

8th Edition

PRINCIPLES OF MODERN
CHEMISTRY

Oxtoby Gillis Butler

PERIODIC TABLE OF THE ELEMENTS

KEY

- Main group metals
- Transition metals
- Metalloids
- Nonmetals, noble gases

Atomic number
 Symbol
 Name
 Atomic mass
 An element

79
Au
 Gold
 196.9665

Period number
 Group number, U.S. system
 Group number, IUPAC system

1
H
 Hydrogen
 1.0079

Group number, U.S. system
 Group number, IUPAC system

1A
 (1)

2	3	4
Li Lithium 6.941	Be Beryllium 9.0122	
3	11	12
Na Sodium 22.9898	Mg Magnesium 24.3050	
4	19	20
K Potassium 39.0983	Ca Calcium 40.078	
5	37	38
Rb Rubidium 85.4678	Sr Strontium 87.62	
6	55	56
Cs Cesium 132.9055	Ba Barium 137.327	
7	87	88
Fr Francium (223)	Ra Radium (226)	

Numbers in parentheses are mass numbers of radioactive isotopes.

5	6	7	8	9	10	18
B Boron 10.811	C Carbon 12.0107	N Nitrogen 14.0067	O Oxygen 15.9994	F Fluorine 18.9984	Ne Neon 20.1797	
13	14	15	16	17	36	54
Al Aluminum 26.9815	Si Silicon 28.0855	P Phosphorus 30.9738	S Sulfur 32.065	Cl Chlorine 35.453	Kr Krypton 83.798	Xe Xenon 131.293
31	32	33	34	35	52	86
Ga Gallium 69.723	Ge Germanium 72.64	As Arsenic 74.9216	Se Selenium 78.96	Br Bromine 79.904	Tellurium 127.60	Rn Radon (222)
49	50	51	80	81	83	118
In Indium 114.818	Sn Tin 118.710	Sb Antimony 121.760	Cd Cadmium 112.411	Hg Mercury 200.59	Pb Lead 207.2	Lv Livermorium (293)
81	82	83	84	85	113	114
Tl Thallium 204.3833	Pb Lead 207.2	Bi Bismuth 208.9804	Po Polonium (209)	At Astatine (210)	Cn Copernicium (285)	Fl Flerovium (288)
113	114	115	116	117	118	119
Bi Bismuth (208)	Po Polonium (209)	At Astatine (210)	Rn Radon (222)	Lv Livermorium (293)	Uue Ununennium (294)	Uuo Ununoctium (294)

66	67	68	69	70	71
Dy Dysprosium 162.500	Ho Holmium 164.9303	Er Erbium 167.259	Tm Thulium 168.9342	Yb Ytterbium 173.054	Lu Lutetium 174.9668
88	89	90	91	92	93
Ra Radium (226)	Ac Actinium (227)	Th Thorium 232.0381	Pa Protactinium 231.0359	U Uranium 238.0289	Np Neptunium (237)
94	95	96	97	98	99
Pu Plutonium (244)	Am Americium (243)	Cm Curium (247)	Bk Berkelium (247)	Cf Californium (251)	Es Einsteinium (252)
100	101	102	103	104	105
Fm Fermium (257)	Md Mendelevium (258)	No Nobelium (259)	Lr Lawrencium (262)	Rf Rutherfordium (261)	Db Dubnium (268)

Atomic masses shown here are March 2013 IUPAC values. Elements for which the International Union of Pure and Applied Chemistry (IUPAC) has officially sanctioned the discovery and approved a name are indicated by their chemical symbols in this table. Elements that have been reported in the literature but not yet officially sanctioned and named are indicated by atomic number.

Standard Atomic Masses
of the Elements 2013, IUPAC

Based on Relative Atomic Mass of $^{12}\text{C} = 12$, where ^{12}C is a neutral atom
in its nuclear and electronic ground state.¹

Name	Symbol	Atomic Number	Atomic Weight	Name	Symbol	Atomic Number	Atomic Weight
Actinium ²	Ac	89	(227)	Neodymium	Nd	60	144.242(3)
Aluminum	Al	13	26.981 5386(8)	Neon	Ne	10	20.1797(6)
Americium ²	Am	95	(243)	Neptunium ²	Np	93	(237)
Antimony	Sb	51	121.760(1)	Nickel	Ni	28	58.6934(4)
Argon	Ar	18	39.948(1)	Niobium	Nb	41	92.906 38(2)
Arsenic	As	33	74.921 60(2)	Nitrogen	N	7	14.0067(2)
Astatine ²	At	85	(210)	Nobelium ²	No	102	(259)
Barium	Ba	56	137.327(7)	Osmium	Os	76	190.23(3)
Berkelium ²	Bk	97	(247)	Oxygen	O	8	15.9994(3)
Beryllium	Be	4	9.012 182(3)	Palladium	Pd	46	106.42(1)
Bismuth	Bi	83	208.980 40(1)	Phosphorus	P	15	30.973 762(2)
Bohrium ²	Bh	107	(270)	Platinum	Pt	78	195.084(9)
Boron	B	5	10.811(7)	Plutonium ²	Pu	94	(244)
Bromine	Br	35	79.904(1)	Polonium ²	Po	84	(209)
Cadmium	Cd	48	112.411(8)	Potassium	K	19	39.0983(1)
Calcium	Ca	20	40.078(4)	Praseodymium	Pr	59	140.907 65(2)
Californium ²	Cf	98	(251)	Promethium ²	Pm	61	(145)
Carbon	C	6	12.0107(8)	Protactinium ²	Pa	91	231.035 88(2)
Cerium	Ce	58	140.116(1)	Radium ²	Ra	88	(226)
Cesium	Cs	55	132.905 4519(2)	Radon ²	Rn	86	(222)
Chlorine	Cl	17	35.453(2)	Rhenium	Re	75	186.207(1)
Chromium	Cr	24	51.9961(6)	Rhodium	Rh	45	102.905 50(2)
Cobalt	Co	27	58.933 195(5)	Roentgenium ²	Rg	111	(280)
Copper	Cu	29	63.546(3)	Rubidium	Rb	37	85.4678(3)
Curium ²	Cm	96	(247)	Ruthenium	Ru	44	101.07(2)
Darmstadtium ²	Ds	110	(281)	Rutherfordium ²	Rf	104	(265)
Dubnium ²	Db	105	(268)	Samarium	Sm	62	150.36(2)
Dysprosium	Dy	66	162.500(1)	Scandium	Sc	21	44.955 912(6)
Einsteinium ²	Es	99	(252)	Seaborgium ²	Sg	106	(271)
Erbium	Er	68	167.259(3)	Selenium	Se	34	78.96(3)
Europium	Eu	63	151.964(1)	Silicon	Si	14	28.0855(3)
Fermium ²	Fm	100	(257)	Silver	Ag	47	107.8682(2)
Fluorine	F	9	18.998 4032(5)	Sodium	Na	11	22.989 769 28(2)
Francium ²	Fr	87	(223)	Strontium	Sr	38	87.62(1)
Gadolinium	Gd	64	157.25(3)	Sulfur	S	16	32.065(5)
Gallium	Ga	31	69.723(1)	Tantalum	Ta	73	180.947 88(2)
Germanium	Ge	32	72.64(1)	Technetium ²	Tc	43	(98)
Gold	Au	79	196.966 569(4)	Tellurium	Te	52	127.60(3)
Hafnium	Hf	72	178.49(2)	Terbium	Tb	65	158.925 35(2)
Hassium ²	Hs	108	(277)	Thallium	Tl	81	204.3833(2)
Helium	He	2	4.002 602(2)	Thorium ²	Th	90	232.038 06(2)
Holmium	Ho	67	164.930 32(2)	Thulium	Tm	69	168.934 21(2)
Hydrogen	H	1	1.00794(7)	Tin	Sn	50	118.710(7)
Indium	In	49	114.818(3)	Titanium	Ti	22	47.867(1)
Iodine	I	53	126.904 47(3)	Tungsten	W	74	183.84(1)
Iridium	Ir	77	192.217(3)	Uranium ²	U	92	238.028 91(3)
Iron	Fe	26	55.845(2)	Vanadium	V	23	50.9415(1)
Krypton	Kr	36	83.798(2)	Xenon	Xe	54	131.293(6)
Lanthanum	La	57	138.905 47(7)	Ytterbium	Yb	70	173.054(5)
Lawrencium ²	Lr	103	(262)	Yttrium	Y	39	88.905 85(2)
Lead	Pb	82	207.2(1)	Zinc	Zn	30	65.38(2)
Lithium	Li	3	6.941	Zirconium	Zr	40	91.224(2)
Lutetium	Lu	71	174.9668(1)	Copernicium ²	Cn	112	(285)
Magnesium	Mg	12	24.3050(6)	— ^{2,3}		113	(284)
Manganese	Mn	25	54.938 045(5)	Flerovium ²	Fl	114	(289)
Meitnerium ²	Mt	109	(276)	— ^{2,3}		115	(288)
Mendelevium ²	Md	101	(258)	Livermorium ²	Lv	116	(293)
Mercury	Hg	80	200.59(2)	— ^{2,3}		117	(294)
Molybdenum	Mo	42	95.96(2)	— ^{2,3}		118	(294)

1. The atomic masses of many elements vary depending on the origin and treatment of the sample. This is particularly true for Li; commercially available lithium-containing materials have Li atomic masses in the range of 6.939 and 6.996. Uncertainties are given in parentheses following the last significant figure to which they are attributed.

2. Elements with no stable nuclide; the value given in parentheses is the atomic mass number of the isotope of longest known half-life. However, three such elements (Th, Pa, and U) have a characteristic terrestrial isotopic composition, and the atomic weight is tabulated for these.

