

INTRODUCTION TO
**ORGANIC
CHEMISTRY**

WILLIAM H. BROWN

THOMAS POON



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Introduction to **Organic Chemistry**

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WILLIAM H. BROWN

Beloit College

THOMAS POON

Claremont McKenna College
Scripps College
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*To Carolyn,
with whom life is a joy*

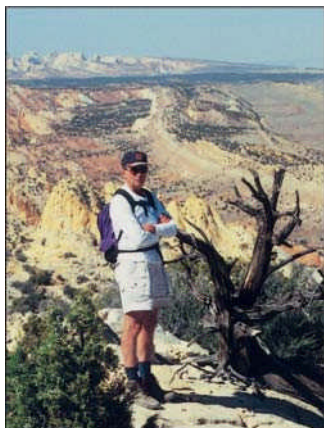
BILL B4OWN

*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.

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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.

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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.

Mechanism Explorer: Sketch and Submission Reaction Explorer Help

(Intermediate) Reactant (Intermediate) Product

Tip: Add curved arrows in this sketcher to represent the electron flows for the next mechanism step

Submitted Mechanism Steps

(Intermediate) Reactant (Intermediate) Product

Overall Reaction

Mix Reactants, Aprotic
Review Examples

Reactants Reagents Target Product 207078

Home Review Links Home

1. Mix Reactants in DMSO or THF (solvent)
2. H₂O (Aqueous workup)

Mix Reactants in Alcohol (solvent)

Select a reagent from the reagent frame.

Pathway (0.000 sec) Help

Reactants Reagents Products

Select a Reactant Select a Reagent Apply Reaction to Generate Product(s)

C06T04Q21B1 Get help answering Molecular Drawing questions.

the product of a substitution reaction.

Edit

Click on the drawing box above to activate the MarvinSketch drawing tool and then draw your answer to this question. If there is no reaction, then check the "no reaction" box below.

no reaction

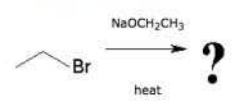
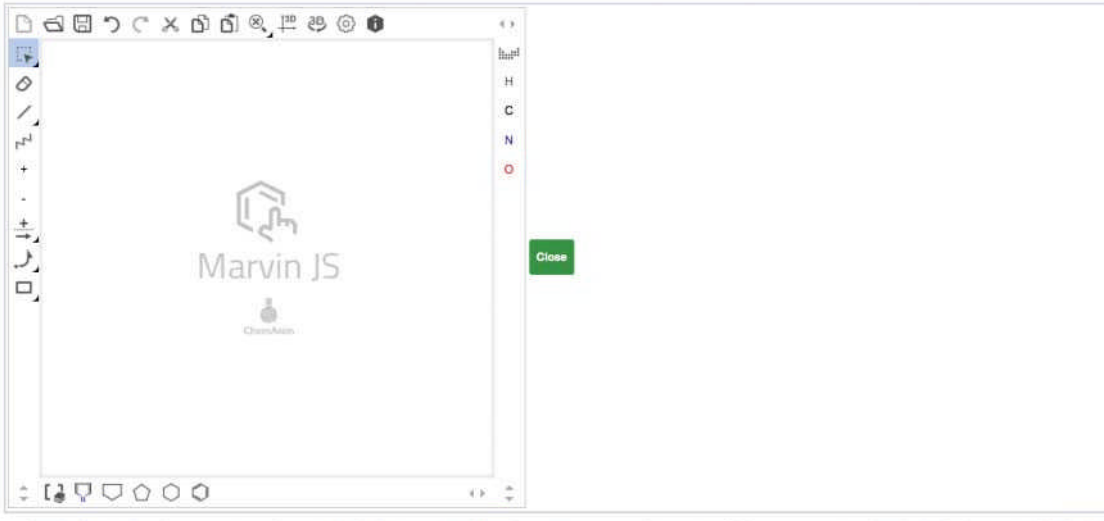
Synthesis Explorer provides meaningful practice of single and multistep synthesis.

