



Pearson New International Edition

Essential Organic Chemistry

Paula Y. Bruice  
Second Edition

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Second Edition

PEARSON

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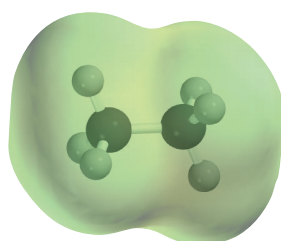
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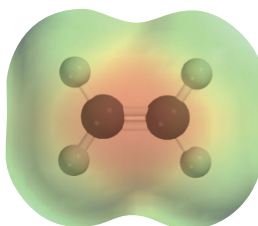
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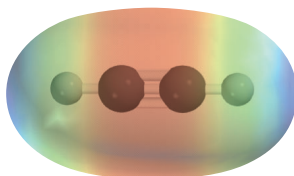
# Electronic Structure and Covalent Bonding



Ethane



Ethene

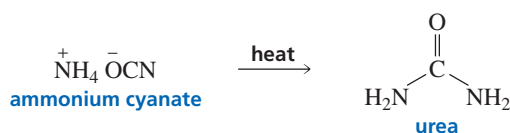


Ethyne

To stay alive, early humans must have been able to tell the difference between two kinds of materials in their world. “You can live on roots and berries,” they might have said, “but you can’t live on dirt. You can stay warm by burning tree branches, but you can’t burn rocks.”

By the early eighteenth century, scientists thought they had grasped the nature of that difference. Compounds derived from living sources were believed to contain an unmeasurable vital force—the essence of life. Because they came from organisms, they were called “organic” compounds. Compounds derived from minerals—those lacking that vital force—were “inorganic.”

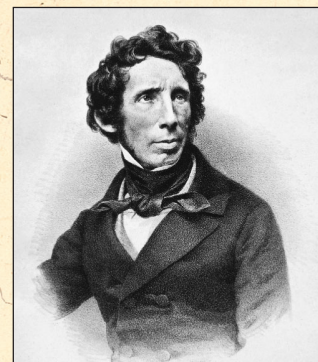
Because chemists could not create life in the laboratory, they assumed they could not create compounds that had a vital force. Since this was their mind-set, you can imagine how surprised chemists were in 1828 when Friedrich Wöhler produced urea—a compound known to be excreted by mammals—by heating ammonium cyanate, an inorganic mineral.



For the first time, an “organic” compound had been obtained from something other than a living organism and certainly without the aid of any kind of vital force. Clearly, chemists needed a new definition for “organic compounds.” **Organic compounds** are now defined as *compounds that contain carbon*.

Why is an entire branch of chemistry devoted to the study of carbon-containing compounds? We study organic chemistry because just about all of the molecules that

## B I O G R A P H Y

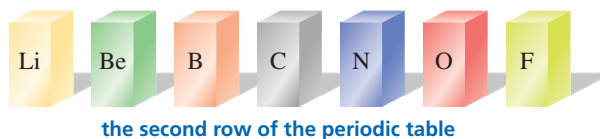


German chemist **Friedrich Wöhler (1800–1882)** began his professional life as a physician and later became a professor of chemistry at the University of Göttingen. Wöhler codiscovered the fact that two different chemicals could have the same molecular formula. He also developed methods of purifying aluminum—at the time, the most expensive metal on Earth—and beryllium.

make life possible—proteins, enzymes, vitamins, lipids, carbohydrates, and nucleic acids—contain carbon; thus, the chemical reactions that take place in living systems, including our own bodies, are reactions of organic compounds. Most of the compounds found in nature—those we rely on for food, medicine, clothing (cotton, wool, silk), and energy (natural gas, petroleum)—are organic compounds as well.

Organic compounds are not, however, limited to those found in nature. Chemists have learned to synthesize millions of organic compounds never found in nature, including synthetic fabrics, plastics, synthetic rubber, medicines, and even things like photographic film and Super Glue. Many of these synthetic compounds prevent shortages of naturally occurring products. For example, it has been estimated that if synthetic materials were not available for clothing, all of the arable land in the United States would have to be used for the production of cotton and wool just to provide enough material to clothe us. Currently, there are about 16 million known organic compounds, and many more are possible.

What makes carbon so special? Why are there so many carbon-containing compounds? The answer lies in carbon's position in the periodic table. Carbon is in the center of the second row of elements. The atoms to the left of carbon have a tendency to give up electrons, whereas the atoms to the right have a tendency to accept electrons (Section 3).



Because carbon is in the middle, it neither readily gives up nor readily accepts electrons. Instead, it shares electrons. Carbon can share electrons with several different kinds of atoms, and it can also share electrons with other carbon atoms. Consequently, carbon is able to form millions of stable compounds with a wide range of chemical properties simply by sharing electrons.

When we study organic chemistry, we study how organic compounds react. When an organic compound reacts, some existing bonds break and some new bonds form. Bonds form when two atoms share electrons, and bonds break when two atoms no longer share electrons. How readily a bond forms and how easily it breaks depend on the particular electrons that are shared, which, in turn, depend on the atoms to which the electrons belong. So if we are going to start our study of organic chemistry at the beginning, we must start with an understanding of the structure of an atom—what electrons an atom has and where they are located.



### NATURAL VERSUS SYNTHETIC

It is a popular belief that natural substances—those made in nature—are superior to synthetic ones—those made in the laboratory. Yet when a chemist synthesizes a compound, such as penicillin, it is exactly the same in all respects as the compound synthesized in nature. Sometimes chemists can improve on nature. For example, chemists have synthesized analogs of morphine—compounds with structures similar to but not identical to that of morphine—that have painkilling effects like morphine but, unlike morphine, are not habit forming. Chemists have synthesized analogs of penicillin that do not produce the allergic responses that a significant fraction of the population experiences from naturally produced penicillin, or that do not have the bacterial resistance of the naturally produced antibiotic.



A field of poppies growing in Afghanistan. Commercial morphine is obtained from opium, the juice obtained from this species of poppy.

## 1 THE STRUCTURE OF AN ATOM

An atom consists of a tiny dense nucleus surrounded by electrons that are spread throughout a relatively large volume of space around the nucleus. The nucleus contains *positively charged protons* and *neutral neutrons*, so it is positively charged. The electrons are *negatively charged*. Because the amount of positive charge on a proton equals the amount of negative charge on an electron, a neutral atom has an equal number of protons and electrons. Atoms can gain electrons and thereby become negatively charged, or they can lose electrons and become positively charged. However, the number of protons in an atom does not change.

Protons and neutrons have approximately the same mass and are about 1800 times more massive than an electron. This means that most of the *mass* of an atom is in its nucleus. However, most of the *volume* of an atom is occupied by its electrons, and that is where our focus will be because it is the electrons that form chemical bonds.

The **atomic number** of an atom equals the *number of protons* in its nucleus. The atomic number is also the number of electrons that surround the nucleus of a neutral atom. For example, the atomic number of carbon is 6, which means that a neutral carbon atom has six protons and six electrons.

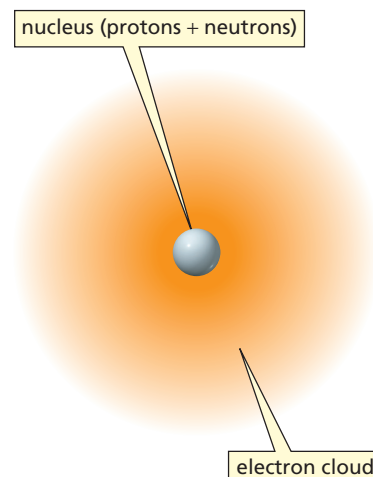
The **mass number** of an atom is the *sum of its protons and neutrons*. All carbon atoms have the same atomic number because they all have the same number of protons. They do not all have the same mass number because they do not all have the same number of neutrons. For example, 98.89% of naturally occurring carbon atoms have six neutrons—giving them a mass number of 12—and 1.11% have seven neutrons—giving them a mass number of 13. These two different kinds of carbon atoms ( $^{12}\text{C}$  and  $^{13}\text{C}$ ) are called isotopes. **Isotopes** have the same atomic number (that is, the same number of protons), but different mass numbers because they have different numbers of neutrons.

Naturally occurring carbon also contains a trace amount of  $^{14}\text{C}$ , which has six protons and eight neutrons. This isotope of carbon is radioactive, decaying with a half-life of 5730 years. (The *half-life* is the time it takes for one-half of the nuclei to decay.) As long as a plant or an animal is alive, it takes in as much  $^{14}\text{C}$  as it excretes or exhales. When it dies, it no longer takes in  $^{14}\text{C}$ , so the  $^{14}\text{C}$  in the organism slowly decreases. Therefore, the age of an organic substance can be determined by its  $^{14}\text{C}$  content.

The **atomic weight** (or **atomic mass**) of a naturally occurring element is the *average mass of its atoms*. For example, carbon has an atomic weight of 12.011 atomic mass units. The **molecular weight** of a compound is the *sum of the atomic weights* of all the atoms in the molecule.

### PROBLEM 1 ♦

Oxygen has three isotopes with mass numbers of 16, 17, and 18. The atomic number of oxygen is eight. How many protons and neutrons does each of the isotopes have?



## 2 HOW THE ELECTRONS IN AN ATOM ARE DISTRIBUTED

The electrons in an atom can be thought of as occupying a set of shells that surround the nucleus. The way in which the electrons are distributed in these shells is based on a theory developed by Einstein. The first shell is the smallest and the one closest to the nucleus; the second shell is larger and extends farther from the nucleus; and the third and higher numbered shells extend even farther out. Each shell consists of subshells known as **atomic orbitals**. The first shell has only an *s* atomic orbital; the second shell consists of *s* and *p* atomic orbitals; and the third shell consists of *s*, *p*, and *d* atomic orbitals (Table 1).



**Table 1** Distribution of Electrons in the First Three Shells That Surround the Nucleus

	First shell	Second shell	Third shell
Atomic orbitals	<i>s</i>	<i>s, p</i>	<i>s, p, d</i>
Number of atomic orbitals	1	1, 3	1, 3, 5
Maximum number of electrons	2	8	18

Each shell contains one *s* orbital. The second and higher shells—in addition to their *s* orbital—each contain three *p* orbitals. The three *p* orbitals have the same energy. The third and higher shells—in addition to their *s* and *p* orbitals—also contain five *d* orbitals. Because an orbital can contain no more than two electrons (see below), the first shell, with only one atomic orbital, can contain no more than two electrons. The second shell, with four atomic orbitals—one *s* and three *p*—can have a total of eight electrons. Eighteen electrons can occupy the nine atomic orbitals—one *s*, three *p*, and five *d*—of the third shell.

An important point to remember is that *the closer the atomic orbital is to the nucleus, the lower is its energy*. Because the *s* orbital in the first shell (called a *1s* orbital) is closer to the nucleus than is the *s* orbital in the second shell (called a *2s* orbital), the *1s* orbital is lower in energy. Comparing orbitals in the same shell, we see that an *s* orbital is lower in energy than a *p* orbital, and a *p* orbital is lower in energy than a *d* orbital.

**Relative energies of atomic orbitals:**  $1s < 2s < 2p < 3s < 3p < 3d$

The **electronic configuration** of an atom describes what orbitals the electrons occupy. The following three rules are used to determine an atom's electronic configuration:

1. An electron always goes into the available orbital with the lowest energy.
2. No more than two electrons can occupy each orbital, and the two electrons must be of opposite spin. (Notice in Table 2 that spin in one direction is designated by  $\uparrow$ , and spin in the opposite direction by  $\downarrow$ .)