3. Not yet named.

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EIGHTH EDITION

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IN APPRECIATION OF

Karl F. Freed

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our Ph.D. advisers

for their distinguished careers in scientific research and education

The search for truth is in one way hard and in another easy, for it is evident that no one can master it fully or miss it completely.

But each adds a little to our knowledge of nature, and from all the facts assembled there arises a certain grandeur.

(Greek inscription, taken from Aristotle, on the facade of the National Academy of Sciences building in Washington, D.C.)

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The eighth edition of *Principles of Modern Chemistry* is written for students in honors and upper-mainstream general chemistry courses who seek to understand and interpret chemical events at the molecular level. The relation of molecular structure to function and properties requires the introduction of molecular structure early in the course and the use of structural arguments in presenting the remaining topics. Moreover, students will soon be introduced to the predictive power of chemical computations and simulations, for which a solid background in the description of molecular structure is essential.

The organization of the eighth edition is fundamentally the same as that of the seventh edition, and presents the material from a unified, molecular point of view that continues to emphasize the central role of structure, but with greater focus on the electronic structure of molecules as a unifying theme. This edition also deepens and broadens the introduction of chemical principles in several chapters. Recognizing that in the top colleges and universities that use this text, over 90% of students taking introductory chemistry have taken a single-variable calculus course in high school, or are taking calculus as a co-requisite for the course, we have improved several portions of the text. These revisions include a more quantitative treatment of the forces and potential energy in molecules (Chapter 3), dipole moments (Chapter 3), molecular collisions (Chapters 9 and 18), and the Maxwell-Boltzmann distribution of molecular speeds (Chapter 9). The eighth edition also includes major revisions in the chapters on quantum mechanics and molecular structure (Chapter 6), electrochemistry (Chapter 17), nuclear chemistry (Chapter 19), and molecular spectroscopy and photochemistry (Chapter 20).

Significant Changes in This Edition

- **OWLv2 for General Chemistry**—Our online learning solution OWLv2 has been revised to offer more flexible student and instructor functionality, new personalized study tools, enhanced integration with learning management systems, and improved analytics. OWLv2 includes Quick Prep, new iPad-compatible visualizations, tutorials, and simulations, and new Adaptive Study Plans. Tutors, Visualizations, and Simulations have been converted from Flash to HTML, allowing for easier navigation and streamlined grading.
- **Revised Writing Style without Loss of Rigor**—The language is more modern and less formal. We have introduced a more conversational writing style, designed to engage our students as active participants in developing the presentation. We have examined every sentence in the book to simplify and lighten the language without compromising intellectual integrity.

- **Greater Flexibility in Topic Coverage**—In response to comments by students, faculty, and reviewers, greater modularity and flexibility have been built into the text to make it compatible with alternative sequences of topics. While keeping the discussion of bonding and structure at the beginning of the book, we have been careful to maintain the option to follow the “macro-to-micro” approach used in previous editions. Selecting alternative approaches is facilitated by the unit structure of the book; we offer several suggestions in the **Teaching Options** section.
- **Streamlined Topic Coverage**—In response to suggestions by both users and reviewers of the text, we have taken care in this revision to retain only those topics that were felt to be critical for students. Chapters 19 and 20, especially, were shortened after extensive surveying of professors who teach the course; what remains (we think) are chapters that are more readily covered within the framework of a conventional two-semester course.
- **New Problems**—We’ve added approximately 30 new and revised problems throughout the book. These follow the unique tradition established in previous editions that all problems are based on actual experimental data measured on real chemical systems. We intend the problems to guide our students in developing intuition for chemical results and the magnitudes of chemical quantities, as well as facility in numerical calculations.

Organizational Approach for Selected Chapters and Major Changes to Content for Eighth Edition

Chapter 1: The Atom in Modern Chemistry

This chapter describes the physical structure of the atom, as determined from the classic experiments of Thomson, Millikan, and Rutherford. For this edition, we added an introduction of the electrostatic force on negatively and positively charged particles (see Section 1.4.3), improved the coverage of the J.J. Thompson experiment measuring the charge-to-mass ratio of the electron (see Section 1.4.3), and incorporated coverage of the mole, counting molecules by weighing (which was Section 2.1 in the seventh edition; it is Section 1.6 here in the eighth edition).

Chapter 3: Atomic Shells and Classical Models of Chemical Bonding

This chapter provides a substantial introduction to molecular structure by coupling experimental observation with interpretation through simple classical models. Today, the tools of classical bonding theory—covalent bonds, ionic bonds, polar covalent bonds, electronegativity, Lewis electron dot diagrams, and VSEPR theory—have all been explained by quantum mechanics. It is a matter of preference whether to present the classical theory first and then gain deeper insight from the quantum explanations, or to cover the quantum theory first and then see the classical theory as a limiting case. Our experience has been that presenting the classical description first enables our students to bring considerably greater sophistication to their first encounter with quantum mechanics and therefore to develop a deeper appreciation for that subject. We have seen that this approach offers definitive pedagogical advantages by enabling students to

- learn the language and vocabulary of the chemical bond starting from familiar physical concepts.

- become familiar with the properties of a broad array of real molecules *before* attempting to explain these results using quantum mechanics.
- develop experience in using physical concepts and equations to describe the behavior of atoms and molecules.

We have organized this chapter to meet these goals. Changes for the eighth edition include the following:

- The chapter now presents attractive and repulsive forces between nuclei and electrons, and between atoms in a diatomic molecule, using simple vectors in two dimensions, so that students may correctly calculate the direction of attractive and repulsive forces between particles (see Section 3.3). We emphasize the physical insight gained from the new quantitative treatment.
- We have streamlined and improved the discussion of polar covalent bonding, removing the application of the virial theorem but retaining the basic description of Coulomb forces between electrons and nuclei (see Sections 3.7 and 3.9).
- We introduce the direction of a molecular dipole moment, in addition to its magnitude (see Section 3.9.4).

Chapter 4: Introduction to Quantum Mechanics

This chapter presents a significant introduction to the concepts and vocabulary of quantum mechanics through very careful choice of language, illustrations with experimental data, interpretation with aid of simple models, and extensive use of graphical presentations.

For the eighth edition we improved the treatment of the particle-in-a-box with examples (Example 4.7 and the solution to Problem 37) that show students how to use the mathematical solutions to answer questions about the probability of the electron being found in different regions of space. We chose the chemical system of 1,3-butadiene for the example. The added material (mainly in Section 4.6) is appropriate both for students who have had integration in their single-variable calculus course and for students who would simply estimate the area under a curve graphically.

Chapter 5: Quantum Mechanics and Atomic Structure

This chapter provides a comprehensive introduction to the hydrogen atomic orbitals, the Hartree orbitals, the shell model of the atom as explained by the Hartree orbitals, and the relation of the shell model to experimental measurements such as photoelectron spectroscopy and the periodic properties of atoms. In this edition, recognizing that students' quantitative understanding of electron density in molecular systems begins with their introduction to atomic wave functions, we added graphical and analytical examples (Examples 5.2 and 5.3) to help students navigate the three-dimensional coordinate system in atoms (see Sections 5.1.2 and 5.1.3). Equation 5.7 reduces the integration over three dimensions to an integral that students may solve using single-variable calculus (or estimate graphically) to aid their understanding of the graphs of $r^2\psi^2$ and r^2R^2 presented in the chapter.

Chapter 6: Quantum Mechanics and Molecular Structure

This chapter provides a gentle ramp-up, starting from a qualitative overview of the quantum picture of the chemical bond and its relation to the potential energy curve for a molecule. The discussion proceeds through molecular orbital theory (MO), then valence bond theory (VB), then the combined use of MO and VB, and ends with a comparison of MO with VB. Changes for this edition include:

- The pedagogy in the introductory section titled Quantum Picture of the Chemical Bond (Section 6.1) has been shortened and improved.
- The graphics and equations presented in the treatment of LCAO-MO theory (see Sections 6.5 and 6.6) have been revised to represent constructive and destructive interference using the same wave functions that are presented in Chapter 5. The linear combinations of atomic orbitals used to construct hybrid atomic orbitals (Section 6.9) have been revised and the pedagogy is shortened and improved.
- The treatment of polyatomic molecules has been improved, including delocalized π bonding in NO_2 , 1,3-butadiene, and benzene.
- The summary and comparison of LCAO-MO theory and the valence bond model was shortened and improved (Section 6.12).

Chapter 7: Bonding in Organic Molecules

The purpose of this chapter is to describe the bonding and nomenclature in alkanes, alkenes, alkynes, aromatics, and conjugated hydrocarbons and in the major functional groups. Our main goal is to illustrate the bonding theories from Chapter 6 with examples from organic chemistry that can be used in conjunction with Chapter 6. For the new edition we updated the nomenclature to give IUPAC names (retaining the common names where advisable) and moved the graphics related to delocalized π molecular orbitals in 1,3-butadiene and benzene to Chapter 6.

Chapter 8: Bonding in Transition Metal Compounds and Coordination Complexes

We present a comprehensive introduction to bonding in transition metal compounds and coordination complexes using MO and VB theory as developed in Chapter 6. Our goal is to demonstrate that MO theory is not limited to the first- and second-period diatomic molecules and that it provides the most satisfactory method for describing bonding in coordination complexes. The material covered in this chapter now provides a self-contained introduction to structure and bonding in inorganic chemistry that should provide sound preparation for an advanced inorganic chemistry course. For the new edition, we have revised and improved the figures related to chiral molecules (see Section 8.3.3) and crystal field theory (see Section 8.4.2).

