

Francis A. Carey  
Robert M. Giuliano

# Organic Chemistry

NINTH EDITION

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**Francis A. Carey**  
University of Virginia

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Villanova University





ORGANIC CHEMISTRY, NINTH EDITION

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# About the Authors

Prior to retiring in 2000, **Frank Carey**'s career teaching chemistry was spent entirely at the University of Virginia.

In addition to this text, he is coauthor (with Robert C. Atkins) of *Organic Chemistry: A Brief Course* and (with Richard J. Sundberg) of *Advanced Organic Chemistry*, a two-volume treatment designed for graduate students and advanced undergraduates.

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# Preface

It's different now.

What's different?

How we read, share information, and learn. That's what's different.

All of these things are more visual, more graphical than before.

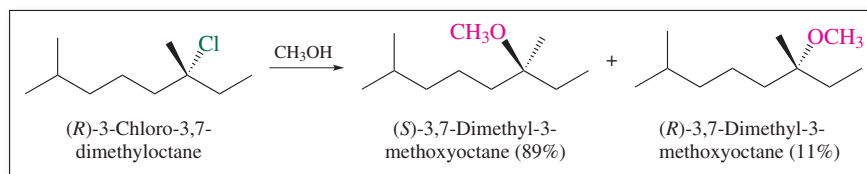
And so is this book.

## Reading and Seeing

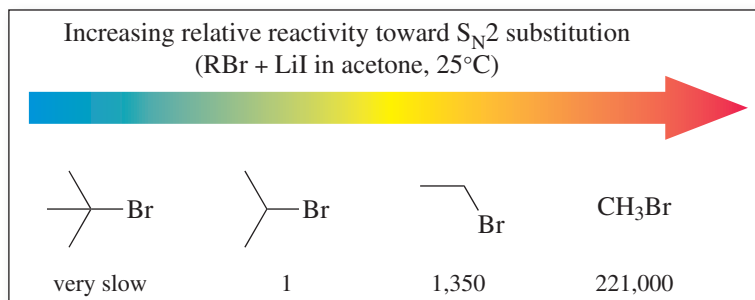
The central message of chemistry is that the properties of a substance come from its structure. What is less obvious, but very powerful, is that someone with training in chemistry can look at the structure of a substance and tell you a lot about its properties. Organic chemistry has always been, and continues to be, the branch of chemistry that best connects structure with properties.

The goal of this text, as it has been through eight previous editions, is to provide students with the conceptual tools to understand and apply the relationship between the structures of organic compounds and their properties. Both the organization of the text and the presentation of individual topics were designed with this objective in mind.

In planning this edition, we committed ourselves to emphasizing line formulas as the primary tool for communicating structural information. Among other features, they replace the act of *reading* and interpreting strings of letters with *seeing* structural relationships between molecules. In order to provide a smooth transition for students as they progress from the textual representations they've used in introductory chemistry, we gradually increase the proportion of bond-line formulas chapter by chapter until they eventually become the major mode of structural representation. Thus, we illustrate  $S_N1$  stereochemistry in Chapter 8 by the equation:



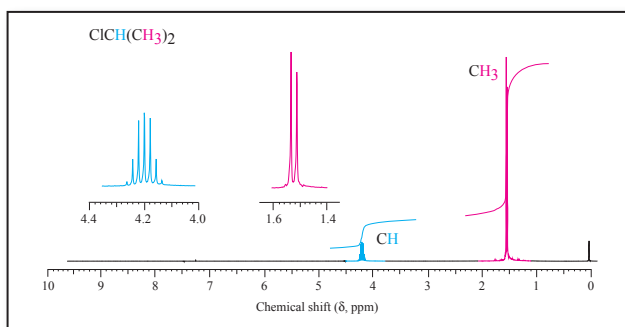
The conversion from reading to seeing is also evident in data recast from a tabular to a graphical format. One example compares  $S_N2$  reaction rates:



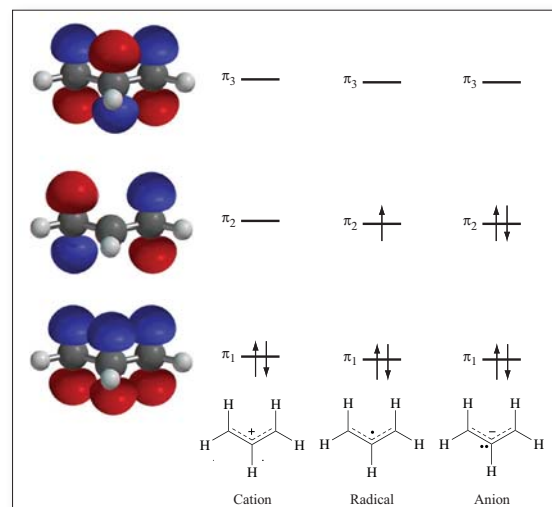
The pace of technological improvements in nuclear magnetic resonance spectroscopy requires regular updating of this core topic, and almost all of the proton spectra in this



edition were obtained at 300 MHz. The spectra themselves were provided courtesy of Sigma-Aldrich, then graphically enhanced to maximize their usefulness as a teaching tool.



The teaching of organic chemistry has especially benefited as powerful modeling and graphics software have become routinely available. Computer-generated molecular models and electrostatic potential maps were integrated into the third edition of this text and their number has increased in each succeeding edition. Also seeing increasing use are molecular orbital theory and the role of orbital interactions in chemical reactivity. These, too, have been adapted to enhance their value as teaching tools as illustrated in Figure 10.2 showing the  $\pi$ -molecular orbitals of allylic carbocations, radicals, and anions.



