

ORGANIC CHEMISTRY

NINTH EDITION

John McMurry



Periodic Table of the Elements

Key

Metals
 Semimetals
 Nonmetals

Atomic number
 Symbol
 Name
 Atomic mass

An element

79	Au	Gold	196.9665
----	-----------	------	----------

Group number,
U.S. system
IUPAC system

1A
(1)

1	H	Hydrogen	1.0079
---	----------	----------	--------

Period number

2A
(2)

3	Li	Lithium	6.941
4	Be	Beryllium	9.0122

11	Na	Sodium	22.9898
12	Mg	Magnesium	24.3050

19	K	Potassium	39.0983
20	Ca	Calcium	40.078

37	Rb	Rubidium	85.4678
38	Sr	Strontium	87.62

55	Cs	Cesium	132.9054
56	Ba	Barium	137.327

87	Fr	Francium	(223)
88	Ra	Radium	227.0278

21	Sc	Scandium	44.9559
22	Ti	Titanium	47.88

23	V	Vanadium	50.9415
24	Cr	Chromium	51.9961

41	Nb	Niobium	92.9064
42	Mo	Molybdenum	95.94

73	Ta	Tantalum	180.9479
74	W	Tungsten	183.85

103	Lr	Lawrencium	(260)
104	Rf	Rutherfordium	(261)

57	La	Lanthanum	138.9055
58	Ce	Cerium	140.115

Lanthanides

Actinides

Numbers in parentheses are mass numbers of radioactive isotopes.

8A
(18)

2	He	Helium	4.0026
---	-----------	--------	--------

10	Ne	Neon	20.1797
18	Ar	Argon	39.948

36	Kr	Krypton	83.80
54	Xe	Xenon	131.29

86	Rn	Radon	(222)
118	Uuo	Ununoctium	(294)

7A	F	Fluorine	18.9984
8A	O	Oxygen	15.9994

17	Cl	Chlorine	35.4527
16	S	Sulfur	32.066

35	Br	Bromine	79.904
53	I	Iodine	126.9045

85	At	Astatine	(210)
117	Uus	Ununseptium	(292)

5A	N	Nitrogen	14.0067
6A	O	Oxygen	15.9994

15	P	Phosphorus	30.9738
16	S	Sulfur	32.066

33	As	Arsenic	74.9216
51	Sb	Antimony	121.757

83	Bi	Bismuth	208.9804
115	Uup	Ununpentium	(289)

4A	C	Carbon	12.011
5A	N	Nitrogen	14.0067

14	Si	Silicon	28.0855
15	P	Phosphorus	30.9738

32	Ge	Germanium	72.61
50	Sn	Tin	118.710

82	Pb	Lead	207.2
114	F	Flerovium	(289)

3A	B	Boron	10.811
4A	C	Carbon	12.011

13	Al	Aluminum	26.9815
14	Si	Silicon	28.0855

31	Ga	Gallium	69.723
49	In	Indium	114.82

81	Tl	Thallium	204.3833
113	Uut	Ununtrium	(289)

2B	Zn	Zinc	65.39
3B	Sc	Scandium	44.9559

28	Ni	Nickel	58.693
46	Pd	Palladium	106.42

78	Pt	Platinum	195.08
110	Ds	Darmstadtium	(285)

80	Hg	Mercury	200.59
112	Cn	Copernicium	(285)

1B	Cu	Copper	63.546
2B	Zn	Zinc	65.39

27	Co	Cobalt	58.9332
45	Rh	Rhodium	102.9055

77	Ir	Iridium	192.22
109	Mt	Mendelevium	(288)

79	Au	Gold	196.9665
111	Rg	Röntgenium	(280)

65	Tb	Terbium	158.9253
66	Dy	Dysprosium	162.50

67	Ho	Holmium	164.9303
68	Er	Erbium	167.26

7B	Mn	Manganese	54.9380
8B	Fe	Iron	55.847

43	Tc	Technetium	(98)
44	Ru	Ruthenium	101.07

75	Re	Rhenium	186.207
107	Bh	Bohrium	(272)

60	Nd	Neodymium	144.24
61	Pm	Promethium	(145)

62	Sm	Samarium	150.36
63	Eu	Europium	151.965

94	Pu	Plutonium	(244)
95	Am	Ameicium	(243)

25	Mn	Manganese	54.9380
26	Fe	Iron	55.847

43	Tc	Technetium	(98)
44	Ru	Ruthenium	101.07

75	Re	Rhenium	186.207
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Organic Chemistry



Ninth Edition

Organic Chemistry

John McMurry

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John McMurry

Product Director: Mary Finch

Product Manager: Maureen Rosener

Content Developers: Nat Chen, Lisa Weber

Product Assistant: Morgan Carney

Marketing Manager: Julie Schuster

Content Project Manager: Teresa Trego

Art Director: Andrei Pasternak

Manufacturing Planner: Judy Inouye

Production Service: Graphic World Inc.

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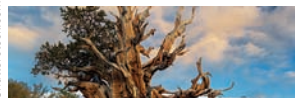
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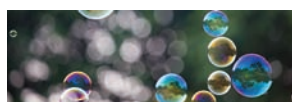


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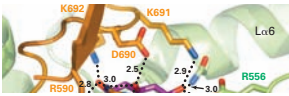
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I love writing, and I love explaining organic chemistry. This book is now in its ninth edition, but I'm still going over every word and every explanation, updating a thousand small details and trying to improve everything. My aim is always to refine the features that made earlier editions so successful, while adding new ones.