From these first two rules, we can assign electrons to atomic orbitals for atoms that contain one, two, three, four, or five electrons. The single electron of a hydrogen atom occupies a *1s* orbital, the second electron of a helium atom fills the *1s* orbital, the third electron of a lithium atom occupies a *2s* orbital, the fourth electron of a beryllium atom fills the *2s* orbital, and the fifth electron of a boron atom occupies one of the *2p* orbitals. (The subscripts *x*, *y*, and *z* distinguish the three *2p* orbitals.) Because the three

The closer the orbital is to the nucleus, the lower is its energy.

**Table 2** The Electronic Configurations of the Smallest Atoms

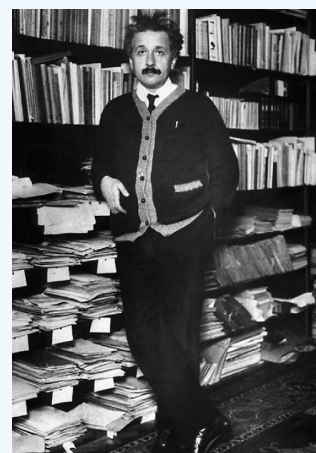
Atom	Name of element	Atomic number	1s	2s	2p <sub>x</sub>	2p <sub>y</sub>	2p <sub>z</sub>	3s
H	Hydrogen	1	$\uparrow$					
He	Helium	2	$\uparrow\downarrow$					
Li	Lithium	3	$\uparrow\downarrow$	$\uparrow$				
Be	Beryllium	4	$\uparrow\downarrow$	$\uparrow\downarrow$				
B	Boron	5	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$			
C	Carbon	6	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$	$\uparrow$		
N	Nitrogen	7	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$	$\uparrow$	$\uparrow$	
O	Oxygen	8	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$	$\uparrow$	
F	Fluorine	9	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$	
Ne	Neon	10	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	
Na	Sodium	11	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$



## ALBERT EINSTEIN

Albert Einstein (1879–1955) was born in Germany. When he was in high school, his father's business failed and his family moved to Milan, Italy. Although Einstein wanted to join his family in Italy, he had to stay behind because German law required compulsory military service after high school. To help him, his high school mathematics teacher wrote a letter saying that Einstein could have a nervous breakdown without his family and also that there was nothing left to teach him. Eventually, Einstein was asked to leave the school because of his disruptive behavior. Popular folklore says he left because of poor grades in Latin and Greek, but his grades in those subjects were fine.

Einstein was visiting the United States when Hitler came to power, so he accepted a position at the Institute for Advanced Study in Princeton, becoming a U.S. citizen in 1940. Although a lifelong pacifist, he wrote a letter to President Roosevelt warning of ominous advances in German nuclear research. This led to the creation of the Manhattan Project, which developed the atomic bomb and tested it in New Mexico in 1945.



$2p$  orbitals have the same energy, the electron can be put into any one of them. Before we can continue to atoms containing six or more electrons, we need the third rule:

- When there are two or more orbitals with the same energy, an electron will occupy an empty orbital before it will pair up with another electron.

The sixth electron of a carbon atom, therefore, goes into an empty  $2p$  orbital, rather than pairing up with the electron already occupying a  $2p$  orbital (Table 2). There is one more empty  $2p$  orbital, so that is where the seventh electron of a nitrogen atom goes. The eighth electron of an oxygen atom pairs up with an electron occupying a  $2p$  orbital rather than going into a higher energy  $3s$  orbital.

Electrons in inner shells (those below the outermost shell) are called **core electrons**. Electrons in the outermost shell are called **valence electrons**. Carbon, for example, has two core electrons and four valence electrons (Table 2).

Lithium and sodium each have one valence electron. Elements in the same column of the periodic table have the same number of valence electrons. Because the number of valence electrons is the major factor determining an element's chemical properties, elements in the same column of the **periodic table** have similar chemical properties. (You can find a periodic table inside the back cover of this book.) Thus, the chemical behavior of an element depends on its electronic configuration.

### PROBLEM 2 ♦

How many valence electrons do the following atoms have?

- a. carbon      b. nitrogen      c. oxygen      d. fluorine

### PROBLEM 3 ♦

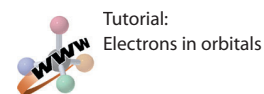
Table 2 shows that lithium and sodium each have one valence electron. Find potassium (K) in the periodic table and predict how many valence electrons it has.

### PROBLEM-SOLVING STRATEGY

Write the ground-state electronic configuration for chlorine.

The periodic table in the back of the book shows that chlorine has 17 electrons. Now we need to assign the electrons to orbitals using the rules that determine an atom's electronic configuration. Two electrons are in the  $1s$  orbital, two are in the  $2s$  orbital, six are in the  $2p$  orbitals, and two are in the  $3s$  orbital. This accounts for 12 of the 17 electrons. The remaining five electrons are in the  $3p$  orbitals. Therefore, the electronic configuration is written as:  $1s^2, 2s^2, 2p^6, 3s^2, 3p^5$

Now continue on to Problem 4.



Shown is a bronze sculpture of **Einstein** on the grounds of the National Academy of Sciences in Washington, D.C. It measures 21 feet from the top of the head to the tip of the feet and weighs 7000 pounds. In his left hand, Einstein holds the mathematical equations that represent his three most important contributions to science: the photoelectric effect, the equivalency of energy and matter, and the theory of relativity. At his feet is a map of the sky.

**PROBLEM 4** ♦

- Compare the ground-state electronic configurations for nitrogen and phosphorus and look at their relative positions in the periodic table. How many valence electrons does each have? How many core electrons does each have?
- Compare the ground-state electronic configurations for oxygen and sulfur and look at their relative positions in the periodic table. How many valence electrons does each have? How many core electrons does each have?

**PROBLEM 5** ♦

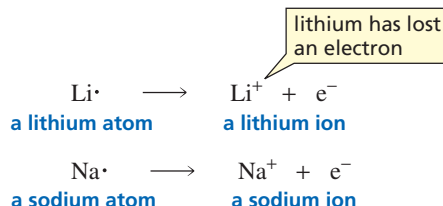
How many valence electrons do chlorine, bromine, and iodine have?

### 3 IONIC AND COVALENT BONDS

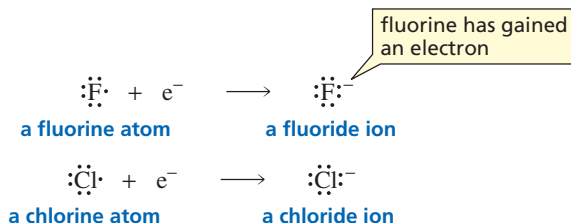
In trying to explain why atoms form bonds, G. N. Lewis proposed that *an atom is most stable if its outer shell is either filled or contains eight electrons and it has no electrons of higher energy*. According to Lewis's theory, an atom will give up, accept, or share electrons in order to achieve a filled outer shell or an outer shell that contains eight electrons. This theory has come to be called the **octet rule** (even though the filled outer shell of hydrogen has only two electrons).

Lithium (Li) has a single electron in its 2s orbital. If it loses this electron, the lithium atom ends up with a filled outer shell—a stable configuration. Lithium, therefore, loses an electron relatively easily. Sodium (Na) has a single electron in its 3s orbital, so it too loses an electron easily.

When we draw the electrons around an atom, as in the following equations, core electrons are not shown; only valence electrons are shown because only valence electrons are used in bonding. Each valence electron is shown as a dot. Notice that when the single valence electron of lithium or sodium is removed, the resulting atom—now called an ion—carries a positive charge.

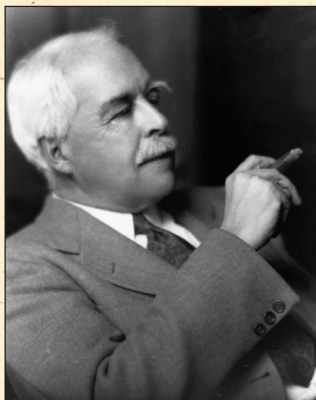


Fluorine and chlorine each have seven valence electrons (Table 2 and Problem 5). Consequently, they readily acquire an electron in order to have an outer shell of eight electrons.



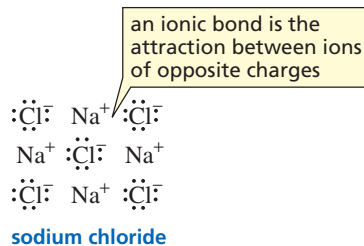
#### Ionic Bonds Are Formed by the Attraction Between Ions of Opposite Charge

We have just seen that sodium gives up an electron easily and chlorine readily acquires an electron. Therefore, when sodium metal and chlorine gas are mixed, each sodium atom transfers an electron to a chlorine atom, and crystalline sodium chloride (table

**B I O G R A P H Y**

American chemist **Gilbert Newton Lewis (1875–1946)** was born in Weymouth, Massachusetts, and received a Ph.D. from Harvard in 1899. He was the first person to prepare “heavy water,” which has deuterium atoms in place of the usual hydrogen atoms ( $\text{D}_2\text{O}$  versus  $\text{H}_2\text{O}$ ). Because heavy water can be used as a moderator of neutrons, it became important in the development of the atomic bomb. Lewis started his career as a professor at the Massachusetts Institute of Technology and joined the faculty at the University of California, Berkeley, in 1912.

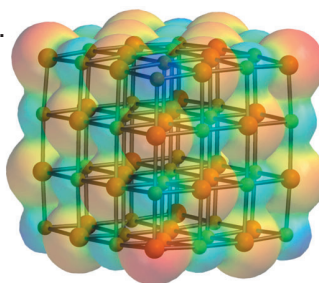
salt) is formed as a result. The positively charged sodium ions and negatively charged chloride ions are independent species held together by the attraction of opposite charges (Figure 1). A **bond** is an attractive force between two ions or between two atoms. A bond that results from the attraction between ions of opposite charge is called an **ionic bond**.



a.



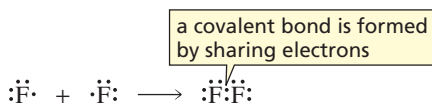
b.

◀ **Figure 1**

(a) Crystalline sodium chloride. (b) The electron-rich chloride ions are red, and the electron-poor sodium ions are blue. Each chloride ion is surrounded by six sodium ions, and each sodium ion is surrounded by six chloride ions. Ignore the sticks holding the balls together; they are there only to keep the model from falling apart.

### Covalent Bonds Are Formed by Sharing Electrons

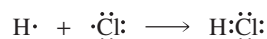
Instead of giving up or acquiring electrons, an atom can achieve a filled outer shell (or an outer shell of eight electrons) by sharing electrons. For example, two fluorine atoms can each attain a filled second shell by sharing their unpaired valence electrons. A bond formed as a result of *sharing electrons* is called a **covalent bond**.



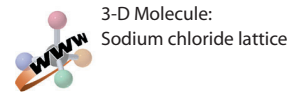
Two hydrogen atoms can form a covalent bond by sharing electrons. As a result of covalent bonding, each hydrogen acquires a stable, filled first shell.



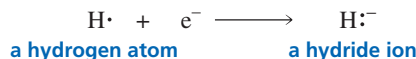
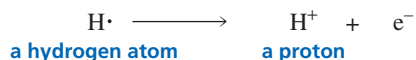
Similarly, hydrogen and chlorine can form a covalent bond by sharing electrons. In doing so, hydrogen fills its only shell and chlorine achieves an outer shell of eight electrons.