## Audience

*Organic Chemistry* is designed to meet the needs of the “mainstream,” two-semester undergraduate organic chemistry course. From the beginning and with each new edition, we have remained grounded in some fundamental notions. These include important issues concerning the intended audience. Is the topic appropriate for them with respect to their interests, aspirations, and experience? Just as important is the need to present an accurate picture of the present state of organic chemistry. How do we know what we know? What makes organic chemistry worth knowing? Where are we now? Where are we headed?

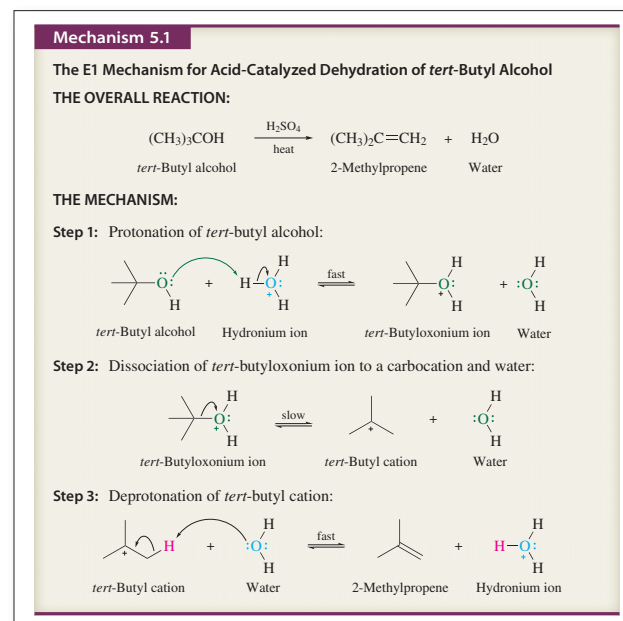
## A Functional Group Organization With a Mechanistic Emphasis

The text is organized according to functional groups—the structural units most closely identified with a molecule’s characteristic properties. This time-tested organization offers two major advantages over alternatives organized according to mechanisms or reaction types.

1. The information content of individual chapters is more manageable in the functional–group approach. A text organized around functional groups typically has more and shorter chapters than one organized according to mechanism.
2. Patterns of reactivity are reinforced when a reaction used to prepare a particular functional–group family reappears as a characteristic reaction of another.

Understanding organic chemistry, however, is impossible without a solid grasp of mechanisms. Our approach is to build this understanding from the ground up beginning in Section 1.12 “Curved Arrows and Chemical Reactions” and continuing through Section 1.16 with applications to Brønsted and Lewis acid–base chemistry. The text contains more than 60 mechanisms that are featured as stand-alone items presented as a series of elementary steps. Numerous other mechanisms—many of them accompanied by potential energy diagrams—are incorporated into the narrative flow.

Numerous other mechanisms—many of them accompanied by potential energy diagrams—are incorporated into the narrative flow.



## Generous and Effective Use of Tables

Annotated summary tables that incorporate commentary have been a staple of *Organic Chemistry* since the first edition. Some review reactions from earlier chapters, others the reactions or concepts of a current chapter. Still others walk the reader step-by-step through skill builders and concepts unique to organic chemistry. Well received by students and faculty alike, these summary tables remain one of the text's strengths.

Reaction and comments	Example
1. <b>Reduction:</b> Carbonyl groups in carbohydrates are reduced by the same methods used for aldehydes and ketones: reduction with sodium borohydride or lithium aluminum hydride or by catalytic hydrogenation.	<p>D-Galactose (90%)</p>
2. <b>Cyanohydrin formation:</b> Reaction of an aldose with HCN gives a mixture of two diastereomeric cyanohydrins.	<p>L-Mannonitrile + L-Gluconitrile</p>
3. <b>Acylation:</b> All available hydroxyl groups of carbohydrates are capable of undergoing acylation to form esters.	<p>1,2,3,4,6-Penta-O-acetyl-D-glucopyranose (88%)</p>
4. <b>Alkylation:</b> Carbohydrate hydroxyl groups react with	<p>Methyl 2,3,4,6-tetra-O-benzyl-alpha-D-glucopyranoside (95%)</p>

## Problems

Problem-solving strategies and skills are emphasized throughout. Understanding is progressively reinforced by problems that appear within topic sections. For many problems, sample solutions are given, including examples of handwritten solutions from the author.

**Problem 14.4**  
Write the structure of the organic product of each of the following reactions.

(a)

(b)

(c)

**Sample Solution**

(a) Carbon-carbon bond formation occurs between the vinyl group and the carbonyl carbon.

Acidification converts the alkoxide to the corresponding alcohol, which is the isolated product.

## Chapter Openers

Each chapter begins with an opener meant to capture the reader's attention. Chemistry that is highlighted in the opener is relevant to chemistry that is included in the chapter.

## Descriptive Passages and Interpretive Problems

Many organic chemistry students later take standardized pre-professional examinations composed of problems derived from a descriptive passage; this text includes comparable passages and problems to familiarize students with this testing style.

Thus, every chapter concludes with a self-contained *Descriptive Passage and Interpretive Problems* unit that complements the chapter's content while emulating the "MCAT style." These 27 passages—listed on page xix—are accompanied by more than 100 total multiple-choice problems. Two of these: *More on Spin-Spin Splitting and Coupling Constants* in Chapter 13 and *Cyclobutadiene and (Cyclobutadiene)tricarbonyliron* in Chapter 14 are new to this edition.