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C06T04Q2181

the product of a substitution reaction.

Click on the drawing box above to activate the MarvinSketch drawing tool and then draw your answer to this question. If there is no reaction, then check the "no reaction" box below.

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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

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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.

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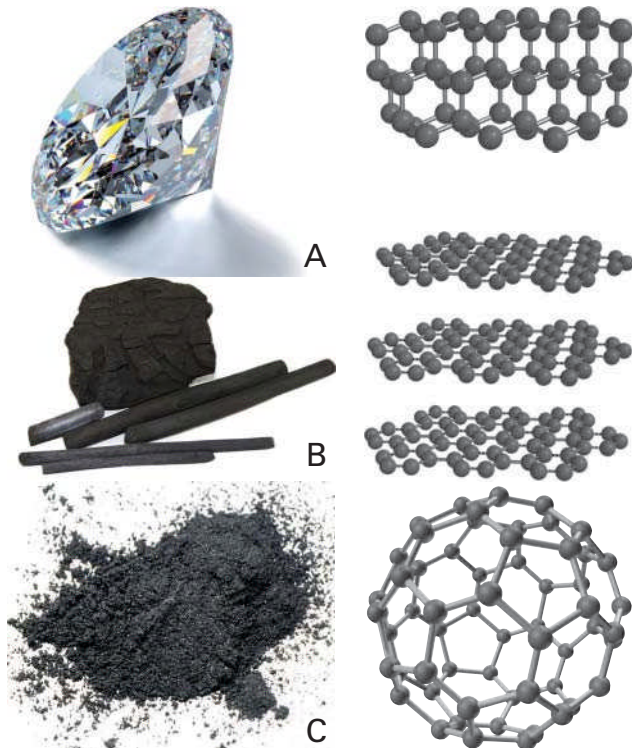
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Covalent Bonding and Shapes of Molecules

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.

1

KEY QUESTIONS

- 1.1 How Do We Describe the Electronic Structure of Atoms?
- 1.2 What Is the Lewis Model of Bonding?
- 1.3 How Do We Predict Bond Angles and the Shapes of Molecules?

- 1.4 How Do We Predict If a Molecule Is Polar or Nonpolar?
- 1.5 What Is Resonance?
- 1.6 What Is the Orbital Overlap Model of Covalent Bonding?
- 1.7 What Are Functional Groups?

HOW TO

- 1.1 How to Draw Lewis Structures for Molecules and Ions

CHEMICAL CONNECTIONS

- 1A Buckyball: A New Form of Carbon

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**.

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.

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

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).

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).

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.