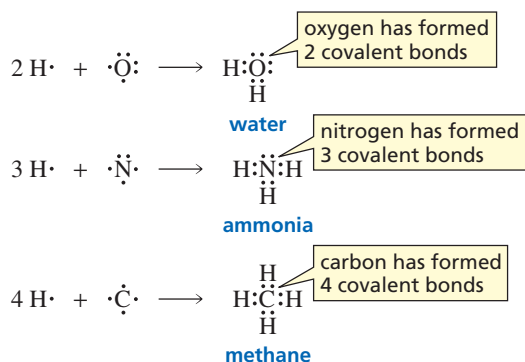
A hydrogen atom can achieve a completely empty shell by losing an electron. Loss of its sole electron results in a positively charged **hydrogen ion**. A positively charged hydrogen ion is called a **proton** because when a hydrogen atom loses its valence electron, only the hydrogen nucleus—which consists of a single proton—remains.



A hydrogen atom can achieve a filled outer shell by gaining an electron, thereby forming a negatively charged hydrogen ion, called a **hydride ion**.



Because oxygen has six valence electrons, it needs to form two covalent bonds to achieve a filled outer shell. Nitrogen, with five valence electrons, must form three covalent bonds, and carbon, with four valence electrons, must form four covalent bonds to achieve a filled outer shell. Notice that all the atoms in water, ammonia, and methane have filled outer shells.



### Nonpolar Covalent Bonds and Polar Covalent Bonds

The atoms that share the bonding electrons in the F—F or the H—H covalent bond are identical. Therefore, they share the electrons equally; that is, each electron spends as much time in the vicinity of one atom as in the other. Such a bond is called a **nonpolar covalent bond**.

In contrast, the bonding electrons in hydrogen chloride, water, and ammonia are more attracted to one atom than to another because the atoms that share the electrons in these molecules are different and have different electronegativities. **Electronegativity** is a measure of the ability of an atom to pull the bonding electrons toward itself. The electronegativities of some of the elements are shown in Table 3. The

**Table 3 The Electronegativities of Selected Elements<sup>a</sup>**

IA	IIA	IB	IIB	IIIA	IVA	VA	VIA	VIIA
H 2.1								
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			Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0							Br 2.8
								I 2.5

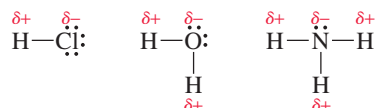
increasing electronegativity →

↑ increasing electronegativity

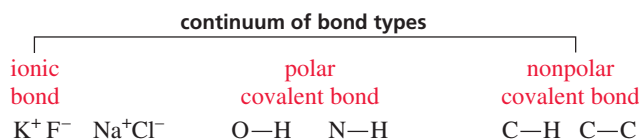
<sup>a</sup>Electronegativity values are relative, not absolute. As a result, there are several scales of electronegativities. The electronegativities listed here are from the scale devised by Linus Pauling.

bonding electrons in hydrogen chloride, water, and ammonia are more attracted to the atom with the greater electronegativity. A **polar covalent bond** is a covalent bond between atoms of different electronegativities. Notice that electronegativity increases from left to right across a row of the periodic table or going up any of the columns.

A polar covalent bond has a slight positive charge on one end and a slight negative charge on the other. Polarity in a covalent bond is indicated by the symbols  $\delta^+$  and  $\delta^-$ , which denote partial positive and partial negative charges, respectively. The negative end of the bond is the end that has the more electronegative atom. The greater the difference in electronegativity between the bonded atoms, the more polar the bond will be. (Notice that a pair of shared electrons can be shown as a line between two atoms.)



You can think of ionic bonds and nonpolar covalent bonds as being at the opposite ends of a continuum of bond types. At one end is an ionic bond, a bond in which there is no sharing of electrons. At the other end is a nonpolar covalent bond, a bond in which the electrons are shared equally. Polar covalent bonds fall somewhere in between, and the greater the difference in electronegativity between the atoms forming the bond, the closer the bond is to the ionic end of the continuum. C—H bonds are relatively nonpolar, because carbon and hydrogen have similar electronegativities (electronegativity difference = 0.4; see Table 3). N—H bonds are relatively polar (electronegativity difference = 0.9), but not as polar as O—H bonds (electronegativity difference = 1.4). Even closer to the ionic end of the continuum is the bond between sodium and chloride ions (electronegativity difference = 2.1), but sodium chloride is not as ionic as potassium fluoride (electronegativity difference = 3.2).

**PROBLEM 6** ♦

Which bond is more polar?

- a. H—CH<sub>3</sub> or Cl—CH<sub>3</sub>      c. H—Cl or H—F  
 b. H—OH or H—H      d. Cl—Cl or Cl—CH<sub>3</sub>

**PROBLEM 7** ♦

Which of the following has

- a. the most polar bond?      b. the least polar bond?  
 NaI    LiBr    Cl<sub>2</sub>    KCl

**PROBLEM 8** ♦

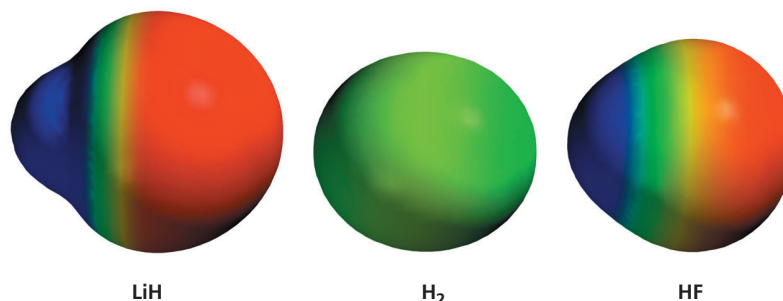
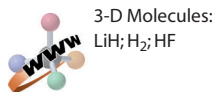
Use the symbols  $\delta^+$  and  $\delta^-$  to show the direction of polarity of the indicated bond in each

of the following compounds (for example,  $\overset{\delta^+}{\text{H}_3\text{C}}-\overset{\delta^-}{\text{OH}}$ )

- a. HO—H      b. H<sub>3</sub>C—NH<sub>2</sub>      c. HO—Br      d. I—Cl



**Electrostatic potential maps** (often simply called potential maps) are models that show how charge is distributed in the molecule under the map. The potential maps for LiH, H<sub>2</sub>, and HF are shown below.



The colors indicate the distribution of charge in the molecule: red signifies electron-rich areas (negative charge); blue signifies electron-deficient areas (positive charge); and green signifies no charge. For example, the potential map for LiH indicates that the hydrogen atom is more negatively charged than the lithium atom. By comparing the three maps, we can tell that the hydrogen in LiH is more negatively charged than a hydrogen in H<sub>2</sub>, and the hydrogen in HF is more positively charged than a hydrogen in H<sub>2</sub>.



#### PROBLEM 9 ♦

After examining the potential maps for LiH, HF, and H<sub>2</sub>, answer the following questions:

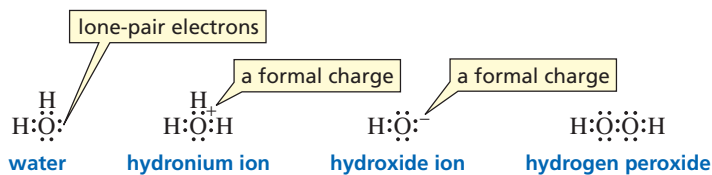
- a. Which compounds are polar?
- b. Which compound has the most positively charged hydrogen?

## 4 HOW THE STRUCTURE OF A COMPOUND IS REPRESENTED

First we will see how compounds are drawn using Lewis structures. Then we will look at the representations of structures that are used more commonly for organic compounds.

### Lewis Structures

The chemical symbols we have been using, in which the valence electrons are represented as dots, are called **Lewis structures** (or electron dot structures) after G. N. Lewis (Section 3). Lewis structures are useful because they show us which atoms are bonded together and tell us whether any atoms *possess lone-pair electrons* or have a *formal charge*, two concepts we describe below. The Lewis structures for H<sub>2</sub>O, H<sub>3</sub>O<sup>+</sup>, HO<sup>-</sup>, and H<sub>2</sub>O<sub>2</sub> are

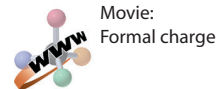
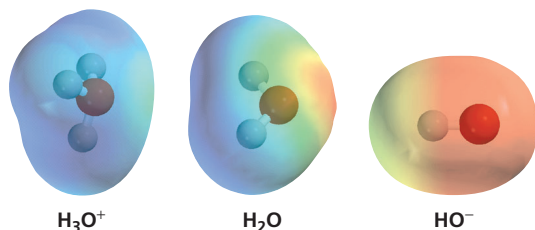


When you draw a Lewis structure, make sure that hydrogen atoms are surrounded by no more than two electrons and that C, O, N, and halogen (F, Cl, Br, I) atoms are surrounded by no more than eight electrons, in accordance with the octet rule. Valence electrons not used in bonding are called **nonbonding electrons, lone-pair electrons**, or simply **lone pairs**.

Once you have all the atoms and the electrons in place, you must examine each atom to see whether a formal charge should be assigned to it. A **formal charge** is the *difference* between the number of valence electrons an atom has when it is not bonded to any other atoms and the number of electrons it “owns” when it is bonded. An atom “owns” all of its lone-pair electrons and half of its bonding (shared) electrons.

$$\text{formal charge} = \text{number of valence electrons} - (\text{number of lone-pair electrons} + 1/2 \text{ number of bonding electrons})$$

For example, an oxygen atom has six valence electrons (Table 2). In water ( $\text{H}_2\text{O}$ ), oxygen “owns” six electrons (four lone-pair electrons and half of the four bonding electrons). Because the number of electrons it “owns” is equal to the number of its valence electrons ( $6 - 6 = 0$ ), the oxygen atom in water does not have a formal charge. The oxygen atom in the hydronium ion ( $\text{H}_3\text{O}^+$ ) “owns” five electrons: two lone-pair electrons plus three (half of six) bonding electrons. Because the number of electrons it “owns” is one less than the number of its valence electrons, its formal charge is +1 ( $6 - 5 = 1$ ). The oxygen atom in hydroxide ion  $\text{HO}^-$  “owns” seven electrons: six lone-pair electrons plus one (half of two) bonding electron. Because it “owns” one more electron than the number of its valence electrons, its formal charge is -1 ( $6 - 7 = -1$ ).



### PROBLEM 10

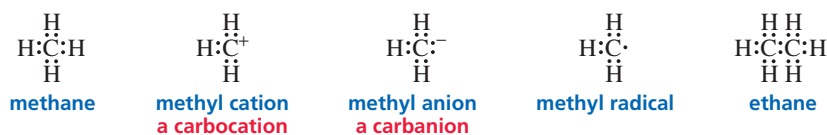
The formal charge does not necessarily indicate that the atom has greater or less electron density than other atoms in the molecule without formal charges. You can see this by examining the potential maps for  $\text{H}_2\text{O}$ ,  $\text{H}_3\text{O}^+$ , and  $\text{HO}^-$ .

- Which atom bears the formal negative charge in the hydroxide ion?
- Which atom has the greater electron density in the hydroxide ion?
- Which atom bears the formal positive charge in the hydronium ion?
- Which atom has the least electron density in the hydronium ion?

