by

$$\begin{aligned} C_{\text{cal}} &= \frac{q_{\text{cal}}}{\Delta t} \\ &= \frac{26.42 \text{ kJ}}{4.673^\circ\text{C}} = 5.654 \text{ kJ}/^\circ\text{C} \end{aligned}$$

Once C_{cal} has been determined, the calorimeter can be used to measure the heat of combustion of other substances.

Note that because reactions in a bomb calorimeter occur under constant-volume rather than constant-pressure conditions, the heat changes correspond to ΔU , *not* the enthalpy change ΔH (see Section 6.4). Equation (6.10) can be used to correct the measured heat changes so that they correspond to ΔH values, but the corrections usually are quite small so we will not concern ourselves with the details here. Finally, it is interesting to note that the energy contents of food and fuel (usually expressed in calories where 1 cal = 4.184 J) are measured with constant-volume calorimeters.

Example 6.6



A quantity of 1.435 g of naphthalene (C_{10}H_8), a pungent-smelling substance used in moth repellents, was burned in a constant-volume bomb calorimeter. Consequently, the temperature of the water rose from 20.28°C to 25.95°C . If the heat capacity of the bomb plus water was $10.17 \text{ kJ}/^\circ\text{C}$, calculate the heat of combustion of naphthalene on a molar basis; that is, find the molar heat of combustion.

Strategy Knowing the heat capacity and the temperature rise, how do we calculate the heat absorbed by the calorimeter? What is the heat generated by the combustion of 1.435 g of naphthalene? What is the conversion factor between grams and moles of naphthalene?

(Continued)

Solution The heat absorbed by the bomb and water is equal to the product of the heat capacity and the temperature change. From Equation (6.16), assuming no heat is lost to the surroundings, we write

$$\begin{aligned} q_{\text{cal}} &= C_{\text{cal}} \Delta t \\ &= (10.17 \text{ kJ}/^{\circ}\text{C})(25.95^{\circ}\text{C} - 20.28^{\circ}\text{C}) \\ &= 57.66 \text{ kJ} \end{aligned}$$

Because $q_{\text{sys}} = q_{\text{cal}} + q_{\text{rxn}} = 0$, $q_{\text{cal}} = -q_{\text{rxn}}$. The heat change of the reaction is -57.66 kJ . This is the heat released by the combustion of 1.435 g of C_{10}H_8 ; therefore, we can write the conversion factor as

$$\frac{-57.66 \text{ kJ}}{1.435 \text{ g } \text{C}_{10}\text{H}_8}$$

The molar mass of naphthalene is 128.2 g, so the heat of combustion of 1 mole of naphthalene is

$$\begin{aligned} \text{molar heat of combustion} &= \frac{-57.66 \text{ kJ}}{1.435 \text{ g } \text{C}_{10}\text{H}_8} \times \frac{128.2 \text{ g } \text{C}_{10}\text{H}_8}{1 \text{ mol } \text{C}_{10}\text{H}_8} \\ &= -5.151 \times 10^3 \text{ kJ/mol} \end{aligned}$$

Check Knowing that the combustion reaction is exothermic and that the molar mass of naphthalene is much greater than 1.4 g, is the answer reasonable? Under the reaction conditions, can the heat change (-57.66 kJ) be equated to the enthalpy change of the reaction?

Practice Exercise A quantity of 1.922 g of methanol (CH_3OH) was burned in a constant-volume bomb calorimeter. Consequently, the temperature of the water rose by 4.20°C . If the heat capacity of the bomb plus water was $10.4 \text{ kJ}/^{\circ}\text{C}$, calculate the molar heat of combustion of methanol.

Similar problem: 6.37.

Constant-Pressure Calorimetry

A simpler device than the constant-volume calorimeter is the constant-pressure calorimeter, which is used to determine the heat changes for noncombustion reactions. A crude constant-pressure calorimeter can be constructed from two Styrofoam coffee cups, as shown in Figure 6.9. This device measures the heat effects of a variety of reactions, such as acid-base neutralization, as well as the heat of solution and heat of dilution. Because the pressure is constant, the heat change for the process (q_{rxn}) is equal to the enthalpy change (ΔH). As in the case of a constant-volume calorimeter, we treat the calorimeter as an isolated system. Furthermore, we neglect the small heat capacity of the coffee cups in our calculations. Table 6.3 lists some reactions that have been studied with the constant-pressure calorimeter.

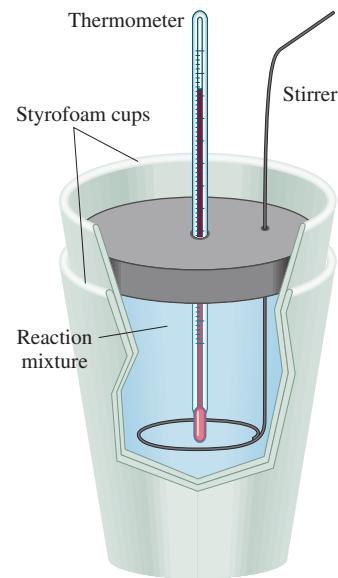


Figure 6.9 A constant-pressure calorimeter made of two Styrofoam coffee cups. The outer cup helps to insulate the reacting mixture from the surroundings. Two solutions of known volume containing the reactants at the same temperature are carefully mixed in the calorimeter. The heat produced or absorbed by the reaction can be determined by measuring the temperature change.

Student Hot Spot

Student data indicate you may struggle with constant-pressure calorimetry. Access your eBook for additional Learning Resources on this topic.

Table 6.3 Heats of Some Typical Reactions Measured at Constant Pressure

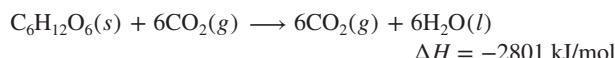
Type of Reaction	Example	ΔH (kJ/mol)
Heat of neutralization	$\text{HCl}(aq) + \text{NaOH}(aq) \rightarrow \text{NaCl}(aq) + \text{H}_2\text{O}(l)$	-56.2
Heat of ionization	$\text{H}_2\text{O}(l) \rightarrow \text{H}^+(aq) + \text{OH}^-(aq)$	56.2
Heat of fusion	$\text{H}_2\text{O}(s) \rightarrow \text{H}_2\text{O}(l)$	6.01
Heat of vaporization	$\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(g)$	44.0*
Heat of reaction	$\text{MgCl}_2(s) + 2\text{Na}(l) \rightarrow 2\text{NaCl}(s) + \text{Mg}(s)$	-180.2

*Measured at 25°C . At 100°C , the value is 40.79 kJ.

CHEMISTRY *in Action*

White Fat Cells, Brown Fat Cells, and a Potential Cure for Obesity

The food we eat is broken down, or metabolized, in stages by a group of complex biological molecules called enzymes. Most of the energy released at each stage is captured for function and growth. One interesting aspect of metabolism is that the overall change in energy is the same as it is in combustion. For example, the total enthalpy change for the conversion of glucose ($C_6H_{12}O_6$) to carbon dioxide and water is the same whether we burn the substance in air or digest it in our bodies:



The energy content of food is generally measured in calories. The *calorie (cal)* is a non-SI unit of energy that is equivalent to 4.184 J:

$$1 \text{ cal} = 4.184 \text{ J}$$

In the context of nutrition, however, the calorie we speak of (sometimes called a “big calorie”) is actually equal to a kilocalorie; that is,

$$1 \text{ Cal} = 1000 \text{ cal} = 4184 \text{ J}$$

The bomb calorimeter described in Section 6.5 is ideally suited for measuring the energy content, or “fuel values,” of foods (see table).

Fuel Values of Foods

Substance	$\Delta H_{\text{combustion}}$ (kJ/g)
Apple	-2
Beef	-8
Beer	-1.5
Bread	-11
Butter	-34
Cheese	-18
Eggs	-6
Milk	-3
Potatoes	-3

The excess energy from food is stored in the body in the form of fats. Fats are a group of organic compounds (triesters of glycerol and fatty acids) that are soluble in organic solvents but insoluble in water. There are two types of fat cells called the white fat cells (WFC) and brown fat cells (BFC). The WFC are designed to store energy for use in time of need for body function. They accumulate under the skin and around internal organs and they cushion and insulate the body. Obese people have a high content of WFC in their bodies. BFC, on the other hand, contain a high concentration of mitochondria, which are specialized subunits within a cell. The main role of BFC is to burn fat molecules and generate heat. Its name is derived from the fact that mitochondria contain iron, giving the tissue a reddish-brown color. In general, women have more BFC than men.

We lose our brown fat as we age, but several studies carried out in 2009 showed that adults possess metabolically active BFC. In one experiment, PET/CT (positron emission tomography and computerized tomography) scans of 24 men exposed to cold and room temperature show that the chilly temperature activates the BFC as they burn off fat molecules to generate heat. Furthermore, it was found that lean people have more active BFC than obese people.

Mice have the same type of fat cells as humans. In 2013 it was demonstrated by genetically labeling the fat cells of mice that WFC could be converted into BFC by exposure to cold (8°C) for one week. Unfortunately, BFC were converted back to WFC a few weeks after the mice were returned to normal room temperature. A separate study suggested that a different type of BFC can be formed from WFC by exercise.