The passages focus on a wide range of topics—from structure, synthesis, mechanism, and natural products. They provide instruc-

# 14

### CHAPTER OUTLINE

14.1 Organometallic Nomenclature	579	<p>Parkinsonism results from a dopamine deficit in the brain that affects the "firing" of neurons. It responds to treatment with a chiral drug (L-dopa), one commercial synthesis of which involves the enantioselective organotin(IV)-catalyzed hydrogenation described in Section 14.12.</p> <h3>Organometallic Compounds</h3> <p>Organometallic compounds are <i>compounds that have a carbon-metal bond</i>; they occupy the place where organic and inorganic chemistry meet. You are already familiar with at least one organometallic compound, sodium acetylide (<math>\text{NaC}\equiv\text{CH}</math>), which has an ionic bond between carbon and sodium. But just because a compound contains both a metal and carbon isn't enough to classify it as organometallic. Like sodium acetylide, sodium methoxide (<math>\text{NaOCH}_3</math>) is an ionic compound. Unlike sodium acetylide, however, the negative charge in sodium methoxide resides on oxygen, not carbon.</p> $\text{Na}^+ \text{:}\overset{\ominus}{\text{C}}\equiv\text{CH} \quad \text{Na}^+ \text{:}\overset{\ominus}{\text{O}}\text{CH}_3$ <p>Sodium acetylide (has a carbon-to-metal bond)      Sodium methoxide (does not have a carbon-to-metal bond)</p> <p>The properties of organometallic compounds are much different from those of the other classes we have studied so far and differ among themselves according to the metal, its oxidation state, and the groups attached to the metal. Many organometallic compounds are sources of nucleophilic carbon, a quality that makes them especially valuable to the synthetic organic chemist who needs to make carbon-carbon bonds. For example, the preparation of alkynes by the reaction of sodium acetylide with alkyl halides (Section 9.6) depends on the presence of a negatively charged, nucleophilic carbon in acetylide ion. Conversely, certain other organometallic compounds behave as electrophiles.</p>
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tors with numerous opportunities to customize their own organic chemistry course while giving students practice in combining new information with what they have already learned.

## What's New

We have already described a number of graphical features designed to foster learning:

- ▶ an emphasis on bond–line structural drawings
- ▶ adoption of 300 MHz as the standard for nuclear magnetic resonance spectra and enhancing them graphically to allow easier interpretation
- ▶ greater integration of molecular orbital diagrams

There have also been significant changes in content.

- ▶ **Chapter 14 (Organometallic Compounds)** has been a prominent part of our text since the first edition and, owing to Nobel-worthy advances based on organic compounds of transition metals, has steadily increased in importance. The chemistry of these transition–metal organic compounds has been expanded in 9e to where it now comprises approximately one-half of the chapter.
- ▶ **Chapter 20 (Enols and Enolates)** has been extensively revised and is much shorter. The new, more conceptual organization allows many synthetic reactions formerly treated independently according to purpose to be grouped efficiently according to mechanism.
- ▶ **Retrosynthetic analysis** is introduced earlier (Section 6.15), elaborated with dedicated sections in subsequent chapters (8.12, 10.13, 11.16, 12.16, 14.7), and used regularly thereafter.
- ▶ **Boxed essays— Fullerenes, Nanotubes, and Graphene** updates the ever-expanding role of elemental carbon in its many forms in Chapter 11. *Sustainability and Organic Chemistry* is a new boxed essay in Chapter 15 that uses real-world examples to illustrate principles of “green” chemistry.

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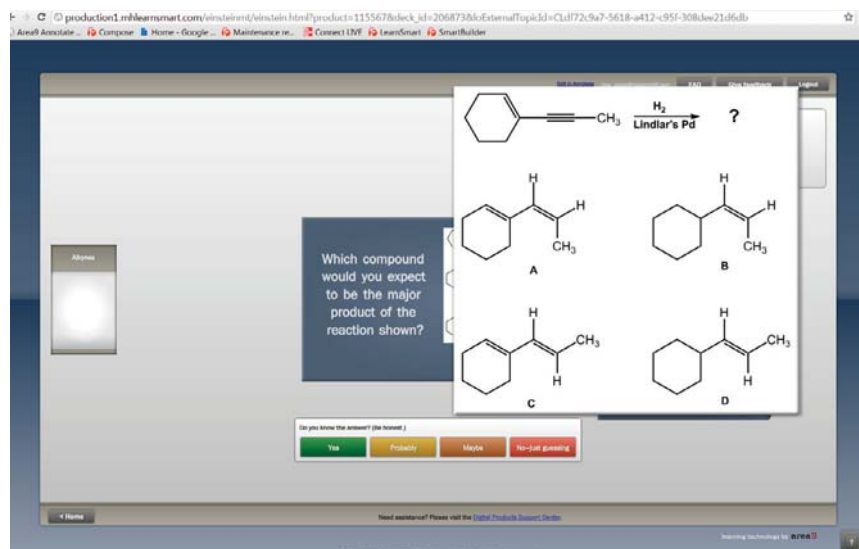


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Enter your answer in the provided box.

To burn 1 molecule of  $C_3H_8$  to form  $CO_2$  and  $H_2O$  (complete combustion), how many molecules of  $O_2$  are required?

molecules

Assistance

- View Hint
- Show Me
- Double Solution
- Print
- Question Help
- Report a Problem

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- **Test Bank** An updated test bank with over 1300 questions is available with the 9th edition. The Test Bank is available as both word files and in a computerized test bank program, which utilizes testing software to quickly create customized exams. This user-friendly program allows instructors to sort questions by format; edit existing questions or add new ones; and scramble questions for multiple versions of the same test.
- **Solutions Manual** This manual provides complete solutions to all end-of-chapter problems in the text. The Solutions Manual includes step-by-step solutions to each problem in the text as well as self-tests to assess student understanding.

## Student Resources

### Solutions Manual

The Solutions Manual provides step-by-step solutions guiding the student through the reasoning behind each problem in the text. There is also a self-test section at the end of each chapter that is designed to assess the student's mastery of the material.

### Schaum's Outline of Organic Chemistry

This helpful study aid provides students with hundreds of solved and supplementary problems for the organic chemistry course.