Chapter 9: The Gaseous State

In this chapter we improved the treatment of the Maxwell-Boltzmann distribution of molecular speeds (see Section 9.5.2) to help students estimate the fraction of molecules with speed in a given range and to understand why the rate of a chemical reaction might increase with temperature. We also introduced the concept of relative velocity in the treatment of molecular collisions (see Section 9.7.2) so that students have a basis for deriving (in Chapter 18) the expression

for the rate of an elementary bimolecular reaction in terms of the product of the concentrations of the two reacting species.

Chapter 10: Solids, Liquids, and Phase Transitions

For the eighth edition, we have introduced calculus to the treatment of compressibility and thermal expansion (see Sections 10.1.2 and 10.1.3).

Chapter 12: Thermodynamic Processes and Thermochemistry

The treatment in this and prior editions gives the instructor flexibility on how to cover traditional thermochemistry in conjunction with direct applications of the laws of thermodynamics. Stronger students may be encouraged to solve problems starting from the axioms and deriving the needed formulas from first principles.

Chapter 13: Spontaneous Processes and Thermodynamic Equilibria

The chapter presents a molecular statistical interpretation of entropy alongside the traditional macroscopic description involving the reversible transfer of heat. It carefully develops the conditions under which one may use the change in Gibbs free energy to assess the spontaneity of a reaction.

Chapter 14: Chemical Equilibrium

To provide flexibility for instructors, this chapter is written to allow thermodynamics to be taught either before or after equilibrium. Each topic is introduced first from the empirical point of view, and then followed immediately with the thermodynamic treatment of the same topic. Instructors who prefer to treat thermodynamics first can use the chapter as written, whereas those who prefer the empirical approach can skip appropriate sections, and then come back and pick up the thermo-based equilibrium sections after they cover basic thermodynamics. “Signposts” are provided in each section to guide these two groups of readers; the options are clearly marked. Specific examples of this flexible approach are:

- Section 14.2 provides a thorough discussion of procedures for writing the empirical law of mass action for gas-phase, solution, and heterogeneous reactions, with specific examples for each.
- Section 14.3 follows with the thermodynamic prescription for calculating equilibrium constants from tabulated Gibbs free energy values for gas-phase, solution, and heterogeneous reactions, with specific examples for each. For students who have covered Chapters 12 and 13, it gives a succinct derivation of $\Delta G = \Delta G^\circ + RT \ln Q$ and the relationship between Q and K .
- Sections 14.4 and 14.5 present a variety of equilibrium calculations based on the empirical law of mass action.
- Section 14.6 discusses direction of change in terms of the empirical reaction quotient Q , with illustrations in gas-phase, solution, and heterogeneous reactions.
- Section 14.7 discusses direction of change from the point of view of thermodynamics, relating Q to the Gibbs free energy change and the equilibrium constant.

Chapter 15: Acid–Base Equilibria

The examples establishing the molecular-level interpretation of acid-base equilibria (see Section 15.8) have been carefully vetted and improved.

Chapter 17: Electrochemistry

This chapter provides a molecular level interpretation of electrochemical processes unique in an undergraduate textbook, as far as we are aware, to complement the standard thermodynamic treatment of the subject. We introduce the idea that a redox potential (a free energy) can be associated with an orbital energy level, which allows us to use energy-level diagrams to help students visualize electron transfer processes pictorially. This approach also allows us to introduce an electrostatic driving force for electrochemical processes and connect it to the thermodynamic driving force. We explicitly identify the conditions under which this approximation is valid (outer sphere electron transfer processes, negligible entropic contribution to the Gibbs free energy) so that our students can use this description with confidence.

For the eighth edition we streamlined and improved the introductory material on electric potential versus potential energy (see Section 17.1), moved the essential material on the molecular interpretation of electrochemical processes to later sections in the chapter to better integrate the pedagogy and applications, and deleted the long subsection on alternative reference electrodes in Section 17.2, moving the essential material to earlier in Section 17.2. We revised the applications in the molecular electrochemistry section (which was Section 17.5 in the seventh edition and is now Section 17.4 in the eighth edition) to shorten the presentation and improve clarity, including the discussion of using semiconductors in solar cells for generating H_2 as an alternative fuel.

Chapter 18: Chemical Kinetics

For the eighth edition we revised and improved the treatment of collision theory (see Section 18.6.1) to allow students to solve problems of importance in atmospheric chemistry, such as the reaction of Cl with methane. The concepts of relative velocity and impact parameter are developed with new graphics and simple examples (Examples 18.9, 18.10, and 18.11) and the connection with molecular collisions (as introduced in Chapter 9) are firmly established. We also expanded the material on molecular beam experiments (see Section 18.6.4). The seventh edition subsection on mechanisms of enzyme-catalyzed reactions is now presented as a *Connection to Biology*.

Chapter 19: Nuclear Chemistry

Chapter 19 has been extensively reorganized and streamlined, with the focus now on balancing nuclear reactions, mass–energy relationships, and predicting the spontaneity of nuclear reactions (with improved notation in the eighth edition), and the kinetics of radioactive decay. This material is followed by a detailed description of selected key applications. The first set of applications, covered under the heading, Radiation in Biology and Medicine (see Section 19.4), retains the *Connection to Medicine* presented in the seventh edition. The chapter ends with applications in nuclear fission, including nuclear power reactors (see Section 19.5.1), and fusion (in the sun and other stars and in proposed energy applications).

Chapter 20: Molecular Spectroscopy and Photochemistry

Chapter 20 has been reorganized in the eighth edition to provide an introduction to molecular energy levels first, including a discussion of how one might probe them using traditional absorption spectroscopy or more modern laser spectroscopy (specifically laser-induced fluorescence). Other changes include:

- A streamlined discussion of direct absorption methods and Raman spectroscopy (see Section 20.2), which included removing the detailed description of Fourier transform methods that was in the middle of the vibrational spectroscopy section in the last edition.
- A reorganized order of topics, so that rotational spectroscopy in diatomic molecules is now treated first, followed by vibrations in diatomics and then infrared spectroscopy of diatomic molecules involving a change in both the vibrational and the rotational quantum number (see consecutive subsections in Section 20.3.1). Rotations and vibrations in polyatomic molecules follow (see Section 20.3.2), ending with material from the seventh edition on characteristic vibrational frequencies of organic functional groups.
- A simplified treatment of nuclear magnetic resonance (NMR) spectroscopy, making it more physically intuitive (see Section 20.4), while retaining material on Fourier-transform NMR from the seventh edition.
- The revision of several figures in the chapter with a focus on scientific accuracy.
- A shortened, streamlined section titled Introduction to Atmospheric Chemistry (see Section 20.6) that retains the discussion of the chemistry of ozone but removes, in response to reviewer feedback, much of the last edition's coverage of climate change. (The full treatment that was found in the seventh edition will be made available on the instructors' website.)
- A shortened, streamlined *A Deeper Look* section (Section 20.8), that retains the coverage on lasers but omits the coverage of the Einstein radiation relations.

Chapter 21: Structure and Bonding in Solids

For the eighth edition we improved the discussion regarding symmetries of the cube primitive (see Section 21.1) and improved the accuracy of several figures.

Chapter 22: Inorganic Materials

For the eighth edition we improved graphics in the section on silicates (see Section 22.1.1).

Appendices

For the eighth edition we added to the appendix on mathematical background for general chemistry a subsection that introduces vectors (see Section C.7). We also improved the notation and pedagogy in portions of the appendix on physics background for general chemistry (see Section B.2).

Teaching Options

The text is structured and written to give instructors significant flexibility in choosing the order in which topics are presented. We suggest several such possibilities here. In all cases we recommend starting with Chapter 1 to provide a contemporary introduction to the structure and properties of the atom, as well as to help our students understand how we came to acquire this understanding. Our own students report that this early introduction to the scientific method, following these historical examples, has been helpful to them in subsequent courses. We then recommend working through the material in Chapter 2 to establish a secure foundation in “chemical accounting methods” that is necessary for studying all the remaining chapters. Particularly well-prepared students can skip Chapter 2, especially if diagnostics are available to ascertain satisfactory background.

Classical Bonding before Introduction to Quantum Theory

Chapters 1–6; selections from Chapters 7 and 8; Chapters 9–23

This is the sequence we have found most effective overall all for two reasons: (1) introducing the classical description before tackling quantum mechanics helps our students see the need to understand the latter approach, and (2) it enables our students to bring substantially greater maturity to their first exposure to quantum theory. This leads to deeper and quicker mastery of quantum theory and its applications to atomic and molecular structure. Instructors who wish to introduce molecular spectroscopy earlier can easily cover Sections 20.1 through 20.4 immediately after Chapter 6.

Introduction to Quantum Theory before Bonding

Chapters 1, 2, 4, 5, 3, 6; selections from Chapters 7 and 8; Chapters 9–23

These sequences are appropriate for instructors who prefer to establish a background in quantum theory before discussing ionic and covalent bonding, Lewis diagrams, and VSEPR theory. Instructors who prefer to cover these classical bonding topics after quantum mechanics but before MO and VB theory would cover Chapter 3 before Chapter 6. Those who want to present the full quantum story first and then present the classical description as the limiting case would cover Chapter 3 after Chapter 6. We recommend that both of these sequences cover Section 3.3 (force and potential energy in atoms) before Chapter 4 to give students a good physical feeling for Rutherford’s planetary model of the atom in preparation for the quantum theory. Instructors who wish to introduce molecular spectroscopy earlier can easily cover Sections 20.1 through 20.4 immediately after Chapter 6.

