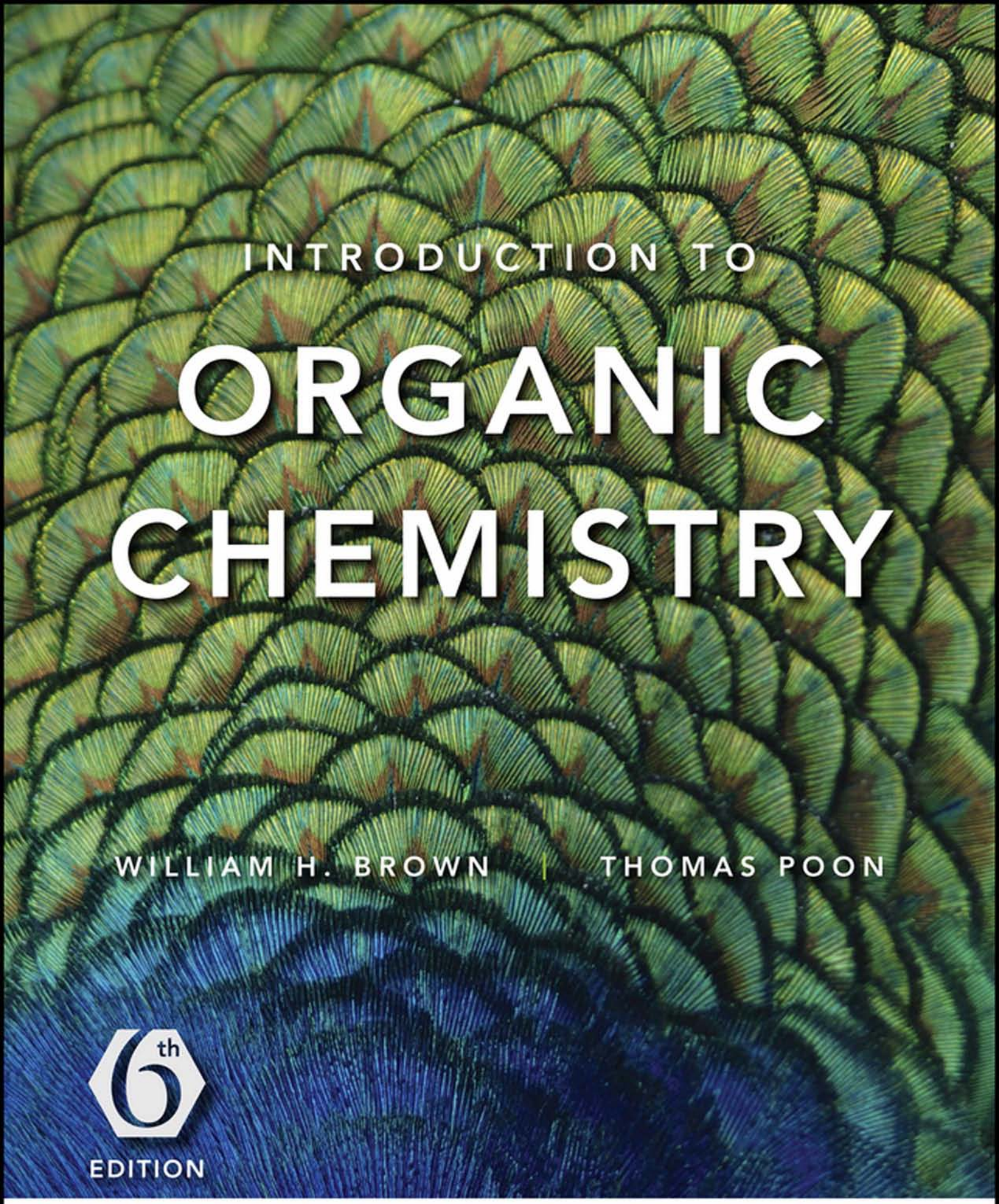

Wiley Binder Version

WILEY

Introduction to **Organic Chemistry**

SIXTH EDITION

WILLIAM H. BROWN
Beloit College

THOMAS POON
Claremont McKenna College
Scripps College
Pitzer College

WILEY

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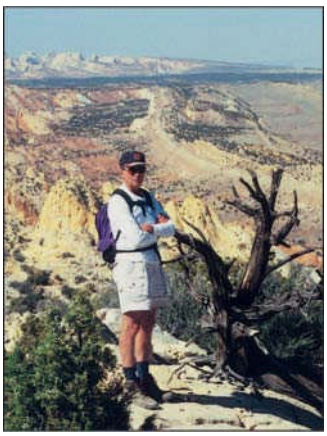
To Carolyn,
with whom life is a joy

Bill Brown

To Cathy and Sophia,
for a lifetime of adventures

Thomas Poon

ABOUT THE AUTHORS



WILLIAM H. BROWN is Professor Emeritus at Beloit College, where he was twice named Teacher of the Year. He is also the author of two other college textbooks: *Organic Chemistry* 5/e, coauthored with Chris Foote, Brent Iverson, and Eric Anslyn, published in 2009, and *General, Organic, and Biochemistry* 9/e, coauthored with Fred Bettelheim, Mary Campbell, and Shawn Farrell, published in 2010. He received his Ph.D. from Columbia University under the direction of Gilbert Stork and did postdoctoral work at California Institute of Technology and the University of Arizona. Twice he was Director of a Beloit College World Affairs Center seminar at the University of Glasgow, Scotland. In 1999, he retired from Beloit College to devote more time to writing and development of educational materials. Although officially retired, he continues to teach Special Topics in Organic Synthesis on a yearly basis.

Bill and his wife Carolyn enjoy hiking in the canyon country of the Southwest. In addition, they both enjoy quilting and quilts.

THOMAS POON is Professor of Chemistry in the W.M. Keck Science Department of Claremont McKenna, Pitzer, and Scripps Colleges, three of the five undergraduate institutions that make up the Claremont Colleges in Claremont, California. He received his B.S. degree from Fairfield University (CT) and his Ph.D. from the University of California, Los Angeles under the direction of Christopher S. Foote. Poon was a Camille and Henry Dreyfus Postdoctoral Fellow under Bradford P. Mundy at Colby College (ME) before joining the faculty at Randolph-Macon College (VA) where he received the Thomas Branch Award for Excellence in Teaching in 1999. He was a visiting scholar at Columbia University (NY) in 2002 (and again in 2004) where he worked on projects in both research and education with his late friend and mentor, Nicholas J. Turro. He has taught organic chemistry, forensic chemistry, upper-level courses in advanced laboratory techniques, and a first-year seminar class titled *Science of Identity*. His favorite activity is working alongside undergraduates in the laboratory on research problems involving the investigation of synthetic methodology in zeolites, zeolite photochemistry, natural products isolation, and reactions of singlet oxygen.

When not in the lab, he likes to play guitar and sing chemistry songs to his students and to his daughter Sophie.

CONTENTS OVERVIEW

CONTENTS

Goals of This Text

This text is designed for an introductory course in organic chemistry and assumes, as background, a prior course of general chemistry. Both its form and content have been shaped by our experiences in the classroom and by our assessment of the present and future direction of the brief organic course.

A brief course in organic chemistry must achieve several goals. First, most students who elect this course are oriented toward careers in science, but few if any intend to become professional chemists; rather, they are preparing for careers in areas that require a grounding in the essentials of organic chemistry. Here is the place to examine the structure, properties, and reactions of rather simple molecules. Students can then build on this knowledge in later course work and professional life.

Second, an introductory course must portray something of the scope and content of organic chemistry as well as its tremendous impact on the ways we live and work. To do this, we have included specific examples of pharmaceuticals, plastics, soaps and detergents, natural and synthetic textile fibers, petroleum refining, petrochemicals, pesticides, artificial flavoring agents, chemical ecology, and so on at appropriate points in the text.

Third, a brief course must convince students that organic chemistry is more than just a catalog of names and reactions. There are certain organizing themes or principles, which not only make the discipline easier to understand, but also provide a way to analyze new chemistry. The relationship between molecular structure and chemical reactivity is one such theme. Electronic theory of organic chemistry, including Lewis structures, atomic orbitals, the hybridization of atomic orbitals, and the theory of resonance are presented in Chapter 1. Chapter 2 explores the relationship between molecular structure and one chemical property, namely, acidity and basicity. Variations in acidity and basicity among organic compounds are correlated using the concepts of electronegativity, the inductive effect, and resonance. These same concepts are used throughout the text in discussions of molecular structure and chemical reactivity. Stereochemistry is a second theme that recurs throughout the text. The concept and importance of the spatial arrangement of atoms is introduced in Chapter 3 with the concept of conformations in alkanes and cycloalkane, followed by *cis/trans* isomerism in Chapters 3 (in cycloalkanes) and 4 (in alkenes). Molecular symmetry and asymmetry, enantiomers and absolute configuration, and the significance of asymmetry in the biological world are discussed in Chapter 6. The concept of a mechanistic understanding of the reactions of organic substances is a third major theme. Reaction mechanisms are first presented in Chapter 5; they not only help to minimize memory work but also provide a satisfaction that comes from an understanding of the molecular logic that governs how and why organic reactions occur as they do. In this chapter we present a set of five fundamental patterns that are foundational to the molecular logic of organic reactions. An understanding and application of these patterns will not only help to minimize memory work but also provide a satisfaction that comes from an understanding of how and why organic reactions occur as they do.

The Audience

This book provides an introduction to organic chemistry for students who intend to pursue careers in the sciences and who require a grounding in organic chemistry. For this reason, we make a special effort throughout to show the interrelation between organic chemistry and other areas of science, particularly the biological and health sciences. While studying with this book, we hope that students will see that organic chemistry is a tool for these many disciplines, and that organic compounds, both natural and synthetic, are all around them—in pharmaceuticals, plastics, fibers, agrochemicals, surface coatings, toiletry preparations and cosmetics, food additives, adhesives, and elastomers. Furthermore, we hope that students will recognize that organic chemistry is a dynamic and ever-expanding area of science waiting openly for those who are prepared, both by training and an inquisitive nature, to ask questions and explore.

New Features

- **Modified Chapter Openers** that employ a Guided Inquiry approach to capture students' attention, getting them excited about the material they are about to read.
- **Key Concept Videos:** Created by co-author Tom Poon, these videos are centered on key topics in the text, helping students better understand important concepts.

  Video lectures are denoted by the following icon which can be found throughout the text.
- **More Practice Problems:** We have added over 130 additional practice problems, while keeping in mind the care and attention instructors put into their courses by *not* changing the basic numbering of problems from the previous addition.
- **More Real World Connections:** In order to show the connections between organic chemistry and other disciplines, we have added over 40 references, either in-text or via column elements, to real world products or applications.
- We have reduced the length of the text. Chapter 19, Lipids, along with Chapter 20 Nucleic Acids, and Chapter 21, The Organic Chemistry of Metabolism, will be available in WileyPLUS and on the text website: www.wiley.com/college/brown.

Hallmark Features

- **"Mechanism"** boxes for each mechanism in the book. These Mechanism boxes serve as road maps and present mechanisms using basic steps and recurring themes that are common to most organic reaction mechanisms. This approach allows students to see that reactions have many steps in common, making the reaction easier to understand and remember.
- **"Group Learning Activities"** appear with the end-of-chapter problems and provide students with the opportunity to learn organic chemistry collaboratively, fostering more active learning.
- **"Key Terms and Concepts"** appear within the "Summary of Key Questions."
- **"How To Boxes":** Step-by-step How To guides for approaching problems and concepts that students often find difficult.

- **Chemical Connection Boxes** include applications of organic chemistry to the world around us, particularly to the biochemical, health, and biological sciences. The topics covered in these boxes represent real-world applications of organic chemistry and highlight the relevance between organic chemistry and the students' future careers.

- **"Putting It Together" Cumulative Review Questions:** In this text, end-of-chapter problems are organized by section, allowing students to easily refer back to the appropriate section if difficulties arise. We offer a section called Putting It Together (PIT) at the end of Chapters 3, 6, 10, 14, and 17. Each PIT section is structured like an exam would be organized, with questions of varying types (multiple choice, short answer, naming, mechanism problems, predict the products, synthesis problems, etc.) and difficulty.

- **Problem-Solving Strategies:** To help students overcome the challenge of knowing where to begin, we include a strategy step for every worked example in the text. The strategy step will help students to determine the starting point for each of the example problems.

- **Quick Quizzes:** A set of true or false questions, provided at the end of every chapter, is designed to test students' understanding of the basic concepts presented in the chapter. The answers to the quizzes are provided at the bottom of the page so that students can quickly check their progress, and if necessary, return to the appropriate section in the chapter to review the material.

- **Greater Attention to Visual Learning:** Research in knowledge and cognition has shown that visualization and organization can greatly enhance learning. We added over 100 callouts (short dialog bubbles) to highlight important features of many of the illustrations throughout the text. This places most of the important information in one location. When students try to recall a concept or attempt to solve a problem, we hope that they will try to visualize the relevant illustration from the text. They may be pleasantly surprised to find that the visual cues provided by the callouts help them to remember the content as well as the context of the illustration.

Organization: An Overview

Chapters 1–10 begin a study of organic compounds by first reviewing the fundamentals of covalent bonding, the shapes of molecules, and acid-base chemistry. The structures and typical reactions of several important classes of organic compounds are then discussed: alkanes; alkenes and alkynes; haloalkanes; alcohols and ethers; benzene and its derivatives; amines, aldehydes, and ketones; and finally carboxylic acids and their derivatives.

Chapter 11 introduces IR spectroscopy, and 1H-NMR and 13C-NMR spectroscopy. Discussion of spectroscopy requires no more background than what students receive in general chemistry. The chapter is freestanding and can be taken up in any order appropriate to a particular course.

Chapters 12–16 continue the study of organic compounds, including aldehydes and ketones, carboxylic acids, and finally carboxylic acids and their derivatives. Chapter 15 concludes with an introduction to the aldol, Claisen, and Michael reactions, all three of which are important means for the formation of new carbon–carbon bonds. Chapter 16 provides a brief introduction to organic polymer chemistry.

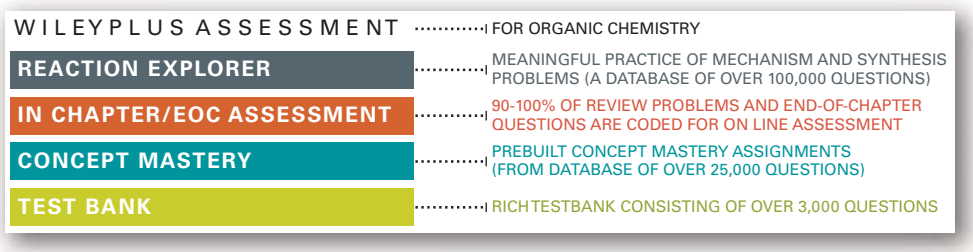
Chapters 17–20 present an introduction to the organic chemistry of carbohydrates; amino acids and proteins; nucleic acids; and lipids. Chapter 21, The Organic Chemistry of Metabolism, demonstrates how the chemistry developed to this point can be applied to an understanding of three major metabolic pathways—glycolysis, the β-oxidation of fatty acids, and the citric acid cycle.

WileyPLUS for Organic Chemistry

What do students receive with WileyPLUS?

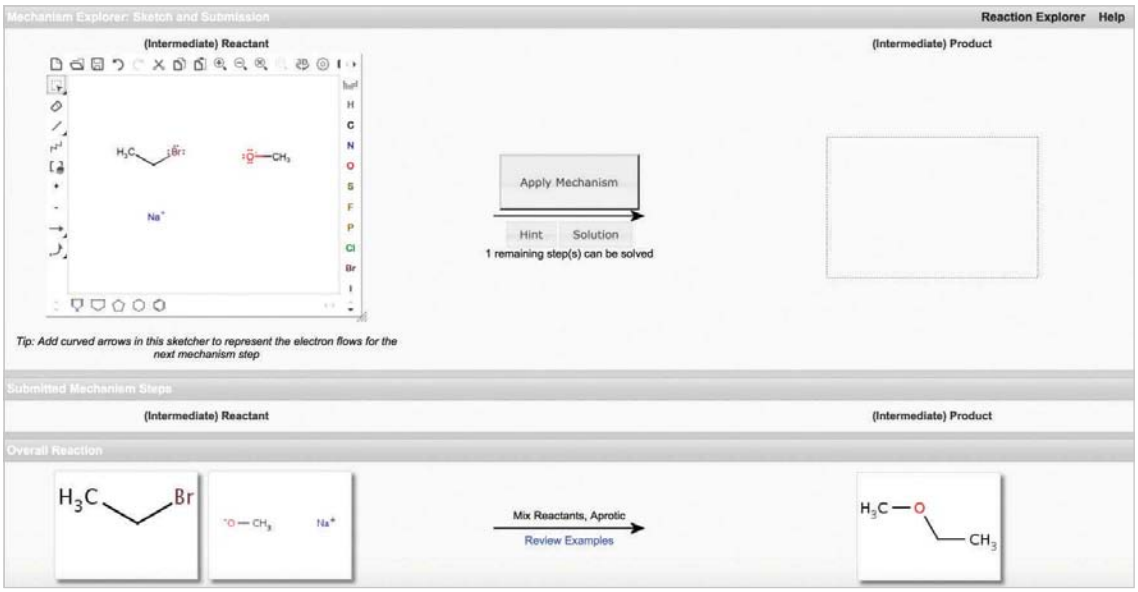
- The complete digital textbook, saving students up to 60% off the cost of the printed text.
- Question assistance, including links to relevant sections in the online digital textbook.
- Immediate feedback and proof of progress, 24/7.
- Integrated, multi-media resources that address your students' unique learning styles, levels of proficiency, and levels of preparation by providing multiple study paths and encourage more active learning.