# ACKNOWLEDGEMENTS

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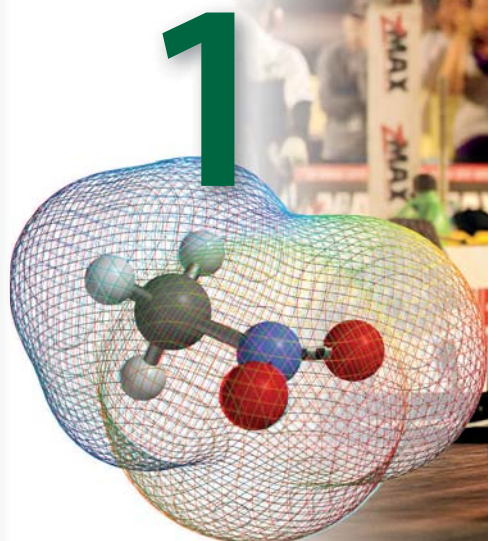
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# Organic Chemistry





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Although function dictates form in the things we build, structure determines properties in molecules. Dragsters are designed to accelerate to high speeds in a short distance from a standing start. Most are powered by nitromethane ( $\text{CH}_3\text{NO}_2$ ), which, because of its structure, makes it more suitable for this purpose than gasoline.

## Structure Determines Properties

**S**tructure\* is the key to everything in chemistry. The properties of a substance depend on the atoms it contains and the way these atoms are connected. What is less obvious, but very powerful, is the idea that someone who is trained in chemistry can look at the structural formula of a substance and tell you a lot about its properties. This chapter begins your training toward understanding the relationship between structure and properties in organic compounds. It reviews some fundamental principles of the Lewis approach to molecular structure and bonding. By applying these principles, you will learn to recognize structural patterns that are more stable than others and develop skills in communicating structural information that will be used throughout your study of organic chemistry. A key relationship between structure and properties will be introduced by examining the fundamentals of acid–base chemistry from a structural perspective.

### 1.1 Atoms, Electrons, and Orbitals

Before discussing structure and bonding in *molecules*, let's first review some fundamentals of *atomic* structure. Each element is characterized by a unique **atomic number Z**, which is equal to

\*A glossary of the terms shown in boldface may be found immediately before the index at the back of the book.

## Organic Chemistry: The Early Days

Eighteenth-century chemists regarded their science as being composed of two branches. One dealt with substances obtained from natural or living sources and was called *organic chemistry*; the other dealt with materials from nonliving matter—minerals and the like—and was called *inorganic chemistry*. Over time, combustion analysis established that the compounds derived from natural sources contained carbon, and a new definition of organic chemistry emerged: *Organic chemistry is the study of carbon compounds*. This is the definition we still use today.

As the eighteenth century gave way to the nineteenth, many scientists still subscribed to a doctrine known as *vitalism*, which held that living systems possessed a “vital force” that was absent in nonliving systems. Substances derived from natural sources (organic) were thought to be fundamentally different from inorganic ones. It was believed that inorganic compounds could be synthesized in the laboratory, but organic compounds could not—at least not from inorganic materials.

In 1823, Friedrich Wöhler, after completing medical studies in Germany, spent a year in Stockholm studying under one of the world’s foremost chemists of the time, Jöns Jacob Berzelius. Wöhler subsequently went on to have a distinguished independent career, spending most of it at the University of Göttingen. He is best remembered for a brief paper he published in 1828 in which he noted that, on evaporating an aqueous solution of ammonium cyanate, he obtained “colorless, clear crystals often more than an inch long,” which were not ammonium cyanate but were instead urea.



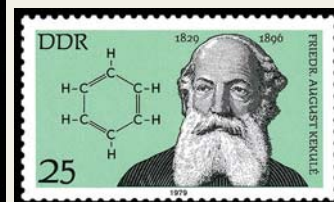
This transformation was remarkable at the time because an *inorganic* salt, ammonium cyanate, was converted to urea, a known *organic* substance earlier isolated from urine. It is now recognized as a significant early step toward overturning the philosophy of vitalism. Although Wöhler himself made no extravagant claims concerning the relationship of his discovery to vitalist theory, the die was cast, and over the next generation organic chemistry outgrew vitalism. What particularly seemed to excite Wöhler and Berzelius had very little to do with vitalism. Berzelius was interested in cases in which two clearly different materials had the same elemental composition, and he invented

the word *isomers* to apply to them. Wöhler’s observation that an inorganic compound (ammonium cyanate) of molecular formula  $\text{CH}_4\text{N}_2\text{O}$  could be transformed into an organic compound (urea) of the same molecular formula had an important bearing on the concept of isomerism.

From the concept of isomerism we can trace the origins of the *structural theory*—the idea that a specific arrangement of atoms uniquely defines a substance. Ammonium cyanate and urea are different compounds because they have different structures.

Three mid-nineteenth-century scientists, August Kekulé, Archibald S. Couper, and Alexander M. Butlerov, stand out for separately proposing the elements of the structural theory. The essential features of Kekulé’s theory, developed and presented while he taught at Heidelberg in 1858, were that carbon normally formed four bonds and had the capacity to bond to other carbons so as to form long chains. Isomers were possible because the same elemental composition (say, the  $\text{CH}_4\text{N}_2\text{O}$  molecular formula common to both ammonium cyanate and urea) accommodates more than one pattern of atoms and bonds. Shortly thereafter, Couper, a Scot working at the École de Médecine in Paris, and Butlerov, a Russian chemist at the University of Kazan, proposed similar theories.

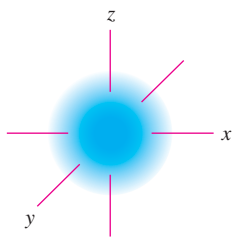
In the late nineteenth and early twentieth centuries, major discoveries about atoms and electrons placed theories of molecular structure and bonding on a more secure, physics-based foundation. Several of these are described at the beginning of this section.



the number of protons in its nucleus. A neutral atom has equal numbers of protons, which are positively charged, and electrons, which are negatively charged.