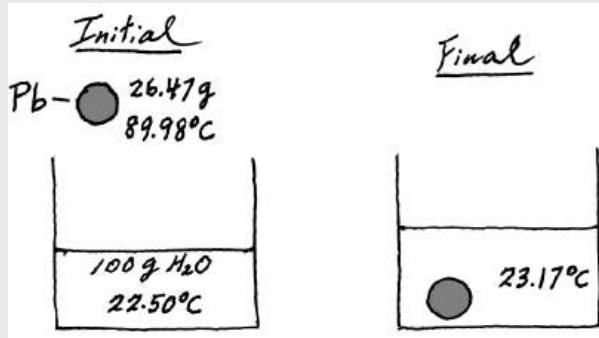
Obesity is a major health hazard in the United States. Treatments for obesity so far are focused on diet to lower the amount of energy consumed, or exercise to increase the amount of energy the body needs. Most current antiobesity drugs work on the diet half of treatment. If scientists can find a way to convert WFC to BFC by biological means, and signs are encouraging, drugs will one day be developed that would fight obesity based on energy expenditure rather than appetite. And one can accomplish this goal without having to exercise in a cold environment.

Example 6.7

A lead (Pb) pellet having a mass of 26.47 g at 89.98°C was placed in a constant-pressure calorimeter of negligible heat capacity containing 100.0 mL of water. The water temperature rose from 22.50°C to 23.17°C. What is the specific heat of the lead pellet?

(Continued)

Strategy Sketches of the initial and final situations are as follows:



We know the masses of water and the lead pellet as well as the initial and final temperatures. Assuming no heat is lost to the surroundings, we can equate the heat lost by the lead pellet to the heat gained by the water. Knowing the specific heat of water, we can then calculate the specific heat of lead.

Solution Treating the calorimeter as an isolated system (no heat lost to the surroundings), we write

$$\begin{aligned} q_{\text{Pb}} + q_{\text{H}_2\text{O}} &= 0 \\ \text{or} \quad q_{\text{Pb}} &= -q_{\text{H}_2\text{O}} \end{aligned}$$

The heat gained by the water is given by

$$q_{\text{H}_2\text{O}} = ms\Delta t$$

where m and s are the mass and specific heat, and $\Delta t = t_{\text{final}} - t_{\text{initial}}$. Therefore,

$$\begin{aligned} q_{\text{H}_2\text{O}} &= (100.0 \text{ g})(4.184 \text{ J/g} \cdot ^\circ\text{C})(23.17^\circ\text{C} - 22.50^\circ\text{C}) \\ &= 280.3 \text{ J} \end{aligned}$$

Because the heat lost by the lead pellet is equal to the heat gained by the water, $q_{\text{Pb}} = -280.3 \text{ J}$. Solving for the specific heat of Pb, we write

$$\begin{aligned} q_{\text{Pb}} &= ms\Delta t \\ -280.3 \text{ J} &= (26.47 \text{ g})(s)(23.17^\circ\text{C} - 89.98^\circ\text{C}) \\ s &= 0.158 \text{ J/g} \cdot ^\circ\text{C} \end{aligned}$$

Practice Exercise A 30.14-g stainless steel ball bearing at 117.82°C is placed in a constant-pressure calorimeter containing 120.0 mL of water at 18.44°C . If the specific heat of the ball bearing is $0.474 \text{ J/g} \cdot ^\circ\text{C}$, calculate the final temperature of the water. Assume the calorimeter to have negligible heat capacity.

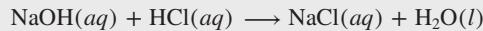
Similar problem: 6.88.

Example 6.8

A quantity of $1.00 \times 10^2 \text{ mL}$ of 0.500 M HCl was mixed with $1.00 \times 10^2 \text{ mL}$ of 0.500 M NaOH in a constant-pressure calorimeter of negligible heat capacity. The initial temperature of the HCl and NaOH solutions was the same, 22.50°C , and the final

(Continued)

temperature of the mixed solution was 25.86°C. Calculate the heat change for the neutralization reaction on a molar basis:



Assume that the densities and specific heats of the solutions are the same as for water (1.00 g/mL and 4.184 J/g · °C, respectively).

Strategy Because the temperature rose, the neutralization reaction is exothermic. How do we calculate the heat absorbed by the combined solution? What is the heat of the reaction? What is the conversion factor for expressing the heat of reaction on a molar basis?

Solution Assuming no heat is lost to the surroundings, $q_{\text{sys}} = q_{\text{soln}} + q_{\text{rxn}} = 0$, so $q_{\text{rxn}} = -q_{\text{soln}}$, where q_{soln} is the heat absorbed by the combined solution. Because the density of the solution is 1.00 g/mL, the mass of a 100-mL solution is 100 g. Thus,

$$\begin{aligned} q_{\text{soln}} &= ms\Delta t \\ &= (1.00 \times 10^2 \text{ g} + 1.00 \times 10^2 \text{ g})(4.184 \text{ J/g} \cdot ^\circ\text{C})(25.86^\circ\text{C} - 22.50^\circ\text{C}) \\ &= 2.81 \times 10^3 \text{ J} \\ &= 2.81 \text{ kJ} \end{aligned}$$

Because $q_{\text{rxn}} = -q_{\text{soln}}$, $q_{\text{rxn}} = -2.81 \text{ kJ}$.

From the molarities given, the number of moles of both HCl and NaOH in $1.00 \times 10^2 \text{ mL}$ solution is

$$\frac{0.500 \text{ mol}}{1 \text{ L}} \times 0.100 \text{ L} = 0.0500 \text{ mol}$$

Therefore, the heat of neutralization when 1.00 mole of HCl reacts with 1.00 mole of NaOH is

$$\text{heat of neutralization} = \frac{-2.81 \text{ kJ}}{0.0500 \text{ mol}} = -56.2 \text{ kJ/mol}$$

Check Is the sign consistent with the nature of the reaction? Under the reaction condition, can the heat change be equated to the enthalpy change?

Practice Exercise A quantity of $4.00 \times 10^2 \text{ mL}$ of 0.600 M HNO_3 is mixed with $4.00 \times 10^2 \text{ mL}$ of 0.300 M Ba(OH)_2 in a constant-pressure calorimeter of negligible heat capacity. The initial temperature of both solutions is the same at 18.46°C . What is the final temperature of the solution? (Use the result in Example 6.8 for your calculation.)

Similar problem: 6.38.

Review of Concepts & Facts

- 6.5.1 A 1-g sample of Al and a 1-g sample of Fe are heated from 40°C to 100°C . Which metal has absorbed a greater amount of heat?
- 6.5.2 A 1.252 g-sample of cyclohexanol ($\text{C}_6\text{H}_{12}\text{O}$) was burned in a constant-volume bomb calorimeter where the temperature of the water increased from 27.00°C to 31.11°C . If the heat capacity of the bomb plus water is $11.3 \text{ kJ}/^\circ\text{C}$, what is the molar heat of combustion of cyclohexanol?
- 6.5.3 A 100.0-g sample of an unknown metal at 125°C is added to 500.0 g of water at 27.5°C . The final temperature of the mixture is 30.0°C . What is the specific heat capacity of the metal?

6.6 Standard Enthalpy of Formation and Reaction

So far we have learned that we can determine the enthalpy change that accompanies a reaction by measuring the heat absorbed or released (at constant pressure). From Equation (6.9) we see that ΔH can also be calculated if we know the actual enthalpies

of all reactants and products. However, as mentioned earlier, there is no way to measure the *absolute* value of the enthalpy of a substance. Only values *relative* to an arbitrary reference can be determined. This problem is similar to the one geographers face in expressing the elevations of specific mountains or valleys. Rather than trying to devise some type of “absolute” elevation scale (perhaps based on distance from the center of Earth?), by common agreement all geographic heights and depths are expressed relative to sea level, an arbitrary reference with a defined elevation of “zero” meters or feet. Similarly, chemists have agreed on an arbitrary reference point for enthalpy.

The “sea level” reference point for all enthalpy expressions is called the ***standard enthalpy of formation*** (ΔH_f°). Substances are said to be in the ***standard state*** at 1 atm,[†] hence the term “standard enthalpy.” The superscript “ $^\circ$ ” represents standard-state conditions (1 atm), and the subscript “f” stands for formation. By convention, *the standard enthalpy of formation of any element in its most stable form is zero*. Take the element oxygen as an example. Molecular oxygen (O_2) is more stable than the other allotropic form of oxygen, ozone (O_3), at 1 atm and 25°C. Thus, we can write $\Delta H_f^\circ(O_2) = 0$, but $\Delta H_f^\circ(O_3) = 142.2 \text{ kJ/mol}$. Similarly, graphite is a more stable allotropic form of carbon than diamond at 1 atm and 25°C, so we have $\Delta H_f^\circ(\text{C, graphite}) = 0$ and $\Delta H_f^\circ(\text{C, diamond}) = 1.90 \text{ kJ/mol}$. Based on this reference for elements, we can now define the standard enthalpy of formation of a compound as *the heat change that results when 1 mole of the compound is formed from its elements at a pressure of 1 atm*. Table 6.4 lists the standard enthalpies of formation for a number of elements and compounds. (For a more



Graphite (top) and diamond (bottom).