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

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

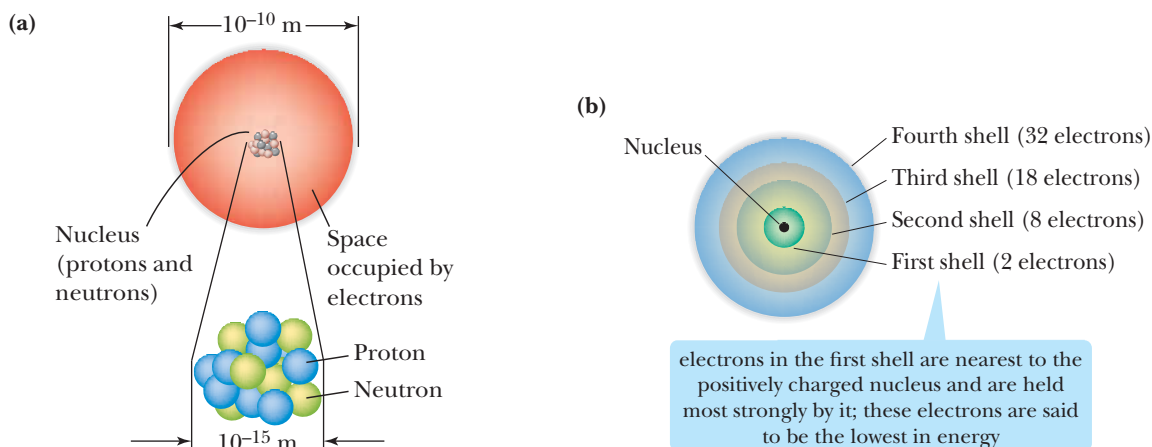


FIGURE 1.1 A schematic view of an atom. (a) Most of the mass of an atom is concentrated in its small, dense nucleus, which has a diameter of 10^{-14} to 10^{-15} meter (m). (b) Each shell can contain up to $2n^2$ electrons, where n is the number of the shell. Thus, the first shell can hold 2 electrons,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

the 2nd shell contains a single orbital called a 1s orbital. The second shell contains one 2s orbital and three 2p orbitals. All p orbitals come in sets of three and can hold up to 6 electrons. The third shell contains one 3s orbital, three 3p orbitals, and five 3d 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 4s, three 4p, five 4d, and seven 4f orbitals	$2 + 6 + 10 + 14 = 32$	Higher
3	One 3s, three 3p, and five 3d orbitals	$2 + 6 + 10 = 18$	↑
2	One 2s and three 2p orbitals	$2 + 6 = 8$	
1	One 1s orbital	2	Lower

A. Electron Configuration of Atoms

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

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

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

*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 $1s$, $2s$, $2p$, $3s$, and $3p$.

Rule 2. Notice that each orbital contains a maximum of two electrons. In neon, there are six additional electrons after the $1s$ and $2s$ orbitals are filled. These are written as $2p_x^2 2p_y^2 2p_z^2$. Alternatively, we can group the three filled $2p$ 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 $3p$ 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.

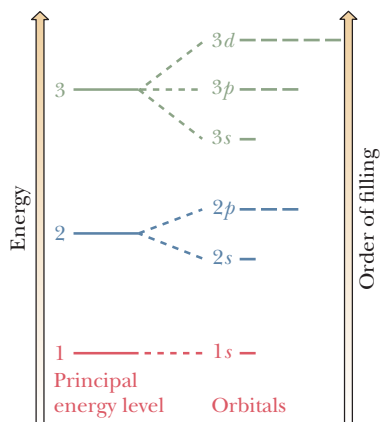
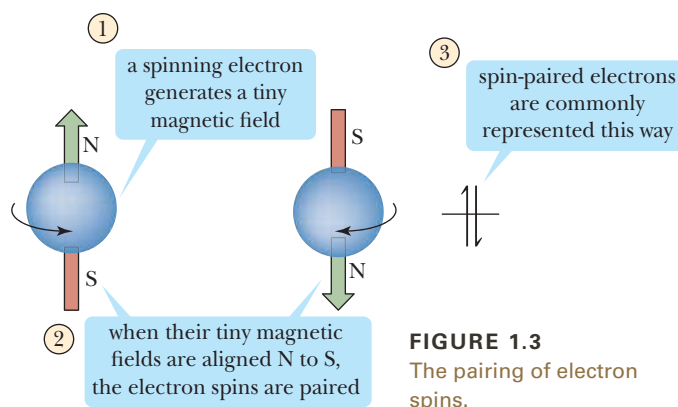


FIGURE 1.2 Relative energies and order of filling of orbitals through the $3d$ orbitals.



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 $1s^2 2s^2 2p^2$, 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 $[\text{He}] 2s^1$.

- (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 $[\text{He}] 2s^2 2p^4$.
- (c) Chlorine (atomic number 17): $1s^2 2s^2 2p^6 3s^2 3p^5$. Alternatively, we can write it as $[\text{Ne}] 3s^2 3p^5$.