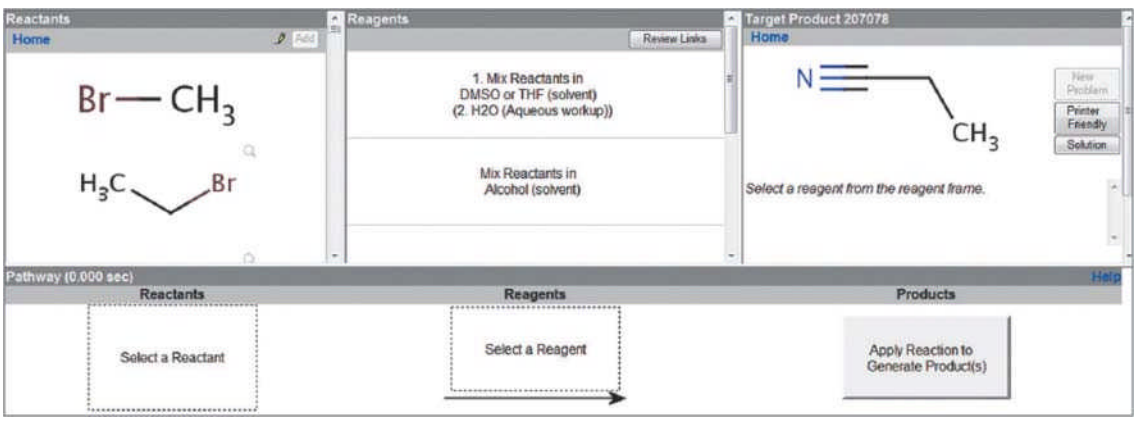
Four unique silos of assessment are available to instructors for creating online homework and quizzes and are designed to enable and support problem-solving skill development and conceptual understanding:

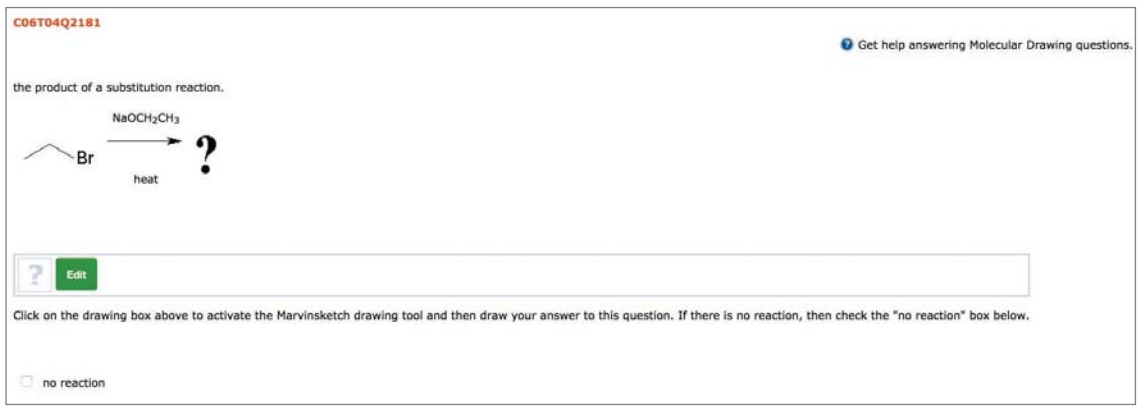


Reaction Explorer—Students' ability to understand mechanisms and predict synthesis reactions greatly impacts their level of success in the course. **Reaction Explorer** is an interactive system for **learning and practicing reactions**, **syntheses**, and **mechanisms** in organic chemistry with advanced support for the automatic generation of random problems and curved arrow mechanism diagrams.

Mechanism Explorer provides valuable practice of reactions and mechanisms.







Synthesis Explorer provides meaningful practice of single and multistep synthesis.
End-of-Chapter Problems—A subset of the end-of-chapter problems is included for use in *WileyPLUS*. Many of the problems are algorithmic and feature structure drawing/assessment functionality using MarvinSketch, with immediate answer feedback.

Prebuilt Concept Mastery Assignments—Students must continuously practice and work organic chemistry problems in order to master the concepts and skills presented in the course. **Prebuilt concept mastery assignments** offer students ample opportunities for practice in each chapter. Each assignment is organized by topic and features feedback for incorrect answers.

These assignments pull from a unique database of over 25,000 questions, over half of which require students to draw a structure using MarvinSketch.
Test Bank—A robust Test Bank, containing over 2,000 questions, is also available within *WileyPLUS* as an additional resource for creating assignments or tests.

With WileyPLUS, students receive:

- **Key Concept Videos**
- **Chapter Zero: General Chemistry Refresher**: To ensure that students have mastered the necessary prerequisite content from General Chemistry, *WileyPLUS* includes a complete chapter of core General Chemistry topics with corresponding assignments.
- **Office Hour Videos, Solved Problem Videos, and Video Mini-Lectures:** In each chapter, several types of video assistance are included to help students with conceptual understanding and problem-solving strategies. The video mini-lectures focus on challenging concepts; the Office Hours videos take these concepts and apply them to example problems, emulating the experience that a student would get if she or he were to attend office hours and ask for assistance in working a problem. The Solved Problem videos use the solved problems from the book, audio, and a whiteboard. The goal is to illustrate good problem solving strategies.
- **Skill-Building Exercises** that utilize animated exercises, with instant feedback, to reinforce the key skills required to succeed in organic chemistry
- **3D Visualization Animations** that use the latest visual and audio technologies to help students understnd concepts. Instructors can assign quizzes based on these visualizations in *WileyPLUS*

With WileyPLUS, instructors receive:

- QuickStart
- Four unique silos of assessment for creating online homework and quizzes
- Reliable resources that reinforce course goals inside and outside of the classroom

- The ability to easily identify those students who are falling behind by tracking their progress and offering assistance early, even before they come to office hours. *WileyPLUS* simplifies and automates such tasks as student performance assessment, creating assignments, scoring student work, keeping grades, and more.
- Media-rich course materials and assessment content that allow customization of the classroom presentation with a wealth of resources and functionality from PowerPoint slides to a database of rich visuals.

Support Package for Students

Student Solutions Manual: Authored by Felix Lee, of The University of Western Ontario, and reviewed by Professors Brown and Poon. The Student Solutions Manual contains detailed solutions to all problems, including the Quick Quiz questions and the Putting It Together questions.

Support Package for Instructors

All Instructor Resources are available within *WileyPLUS* or they can be accessed by contacting your local Wiley Sales Representative.

PowerPoint Presentations: Authored by William Brown, the PPT lecture slides provide a pre-built set of approximately 700 slides corresponding to every chapter in the text. The slides include examples and illustrations that help reinforce and test students' grasp of organic chemistry concepts. An additional set of PPT slides, featuring the illustrations, figures, and tables from the text, are also available. All PPT slide presentations are customizable to fit your course.

Test Bank: Authored by Stefan Bossmann of Kansas State University, the Test Bank for this edition has been revised and updated to include over 2,000 short-answer, multiple-choice, and true-false questions. It is available in both printed and computerized versions.

Digital Image Library: Images from the text are available online in JPEG format. Instructors may use these to customize their presentations and to provide additional visual support for quizzes and exams.

Acknowledgments

While one or a few persons are listed as "authors" of any textbook, the book is in fact the product of collaboration of many individuals, some obvious and some not so obvious. It is with gratitude that we acknowledge the contributions of the many. We begin with Felix Lee, who has worked with us for so many years on both the solutions manual and the solutions to problems in all parts of the text. His keen eye and chemical expertise has helped to improve this edition in so many ways. A special thanks go to Professor Robert White of Dalhousie University for taking the time to inform us of errors that he found in the previous edition. We also thank Senior Production Editor Patty Donovan at SPi Global for her incredible organizational skills and patience. Speaking of patience, the entire Wiley production and editorial team is to be commended for their patience, skill and professionalism on this project including Joan Kakut, Chemistry Development Editor; Alyson Rentrop, Associate Development Editor, Mallory Fryc, Chemistry Editorial Assistant; Sandra Dumas, Senior Production Editor, and Wendy Lai, Senior Graphic Designer, for her creative contributions to the covers of both this and the previous edition of the text. We thank Sophia Brown for a student's eye view of the PowerPoint Lecture series. Finally, we thank all our students, both past and present, for their many positive interactions over the years that have guided us in creating this textbook.

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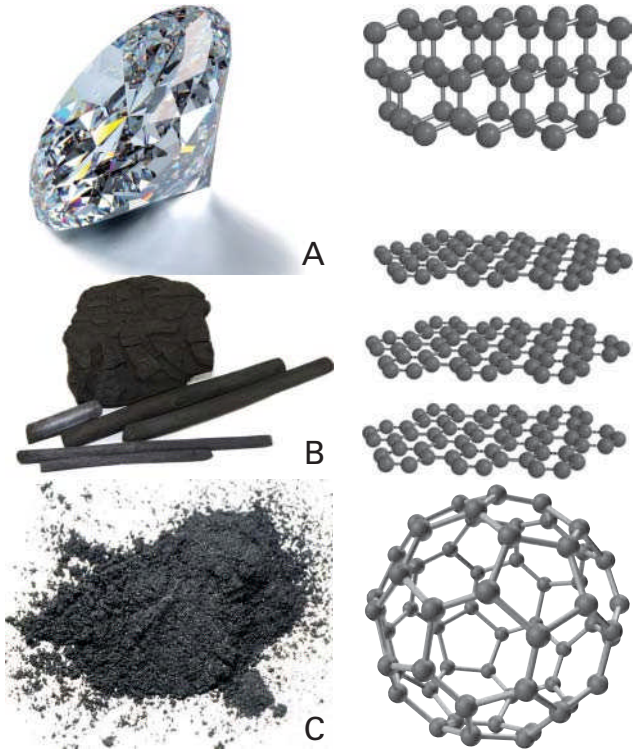

(A) James Steidl/Shutterstock, (B) PortiadeCastro/Getty Images, Inc.
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Three forms of elemental carbon, (A) diamond, (B) graphite, and (C) buckminsterfullerene, along with their molecular models. Notice how vastly different their molecular structures are with diamond having an interconnected network of atoms, graphite existing as sheets, and buckminsterfullerene's atoms arranged like a soccer ball.

Covalent Bonding and Shapes of Molecules

1

KEY QUESTIONS

HOW TO

CHEMICAL CONNECTIONS

WHAT DO THE FOODS THAT WE EAT, the fragrances that we smell, the medicines that we take, the tissues that make up all living things, the fuels that we burn, and the many products that constitute our modern conveniences in life have in common? They all contain **organic compounds**, compounds that consist of at least one carbon and oftentimes other elements such as hydrogen, oxygen, nitrogen, sulfur, and others from the Periodic Table. The study of these compounds is known as **organic chemistry**.

Organic chemistry The study of the chemical and physical properties of the compounds of carbon.

You are about to embark on an exploration of organic chemistry, which spans a large majority of the roughly 88 million chemical substances that have been cataloged. How can one book cover the chemistry of tens of millions of compounds? It turns out that elements commonly arrange themselves in ways that are predictable and that consistently exhibit similar properties. In this chapter, we review how these arrangements of elements such as carbon, hydrogen, oxygen, and nitrogen are achieved through the sharing of electrons to form molecules. We will then learn chemical trends found in these arrangements and use this knowledge to make our study of organic chemistry manageable and fun.

1.1 How Do We Describe the Electronic Structure of Atoms?

You are already familiar with the fundamentals of the electronic structure of atoms from a previous study of chemistry. Briefly, an atom contains a small, dense nucleus made of neutrons and positively charged protons (Figure 1.1a).

Shells A region of space around a nucleus where electrons are found.

Electrons do not move freely in the space around a nucleus, but rather are confined to regions of space called **principal energy levels** or, more simply, **shells**. We number these shells 1, 2, 3, and so forth from the inside out (Figure 1.1b).

Orbital A region of space where an electron or pair of electrons spends 90 to 95% of its time.

Shells are divided into subshells designated by the letters *s*, *p*, *d*, and *f*, and within these subshells, electrons are grouped in orbitals (Table 1.1). An **orbital** is a region of space that can hold 2 electrons. In this course, we focus on compounds of carbon with hydrogen, oxygen, and nitrogen, all of which use only electrons in *s* and *p* orbitals for covalent bonding. Therefore, we are concerned primarily with *s* and *p* orbitals.

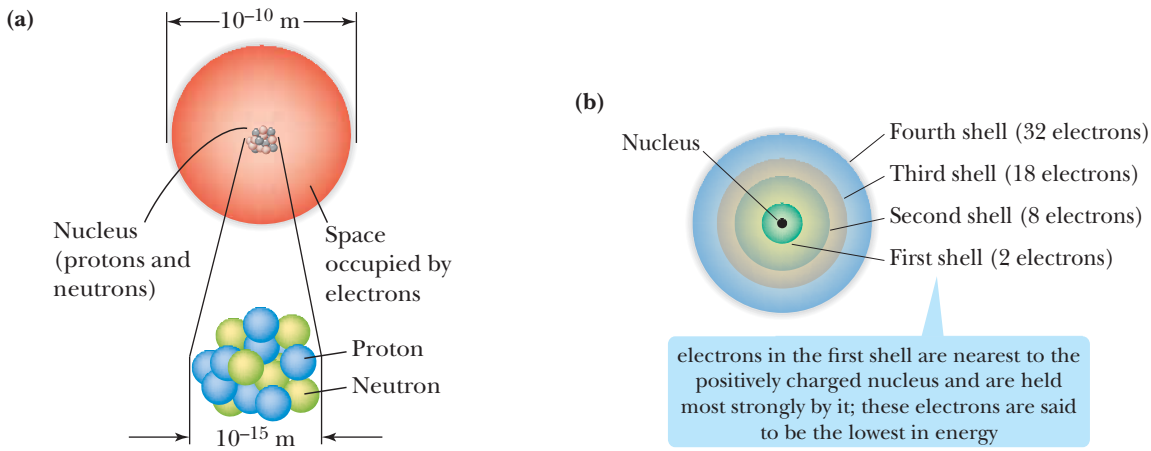


FIGURE 1.1 A schematic view of an atom. (a) Most of the mass of an atom is concentrated in its small, dense nucleus, which has a diameter of 10^{-14} to 10^{-15} meter (m). (b) Each shell can contain up to $2n^2$ electrons, where n is the number of the shell. Thus, the first shell can hold 2 electrons, the second 8 electrons, the third 18, the fourth 32, and so on (Table 1.1).

the first shell contains a single orbital called a 1*s* orbital. The second shell contains one 2*s* orbital and three 2*p* orbitals. All *p* orbitals come in sets of three and can hold up to 6 electrons. The third shell contains one 3*s* orbital, three 3*p* orbitals, and five 3*d* orbitals. All *d* orbitals come in sets of five and can hold up to 10 electrons. All *f* orbitals come in sets of seven and can hold up to 14 electrons

TABLE 1.1 Distribution of Orbitals within Shells

Shell	Orbitals Contained in Each Shell	Maximum Number of Electrons Shell Can Hold	Relative Energies of Electrons in Each Shell
4	One 4*s*, three 4*p*, five 4*d*, and seven 4*f* orbitals	2 + 6 + 10 + 14 = 32	Higher
3	One 3*s*, three 3*p*, and five 3*d* orbitals	2 + 6 + 10 = 18	
2	One 2*s* and three 2*p* orbitals	2 + 6 = 8	
1	One 1*s* orbital	2	Lower

A. Electron Configuration of Atoms

Ground-state electron configuration The electron configuration of lowest energy for an atom, molecule, or ion.

The electron configuration of an atom is a description of the orbitals the electrons in the atom occupy. Every atom has an infinite number of possible electron configurations. At this stage, we are concerned only with the **ground-state electron configuration**—the electron configuration of lowest energy. Table 1.2 shows ground-state electron configurations

TABLE 1.2 Ground-State Electron Configurations for Elements 1–18*

First Period	H	1	$1s^1$	
	He	2	$1s^2$	
Second Period	Li	3	$1s^2s^1$	[He] $2s^1$
	Be	4	$1s^22s^2$	[He] $2s^2$
	B	5	$1s^22s^22p_x^1$	[He] $2s^22p_x^1$
	C	6	$1s^22s^22p_x^12p_y^1$	[He] $2s^22p_x^12p_y^1$
	N	7	$1s^22s^22p_x^12p_y^12p_z^1$	[He] $2s^22p_x^12p_y^12p_z^1$
	O	8	$1s^22s^22p_x^22p_y^12p_z^1$	[He] $2s^22p_x^22p_y^12p_z^1$
	F	9	$1s^22s^22p_x^22p_y^22p_z^1$	[He] $2s^22p_x^22p_y^22p_z^1$
	Ne	10	$1s^22s^22p_x^22p_y^22p_z^2$	[He] $2s^22p_x^22p_y^22p_z^2$
Third Period	Na	11	$1s^22s^22p_x^22p_y^22p_z^23s^1$	[Ne] $3s^1$
	Mg	12	$1s^22s^22p_x^22p_y^22p_z^23s^2$	[Ne] $3s^2$
	Al	13	$1s^22s^22p_x^22p_y^22p_z^23s^23p_x^1$	[Ne] $3s^23p_x^1$
	Si	14	$1s^22s^22p_x^22p_y^22p_z^23s^23p_x^13p_y^1$	[Ne] $3s^23p_x^13p_y^1$
	P	15	$1s^22s^22p_x^22p_y^22p_z^23s^23p_x^13p_y^13p_z^1$	[Ne] $3s^23p_x^13p_y^13p_z^1$
	S	16	$1s^22s^22p_x^22p_y^22p_z^23s^23p_x^23p_y^13p_z^1$	[Ne] $3s^23p_x^23p_y^13p_z^1$
	Cl	17	$1s^22s^22p_x^22p_y^22p_z^23s^23p_x^23p_y^23p_z^1$	[Ne] $3s^23p_x^23p_y^23p_z^1$
	Ar	18	$1s^22s^22p_x^22p_y^22p_z^23s^23p_x^23p_y^23p_z^2$	[Ne] $3s^23p_x^23p_y^23p_z^2$

*Elements are listed by symbol, atomic number, ground-state electron configuration, and shorthand notation for the ground-state electron configuration, in that order.

Rule 1. Orbitals in these elements fill in the order 1*s*, 2*s*, 2*p*, 3*s*, and 3*p*.