(top): ©McGraw-Hill Education/Ken Karp; (bottom): ©JewelryStock/Alamy Stock Photo

Table 6.4 Standard Enthalpies of Formation of Some Inorganic Substances at 25°C

Substance	$\Delta H_f^\circ(\text{kJ/mol})$	Substance	$\Delta H_f^\circ(\text{kJ/mol})$
$\text{Ag}(s)$	0	$\text{H}_2\text{O}_2(l)$	-187.6
$\text{AgCl}(s)$	-127.0	$\text{Hg}(l)$	0
$\text{Al}(s)$	0	$\text{I}_2(s)$	0
$\text{Al}_2\text{O}_3(s)$	-1669.8	$\text{HI}(g)$	25.9
$\text{Br}_2(l)$	0	$\text{Mg}(s)$	0
$\text{HBr}(g)$	-36.2	$\text{MgO}(s)$	-601.8
$\text{C}(\text{graphite})$	0	$\text{MgCO}_3(s)$	-1112.9
$\text{C}(\text{diamond})$	1.90	$\text{N}_2(g)$	0
$\text{CO}(g)$	-110.5	$\text{NH}_3(g)$	-46.3
$\text{CO}_2(g)$	-393.5	$\text{NO}(g)$	90.4
$\text{Ca}(s)$	0	$\text{NO}_2(g)$	33.85
$\text{CaO}(s)$	-635.6	$\text{N}_2\text{O}(g)$	81.56
$\text{CaCO}_3(s)$	-1206.9	$\text{N}_2\text{O}_4(g)$	9.66
$\text{Cl}_2(g)$	0	$\text{O}(g)$	249.4
$\text{HCl}(g)$	-92.3	$\text{O}_2(g)$	0
$\text{Cu}(s)$	0	$\text{O}_3(g)$	142.2
$\text{CuO}(s)$	-155.2	$\text{S}(\text{rhombic})$	0
$\text{F}_2(g)$	0	$\text{S}(\text{monoclinic})$	0.30
$\text{HF}(g)$	-271.6	$\text{SO}_2(g)$	-296.1
$\text{H}(g)$	218.2	$\text{SO}_3(g)$	-395.2
$\text{H}_2(g)$	0	$\text{H}_2\text{S}(g)$	-20.15
$\text{H}_2\text{O}(g)$	-241.8	$\text{Zn}(s)$	0
$\text{H}_2\text{O}(l)$	-285.8	$\text{ZnO}(s)$	-348.0

[†]In thermodynamics, the standard pressure is defined as 1 bar, where 1 bar = $10^5 \text{ Pa} = 0.987 \text{ atm}$. Because 1 bar differs from 1 atm by only 1.3 percent, we will continue to use 1 atm as the standard pressure. Note that the normal melting point and boiling point of a substance are defined in terms of 1 atm.

complete list of ΔH_f° values, see Appendix 2.) Note that although the standard state does not specify a temperature, we will always use ΔH_f° values measured at 25°C for our discussion because most of the thermodynamic data are collected at this temperature.

The importance of the standard enthalpies of formation is that once we know their values, we can readily calculate the **standard enthalpy of reaction**, ΔH_{rxn}° , defined as *the enthalpy of a reaction carried out at 1 atm*. For example, consider the hypothetical reaction



where a , b , c , and d are stoichiometric coefficients. For this reaction, ΔH_{rxn}° is given by

$$\Delta H_{rxn}^\circ = [c\Delta H_f^\circ(C) + d\Delta H_f^\circ(D)] - [a\Delta H_f^\circ(A) + b\Delta H_f^\circ(B)] \quad (6.17)$$

We can generalize Equation (6.17) as

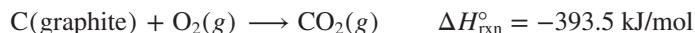
$$\Delta H_{rxn}^\circ = \Sigma n\Delta H_f^\circ(\text{products}) - \Sigma m\Delta H_f^\circ(\text{reactants}) \quad (6.18)$$

where m and n denote the stoichiometric coefficients for the reactants and products, and Σ (sigma) means “the sum of.” Note that in calculations, the stoichiometric coefficients are just numbers without units.

To use Equation (6.18) to calculate ΔH_{rxn}° , we must know the ΔH_f° values of the compounds that take part in the reaction. These values can be determined by applying the direct method or the indirect method.

The Direct Method

This method of measuring ΔH_f° works for compounds that can be readily synthesized from their elements. Suppose we want to know the enthalpy of formation of carbon dioxide. We must measure the enthalpy of the reaction when carbon (graphite) and molecular oxygen in their standard states are converted to carbon dioxide in its standard state:



We know from experience that this combustion easily goes to completion. Thus, from Equation (6.18) we can write

$$\begin{aligned} \Delta H_{rxn}^\circ &= \Delta H_f^\circ(\text{CO}_2, g) - [\Delta H_f^\circ(\text{C, graphite}) + \Delta H_f^\circ(\text{O}_2, g)] \\ &= -393.5 \text{ kJ/mol} \end{aligned}$$

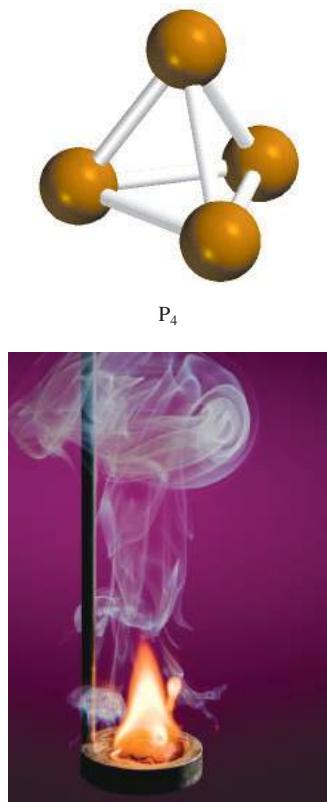
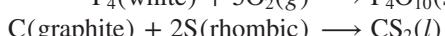
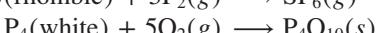
Because both graphite and O_2 are stable allotropic forms of the elements, it follows that $\Delta H_f^\circ(\text{C, graphite})$ and $\Delta H_f^\circ(\text{O}_2, g)$ are zero. Therefore,

$$\Delta H_{rxn}^\circ = \Delta H_f^\circ(\text{CO}_2, g) = -393.5 \text{ kJ/mol}$$

or $\Delta H_f^\circ(\text{CO}_2, g) = -393.5 \text{ kJ/mol}$

Note that arbitrarily assigning zero ΔH_f° for each element in its most stable form at the standard state does not affect our calculations in any way. Remember, in thermochemistry we are interested only in enthalpy *changes* because they can be determined experimentally, whereas the absolute enthalpy values cannot. The choice of a zero “reference level” for enthalpy makes calculations easier to handle. Again referring to the terrestrial altitude analogy, we find that Mt. Everest is 8708 ft higher than Mt. McKinley (now officially known as Denali). This difference in altitude is unaffected by the decision to set sea level at 0 ft or at 1000 ft.

Other compounds that can be studied by the direct method are SF_6 , P_4O_{10} , and CS_2 . The equations representing their syntheses are



White phosphorus burns in air to form P_4O_{10} .

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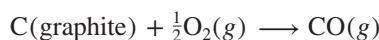
Note that S(rhombic) and P(white) are the most stable allotropes of sulfur and phosphorus, respectively, at 1 atm and 25°C, so their ΔH_f° values are zero.

The Indirect Method

Many compounds cannot be directly synthesized from their elements. In some cases, the reaction proceeds too slowly, or side reactions produce substances other than the desired compound. In these cases, ΔH_f° can be determined by an indirect approach, which is based on Hess's law of heat summation, or simply Hess's law, named after the Swiss-Russian chemist Germain Hess.[†] **Hess's law** can be stated as follows: *When reactants are converted to products, the change in enthalpy is the same whether the reaction takes place in one step or in a series of steps.* In other words, if we can break down the reaction of interest into a series of reactions for which ΔH_{rxn}° can be measured, we can calculate ΔH_{rxn}° for the overall reaction. Hess's law is based on the fact that because H is a state function, ΔH depends only on the initial and final state (that is, only on the nature of reactants and products). The enthalpy change would be the same whether the overall reaction takes place in one step or many steps.

An analogy for Hess's law is as follows. Suppose you go from the first floor to the sixth floor of a building by elevator. The gain in your gravitational potential energy (which corresponds to the enthalpy change for the overall process) is the same whether you go directly there or stop at each floor on your way up (breaking the trip into a series of steps).

Let's say we are interested in the standard enthalpy of formation of carbon monoxide (CO). We might represent the reaction as



However, burning graphite also produces some carbon dioxide (CO₂), so we cannot measure the enthalpy change for CO directly as shown. Instead, we must employ an indirect route, based on Hess's law. It is possible to carry out the following two separate reactions, which do go to completion:

- (a) $\text{C(graphite)} + \text{O}_2(g) \longrightarrow \text{CO}_2(g) \quad \Delta H_{rxn}^\circ = -393.5 \text{ kJ/mol}$
 (b) $\text{CO}(g) + \frac{1}{2}\text{O}_2(g) \longrightarrow \text{CO}_2(g) \quad \Delta H_{rxn}^\circ = -283.0 \text{ kJ/mol}$

First, we reverse Equation (b) to get



Remember to reverse the sign of ΔH when you reverse a chemical equation.

Because chemical equations can be added and subtracted just like algebraic equations, we carry out the operation (a) + (c) and obtain

- | | | |
|-----|---|--|
| (a) | $\text{C(graphite)} + \text{O}_2(g) \longrightarrow \text{CO}_2(g) \quad \Delta H_{rxn}^\circ = -393.5 \text{ kJ/mol}$ | |
| (c) | $\text{CO}_2(g) \longrightarrow \text{CO}(g) + \frac{1}{2}\text{O}_2(g) \quad \Delta H_{rxn}^\circ = +283.0 \text{ kJ/mol}$ | |
| (d) | <hr/> | |
| (d) | $\text{C(graphite)} + \frac{1}{2}\text{O}_2(g) \longrightarrow \text{CO}(g) \quad \Delta H_{rxn}^\circ = -110.5 \text{ kJ/mol}$ | |

Thus, $\Delta H_f^\circ(\text{CO}) = -110.5 \text{ kJ/mol}$. Looking back, we see that the overall reaction is the formation of CO₂ [Equation (a)], which can be broken down into two parts [Equations (d) and (b)]. Figure 6.10 shows the overall scheme of our procedure.