Traditional “Macro-to-Micro” Approach

Chapters 1, 2, 9–19, 3–8, 20–23

This sequence covers fully the macroscopic descriptions of chemical phenomena and then begins to interpret them in terms of molecular structure. Instructors could choose either of the two bonding approaches suggested earlier for the specific order of Chapters 3 through 6 late in this course. This sequence repre-

sents a rather pure form of the “macro-to-micro” approach that was followed in the first three editions. Alternatively, they could cover Chapter 3 between Chapter 2 and Chapter 9, as was done in the fourth and fifth editions. This approach has the advantage of building a substantial foundation in structure—and a complete discussion of chemical nomenclature—as the basis for the macroscopic descriptions, while leaving the quantum theory of bonding to come later in the course.

Thermodynamics before Chemical Equilibrium

Chapters 12–17

This is the sequence we have found to be the most effective. If students first have a good understanding for the physical basis of equilibrium, then the facts and trends of chemical equilibrium quickly begin to form patterns around molecular structure. The equilibrium state is determined by the changes in entropy and bond energies associated with each chemical reaction.

Empirical Chemical Equilibrium before Thermodynamics

Chapter 14 (omit Sections 14.3, 14.7); Chapters 15, 16, 12, 13; Sections 14.3, 14.7; Chapter 17

Perhaps to provide background for quantitative laboratory work, others may wish to present chemical equilibrium earlier in the course in a more empirical fashion, before the presentation of thermodynamics. Chapter 14 is clearly marked with “signposts” to facilitate this sequence.

Modified “Macro-to-Micro” Approach

Chapters 1–3, 9, 10, 12–14, 11, 15, 4–7, 20, 16–19, 8, and 21; selections from Chapters 22 and 23

The syllabus currently in use at The University of Chicago follows the approach of thermodynamics before chemical equilibrium, and covers most of quantum mechanics in the winter months (so students co-enrolled in calculus are up to speed by then). Molecular spectroscopy (Chapter 20) and applications to organic chemistry (selected from Chapter 7) immediately follow, or are interleaved with, the coverage of quantum mechanics and molecular structure during the winter. Chapters 16 to 19 and Chapter 21 follow in the spring with Chapter 8 immediately following Chapter 19 in our regular course and Chapter 7 in our honors course. This allows students to switch between our honors and regular course in the winter if they desire. For an honors course populated primarily by students who have scored a 4 or 5 in AP chemistry, we retain the student’s interest by covering only selected sections of Chapters 1, 3, 9 (focusing on the material in Section 9.5 and later), 10, and 11, and we skip Chapter 2. We then focus on a first-principles development of thermodynamics and chemical equilibrium in Chapters 12 to 14, immediately followed by chemical applications in Chapter 15 and selected portions of Chapter 16. This is followed by the comprehensive treatment of quantum mechanics, Chapters 4 to 6, the last with added material on molecular orbitals for a variety of polyatomics covered in Chapter 7 along with some radical species such as the allyl radical. Chapters 8 and 20 are typically covered then, followed by Chapters 16 through 21 in the spring and special topics selected by the instructor.

General Aspects of Flexibility

Certain topics may be omitted without loss of continuity. For example, a principles-oriented course might cover the first 20 chapters thoroughly and then select one or two specific topics in the last chapters for close attention. A course with a more descriptive orientation might omit the sections entitled *A Deeper Look . . .*, which are more advanced conceptually and mathematically than the sections in the main part of the book, and cover the last three chapters more systematically. Additional suggestions are given in the *Instructor's Manual* that accompanies the book.

Features

Mathematical Level

This book presupposes a solid high school background in algebra and coordinate geometry. The concepts of slope and area are introduced in the physical and chemical contexts in which they arise, and differential and integral notation is used in parallel with these concepts. Thus, students with a single-variable calculus background are engaged fully, while students without that background will not be at a disadvantage. Simple vectors are introduced to aid in discussing force and velocity, with an elementary section in Appendix C covering vectors in Cartesian coordinates. The book is fully self-contained in its use of mathematical methods. Methods are introduced at “point of use,” and Appendix C provides a more comprehensive introduction (or review) of the material as needed.

Key equations in the text are highlighted in color and numbered on the right side of the text column. Students should practice using them for chemical calculations. The steps to derive each of these equations are presented in the text, so students do not conclude they must simply memorize these equations. Rather they are taught how to develop these relationships from first principles.

Updated Design and New Illustrations and Photographs

This eighth edition features a modern design, whose elements have been carefully arranged for maximum clarity and whose aesthetics should engage today's visually oriented students. We have selected photographs and illustrations to amplify and illuminate concepts in the narrative text. All illustrations of atomic and molecular orbitals, charge density, and electrostatic potential energy maps were generated expressly for this textbook. Most orbitals and charge densities were calculated by Mr. Hatem Helal (Cambridge University, UK) in the Materials Simulation Center at the California Institute of Technology, directed by Professor William A. Goddard III. Dr. Kelly Gaither (Director, Visualization and Data Analysis group, Texas Advanced Computing Center) plotted the images using state-of-the-art software at the Scientific Visualization Laboratory at The University of Texas at Austin. The colors, lighting effects, and viewing angles were chosen to display three-dimensional objects with maximum clarity and to provide chemical insight. In many cases quantitative contour plots accompany the three-dimensional isosurfaces representing orbitals to help our students understand how the appearances of isosurfaces depend on choices made by scientists and that these isosurfaces are not unique.

Molecular Art

The sixth edition introduced an art program in which molecular shapes are rendered with quantitative accuracy and in modern graphical style. Most of the illustrations of atomic and molecular orbitals, charge density, and electrostatic potential energy maps were generated from accurate quantum chemistry calculations carried out at the California Institute of Technology. Orbitals were plotted using state-of-the-art visualization software at the Texas Advanced Computing Center, University of Texas at Austin. The colors, lighting effects, and viewing angles were chosen to display three-dimensional objects with maximum clarity and to provide chemical insight.

Worked Examples

This textbook includes worked examples that demonstrate the methods of reasoning applied in solving chemical problems. The examples are inserted immediately after the presentation of the corresponding principles, and cross-references are made to related problems appearing at the end of the chapter.

A Deeper Look

Sections entitled *A Deeper Look . . .* provide students with a discussion of the physical origins of chemical behavior. The material that they present is sometimes more advanced mathematically than that in the main parts of the book. The material provided in these sections allows instructors to more easily tailor the breadth and depth of their courses to meet their specific objectives.

Key Terms

Key terms appear in boldface where they are first introduced. Definitions for all key terms are also included in the Index/Glossary for ready reference.

“Connections to...”

A number of essays provide “Connections to...” other branches of science, engineering, and medicine. Coupled with the interdisciplinary Cumulative Exercises that have long been a hallmark of *Principles of Modern Chemistry*, these “Connections” give a substantial sampling of applications of the principles of chemistry.

Chapter Summary

Immediately at the end of each chapter is a summary that ties together the main themes of the chapter in a retrospective narrative. This complements the introductory passage at the beginning of the chapter in a manner that conveys the importance of the chapter. The summary is the first in a set of four end-of-chapter features that constitute a comprehensive set of tools for organizing, studying, and evaluating mastery of the chapter.

Cumulative Exercise

At the end of each of Chapters 2 through 21 is a cumulative exercise, a unique feature of *Principles* since its inception that focuses on a problem of chemical interest and draws on material from the entire chapter for its solution. Working through a chapter's cumulative exercise provides a useful review of material in the chapter, helps our students put principles into practice, and prepares them to solve the problems that follow.

Concepts and Skills

Each chapter concludes with a list of concepts and skills (task-oriented) for each section in the chapter for review by our students. Included in this list are cross-references to the section in which the topic was covered, a concise review of material essential to that topic, the key equations for each topic, and cross-references to end-of-chapter problems that help test mastery of the particular skill involved. Our own students report that this feature has been very helpful to them for self-testing and review of material.

Problems

Problems are grouped into three categories. Answers to odd-numbered “paired problems” (which have red problem numbers) are provided in Appendix G; they enable students to check the answer to the first problem in a pair before tackling the second problem. *Additional Problems*, which are unpaired, illustrate further applications of the principles developed in the chapter. *Cumulative Problems* integrate material from the chapter with topics presented earlier in the book. We integrate more challenging problems throughout the problems sets and identify them with asterisks.

Appendices

Appendices A, B, and C are important pedagogically. Appendix A discusses experimental error and scientific notation. Appendix B introduces the SI system of units used throughout the book and describes the methods used for converting units. Appendix B also provides a brief review of some fundamental principles in physics, which may be particularly helpful to students in understanding topics covered in Chapters 3, 4, 5, 6, 9, 10, 12, 13, 17, 18, 19, and 20. Appendix C provides a review of mathematics for general chemistry. Appendices D, E, and F are compilations of thermodynamic, electrochemical, and physical data, respectively.

Index/Glossary

The Index/Glossary at the back of the book provides brief definitions of all bold-faced key terms, as well as cross-references to the pages on which the terms appear.

Supporting Materials

Student Resources

Please visit <http://www.cengage.com/chemistry/oxtoby/POMC8e> for information about student resources for this text.

Instructor Resources

Please visit <http://www.cengage.com/chemistry/oxtoby/POMC8e> for information about instructor resources for this text.