Nitrogen has five valence electrons (Table 2). Prove to yourself that the appropriate formal charges have been assigned to the nitrogen atoms in the following Lewis structures:



Carbon has four valence electrons. Take a moment to understand why the carbon atoms in the following Lewis structures have the indicated formal charges:

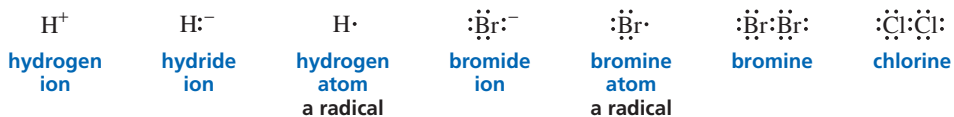




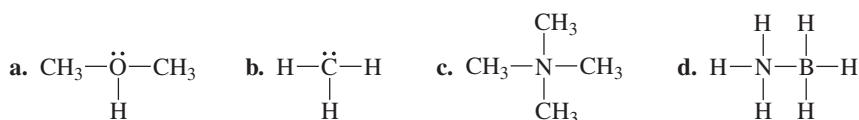
## Electronic Structure and Covalent Bonding

A species containing a positively charged carbon atom is called a **carbocation**, and a species containing a negatively charged carbon atom is called a **carbanion**. (Recall that a *cation* is a positively charged ion and an *anion* is a negatively charged ion.) A species containing an atom with a single unpaired electron is called a **radical** (often called a **free radical**).

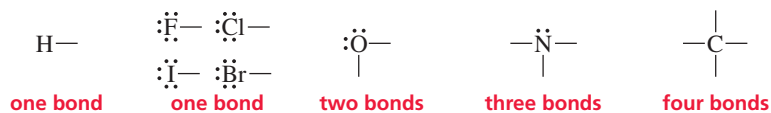
Hydrogen has one valence electron, and each halogen (F, Cl, Br, I) has seven valence electrons, so the following species have the indicated formal charges:


**PROBLEM 11**

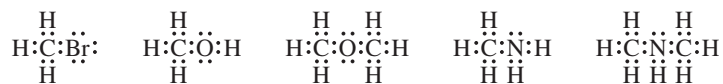
Give each atom the appropriate formal charge:



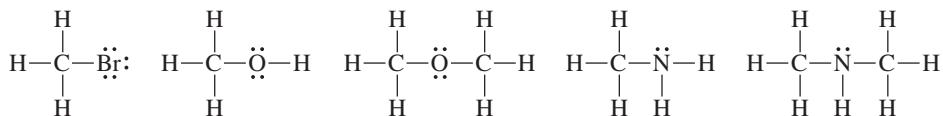
In studying the molecules in this section, notice that when the atoms do not bear a formal charge or an unpaired electron, hydrogen and the halogens always have *one* covalent bond, oxygen always has *two* covalent bonds, nitrogen always has *three* covalent bonds, and carbon has *four* covalent bonds. Atoms that have more bonds or fewer bonds than the number required for a neutral atom will have either a formal charge or an unpaired electron. These numbers are very important to remember when you are first drawing structures of organic compounds because they provide a quick way to recognize when you have made a mistake.



In the following Lewis structures, notice that each atom has a filled outer shell. Also notice that since none of the molecules has a formal charge or an unpaired electron, C forms four bonds, N forms three bonds, O forms two bonds, and H and Br each form one bond.



Because a pair of shared electrons can be shown as a line between two atoms, compare the preceding structures with the following ones:

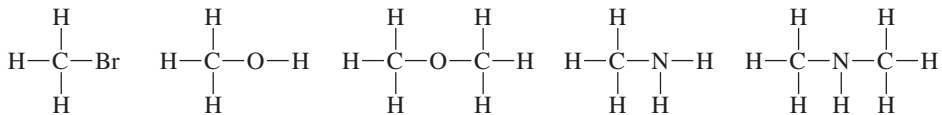

**PROBLEM 12**

Draw the Lewis structure for each of the following:



## Kekulé Structures

In **Kekulé structures**, the bonding electrons are drawn as lines and the lone-pair electrons are usually left out entirely, unless they are needed to draw attention to some chemical property of the molecule. (Although lone-pair electrons are not shown, you should remember that neutral nitrogen, oxygen, and halogen atoms always have them: one pair in the case of nitrogen, two pairs in the case of oxygen, and three pairs in the case of a halogen.)



## Condensed Structures

Frequently, structures are simplified by omitting some (or all) of the covalent bonds and listing atoms bonded to a particular carbon (or nitrogen or oxygen) next to it with subscripts as necessary. These structures are called **condensed structures**. Compare the following examples with the Kekulé structures shown above:



You can find more examples of condensed structures and the conventions commonly used to create them in Table 4.

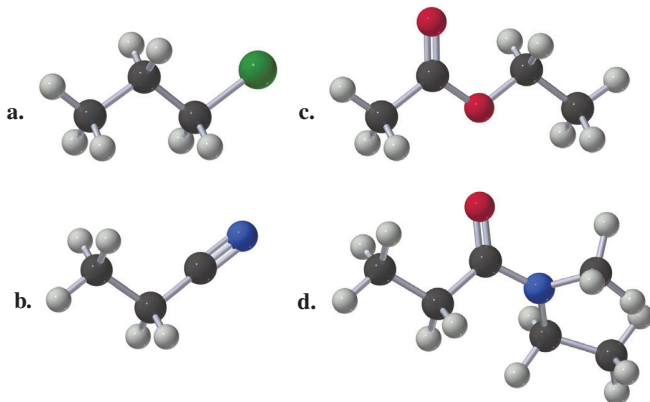
### PROBLEM 13

Draw the lone-pair electrons that are not shown in the following structures:

- a.  $\text{CH}_3\text{CH}_2\text{NH}_2$       c.  $\text{CH}_3\text{CH}_2\text{OH}$       e.  $\text{CH}_3\text{CH}_2\text{Cl}$   
 b.  $\text{CH}_3\text{NHCH}_3$       d.  $\text{CH}_3\text{OCH}_3$       f.  $\text{HONH}_2$

### PROBLEM 14

Draw condensed structures for the compounds represented by the following models (black = C, white = H, red = O, blue = N, green = Cl):



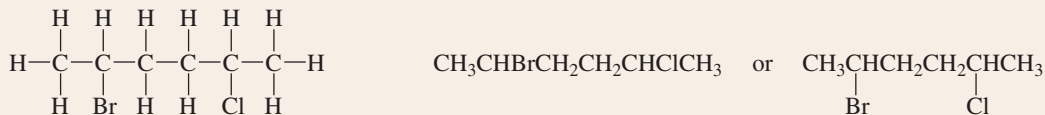
### PROBLEM 15

Which of the atoms in the molecular models in Problem 14 have

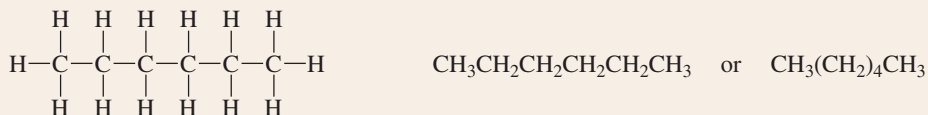
- a. three lone pairs?      b. two lone pairs?      c. one lone pair?      d. no lone pairs?

**Table 4 Kekulé and Condensed Structures****Kekulé structure****Condensed structures**

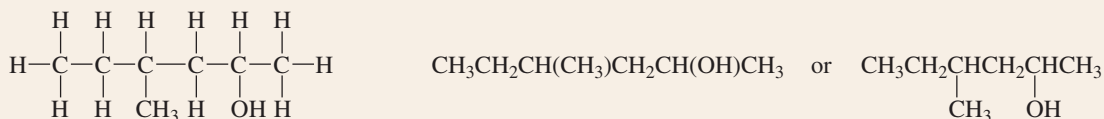
Atoms bonded to a carbon are shown to the right of the carbon. Atoms other than H can be shown hanging from the carbon.



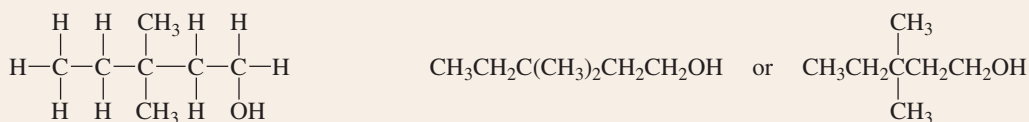
Repeating  $\text{CH}_2$  groups can be shown in parentheses.



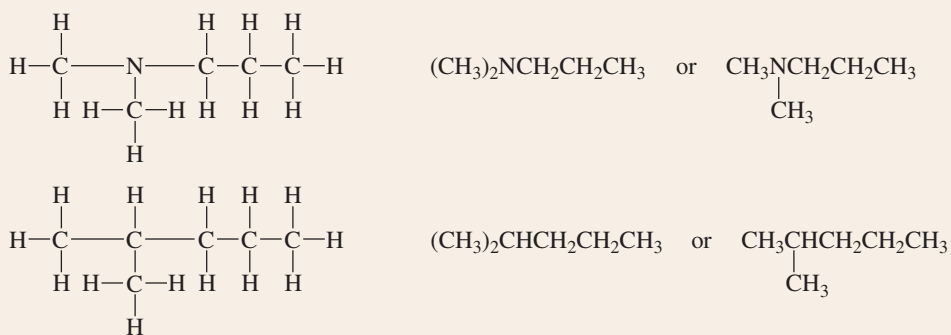
Groups bonded to a carbon can be shown (in parentheses) to the right of the carbon, or hanging from the carbon.



Groups bonded to the far-right carbon are not put in parentheses.



Two or more identical groups considered bonded to the “first” atom on the left can be shown (in parentheses) to the left of that atom, or hanging from the atom.

**PROBLEM 16**

Which of the following molecular formulas are not possible for an organic compound?



**PROBLEM 17**

- a. Draw two Lewis structures for  $C_2H_6O$ .  
 b. Draw three Lewis structures for  $C_3H_8O$ .  
 (*Hint:* The two Lewis structures in part a are **constitutional isomers**; they have the same atoms, but differ in the way the atoms are connected. The three Lewis structures in part b are also constitutional isomers.)

**PROBLEM 18**

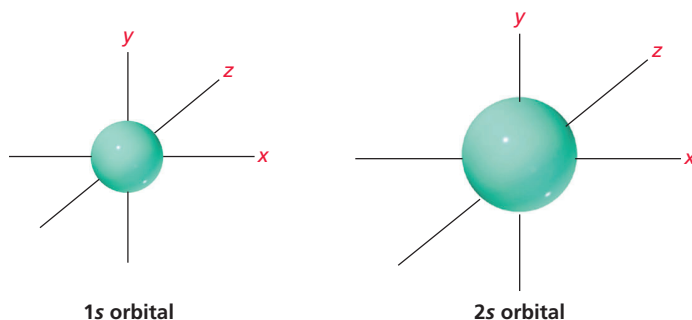
Expand the following condensed structures to show the covalent bonds and lone pairs:

- a.  $CH_3NH(CH_2)_2CH_3$                       c.  $(CH_3)_3COH$   
 b.  $(CH_3)_2CHCl$                                 d.  $(CH_3)_3C(CH_2)_3CH(CH_3)_2$

## 5 ATOMIC ORBITALS

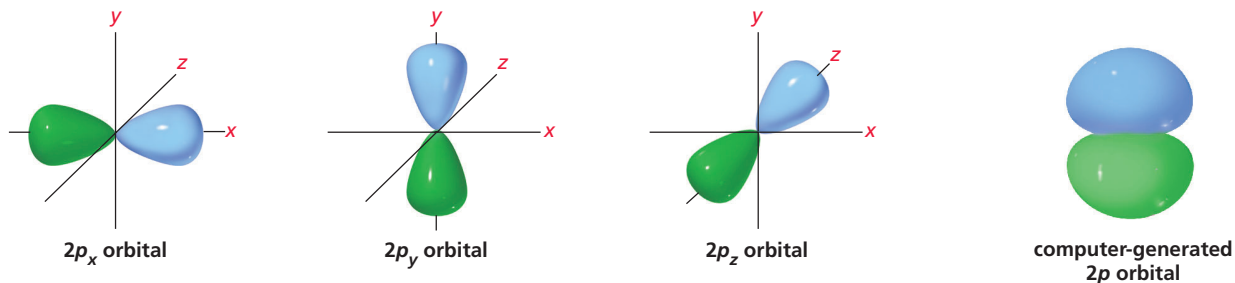
We have seen that electrons are distributed into different atomic orbitals (Table 2). An **orbital** is a three-dimensional region around the nucleus where an electron is most likely to be found. But what does an orbital look like? The  $s$  orbital is a sphere with the nucleus at its center. Thus, when we say that an electron occupies a  $1s$  orbital, we mean that there is a greater than 90% probability that the electron is in the space defined by the sphere.