Electrons were believed to be particles from the time of their discovery in 1897 until 1924, when the French physicist Louis de Broglie suggested that they have wavelike properties as well. Two years later Erwin Schrödinger took the next step and calculated the energy of an electron in a hydrogen atom by using equations that treated the electron as if it were a wave. Instead of a single energy, Schrödinger obtained a series of them, each of which corresponded to a different mathematical description of the electron wave. These mathematical descriptions are called **wave functions** and are symbolized by the Greek letter  $\psi$  (psi).





**Figure 1.1**

Probability distribution ( $\psi^2$ ) for an electron in a  $1s$  orbital.

According to the Heisenberg uncertainty principle, we can't tell exactly where an electron is, but we can tell where it is most likely to be. The probability of finding an electron at a particular spot relative to an atom's nucleus is given by the square of the wave function ( $\psi^2$ ) at that point. Figure 1.1 illustrates the probability of finding an electron at various points in the lowest energy (most stable) state of a hydrogen atom. The darker the color in a region, the higher the probability. The probability of finding an electron at a particular point is greatest near the nucleus and decreases with increasing distance from the nucleus but never becomes zero.

Wave functions are also called **orbitals**. For convenience, chemists use the term "orbital" in several different ways. A drawing such as Figure 1.1 is often said to represent an orbital. We will see other kinds of drawings in this chapter, and use the word "orbital" to describe them too.

Orbitals are described by specifying their size, shape, and directional properties. Spherically symmetrical ones such as shown in Figure 1.1 are called *s orbitals*. The letter *s* is preceded by the **principal quantum number**  $n$  ( $n = 1, 2, 3$ , etc.), which specifies the **shell** and is related to the energy of the orbital. An electron in a  $1s$  orbital is likely to be found closer to the nucleus, is lower in energy, and is more strongly held than an electron in a  $2s$  orbital.

Instead of probability distributions, it is more common to represent orbitals by their **boundary surfaces**, as shown in Figure 1.2 for the  $1s$  and  $2s$  orbitals. The region enclosed by a boundary surface is arbitrary but is customarily the volume where the probability of finding an electron is high—on the order of 90–95%. Like the probability distribution plot from which it is derived, a picture of a boundary surface is usually described as a drawing of an orbital.

A hydrogen atom ( $Z = 1$ ) has one electron; a helium atom ( $Z = 2$ ) has two. The single electron of hydrogen occupies a  $1s$  orbital, as do the two electrons of helium. We write their electron configurations as:



In addition to being negatively charged, electrons possess the property of **spin**. The **spin quantum number** of an electron can have a value of either  $+\frac{1}{2}$  or  $-\frac{1}{2}$ . According to the **Pauli exclusion principle**, two electrons may occupy the same orbital only when they have opposite, or "paired," spins. For this reason, no orbital can contain more than two electrons. Because two electrons fill the  $1s$  orbital, the third electron in lithium ( $Z = 3$ ) must occupy an orbital of higher energy. After  $1s$ , the next higher energy orbital is  $2s$ . The third electron in lithium therefore occupies the  $2s$  orbital, and the electron configuration of lithium is



The **period** (or **row**) of the periodic table in which an element appears corresponds to the principal quantum number of the highest numbered occupied orbital ( $n = 1$  in the case of hydrogen and helium). Hydrogen and helium are first-row elements; lithium ( $n = 2$ ) is a second-row element.

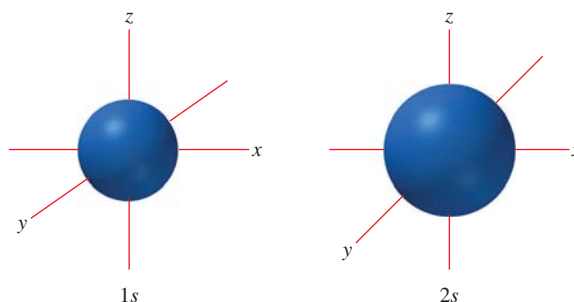
With beryllium ( $Z = 4$ ), the  $2s$  level becomes filled and, beginning with boron ( $Z = 5$ ), the next orbitals to be occupied are  $2p_x$ ,  $2p_y$ , and  $2p_z$ . These three orbitals (Figure 1.3) are of equal energy and are characterized by boundary surfaces that are usually

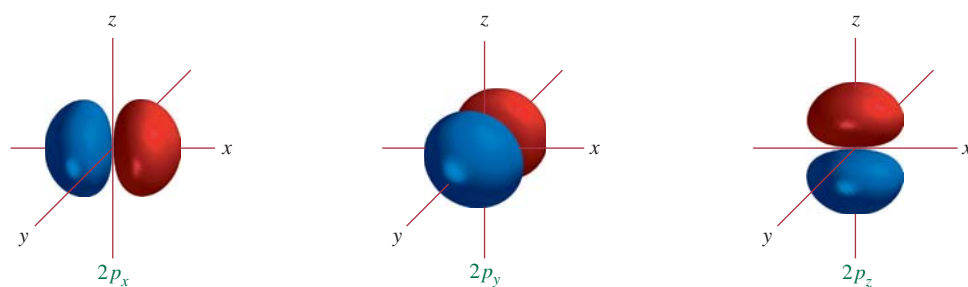
A complete periodic table of the elements is presented at the back of the book.

Other methods are also used to contrast the regions of an orbital where the signs of the wave function are different. Some mark one lobe of a  $p$  orbital  $+$  and the other  $-$ . Others shade one lobe and leave the other blank. When this level of detail isn't necessary, no differentiation is made between the two lobes.