▶ Changes and Additions for This Ninth Edition

Text content has been updated for greater accuracy as a response to user feedback. Discussions of NMR spectroscopy and opportunities to practice mechanism problems have been expanded substantially for this ninth edition. Changes include:

- Discussions of interpreting mass spectra have been expanded with new spectroscopy problems included throughout the book.
- Discussions of the theory of nuclear magnetic resonance and interpretation of NMR data have been reorganized and expanded with new NMR problems.
- *Why This Chapter* now precedes the introduction in each chapter, immediately setting the context for what to expect.
- Mechanism problems at the ends of chapters are now grouped together so that they are easily located.
- Many new problems at the ends of chapters have been added, including 108 new mechanism-drawing practice problems and new spectroscopy and NMR problems.
- *Deeper Look* features have been changed to *Something Extra*, with updated coverage on each topic.
- Seven new *Practice Your Scientific Analysis and Reasoning* essays and corresponding questions modeled on professional tests such as the MCAT. Topics focus on the latest developments in the medical, pharmaceutical, or biological application of organic chemistry. Topics include: *The Chiral Drug Thalidomide*, *From Mustard Gas to Alkylating Anticancer Drugs*, *Photodynamic Therapy (PDT)*, *Selective Serotonin Reuptake Inhibitors (SSRIs)*, *Thymine in DNA*, *Melatonin and Serotonin*, and *The Potent Antibiotic Traits of Endiandric Acid C*.



In addition to seven new *Practice Your Scientific Analysis and Reasoning* sections, specific changes within individual chapters include:

- Chapter 2—*Polar Covalent Bonds; Acids and Bases*. Formal charge figures have been added for greater accuracy. New mechanism problems have been added at the end of the chapter.
- Chapter 3—*Organic Compounds: Alkanes and Their Stereochemistry*. Figures and steps for naming alkanes have been revised based on user feedback.
- Chapter 6—*An Overview of Organic Reactions*. New problems have been added to the end of the chapter, including new reaction mechanism problems.
- Chapter 7—*Alkenes: Structure and Reactivity*. Alkene Stereochemistry has been updated with expanded examples for practicing *E* and *Z* geometry. Additional practice problems on mechanisms have been added to the end of the chapter.
- Chapter 8—*Alkenes: Reactions and Synthesis*. New mechanism practice problems have been added at the end of the chapter.
- Chapter 9—*Alkynes: An Introduction to Organic Synthesis*. Sections on alkyne nomenclature and reactions of alkynes have been updated for greater accuracy. New mechanism problems have been added to the end of the chapter.
- Chapter 10—*Organohalides*. Suzuki–Miyaura reactions, curved-arrow drawings, and electron-pushing mechanisms are emphasized in new problems at the end of the chapter.
- Chapter 11—*Reactions of Alkyl Halides: Nucleophilic Substitutions and Eliminations*. There are additional end-of-chapter problems, with particular focus on elimination-reaction mechanisms.
- Chapter 12—*Structure Determination: Mass Spectrometry and Infrared Spectroscopy*. Expanded discussion on interpreting mass spectra, additional examples, and new problems have been added.
- Chapter 13—*Structure Determination: Nuclear Magnetic Resonance Spectroscopy*. Discussions on the theory of nuclear magnetic resonance and the interpretation of NMR data have been expanded and reorganized, and new NMR problems have been added.
- Chapter 14—*Conjugated Compounds and Ultraviolet Spectroscopy*. New problems have been added to the end of the chapter, including mechanism problems.
- Chapter 15—*Benzene and Aromaticity*. The discussion of spectroscopic characterization of benzene derivatives has been expanded. New mechanism and spectroscopy problems have been added to the end of the chapter.
- Chapter 16—*Chemistry of Benzene: Electrophilic Aromatic Substitution*. New problems have been added to the end of the chapter, including mechanism practice problems.
- Chapter 17—*Alcohols and Phenols*. New spectroscopy examples and problems have been added, along with new mechanism problems at the end of the chapter.
- Chapter 18—*Ethers and Epoxides; Thiols and Sulfides*. New spectroscopy examples and problems have been added, along with new mechanism problems at the end of the chapter.

- Chapter 19—*Aldehydes and Ketones: Nucleophilic Addition Reactions*. The discussion of IR and NMR spectroscopy of aldehydes/ketones has been expanded. New NMR problems and mechanism practice problems have been added.
- Chapter 20—*Carboxylic Acids and Nitriles*. The discussion of IR and NMR spectroscopy of carboxylic acid has been updated. New problems have been added to the end of the chapter, including mechanism and spectroscopy problems.
- Chapter 21—*Carboxylic Acid Derivatives: Nucleophilic Acyl Substitution Reactions*. The discussion of electronic effects in the IR and NMR spectroscopy of carboxylic acid derivatives has been expanded with two new end-of-chapter IR spectroscopy problems, along with new mechanism problems. Four new worked examples on synthesizing esters, amides, and amines have also been added.
- Chapter 22 and Chapter 23—*Carbonyl Alpha-Substitution Reactions; Carbonyl Condensation Reactions*. New problems have been added to the end of the chapter, including additional mechanism practice problems.
- Chapter 24—*Amines and Heterocycles*. The discussion of IR and NMR spectroscopy of amines has been updated, and new spectroscopy and mechanism practice problems have been added to the end of the chapter.
- Chapter 25—*Biomolecules: Carbohydrates*. The coverage of other important carbohydrates was expanded, and the worked examples related to drawing Fischer projections were revised.
- Chapter 26—*Biomolecules: Amino Acids, Peptides, and Proteins*. The *Something Extra* feature on the Protein Data Bank was revised and updated to make it more current.
- Chapter 28—*Biomolecules: Nucleic Acids*. Content on DNA sequencing and DNA synthesis was updated and revised.