An orbital tells us the volume of space around the nucleus where an electron is most likely to be found.

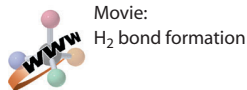


Because the second shell lies farther from the nucleus than the first shell (Section 2), the average distance from the nucleus is greater for an electron in a  $2s$  orbital than for an electron in a  $1s$  orbital. A  $2s$  orbital, therefore, is represented by a larger sphere. Because of the greater size of the  $2s$  orbital, its average electron density is less than the average electron density of a  $1s$  orbital.

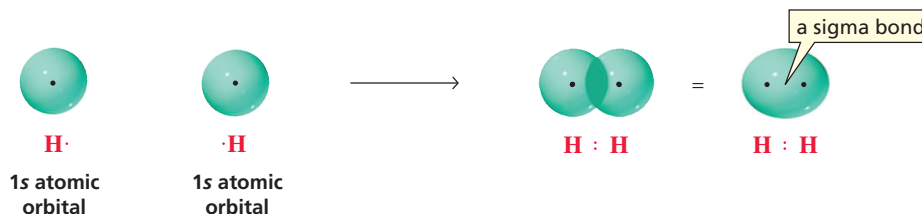
Unlike  $s$  orbitals, which resemble spheres, a  $p$  orbital has two lobes. Generally, the lobes are depicted as teardrop-shaped, but computer-generated representations reveal that they are shaped more like doorknobs. In Section 2, we saw that the second and higher numbered shells each contain three  $p$  orbitals, and the three  $p$  orbitals have the same energy. The  $p_x$  orbital is symmetrical about the  $x$ -axis, the  $p_y$  orbital is symmetrical about the  $y$ -axis, and the  $p_z$  orbital is symmetrical about the  $z$ -axis. This means that each  $p$  orbital is perpendicular to the other two  $p$  orbitals. The energy of a  $2p$  orbital is greater than that of a  $2s$  orbital because the average location of an electron in a  $2p$  orbital is farther away from the nucleus.



## 6 HOW ATOMS FORM COVALENT BONDS



How do atoms form covalent bonds in order to form molecules? Let's look first at the bonding in a hydrogen molecule (H<sub>2</sub>). The covalent bond is formed when the 1s orbital of one hydrogen atom overlaps the 1s orbital of a second hydrogen atom. The covalent bond that is formed when the two orbitals overlap is called a **sigma ( $\sigma$ ) bond**.



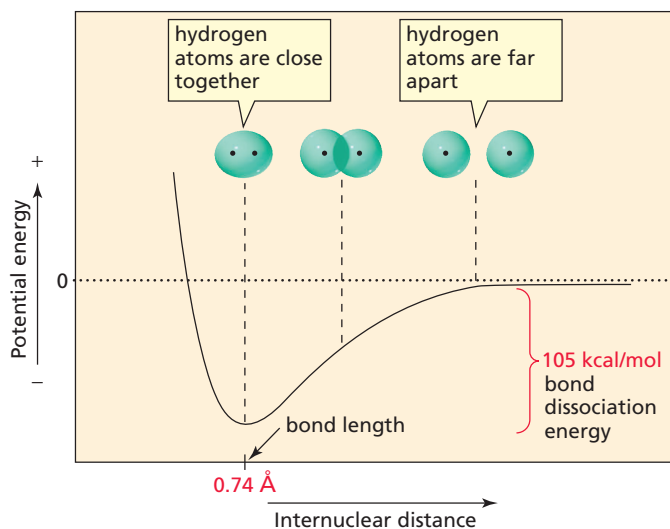
Why do atoms form covalent bonds? As the two orbitals start to overlap to form the covalent bond, energy is released (and stability increases) because the electron in each atom is attracted both to its own nucleus and to the positively charged nucleus of the other atom (Figure 2). Thus atoms form covalent bonds because the covalently bonded atoms are more stable than the individual atoms. The attraction of the negatively charged electrons for the positively charged nuclei is what holds the atoms together. The more the orbitals overlap, the more the energy decreases until the atoms are so close together that their positively charged nuclei start to repel each other. This repulsion causes a large increase in energy. Maximum stability (that is, minimum energy) is achieved when the nuclei are a certain distance apart. This distance is the **bond length** of the new covalent bond. The length of the H—H bond is 0.74 Å.

As Figure 2 shows, energy is released when a covalent bond forms. When the H—H bond forms, 105 kcal/mol or 439 kJ/mol of energy is released (1 kcal = 4.184 kJ).<sup>\*</sup> Breaking the bond requires precisely the same amount of energy. Thus, the **bond strength**—also called the **bond dissociation energy**—is the energy required to break the bond, or the energy released when the bond is formed. Every covalent bond has a characteristic bond length and bond strength.

Maximum stability corresponds to minimum energy.

### ► Figure 2

The change in energy that occurs as two 1s atomic orbitals approach each other. The internuclear distance at minimum energy is the length of the H—H covalent bond.



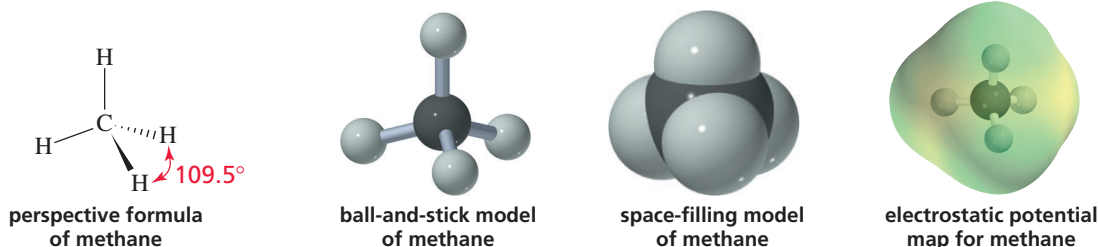
<sup>\*</sup>Joules are the Système International (SI) units for energy, although many chemists use calories. We will use both in this book.

## 7 HOW SINGLE BONDS ARE FORMED IN ORGANIC COMPOUNDS

We will begin the discussion of bonding in organic compounds by looking at the bonding in methane, a compound with only one carbon atom. Then we will examine the bonding in ethane, a compound with two carbons attached by a carbon–carbon *single bond*.

### The Bonds in Methane

Methane ( $\text{CH}_4$ ) has four covalent C—H bonds. Because all four bonds have the same length and all the bond angles are the same ( $109.5^\circ$ ), we can conclude that the four C—H bonds in methane are identical. Four different ways to represent a methane molecule are shown here.



3-D Molecule:  
Methane

In a **perspective formula**, bonds in the plane of the paper are drawn as solid lines, bonds protruding out of the plane of the paper toward the viewer are drawn as solid wedges, and those protruding back from the plane of the paper away from the viewer are drawn as hatched wedges.

The potential map of methane shows that neither carbon nor hydrogen carries much of a charge: there are neither red areas, representing partially negatively charged atoms, nor blue areas, representing partially positively charged atoms. (Compare this map with the potential map for water). The absence of partially charged atoms is due to the similar electronegativities of carbon and hydrogen, which cause them to share their bonding electrons relatively equally. Methane is therefore a **nonpolar molecule**.

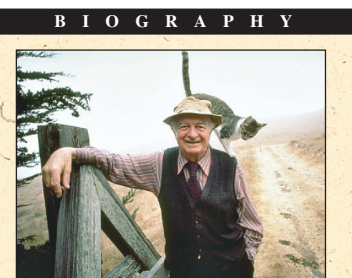
You may be surprised to learn that carbon forms four covalent bonds since you know that carbon has only two unpaired electrons in its electronic configuration (Table 2). But if carbon formed only two covalent bonds, it would not complete its octet. We therefore need to come up with an explanation that accounts for carbon's forming four covalent bonds.

If one of the electrons in carbon's  $2s$  orbital were promoted into the empty  $2p$  orbital, the new electronic configuration would have four unpaired electrons; thus, four covalent bonds could be formed.



If carbon used an  $s$  orbital and three  $p$  orbitals to form these four bonds, the bond formed with the  $s$  orbital would be different from the three bonds formed with  $p$  orbitals. What could account for the fact that the four C—H bonds in methane are identical if they are made using one  $s$  and three  $p$  orbitals? The answer is that carbon uses *hybrid orbitals*.

**Hybrid orbitals** are mixed orbitals that result from combining atomic orbitals. The concept of combining orbitals was first proposed by Linus Pauling in 1931. If the one  $s$  and three  $p$  orbitals of the second shell are all combined and then apportioned into



#### Linus Carl Pauling

(1901–1994) was born in Portland, Oregon. A friend's home chemistry laboratory sparked Pauling's early interest in science. He received a Ph.D. from the California Institute of Technology and remained there for most of his academic career. He received the Nobel Prize in chemistry in 1954 for his work on molecular structure. Like Einstein, Pauling was a pacifist, winning the 1962 Nobel Peace Prize for his work on behalf of nuclear disarmament.

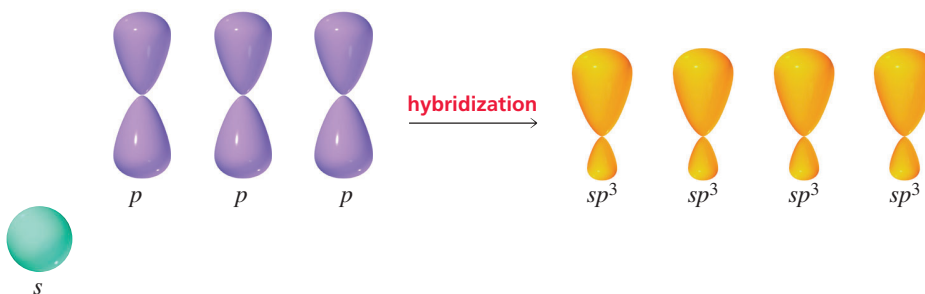
four equal orbitals, each of the four resulting orbitals will be one part  $s$  and three parts  $p$ . Therefore, each orbital has 25%  $s$  character and 75%  $p$  character. This type of mixed orbital is called an  $sp^3$  (stated “ $s$ - $p$ -three” not “ $s$ - $p$ -cubed”) orbital. (The superscript 3 means that three  $p$  orbitals were mixed with one  $s$  orbital to form the hybrid orbitals.) Each of the four  $sp^3$  orbitals has the same energy.



Like a  $p$  orbital, an  $sp^3$  orbital has two lobes. Unlike the lobes of a  $p$  orbital, the two lobes of an  $sp^3$  orbital are not the same size (Figure 3). The larger lobe of the  $sp^3$  orbital is used in covalent bond formation.