The general rule in applying Hess's law is to arrange a series of chemical equations (corresponding to a series of steps) in such a way that, when added together, all species will cancel except for the reactants and products that appear in the overall reaction. This means that we want the elements on the left and the compound of interest on the right

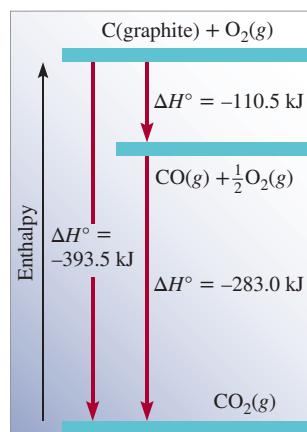
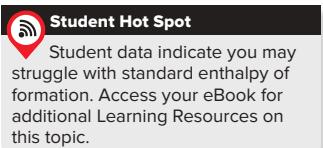


Figure 6.10 The enthalpy change for the formation of 1 mole of CO₂ from graphite and O₂ can be broken down into two steps according to Hess's law.

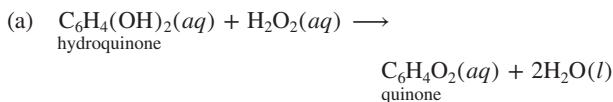
[†]Germain Henri Hess (1802–1850). Swiss-Russian chemist. Hess was born in Switzerland but spent most of his life in Russia. For formulating Hess's law, he is called the father of thermochemistry.

CHEMISTRY *in Action*

How a Bombardier Beetle Defends Itself

Survival techniques of insects and small animals in a fiercely competitive environment take many forms. For example, chameleons have developed the ability to change color to match their surroundings, and the butterfly *Limenitis* has evolved into a form that mimics the poisonous and unpleasant-tasting monarch butterfly (*Danaus*). A less passive defense mechanism is employed by bombardier beetles (*Brachinus*), which repel predators with a “chemical spray.”

The bombardier beetle has a pair of glands at the tip of its abdomen. Each gland consists of two compartments. The inner compartment contains an aqueous solution of hydroquinone and hydrogen peroxide, and the outer compartment holds a mixture of enzymes. (Enzymes are biological molecules that can speed up a reaction.) When threatened, the beetle squeezes some fluid from the inner compartment into the outer compartment, where, in the presence of the enzymes, an exothermic reaction takes place:



To estimate the heat of reaction, let us consider the following steps:

- (b) $\text{C}_6\text{H}_4(\text{OH})_2(aq) \longrightarrow \text{C}_6\text{H}_4\text{O}_2(aq) + \text{H}_2(g)$ $\Delta H^\circ = 177 \text{ kJ/mol}$
(c) $\text{H}_2\text{O}_2(aq) \longrightarrow \text{H}_2\text{O}(l) + \frac{1}{2}\text{O}_2(g)$ $\Delta H^\circ = -94.6 \text{ kJ/mol}$
(d) $\text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \longrightarrow \text{H}_2\text{O}(l)$ $\Delta H^\circ = -286 \text{ kJ/mol}$

Recalling Hess’s law, we find that the heat of reaction for (a) is simply the *sum* of those for (b), (c), and (d).



A bombardier beetle discharging a chemical spray.
©Thomas Eisner and Daniel Aneshansley/Cornell University

Therefore, we write

$$\begin{aligned}\Delta H_a^\circ &= \Delta H_b^\circ + \Delta H_c^\circ + \Delta H_d^\circ \\ &= (177 - 94.6 - 286) \text{ kJ/mol} \\ &= -204 \text{ kJ/mol}\end{aligned}$$

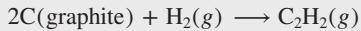
The large amount of heat generated is sufficient to bring the mixture to its boiling point. By rotating the tip of its abdomen, the beetle can quickly discharge the vapor in the form of a fine mist toward an unsuspecting predator. In addition to the thermal effect, the quinones also act as a repellent to other insects and animals. One bombardier beetle carries enough reagents to produce 20 to 30 discharges in quick succession, each with an audible detonation.

Student Hot Spot
Student data indicate you may struggle with Hess's law. Access your eBook for additional Learning Resources on this topic.

of the arrow. Further, we often need to multiply some or all of the equations representing the individual steps by the appropriate coefficients.

Example 6.9

Calculate the standard enthalpy of formation of acetylene (C_2H_2) from its elements:



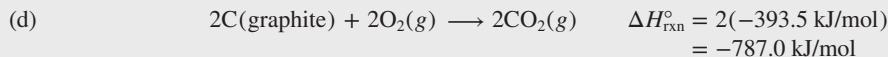
The equations for each step and the corresponding enthalpy changes are

- (a) $\text{C(graphite)} + \text{O}_2(g) \longrightarrow \text{CO}_2(g)$ $\Delta H_{rxn}^\circ = -393.5 \text{ kJ/mol}$
(b) $\text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \longrightarrow \text{H}_2\text{O}(l)$ $\Delta H_{rxn}^\circ = -285.8 \text{ kJ/mol}$
(c) $2\text{C}_2\text{H}_2(g) + 5\text{O}_2(g) \longrightarrow 4\text{CO}_2(g) + 2\text{H}_2\text{O}(l)$ $\Delta H_{rxn}^\circ = -2598.8 \text{ kJ/mol}$

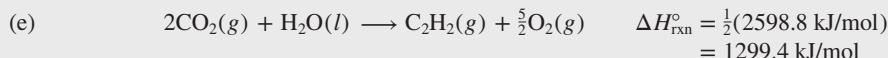
(Continued)

Strategy Our goal here is to calculate the enthalpy change for the formation of C₂H₂ from its elements C and H₂. The reaction does not occur directly, however, so we must use an indirect route using the information given by Equations (a), (b), and (c).

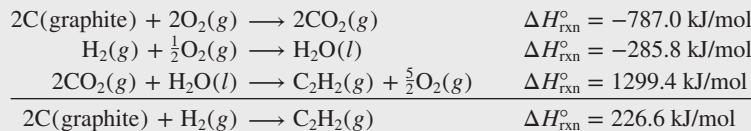
Solution Looking at the synthesis of C₂H₂, we need 2 moles of graphite as reactant. So we multiply Equation (a) by 2 to get



Next, we need 1 mole of H₂ as a reactant and this is provided by Equation (b). Last, we need 1 mole of C₂H₂ as a product. Equation (c) has 2 moles of C₂H₂ as a reactant so we need to reverse the equation and divide it by 2:

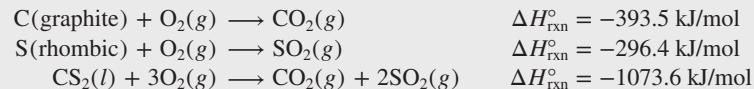


Adding Equations (d), (b), and (e) together, we get



Therefore, $\Delta H_f^{\circ} = \Delta H_{\text{rxn}}^{\circ} = 226.6 \text{ kJ/mol}$. The ΔH_f° value means that when 1 mole of C₂H₂ is synthesized from 2 moles of C(graphite) and 1 mole of H₂, 226.6 kJ of heat are absorbed by the reacting system from the surroundings. Thus, this is an endothermic process.

Practice Exercise Calculate the standard enthalpy of formation of carbon disulfide (CS₂) from its elements, given that



Similar problems: 6.62, 6.63.

We can calculate the enthalpy of reactions from the values of ΔH_f° , as shown in Example 6.10.

Example 6.10

The thermite reaction involves aluminum and iron(III) oxide



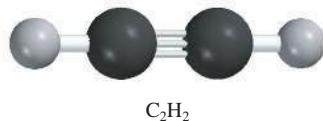
This reaction is highly exothermic and the liquid iron formed is used to weld metals. Calculate the heat released in kilojoules per gram of Al reacted with Fe₂O₃. The ΔH_f° for Fe(l) is 12.40 kJ/mol.

Strategy The enthalpy of a reaction is the difference between the sum of the enthalpies of the products and the sum of the enthalpies of the reactants. The enthalpy of each species (reactant or product) is given by its stoichiometric coefficient times the standard enthalpy of formation of the species.

Solution Using the given ΔH_f° value for Fe(l) and other ΔH_f° values in Appendix 2 and Equation (6.18), we write

$$\begin{aligned} \Delta H_{\text{rxn}}^{\circ} &= [\Delta H_f^{\circ}(\text{Al}_2\text{O}_3) + 2\Delta H_f^{\circ}(\text{Fe})] - [2\Delta H_f^{\circ}(\text{Al}) + \Delta H_f^{\circ}(\text{Fe}_2\text{O}_3)] \\ &= [(-1669.8 \text{ kJ/mol}) + 2(12.40 \text{ kJ/mol})] - [2(0) + (-822.2 \text{ kJ/mol})] \\ &= -822.8 \text{ kJ/mol} \end{aligned}$$

(Continued)



An oxyacetylene torch has a high flame temperature (3000°C) and is used to weld metals.

©Charles D. Winters/Science Source



The molten iron formed in a thermite reaction is run down into a mold between the ends of two railroad rails. On cooling, the rails are welded together.