Features

- The “Why This Chapter?” section is a short paragraph that appears before the introduction to every chapter and tells students why the material about to be covered is important.
- Each Worked Example includes a Strategy and a detailed Solution and is followed by problems for students to try on their own. This book has more than 1800 in-text and end-of-chapter problems.
- An overview chapter, *A Preview of Carbonyl Chemistry*, follows Chapter 18 and emphasizes the idea that studying organic chemistry requires both summarizing and looking ahead.
- The *Visualizing Chemistry Problems* that begin the exercises at the end of each chapter offer students an opportunity to see chemistry in a different way by visualizing molecules rather than by simply interpreting structural formulas.
- New *Mechanism Problems* sections were added to the end-of-chapter problems for most of the chapters. Mechanism-type problems are now grouped together under this topic title.

- The new *Practice Your Scientific Analysis and Reasoning* feature provides two-page essays and corresponding professional exam-style questions on special topics related to medical, pharmaceutical, and biological applications of organic chemistry. These sections are located at various points throughout the book. Essays and questions touch on organic chemistry content from preceding chapters. The multiple-choice format of the questions is modeled on professional exams such as the MCAT. The focus is on reinforcing the foundations of organic chemistry through practical application and real-world examples.
- Applied essays called *Something Extra* complement the text and highlight applications to chemistry. They include, “Where Do Drugs Come From?” in Chapter 6 and “Molecular Mechanics” in Chapter 4.
- *Summaries* and *Key Word* lists help students by outlining the key concepts of each chapter.
- *Summaries of Reactions* at the ends of appropriate chapters bring together the key reactions from the chapter in one complete list.

Alternate Editions

***Organic Chemistry*, Ninth Edition Hybrid Version with Access (24 months) to OWLv2 with MindTap Reader**

ISBN: 9781305084445

This briefer, paperbound version of *Organic Chemistry*, Ninth Edition does not contain the end-of-chapter problems, which can be assigned in OWL, the online homework and learning system for this book. Access to OWLv2 and the MindTap Reader eBook is included with the Hybrid version. The MindTap Reader version includes the full text, with all end-of-chapter questions and problem sets.

Supporting Materials

Please visit <http://www.cengage.com/chemistry/mcmurry/oc9e> to learn about student and instructor resources for this text, including custom versions and laboratory manuals.

Special Contributions

This revision would not have been possible without the work of several key contributors. Special thanks go to KC Russell of Northern Kentucky University for writing the many new mechanism questions that appear in this edition; to James S. Vyvyan of Western Washington University for reshaping the NMR and spectroscopy discussions and corresponding problems throughout the book; to Andrew Frazer of the University of Central Florida for creating the new *Practice Your Scientific Analysis and Reasoning* sections and Gordon W. Gribble of Dartmouth College for assisting in their development; and to Jordan

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Reviewers

This book has benefited greatly from the helpful comments and suggestions of those who have reviewed it. They include:

Reviewers of the Ninth Edition

Peter Bell, Tarleton State University
Andrew Frazer, University of Central Florida
Stephen Godleski, State University of New York–Brockport
Susan Klein, Manchester College
Barbara Mayer, California State University–Fresno
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Pauline Schwartz, University of New Haven
Gabriela Smeureanu, Hunter College
Douglas C. Smith, California State University–San Bernardino
Linfeng Xie, University of Wisconsin–Oshkosh
Yan Zhao, Iowa State University

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Darren Johnson, University of Oregon
Ernest G. Nolen, Colgate University
Douglas C. Smith, California State University–San Bernardino
Gary Sulikowski, Vanderbilt University
Richard Weiss, Georgetown University
Yan Zhao, Iowa State University

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Arthur W. Bull, Oakland University
Robert Coleman, Ohio State University
Nicholas Drapela, Oregon State University
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Joseph B. Lambert, Northwestern University

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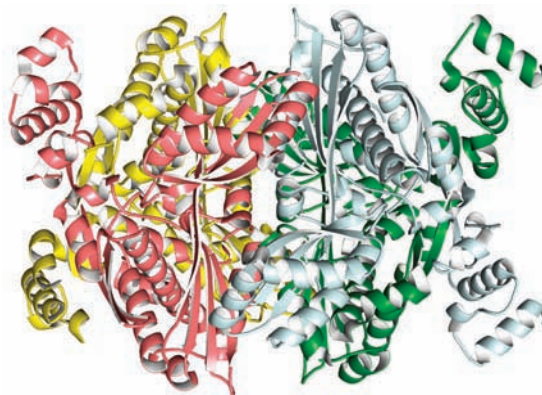
Thomas A. Newton, University of Southern Maine

Michael Rathke, Michigan State University

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Structure and Bonding

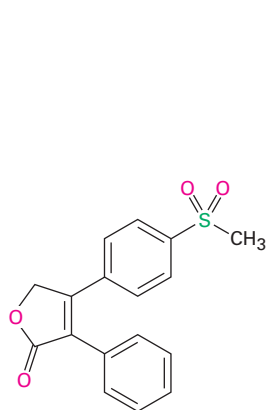
The enzyme HMG-CoA reductase, shown here as a so-called ribbon model, catalyzes a crucial step in the body's synthesis of cholesterol. Understanding how this enzyme functions has led to the development of drugs credited with saving millions of lives.