**Figure 1.2**

Boundary surfaces of a  $1s$  orbital and a  $2s$  orbital.





**Figure 1.3**

Boundary surfaces of the  $2p$  orbitals. The wave function changes sign at the nucleus. The two halves of each orbital are indicated by different colors. The  $yz$ -plane is a nodal surface for the  $2p_x$  orbital. The probability of finding a  $2p_x$  electron in the  $yz$ -plane is zero. Analogously, the  $xz$ -plane is a nodal surface for the  $2p_y$  orbital, and the  $xy$ -plane is a nodal surface for the  $2p_z$  orbital.

described as “dumbbell-shaped.” The axes of the three  $2p$  orbitals are at right angles to one another. Each orbital consists of two “lobes,” represented in Figure 1.3 by regions of different colors. Regions of a single orbital, in this case, each  $2p$  orbital, may be separated by **nodal surfaces** where the wave function changes sign and the probability of finding an electron is zero.

The electron configurations of the first 12 elements, hydrogen through magnesium, are given in Table 1.1. In filling the  $2p$  orbitals, notice that each is singly occupied before any one is doubly occupied. This general principle for orbitals of equal energy is known as **Hund’s rule**. Of particular importance in Table 1.1 are *hydrogen*, *carbon*, *nitrogen*, and *oxygen*. Countless organic compounds contain nitrogen, oxygen, or both in addition to carbon, the essential element of organic chemistry. Most of them also contain hydrogen.

It is often convenient to speak of the **valence electrons** of an atom. These are the outermost electrons, the ones most likely to be involved in chemical bonding and

**TABLE 1.1** Electron Configurations of the First Twelve Elements of the Periodic Table

Element	Atomic number $Z$	Number of electrons in indicated orbital					
		$1s$	$2s$	$2p_x$	$2p_y$	$2p_z$	$3s$
Hydrogen	1	1					
Helium	2	2					
Lithium	3	2	1				
Beryllium	4	2	2				
Boron	5	2	2	1			
Carbon	6	2	2	1	1		
Nitrogen	7	2	2	1	1	1	
Oxygen	8	2	2	2	1	1	
Fluorine	9	2	2	2	2	1	
Neon	10	2	2	2	2	2	
Sodium	11	2	2	2	2	2	1
Magnesium	12	2	2	2	2	2	2

reactions. For second-row elements these are the  $2s$  and  $2p$  electrons. Because four orbitals ( $2s$ ,  $2p_x$ ,  $2p_y$ ,  $2p_z$ ) are involved, the maximum number of electrons in the **valence shell** of any second-row element is 8. Neon, with all its  $2s$  and  $2p$  orbitals doubly occupied, has eight valence electrons and completes the second row of the periodic table. For **main-group elements**, the number of valence electrons is equal to its group number in the periodic table.

Detailed solutions to all of the problems are found in the *Student Solutions Manual* along with a brief discussion and advice on how to do problems of the same type.

In-chapter problems that contain multiple parts are accompanied by a sample solution to part (a).

### Problem 1.1

How many electrons does carbon have? How many are valence electrons? What third-row element has the same number of valence electrons as carbon?

Once the  $2s$  and  $2p$  orbitals are filled, the next level is the  $3s$ , followed by the  $3p_x$ ,  $3p_y$ , and  $3p_z$  orbitals. Electrons in these orbitals are farther from the nucleus than those in the  $2s$  and  $2p$  orbitals and are of higher energy.

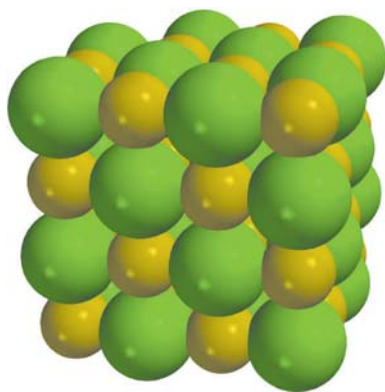
### Problem 1.2

Referring to the periodic table as needed, write electron configurations for all the elements in the third period.

**Sample Solution** The third period begins with sodium and ends with argon. The atomic number  $Z$  of sodium is 11, and so a sodium atom has 11 electrons. The maximum number of electrons in the  $1s$ ,  $2s$ , and  $2p$  orbitals is ten, and so the eleventh electron of sodium occupies a  $3s$  orbital. The electron configuration of sodium is  $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2 3s^1$ .

Neon, in the second period, and argon, in the third, have eight electrons in their valence shell; they are said to have a complete **octet** of electrons. Helium, neon, and argon belong to the class of elements known as **noble gases** or **rare gases**. The noble gases are characterized by an extremely stable “closed-shell” electron configuration and are very unreactive.

*Structure determines properties* and the properties of atoms depend on atomic structure. All of an element’s protons are in its nucleus, but the element’s electrons are distributed among orbitals of various energy and distance from the nucleus. More than anything else, we look at its electron configuration when we wish to understand how an element behaves. The next section illustrates this with a brief review of ionic bonding.



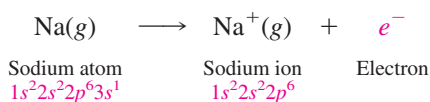
**Figure 1.4**

An ionic bond is the force of attraction between oppositely charged ions. Each  $\text{Na}^+$  ion in the crystal lattice of solid  $\text{NaCl}$  is involved in ionic bonding to each of six surrounding  $\text{Cl}^-$  ions and vice versa. The smaller balls are  $\text{Na}^+$  and the larger balls are  $\text{Cl}^-$ .

## 1.2 Ionic Bonds

Atoms combine with one another to give **compounds** having properties different from the atoms they contain. The attractive force between atoms in a compound is a **chemical bond**. One type of chemical bond, called an **ionic bond**, is the force of attraction between oppositely charged species (**ions**) (Figure 1.4). Positively charged ions are referred to as **cations**; negatively charged ions are **anions**.