©Orgo-Thermite

This is the amount of heat released for 2 moles of Al reacted. We use the following ratio

$$\frac{-822.8 \text{ kJ}}{2 \text{ mol Al}}$$

to convert to kJ/g Al. The molar mass of Al is 26.98 g, so

$$\begin{aligned} \text{heat released per gram of Al} &= \frac{-822.8 \text{ kJ}}{2 \text{ mol Al}} \times \frac{1 \text{ mol Al}}{26.98 \text{ g Al}} \\ &= -15.25 \text{ kJ/g} \end{aligned}$$

Check Is the negative sign consistent with the exothermic nature of the reaction? As a quick check, we see that 2 moles of Al weigh about 54 g and give off about 823 kJ of heat when reacted with Fe_2O_3 . Therefore, the heat given off per gram of Al reacted is approximately $-830 \text{ kJ}/54 \text{ g}$ or -15.4 kJ/g .

Practice Exercise Benzene (C_6H_6) burns in air to produce carbon dioxide and liquid water. Calculate the heat released (in kilojoules) per gram of the compound reacted with oxygen. The standard enthalpy of formation of benzene is 49.04 kJ/mol.

Similar problems: 6.54, 6.57.

Review of Concepts & Facts

6.6.1 Which of the following does not have $\Delta H_f^\circ = 0$ at 25°C?

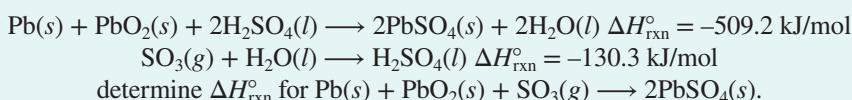


6.6.2 Explain why reactions involving reactant compounds with positive ΔH_f° values are generally more exothermic than those with negative ΔH_f° values.

6.6.3 Using data from Appendix 2, calculate $\Delta H_{\text{rxn}}^\circ$ for



6.6.4 Given the following information



6.7 Heat of Solution and Dilution

Although we have focused so far on the thermal energy effects resulting from chemical reactions, many physical processes, such as the melting of ice or the condensation of a vapor, also involve the absorption or release of heat. Enthalpy changes occur as well when a solute dissolves in a solvent or when a solution is diluted. Let us look at these two related physical processes, involving heat of solution and heat of dilution.

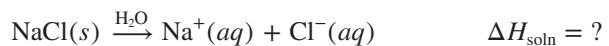
Heat of Solution

In the vast majority of cases, dissolving a solute in a solvent produces measurable heat change. At constant pressure, the heat change is equal to the enthalpy change. The **heat of solution**, or **enthalpy of solution**, ΔH_{soln} , is the heat generated or absorbed when a certain amount of solute dissolves in a certain amount of solvent. The quantity ΔH_{soln} represents the difference between the enthalpy of the final solution and the enthalpies of its original components (that is, solute and solvent) before they are mixed. Thus,

$$\Delta H_{\text{soln}} = H_{\text{soln}} - H_{\text{components}} \tag{6.19}$$

Neither H_{soln} nor $H_{\text{components}}$ can be measured, but their difference, ΔH_{soln} , can be readily determined in a constant-pressure calorimeter. Like other enthalpy changes, ΔH_{soln} is positive for endothermic (heat-absorbing) processes and negative for exothermic (heat-generating) processes.

Consider the heat of solution of a process in which an ionic compound is the solute and water is the solvent. For example, what happens when solid NaCl dissolves in water? In solid NaCl, the Na^+ and Cl^- ions are held together by strong positive-negative (electrostatic) forces, but when a small crystal of NaCl dissolves in water, the three-dimensional network of ions breaks into its individual units. (The structure of solid NaCl is shown in Figure 2.13.) The separated Na^+ and Cl^- ions are stabilized in solution by their interaction with water molecules (see Figure 4.2). These ions are said to be *hydrated*. In this case water plays a role similar to that of a good electrical insulator. Water molecules shield the ions (Na^+ and Cl^-) from each other and effectively reduce the electrostatic attraction that held them together in the solid state. The heat of solution is defined by the following process:



Dissolving an ionic compound such as NaCl in water involves complex interactions among the solute and solvent species. However, for the sake of analysis we can imagine that the solution process takes place in two separate steps, illustrated in Figure 6.11. First, the Na^+ and Cl^- ions in the solid crystal are separated from each other and converted to the gaseous state:

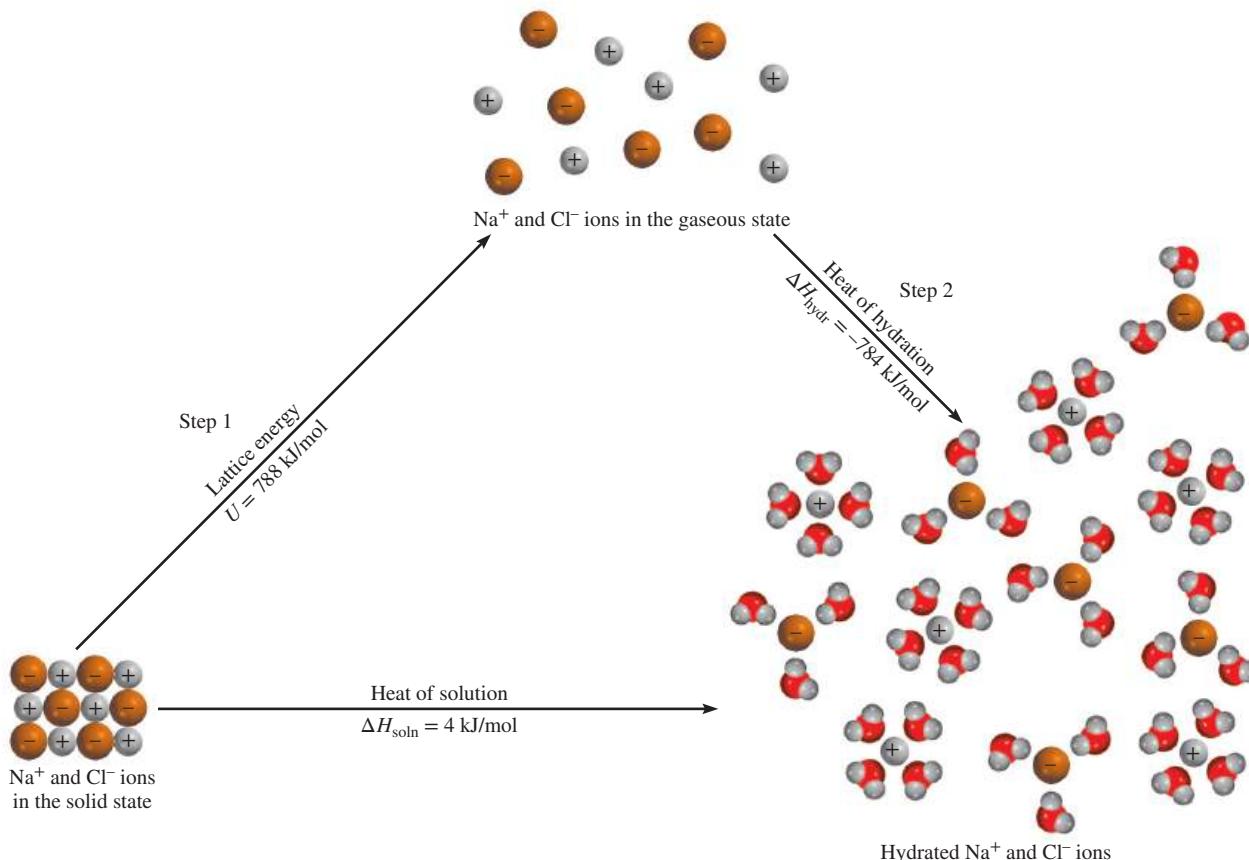
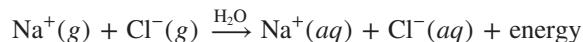


Figure 6.11 The solution process for NaCl. The process can be considered to occur in two separate steps: (1) separation of ions from the crystal state to the gaseous state and (2) hydration of the gaseous ions. The heat of solution is equal to the energy changes for these two steps, $\Delta H_{\text{soln}} = U + \Delta H_{\text{hydr}}$.

The word “lattice” describes arrangement in space of isolated points (occupied by ions) in a regular pattern. Lattice energy is a positive quantity. Beware that lattice energy and internal energy share the same symbol.

The energy required to completely separate one mole of a solid ionic compound into gaseous ions is called **lattice energy (U)**. The lattice energy of NaCl is 788 kJ/mol. In other words, we would need to supply 788 kJ of energy to break 1 mole of solid NaCl into 1 mole of Na^+ ions and 1 mole of Cl^- ions.

Next, the “gaseous” Na^+ and Cl^- ions enter the water and become hydrated:



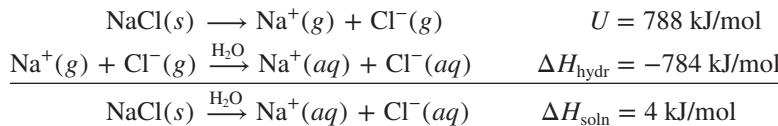
The enthalpy change associated with the hydration process is called the **heat of hydration, ΔH_{hydr}** (heat of hydration is a negative quantity for cations and anions). Applying Hess’s law, it is possible to consider ΔH_{soln} as the sum of two related quantities, lattice energy (U) and heat of hydration (ΔH_{hydr}), as shown in Figure 6.11:

Table 6.5

Heats of Solution of Some Ionic Compounds	
Compound	ΔH_{soln} (kJ/mol)
LiCl	-37.1
CaCl ₂	-82.8
NaCl	4.0
KCl	17.2
NH ₄ Cl	15.2
NH ₄ NO ₃	26.6

$$\Delta H_{\text{soln}} = U + \Delta H_{\text{hydr}} \quad (6.20)$$

Therefore,



Thus, when 1 mole of NaCl dissolves in water, 4 kJ of heat will be absorbed from the surroundings. We would observe this effect by noting that the beaker containing the solution becomes slightly colder. Table 6.5 lists the ΔH_{soln} of several ionic compounds. Depending on the nature of the cation and anion involved, ΔH_{soln} for an ionic compound may be either negative (exothermic) or positive (endothermic).