► **Figure 3**

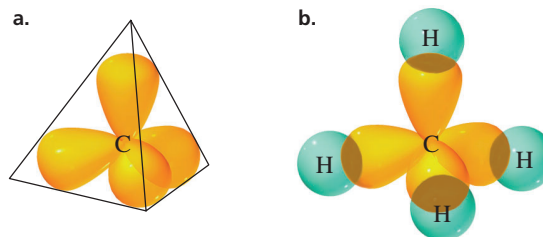
An  $s$  orbital and three  $p$  orbitals hybridize to form four  $sp^3$  orbitals. An  $sp^3$  orbital is more stable than a  $p$  orbital, but not as stable as an  $s$  orbital.



The four  $sp^3$  orbitals adopt a spatial arrangement that keeps them as far away from each other as possible (Figure 4a). They do this because electrons repel each other, and moving the orbitals as far from each other as possible minimizes the repulsion. When four orbitals move as far from each other as possible, they point toward the corners of a regular tetrahedron (a pyramid with four faces, each an equilateral triangle). Each of the four C—H bonds in methane is formed from overlap of an  $sp^3$  orbital of carbon with the  $s$  orbital of a hydrogen (Figure 4b). This explains why the four C—H bonds are identical.

► **Figure 4**

(a) The four  $sp^3$  orbitals are directed toward the corners of a tetrahedron, causing each bond angle to be  $109.5^\circ$ . (b) An orbital picture of methane, showing the overlap of each  $sp^3$  orbital of carbon with the  $s$  orbital of a hydrogen. (For clarity, the smaller lobes of the  $sp^3$  orbitals are not shown.)



The angle between any two bonds that point from the center to the corners of a tetrahedron are  $109.5^\circ$ . The bond angles in methane therefore are  $109.5^\circ$ . This is called a **tetrahedral bond angle**. A carbon, such as the one in methane, that forms covalent bonds using four equivalent  $sp^3$  orbitals is called a **tetrahedral carbon**.

Hybrid orbitals may appear to have been contrived just to make things fit—and that is exactly the case. Nevertheless, they give us a very good picture of the bonding in organic compounds.

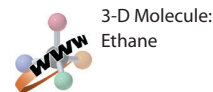
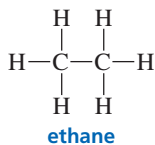
**Electron pairs stay as far from each other as possible.**

**Note to the student**

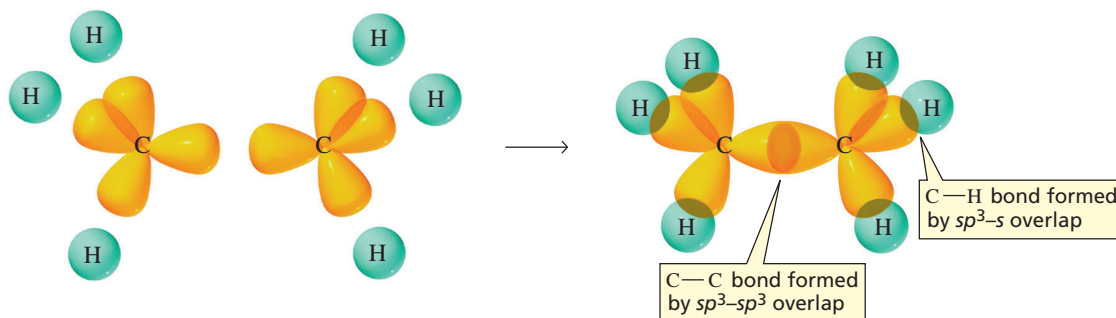
It is important to understand what molecules look like in three dimensions. Therefore be sure to visit the textbook's website (<http://www.chemplace.com>) and look at the three-dimensional representations of molecules that can be found in the molecule gallery prepared for each chapter.

## The Bonds in Ethane

The two carbon atoms in ethane ( $\text{CH}_3\text{CH}_3$ ) are tetrahedral. Each carbon uses four  $sp^3$  orbitals to form four covalent bonds:



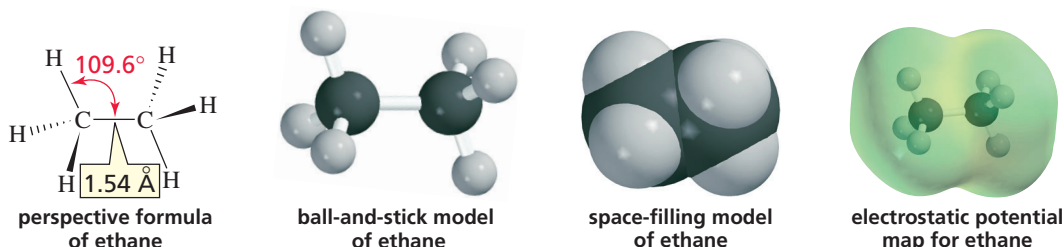
One  $sp^3$  orbital of one carbon overlaps an  $sp^3$  orbital of the other carbon to form the C—C bond. Each of the remaining three  $sp^3$  orbitals of each carbon overlaps the  $s$  orbital of a hydrogen to form a C—H bond. Thus, the C—C bond is formed by  $sp^3-sp^3$  overlap, and each C—H bond is formed by  $sp^3-s$  overlap (Figure 5).



▲ **Figure 5**

An orbital picture of ethane. The C—C bond is formed by  $sp^3-sp^3$  overlap, and each C—H bond is formed by  $sp^3-s$  overlap. (The smaller lobes of the  $sp^3$  orbitals are not shown.)

Each of the bond angles in ethane is nearly the tetrahedral bond angle of  $109.5^\circ$ , and the length of the C—C bond is  $1.54 \text{ \AA}$ . Ethane, like methane, is a nonpolar molecule.



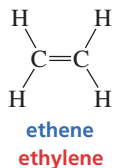
All the bonds in methane and ethane are sigma ( $\sigma$ ) bonds. We will see that all **single bonds** found in organic compounds are *sigma bonds*.

### PROBLEM 19 ♦

What orbitals are used to form the 10 covalent bonds in propane ( $\text{CH}_3\text{CH}_2\text{CH}_3$ )?

## 8 HOW A DOUBLE BOND IS FORMED: THE BONDS IN ETHENE

Each of the carbon atoms in ethene (also called ethylene) forms four bonds, but each is bonded to only three atoms:







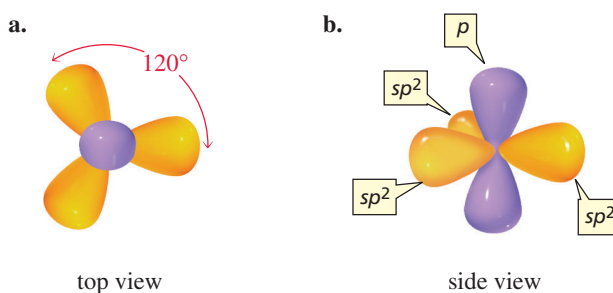
To bond to three atoms, each carbon hybridizes three atomic orbitals: an  $s$  orbital and two of the  $p$  orbitals). Because three orbitals are hybridized, three hybrid orbitals are formed. These are called  $sp^2$  orbitals. After hybridization, each carbon atom has three identical  $sp^2$  orbitals and one  $p$  orbital:



The axes of the three  $sp^2$  orbitals lie in a plane (Figure 6a). To minimize electron repulsion, the three orbitals need to get as far from each other as possible. Therefore the bond angles are all close to  $120^\circ$ . The unhybridized  $p$  orbital is perpendicular to the plane defined by the axes of the  $sp^2$  orbitals (Figure 6b).

► **Figure 6**

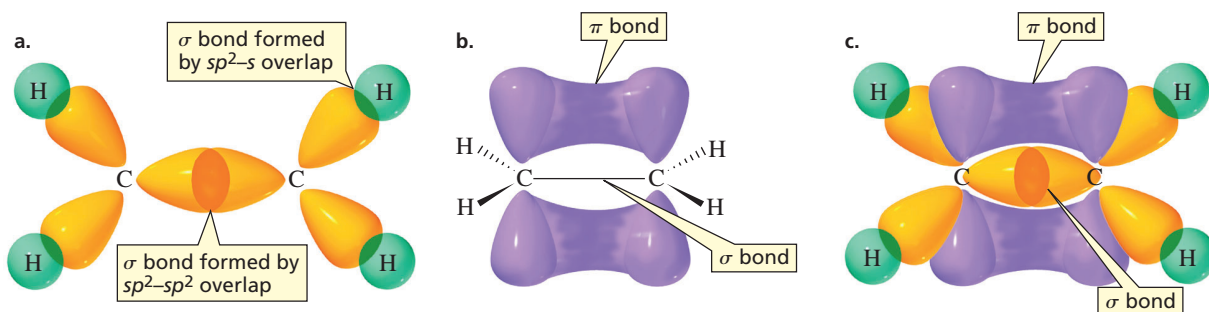
- (a) The three  $sp^2$  orbitals lie in a plane.  
(b) The unhybridized  $p$  orbital is perpendicular to the plane. (The smaller lobes of the  $sp^2$  orbitals are not shown.)



The carbons in ethene are held together by two bonds. Two bonds connecting two atoms is called a **double bond**. The two carbon-carbon bonds in the double bond are not identical. One of them results from the overlap of an  $sp^2$  orbital of one carbon with an  $sp^2$  orbital of the other carbon; this is a sigma ( $\sigma$ ) bond. Each carbon uses its other two  $sp^2$  orbitals to overlap the  $s$  orbital of a hydrogen to form the C—H bonds (Figure 7a). The second carbon-carbon bond results from side-to-side overlap of the two unhybridized  $p$  orbitals (Figure 7b). Side-to-side overlap of  $p$  orbitals forms a **pi ( $\pi$ ) bond**. Thus, one of the bonds in a double bond is a  $\sigma$  bond, and the other is a  $\pi$  bond. All the C—H bonds are  $\sigma$  bonds.

Side-to-side overlap of two  $p$  atomic orbitals forms a  $\pi$  bond.

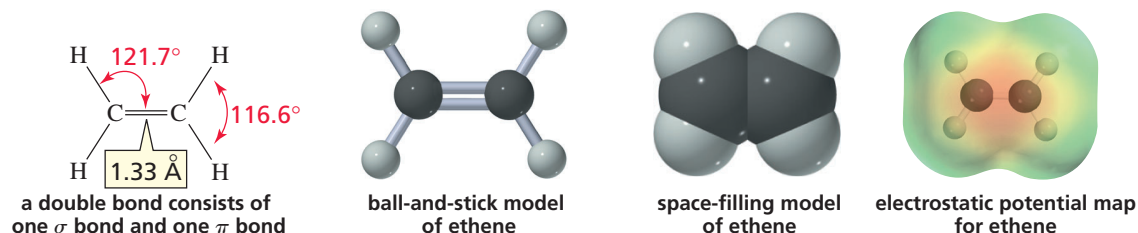
The two  $p$  orbitals that overlap to form the  $\pi$  bond must be parallel to each other for maximum overlap to occur. This forces the triangle formed by one carbon and two hydrogens to lie in the same plane as the triangle formed by the other carbon and two



▲ **Figure 7**

- (a) One C—C bond in ethene is a  $\sigma$  bond formed by  $sp^2$ – $sp^2$  overlap, and the C—H bonds are formed by  $sp^2$ – $s$  overlap.  
(b) The second C—C bond is a  $\pi$  bond formed by side-to-side overlap of a  $p$  orbital of one carbon with a  $p$  orbital of the other carbon.  
(c) There is an accumulation of electron density above and below the plane containing the two carbons and four hydrogens.

hydrogens. As a result, all six atoms of ethene lie in the same plane, and the electrons in the  $p$  orbitals occupy a volume of space above and below the plane (Figure 7c). The potential map for ethene shows that it is a nonpolar molecule with a slight accumulation of negative charge (the pale orange area) above the two carbons. (If you could turn the potential map over to show the hidden side, a similar accumulation of negative charge would be found there.)