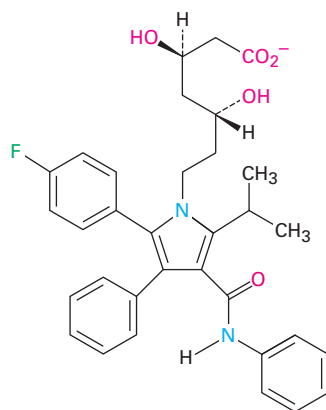
WHY THIS CHAPTER?

We'll ease into the study of organic chemistry by first reviewing some ideas about atoms, bonds, and molecular geometry that you may recall from your general chemistry course. Much of the material in this chapter and the next is likely to be familiar to you, but it's nevertheless a good idea to make sure you understand it before moving on.

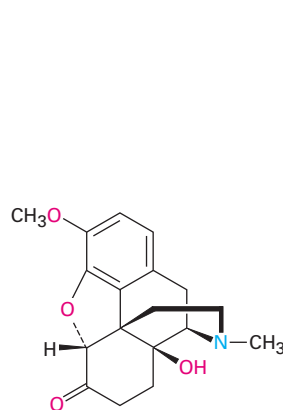
What is organic chemistry, and why should you study it? The answers to these questions are all around you. Every living organism is made of organic chemicals. The proteins that make up your hair, skin, and muscles; the DNA that controls your genetic heritage; the foods that nourish you; and the medicines that heal you are all organic chemicals. Anyone with a curiosity about life and living things, and anyone who wants to be a part of the remarkable advances now occurring in medicine and the biological sciences, must first understand organic chemistry. Look at the following drawings for instance, which show the chemical structures of some molecules whose names might be familiar to you. Although the drawings may appear unintelligible at this point, don't worry. Before long, they'll make perfectly good sense, and you'll soon be drawing similar structures for any substance you're interested in.



Rofecoxib
(Vioxx)



Atorvastatin
(Lipitor)



Oxycodone
(OxyContin)

1

Continued ►

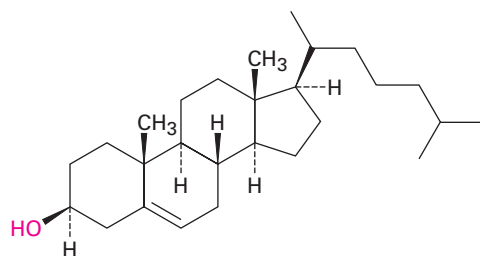
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- 1-2 Atomic Structure: Orbitals
- 1-3 Atomic Structure: Electron Configurations
- 1-4 Development of Chemical Bonding Theory
- 1-5 Describing Chemical Bonds: Valence Bond Theory
- 1-6 sp^3 Hybrid Orbitals and the Structure of Methane
- 1-7 sp^3 Hybrid Orbitals and the Structure of Ethane
- 1-8 sp^2 Hybrid Orbitals and the Structure of Ethylene
- 1-9 sp Hybrid Orbitals and the Structure of Acetylene
- 1-10 Hybridization of Nitrogen, Oxygen, Phosphorus, and Sulfur
- 1-11 Describing Chemical Bonds: Molecular Orbital Theory
- 1-12 Drawing Chemical Structures

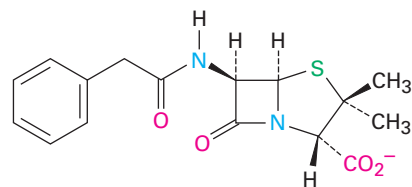
SOMETHING EXTRA

Organic Foods: Risk versus Benefit





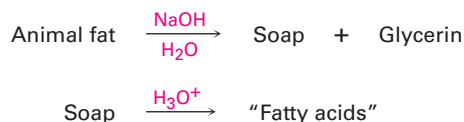
Cholesterol



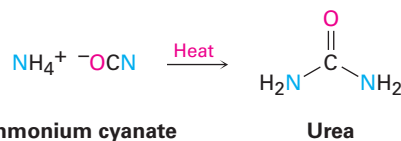
Benzylpenicillin

The foundations of organic chemistry date from the mid-1700s, when chemistry was evolving from an alchemist's art into a modern science. Little was known about chemistry at that time, and the behavior of the “organic” substances isolated from plants and animals seemed different from that of the “inorganic” substances found in minerals. Organic compounds were generally low-melting solids and were usually more difficult to isolate, purify, and work with than high-melting inorganic compounds.

To many chemists, the simplest explanation for the difference in behavior between organic and inorganic compounds was that organic compounds contained a peculiar “vital force” as a result of their origin in living sources. Because of this vital force, chemists believed, organic compounds could not be prepared and manipulated in the laboratory as could inorganic compounds. As early as 1816, however, this vitalistic theory received a heavy blow when Michel Chevreul found that soap, prepared by the reaction of alkali with animal fat, could be separated into several pure organic compounds, which he termed *fatty acids*. For the first time, one organic substance (fat) was converted into others (fatty acids plus glycerin) without the intervention of an outside vital force.