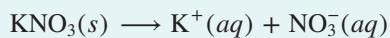
Heat of Dilution

Generations of chemistry students have been reminded of the safe procedure for diluting acids by the venerable saying, “Do as you oughter, add acid to water.”

When a previously prepared solution is *diluted*, that is, when more solvent is added to lower the overall concentration of the solute, additional heat is usually given off or absorbed. The **heat of dilution** is the heat change associated with the dilution process. If a certain solution process is endothermic and the solution is subsequently diluted, *more* heat will be absorbed by the same solution from the surroundings. The converse holds true for an exothermic solution process—more heat will be liberated if additional solvent is added to dilute the solution. Therefore, always be cautious when working on a dilution procedure in the laboratory. Because of its highly exothermic heat of dilution, concentrated sulfuric acid (H_2SO_4) poses a particularly hazardous problem if its concentration must be reduced by mixing it with additional water. Concentrated H_2SO_4 is composed of 98 percent acid and 2 percent water by mass. Diluting it with water releases considerable amount of heat to the surroundings. This process is so exothermic that you must *never* attempt to dilute the concentrated acid by adding water to it. The heat generated could cause the acid solution to boil and splatter. The recommended procedure is to add the concentrated acid slowly to the water (while constantly stirring).

Review of Concepts & Facts

- 6.7.1** Use the data in Appendix 2 to calculate the heat of solution for the following process:



Learning Objectives

- Distinguish between kinetic energy and potential, and identify specific examples of each. (Section 6.1)
- Discriminate between the system and surroundings for a given experiment. (Section 6.2)
- Classify a system as being open, closed, or isolated. (Section 6.2)
- Categorize a process as endothermic or exothermic. (Section 6.2)
- Explain what a state function is and be able to identify state functions and nonstate functions. (Section 6.3)
- Summarize the first law of thermodynamics. (Section 6.3)
- Define work and heat, and predict the sign conventions associated with each term. (Section 6.3)
- Discuss enthalpy and enthalpy changes. (Section 6.4)
- Calculate the enthalpy change of a reaction and illustrate how it depends on the stoichiometry of the reactants and products. (Section 6.4)
- Perform calorimetric calculations involving specific heat or heat capacity. (Section 6.5)
- Describe constant-pressure calorimetry. (Section 6.5)
- Employ standard heats of formation of substances to determine the enthalpy change of a reaction. (Section 6.6)
- Apply Hess's law to determine the enthalpy change of a reaction. (Section 6.6)
- Appraise the physical processes of heat of solution and heat of hydration. (Section 6.7)

Key Equations

$$\Delta U = q + w \quad (6.1)$$

$$w = -P\Delta V \quad (6.3)$$

$$H = U + PV \quad (6.6)$$

$$\Delta H = \Delta U + P\Delta V \quad (6.8)$$

$$C = ms \quad (6.11)$$

$$q = ms\Delta t \quad (6.12)$$

$$q = C\Delta t \quad (6.13)$$

$$\Delta H_{rxn}^{\circ} = \sum n\Delta H_f^{\circ} (\text{products}) - \sum m\Delta H_f^{\circ} (\text{reactants}) \quad (6.18)$$

$$\Delta H_{soln} = U + \Delta H_{hydr} \quad (6.20)$$

Mathematical statement of the first law of thermodynamics.

Calculating work done in gas expansion or gas compression.

Definition of enthalpy.

Calculating enthalpy (or energy) change for a constant-pressure process.

Definition of heat capacity.

Calculating heat change in terms of specific heat.

Calculating heat change in terms of heat capacity.

Calculating standard enthalpy of reaction.

Lattice energy and hydration contributions to heat of solution.

Summary of Concepts & Facts

1. Energy is the capacity to do work. There are many forms of energy, and they are interconvertible. The law of conservation of energy states that the total amount of energy in the universe is constant.
2. A process that gives off heat to the surroundings is exothermic; a process that absorbs heat from the surroundings is endothermic.
3. The state of a system is defined by properties such as composition, volume, temperature, and pressure. These properties are called state functions.
4. The change in a state function for a system depends only on the initial and final states of the system, and not

on the path by which the change is accomplished. Energy is a state function; work and heat are not.

5. Energy can be converted from one form to another, but it cannot be created or destroyed (first law of thermodynamics). In chemistry we are concerned mainly with thermal energy, electrical energy, and mechanical energy, which is usually associated with pressure-volume work.
6. Enthalpy is a state function. A change in enthalpy ΔH is equal to $\Delta U + P\Delta V$ for a constant-pressure process.
7. The change in enthalpy (ΔH , usually given in kilojoules) is a measure of the heat of reaction (or any other process) at constant pressure.

8. Constant-volume and constant-pressure calorimeters are used to measure heat changes that occur in physical and chemical processes.
9. Hess's law states that the overall enthalpy change in a reaction is equal to the sum of enthalpy changes for individual steps in the overall reaction.
10. The standard enthalpy of a reaction can be calculated from the standard enthalpies of formation of reactants and products.
11. The heat of solution of an ionic compound in water is the sum of the lattice energy of the compound and the heat of hydration. The relative magnitudes of these two quantities determine whether the solution process is endothermic or exothermic. The heat of dilution is the heat absorbed or evolved when a solution is diluted.

Key Words

Calorimetry, p. 246	First law of thermodynamics, p. 235	Lattice energy (U), p. 260	Standard state, p. 253
Chemical energy, p. 232	Law of conservation of energy, p. 232	State function, p. 234	State of a system, p. 234
Closed system, p. 232	Heat, p. 232	Surroundings, p. 232	System, p. 232
Endothermic process, p. 234	Heat capacity (C), p. 246	Radiant energy, p. 231	Thermal energy, p. 231
Energy, p. 231	Heat of dilution, p. 260	Specific heat (s), p. 246	Thermochemical equation, p. 243
Enthalpy (H), p. 241	Heat of hydration (ΔH_{hydr}), p. 260	Standard enthalpy of formation (ΔH_f°), p. 253	Thermochemistry, p. 232
Enthalpy of reaction (ΔH_{rxn}), p. 242	Heat of solution (ΔH_{soln}), p. 258	Standard enthalpy of reaction ($\Delta H_{\text{rxn}}^\circ$), p. 254	Thermodynamics, p. 234
Enthalpy of solution (ΔH_{soln}), p. 255	Hess's law, p. 255		Work, p. 231
Exothermic process, p. 233	Isolated system, p. 232		

Questions & Problems

Red numbered problems solved in Student Solutions Manual

6.1 The Nature of Energy and Types of Energy

Review Questions

- 6.1 Define these terms: *system, surroundings, open system, closed system, isolated system, thermal energy, chemical energy, potential energy, kinetic energy, law of conservation of energy*.
- 6.2 What is heat? How does heat differ from thermal energy? Under what condition is heat transferred from one system to another?
- 6.3 What are the units for energy commonly employed in chemistry?
- 6.4 A truck initially traveling at 60 km per hour is brought to a complete stop at a traffic light. Does this change violate the law of conservation of energy? Explain.
- 6.5 These are various forms of energy: chemical, heat, light, mechanical, and electrical. Suggest ways of interconverting these forms of energy.
- 6.6 Describe the interconversions of forms of energy occurring in these processes: (a) You throw a softball up into the air and catch it. (b) You switch on a flashlight. (c) You ride the ski lift to the top of the hill and then ski down. (d) You strike a match and let it burn down.

6.2 Energy Changes in Chemical Reactions

Review Questions

- 6.7 Define these terms: *thermochemistry, exothermic process, endothermic process*.
- 6.8 Stoichiometry is based on the law of conservation of mass. On what law is thermochemistry based?
- 6.9 Describe two exothermic processes and two endothermic processes.
- 6.10 Decomposition reactions are usually endothermic, whereas combination reactions are usually exothermic. Give a qualitative explanation for these trends.

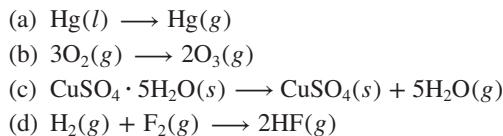
6.3 Introduction to Thermodynamics

Review Questions

- 6.11 On what law is the first law of thermodynamics based? Explain the sign conventions in the equation $\Delta U = q + w$.
- 6.12 Explain what is meant by a state function. Give two examples of quantities that are state functions and two that are not.
- 6.13 The internal energy of an ideal gas depends only on its temperature. Do a first-law analysis of this process. A sample of an ideal gas is allowed to expand at constant temperature against atmospheric

pressure. (a) Does the gas do work on its surroundings? (b) Is there heat exchange between the system and the surroundings? If so, in which direction? (c) What is ΔU for the gas for this process?

- 6.14 Consider these changes:



At constant pressure, in which of the reactions is work done by the system on the surroundings? By the surroundings on the system? In which of them is no work done?

Problems

- 6.15 A sample of nitrogen gas expands in volume from 1.6 L to 5.4 L at constant temperature. Calculate the work done in joules if the gas expands (a) against a vacuum, (b) against a constant pressure of 0.80 atm, and (c) against a constant pressure of 3.7 atm.

- 6.16 A gas expands in volume from 26.7 mL to 89.3 mL at constant temperature. Calculate the work done (in joules) if the gas expands (a) against a vacuum, (b) against a constant pressure of 1.5 atm, and (c) against a constant pressure of 2.8 atm.