Rule 2. Notice that each orbital contains a maximum of two electrons. In neon, there are six additional electrons after the 1*s* and 2*s* orbitals are filled. These are written as $2p_x^22p_y^22p_z^2$. Alternatively, we can group the three filled 2*p* orbitals and write them in a condensed form as $2p^6$.

Rule 3. Because the p_x, p_y, and p_z orbitals are equal in energy, we fill each with one electron before adding a second electron. That is, only after each 3*p* orbital contains one electron do we add a second electron to the $3p_x$ orbital.

for the first 18 elements of the Periodic Table. We determine the ground-state electron configuration of an atom with the use of the following three rules:

Rule 1. *Orbitals fill in order of increasing energy from lowest to highest* (Figure 1.2).

Rule 2. *Each orbital can hold up to two electrons with their spins paired. Spin pairing* means that each electron spins in a direction opposite that of its partner (Figure 1.3). We show this pairing by writing two arrows, one with its head up and the other with its head down.

Rule 3. *When orbitals of equivalent energy are available, but there are not enough electrons to fill them completely, then we add one electron to each equivalent orbital before we add a second electron to any one of them.*

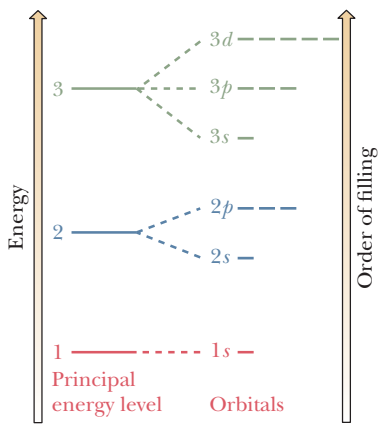


FIGURE 1.2 Relative energies and order of filling of orbitals through the 3*d* orbitals.

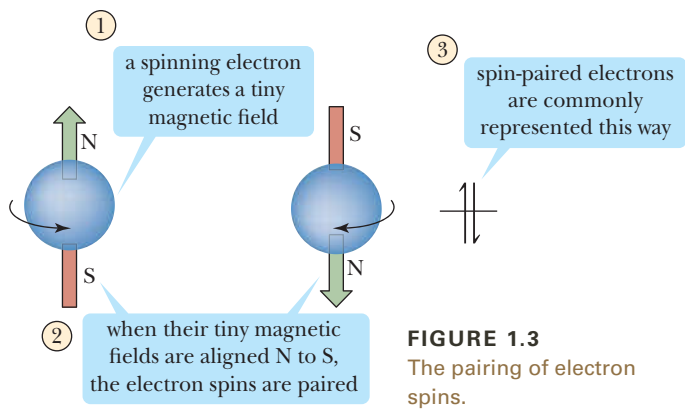


FIGURE 1.3 The pairing of electron spins.

B. Lewis Structures

In discussing the physical and chemical properties of an element, chemists often focus on the outermost shell of its atoms, because electrons in this shell are the ones involved in the formation of chemical bonds and in chemical reactions. We call outer-shell electrons **valence electrons**, and we call the energy level in which they are found the **valence shell**. Carbon, for example, with a ground-state electron configuration of $1s^22s^22p^2$, has four valence (outer-shell) electrons.

Valence electrons Electrons in the valence (outermost) shell of an atom.

Valence shell The outermost electron shell of an atom.

EXAMPLE 1.1

Write ground-state electron configurations for these elements:
(a) Lithium **(b)** Oxygen **(c)** Chlorine

STRATEGY

Locate each atom in the Periodic Table and determine its atomic number. The order of filling of orbitals is $1s$, $2s$, $2p_x$, $2p_y$, $2p_z$, and so on.

SOLUTION

(a) Lithium (atomic number 3): $1s^2 2s^1$. Alternatively, we can write the ground-state electron configuration as [He] $2s^1$.

(b) Oxygen (atomic number 8): $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$. Alternatively, we can group the four electrons of the $2p$ orbitals together and write the ground-state electron configuration as $1s^2 2s^2 2p^4$. We can also write it as [He] $2s^2 2p^4$.

(c) Chlorine (atomic number 17): $1s^2 2s^2 2p^6 3s^2 3p^5$. Alternatively, we can write it as [Ne] $3s^2 3p^5$.

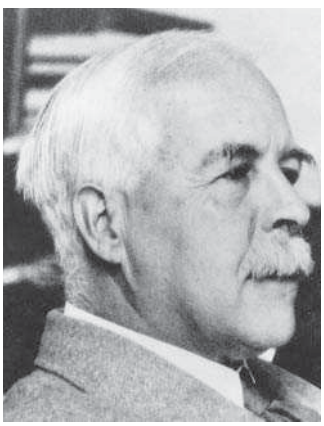
See problems 1.17–1.20

PROBLEM 1.1

Write and compare the ground-state electron configurations for the elements in each set. What can be said about the outermost shell of orbitals for each pair of elements?

(a) Carbon and silicon
(b) Oxygen and sulfur
(c) Nitrogen and phosphorus

Lewis structure of an atom The symbol of an element surrounded by a number of dots equal to the number of electrons in the valence shell of the atom.



UPI/© Corbis

Gilbert N. Lewis (1875–1946) introduced the theory of the electron pair that extended our understanding of covalent bonding and of the concept of acids and bases. It is in his honor that we often refer to an "electron dot" structure as a Lewis structure.

To show the outermost electrons of an atom, we commonly use a representation called a **Lewis structure**, after the American chemist Gilbert N. Lewis (1875–1946), who devised this notation. A Lewis structure shows the symbol of the element, surrounded by a number of dots equal to the number of electrons in the outer shell of an atom of that element. In Lewis structures, the atomic symbol represents the nucleus and all filled inner shells. Table 1.3 shows Lewis structures for the first 18 elements of the Periodic Table. As you study the entries in the table, note that, with the exception of helium, the number of valence electrons of the element corresponds to the group number of the element in the Periodic Table; for example, oxygen, with six valence electrons, is in Group 6A.

At this point, we must say a word about the numbering of the columns (families or groups) in the Periodic Table. Dmitri Mendeleev gave them numerals and added the letter A for some columns and B for others. This pattern remains in common use in the United States today. In 1985, however, the International Union of Pure and Applied Chemistry (IUPAC) recommended an alternative system in which the columns are numbered 1 to 18 beginning on the left and without added letters. Although we use the original Mendeleev system in this text, the Periodic Table at the front of the text shows both.

Notice from Table 1.3 that, because of the differences in number and kind of valence shell orbitals available to elements of the second and third periods, significant differences exist in the covalent bonding of oxygen and sulfur and of nitrogen and phosphorus. For example, although oxygen and nitrogen can accommodate no more than 8 electrons in their valence shells, many phosphorus-containing compounds have 10 electrons in the valence shell of phosphorus, and many sulfur-containing compounds have 10 and even 12 electrons in the valence shell of sulfur.

the valence shell of 1st period elements contain only *s* orbitals

the valence shell of 2nd period elements contains *s* and *p* orbitals

TABLE 1.3 Lewis Structures for Elements 1–18 of the Periodic Table

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

the valence shell of 3rd period elements contains *s*, *p*, and *d* orbitals. The *d* orbitals allow for expanded covalent bonding opportunities for 3rd period elements

1.2 What Is the Lewis Model of Bonding?

A. Formation of Ions

In 1916, Lewis devised a beautifully simple model that unified many of the observations about chemical bonding and reactions of the elements. He pointed out that the chemical inertness of the noble gases (Group 8A) indicates a high degree of stability of the electron configurations of these elements: helium with a valence shell of two electrons ($1s^2$), neon with a valence shell of eight electrons ($2s^2 2p^6$), argon with a valence shell of eight electrons ($3s^2 3p^6$), and so forth.

Noble Gas	Noble Gas Notation
He	$1s^2$
Ne	[He] $2s^2 2p^6$
Ar	[Ne] $3s^2 3p^6$
Kr	[Ar] $4s^2 4p^6 3d^{10}$
Xe	[Kr] $5s^2 5p^6 4d^{10}$

The tendency of atoms to react in ways that achieve an outer shell of eight valence electrons is particularly common among elements of Groups 1A–7A (the main-group elements). We give this tendency the special name, the **octet rule**. An atom with almost eight valence electrons tends to gain the needed electrons to have eight electrons in its valence shell and an electron configuration like that of the noble gas nearest it in atomic number. In gaining electrons, the atom becomes a negatively charged ion called an **anion**. An atom with only one or two valence electrons tends to lose the number of electrons required to have the same electron configuration as the noble gas nearest it in atomic number. In losing one or more electrons, the atom becomes a positively charged ion called a **cation**.

Octet rule The tendency among atoms of Group 1A–7A elements to react in ways that achieve an outer shell of eight valence electrons.

Anion An atom or group of atoms bearing a negative charge.

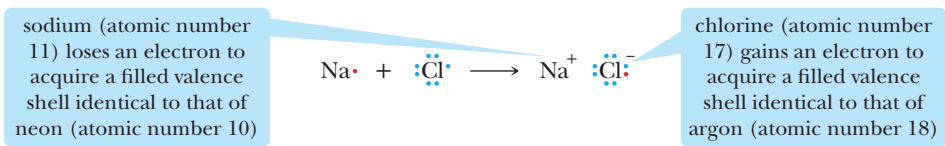
Cation An atom or group of atoms bearing a positive charge.

B. Formation of Chemical Bonds

According to the Lewis model of bonding, atoms interact with each other in such a way that each atom participating in a chemical bond acquires a valence-shell electron configuration the same as that of the noble gas closest to it in atomic number. Atoms acquire completed valence shells in two ways:

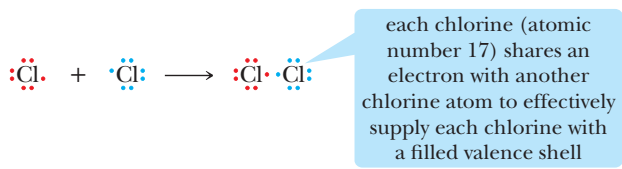
1. An atom may lose or gain enough electrons to acquire a filled valence shell. An atom that gains electrons becomes an anion, and an atom that loses electrons becomes a cation. A chemical bond between an anion and a cation is called an **ionic bond**.

Ionic bond A chemical bond resulting from the electrostatic attraction of an anion and a cation.



2. An atom may share electrons with one or more other atoms to acquire a filled valence shell. A chemical bond formed by sharing electrons is called a **covalent bond**.

Covalent bond A chemical bond resulting from the sharing of one or more pairs of electrons.



We now ask how we can find out whether two atoms in a compound are joined by an ionic bond or a covalent bond. One way to answer this question is to consider the relative positions of the two atoms in the Periodic Table. Ionic bonds usually form between a metal and a nonmetal. An example of an ionic bond is that formed between the metal sodium and the nonmetal chlorine in the compound sodium chloride, Na^+Cl^-. By contrast, when two nonmetals or a metalloid and a nonmetal combine, the bond between them is usually covalent. Examples of compounds containing covalent bonds between nonmetals include Cl_2, H_2O, CH_4, and NH_3. Examples of compounds containing covalent bonds between a metalloid and a nonmetal include BF_3, $SiCl_4$, and AsH_4.

EXAMPLE 1.2

Show how the loss of one electron from a sodium atom to form a sodium ion leads to a stable octet:

$$\underset{\text{A sodium atom}}{Na} \longrightarrow \underset{\text{A sodium ion}}{Na^+} + \underset{\text{An electron}}{e^-}$$

STRATEGY

To see how this chemical change leads to a stable octet, write the condensed ground-state electron configuration for a sodium atom and for a sodium ion, and then compare the two to the noble gas nearest to sodium in atomic number.

SOLUTION

A sodium atom has one electron in its valence shell. The loss of this one valence electron changes the sodium atom to a sodium ion, Na^+, which has a complete octet of electrons in its valence shell and the same electron configuration as neon, the noble gas nearest to it in atomic number.

Na (11 electrons): $1s^2 2s^2 2p^6 3s^1$

Na^+ (10 electrons): $1s^2 2s^2 2p^6$

Ne (10 electrons): $1s^2 2s^2 2p^6$

See problems 1.22, 1.23

PROBLEM 1.2

Show how the gain of two electrons by a sulfur atom to form a sulfide ion leads to a stable octet:

$$S + 2e^- \longrightarrow S^{2-}$$

Another way to identify the type of bond is to compare the electronegativities of the atoms involved, which is the subject of the next subsection.

C. Electronegativity and Chemical Bonds

Electronegativity A measure of the force of an atom's attraction for electrons it shares in a chemical bond with another atom.

Electronegativity is a measure of the force of an atom's attraction for electrons that it shares in a chemical bond with another atom. The most widely used scale of electronegativities (Table 1.4) was devised by Linus Pauling in the 1930s. On the Pauling scale, fluorine, the most electronegative element, is assigned an electronegativity of 4.0, and all other elements are assigned values in relation to fluorine.

As you study the electronegativity values in this table, note that they generally increase from left to right within a period of the Periodic Table and generally increase from bottom to top within a group. Values increase from left to right because of the increasing positive charge on the nucleus, which leads to a stronger attraction for electrons in the valence shell. Values increase going up a column because of the decreasing distance of the valence electrons from the nucleus, which leads to stronger attraction between a nucleus and its valence electrons.

Note that the values given in Table 1.4 are only approximate. The electronegativity of a particular element depends not only on its position in the Periodic Table, but also on its oxidation state. The electronegativity of Cu(I) in Cu_2O, for example, is 1.8, whereas the electronegativity of Cu(II) in CuO is 2.0. In spite of these variations, electronegativity is still a useful guide to the distribution of electrons in a chemical bond.

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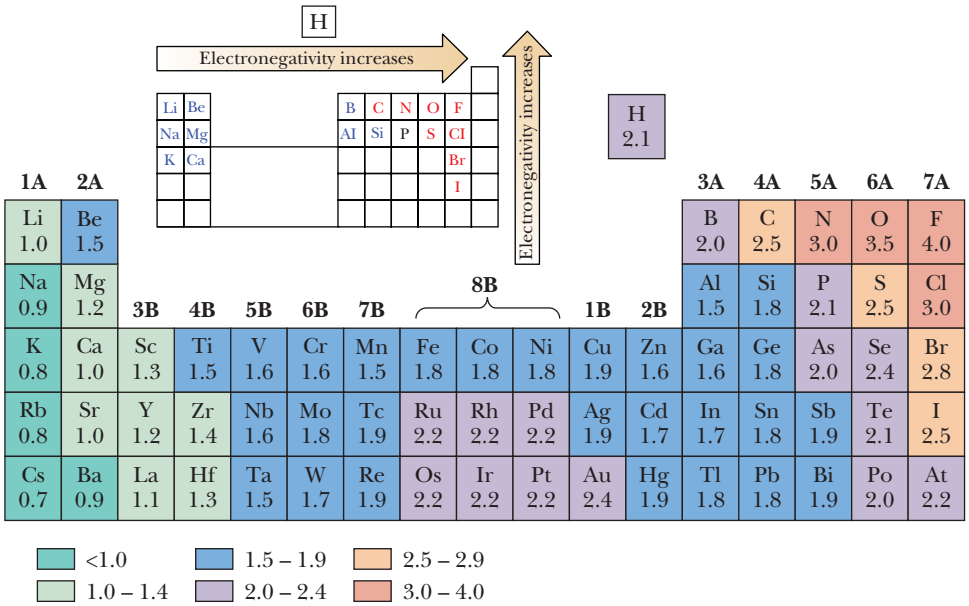
Linus Pauling (1901–1994) was the first person ever to receive two unshared Nobel Prizes. He received the Nobel Prize for Chemistry in 1954 for his contributions to the nature of chemical bonding. He received the Nobel Prize for Peace in 1962 for his efforts on behalf of international control of nuclear weapons and against nuclear testing.

Ionic Bonds

An ionic bond forms by the transfer of electrons from the valence shell of an atom of lower electronegativity to the valence shell of an atom of higher electronegativity. The more electronegative atom gains one or more valence electrons and becomes an anion; the less electronegative atom loses one or more valence electrons and becomes a cation.

As a guideline, we say that this type of electron transfer to form an ionic compound is most likely to occur if the difference in electronegativity between two atoms is approximately 1.9 or greater. A bond is more likely to be covalent if this difference is less than 1.9. Note that the value 1.9 is somewhat arbitrary: Some chemists prefer a slightly larger value, others a slightly smaller value. The essential point is that the value 1.9 gives us a guidepost against which to decide whether a bond is more likely to be ionic or more likely to be covalent.

TABLE 1.4 Electronegativity Values and Trends for Some Atoms (Pauling Scale)



Partial Periodic Table showing commonly encountered elements in organic chemistry. Electronegativity generally increases from left to right within a period and from bottom to top within a group. Hydrogen is less electronegative than the elements in red and more electronegative than those in blue. Hydrogen and phosphorus have the same electronegativity on the Pauling scale.

An example of an ionic bond is that formed between sodium (electronegativity 0.9) and fluorine (electronegativity 4.0). The difference in electronegativity between these two elements is 3.1. In forming Na^+F^-, the single $3s$ valence electron of sodium is transferred to the partially filled valence shell of fluorine:

$$Na(1s^2\,2s^2\,2p^6\,\boxed{3s^1}) + F(1s^2\,2s^2\,\boxed{2p^5}) \longrightarrow Na^+(1s^2 2s^2 2p^6) + F^-(1s^2 2s^2\,\boxed{2p^6})$$

As a result of this transfer of one electron, both sodium and fluorine form ions that have the same electron configuration as neon, the noble gas closest to each in atomic number. In the following equation, we use a single-headed curved arrow to show the transfer of one electron from sodium to fluorine:

EXAMPLE 1.3

Judging from their relative positions in the Periodic Table, which element in each pair has the larger electronegativity?

(a) Lithium or carbon
(b) Nitrogen or oxygen
(c) Carbon or oxygen

STRATEGY

Determine whether the pair resides in the same period (row) or group (column) of the Periodic Table. For those in the same period, electronegativity increases from left to right. For those in the same group, electronegativity increases from bottom to top.