Little more than a decade later, the vitalistic theory suffered further when Friedrich Wöhler discovered in 1828 that it was possible to convert the “inorganic” salt ammonium cyanate into the “organic” substance urea, which had previously been found in human urine.



By the mid-1800s, the weight of evidence was clearly against the vitalistic theory and it was clear that there was no fundamental difference between organic and inorganic compounds. The same fundamental principles explain the behaviors of all substances, regardless of origin or complexity. The only distinguishing characteristic of organic compounds is that all contain the element carbon.

Organic chemistry, then, is the study of carbon compounds. But why is carbon special? Why, of the more than 50 million presently known chemical

compounds, do most of them contain carbon? The answers to these questions come from carbon's electronic structure and its consequent position in the periodic table (FIGURE 1-1). As a group 4A element, carbon can share four valence electrons and form four strong covalent bonds. Furthermore, carbon atoms can bond to one another, forming long chains and rings. Carbon, alone of all elements, is able to form an immense diversity of compounds, from the simple methane, with one carbon atom, to the staggeringly complex DNA, which can have more than *100 million* carbons.

Group 1A																	8A
H	2A											3A	4A	5A	6A	7A	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	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															

FIGURE 1-1 The position of carbon in the periodic table. Other elements commonly found in organic compounds are shown in the colors typically used to represent them.

Of course, not all carbon compounds are derived from living organisms. Modern chemists have developed a remarkably sophisticated ability to design and synthesize new organic compounds in the laboratory—medicines, dyes, polymers, and a host of other substances. Organic chemistry touches the lives of everyone; its study can be a fascinating undertaking.

1-1 Atomic Structure: The Nucleus

As you probably know from your general chemistry course, an atom consists of a dense, positively charged nucleus surrounded at a relatively large distance by negatively charged electrons (FIGURE 1-2). The nucleus consists of subatomic particles called protons, which are positively charged, and neutrons, which are electrically neutral. Because an atom is neutral overall, the number of positive protons in the nucleus and the number of negative electrons surrounding the nucleus are the same.

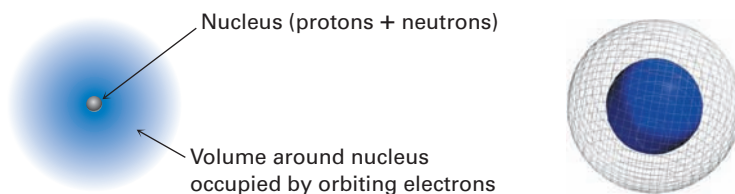


FIGURE 1-2 A schematic view of an atom. The dense, positively charged nucleus contains most of the atom's mass and is surrounded by negatively charged electrons. The three-dimensional view on the right shows calculated electron-density surfaces. Electron density increases steadily toward the nucleus and is 40 times greater at the blue solid surface than at the gray mesh surface.

Although extremely small—about 10^{-14} to 10^{-15} meter (m) in diameter—the nucleus nevertheless contains essentially all the mass of the atom. Electrons have negligible mass and circulate around the nucleus at a distance of approximately 10^{-10} m. Thus, the diameter of a typical atom is about 2×10^{-10} m, or 200 picometers (pm), where $1 \text{ pm} = 10^{-12}$ m. To give you an idea of how small this is, a thin pencil line is about 3 million carbon atoms wide. Many organic chemists and biochemists, particularly in the United States, still use the unit *angstrom* (Å) to express atomic distances, where $1 \text{ Å} = 100 \text{ pm} = 10^{-10}$ m, but we'll stay with the SI unit picometer in this book.

A specific atom is described by its *atomic number* (Z), which gives the number of protons (or electrons) it contains, and its *mass number* (A), which gives the total number of protons and neutrons in its nucleus. All the atoms of a given element have the same atomic number—1 for hydrogen, 6 for carbon, 15 for phosphorus, and so on—but they can have different mass numbers depending on how many neutrons they contain. Atoms with the same atomic number but different mass numbers are called **isotopes**.

The weighted-average mass in atomic mass units (amu) of an element's naturally occurring isotopes is called atomic mass (or atomic weight)—1.008 amu for hydrogen, 12.011 amu for carbon, 30.974 amu for phosphorus, and so on. Atomic masses of the elements are given in the periodic table in the front of this book.

1-2 Atomic Structure: Orbitals

How are the electrons distributed in an atom? You might recall from your general chemistry course that, according to the quantum mechanical model, the behavior of a specific electron in an atom can be described by a mathematical expression called a *wave equation*—the same type of expression used to describe the motion of waves in a fluid. The solution to a wave equation is called a *wave function*, or **orbital**, and is denoted by the Greek letter psi (ψ).

By plotting the square of the wave function, ψ^2 , in three-dimensional space, an orbital describes the volume of space around a nucleus that an electron is most likely to occupy. You might therefore think of an orbital as looking like a photograph of the electron taken at a slow shutter speed. In such a photo, the orbital would appear as a blurry cloud, indicating the region of space where the electron has been. This electron cloud doesn't have a sharp boundary, but for practical purposes we can set its limits by saying that an orbital represents the space where an electron spends 90% to 95% of its time.

What do orbitals look like? There are four different kinds of orbitals, denoted s , p , d , and f , each with a different shape. Of the four, we'll be concerned primarily with s and p orbitals because these are the most common in organic and biological chemistry. An s orbital is spherical, with the nucleus at its center; a p orbital is dumbbell-shaped; and four of the five d orbitals are cloverleaf-shaped, as shown in **FIGURE 1-3**. The fifth d orbital is shaped like an elongated dumbbell with a doughnut around its middle.