- 6.17 A gas expands and does $P\text{-}V$ work on the surroundings equal to 325 J. At the same time, it absorbs 127 J of heat from the surroundings. Calculate the change in energy of the gas.

- 6.18 The work done to compress a gas is 74 J. As a result, 26 J of heat is given off to the surroundings. Calculate the change in energy of the gas.

- 6.19 Calculate the work done when 50.0 g of tin dissolves in excess acid at 1.00 atm and 25°C:



Assume ideal gas behavior.

- 6.20 Calculate the work done in joules when 1.0 mole of water vaporizes at 1.0 atm and 100°C. Assume that the volume of liquid water is negligible compared with that of steam at 100°C, and ideal gas behavior.

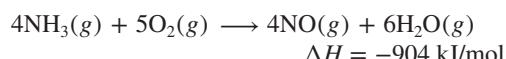
6.4 Enthalpy of Chemical Reactions

Review Questions

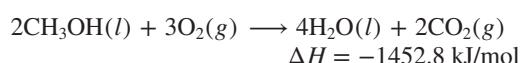
- 6.21 Define these terms: *enthalpy*, *enthalpy of reaction*. Under what condition is the heat of a reaction equal to the enthalpy change of the same reaction?

- 6.22 In writing thermochemical equations, why is it important to indicate the physical state (that is, gaseous, liquid, solid, or aqueous) of each substance?

- 6.23 Explain the meaning of this thermochemical equation:



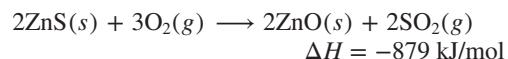
- 6.24 Consider this reaction:



What is the value of ΔH if (a) the equation is multiplied throughout by 2, (b) the direction of the reaction is reversed so that the products become the reactants and vice versa, (c) water vapor instead of liquid water is formed as the product?

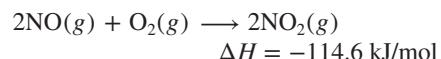
Problems

- 6.25 The first step in the industrial recovery of zinc from the zinc sulfide ore is roasting, that is, the conversion of ZnS to ZnO by heating:

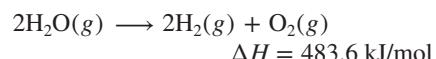


Calculate the heat evolved (in kJ) per gram of ZnS roasted.

- 6.26 Determine the amount of heat (in kJ) given off when 1.26×10^4 g of NO₂ are produced according to the equation

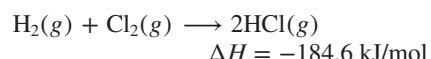


- 6.27 Consider the reaction



If 2.0 moles of H₂O(g) are converted to H₂(g) and O₂(g) against a pressure of 1.0 atm at 125°C, what is ΔU for this reaction?

- 6.28 Consider the reaction



If 3 moles of H₂ react with 3 moles of Cl₂ to form HCl, calculate the work done (in joules) against a pressure of 1.0 atm at 25°C. What is ΔU for this reaction? Assume the reaction goes to completion.

6.5 Calorimetry

Review Questions

- 6.29 What is the difference between specific heat and heat capacity? What are the units for these two quantities? Which is the intensive property and which is the extensive property?

- 6.30 Define calorimetry and describe two commonly used calorimeters. In a calorimetric measurement, why is it important that we know the heat capacity of the calorimeter? How is this value determined?

Problems

- 6.31 Consider the following data:

Metal	Al	Cu
Mass (g)	10	30
Specific heat (J/g • °C)	0.900	0.385
Temperature (°C)	40	60

When these two metals are placed in contact, which of the following will take place?

- (a) Heat will flow from Al to Cu because Al has a larger specific heat.
 (b) Heat will flow from Cu to Al because Cu has a larger mass.
 (c) Heat will flow from Cu to Al because Cu has a larger heat capacity.
 (d) Heat will flow from Cu to Al because Cu is at a higher temperature.
 (e) No heat will flow in either direction.
- 6.32** A piece of silver of mass 362 g has a heat capacity of 85.7 J°C. What is the specific heat of silver?
- 6.33** A 6.22-kg piece of copper metal is heated from 20.5°C to 324.3°C. Calculate the heat absorbed (in kJ) by the metal.
- 6.34** Calculate the amount of heat liberated (in kJ) from 366 g of mercury when it cools from 77.0°C to 12.0°C.
- 6.35** A sheet of gold weighing 10.0 g and at a temperature of 18.0°C is placed flat on a sheet of iron weighing 20.0 g and at a temperature of 55.6°C. What is the final temperature of the combined metals? Assume that no heat is lost to the surroundings. (*Hint:* The heat gained by the gold must be equal to the heat lost by the iron. The specific heats of the metals are given in Table 6.2.)
- 6.36** To a sample of water at 23.4°C in a constant-pressure calorimeter of negligible heat capacity is added a 12.1-g piece of aluminum whose temperature is 81.7°C. If the final temperature of water is 24.9°C, calculate the mass of the water in the calorimeter. (*Hint:* See Table 6.2.)
- 6.37** A 0.1375-g sample of solid magnesium is burned in a constant-volume bomb calorimeter that has a heat capacity of 3024 J°C. The temperature increases by 1.126°C. Calculate the heat given off by the burning Mg, in kJ/g and in kJ/mol.
- 6.38** A quantity of 85.0 mL of 0.900 M HCl is mixed with 85.0 mL of 0.900 M KOH in a constant-pressure calorimeter that has a heat capacity of 325 J°C. If the initial temperatures of both solutions are the same at 18.24°C, what is the final temperature of the mixed solution? The heat of neutralization is –56.2 kJ/mol. Assume the density and specific heat of the solutions are the same as those for water.
- 6.6 Standard Enthalpy of Formation and Reaction**
- Review Questions**
- 6.39** What is meant by the standard-state condition?
- 6.40** How are the standard enthalpies of an element and a compound determined?
- 6.41** What is meant by the standard enthalpy of a reaction?
- 6.42** Write the equation for calculating the enthalpy of a reaction. Define all the terms.
- 6.43** State Hess's law. Explain, with one example, the usefulness of this law in thermochemistry.
- 6.44** Describe how chemists use Hess's law to determine the ΔH_f° of a compound by measuring its heat (enthalpy) of combustion.
- Problems**
- 6.45** Which of the following standard enthalpy of formation values is not zero at 25°C? Na(s), Ne(g), CH₄(g), S₈(s), Hg(l), H(g).
- 6.46** The ΔH_f° values of the two allotropes of oxygen, O₂ and O₃, are 0 and 142.2 kJ/mol, respectively, at 25°C. Which is the more stable form at this temperature?
- 6.47** Which is the more negative quantity at 25°C: ΔH_f° for H₂O(l) or ΔH_f° for H₂O(g)?
- 6.48** Predict the value of ΔH_f° (greater than, less than, or equal to zero) for these elements at 25°C: (a) Br₂(g); Br₂(l). (b) I₂(g); I₂(s).
- 6.49** In general, compounds with negative ΔH_f° values are more stable than those with positive ΔH_f° values. H₂O₂(l) has a negative ΔH_f° (see Table 6.4). Why, then, does H₂O₂(l) have a tendency to decompose to H₂O(l) and O₂(g)?
- 6.50** Suggest ways (with appropriate equations) that would enable you to measure the ΔH_f° values of Ag₂O(s) and CaCl₂(s) from their elements. No calculations are necessary.
- 6.51** Calculate the heat of decomposition for this process at constant pressure and 25°C:
- $$\text{CaCO}_3(s) \longrightarrow \text{CaO}(s) + \text{CO}_2(g)$$
- (Look up the standard enthalpy of formation of the reactant and products in Table 6.4.)
- 6.52** The standard enthalpies of formation of ions in aqueous solutions are obtained by arbitrarily assigning a value of zero to H⁺ ions; that is, ΔH_f° [H⁺(aq)] = 0.
- (a) For the following reaction
- $$\text{HCl}(g) \xrightarrow{\text{H}_2\text{O}} \text{H}^+(aq) + \text{Cl}^-(aq)$$
- $$\Delta H^\circ = -74.9 \text{ kJ/mol}$$
- calculate ΔH_f° for the Cl[–] ions.
- (b) Given that ΔH_f° for OH[–] ions is –229.6 kJ/mol, calculate the enthalpy of neutralization when 1 mole of a strong monoprotic acid (such as HCl) is titrated by 1 mole of a strong base (such as KOH) at 25°C.
- 6.53** Calculate the heats of combustion for the following reactions from the standard enthalpies of formation listed in Appendix 2:
- (a) 2H₂(g) + O₂(g) → 2H₂O(l)
 (b) 2C₂H₂(g) + 5O₂(g) → 4CO₂(g) + 2H₂O(l)
- 6.54** Calculate the heats of combustion for the following reactions from the standard enthalpies of formation listed in Appendix 2:
- (a) C₂H₄(g) + 3O₂(g) → 2CO₂(g) + 2H₂O(l)
 (b) 2H₂S(g) + 3O₂(g) → 2H₂O(l) + 2SO₂(g)
- 6.55** Methanol, ethanol, and *n*-propanol are three common alcohols. When 1.00 g of each of these alcohols is burned in air, heat is liberated as shown by the following data: (a) methanol (CH₃OH),

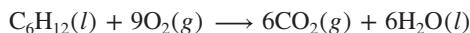
–22.6 kJ; (b) ethanol (C_2H_5OH), –29.7 kJ; (c) *n*-propanol (C_3H_7OH), –33.4 kJ. Calculate the heats of combustion of these alcohols in kJ/mol.

- 6.56** The standard enthalpy change for the following reaction is 436.4 kJ/mol:



Calculate the standard enthalpy of formation of atomic hydrogen (H).