SOLUTION

The elements in these pairs are all in the second period of the Periodic Table. Electronegativity in this period increases from left to right.

(a) C > Li
(b) O > N
(c) O > C

See problem 1.24

PROBLEM 1.3

Judging from their relative positions in the Periodic Table, which element in each pair has the larger electronegativity?

(a) Lithium or potassium
(b) Nitrogen or phosphorus
(c) Carbon or silicon
(d) Oxygen or phosphorus
(e) Oxygen or silicon

Covalent Bonds

A covalent bond forms when electron pairs are shared between two atoms whose difference in electronegativity is 1.9 or less. According to the Lewis model, an electron pair in a covalent bond functions in two ways simultaneously: It is shared by two atoms, and, at the same time, it fills the valence shell of each atom.

The simplest example of a covalent bond is that in a hydrogen molecule, H_2. When two hydrogen atoms bond, the single electrons from each atom combine to form an electron pair with the release of energy. A bond formed by sharing a pair of electrons is called a *single bond* and is represented by a single line between the two atoms. The electron pair shared between the two hydrogen atoms in H_2 completes the valence shell of each hydrogen. Thus, in H_2, each hydrogen has two electrons in its valence shell and an electron configuration like that of helium, the noble gas nearest to it in atomic number:

$$H\cdot + \cdot H \rightarrow H{-}H \qquad \Delta H^0 = -435 \text{ kJ / mol } (-104 \text{ kcal / mol})$$

The Lewis model accounts for the stability of covalently bonded atoms in the following way: In forming a covalent bond, an electron pair occupies the region between two nuclei and serves to shield one positively charged nucleus from the repulsive force of the other positively charged nucleus. At the same time, an electron pair attracts both nuclei. In other words, an electron pair in the space between two nuclei bonds them together and fixes the internuclear distance to within very narrow limits. The distance between nuclei participating in a chemical bond is called a **bond length**. Every covalent bond has a definite bond length. In H—H, it is 74 pm, where 1 pm = 10^{-12} m.

Although all covalent bonds involve the sharing of electrons, they differ widely in the degree of sharing. We classify covalent bonds into two categories—nonpolar covalent and polar covalent—depending on the difference in electronegativity between the bonded atoms. In a **nonpolar covalent bond**, electrons are shared equally. In a **polar covalent bond**, they are shared unequally. It is important to realize that no sharp line divides these two categories, nor, for that matter, does a sharp line divide polar covalent bonds and ionic bonds. Nonetheless, the rule-of-thumb guidelines in Table 1.5 will help you decide whether a given bond is more likely to be nonpolar covalent, polar covalent, or ionic.

Nonpolar covalent bond A covalent bond between atoms whose difference in electronegativity is less than approximately 0.5.

Polar covalent bond A covalent bond between atoms whose difference in electronegativity is between approximately 0.5 and 1.9.

A covalent bond between carbon and hydrogen, for example, is classified as non-polar covalent because the difference in electronegativity between these two atoms is 2.5 − 2.1 = 0.4 unit. An example of a polar covalent bond is that of H—Cl. The difference in electronegativity between chlorine and hydrogen is 3.0 − 2.1 = 0.9 unit.

An important consequence of the unequal sharing of electrons in a polar covalent bond is that the more electronegative atom gains a greater fraction of the shared electrons and acquires a partial negative charge, which we indicate by the symbol $\delta-$ (read "delta minus"). The less electronegative atom has a lesser fraction of the shared electrons and acquires a partial positive charge, which we indicate by the symbol $\delta+$ (read "delta plus"). This separation of charge produces a **dipole** (two poles). We can also show the presence of a bond dipole by an arrow, with the head of the arrow near the negative end of the dipole and a cross on the tail of the arrow near the positive end (Figure 1.4).

We can display the polarity of a covalent bond by a type of molecular model called an *electron density model*. In this type of model, a blue color shows the presence of a $\delta+$ charge, and a red color shows the presence of a $\delta-$ charge. Figure 1.4 shows an electron density model of HCl. The ball-and-stick model in the center shows the orientation of the two atoms in space. The transparent surface surrounding the ball-and-stick model shows the relative sizes of the atoms (equivalent to the size shown by a space-filling model). Colors on

TABLE 1.5 Classification of Chemical Bonds

Difference in Electronegativity between Bonded Atoms	Type of Bond	Most Likely Formed Between
Less than 0.5	Nonpolar covalent	Two nonmetals or a nonmetal and a metalloid
0.5 to 1.9	Polar covalent	
Greater than 1.9	Ionic	A metal and a nonmetal

EXAMPLE 1.4

Classify each bond as nonpolar covalent, polar covalent, or ionic:

(a) O—H
(b) N—H
(c) Na—F
(d) C—Mg

STRATEGY

Use the difference in electronegativity between the two atoms and compare this value with the range of values given in Table 1.5.

SOLUTION

On the basis of differences in electronegativity between the bonded atoms, three of these bonds are polar covalent and one is ionic:

Bond	Difference in Electronegativity	Type of Bond
(a) O—H	3.5 – 2.1 = 1.4	polar covalent
(b) N—H	3.0 – 2.1 = 0.9	polar covalent
(c) Na—F	4.0 – 0.9 = 3.1	ionic
(d) C—Mg	2.5 – 1.2 = 1.3	polar covalent

See problem 1.25

PROBLEM 1.4

Classify each bond as nonpolar covalent, polar covalent, or ionic:
(a) S—H **(b)** P—H **(c)** C—F **(d)** C—Cl

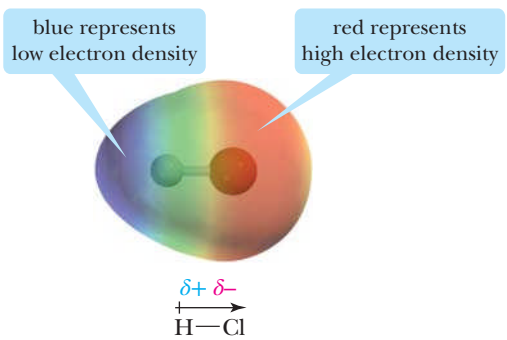


FIGURE 1.4 An electron density model of HCl. Red indicates a region of high electron density, and blue indicates a region of low electron density.

the surface show the distribution of electron density. We see by the blue color that hydrogen bears a $\delta+$ charge and by the red color that chlorine bears a $\delta-$ charge.

In summary, the twin concepts of electronegativity and the polarity of covalent bonds will be very helpful in organic chemistry as a guide to locating centers of chemical reactions. In many of the reactions we will study, reaction is initiated by the attraction between a center of partial positive charge and a center of partial negative charge.

From the study of the compounds in Table 1.6 and other organic compounds, we can make the following generalizations: In neutral (uncharged) organic compounds,

- H has one bond.
- C has four bonds.
- N has three bonds and one unshared pair of electrons.
- O has two bonds and two unshared pair of electrons.
- F, Cl, Br, and I have one bond and three unshared pairs of electrons.

D. Formal Charge

Throughout this course, we deal not only with molecules, but also with polyatomic cations and polyatomic anions. Examples of polyatomic cations are the hydronium ion, H_3O^+, and the ammonium ion, NH_4^+. An example of a polyatomic anion is the bicarbonate ion, HCO_3^-.

EXAMPLE 1.5

Using a bond dipole arrow and the symbols $\delta-$ and $\delta+$, indicate the direction of polarity in these polar covalent bonds:

(a) C—O **(b)** N—H **(c)** C—Mg

STRATEGY

To determine the polarity of a covalent bond and the direction of the polarity, compare the electronegativities of the bonded atoms. Remember that a bond dipole arrow always points toward the more electronegative atom.

SOLUTION

For (a), carbon and oxygen are both in period 2 of the Periodic Table. Because oxygen is farther to the right than carbon, it is more electronegative. For (b), nitrogen is more electronegative than hydrogen. For (c), magnesium is a metal located at the far left of the Periodic Table, and carbon is a nonmetal located at the right. All nonmetals, including hydrogen, have a greater electronegativity than do the metals in columns 1A and 2A. The electronegativity of each element is given below the symbol of the element:

(a) $\overset{\delta+}{\underset{2.5}{C}}—\overset{\delta-}{\underset{3.5}{O}}$ **(b)** $\overset{\delta-}{\underset{3.0}{N}}—\overset{\delta+}{\underset{2.1}{H}}$ **(c)** $\overset{\delta-}{\underset{2.5}{C}}—\overset{\delta+}{\underset{1.2}{Mg}}$

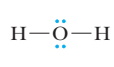
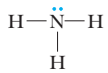
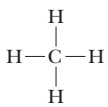
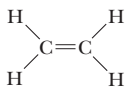
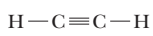
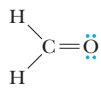
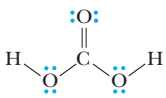
See problems 1.26, 1.38, 1.40

PROBLEM 1.5

Using a bond dipole arrow and the symbols $\delta-$ and $\delta+$, indicate the direction of polarity in these polar covalent bonds:

(a) C—N **(b)** N—O **(c)** C—Cl

TABLE 1.6 Lewis Structures for Several Molecules. The number of valence electrons in each molecule is given in parentheses after the molecule's molecular formula

 H_2O (8) Water	 NH_3 (8) Ammonia	 CH_4 (8) Methane	 HCl (8) Hydrogen chloride
 C_2H_4 (12) Ethylene	 C_2H_2 (10) Acetylene	 CH_2O (12) Formaldehyde	 H_2CO_3 (24) Carbonic acid

Formal charge The charge on an atom in a molecule or polyatomic ion.

Nonbonding electrons Valence electrons not involved in forming covalent bonds, that is, unshared electrons.

Bonding electrons Valence electrons shared in a covalent bond.

It is important that you be able to determine which atom or atoms in a molecule or polyatomic ion bear the positive or negative charge. The charge on an atom in a molecule or polyatomic ion is called its **formal charge**. To derive a formal charge,

Step 1: *Write a correct Lewis structure for the molecule or ion.*

Step 2: *Assign to each atom all its unshared* ***(nonbonding) electrons*** *and one-half its shared* ***(bonding) electrons****.*

Step 3: *Compare the number arrived at in Step 2 with the number of valence electrons in the neutral, unbonded atom.* If the number of electrons assigned to a bonded atom is less than that assigned to the unbonded atom, then more positive charges are in the nucleus than counterbalancing negative charges, and the atom has a positive formal charge. Conversely, if the number of electrons assigned to a bonded atom is greater than that assigned to the unbonded atom, then the atom has a negative formal charge.

$$\text{Formal charge} = \begin{array}{c}\text{Number of valence}\\ \text{electrons in neutral}\\ \text{unbonded atom}\end{array} - \left(\begin{array}{c}\text{All unshared}\\ \text{electrons}\end{array} + \begin{array}{c}\text{One-half of all}\\ \text{shared electrons}\end{array}\right)$$

HOW TO 1.1

Draw Lewis Structures of Molecules and Ions

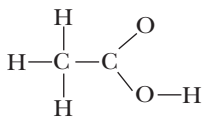
The ability to draw Lewis structures for molecules and ions is a fundamental skill in the study of organic chemistry. The following steps will help you to do this (as you study these steps look at the examples in Table 1.6). As an example, let us draw a Lewis structure of acetic acid, molecular formula $C_2H_4O_2$. Its structural formula, CH_3COOH, gives a hint of the connectivity.

STEP 1: *Determine the number of valence electrons in the molecule or ion.*

To do so, add the number of valence electrons contributed by each atom. For ions, add one electron for each negative charge on the ion, and subtract one electron for each positive charge on the ion. For example, the Lewis structure of the water molecule, H_2O, must show eight valence electrons: one from each hydrogen and six from oxygen. The Lewis structure for the hydroxide ion, OH^-, must also show eight valence electrons: one from hydrogen, six from oxygen, plus one for the negative charge on the ion. For acetic acid the molecular formula is $C_2H_4O_2$. The Lewis structure must show 8(2 carbons) + 4(4 hydrogens) + 12(2 oxygens) = 24 valence electrons.

STEP 2: *Determine the arrangement of atoms in the molecule or ion.*

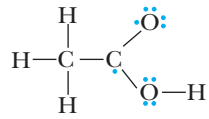
This step is the most difficult part of drawing a Lewis structure. Fortunately, the structural formula of a compound can provide valuable information about connectivity. The order in which the atoms are listed in a structural formula is a guide. For example, the CH_3 part of the structural formula of acetic acid tells you that three hydrogen atoms are bonded to the carbon written on the left, and the COOH part tells you that both oxygens are bonded to the same carbon and a hydrogen is bonded to one of the oxygens.



Except for the simplest molecules and ions, the connectivity must be determined experimentally. For some molecules and ions we give as examples, we ask you to propose a connectivity of the atoms. For most, however, we give you the experimentally determined arrangement.

STEP 3: *Arrange the remaining electrons in pairs so that each atom in the molecule or ion has a complete outer shell. Show a pair of* **bonding electrons** *as a single line between the bonded atoms; show a pair of* **nonbonding electrons** *as a pair of Lewis dots.*

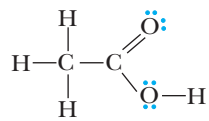
To accomplish this, connect the atoms with single bonds. Then arrange the remaining electrons in pairs so that each atom in the molecule or ion has a complete outer shell. Each hydrogen atom must be surrounded by two electrons. Each atom of carbon, oxygen, and nitrogen, as well as each halogen, must be surrounded by eight electrons (per the octet rule). Recall that each neutral carbon atom has four valence electrons and each neutral oxygen atom has six valence electrons. The structure here shows the required 24 valence electrons. The left carbon has four single bonds and a complete valence shell. Each hydrogen also has a complete valence shell. The lower oxygen has two single bonds and two unshared pairs of electrons and, therefore, has a complete valence shell. The original six valence electrons of the upper oxygen are accounted for, but it does not yet have a filled valence shell. Similarly, the original four valence electrons of the right carbon atom are accounted for but it still does not have a complete valence shell.



Notice that in the structure so far, we have accounted for all valence electrons, but two atoms do not yet have completed valence shells. Furthermore, one carbon atom and one oxygen atom each have a single unpaired electron.

STEP 4: *Use multiple bonds where necessary to eliminate unpaired electrons.*

In a **single bond**, two atoms share one pair of electrons. It is sometimes necessary for atoms to share more than one pair of electrons. In a **double bond**, they share two pairs of electrons; we show a double bond by drawing two parallel lines between the bonded atoms. In a **triple bond**, two atoms share three pairs of electrons; we show a triple bond by three parallel lines between the bonded atoms. The following structure combines the unpaired electrons on carbon and oxygen and creates a double bond (C═O) between these two atoms. The Lewis structure is now complete.



EXAMPLE 1.6

Draw Lewis structures, showing all valence electrons, for these molecules:

(a) H_2O_2 **(b)** CH_3OH **(c)** CH_3Cl

STRATEGY

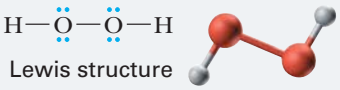
Determine the number of valence electrons and the connectivity of the atoms in each molecule. Connect the bonded atoms by single bonds and then arrange the remaining valence electrons so that each atom has a filled valence shell.

SOLUTION

(a) A Lewis structure for hydrogen peroxide, H_2O_2, must show 6 valence electrons from each oxygen and 1 from each hydrogen, for a total of 12 + 2 = 14 valence electrons. We know that hydrogen forms only one covalent bond, so the connectivity of the atoms must be as follows:

H—O—O—H

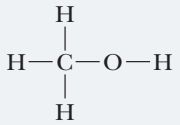
The three single bonds account for 6 valence electrons. We place the remaining 8 valence electrons on the oxygen atoms to give each a complete octet:



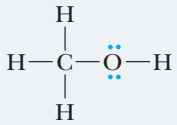
Lewis structure

Ball-and-stick models show only nuclei and covalent bonds; they do not show unshared pairs of electrons

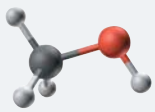
(b) A Lewis structure for methanol, CH_3OH, must show 4 valence electrons from carbon, 1 from each hydrogen, and 6 from oxygen, for a total of 4 + 4 + 6 = 14 valence electrons. The connectivity of the atoms in methanol is given on the left. The five single bonds in this partial structure account for 10 valence electrons. We place the remaining 4 valence electrons on oxygen as two Lewis dot pairs to give it a complete octet.



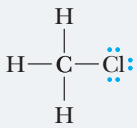
The order of attachment of atoms



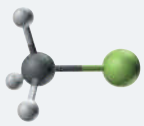
Lewis structure



(c) A Lewis structure for chloromethane, CH_3Cl, must show 4 valence electrons from carbon, 1 from each hydrogen, and 7 from chlorine, for a total of 4 + 3 + 7 = 14. Carbon has four bonds, one to each of the hydrogens and one to chlorine. We place the remaining 6 valence electrons on chlorine as three Lewis dot pairs to complete its octet.



Lewis structure



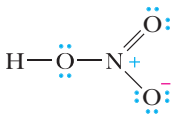
See problems 1.27, 1.28

PROBLEM 1.6

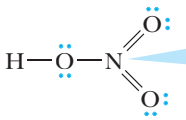
Draw Lewis structures, showing all valence electrons, for these molecules:

(a) C_2H_6 **(b)** CS_2 **(c)** HCN **(d)** HCHO

In writing Lewis structures for molecules and ions, you must remember that elements of the second period, including carbon, nitrogen, and oxygen, can accommodate no more than eight electrons in the four orbitals (2*s*, 2p_x, 2p_y, and 2p_z) of their valence shells. Following are two Lewis structures for nitric acid, HNO_3, each with the correct number of valence electrons, namely, 24; one structure is acceptable and the other is not:



An acceptable Lewis structure



Not an acceptable Lewis structure

The structure on the left is an acceptable Lewis structure. It shows the required 24 valence electrons, and each oxygen and nitrogen has a completed valence shell of 8 electrons. Further, the structure on the left shows a positive formal charge on nitrogen and a negative formal charge on one of the oxygens. An acceptable Lewis structure must show these formal charges. The structure on the right is *not* an acceptable Lewis structure. Although it shows the correct number of valence electrons, it places 10 electrons in the valence shell of

EXAMPLE 1.7

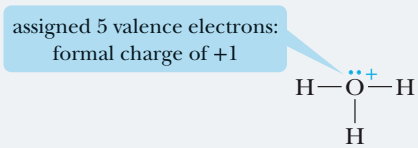
Draw Lewis structures for these ions, and show which atom in each bears the formal charge:
(a) H_3O^+ **(b)** CH_3O^-

STRATEGY

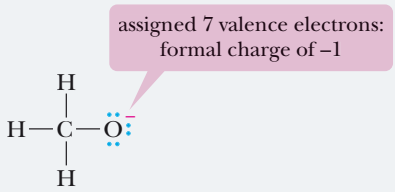
Draw a correct Lewis structure molecule showing all valence electrons on each atom. Then determine the location of the formal charge.