The orbitals in an atom are organized into different **electron shells**, centered around the nucleus and having successively larger size and energy. Different shells contain different numbers and kinds of orbitals, and each orbital

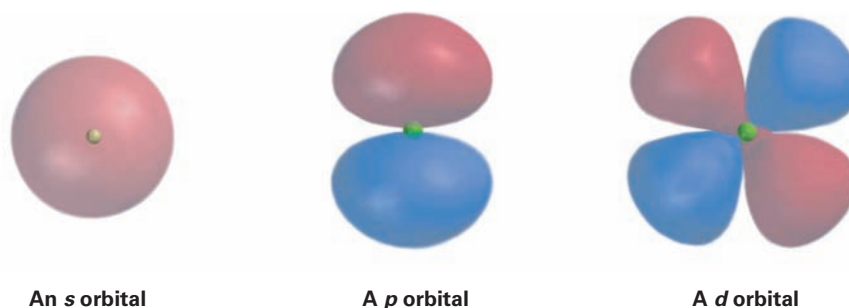


FIGURE 1-3 Representations of *s*, *p*, and *d* orbitals. An *s* orbital is spherical, a *p* orbital is dumbbell-shaped, and four of the five *d* orbitals are cloverleaf-shaped. Different colors of *p* and *d* orbitals are often drawn for convenience as teardrops, but their actual shape is more like that of a doorknob, as indicated.

within a shell can be occupied by two electrons. The first shell contains only a single *s* orbital, denoted $1s$, and thus holds only 2 electrons. The second shell contains one $2s$ orbital and three $2p$ orbitals and thus holds a total of 8 electrons. The third shell contains a $3s$ orbital, three $3p$ orbitals, and five $3d$ orbitals, for a total capacity of 18 electrons. These orbital groupings and their energy levels are shown in **FIGURE 1-4**.

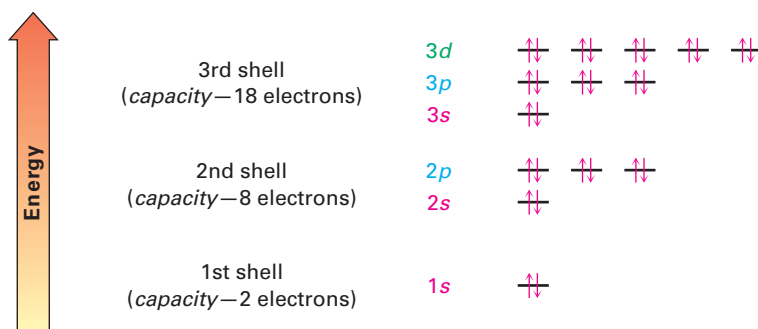


FIGURE 1-4 The energy levels of electrons in an atom. The first shell holds a maximum of 2 electrons in one $1s$ orbital; the second shell holds a maximum of 8 electrons in one $2s$ and three $2p$ orbitals; the third shell holds a maximum of 18 electrons in one $3s$, three $3p$, and five $3d$ orbitals; and so on. The two electrons in each orbital are represented by up and down arrows, $\uparrow\downarrow$. Although not shown, the energy level of the $4s$ orbital falls between $3p$ and $3d$.

The three different *p* orbitals within a given shell are oriented in space along mutually perpendicular directions, denoted p_x , p_y , and p_z . As shown in **FIGURE 1-5**, the two lobes of each *p* orbital are separated by a region of zero electron density called a **node**. Furthermore, the two orbital regions separated by the node have different algebraic signs, + and −, in the wave function, as represented by the different colors in Figure 1-5. We'll see in **Section 1-11** that these algebraic signs for different orbital lobes have important consequences with respect to chemical bonding and chemical reactivity.

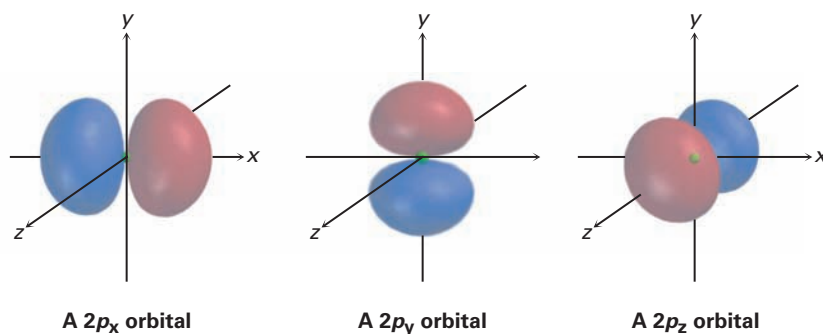


FIGURE 1-5 Shapes of the $2p$ orbitals. Each of the three mutually perpendicular, dumbbell-shaped orbitals has two lobes separated by a node. The two lobes have different algebraic signs in the corresponding wave function, as indicated by the different colors.

1-3 Atomic Structure: Electron Configurations

The lowest-energy arrangement, or **ground-state electron configuration**, of an atom is a listing of the orbitals occupied by its electrons. We can predict this arrangement by following three rules.

RULE 1

The lowest-energy orbitals fill up first, according to the order $1s \rightarrow 2s \rightarrow 2p \rightarrow 3s \rightarrow 3p \rightarrow 4s \rightarrow 3d$, a statement called the *Aufbau principle*. Note that the $4s$ orbital lies between the $3p$ and $3d$ orbitals.