Acknowledgments

In preparing the eighth edition, we have benefited greatly from the comments of students who used the first seven editions over the years. We would also like to acknowledge the many helpful suggestions of colleagues at Pomona College, The University of Chicago, the University of California–Los Angeles, and other colleges and universities who have taught from this book. We are particularly grateful to Professors Robin Garrell, Ken Houk, Herb Kaesz, and Thomas Mason of UCLA, Professor Greg Engel of The University of Chicago, Professor Michael Topp of the University of Pennsylvania, Professor Gina Frey of Washington University, and Professors Eric Anslyn, Al Bard, Ray Davis, Brad Holliday, Simon Humphrey, Brent Iverson, Richard Jones, Peter Rossky, Jason Shear, John Stanton, Keith Stevenson, David Vanden Bout, Grant Willson, and Robert Wyatt of The University of Texas–Austin, Professor Samir Anz of California Polytechnic State University–Pomona, and Professor Andrew J. Pounds of Mercer University for their helpful comments and advice.

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We are much indebted to our longtime friend Professor Eric J. Heller of Harvard University for the beautiful and striking images that grace the covers

of the sixth, seventh, and eighth editions of our book. Professor Heller's work demonstrates that images of great beauty can arise from scientific research and that artistic renderings effectively convey the meaning of scientific results. We are certain this image will entice readers to peek between the covers of our book, and we hope they find scientific beauty on the inside as well as on the cover!

We are particularly grateful to friends and colleagues who provided original scientific illustrations for the book. They are Professor Wilson Ho (University of California–Irvine), Dr. Gilberto Medeiros-Ribeiro and Dr. R. Stanley Williams (Hewlett-Packard Research Laboratories), Professor Leonard Fine (Columbia University), Professor Andrew J. Pounds (Mercer University) and Dr. Mark Iken (Scientific Visualization Laboratory, Georgia Institute of Technology), Dr. Stuart Watson and Professor Emily Carter (Princeton University), Professor Nathan Lewis (California Institute of Technology), Dr. Don Eigler (IBM Almaden Research Center), Dr. Gerard Parkinsen and Mr. William Gerace (OMICRON Vakuumphysik), Dr. Richard P. Muller and Professor W.A. Goddard III (California Institute of Technology), Professor Mounji Bawendi and Ms. Felice Frankel (Massachusetts Institute of Technology), Professor Graham Fleming (University of California–Berkeley), Professors Donald Levy, Philippe Guyot-Sionnest, and David Mazziotti (The University of Chicago), Professor W.E. Moerner (Stanford University), Dr. Jane Strouse (University of California–Los Angeles), Professor James Speck and Professor Stephen Den Baars (University of California–Santa Barbara), Professor John Baldeschwieler (California Institute of Technology), and Dr. Thomas Koop (Bielefeld University).

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We are also indebted to Professor Charles M. Knobler of the University of California–Los Angeles; Professor Jurg Waser, formerly of the California Institute of Technology; and Mrs. Jean T. Trueblood (widow of the late Professor Kenneth N. Trueblood of the University of California–Los Angeles) for permission to incorporate selected problems from their distinguished textbook *ChemOne*, Second Edition, McGraw-Hill, New York (1980).

On a personal note, it gives us genuine pleasure to dedicate this eighth edition of our textbook to our own Ph.D. research advisers Professors Bill Gelbart (Oxtoby), Karl Freed (Gillis), and Yuan T. Lee (Butler). They showed us the excitement of doing scientific research and the joy of transmitting scientific knowledge to the next generation. Their legacy inspires our work with our own students in the laboratory, in the classroom, and in the pages of this textbook.

The staff members at Cengage Learning have been most helpful in preparing this eighth edition. In particular, we gratefully acknowledge the superb work of content developer Ed Dodd, who made sure all the changes to the text and graphics for the eighth edition were done perfectly. We also acknowledge the role of our associate product manager, chemistry, Krista M. Mastroianni. Content developer Elizabeth Woods coordinated production of the ancillary materials. Senior content developer Lisa Weber handled the media products. Senior content project manager, Teresa L. Trego, at Cengage, and Cassie Carey, senior production editor at Graphic World Publishing Services, kept the schedule mov-

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November 2014

David W. Oxtoby

David W. Oxtoby became the ninth president of Pomona College on July 1, 2003. An internationally noted chemist, he previously served as dean of physical sciences at The University of Chicago. At Pomona, he holds a coterminous appointment as president and professor of chemistry. Before coming to Pomona, he was associated with the University of Chicago for nearly three decades, with brief interludes to serve as a visiting professor at such places as the University of Paris; the University of Bristol in Great Britain; and the University of Sydney in Australia. Oxtoby is a fellow of the American Physical Society and a member of the American Chemical Society and the American Association for the Advancement of Science. After earning his bachelor's degree, summa cum laude, from Harvard University, he went on to earn his Ph.D. at the University of California, Berkeley. As a research chemist, he is author or co-author of more than 165 scientific articles on such subjects as light scattering, chemical reaction dynamics, and phase transitions. In addition to co-authoring *Principles of Modern Chemistry* and *Chemistry: Science of Change*, he has received fellowships from the Guggenheim, von Humboldt, Dreyfus, Sloan, Danforth, and National Science foundations.

H.P. Gillis

H.P. Gillis conducts experimental research in the physical chemistry of electronic materials, emphasizing phenomena at solid surfaces and interfaces. Dr. Gillis received his B.S. (Chemistry and Physics) at Louisiana State University and his Ph.D. (Chemical Physics) at The University of Chicago. After postdoctoral research at the University of California–Los Angeles and 10 years with the technical staff at Hughes Research Laboratories in Malibu, California, Dr. Gillis joined the faculty of Georgia Institute of Technology. Dr. Gillis moved to University of California–Los Angeles, where he currently serves as adjunct professor of materials science and engineering. He has taught courses in general chemistry, physical chemistry, quantum mechanics, surface science, and materials science at UCLA and at Georgia Institute of Technology.

Laurie J. Butler

Laurie J. Butler uses molecular beam and laser spectroscopic techniques, along with associated computational modeling, to study the chemical reaction dynamics of radical intermediates and of electronically excited molecules. She received her B.S. (Chemistry) at the Massachusetts Institute of Technology and her Ph.D. (Physical Chemistry) at the University of California, Berkeley (the latter under the direction of Nobel Laureate Y.T. Lee). After a short postdoctoral position at University of Wisconsin–Madison, she accepted a faculty position at The University of Chicago. Fellow of the AAAS, the American Chemical Society, and the American Physical Society, she has co-authored over a hundred scientific papers. She teaches introductory and physical chemistry to the brilliant undergraduates at Chicago, for which she received the University's Quantrell teaching award, as well as graduate-level courses in quantum mechanics and in chemical reaction dynamics.

Introduction to the Study of Modern Chemistry

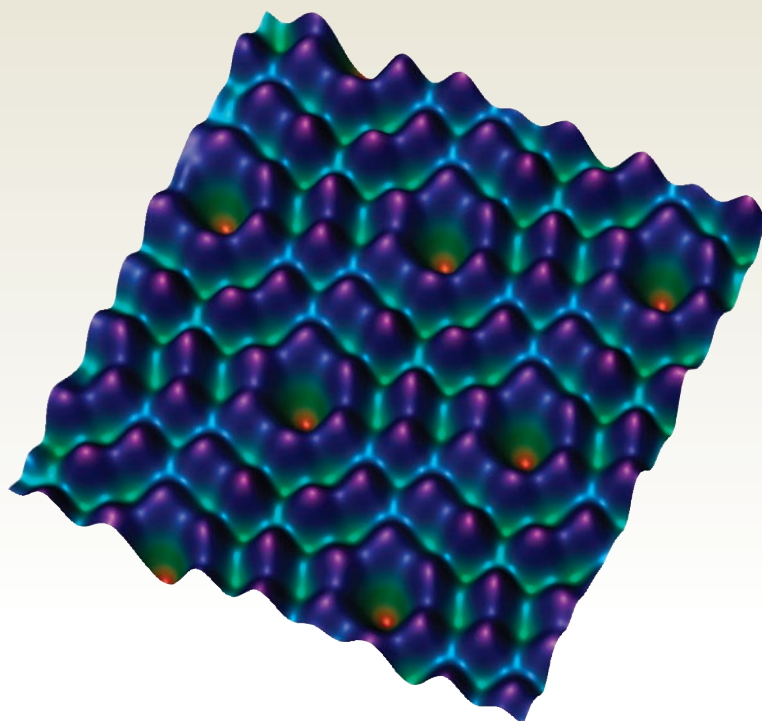


Photo courtesy of Wilson Ho, University of California, Irvine. Reprinted by permission of Physical Review Letters, Fig 1, vol. 79, 4397-4400, © 1997 by the American Physical Society

The surface of a silicon crystal imaged using a scanning tunneling microscope. Individual silicon atoms appear as purple protrusions above the background. The surface was cleaned in an ultrahigh vacuum to remove all impurity atoms and the image was taken at very low temperatures (-220°C) to obtain the high resolution shown here. There are two kinds of surface silicon atoms shown in this image: "corner" silicon atoms that form hexagonal rings around a hole in the surface layer and "center" silicon atoms that appear as pairs arranged around the hexagonal rings.

Modern chemistry explores the world of atoms and molecules, seeking to explain not only their bonding, structures, and properties, but also how these very structures are transformed in chemical reactions. The search for atoms and molecules began with the speculations of ancient philosophers and—stimulated by the classic experiments of the 18th and 19th centuries—led to John Dalton’s famous atomic hypothesis in 1808. The quest continues. The invention of the scanning tunneling microscope (STM) in the 1980s, along with other microscopic and spectroscopic techniques, has enabled contemporary scientists to detect and manipulate individual atoms and molecules.