See problems 1.17–1.20

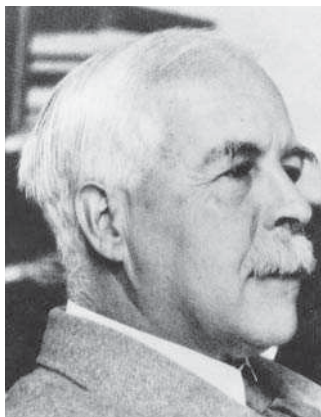
PROBLEM 1.1

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.



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.

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 1st period elements contain only s orbitals

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

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 4 electron configurations of these elements: helium with a valence shell of two electrons ($1s^2$), neon with a valence shell of eight electrons ($2s^22p^6$), argon with a valence shell of eight electrons ($3s^23p^6$), and so forth.

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**.

Noble Gas	Noble Gas Notation
He	$1s^2$
Ne	$[\text{He}] 2s^22p^6$
Ar	$[\text{Ne}] 3s^23p^6$
Kr	$[\text{Ar}] 4s^24p^63d^{10}$
Xe	$[\text{Kr}] 5s^25p^64d^{10}$

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**.

sodium (atomic number 11) loses an electron to acquire a filled valence shell identical to that of neon (atomic number 10)



chlorine (atomic number 17) gains an electron to acquire a filled valence shell identical to that of argon (atomic number 18)

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**.



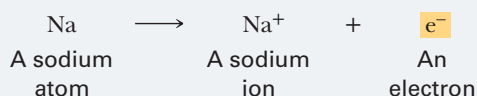
each chlorine (atomic number 17) shares an electron with another chlorine atom to effectively supply each chlorine with a filled valence shell

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:

**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): $1s^2 2s^2 2p^6 3s^1$

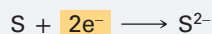
Na^+ (10 electrons): $1s^2 2s^2 2p^6$

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:



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.

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.



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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.

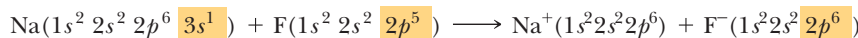
TABLE 1.4 Electronegativity Values and Trends for Some Atoms (Pauling Scale)

1A	2A											3A	4A	5A	6A	7A
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2	3B	4B	5B	6B	7B	8B			1B	2B	Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5
Cs 0.7	Ba 0.9	La 1.1	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2

<1.0
 1.5 – 1.9
 2.5 – 2.9
1.0 – 1.4
 2.0 – 2.4
 3.0 – 4.0

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:



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 (c) Carbon or oxygen
 (b) Nitrogen 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) $\text{C} > \text{Li}$
 (b) $\text{O} > \text{N}$
 (c) $\text{O} > \text{C}$

See problem 1.24

PROBLEM 1.3

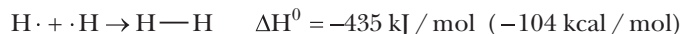
Judging from their relative positions in the Periodic Table, which element in each pair has the larger electronegativity?

- (a) Lithium or potassium (c) Carbon or silicon
 (b) Nitrogen or phosphorus (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:



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

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.

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 $-$ (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 $+$ (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 $+$ charge, and a red color shows the presence of a $-$ 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

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.

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

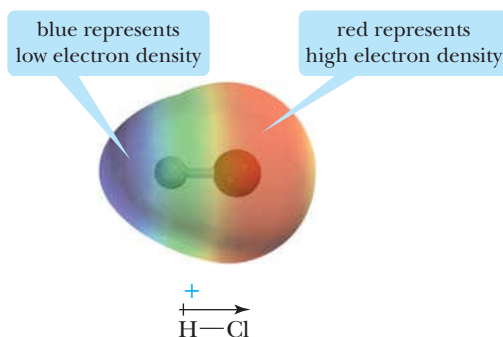
See problem 1.25

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 + charge and by the red color that chlorine bears a - 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^- .