RULE 2

Electrons act in some ways as if they were spinning around an axis, somewhat like how the earth spins. This spin can have two orientations, denoted as up (\uparrow) and down (\downarrow). Only two electrons can occupy an orbital, and they must be of opposite spin, a statement called the *Pauli exclusion principle*.

RULE 3

If two or more empty orbitals of equal energy are available, one electron occupies each with spins parallel until all orbitals are half-full, a statement called *Hund's rule*.

Some examples of how these rules apply are shown in **TABLE 1-1**. Hydrogen, for instance, has only one electron, which must occupy the lowest-energy orbital. Thus, hydrogen has a $1s$ ground-state configuration. Carbon has six electrons and the ground-state configuration $1s^2 2s^2 2p_x^1 2p_y^1$, and so forth. Note that a superscript is used to represent the number of electrons in a particular orbital.

PROBLEM 1-1

Give the ground-state electron configuration for each of the following elements:

(a) Oxygen (b) Nitrogen (c) Sulfur

PROBLEM 1-2

How many electrons does each of the following elements have in its outermost electron shell?

(a) Magnesium (b) Cobalt (c) Selenium

TABLE 1-1 Ground-State Electron Configurations of Some Elements

Element	Atomic number	Configuration	Element	Atomic number	Configuration
Hydrogen	1	$1s \uparrow$	Phosphorus	15	$3p \uparrow \uparrow \uparrow$
Carbon	6	$2p \uparrow \uparrow \text{—}$			$3s \uparrow\downarrow$
		$2s \uparrow\downarrow$			$2p \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow$
		$1s \uparrow\downarrow$			$2s \uparrow\downarrow$
					$1s \uparrow\downarrow$

1-4 Development of Chemical Bonding Theory

By the mid-1800s, the new science of chemistry was developing rapidly and chemists had begun to probe the forces holding compounds together. In 1858, August Kekulé and Archibald Couper independently proposed that, in all organic compounds, carbon is *tetravalent*—it always forms four bonds when it joins other elements to form stable compounds. Furthermore, said Kekulé, carbon atoms can bond to one another to form extended chains of linked atoms. In 1865, Kekulé provided another major advance when he suggested that carbon chains can double back on themselves to form *rings* of atoms.

Although Kekulé and Couper were correct in describing the tetravalent nature of carbon, chemistry was still viewed in a two-dimensional way until 1874. In that year, Jacobus van 't Hoff and Joseph Le Bel added a third dimension to our ideas about organic compounds when they proposed that the four bonds of carbon are not oriented randomly but have specific spatial directions. Van 't Hoff went even further and suggested that the four atoms to which carbon is bonded sit at the corners of a regular tetrahedron, with carbon in the center.

A representation of a tetrahedral carbon atom is shown in **FIGURE 1-6**. Note the conventions used to show three-dimensionality: solid lines represent bonds in the plane of the page, the heavy wedged line represents a bond coming out of the page toward the viewer, and the dashed line represents a bond receding back behind the page, away from the viewer. These representations will be used throughout the text.

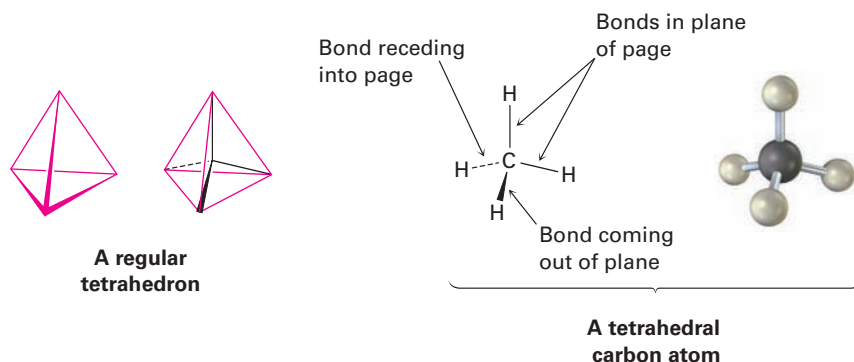


FIGURE 1-6 A representation of a tetrahedral carbon atom. The solid lines represent bonds in the plane of the paper, the heavy wedged line represents a bond coming out of the plane of the page, and the dashed line represents a bond going back behind the plane of the page.

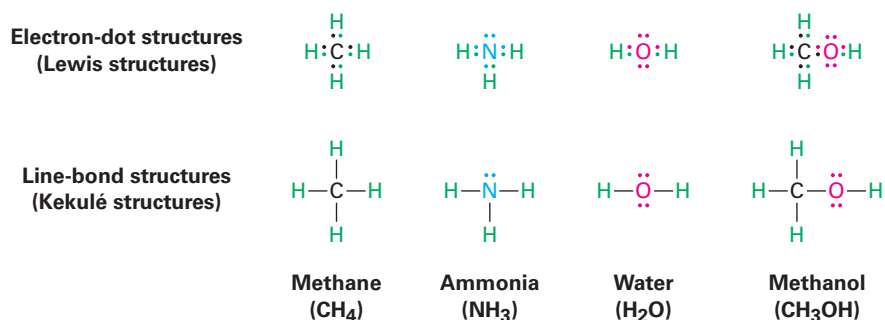
Why, though, do atoms bond together, and how can bonds be described electronically? The *why* question is relatively easy to answer: atoms bond together because the compound that results is more stable and lower in energy than the separate atoms. Energy—usually as heat—always flows out of the chemical system when a bond forms. Conversely, energy must be put into the chemical system to break a bond. Making bonds always releases energy, and breaking bonds always absorbs energy. The *how* question is more difficult. To answer it, we need to know more about the electronic properties of atoms.