Unit Chapters

CHAPTER 1

The Atom in Modern Chemistry

CHAPTER 2

Chemical Formulas, Equations, and Reaction Yields

Unit Goals

- To describe the key experiments and the underlying physical models that justify the central role of the atom in modern chemistry
 - Chemical evidence for the existence and properties of atoms and molecules
 - Physical evidence for the existence and properties of atoms and molecules
 - The modern, planetary model of the atom
- To introduce the established quantitative procedures that describe chemical reactions as rearrangements of atoms, forming products from reactants
 - The mole concept that relates weighing and counting of molecules and atoms
 - Balanced chemical equations that relate moles of reactants to moles of products

1

CHAPTER

The Atom in Modern Chemistry

- 1.1 The Nature of Modern Chemistry
 - 1.2 Elements: The Building Blocks of Matter
 - 1.3 Indirect Evidence for the Existence of Atoms: Laws of Chemical Combination
 - 1.4 The Physical Structure of Atoms
 - 1.5 Mass Spectrometry, Isotopes, and the Measurement of Relative Mass
 - 1.6 The Mole: Counting Molecules by Weighing
- Connection to Nanotechnology:*
Imaging Atoms, Molecules, and Chemical Reactions by Scanning Tunneling Microscopy

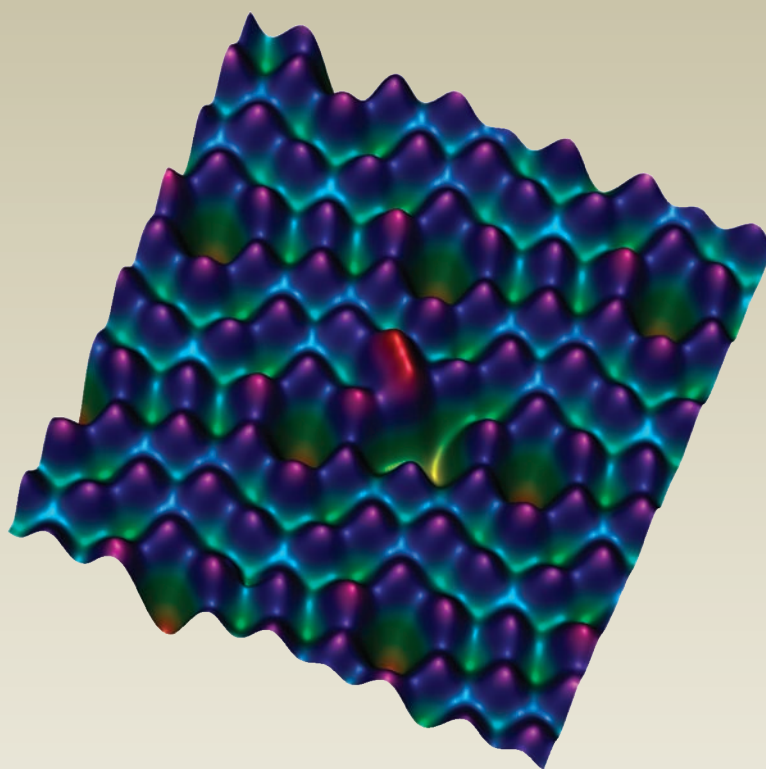


Photo courtesy of Wilson Ho, University of California, Irvine. Reprinted by permission of Physical Review Letters, 79, 4357–4400 (1997).

Reversible single atom transfer using the scanning tunneling microscope. This image was taken under the same conditions as the one shown opposite page 1. One of the “center” silicon atoms (imaged in red) has been transferred halfway to another center atom site by the scanning tunneling microscope tip. The atom is stable in this position at low temperatures but returns to its home site as the temperature is raised above -100°C .

1.1 The Nature of Modern Chemistry

Chemists study the properties of substances and the reactions that transform substances into other substances. Chemists are particularly interested in understanding how and why specific chemical reactions occur, in order to tailor the properties of existing substances to meet particular needs—and to create entirely new substances designed to have specific properties. Chemistry has improved agricultural production, helped prevent and cure many diseases, increased the efficiency of energy production, and reduced environmental pollution, to cite just a few advances. A particularly exciting challenge for modern chemical research is to understand the dynamics of these chemical transformations, because they govern phenomena as diverse as the evolution of small carbon-containing molecules in interstellar space, changes in terrestrial atmospheric and climatic patterns caused by pollutants, and the unfolding of life processes in living organisms.



Painting: The Alchemist by Hendrick Heerschoop, 1671. Courtesy of Dr. Alfred Bader

FIGURE 1.1 Alchemists searched in vain for procedures that would turn base metals into gold. Their apparatus foreshadowed equipment in modern chemical laboratories.

Chemistry influences almost every area of science and technology; advances in chemistry inform disciplines as different as solid-state physics and molecular biology, and the synthetic methods and analytical techniques developed by chemists support research and manufacturing in important areas like medicine and microelectronics. Perhaps no other science covers as broad a range of topics as does chemistry. Within a single modern chemistry department, you're likely to find chemists creating new materials and developing strategies for sustainable energy, devising synthetic routes that conserve all of the atoms in starting materials, detecting and identifying single molecules, designing new molecules for therapeutic purposes and translating those developments into clinical trials, and developing highly selective integrated sensors for a variety of applications in science and technology. Despite the diversity of these areas of scientific inquiry, they are all unified by a single set of fundamental scientific principles, which we will introduce in this textbook.

Chemistry is a relatively young science, and its foundations weren't established until the last quarter of the 18th century. Before that, most chemists were known as *alchemists*—early entrepreneurs who sought to transform the properties of materials for economic gain (Fig. 1.1). For centuries their obsession was to transform “base” metals, such as lead, into gold. They boldly assumed that the properties of one material could somehow be extracted and transferred to another. If the essential properties—such as yellow color, softness, and ductility—could be assembled from various inexpensive sources, then gold could be created at great profit.

The alchemists persisted in their efforts for more than a thousand years. Although they collected many useful, empirical results that have since been incorporated into modern chemistry, they never transformed base metals into gold. Many scientists had begun to challenge the basic assumptions of the alchemists by the middle of the 17th century. These doubts culminated with the publication of *The Sceptical Chymist* by Robert Boyle in England in the 1660s, one of the pivotal events that marked the beginning of modern chemistry. Another century was required to establish the conceptual foundations of modern chemistry, a field that flourished throughout the 19th and 20th centuries and remains vibrant today.

The error of the alchemists is obvious to modern observers: they did not follow the scientific method. A new idea is accepted only temporarily in the scientific method, in the form of a **hypothesis**. It is then subjected to rigorous testing, in carefully controlled experiments. A hypothesis is elevated to a **scientific law** only after it has survived many such tests. Concepts or ideas that have earned the status of scientific laws by direct and repeated testing then can be applied with confidence in new situations. A scientific law must be predictive, in addition to being explanatory; failure to accurately predict the results of a new experiment is sufficient to invalidate a scientific law. Had a proper set of tests been made in separate, independent experiments, the alchemists would have recognized that the properties of a material are, in fact, intrinsic, inherent characteristics of that material and cannot be extracted from it.

The history of the alchemists shows the origin of a certain duality in the nature of modern chemistry, which persists to the present. Because chemistry contributes to the foundations of numerous professions and industries, we see the urge to apply established chemical knowledge for profit. But we also see the urge to create new chemical knowledge, driven by both intellectual curiosity and by the desire to have reliable information for applications. Many scientists and engineers from different disciplines contribute to both basic and applied chemical research and development. Irrespective of the specific context, conducting chemical research requires scrupulous adherence to the scientific method, in which the new knowledge generated is subjected to rigorous scrutiny before it earns the confidence of the scientific community.

Most students who study chemistry will apply what they have learned during the course of their professional careers rather than conduct research in chemistry. Still, a useful strategy for learning to think like an experienced chemist is to assume that you are personally responsible for establishing the scientific foundations of chemistry for the very first time. Upon encountering a new topic, try this: imagine that you are the first person ever to see the laboratory results on which it is based. Imagine that you must construct the new concepts and explanations to interpret these results, and that you will present and defend your conclusions before the scientific community. Be suspicious. Cross-check everything. Demand independent confirmations. Always remain, with Boyle, the “skeptical chemist.” Follow the scientific method in your acquisition of knowledge, even from textbooks. In this way, you will make the science of chemistry your own, and you will experience the intellectual joys of discovery and interpretation. Most important, you will recognize that chemistry is hardly a closed set of facts and formulas. Quite the contrary, it is a living, growing method for investigating all aspects of human experience that depend on changes in the composition of substances. Finally, learning to examine critically what we call “the nature of the evidence” will help you make better decisions as consumers and citizens in a world where science and technology continue to become increasingly important parts of modern life.

1.1.1 Conservation of Matter and Energy

The science of chemistry rests on two well-established principles: the conservation of matter and the conservation of energy. The total amount of matter involved in chemical reactions is conserved—that is, it remains constant during the course of every chemical reaction. Matter is neither created nor destroyed in chemical reactions; the components of the reactants are simply rearranged to form products.