Four electrons hold the carbons together in a carbon–carbon double bond; only two electrons hold the carbons together in a carbon–carbon single bond. This means that a carbon–carbon double bond is stronger and shorter than a carbon–carbon single bond.



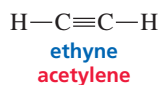
### DIAMOND AND GRAPHITE: SUBSTANCES THAT CONTAIN ONLY CARBON ATOMS

Diamond is the hardest of all substances. Graphite, in contrast, is a slippery, soft solid most familiar to us as the “lead” in pencils. Both materials, in spite of their very different physical properties, contain only carbon atoms. The two substances differ solely in the nature of the bonds holding the carbon atoms together. Diamond consists of a rigid three-dimensional network of

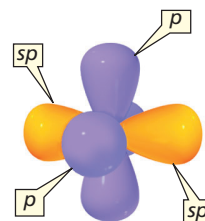
atoms, with each carbon bonded to four other carbons via  $sp^3$  orbitals. The carbon atoms in graphite, on the other hand, are  $sp^2$  hybridized, so each bonds to only three other carbons. This planar arrangement causes the atoms in graphite to lie in flat, layered sheets that can shear off of neighboring sheets. When you write with a pencil, sheets of carbon atoms shear off to leave a thin trail of graphite.

## 9 HOW A TRIPLE BOND IS FORMED: THE BONDS IN ETHYNE

The carbon atoms in ethyne (also called acetylene) are each bonded to only two atoms—a hydrogen and another carbon:



Because each carbon forms covalent bonds with two atoms, only two orbitals (an  $s$  and a  $p$ ) are hybridized. Two identical  $sp$  orbitals result. Each carbon atom in ethyne, therefore, has two hybridized  $sp$  orbitals and two unhybridized  $p$  orbitals (Figure 8).

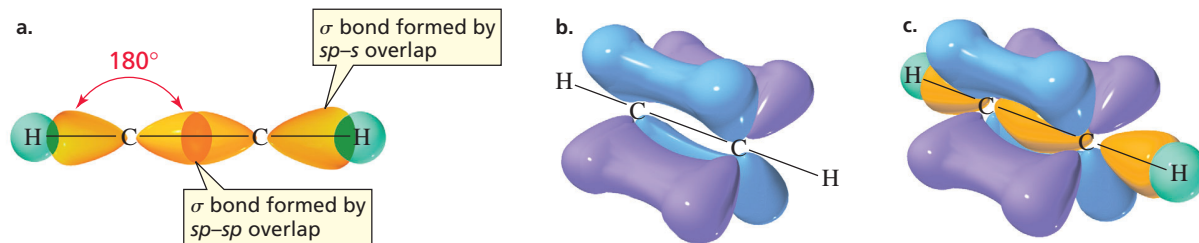


To minimize electron repulsion, the two  $sp$  orbitals point in opposite directions (Figure 8).

The carbons in ethyne are held together by three bonds. Three bonds connecting two atoms is called a **triple bond**. One of the  $sp$  orbitals of one carbon in ethyne overlaps an  $sp$  orbital of the other carbon to form a carbon–carbon  $\sigma$  bond. The other  $sp$  orbital of each carbon overlaps the  $s$  orbital of a hydrogen to form a C—H  $\sigma$  bond

▲ **Figure 8**  
The two  $sp$  orbitals are oriented  $180^\circ$  away from each other, perpendicular to the two unhybridized  $p$  orbitals. (The smaller lobes of the  $sp$  orbitals are not shown.)

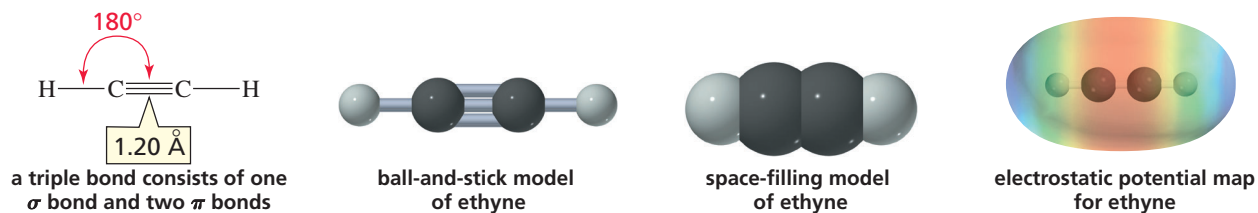
(Figure 9a). Because the two  $sp$  orbitals point in opposite directions, the bond angles are  $180^\circ$ . The two unhybridized  $p$  orbitals are perpendicular to each other, and both are perpendicular to the  $sp$  orbitals. Each of the unhybridized  $p$  orbitals engages in side-to-side overlap with a parallel  $p$  orbital on the other carbon, with the result that two  $\pi$  bonds are formed (Figure 9b).



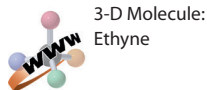
▲ **Figure 9**

(a) The C—C  $\sigma$  bond in ethyne is formed by  $sp$ – $sp$  overlap, and the C—H bonds are formed by  $sp$ – $s$  overlap. The carbon atoms and the atoms bonded to them are in a straight line.  
 (b) The two  $\pi$  bonds are formed by side-to-side overlap of the  $p$  orbitals of one carbon with the  $p$  orbitals of the other carbon.  
 (c) The triple bond has an electron-dense region above and below and in front of and in back of the internuclear axis of the molecule.

A **triple bond** therefore consists of one  $\sigma$  bond and two  $\pi$  bonds. Because the two unhybridized  $p$  orbitals on each carbon are perpendicular to each other, there is a region of high electron density above and below, *and* in front of and in back of, the internuclear axis of the molecule (Figure 9c). The potential map for ethyne shows that negative charge accumulates in a cylinder that wraps around the egg-shaped molecule.



Because the two carbon atoms in a triple bond are held together by six electrons, a triple bond is stronger and shorter than a double bond.

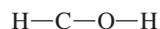


**PROBLEM 20 SOLVED**

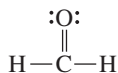
For each of the following species:

- Draw its Lewis structure.
  - Describe the orbitals used by each carbon atom in bonding and indicate the approximate bond angles.
- HCOH
  - $\text{CCl}_4$
  - HCN

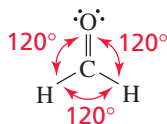
**Solution to 20a** Because HCOH is neutral, we know that each H forms one bond, the oxygen forms two bonds, and the carbon forms four bonds. Our first attempt at a Lewis structure (drawing the atoms in the order given by the Kekulé structure) shows that carbon is the only atom that does not form the needed number of bonds.



If we place a double bond between the carbon and the oxygen and move an H, all the atoms end up with the correct number of bonds. All the C and H atoms have filled outer shells but lone-pair electrons need to be added to give the oxygen atom a filled outer shell. When we check to see if any atom needs to be assigned a formal charge, we find that none of them does.



**Solution to 20b** Because the carbon atom forms a double bond, we know that carbon uses  $sp^2$  orbitals (as it does in ethene) to bond to the two hydrogens and the oxygen. It uses its “leftover”  $p$  orbital to form the second bond to oxygen. Because carbon is  $sp^2$  hybridized, the bond angles are approximately  $120^\circ$ .

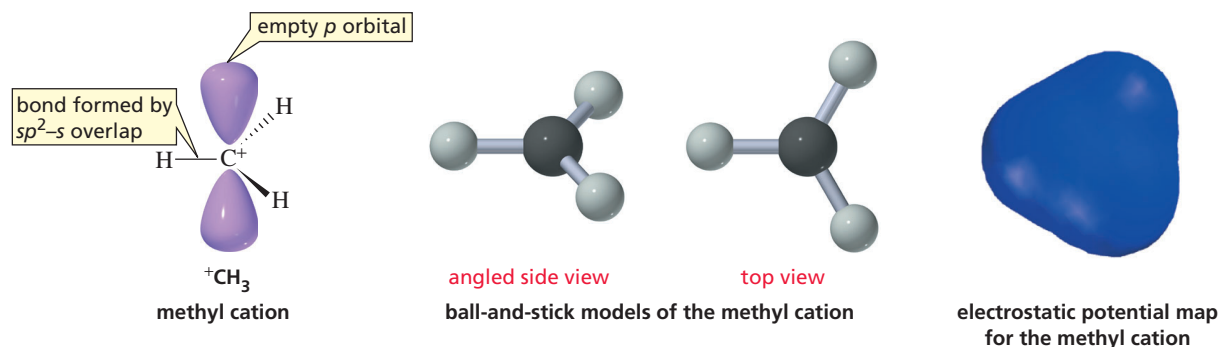


## 10 BONDING IN THE METHYL CATION, THE METHYL RADICAL, AND THE METHYL ANION

Not all carbon atoms form four bonds. A carbon with a positive charge, a negative charge, or an unpaired electron forms only three bonds. Now we will see what orbitals carbon uses when it forms three bonds.

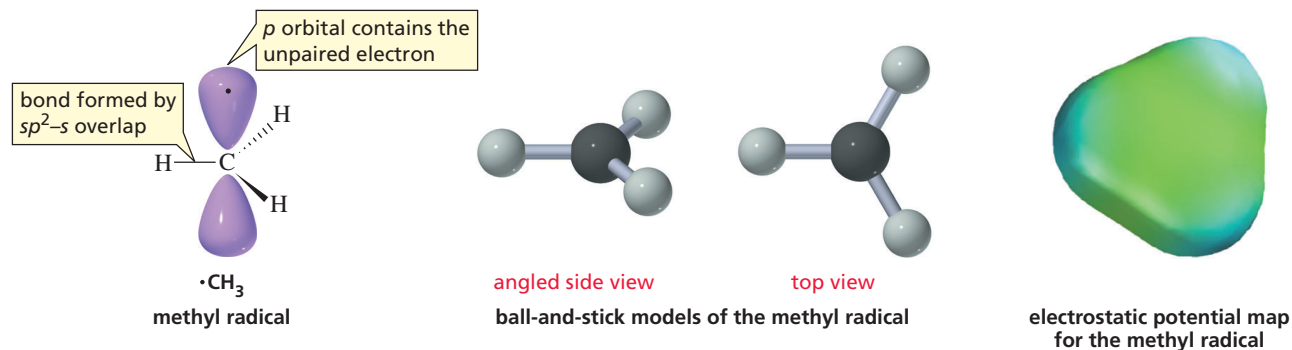
### The Methyl Cation ( $^+\text{CH}_3$ )

The positively charged carbon in the methyl cation is bonded to three atoms, so it hybridizes three orbitals—an  $s$  orbital and two  $p$  orbitals. Therefore, it forms its three covalent bonds using  $sp^2$  orbitals. Its unhybridized  $p$  orbital remains empty. The positively charged carbon and the three atoms bonded to it lie in a plane. The  $p$  orbital stands perpendicular to the plane.