SOLUTION

(a) The Lewis structure for the hydronium ion must show 8 valence electrons: 3 from the three hydrogens, 6 from oxygen, minus 1 for the single positive charge. A neutral, unbonded oxygen atom has 6 valence electrons. To the oxygen atom in H_3O^+, we assign two unshared electrons and one from each shared pair of electrons, giving it a formal charge of 6 – (2 + 3) = +1.



(b) The Lewis structure for the methoxide ion, CH_3O^-, must show 14 valence electrons: 4 from carbon, 6 from oxygen, 3 from the hydrogens, plus 1 for the single negative charge. To carbon, we assign 1 electron from each shared pair, giving it a formal charge of 4 – 4 = 0. To oxygen, we assign 7 valence electrons, giving it a formal charge of 6 – 7 = –1.



See problems 1.30–1.32, 1.34

PROBLEM 1.7

Draw Lewis structures for these ions, and show which atom in each bears the formal charge(s):
(a) $CH_3NH_3^+$ **(b)** CH_3^+

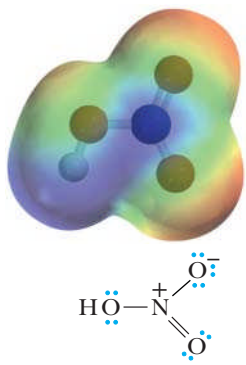
nitrogen, yet the four orbitals of the second shell (2*s*, 2p_x, 2p_y, and 2p_z) can hold no more than 8 valence electrons!

1.3 How Do We Predict Bond Angles and the Shapes of Molecules?

In Section 1.2, we used a shared pair of electrons as the fundamental unit of a covalent bond and drew Lewis structures for several small molecules containing various combinations of single, double, and triple bonds. (See, for example, Table 1.6.) We can predict bond angles in these and other molecules in a very straightforward way by using the concept of **valence-shell electron-pair repulsion (VSEPR)**. According to this concept, the valence electrons of an atom may be involved in the formation of single, double, or triple bonds, or they may be unshared. Each combination creates a region of electron density that, because it is occupied by electrons, is negatively charged. Because like charges repel each other, the various regions of electron density around an atom spread so that each is as far away from the others as possible.

Recall from your prior studies in chemistry that VSEPR can be used to predict the shapes of molecules. This can be demonstrated in a very simple way by using balloons as shown in Figure 1.5.

We can use the example of the balloons to model the shapes that methane (CH_4), ammonia (NH_3), and water (H_2O) assume. As you look at each of these molecules in Figures 1.6–1.8, take note of (1) the number of regions of electron density shown by the Lewis structure, (2) the geometry that is required to maximize the separation of these regions of electron density, and (3) the names of the shapes that result from this treatment using VSEPR.



The Lewis structure of HNO_3 shows the negative formal charge localized on one of the oxygen atoms. The electron density model, on the other hand, shows that the negative charge is distributed equally over the two oxygen atoms on the right. The concept of resonance can explain this phenomenon and will be discussed in Section 1.6. Notice also the intense blue color on nitrogen, which is due to its positive formal charge.

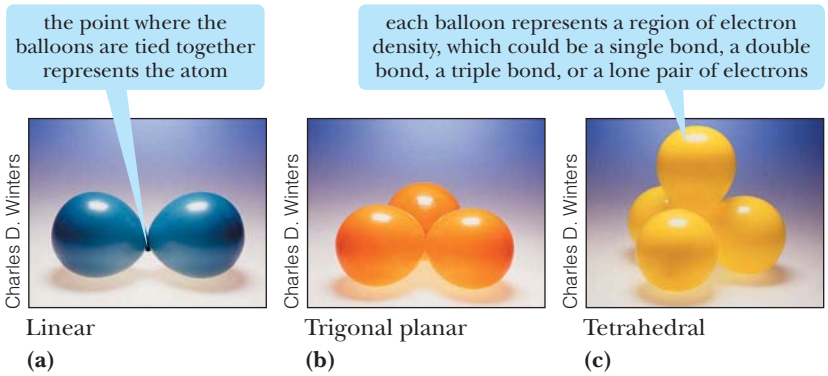


FIGURE 1.5 Balloon models used to predict bond angles. (a) Two balloons assume a linear shape with a bond angle of 180° about the tie point. (b) Three balloons assume a trigonal planar shape with bond angles of 120° about the tie point. (c) Four balloons assume a tetrahedral shape with bond angles of 109.5° about the tie point.

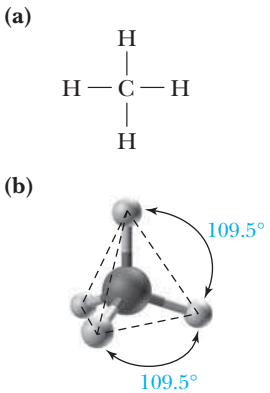


FIGURE 1.6 The shape of a methane molecule, CH_4. (a) Lewis structure and (b) ball-and-stick model. The single bonds occupy four regions of electron density, causing the molecule to be **tetrahedral**. The hydrogens occupy the four corners of a regular tetrahedron, and all H—C—H bond angles are 109.5°.

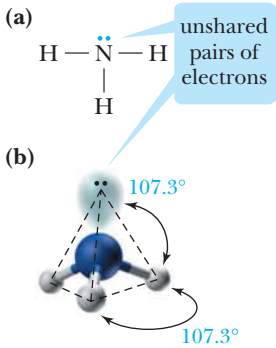


FIGURE 1.7 The shape of an ammonia molecule, NH_3. (a) Lewis structure and (b) ball-and-stick model. The three single bonds and one lone pair of electrons create four regions of electron density. This allows the lone pair and the three hydrogens to occupy the four corners of a tetrahedron. However, we do not take lone pairs of electrons into account when describing the shape of the molecule. For this reason, we describe the geometry of an ammonia molecule as **pyramidal**; that is, the molecule has a shape like a triangular-based pyramid with the three hydrogens at the base and nitrogen at the apex. The observed bond angles are 107.3°. We account for this small difference between the predicted and observed angles by proposing that the unshared pair of electrons on nitrogen repels adjacent electron pairs more strongly than bonding pairs repel each other.

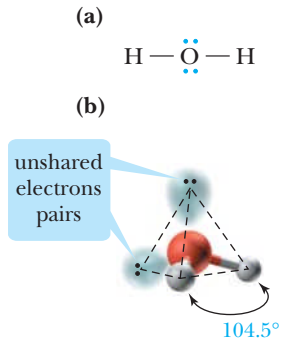


FIGURE 1.8 The shape of a water molecule, H_2O. (a) A Lewis structure and (b) a ball-and-stick model. Using VSEPR, we predict that the four regions of electron density around oxygen are arranged in a tetrahedral manner and that the H—O—H bond angle is 109.5°. Experimental measurements show that the actual H—O—H bond angle is 104.5°, a value smaller than that predicted. We explain this difference between the predicted and observed bond angle by proposing, as we did for NH_3, that unshared pairs of electrons repel adjacent pairs more strongly than do bonding pairs. Note that the distortion from 109.5° is greater in H_2O, which has two unshared pairs of electrons, than it is in NH_3, which has only one unshared pair. We describe the shape of water as **bent**.

A general prediction emerges from this discussion of the shapes of CH_4, NH_3, and H_2O molecules. If a Lewis structure shows four regions of electron density around an atom, then VSEPR predicts a tetrahedral distribution of electron density and bond angles of approximately 109.5°.

In many of the molecules we encounter, an atom is surrounded by three regions of electron density. Figure 1.9 shows Lewis structures for formaldehyde (CH_2O) and ethylene (C_2H_4). As you look at these two molecules, take note of (1) the number of regions of electron density shown by the Lewis structure, (2) the geometry that is required to maximize the separation of these regions of electron density, and (3) the names of the shapes that result from this treatment using VSEPR. Also notice that using VSEPR, we treat a double bond as a single region of electron density.

In still other types of molecules, a central atom is surrounded by only two regions of electron density. Figure 1.10 shows Lewis structures and ball-and-stick models of carbon dioxide (CO_2) and acetylene (C_2H_2). As with double bonds, VSEPR treats triple bonds as one region of electron density.

Table 1.7 summarizes the predictions of VSEPR.

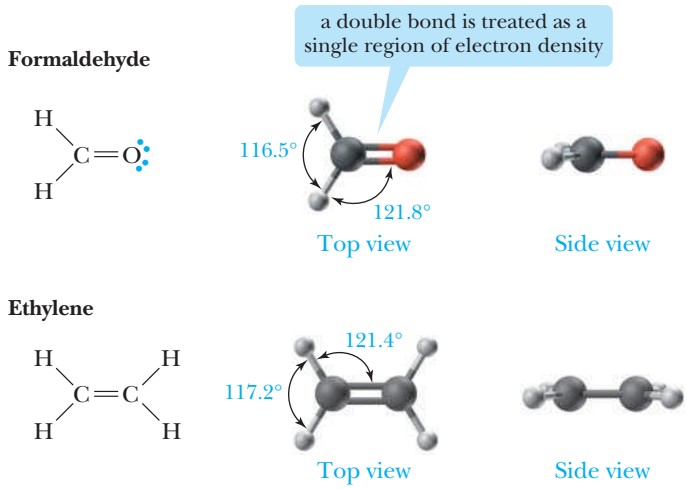


FIGURE 1.9 Shapes of formaldehyde (CH_2O) and ethylene (C_2H_4). In each molecule, the carbons are surrounded by three regions of electron density. Three regions of electron density about an atom are farthest apart when they lie in a plane and make angles of approximately 120° with each other. We describe the geometry about each carbon atom as **trigonal planar**.

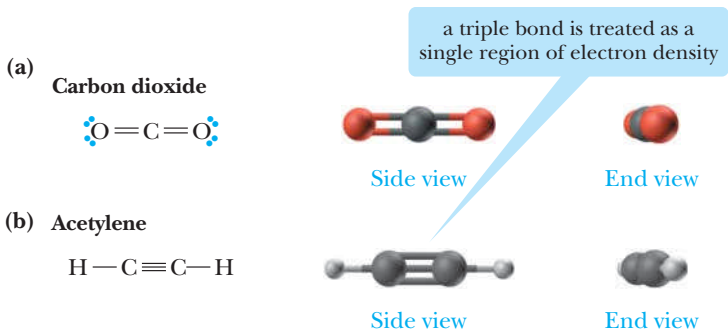


FIGURE 1.10 Shapes of (a) carbon dioxide (CO_2) and (b) acetylene (C_2H_2). In each case, the two regions of electron density are farthest apart if they form a straight line through the central atom and create an angle of 180°. Both carbon dioxide and acetylene are referred to as **linear** molecules.

TABLE 1.7 Predicted Molecular Shapes (VSEPR)

Regions of Electron Density around Central Atom	Predicted Distribution of Electron Density about the Central Atom	Predicted Bond Angles	Examples (Shape of the Molecule)
4	Tetrahedral	109.5°	a solid wedge-shaped bond represents a bond extending out of the plane of the page; a dashed wedge-shaped bond represents a bond extending behind the plane of the page; Methane (tetrahedral); Ammonia (pyramidal); Water (bent)
3	Trigonal planar	120°	Ethylene (planar); Formaldehyde (planar)
2	Linear	180°	Carbon dioxide (linear); Acetylene (linear)

EXAMPLE 1.8

Predict all bond angles in these molecules:

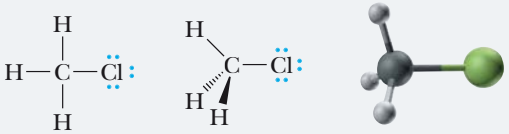
(a) CH_3Cl **(b)** $CH_2{=}CHCl$

STRATEGY

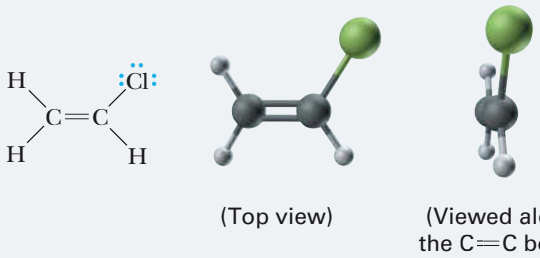
To predict bond angles, first draw a correct Lewis structure for the molecule. Be certain to show all unpaired electrons. Then determine the number of regions of electron density (either 2, 3, or 4) around each atom and use that number to predict bond angles (either 180°, 120°, or 109.5°).

SOLUTION

(a) The Lewis structure for CH_3Cl shows carbon surrounded by four regions of electron density. Therefore, we predict that the distribution of electron pairs about carbon is tetrahedral, that all bond angles are 109.5°, and that the shape of CH_3Cl is tetrahedral:



(b) The Lewis structure for $CH_2{=}CHCl$ shows each carbon surrounded by three regions of electron density. Therefore, we predict that all bond angles are 120°.



(Top view) (Viewed along the C=C bond)

See problems 1.41–1.43

PROBLEM 1.8

Predict all bond angles for these molecules:

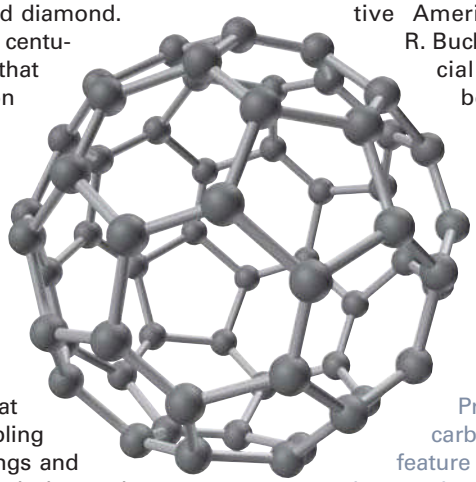
(a) CH_3OH **(b)** CH_2Cl_2 **(c)** H_2CO_3 (carbonic acid)

Chemical Connections 1A

BUCKYBALL: A NEW FORM OF CARBON

Many elements in the pure state can exist in different forms. We are all familiar with the fact that pure carbon is found in two forms: graphite and diamond. These forms have been known for centuries, and it was generally believed that they were the only forms of carbon having extended networks of C atoms in well-defined structures.

But that is not so! The scientific world was startled in 1985 when Richard Smalley of Rice University and Harry W. Kroto of the University of Sussex, England, and their coworkers announced that they had detected a new form of carbon with a molecular formula C_{60}. They suggested that the molecule has a structure resembling a soccer ball: 12 five-membered rings and 20 six-membered rings arranged such that each five-membered ring is surrounded by six-membered rings. This structure reminded its discoverers of a geodesic dome, a structure invented by the innovative American engineer and philosopher R. Buckminster Fuller. Therefore, the official name of the new allotrope of carbon has become fullerene. Kroto, Smalley, and Robert F. Curl were awarded the Nobel Prize for Chemistry in 1996 for their work with fullerenes. Many higher fullerenes, such as C_{70} and C_{84}, have also been isolated and studied.



Question

Predict the bond angles about the carbon atoms in C_{60}. What geometric feature distinguishes the bond angles about each carbon in C_{60} from the bond angles of a compound containing typical carbon–carbon bonds?

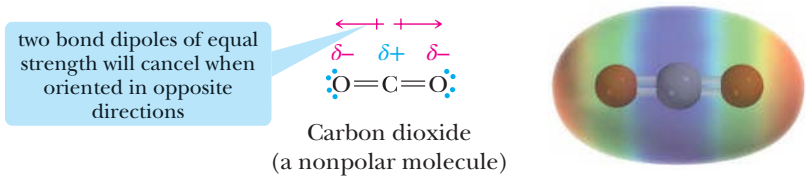
1.4 How Do We Predict If a Molecule Is Polar or Nonpolar?

In Section 1.2C, we used the terms *polar* and *dipole* to describe a covalent bond in which one atom bears a partial positive charge and the other bears a partial negative charge. We also saw that we can use the difference in electronegativity between bonded atoms to determine the polarity of a covalent bond and the direction of its polarity. We can now combine our understanding of bond polarity and molecular geometry (Section 1.3) to predict the polarity of molecules.

A molecule will be nonpolar if (1) it has all nonpolar bonds, or (2) it has polar bonds and the vector sum of its bond dipoles is zero (i.e., the bond dipoles cancel each other). Consider first carbon dioxide, CO_2, a molecule with two polar carbon–oxygen double bonds. Because carbon dioxide is a linear molecule, the vector sum of its two bond dipoles is zero; therefore, this molecule is nonpolar.

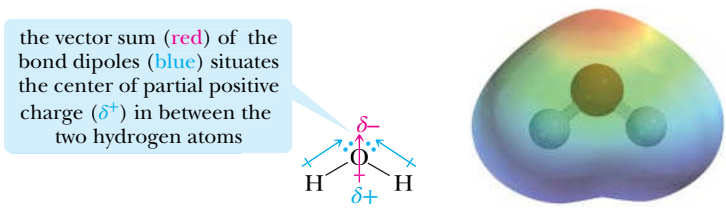
Charles D. Winters/Science Source Images

Carbon dioxide, CO_2, is a nonpolar molecule. Its solid state is often referred to as dry ice.