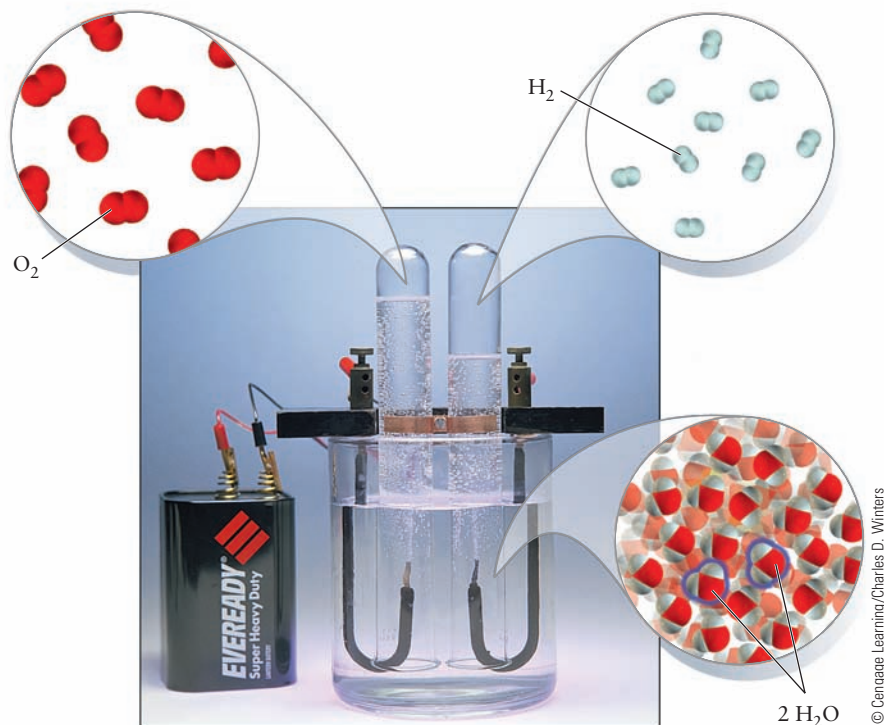
These rearrangements are inevitably accompanied by changes in energy, which brings us to the second principle. The total amount of chemical energy stored in the reactants is almost always different than that stored in the products; this difference manifests itself in the form of thermal, electrical, or mechanical energy required for, or produced by, chemical reactions. But energy is neither created nor destroyed during chemical reactions; it has always been found to be conserved.

These two core principles must be modified slightly for nuclear reactions, which occur at energies so high that matter and energy can be converted into one another through Einstein’s relation, $E = mc^2$. The *sum* of mass and energy is conserved in nuclear reactions.

1.1.2 Macroscopic Methods and Nanoscopic Models

Chemical reasoning, as used both in applications and in basic research, resembles a detective story in which tangible clues lead to a mental picture of events never directly witnessed by the detective. Chemical experiments are conducted in laboratories equipped with beakers, flasks, analytical balances, pipettes, optical and infrared spectrometers, lasers, vacuum pumps, pressure gauges, mass spectrometers, centrifuges, and other apparatus. Each of these devices exists on the *macroscopic* scale—that is, it is perceptible by ordinary human senses. Macroscopic objects range in size from about 1 meter (m) down to about 1 millimeter (mm), which is 1×10^{-3} m. But the actual chemical transformation events occur in the *nanoscopic* world of atoms and molecules—objects far too small to be detected by the naked eye, even with the aid of a first-class microscope. One nanometer (nm) is 1×10^{-9} m. So our modern laboratory instruments are the bridge between these worlds, giving us the means not only to influence the actions of

FIGURE 1.2 Hydrogen and oxygen gas are produced in the ratio 2:1 when an electrical current is passed through water that contains dissolved sulfuric acid. The insert illustrates how chemists view this macroscopic chemical reaction as arising from the rearrangement of atoms on the nanoscale.



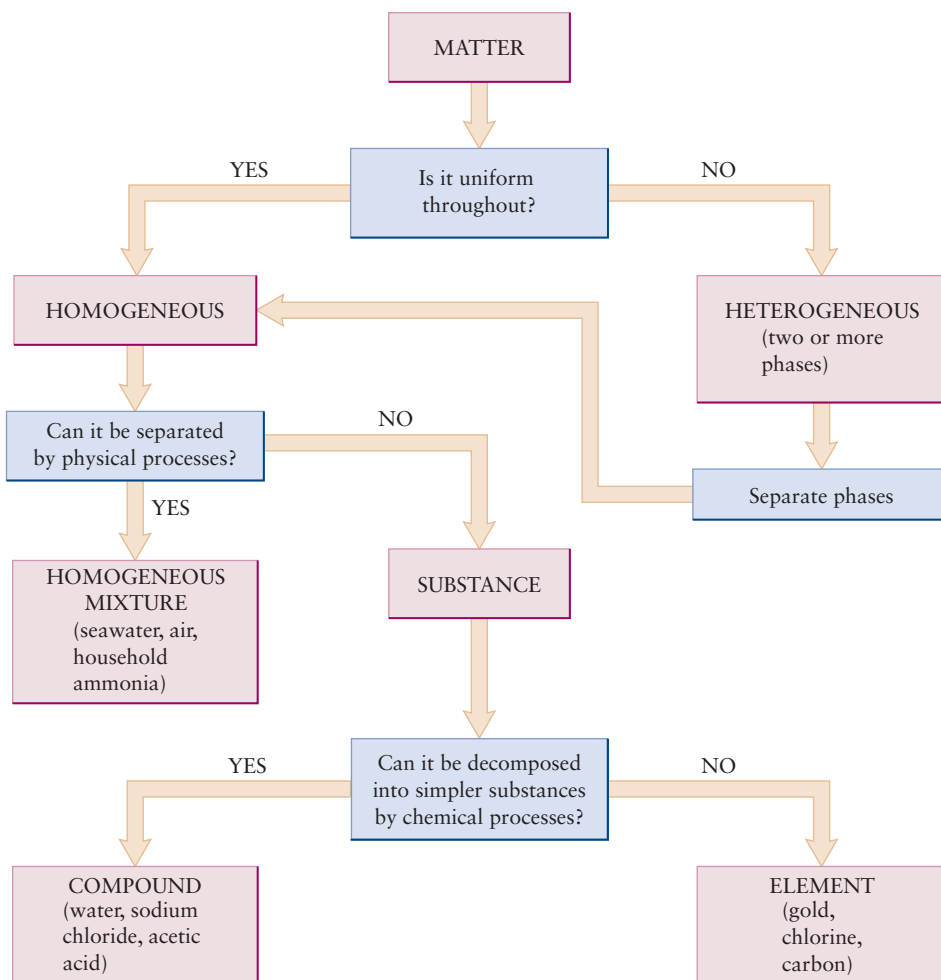
the atoms and molecules but also to measure their response. Figure 1.2 shows views of both worlds simultaneously. In illustrating the chemical decomposition of water into gaseous hydrogen and oxygen by electrolysis, the figure shows the relationship between events on the macroscale and on the nanoscale. Chemists *think* in the highly visual nanoscopic world of atoms and molecules, but they *work* in the tangible world of macroscopic laboratory apparatus. These two approaches to the chemical sciences cannot be divorced, and we emphasize their interplay throughout this textbook. Students of chemistry must master not only the fascinating concepts of chemistry, which describe the nanoscopic world of atoms and molecules, but also the macroscopic procedures of chemistry on which those concepts are founded.

1.2 Elements: The Building Blocks of Matter

Chemists study how sets of pure substances transform into other sets of pure substances in chemical reactions. These investigations apply two modes of reasoning and physical procedures—analysis (taking things apart) and synthesis (putting things together)—that go back to early Greek philosophers, who sought to identify the constituents of all matter as four elements: air, earth, fire, and water. Contemporary chemists classify matter using a very different set of fundamental building blocks, but the analysis and synthesis steps are basically unchanged.

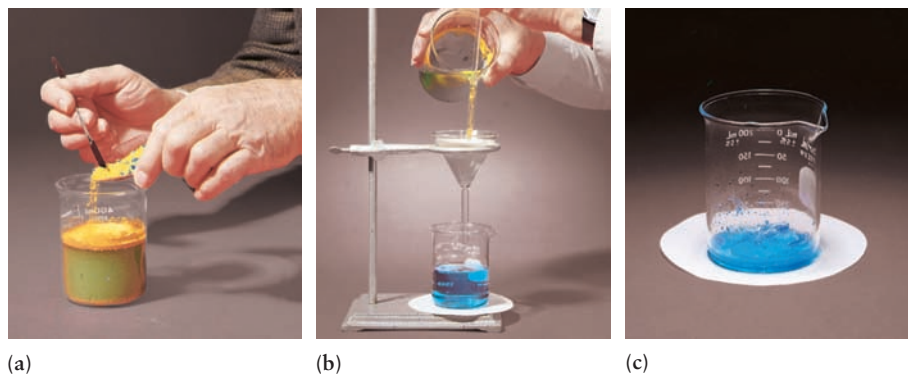
1.2.1 Substances and Mixtures

Investigating chemical reactions can be greatly complicated and often obscured by the presence of extraneous materials. The first step is to learn how to analyze and classify materials to ensure that you are working with *pure* substances before initiating any reactions (Fig. 1.3). Suppose you take a sample of a

FIGURE 1.3 Process flowchart for analyzing matter.

material—a gas, liquid, or solid—and examine its various properties or distinguishing characteristics, such as its color, odor, or density. How uniform are those properties throughout the sample? Different regions of a piece of wood, for example, have different properties, such as variations in color and texture. Wood, then, is said to be **heterogeneous**. Other materials, such as air or mixtures of salt and water, are classified as **homogeneous** materials because their properties are the same throughout a given sample. But these mixtures, although homogeneous, cannot be called pure substances. Thus, call a substance a **mixture** when it is possible to separate it into components by ordinary physical means such as melting, freezing, boiling, or dissolving in solvents (Fig. 1.4). These operations provide

FIGURE 1.4 (a) A solid mixture of blue $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and yellow CdS is added to water. (b) Although the $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ dissolves readily and passes through the filter, the CdS remains largely undissolved and is retained by the filter. (c) Evaporation of the solution leaves nearly pure crystals of $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$.