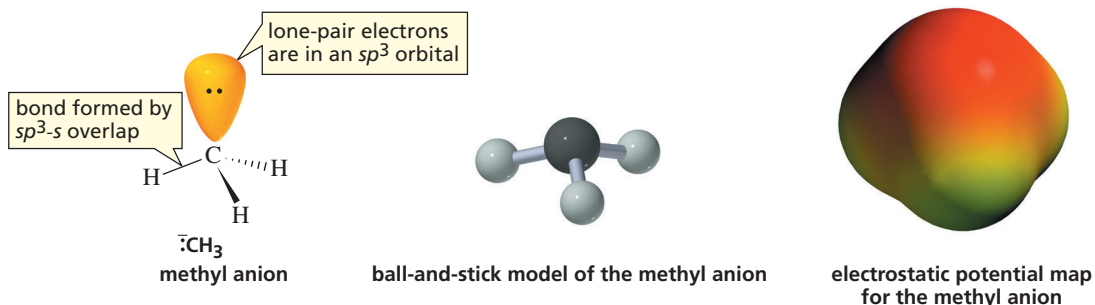
### The Methyl Radical ( $\cdot\text{CH}_3$ )

The carbon atom in the methyl radical is also  $sp^2$  hybridized. The methyl radical differs by one unpaired electron from the methyl cation. That electron is in the  $p$  orbital. Notice the similarity in the ball-and-stick models of the methyl cation and the methyl radical. The potential maps, however, are quite different because of the additional electron in the methyl radical.



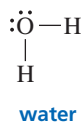
## The Methyl Anion ( $\text{:CH}_3^-$ )

The negatively charged carbon in the methyl anion has three pairs of bonding electrons and one lone pair. The four pairs of electrons are farthest apart when the four orbitals containing the bonding and lone-pair electrons point toward the corners of a tetrahedron. In other words, a negatively charged carbon is  $sp^3$  hybridized. In the methyl anion, three of carbon's  $sp^3$  orbitals each overlap the  $s$  orbital of a hydrogen, and the fourth  $sp^3$  orbital holds the lone pair.



Take a moment to compare the potential maps for the methyl cation, the methyl radical, and the methyl anion.

## 11 THE BONDS IN WATER

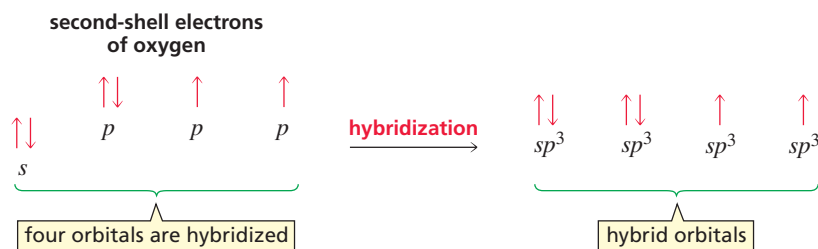


The bond angles in a molecule indicate which orbitals are used in bond formation.

The oxygen atom in water ( $\text{H}_2\text{O}$ ) forms two covalent bonds and has two lone pairs.

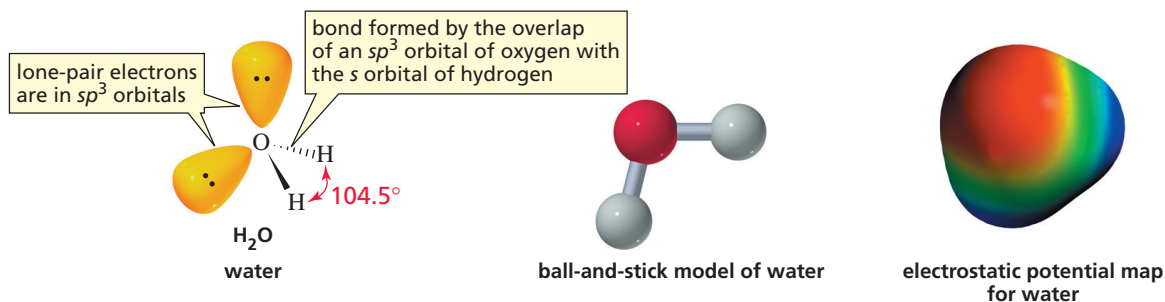
Because the electronic configuration of oxygen shows that it has two unpaired electrons (Table 2), oxygen does not need to promote an electron to form the number (two) of covalent bonds required to complete its octet. If we assume that oxygen uses  $p$  orbitals to form the two  $\text{O—H}$  bonds, as predicted by oxygen's electronic configuration, we would expect a bond angle of about  $90^\circ$  because the two  $p$  orbitals are at right angles to each other. However, the experimentally observed bond angle is  $104.5^\circ$ . In addition, we would expect the lone pairs to be chemically different because one pair would be in an  $s$  orbital and the other would be in a  $p$  orbital. The lone pairs, however, are known to be identical.

To explain the observed bond angle and the fact that the lone pairs are identical, oxygen must use hybrid orbitals to form covalent bonds—just as carbon does. The  $s$  orbital and the three  $p$  orbitals must hybridize to produce four identical  $sp^3$  orbitals.



Each of the two  $\text{O—H}$  bonds is formed by the overlap of an  $sp^3$  orbital of oxygen with the  $s$  orbital of a hydrogen. A lone pair occupies each of the two remaining  $sp^3$  orbitals.

The bond angle in water ( $104.5^\circ$ ) is a little smaller than the bond angle in methane ( $109.5^\circ$ ) presumably because each of the lone pairs is held by only one nucleus, which makes a lone pair more diffuse than a bonding pair that is held by two nuclei and is therefore relatively confined between them. Consequently, there is more electron repulsion between lone pairs, causing the  $\text{O—H}$  bonds to squeeze closer together, thereby decreasing the bond angle.



Compare the potential map for water with that for methane. Water is a polar molecule; methane is nonpolar.

### PROBLEM 21

The bond angles in  $H_3O^+$  are greater than \_\_\_\_\_ and less than \_\_\_\_\_.



### WATER—A UNIQUE COMPOUND

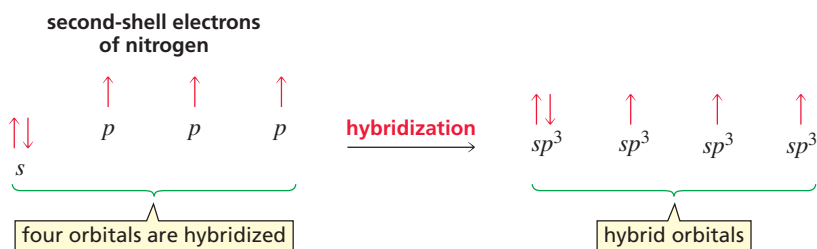
Water is the most abundant compound found in living organisms. Its unique properties have allowed life to originate and evolve. Its high heat of fusion (the heat required to convert a solid to a liquid) protects organisms from freezing at low temperatures because a lot of heat must be removed from water to freeze it. Its high heat capacity (the heat required to raise the temperature of a substance a

given amount) minimizes temperature changes in organisms, and its high heat of vaporization (the heat required to convert a liquid to a gas) allows animals to cool themselves with a minimal loss of body fluid. Because liquid water is denser than ice, ice formed on the surface of water floats and insulates the water below. That is why oceans and lakes don't freeze from the bottom up. It is also why plants and aquatic animals can survive when the ocean or lake they live in freezes.

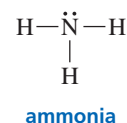
## 12 THE BONDS IN AMMONIA AND IN THE AMMONIUM ION

The nitrogen atom in ammonia ( $NH_3$ ) forms three covalent bonds and has one lone pair.

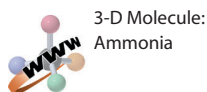
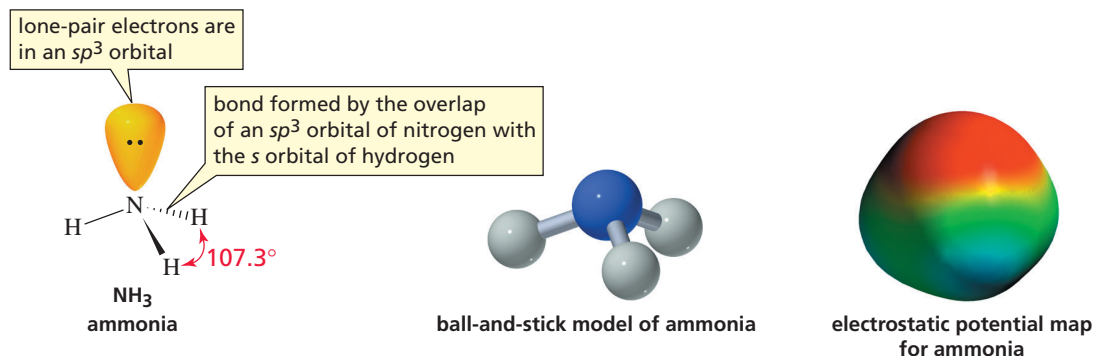
Because nitrogen has three unpaired electrons in its electronic configuration (Table 2), it can form three covalent bonds without having to promote an electron. The experimentally observed bond angles in  $NH_3$  are  $107.3^\circ$ , indicating that nitrogen also uses hybrid orbitals when it forms covalent bonds. Like carbon and oxygen, the one  $s$  and three  $p$  orbitals of the second shell of nitrogen hybridize to form four identical  $sp^3$  orbitals:



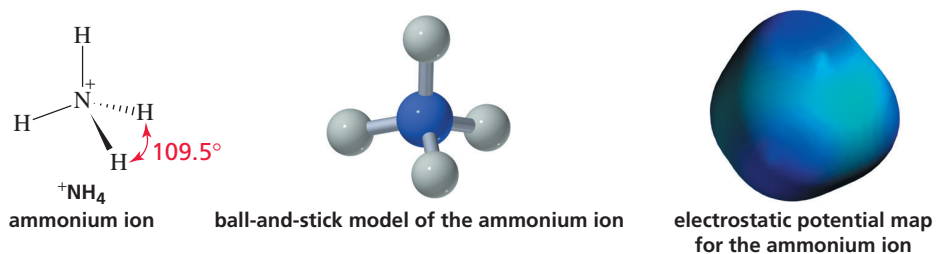
Each of the N—H bonds in  $NH_3$  is formed by the overlap of an  $sp^3$  orbital of nitrogen with the  $s$  orbital of a hydrogen. The single lone pair occupies an  $sp^3$  orbital. The bond angle ( $107.3^\circ$ ) is smaller than the tetrahedral bond angle ( $109.5^\circ$ ) because of the relatively diffuse lone pair. Notice that the bond angles in  $NH_3$  ( $107.3^\circ$ ) are larger than



the bond angles in  $\text{H}_2\text{O}$  ( $104.5^\circ$ ) because nitrogen has only one lone pair, whereas oxygen has two lone pairs.



Because the ammonium ion ( $^+\text{NH}_4$ ) has four identical N—H bonds and no lone pairs, all the bond angles are  $109.5^\circ$ , just like the bond angles in methane.

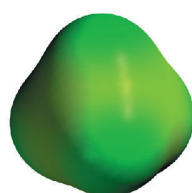


#### PROBLEM 22

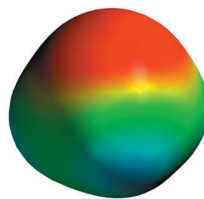
According to the potential map for the ammonium ion, which atom(s) has (have) the least electron density?

#### PROBLEM 23

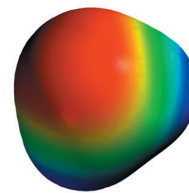
Compare the potential maps for methane, ammonia, and water. Which is the most polar molecule? Which is the least polar?



electrostatic potential map for methane



electrostatic potential map for ammonia



electrostatic potential map for water

#### PROBLEM 24

Predict the approximate bond angles in the methyl carbanion.

## 13 THE BOND IN A HYDROGEN HALIDE

Fluorine, chlorine, bromine, and iodine are known as the halogens; HF, HCl, HBr, and HI are called hydrogen halides. Bond angles will not help us determine the orbitals that form the hydrogen halide bond, as they did with other molecules, because a