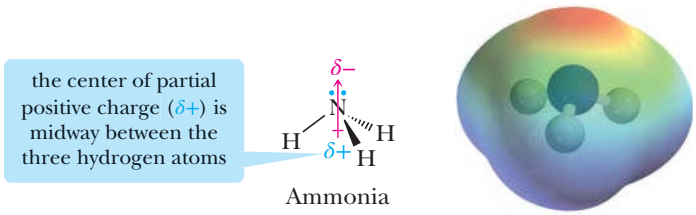
Carbon dioxide
(a nonpolar molecule)

A molecule will be polar if it has polar bonds and the vector sum of its bond dipoles is non-zero. In a water molecule, each O—H bond is polar, with oxygen, the more electronegative atom, bearing a partial negative charge and each hydrogen bearing a partial positive charge. Because water is a bent molecule, the center of its partial positive charge is between the two hydrogen atoms, and the center of its partial negative charge is on oxygen. Thus, water has polar bonds and, because of its geometry, it is a polar molecule.



Water
(a polar molecule)

Ammonia has three polar N—H bonds, and because of its geometry, the vector sum of their bond dipoles does not equal zero. Thus, ammonia is a polar molecule.



Ammonia
(a polar molecule)

EXAMPLE 1.9

Which of these molecules are polar? For each that is polar, specify the direction of its polarity.

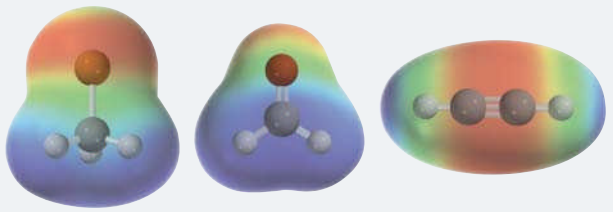
(a) CH_3Cl (b) CH_2O (c) C_2H_2

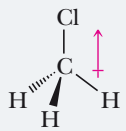
STRATEGY

To determine whether a molecule is polar, first determine if it has polar bonds, and if it does, determine whether the vector sum of the bond dipoles is zero. If the vector sum of the bond dipoles is not zero, the molecule is polar.

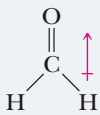
SOLUTION

Both chloromethane (CH_3Cl) and formaldehyde (CH_2O) have polar bonds and, because of their geometry, are polar molecules. Because acetylene (C_2H_2) is linear, and each of its C—H bonds is nonpolar covalent, the molecule is nonpolar.

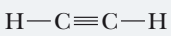




Chloromethane (polar)



Formaldehyde (polar)



Acetylene (nonpolar)

See problems 1.44, 1.46

PROBLEM 1.9

Both carbon dioxide (CO_2) and sulfur dioxide (SO_2) are triatomic molecules. Account for the fact that carbon dioxide is a nonpolar molecule, whereas sulfur dioxide is a polar molecule.

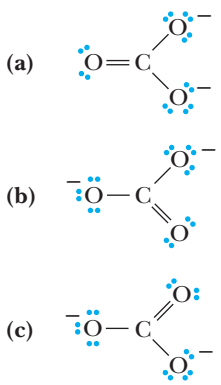


FIGURE 1.11 Three Lewis structures for the carbonate ion.

1.5 What Is Resonance?

As chemists developed a better understanding of covalent bonding in organic compounds, it became obvious that, for a great many molecules and ions, no single Lewis structure provides a truly accurate representation. For example, Figure 1.11 shows three Lewis structures for the carbonate ion, CO_3^{2-}, each of which shows carbon bonded to three oxygen atoms by a combination of one double bond and two single bonds. Each Lewis structure implies that one carbon–oxygen bond is different from the other two. This, however, is not the case; it has been shown that all three carbon–oxygen bonds are identical.

To describe the carbonate ion, as well as other molecules and ions for which no single Lewis structure is adequate, we turn to the theory of resonance.

A. The Theory of Resonance

The theory of resonance was developed by Linus Pauling in the 1930s. According to this theory, many molecules and ions are best described by writing two or more Lewis structures and considering the real molecule or ion to be a composite of these structures. We call

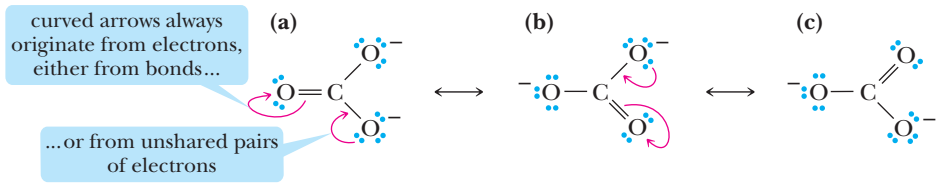


FIGURE 1.12 The carbonate ion represented as a hybrid of three equivalent contributing structures. Curved arrows show the redistribution of valence electrons between one contributing structure and the next.

individual Lewis structures **resonance contributing structures**. We show that the real molecule or ion is a **resonance hybrid** of the various contributing structures by interconnecting them with **double-headed arrows**.

Resonance contributing structures Representations of a molecule or ion that differ only in the distribution of valence electrons.

Resonance hybrid A molecule or ion that is best described as a composite of a number of contributing structures.

Double-headed arrow A symbol used to connect contributing structures.

Figure 1.12 shows three resonance contributing structures for the carbonate ion. The three are equivalent, meaning that they have identical patterns of covalent bonding (each contributing structure has one double bond and two single bonds) and are of equal energy.

Use of the term *resonance* for this theory of covalent bonding might suggest to you that bonds and electron pairs constantly change back and forth from one position to another over time. This notion is not at all correct. The carbonate ion, for example, has one and only one real structure. The problem is ours: How do we draw that one real structure? The resonance method is a way to describe the real structure and at the same time retain Lewis structures with electron-pair bonds. Thus, although we realize that the carbonate ion is not accurately represented by any one contributing structure shown in Figure 1.12, we continue to represent it as one of these for convenience. We understand, of course, that what is intended is the resonance hybrid.

A final note. Do not confuse resonance contributing structures with equilibration among different species. A molecule described as a resonance hybrid is not equilibrating among individual electron configurations. Rather, the molecule has only one structure, which is best described as a hybrid of its various contributing structures. The colors of the color wheel provide a good analogy. Green is not a primary color; the colors yellow and blue are mixed to make green. You can think of molecules represented by resonance hybrids as being green. Green is not sometimes yellow and sometimes blue. Green is green! In an analogous way, a molecule described as a resonance hybrid is not sometimes one contributing structure and sometimes another. It is a single structure all of the time—the resonance hybrid.

B. Curved Arrows and Electron Pushing

Notice in Figure 1.12 that the only change from resonance contributing structure (a) to (b) and then from (b) to (c) is a redistribution of valence electrons. To show how this redistribution of valence electrons occurs, chemists use a symbol called a **curved arrow**, which shows the repositioning of an electron pair from its origin (the tail of the arrow) to its destination (the head of the arrow). The repositioning may be from an atom to an adjacent bond or from a bond to an adjacent atom.

Curved arrow A symbol used to show the redistribution of valence electrons.

A curved arrow is nothing more than a bookkeeping symbol for keeping track of electron pairs or, as some call it, **electron pushing**. Do not be misled by its simplicity. Electron pushing will help you see the relationship between contributing structures. Furthermore, it will help you follow bond-breaking and bond-forming steps in organic reactions. Understanding this type of electron pushing is a survival skill in organic chemistry; your success in this course depends on it.

C. Rules for Writing Acceptable Resonance Contributing Structures

You must follow these four rules in writing acceptable resonance contributing structures:

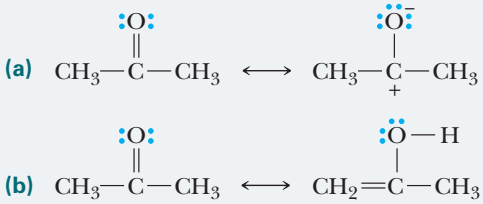
1. All contributing structures must have the same number of valence electrons.
2. All contributing structures must obey the rules of covalent bonding; thus, no contributing structure may have more than 2 electrons in the valence shell of hydrogen or more

than 8 electrons in the valence shell of a second-period element. Third-period elements, such as sulfur and phosphorus, may have up to 12 electrons in their valence shells.

3. The positions of all nuclei must be the same; that is, contributing structures differ only in the distribution of valence electrons.
4. All contributing structures must have the same total number of paired and unpaired electrons.

EXAMPLE 1.10

Which sets are pairs of acceptable resonance contributing structures?



STRATEGY

The concept being examined here is that resonance involves the redistribution of valence electrons; the connectivity of atoms does not change.

SOLUTION

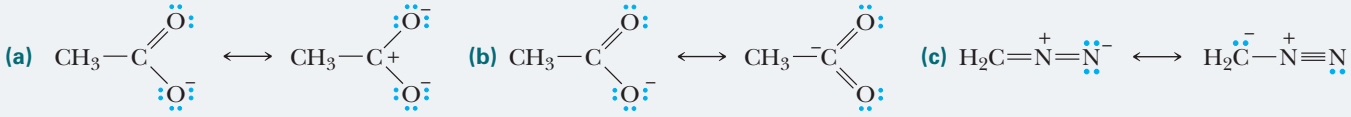
(a) A pair of resonance contributing structures. They differ only in the distribution of valence electrons.

(b) Not a pair of resonance contributing structures. They differ in the arrangement of their atoms. Oxygen is bonded to a hydrogen atom in the Lewis structure on the right, but the other structure contains no such bond.

See problem 1.47

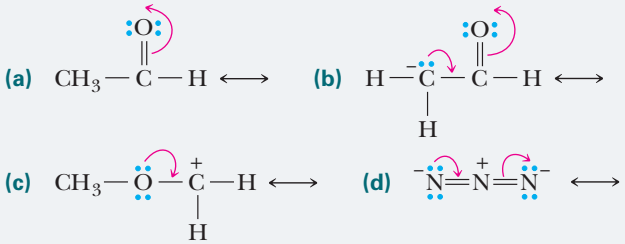
PROBLEM 1.10

Which sets are pairs of resonance contributing structures?



EXAMPLE 1.11

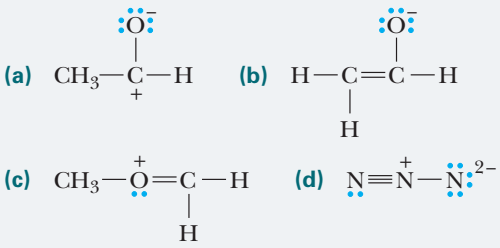
Draw the resonance contributing structure indicated by the curved arrows. Be certain to show all valence electrons and all formal charges.



STRATEGY

Any curved arrow that points to an atom will generate a lone pair of electrons. Any curved arrow that points to a bond will result in an additional bond on top of the original bond. That is, a single bond will become a double bond and a double bond will become a triple bond.

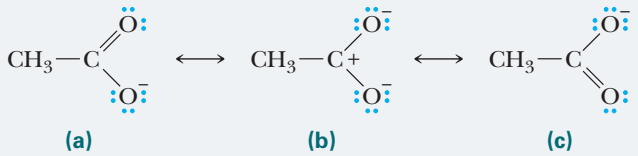
SOLUTION



See problems 1.48, 1.50

PROBLEM 1.11

Use curved arrows to show the redistribution of valence electrons in converting resonance contributing structure (a) to (b) and then (b) to (c). Also show, using curved arrows, how (a) can be converted to (c) without going through (b).



1.6 What Is the Orbital Overlap Model of Covalent Bonding?

As much as the Lewis and VSEPR models help us to understand covalent bonding and the geometry of molecules, they leave many questions unanswered. The most important of these questions is the relation between molecular structure and chemical reactivity. For example, carbon–carbon double bonds are different in chemical reactivity from carbon–carbon single bonds. Most carbon–carbon single bonds are quite unreactive but carbon–carbon double bonds, as we will see in Chapter 5, react with a wide variety of reagents. The Lewis model and VSEPR give us no way to account for these differences. Therefore, let us turn to a newer model of covalent bonding, namely, the formation of covalent bonds by the overlap of atomic orbitals.

A. Shapes of Atomic Orbitals

One way to visualize the electron density associated with a particular orbital is to draw a boundary surface around the region of space that encompasses some arbitrary percentage of the charge density associated with that orbital. Most commonly, we draw the boundary surface at 95%. Drawn in this manner, all *s* orbitals have the shape of a sphere with its center at the nucleus (Figure 1.13). Of the various *s* orbitals, the sphere representing the 1*s* orbital is the smallest. A 2*s* orbital is a larger sphere, and a 3*s* orbital is an even larger sphere.

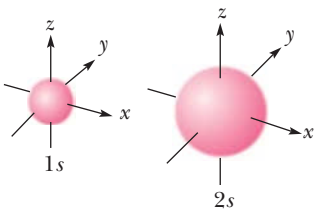


FIGURE 1.13 Shapes of 1*s* and 2*s* atomic orbitals.

Figure 1.14 shows the three-dimensional shapes of the three 2*p* orbitals, combined in one diagram to illustrate their relative orientations in space. Each 2*p* orbital consists of two lobes arranged in a straight line with the nucleus in the middle. The three 2*p* orbitals are mutually perpendicular and are designated $2p_x$, $2p_y$, and $2p_z$.

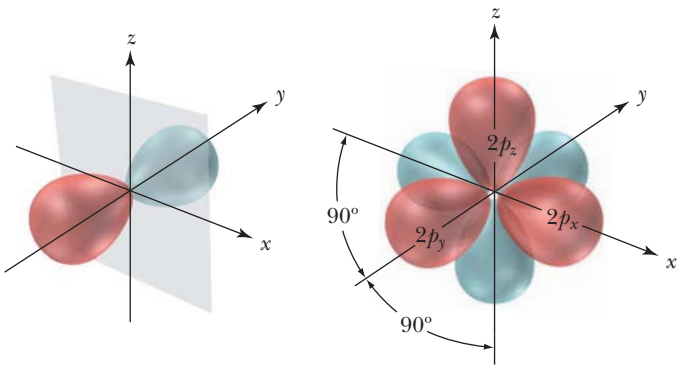


FIGURE 1.14 Shapes of $2p_x$, $2p_y$, and $2p_z$ atomic orbitals. The three 2*p* orbitals are mutually perpendicular. One lobe of each orbital is shown in red, the other in blue.

B. Formation of a Covalent Bond by the Overlap of Atomic Orbitals

Sigma (σ) bond A covalent bond in which the overlap of atomic orbitals is concentrated along the bond axis.

According to the orbital overlap model, a covalent bond is formed when a portion of an atomic orbital of one atom overlaps a portion of an atomic orbital of another atom. In forming the covalent bond in H_2, for example, two hydrogens approach each other so that their 1*s* atomic orbitals overlap to form a sigma covalent bond (Figure 1.15). A **sigma (σ) bond** is a covalent bond in which orbitals overlap along the axis joining the two nuclei.

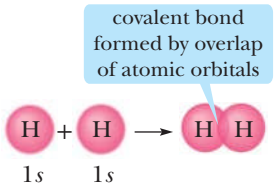
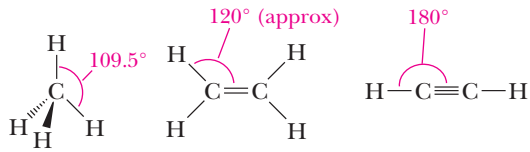


FIGURE 1.15 Formation of the covalent bond in H_2 by the overlap of the 1*s* atomic orbitals of each hydrogen.

C. Hybridization of Atomic Orbitals

The formation of a covalent bond between two hydrogen atoms is straightforward. The formation of covalent bonds with second-period elements, however, presents the following problem: In forming covalent bonds, atoms of carbon, nitrogen, and oxygen (all second-period elements) use 2*s* and 2*p* atomic orbitals. The three 2*p* atomic orbitals are at angles of 90° to one another (Figure 1.14), and if atoms of second-period elements used these orbitals to form covalent bonds, the bond angles around each would be approximately 90°. Bond angles of 90°, however, are rarely observed in organic molecules. What we find, instead, are bond angles of approximately 109.5° in molecules with only single bonds, 120° in molecules with double bonds, and 180° in molecules with triple bonds:



Hybrid orbitals An orbital produced from the combination of two or more atomic orbitals.

To account for these observed bond angles, Pauling proposed that atomic orbitals combine to form new orbitals, called **hybrid orbitals**. In your introductory chemistry course, you learned about several types of hybrid orbitals made up from *s*, *p*, and even *d* atomic orbitals. In organic chemistry, because we deal almost exclusively with elements of the first and second periods of the Periodic Table, we are mostly concerned with the hybrid orbitals that result from the combination of *s* and *p* atomic orbitals. These are aptly named the *sp*-type hybrid orbitals, of which there are three types. The type and number of hybrid orbitals formed are equal to the number of atomic orbitals combined. Elements of the second period form these three types of hybrid orbitals, designated sp^3, sp^2, and *sp*, each of which can contain up to two electrons. We review these hybrid orbitals for you here. Keep in mind that superscripts in the designation of hybrid orbitals tell you how many atomic orbitals have been combined to form the hybrid orbitals. The designation sp^3, for example, tells you that *one s* atomic orbital and *three p* atomic orbitals are combined in forming the hybrid orbital. Do not confuse this use of superscripts with how we use superscripts in writing a ground-state electron configuration—for example, $1s^2 2s^2 2p^5$ for fluorine. In the case of an electron configuration, superscripts tell you the number of electrons in each orbital or set of orbitals.