We know through observation that eight electrons (an electron *octet*) in an atom's outermost shell, or **valence shell**, impart special stability to the noble-gas elements in group 8A of the periodic table: Ne (2 + 8); Ar (2 + 8 + 8); Kr (2 + 8 + 18 + 8). We also know that the chemistry of main-group elements

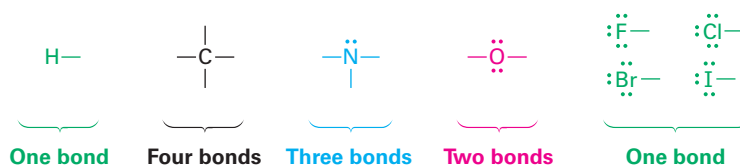
is governed by their tendency to take on the electron configuration of the nearest noble gas. The alkali metals in group 1A, for example, achieve a noble-gas configuration by losing the single s electron from their valence shell to form a cation, while the halogens in group 7A achieve a noble-gas configuration by gaining a p electron to fill their valence shell and form an anion. The resultant ions are held together in compounds like $\text{Na}^+ \text{Cl}^-$ by an electrostatic attraction that we call an *ionic bond*.

But how do elements closer to the middle of the periodic table form bonds? Look at methane, CH_4 , the main constituent of natural gas, for example. The bonding in methane is not ionic because it would take too much energy for carbon ($1s^2 2s^2 2p^2$) either to gain or lose four electrons to achieve a noble-gas configuration. As a result, carbon bonds to other atoms, not by gaining or losing electrons, but by sharing them. Such a shared-electron bond, first proposed in 1916 by G. N. Lewis, is called a **covalent bond**. The neutral collection of atoms held together by covalent bonds is called a **molecule**.

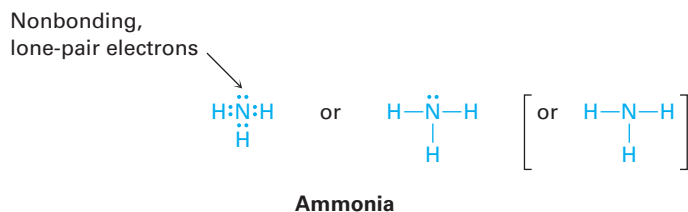
A simple way of indicating the covalent bonds in molecules is to use what are called *Lewis structures*, or **electron-dot structures**, in which the valence-shell electrons of an atom are represented as dots. Thus, hydrogen has one dot representing its $1s$ electron, carbon has four dots ($2s^2 2p^2$), oxygen has six dots ($2s^2 2p^4$), and so on. A stable molecule results whenever a noble-gas configuration is achieved for all the atoms—eight dots (an octet) for main-group atoms or two dots for hydrogen. Simpler still is the use of *Kekulé structures*, or **line-bond structures**, in which a two-electron covalent bond is indicated as a line drawn between atoms.



The number of covalent bonds an atom forms depends on how many additional valence electrons it needs to reach a noble-gas configuration. Hydrogen has one valence electron ($1s$) and needs one more to reach the helium configuration ($1s^2$), so it forms one bond. Carbon has four valence electrons ($2s^2 2p^2$) and needs four more to reach the neon configuration ($2s^2 2p^6$), so it forms four bonds. Nitrogen has five valence electrons ($2s^2 2p^3$), needs three more, and forms three bonds; oxygen has six valence electrons ($2s^2 2p^4$), needs two more, and forms two bonds; and the halogens have seven valence electrons, need one more, and form one bond.



Valence electrons that are not used for bonding are called **lone-pair electrons**, or *nonbonding electrons*. The nitrogen atom in ammonia, NH_3 , for instance, shares six valence electrons in three covalent bonds and has its remaining two valence electrons in a nonbonding lone pair. As a time-saving shorthand, nonbonding electrons are often omitted when drawing line-bond structures, but you still have to keep them in mind since they're often crucial in chemical reactions.



Predicting the Number of Bonds Formed by an Atom

Worked Example 1-1

How many hydrogen atoms does phosphorus bond to in forming phosphine, PH_3 ?

Strategy

Identify the periodic group of phosphorus, and find from that how many electrons (bonds) are needed to make an octet.

Solution

Phosphorus is in group 5A of the periodic table and has five valence electrons. It thus needs to share three more electrons to make an octet and therefore bonds to three hydrogen atoms, giving PH_3 .

Drawing Electron-Dot and Line-Bond Structures

Worked Example 1-2

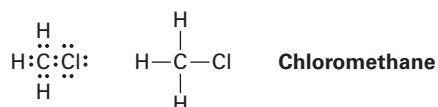
Draw both electron-dot and line-bond structures for chloromethane, CH_3Cl .

Strategy

Remember that a bond—that is, a pair of shared electrons—is represented as a line between atoms.

Solution

Hydrogen has one valence electron, carbon has four valence electrons, and chlorine has seven valence electrons. Thus, chloromethane is represented as



PROBLEM 1-3

Draw a molecule of chloroform, CHCl_3 , using solid, wedged, and dashed lines to show its tetrahedral geometry.