- 6.57** From the standard enthalpies of formation, calculate ΔH_{rxn}° for the reaction



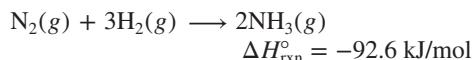
For $C_6H_{12}(l)$, $\Delta H_f^{\circ} = -151.9$ kJ/mol.

- 6.58** Pentaborane-9, B_5H_9 , is a colorless, highly reactive liquid that will burst into flame when exposed to oxygen. The reaction is



Calculate the kilojoules of heat released per gram of the compound reacted with oxygen. The standard enthalpy of formation of B_5H_9 is 73.2 kJ/mol.

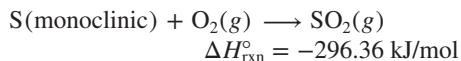
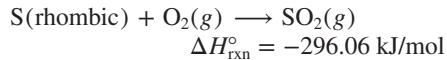
- 6.59** Determine the amount of heat (in kJ) given off when 1.26×10^4 g of ammonia are produced according to the equation



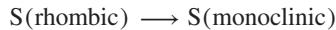
Assume that the reaction takes place under standard-state conditions at 25°C.

- 6.60** At 850°C, $CaCO_3$ undergoes substantial decomposition to yield CaO and CO_2 . Assuming that the ΔH_f° values of the reactant and products are the same at 850°C as they are at 25°C, calculate the enthalpy change (in kJ) if 66.8 g of CO_2 are produced in one reaction.

- 6.61** From these data,

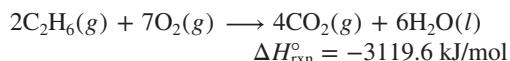
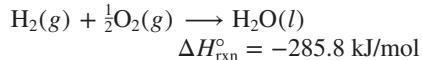
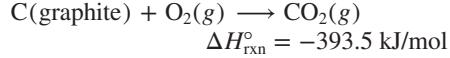


calculate the enthalpy change for the transformation



(Monoclinic and rhombic are different allotropic forms of elemental sulfur.)

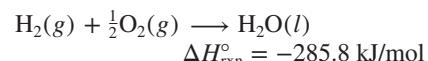
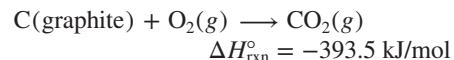
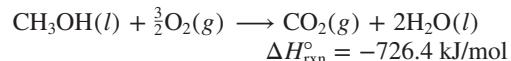
- 6.62** From the following data,



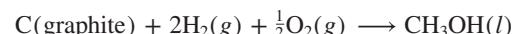
calculate the enthalpy change for the reaction



- 6.63** From the following heats of combustion,



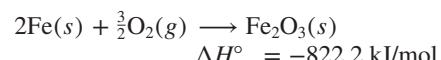
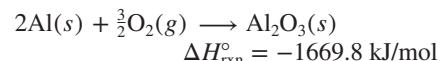
calculate the enthalpy of formation of methanol (CH_3OH) from its elements:



- 6.64** Calculate the standard enthalpy change for the reaction



given that



6.7 Heat of Solution and Dilution

Review Questions

- 6.65** Define the following terms: *enthalpy of solution*, *heat of hydration*, *lattice energy*, *heat of dilution*.

- 6.66** Why is the lattice energy of a solid always a positive quantity? Why is the hydration of ions always a negative quantity?

- 6.67** Consider two ionic compounds A and B. A has a larger lattice energy than B. Which of the two compounds is more stable?

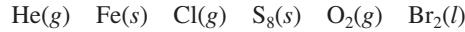
- 6.68** Mg^{2+} is a smaller cation than Na^+ and also carries more positive charge. Which of the two species has a larger hydration energy (in kJ/mol)? Explain.

- 6.69** Consider the dissolution of an ionic compound such as potassium fluoride in water. Break the process into the following steps: separation of the cations and anions in the vapor phase and the hydration of the ions in the aqueous medium. Discuss the energy changes associated with each step. How does the heat of solution of KF depend on the relative magnitudes of these two quantities? On what law is the relationship based?

- 6.70** Why is it dangerous to add water to a concentrated acid such as sulfuric acid in a dilution process?

Additional Problems

- 6.71** Which of the following does not have $\Delta H_f^{\circ} = 0$ at 25°C?

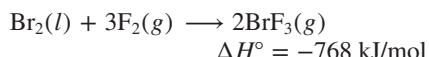
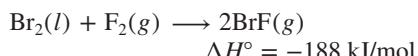


- 6.72** Calculate the expansion work done when 3.70 moles of ethanol are converted to vapor at its boiling point (78.3°C) and 1.0 atm.

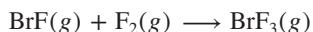
- 6.73** The convention of arbitrarily assigning a zero enthalpy value for the most stable form of each element in the standard state at 25°C is a convenient way of

dealing with enthalpies of reactions. Explain why this convention cannot be applied to nuclear reactions.

6.74 Given the thermochemical equations:



calculate the $\Delta H_{\text{rxn}}^\circ$ for the reaction



6.75 The standard enthalpy change ΔH° for the thermal decomposition of silver nitrate according to the following equation is +78.67 kJ:



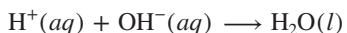
The standard enthalpy of formation of $\text{AgNO}_3(s)$ is -123.02 kJ/mol . Calculate the standard enthalpy of formation of $\text{AgNO}_2(s)$.

6.76 Hydrazine, N_2H_4 , decomposes according to the following reaction:



(a) Given that the standard enthalpy of formation of hydrazine is 50.42 kJ/mol , calculate ΔH° for its decomposition. (b) Both hydrazine and ammonia burn in oxygen to produce $\text{H}_2\text{O}(l)$ and $\text{N}_2(g)$. Write balanced equations for each of these processes and calculate ΔH° for each of them. On a mass basis (per kg), would hydrazine or ammonia be the better fuel?

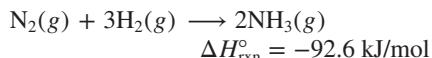
6.77 A quantity of $2.00 \times 10^2 \text{ mL}$ of 0.862 M HCl is mixed with an equal volume of 0.431 M Ba(OH)_2 in a constant-pressure calorimeter of negligible heat capacity. The initial temperature of the HCl and Ba(OH)_2 solutions is the same at 20.48°C . For the process



the heat of neutralization is -56.2 kJ/mol . What is the final temperature of the mixed solution?

6.78 A 3.53-g sample of ammonium nitrate (NH_4NO_3) was added to 80.0 mL of water in a constant-pressure calorimeter of negligible heat capacity. As a result, the temperature of the water decreased from 21.6°C to 18.1°C . Calculate the heat of solution (ΔH_{soln}) of ammonium nitrate.

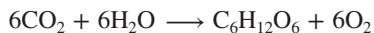
6.79 Consider the reaction



If 2.0 moles of N_2 react with 6.0 moles of H_2 to form NH_3 , calculate the work done (in joules) against a pressure of 1.0 atm at 25°C . What is ΔU for this reaction? Assume the reaction goes to completion.

6.80 Calculate the heat released when 2.00 L of $\text{Cl}_2(g)$ with a density of 1.88 g/L react with an excess of sodium metal at 25°C and 1 atm to form sodium chloride.

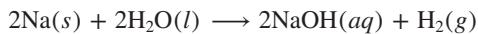
6.81 Photosynthesis produces glucose, $\text{C}_6\text{H}_{12}\text{O}_6$, and oxygen from carbon dioxide and water:



(a) How would you determine experimentally the $\Delta H_{\text{rxn}}^\circ$ value for this reaction? (b) Solar radiation produces about $7.0 \times 10^{14} \text{ kg}$ glucose a year on Earth. What is the corresponding ΔH° change?

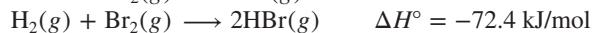
6.82 A 2.10-mole sample of crystalline acetic acid, initially at 17.0°C , is allowed to melt at 17.0°C and is then heated to 118.1°C (its normal boiling point) at 1.00 atm. The sample is allowed to vaporize at 118.1°C and is then rapidly quenched to 17.0°C , so that it recrystallizes. Calculate ΔH° for the total process as described.

6.83 Calculate the work done in joules by the reaction

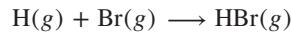


when 0.34 g of Na reacts with water to form hydrogen gas at 0°C and 1.0 atm.

6.84 You are given the following data:



Calculate ΔH° for the reaction



6.85 A gaseous mixture consists of 28.4 mole percent of hydrogen and 71.6 mole percent of methane. A 15.6-L gas sample, measured at 19.4°C and 2.23 atm, is burned in air. Calculate the heat released.

6.86 When 2.740 g of Ba reacts with O_2 at 298 K and 1 atm to form BaO , 11.14 kJ of heat are released. What is ΔH_f° for BaO ?

6.87 Methanol (CH_3OH) is an organic solvent and is also used as a fuel in some automobile engines. From the following data, calculate the standard enthalpy of formation of methanol:



$$\Delta H_{\text{rxn}}^\circ = -1452.8 \text{ kJ/mol}$$

6.88 A 44.0-g sample of an unknown metal at 99.0°C was placed in a constant-pressure calorimeter containing 80.0 g of water at 24.0°C . The final temperature of the system was found to be 28.4°C . Calculate the specific heat of the metal. (The heat capacity of the calorimeter is $12.4 \text{ J}/^\circ\text{C}$.)

6.89 Using the data in Appendix 2, calculate the enthalpy change for the gaseous reaction shown here. (Hint: First determine the limiting reagent.)