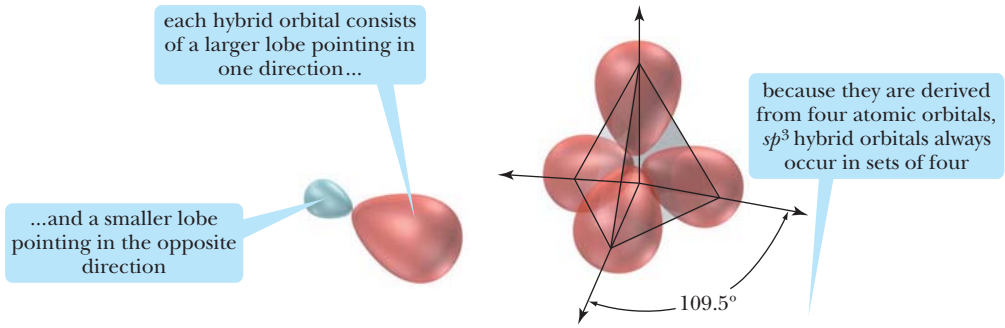
As you review each type of hybrid orbital in the following subsections, take note of (1) the number and types of atomic orbitals that were combined to make the hybrid orbitals, (2) the number of *p* orbitals that remain uncombined, and (3) the three-dimensional arrangement in space of the hybrid orbitals and any uncombined *p* orbitals. In particular, you will find that these three-dimensional arrangements will retain the names (tetrahedral, trigonal planar, linear) and bond angles (109.5°, 120°, and 180°) used to describe the shapes of molecules in our section on VSEPR (Section 1.3).

D. sp^3 Hybrid Orbitals: Bond Angles of Approximately 109.5°

sp^3 Hybrid orbital An orbital produced by the combination of one *s* atomic orbital and three *p* atomic orbitals.

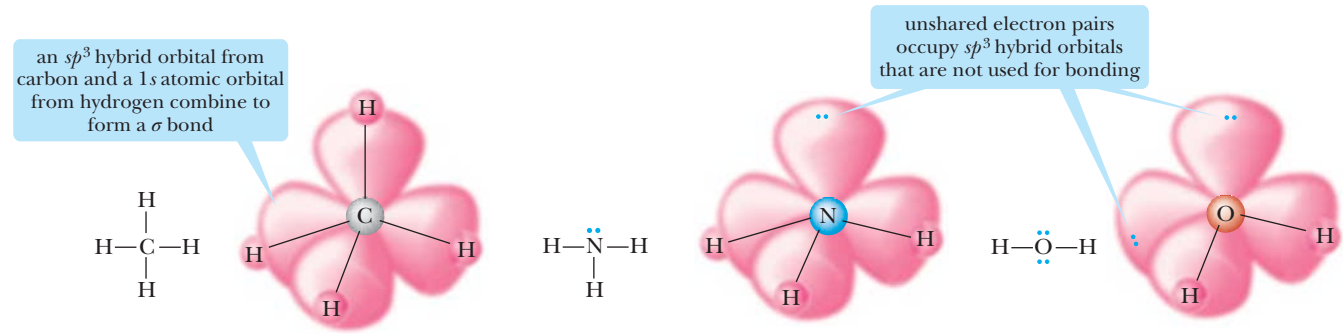
The combination of one 2*s* atomic orbital and three 2*p* atomic orbitals forms four equivalent **sp^3 hybrid orbitals** (Figure 1.16).

In Section 1.2, we described the covalent bonding in CH_4, NH_3, and H_2O in terms of the Lewis model, and in Section 1.3 we used VSEPR to predict bond angles of approximately 109.5° in each molecule. Figure 1.17 shows the bonding in these molecules in terms of the overlap of orbitals. Notice that the central atom in each compound uses four sp^3



(a) An sp^3 orbital **(b)** Four tetrahedral sp^3 orbitals

FIGURE 1.16 sp^3 Hybrid orbitals. (a) Representation of a single sp^3 hybrid orbital showing two lobes of unequal size. (b) Three-dimensional representation of four sp^3 hybrid orbitals, which point toward the corners of a regular tetrahedron. The smaller lobes of each sp^3 hybrid orbital are hidden behind the larger lobes.



	Methane	**Ammonia**	**Water**
Arrangement of orbitals:	Tetrahedral	Tetrahedral	Tetrahedral
Shape of molecule:	Tetrahedral	Pyramidal	Bent

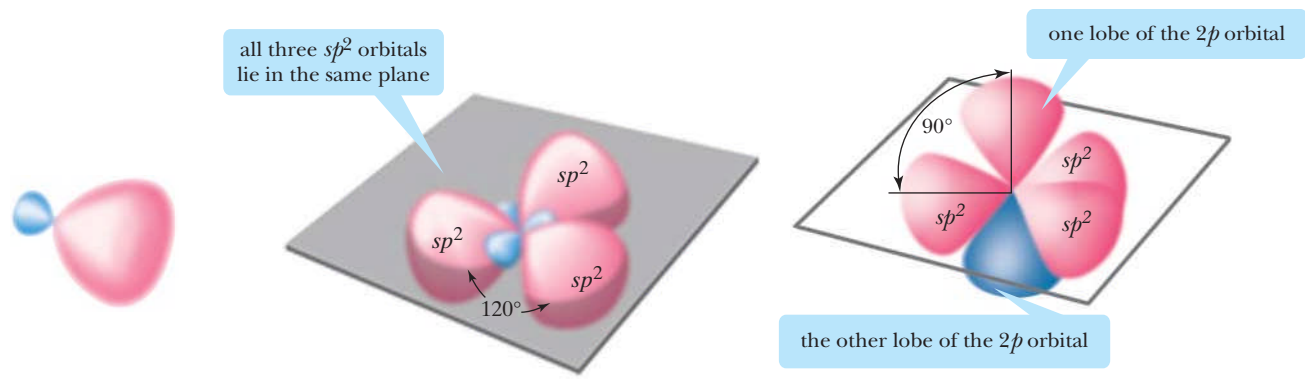
FIGURE 1.17 Orbital overlap models of methane, ammonia, and water.

hybrid orbitals to either form a sigma (σ) bond with a hydrogen atom or to hold unshared pairs of electrons. In each case, the orbitals are arranged tetrahedrally, while the shape that describes each molecule is based only on the arrangement of atoms.

E. sp^2 Hybrid Orbitals: Bond Angles of Approximately 120°

The combination of one 2s atomic orbital and two 2p atomic orbitals forms three equivalent ***sp*² hybrid orbitals** (Figure 1.18). Because they are derived from three atomic orbitals, sp^2 hybrid orbitals always occur in sets of three. The third 2p atomic orbital (remember $2p_x$, $2p_y$, and $2p_z$) is not involved in hybridization and consists of two lobes lying perpendicular to the plane of the hybrid orbitals [Figure 1.18(c)].

***sp*² Hybrid orbital** An orbital produced by the combination of one *s* atomic orbital and two *p* atomic orbitals.



(a) An sp^2 orbital **(b)** Three sp^2 orbitals **(c)**

FIGURE 1.18 sp^2 Hybrid orbitals. (a) A single sp^2 hybrid orbital showing two lobes of unequal size. (b) The three sp^2 hybrid orbitals with their axes in a plane at angles of 120°. (c) The unhybridized 2p atomic orbital perpendicular to the plane created by the three sp^2 hybrid orbitals.

Second-period elements use sp^2 hybrid orbitals to form double bonds. Figure 1.19(a) shows a Lewis structure for ethylene, C_2H_4. A sigma bond between the carbons in ethylene forms by the overlap of sp^2 hybrid orbitals along a common axis [Figure 1.19(b)]. Each carbon also forms sigma bonds to two hydrogens. The remaining $2p$ orbitals on adjacent carbon atoms lie parallel to each other and overlap to form a pi bond [Figure 1.19(c)]. A **pi (π) bond** is a covalent bond formed by the overlap of parallel p orbitals. Because of the lesser degree of overlap of orbitals forming pi bonds compared with those forming sigma bonds, pi bonds are generally weaker than sigma bonds.

Pi (π) bond A covalent bond formed by the overlap of parallel *p* orbitals.

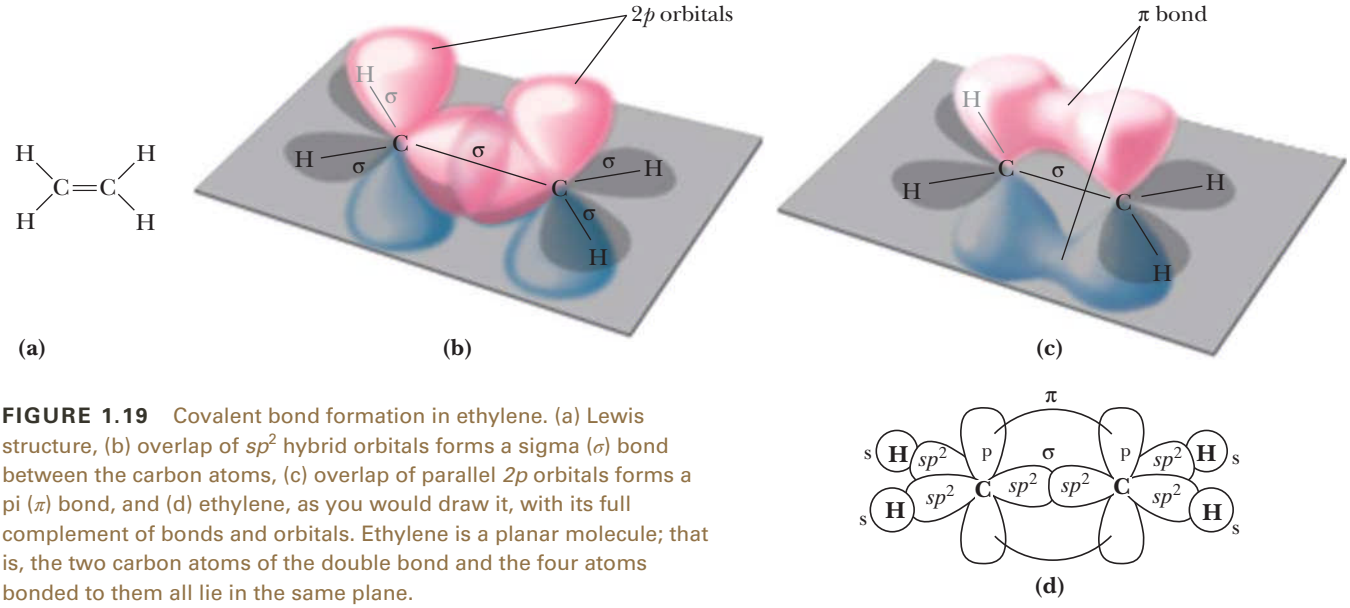


FIGURE 1.19 Covalent bond formation in ethylene. (a) Lewis structure, (b) overlap of sp^2 hybrid orbitals forms a sigma (σ) bond between the carbon atoms, (c) overlap of parallel *2p* orbitals forms a pi (π) bond, and (d) ethylene, as you would draw it, with its full complement of bonds and orbitals. Ethylene is a planar molecule; that is, the two carbon atoms of the double bond and the four atoms bonded to them all lie in the same plane.

The orbital overlap model describes all double bonds in the same way that we have described a carbon–carbon double bond. In formaldehyde, CH_2O, the simplest organic molecule containing a carbon–oxygen double bond, carbon forms sigma bonds to two hydrogens by the overlap of an sp^2 hybrid orbital of carbon and the $1s$ atomic orbital of each hydrogen. Carbon and oxygen are joined by a sigma bond formed by the overlap of sp^2 hybrid orbitals and a pi bond formed by the overlap of unhybridized $2p$ atomic orbitals (Figure 1.20).

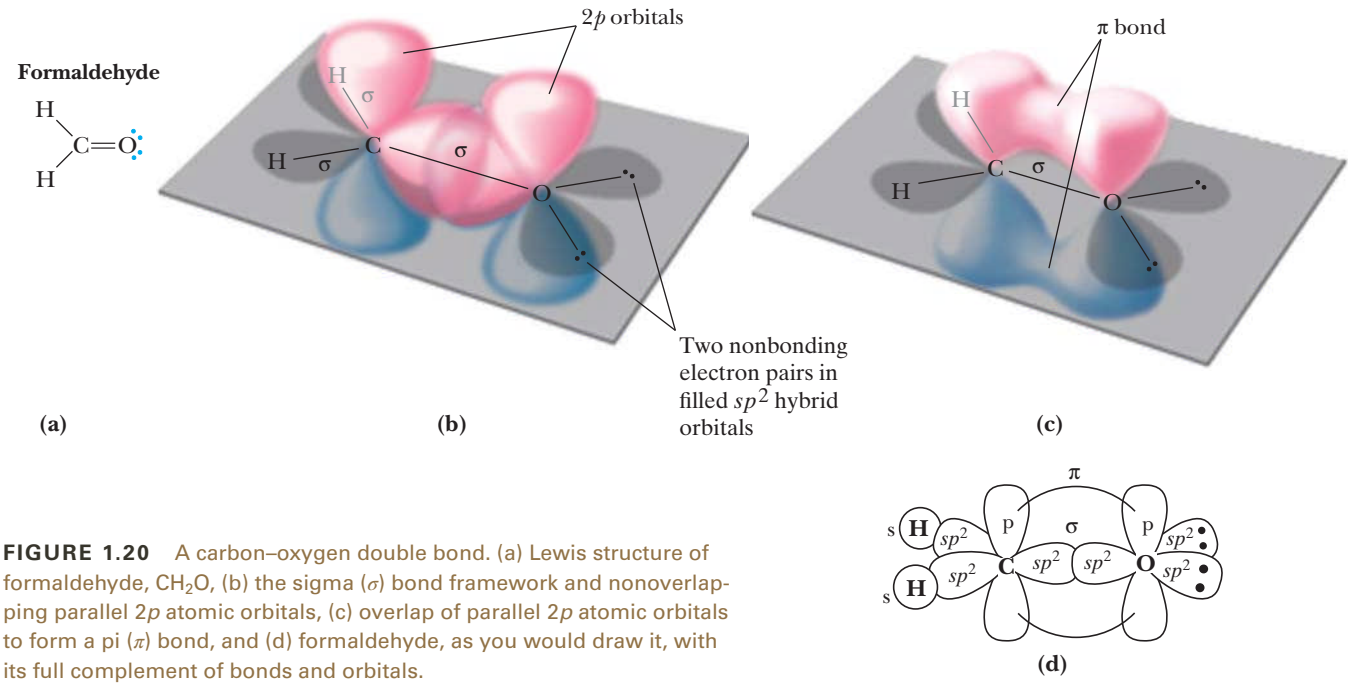


FIGURE 1.20 A carbon–oxygen double bond. (a) Lewis structure of formaldehyde, CH_2O, (b) the sigma (σ) bond framework and nonoverlapping parallel $2p$ atomic orbitals, (c) overlap of parallel $2p$ atomic orbitals to form a pi (π) bond, and (d) formaldehyde, as you would draw it, with its full complement of bonds and orbitals.

F. *sp* Hybrid Orbitals: Bond Angles of Approximately 180°

The combination of one 2*s* atomic orbital and one 2*p* atomic orbital forms two equivalent ***sp* hybrid orbitals**. Because they are derived from two atomic orbitals, *sp* hybrid orbitals always occur in sets of two (Figure 1.21).

Figure 1.22 shows a Lewis structure and an orbital overlap diagram for acetylene, C_2H_2. A carbon–carbon triple bond consists of one sigma bond and two pi bonds. The sigma bond is formed by the overlap of *sp* hybrid orbitals. One pi bond is formed by the overlap of a pair of parallel 2*p* atomic orbitals. The second pi bond is formed by the overlap of a second pair of parallel 2*p* atomic orbitals.

***sp* Hybrid orbitals** A hybrid atomic orbital produced by the combination of one *s* atomic orbital and one *p* atomic orbital.

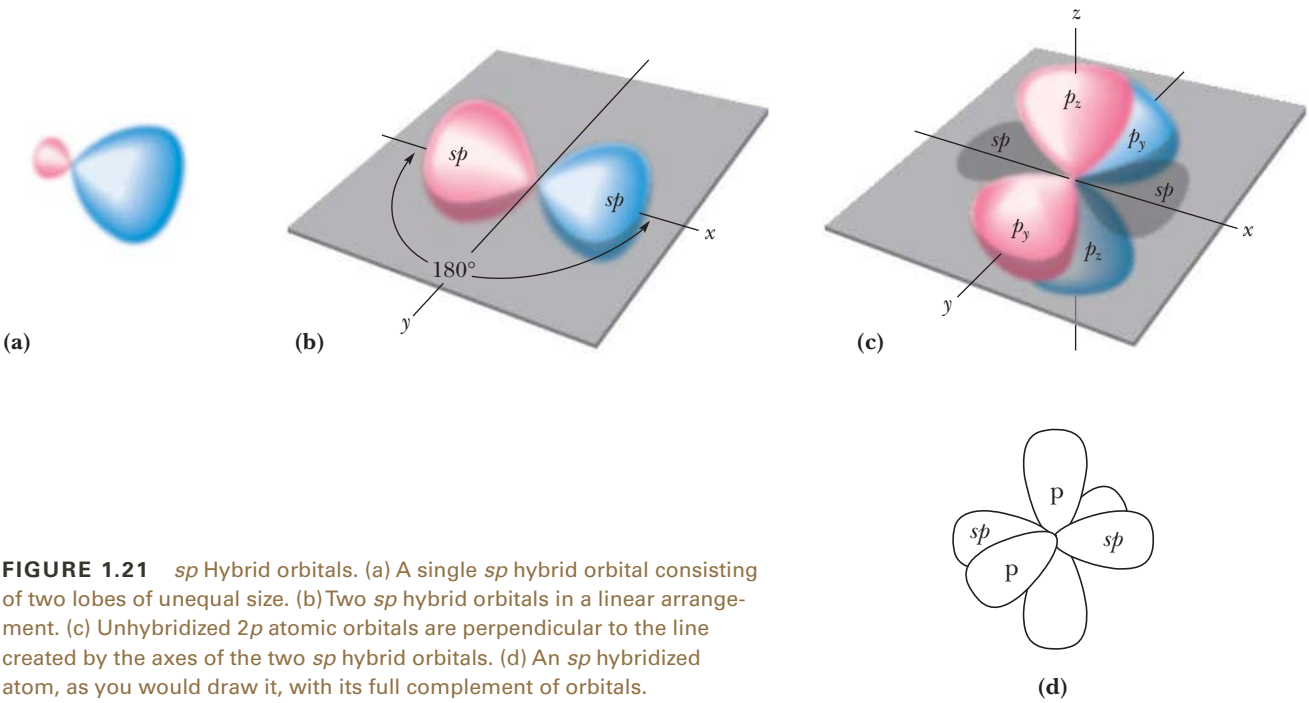


FIGURE 1.21 *sp* Hybrid orbitals. (a) A single *sp* hybrid orbital consisting of two lobes of unequal size. (b) Two *sp* hybrid orbitals in a linear arrangement. (c) Unhybridized 2*p* atomic orbitals are perpendicular to the line created by the axes of the two *sp* hybrid orbitals. (d) An *sp* hybridized atom, as you would draw it, with its full complement of orbitals.