Whether an element is the source of the cation or anion in an ionic bond depends on several factors, for which the periodic table can serve as a guide. In forming ionic compounds, elements at the left of the periodic table typically lose electrons, giving a cation that has the same electron configuration as the preceding noble gas. Loss of an electron from sodium, for example, yields  $\text{Na}^+$ , which has the same electron configuration as neon.



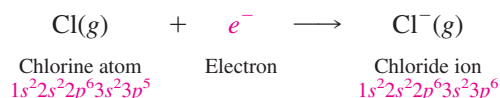
[The symbol (g) indicates that the species is present in the gas phase.]

### Problem 1.3

Species that have the same number of electrons are described as *isoelectronic*. What +2 ion is isoelectronic with Na<sup>+</sup>? What -2 ion?

A large amount of energy, called the **ionization energy**, must be transferred to any atom to dislodge an electron. The ionization energy of sodium, for example, is 496 kJ/mol (119 kcal/mol). Processes that absorb energy are said to be **endothermic**. Compared with other elements, sodium and its relatives in group 1A have relatively low ionization energies. In general, ionization energy increases across a row in the periodic table.

Elements at the right of the periodic table tend to gain electrons to reach the electron configuration of the next higher noble gas. Adding an electron to chlorine, for example, gives the anion Cl<sup>-</sup>, which has the same closed-shell electron configuration as the noble gas argon.



### Problem 1.4

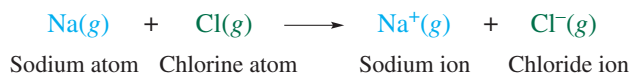
Which of the following ions possess a noble gas electron configuration?

- (a) K<sup>+</sup>                      (c) H<sup>-</sup>                      (e) F<sup>-</sup>  
 (b) He<sup>+</sup>                      (d) O<sup>-</sup>                      (f) Ca<sup>2+</sup>

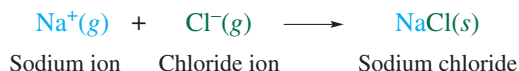
**Sample Solution** (a) Potassium has atomic number 19, and so a potassium atom has 19 electrons. The ion K<sup>+</sup>, therefore, has 18 electrons, the same as the noble gas argon. The electron configurations of both K<sup>+</sup> and Ar are 1s<sup>2</sup>2s<sup>2</sup>2p<sup>6</sup>3s<sup>2</sup>3p<sup>6</sup>.

Energy is released when a chlorine atom captures an electron. Energy-releasing reactions are described as **exothermic**, and the energy change for an exothermic process has a negative sign. The energy change for addition of an electron to an atom is referred to as its **electron affinity** and is -349 kJ/mol (-83.4 kcal/mol) for chlorine.

We can use the ionization energy of sodium and the electron affinity of chlorine to calculate the energy change for the reaction:



Were we to simply add the ionization energy of sodium (496 kJ/mol) and the electron affinity of chlorine (-349 kJ/mol), we would conclude that the overall process is endothermic by +147 kJ/mol. The energy liberated by adding an electron to chlorine is insufficient to override the energy required to remove an electron from sodium. This analysis, however, fails to consider the force of attraction between the oppositely charged ions Na<sup>+</sup> and Cl<sup>-</sup>, as expressed in terms of the energy released in the formation of solid NaCl from the separated gas-phase ions:



This *lattice energy* is 787 kJ/mol and is more than sufficient to make the overall process for formation of sodium chloride from the elements exothermic. Forces between oppositely charged particles are called **electrostatic**, or **Coulombic**, and constitute an ionic bond when they are attractive.

### Problem 1.5

What is the electron configuration of C<sup>+</sup>? Of C<sup>-</sup>? Does either one of these ions have a noble gas (closed-shell) electron configuration?

The SI (*Système International d'Unites*) unit of energy is the *joule* (J). An older unit is the *calorie* (cal). Many chemists still express energy changes in units of kilocalories per mole (1 kcal/mol = 4.184 kJ/mol).

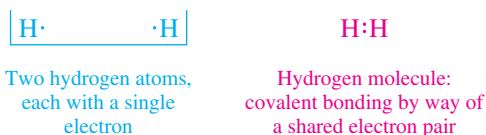
Ionic bonding was proposed by the German physicist Walther Kossel in 1916, in order to explain the ability of substances such as molten sodium chloride to conduct an electric current. He was the son of Albrecht Kossel, winner of the 1910 Nobel Prize in Physiology or Medicine for early studies of nucleic acids.

Ionic bonds are very common in *inorganic* compounds, but rare in *organic* ones. The ionization energy of carbon is too large and the electron affinity too small for carbon to realistically form a  $C^{4+}$  or  $C^{4-}$  ion. What kinds of bonds, then, link carbon to other elements in millions of organic compounds? Instead of losing or gaining electrons, carbon *shares* electrons with other elements (including other carbon atoms) to give what are called covalent bonds.

### 1.3 Covalent Bonds, Lewis Formulas, and the Octet Rule

Gilbert Newton Lewis has been called the greatest American chemist.

The **covalent**, or **shared electron pair**, model of chemical bonding was first suggested by G. N. Lewis of the University of California in 1916. Lewis proposed that a *sharing* of two electrons by two hydrogen atoms permits each one to have a stable closed-shell electron configuration analogous to helium.



The amount of energy required to dissociate a hydrogen molecule  $H_2$  to two separate hydrogen atoms is its **bond dissociation enthalpy**. For  $H_2$  it is quite large, amounting to +435 kJ/mol (+104 kcal/mol). The main contributor to the strength of the covalent bond in  $H_2$  is the increased Coulombic force exerted on its two electrons. Each electron in  $H_2$  “feels” the attractive force of two nuclei, rather than one as it would in an isolated hydrogen atom.