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ways of separating materials from one another by their properties: freezing points, boiling points, and solubilities. Air, for example, is a mixture of several components—oxygen, nitrogen, argon, and various other gases. If air is liquefied and then warmed slowly, the gases with the lowest boiling points evaporate first, leaving behind in the liquid those with higher boiling points. Such a separation would not be perfect, but the processes of liquefaction and evaporation could be repeated to improve the purity of the component gases to any required degree.

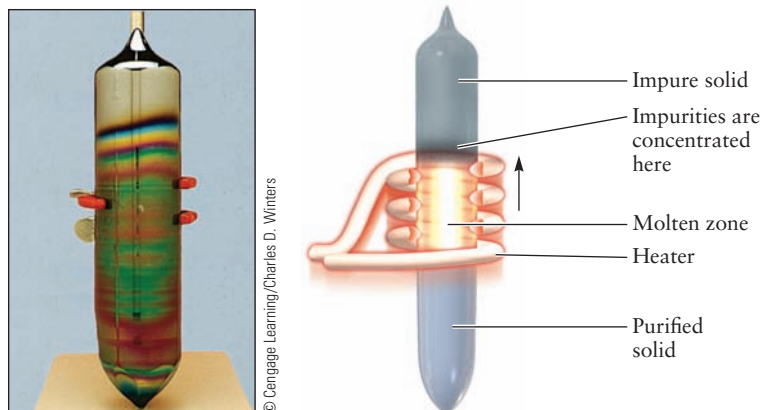
If all these physical procedures (and many others) fail to separate matter into portions that have different properties, the material is said to be a **pure substance**. What about the common material sodium chloride, which we call table salt? Is it a substance? The answer is yes if we use the term *sodium chloride* (NaCl), but no if we use the term *table salt*. Table salt is a mixture of mostly sodium chloride but also small amounts of sodium iodide (needed by the thyroid gland) and magnesium carbonate (needed to prevent the salt from caking). Even if these two components were not added, table salt contains other impurities that had not been removed in its preparation, so to that extent, table salt is a mixture. In contrast, when we refer to sodium chloride, we imply that it is a pure substance that contains only NaCl. The pure substance sodium chloride is a compound, not an element.

Nothing is absolutely pure in practice, so the word **substance** is an idealization. Among the purest materials ever prepared are silicon (Fig. 1.5) and germanium. These elements are used in electronic devices and solar cells, and their electronic properties require either high purity or else precisely controlled concentrations of deliberately added impurities. Meticulous chemical and physical methods have enabled scientists to prepare germanium and silicon with concentrations of impurities that are less than one part per billion. Any higher concentrations of certain impurities would alter the electrical properties of these materials.

1.2.2 Elements

Literally millions of substances have so far been either discovered or synthesized and formally identified. Are these the fundamental building blocks of matter? Happily not, for their classification alone would pose an insurmountable task. In fact, all of these substances are merely combinations of much smaller numbers of building blocks called **elements**. Elements are substances that cannot be decomposed into two or more simpler substances by ordinary physical or chemical means. The word *ordinary* excludes the processes of radioactive decay, whether natural or artificial, and high-energy nuclear reactions that *do* transform elements into one another. When a substance contains two or more chemical elements, we call it a **compound**. For example, hydrogen and oxygen are elements because no further chemical separation is possible, whereas water is a

FIGURE 1.5 Nearly pure elemental silicon is produced by pulling a 10-inch-long solid cylinder (called a boule) out of the melt, leaving most of the impurities behind.



compound because it can be separated into hydrogen and oxygen by passing an electric current through it (see Fig. 1.2). *Binary* compounds are substances, such as water, that contain two elements, *ternary* compounds contain three elements, *quaternary* compounds contain four elements, and so on.

At present, scientists have identified some 118 chemical elements. A few have been known since before recorded history, principally because they occur in nature as elements rather than in combination with one another in compounds. Gold, silver, lead, copper, and sulfur are the most common of these. Gold is found in streams in the form of little granules (placer gold) or nuggets in loosely consolidated rock. Sulfur is associated with volcanoes, and copper often can be found in its native state in shallow mines. Iron occurs (only rarely) in its elemental state (in meteorites); it usually is combined with oxygen or other elements. Ancient metallurgists, in the second millennium B.C., somehow learned to reduce iron oxide to metallic iron using charcoal in forced-draft fires, and the Iron Age was born.

The names of the chemical elements and the symbols that designate them have a fascinating history. The symbols for many elements come from their Latin names, such as gold (aurum, symbol Au), copper (cuprum, Cu), and iron (ferrum, Fe). Some elements have names that describe their characteristic reactions or source; hydrogen (H), for example, means “water former” and potassium (kalium, K) takes its common name from potash (potassium carbonate), a useful chemical obtained in early times by leaching the ashes of wood fires with water. Many elements take their names from Greek and Roman mythology: cerium (Ce) from Ceres, goddess of plenty; tantalum (Ta) from Tantalus, who was condemned in the afterlife to an eternity of hunger and thirst while close to water and fruit that were always tantalizingly just out of reach; niobium (Nb) from Niobe, daughter of Tantalus; and mercury (hydrargyrum, Hg), which means silver water, named after the quickly moving god. Some elements are named for continents: europium (Eu) and americium (Am). Other elements are named after countries: germanium (Ge), francium (Fr), and polonium (Po). Cities provided the names of other elements: holmium (Stockholm, Ho), ytterbium (Ytterby, Yb), and berkelium (Berkeley, Bk). Some are named for the planets: uranium (U), plutonium (Pu), and neptunium (Np). Other elements take their names from colors: praseodymium (green, Pr), rubidium (red, Rb), and cesium (sky blue, Cs). Still others honor great scientists: curium (Marie Curie, Cm), mendelevium (Dmitri Mendeleev, Md), fermium (Enrico Fermi, Fm), einsteinium (Albert Einstein, Es), and seaborgium (Glenn Seaborg, Sg).

1.3 Indirect Evidence for the Existence of Atoms: Laws of Chemical Combination

How did we acquire the chemical evidence for the existence of atoms and the scale of relative atomic masses? It is an instructive story, both in its own right and as an illustration of how science progresses.

We may know the elements to be the most fundamental substances, and we may know that they can be combined chemically to form compound substances, but that knowledge provides us no information about the nanoscopic structure of matter or how that nanoscopic structure controls and is revealed by chemical reactions. Ancient philosophers dealt with these fascinating questions by proposing assumptions, or *postulates*, about the structure of matter. The Greek philosopher Democritus (c. 460–370 B.C.) postulated the existence of unchangeable *atoms* of the elements, which he imagined to undergo continuous random motion in the vacuum, a remarkably modern point of view. It follows from this postulate that matter is not divisible without limit; there is a lower limit to

which a compound can be divided before it becomes separated into atoms of the elements from which it is made. Lacking both experimental capabilities and the essentially modern scientific view that theories must be tested and refined by experiment, the Greek philosophers were content to leave their views in the form of assertions.

Experimental measurements showed that the ratios of the masses of compounds that react to form other compounds is also fixed. These results could be interpreted only by inferring that the smallest indivisible units of the elements (atoms) combined to form the smallest indivisible units of the compounds (molecules). The definite mass ratios involved in reactions suggested a convenient method for counting the number of atoms of each element participating in the reaction. These results, summarized as the **laws of chemical combination**, provided overwhelming, if indirect, evidence for the existence of atoms and molecules.

For more than a century, we have become so accustomed to speaking of atoms that we rarely stop to consider the experimental evidence for their existence that was collected in the 18th and 19th centuries. Twentieth-century science developed a number of sophisticated techniques to measure the properties of single atoms and powerful microscopes to observe them (see *Connection to Nanotechnology*). But long before single atoms were detected, chemists could speak with confidence about their existence and the ways in which they combine to form molecules. Moreover, although the absolute masses of single atoms of oxygen and hydrogen were not measured until the early 20th century, chemists could assert (correctly) some 50 years earlier that the *ratio* of their masses was close to 16:1.

1.3.1 Law of Conservation of Mass

The first steps toward formulating the laws of chemical composition were taken during the 18th century in the course of studies of heat and combustion. It had been observed that an organic material, such as wood, left a solid residue of ash when burned; similarly, a metal heated in air was transformed into a “calx,” which we now call an oxide. The popular explanation for these phenomena in the early 18th century was that a property called *phlogiston* was driven out of wood or metal by the heat of a fire. From the modern perspective, this seems absurd, because the ash weighed less than the original wood, whereas the calx weighed more than the metal. The principle of conservation of mass had not yet been established at that time, and people saw no reason why the mass of a material should not change when heated.

Further progress could be made only by carefully measuring the changes in mass¹ that occur in chemical reactions. The balance had been known since antiquity, but it had been used principally as an assayer’s tool and for verifying the masses of coins or commodities in commerce. The analytical balance developed in the 18th century was accurate to perhaps 1 part in 10,000, enabling much more accurate measurements of mass changes accompanying chemical reactions than had been possible previously. French chemist Antoine Lavoisier used the analytical balance (see the photo on page 35) to demonstrate that the sum of the masses of the products of a chemical reaction equals the sum of the masses of the reactants to the high degree of accuracy provided by the instrument. Lavoisier heated mercury in a sealed flask that contained air. After several

¹Chemists sometimes use the term *weight* in place of *mass*. Strictly speaking, weight and mass are not the same. The mass of a body is an invariant quantity, but its weight is the force exerted on it by gravitational attraction (usually by the Earth). Newton’s second law relates the two ($weight = m \times g$, where g is the acceleration due to gravity). As g varies from place to place on the Earth’s surface, so does the weight of a body. In chemistry, we deal mostly with ratios, which are the same for masses and weights. In this textbook we use the term *mass* exclusively, but *weight* is still in colloquial chemical use.