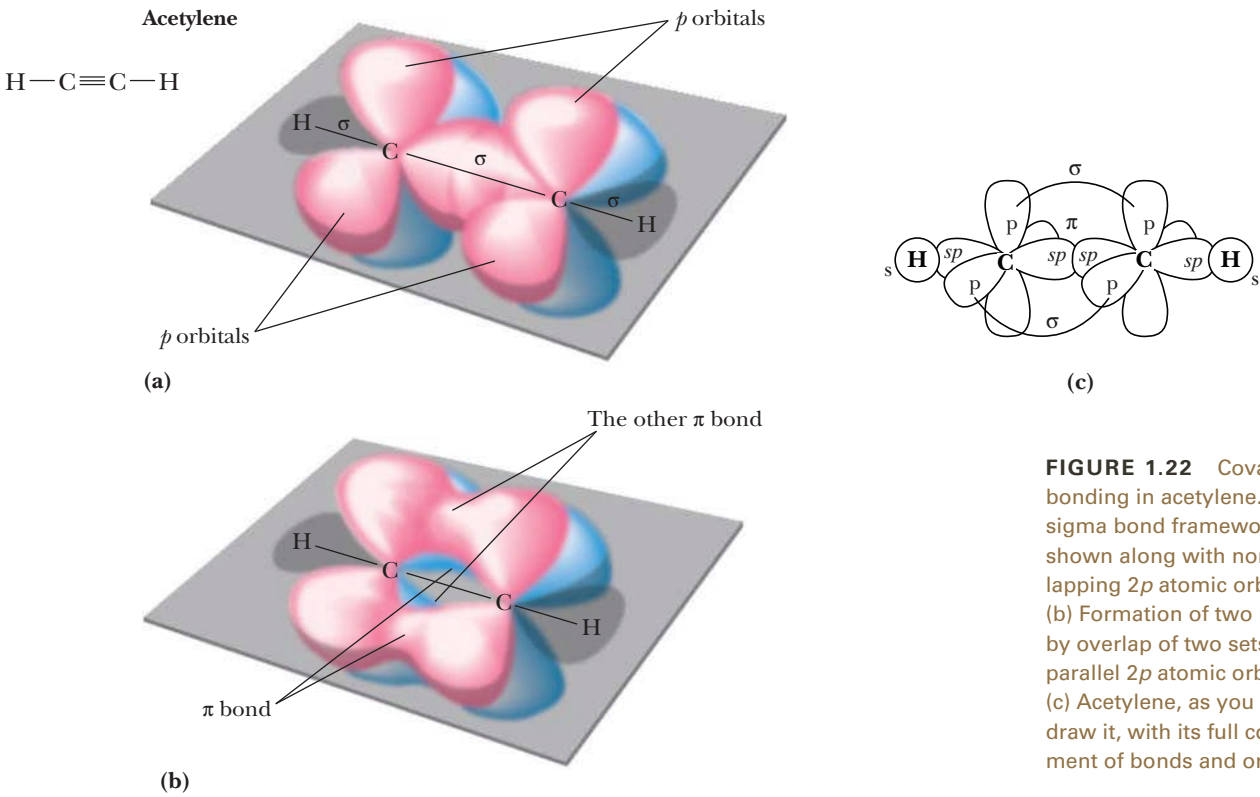
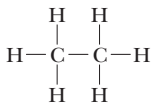
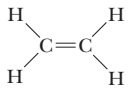


FIGURE 1.22 Covalent bonding in acetylene. (a) The sigma bond framework shown along with nonoverlapping 2*p* atomic orbitals. (b) Formation of two pi bonds by overlap of two sets of parallel 2*p* atomic orbitals. (c) Acetylene, as you would draw it, with its full complement of bonds and orbitals.

Table 1.8 summarizes the relationship among the number of groups bonded to carbon, orbital hybridization, and the types of bonds involved.

TABLE 1.8 Covalent Bonding of Carbon

Groups Bonded to Carbon	Orbital Hybridization	Predicted Bond Angles	Types of Bonds to Carbon	Example	Name
4	sp^3	109.5°	four sigma bonds		ethane
3	sp^2	120°	three sigma bonds and one pi bond		ethylene
2	sp	180°	two sigma bonds and two pi bonds		acetylene

EXAMPLE 1.12

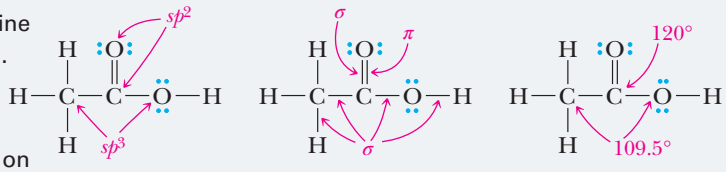
Describe the bonding in acetic acid, CH_3COOH, in terms of the orbitals involved, and predict all bond angles.

STRATEGY

First draw a Lewis structure for acetic acid and then determine the number of regions of electron density about each atom.

SOLUTION

The following are three identical Lewis structures. Labels on the first structure point to atoms and show hybridization. Labels on the second structure point to bonds and show the type of bond, either sigma or pi. Labels on the third structure point to atoms and show bond angles about each atom as predicted by valence-shell electron-pair repulsion.



See problems 1.51, 1.52

PROBLEM 1.12

Describe the bonding in these molecules in terms of the atomic orbitals involved, and predict all bond angles:

(a) $CH_3CH{=}CH_2$
(b) CH_3NH_2

1.7 What Are Functional Groups?

Over 10 million organic compounds have been discovered or made by organic chemists! Surely it would seem to be an almost impossible task to learn the physical and chemical properties of this many compounds. Fortunately, the study of organic compounds is not as formidable a task as you might think. While organic compounds can undergo a wide variety of chemical reactions, only certain portions of their structure are changed in any particular reaction. The part of an organic molecule that undergoes chemical reactions is called a **functional group**, and, as we will see, the same functional group, in whatever organic molecule we find it, undergoes the same types of chemical reactions. Therefore, you do not have to study the chemical reactions of even a fraction of the 10 million known organic compounds. Instead you need only to identify a few characteristic types of functional groups and then study the chemical reactions that each undergoes.

Functional group An atom or a group of atoms within a molecule that shows a characteristic set of physical and chemical properties.

Functional groups are also important because they are the units by which we divide organic compounds into families of compounds. For example, we group those compounds which contain an —OH (hydroxyl) group bonded to a tetrahedral carbon into a family called alcohols, and compounds containing a —COOH (carboxyl) group into a family called carboxylic acids. In Table 1.9, we introduce seven of the most common functional groups. A complete list of all functional groups we will study is on page I.10 at the end of the text.

TABLE 1.9 Seven Common Functional Groups

Functional Group	Name of Group	Present In	Example	Name of Example
—OH	hydroxyl	alcohols	CH_3CH_2OH	Ethanol
$-NH_2$	amino	amines	$CH_3CH_2NH_2$	Ethanamine
$-\overset{\overset{O}{\|}}{C}-H$	carbonyl	aldehydes	$CH_3\overset{\overset{O}{\|}}{C}H$	Ethanal
$-\overset{\overset{O}{\|}}{C}-$	carbonyl	ketones	$CH_3\overset{\overset{O}{\|}}{C}CH_3$	Acetone
$-\overset{\overset{O}{\|}}{C}-OH$	carboxyl	carboxylic acids	$CH_3\overset{\overset{O}{\|}}{C}OH$	Acetic acid
$-\overset{\overset{O}{\|}}{C}-O-$	carboxylate	esters	$CH_3\overset{\overset{O}{\|}}{C}OCH_3$	Ethyl acetate
$-\overset{\overset{O}{\|}}{C}-\underset{\|}{N}-$	carbamide	amides	$CH_3\overset{\overset{O}{\|}}{C}NH_2$	Acetamide

At this point, our concern is only pattern recognition—that is, how to recognize these seven functional groups when you see them and how to draw structural formulas of molecules containing them.

Finally, functional groups serve as the basis for naming organic compounds. Ideally, each of the 10 million or more organic compounds must have a name that is different from every other compound.

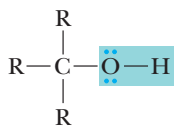
To summarize, functional groups

- are sites of chemical reaction; a particular functional group, in whatever compound we find it, undergoes the same types of chemical reactions.
- determine, in large measure, the physical properties of a compound.
- are the units by which we divide organic compounds into families.
- serve as a basis for naming organic compounds.

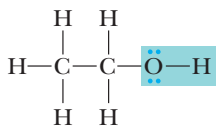
A. Alcohols

Hydroxyl group An —OH group.

The functional group of an **alcohol** is an **—OH (hydroxyl) group** bonded to a tetrahedral (sp^3 hybridized) carbon atom. In the general formula that follows, we use the symbol R to indicate either a hydrogen or another carbon group. The important point in the general structure is that the —OH group is bonded to a tetrahedral carbon atom:



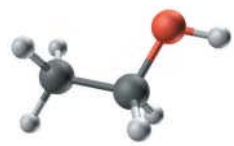
Functional group (R=H or carbon group)



Structural formula

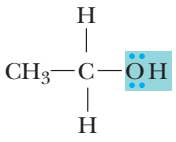
CH_3CH_2OH

Condensed structural formula

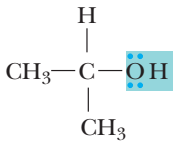


The rightmost representation of this alcohol is a **condensed structural formula**, CH_3CH_2OH. In a condensed structural formula, CH_3 indicates a carbon bonded to three hydrogens, CH_2 indicates a carbon bonded to two hydrogens, and CH indicates a carbon bonded to one hydrogen. We generally do not show unshared pairs of electrons in a condensed structural formula.

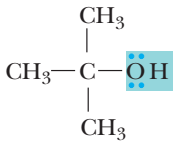
Alcohols are classified as **primary (1°)**, **secondary (2°)**, or **tertiary (3°)**, depending on the number of carbon atoms bonded to the carbon bearing the —OH group:



A 1° alcohol



A 2° alcohol



A 3° alcohol

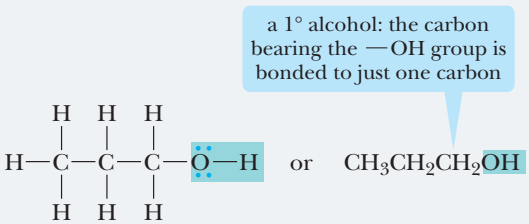
EXAMPLE 1.13

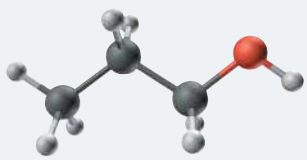
Write condensed structural formulas for the two alcohols with the molecular formula C_3H_8O. Classify each as primary, secondary, or tertiary.

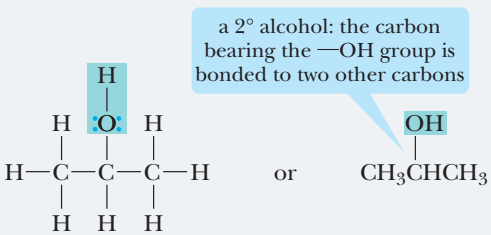
STRATEGY

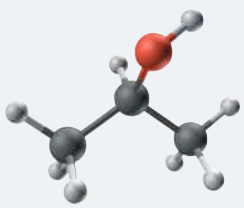
First, bond the three carbon atoms in a chain with the —OH (hydroxyl) group bonded to either an end carbon or the middle carbon of the chain. Then, to complete each structural formula, add seven hydrogens so that each carbon has four bonds to it.

SOLUTION









See problems 1.53–1.56, 1.58, 1.59

PROBLEM 1.13

Write condensed structural formulas for the four alcohols with the molecular formula $C_4H_{10}O$. Classify each as primary, secondary, or tertiary.

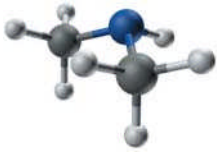
B. Amines

Amino group An sp^3 hybridized nitrogen atom bonded to one, two, or three carbon groups.

The functional group of an amine is an **amino group**—a nitrogen atom bonded to one, two, or three carbon atoms. In a **primary (1°) amine**, nitrogen is bonded to one carbon atom. In a **secondary (2°) amine**, it is bonded to two carbon atoms, and in a **tertiary (3°) amine**, it is bonded to three carbon atoms. The second and third structural formulas that follow can be written in a more abbreviated form by collecting the CH_3 groups and writing them as $(CH_3)_2NH$ and $(CH_3)_3N$, respectively.

$CH_3\ddot{N}H_2$

Methylamine
(a 1° amine)



$CH_3\ddot{N}H$ or $(CH_3)_2\ddot{N}H$
|
CH_3

Dimethylamine
(a 2° amine)

$CH_3\ddot{N}CH_3$ or $(CH_3)_3\ddot{N}$
|
CH_3

Trimethylamine
(a 3° amine)

EXAMPLE 1.14

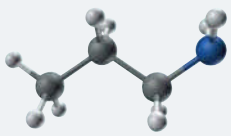
Write condensed structural formulas for the two primary (1°) amines with the molecular formula C_3H_9N.

STRATEGY

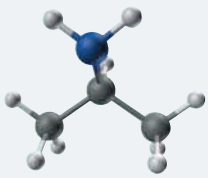
For a primary amine, draw a nitrogen atom bonded to two hydrogens and one carbon. The nitrogen may be bonded to the three-carbon chain in two different ways. Then add the seven hydrogens to give each carbon four bonds and give the correct molecular formula.

SOLUTION

$CH_3CH_2CH_2\ddot{N}H_2$



$CH_3CH(\ddot{N}H_2)CH_3$



See problems 1.53–1.56, 1.58, 1.59

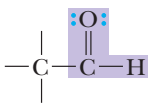
PROBLEM 1.14

Write condensed structural formulas for the three secondary amines with molecular formula $C_4H_{11}N$.

C. Aldehydes and Ketones

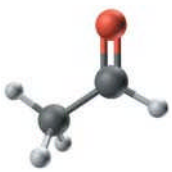
Both aldehydes and ketones contain a **C═O (carbonyl) group**. The **aldehyde** functional group contains a carbonyl group bonded to a hydrogen. In formaldehyde, CH_2O, the simplest aldehyde, the carbonyl carbon is bonded to two hydrogen atoms. In a condensed structural formula, the aldehyde group may be written showing the carbon–oxygen double bond as CH═O, or, alternatively, it may be written —CHO. The functional group of a **ketone** is a carbonyl group bonded to two carbon atoms.

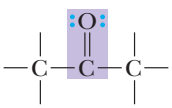
Carbonyl group A C═O group.



Functional group

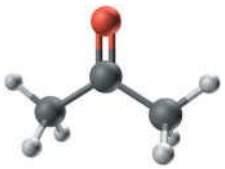
An aldehyde





Functional group

A ketone



EXAMPLE 1.15

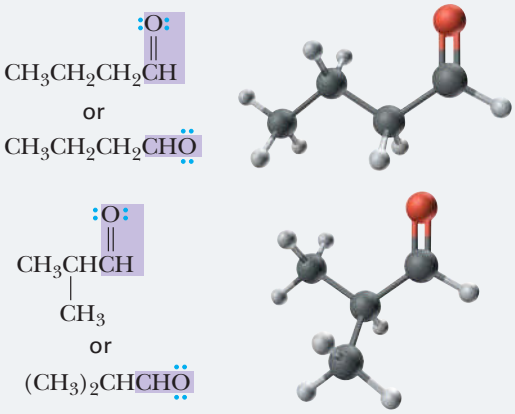
Write condensed structural formulas for the two aldehydes with the molecular formula C_4H_8O.

STRATEGY

First, draw the functional group of an aldehyde and add the remaining carbons, which in this case may be bonded in two different ways. Then, add seven hydrogens to complete the four bonds of each carbon and give the correct molecular formula: Note that the aldehyde group may be written showing the carbon–oxygen double bond as C═O, or, alternatively, it may be written —CHO.

See problems 1.53–1.56, 1.58, 1.59

SOLUTION



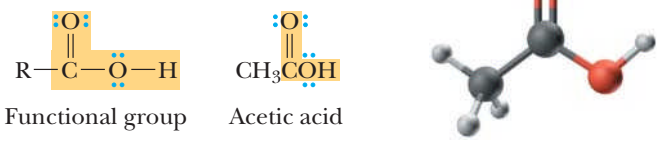
PROBLEM 1.15

Write condensed structural formulas for the three ketones with the molecular formula $C_5H_{10}O$.

D. Carboxylic Acids, Esters, and Amides

Carboxyl group A —COOH group.

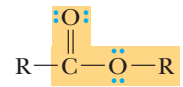
The functional group of a **carboxylic acid** is a **—COOH (carboxyl:** *carb*onyl + hydr*oxyl*) group. In an **ester**, the —OH group is replaced with an —OR group, and in an **amide**, an $—NH_2$, —NHR, or $—NR_2$ group is bonded to the carbonyl group:



Functional group

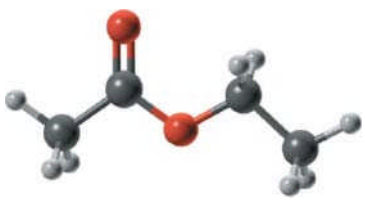
Acetic acid

Carboxylic acid

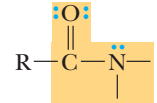


Functional group

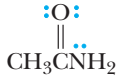
Ethyl acetate



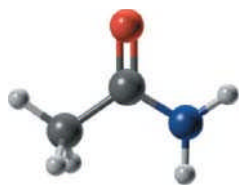
Ester



Functional group



Acetamide



Amide