Only the electrons in an atom’s valence shell are involved in covalent bonding. Fluorine, for example, has nine electrons, but only seven are in its valence shell. Pairing a valence electron of one fluorine atom with one of a second fluorine gives a fluorine molecule ( $F_2$ ) in which each fluorine has eight valence electrons and an electron configuration equivalent to that of the noble gas neon. Shared electrons count toward satisfying the octet of both atoms.



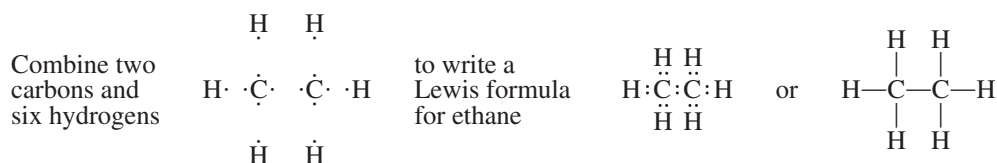
Unshared pairs are also called *lone pairs*.

The six valence electrons of each fluorine that are not involved in bonding comprise three **unshared pairs**.

Structural formulas such as those just shown for  $H_2$  and  $F_2$  where electrons are represented as dots are called **Lewis formulas**, or **Lewis structures**. It is usually more convenient to represent shared electron-pair bonds as lines and to sometimes omit electron pairs.

The Lewis model limits second-row elements (Li, Be, B, C, N, O, F, Ne) to a total of eight electrons (shared plus unshared) in their valence shells. Hydrogen is limited to two. Most of the elements that we’ll encounter in this text obey the **octet rule**: *In forming compounds they gain, lose, or share electrons to achieve a stable electron configuration characterized by eight valence electrons*. When the octet rule is satisfied for carbon, nitrogen, oxygen, and fluorine, each has an electron configuration analogous to the noble gas neon. The Lewis formulas of methane ( $CH_4$ ), ammonia ( $NH_3$ ), water ( $H_2O$ ), and hydrogen fluoride ( $HF$ ) given in Table 1.2 illustrate the octet rule.

With four valence electrons, carbon normally forms four covalent bonds as shown in Table 1.2 for  $CH_4$ . In addition to  $C-H$  bonds, most organic compounds contain covalent  $C-C$  bonds. Ethane ( $C_2H_6$ ) is an example.



**TABLE 1.2** Lewis Formulas of Methane, Ammonia, Water, and Hydrogen Fluoride

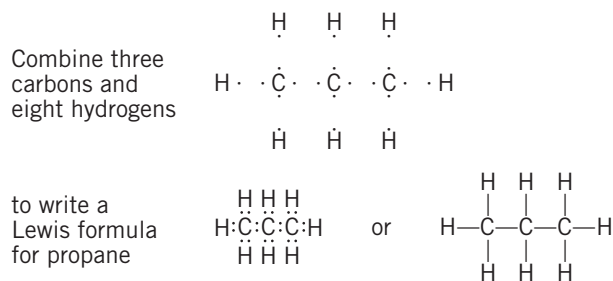
Compound	Atom	Number of valence electrons in atom	Atom and sufficient number of hydrogen atoms to complete octet	Lewis formula	
				Dot	Line
Methane	Carbon	4	$\begin{array}{c} \text{H} \\   \\ \text{H} \cdot \text{C} \cdot \text{H} \\   \\ \text{H} \end{array}$	$\begin{array}{c} \text{H} \\   \\ \text{H}:\text{C}:\text{H} \\   \\ \text{H} \end{array}$	$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{C}-\text{H} \\   \\ \text{H} \end{array}$
Ammonia	Nitrogen	5	$\begin{array}{c} \text{H} \cdot \ddot{\text{N}} \cdot \text{H} \\   \\ \text{H} \end{array}$	$\begin{array}{c} \text{H}:\ddot{\text{N}}:\text{H} \\   \\ \text{H} \end{array}$	$\begin{array}{c} \text{H}-\ddot{\text{N}}-\text{H} \\   \\ \text{H} \end{array}$
Water	Oxygen	6	$\text{H} \cdot \ddot{\text{O}} \cdot \text{H}$	$\text{H}:\ddot{\text{O}}:\text{H}$	$\text{H}-\ddot{\text{O}}-\text{H}$
Hydrogen fluoride	Fluorine	7	$\text{H} \cdot \ddot{\text{F}} \cdot$	$\text{H}:\ddot{\text{F}} \cdot$	$\text{H}-\ddot{\text{F}} \cdot$

**Problem 1.6**

Write Lewis formulas, including unshared pairs, for each of the following. Carbon has four bonds in each compound.

- (a) Propane ( $\text{C}_3\text{H}_8$ )                      (c) Methyl fluoride ( $\text{CH}_3\text{F}$ )  
 (b) Methanol ( $\text{CH}_4\text{O}$ )                      (d) Ethyl fluoride ( $\text{C}_2\text{H}_5\text{F}$ )

**Sample Solution** (a) The Lewis formula of propane is analogous to that of ethane but the chain has three carbons instead of two.



The ten covalent bonds in the Lewis formula shown account for 20 valence electrons, which is the same as that calculated from the molecular formula ( $\text{C}_3\text{H}_8$ ). The eight hydrogens of  $\text{C}_3\text{H}_8$  contribute 1 electron each and the three carbons 4 each, for a total of 20 (8 from the hydrogens and 12 from the carbons). Therefore, all the valence electrons are in covalent bonds; propane has no unshared pairs.

**1.4 Double Bonds and Triple Bonds**

Lewis's concept of shared electron pair bonds allows for four-electron double bonds and six-electron triple bonds. Ethylene ( $\text{C}_2\text{H}_4$ ) has 12 valence electrons, which can be distributed as follows:

