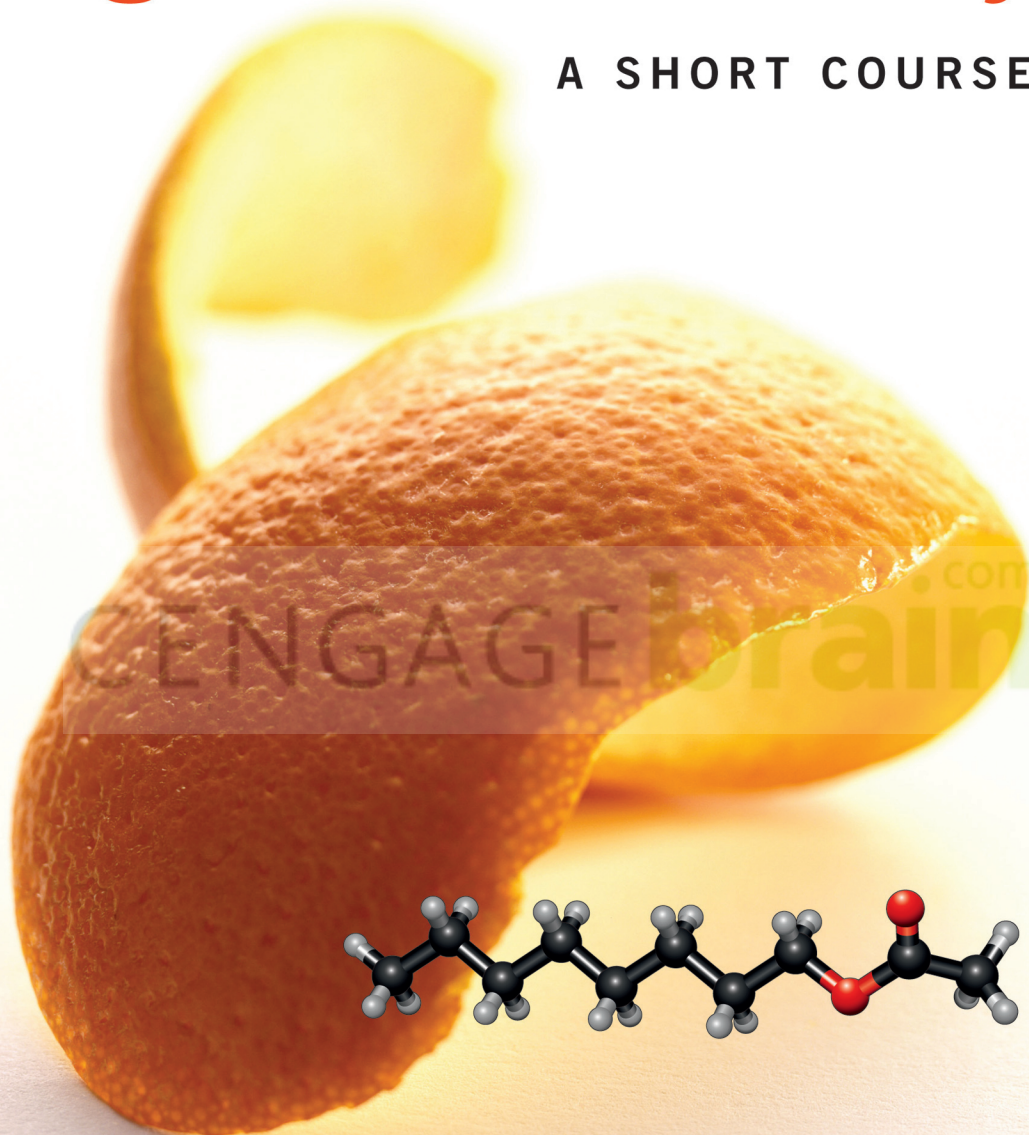


Organic Chemistry

A SHORT COURSE



HART // HADAD // CRAINE // HART

**Organic Chemistry: A Short Course,
13th Edition**

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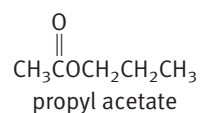
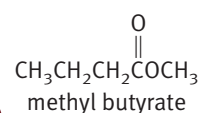
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1 2 3 4 5 6 7 14 13 12 11 10

Methyl butyrate and propyl acetate, organic flavor and fragrance molecules found in apples and pears, respectively, are structural isomers (Sec. 1.8).



Jerry Howard/Positive Images



Bonding and Isomerism

Why does sucrose (table sugar) melt at 185°C, while sodium chloride (table salt)—melts at a much higher temperature, 801°C? Why do both of these substances dissolve in water, while olive oil does not? Why does the molecule methyl butyrate smell like apples, while the molecule propyl acetate, which contains the same number and kind of atoms, smells like pears? To answer questions such as these, you must understand how atoms bond with one another and how molecules interact with one another. Bonding is the key to the structure, physical properties, and chemical behavior of different kinds of matter.

Perhaps you have already studied bonding and related concepts in a beginning chemistry course. Browse through each section of this chapter to see whether it is familiar, and try to work the problems. If you can work the problems, you can safely skip that section. But if you have difficulty with any of the problems within or at the end of this chapter, study the entire chapter carefully because we will use the ideas developed here throughout the rest of the book.

- 1.1 How Electrons Are Arranged in Atoms
- 1.2 Ionic and Covalent Bonding
- 1.3 Carbon and the Covalent Bond
- 1.4 Carbon–Carbon Single Bonds
- 1.5 Polar Covalent Bonds
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- A CLOSER LOOK AT... Green Chemistry**
- 1.8 Isomerism
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- 1.12 Resonance
- 1.13 Arrow Formalism
- 1.14 The Orbital View of Bonding; the Sigma Bond
- 1.15 Carbon sp^3 Hybrid Orbitals
- 1.16 Tetrahedral Carbon; the Bonding in Methane
- 1.17 Classification According to Molecular Framework
- 1.18 Classification According to Functional Group



Online homework for this chapter can be assigned in OWL, an online homework assessment tool.

An **atom** consists of a small, dense **nucleus** containing positively charged **protons** and neutral **neutrons** and surrounded by negatively charged **electrons**. The **atomic number** of an element equals the number of protons in its nucleus; its **atomic weight** is the sum of the number of protons and neutrons in its nucleus.

Electrons are located in **orbitals**. Orbitals are grouped in **shells**. An orbital can hold a maximum of two electrons.

Valence electrons are located in the outermost shell. The **kernel** of the atom contains the nucleus and the inner electrons.

1.1 How Electrons Are Arranged in Atoms

Atoms contain a small, dense **nucleus** surrounded by **electrons**. The nucleus is positively charged and contains most of the mass of the atom. The nucleus consists of **protons**, which are positively charged, and **neutrons**, which are neutral. (The only exception is hydrogen, whose nucleus consists of only a single proton.) In a neutral atom, the positive charge of the nucleus is exactly balanced by the negative charge of the electrons that surround it. The **atomic number** of an element is equal to the number of protons in its nucleus (and to the number of electrons around the nucleus in a neutral atom). The **atomic weight** is approximately equal to the sum of the number of protons and the number of neutrons in the nucleus; the electrons are not counted because they are very light by comparison. The periodic table on the inside back cover of this book shows all the elements with their atomic numbers and weights.

We are concerned here mainly with the atom's electrons because their number and arrangement provide the key to how a particular atom reacts with other atoms to form molecules. Also, we will deal only with electron arrangements in the lighter elements because these elements are the most important in organic molecules.

Electrons are concentrated in certain regions of space around the nucleus called **orbitals**. Each orbital can contain a maximum of two electrons. The orbitals, which differ in shape, are designated by the letters *s*, *p*, and *d*. In addition, orbitals are grouped in **shells** designated by the numbers 1, 2, 3, and so on. Each shell contains different types and numbers of orbitals, corresponding to the shell number. For example, shell 1 contains only one type of orbital, designated the 1*s* orbital. Shell 2 contains two types of orbitals, 2*s* and 2*p*, and shell 3 contains three types, 3*s*, 3*p*, and 3*d*. Within a particular shell, the number of *s*, *p*, and *d* orbitals is 1, 3, and 5, respectively (Table 1.1). These rules permit us to count how many electrons each shell will contain when it is filled (last column in Table 1.1). Table 1.2 shows how the electrons of the first 18 elements are arranged.

The first shell is filled for helium (He) and all elements beyond, and the second shell is filled for neon (Ne) and all elements beyond. Filled shells play almost no role in chemical bonding. Rather, the outer electrons, or **valence electrons**, are mainly involved in chemical bonding, and we will focus our attention on them.

Table 1.3 shows the valence electrons, the electrons in the outermost shell, for the first 18 elements. The element's symbol stands for the **kernel** of the element (the nucleus plus the filled electron shells), and the dots represent the valence electrons. The elements are arranged in groups according to the periodic table, and (except for helium) these group numbers correspond to the number of valence electrons.

Armed with this information about atomic structure, we are now ready to tackle the problem of how elements combine to form chemical bonds.

Table 1.1 Numbers of Orbitals and Electrons in the First Three Shells

Shell number	Number of orbitals of each type			Total number of electrons when shell is filled
	<i>s</i>	<i>p</i>	<i>d</i>	
1	1	0	0	2
2	1	3	0	8
3	1	3	5	18

Table 1.2 ■ Electron Arrangements of the First 18 Elements

Atomic number	Element	Number of electrons in each orbital				
		1s	2s	2p	3s	3p
1	H	1				
2	He	2				
3	Li	2	1			
4	Be	2	2			
5	B	2	2	1		
6	C	2	2	2		
7	N	2	2	3		
8	O	2	2	4		
9	F	2	2	5		
10	Ne	2	2	6		
11	Na	2	2	6	1	
12	Mg	2	2	6	2	
13	Al	2	2	6	2	1
14	Si	2	2	6	2	2
15	P	2	2	6	2	3
16	S	2	2	6	2	4
17	Cl	2	2	6	2	5
18	Ar	2	2	6	2	6

Table 1.3 ■ Valence Electrons of the First 18 Elements

Group	I	II	III	IV	V	VI	VII	VIII
	H ·							He :
	Li ·	Be ·	·B ·	·C ·	·N :	·O :	·F :	·Ne :
	Na ·	Mg ·	·Al ·	·Si ·	·P :	·S :	·Cl :	·Ar :

1.2 Ionic and Covalent Bonding

An early, but still useful, theory of chemical bonding was proposed in 1916 by Gilbert Newton Lewis, then a professor at the University of California, Berkeley. Lewis noticed that the **inert gas** helium had only two electrons surrounding its nucleus and that the next inert gas, neon, had 10 such electrons ($2 + 8$; see Table 1.2). He concluded that atoms of these gases must have very stable electron arrangements *because these elements do not combine with other atoms*. He further suggested that other atoms might react in such a way in order to achieve these stable arrangements. This stability could be achieved in one of two ways: by complete transfer of electrons from one atom to another or by sharing of electrons between atoms.

An **inert gas** has a stable electron configuration.

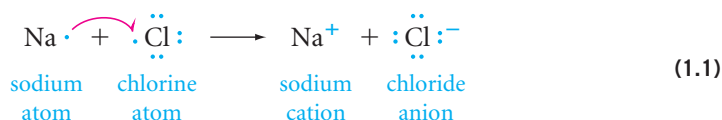
Ionic compounds are composed of positively charged **cations** and negatively charged **anions**.

Electropositive atoms give up electrons and form cations.

Electronegative atoms accept electrons and form anions.

1.2.a Ionic Compounds

Ionic bonds are formed by the transfer of one or more valence electrons from one atom to another. Because electrons are negatively charged, the atom that gives up electrons becomes positively charged, a **cation**. The atom that receives electrons becomes negatively charged, an **anion**. The reaction between sodium and chlorine atoms to form sodium chloride (ordinary table salt) is a typical electron-transfer reaction.*



The sodium atom has only one valence electron (it is in the third shell; see Table 1.2). By giving up that electron, sodium achieves the electron arrangement of neon. At the same time, it becomes positively charged, a sodium cation. The chlorine atom has seven valence electrons. By accepting an additional electron, chlorine achieves the electron arrangement of argon and becomes negatively charged, a chloride anion. Atoms, such as sodium, that tend to give up electrons are said to be **electropositive**. Often such atoms are metals. Atoms, such as chlorine, that tend to accept electrons are said to be **electronegative**. Often such atoms are nonmetals.

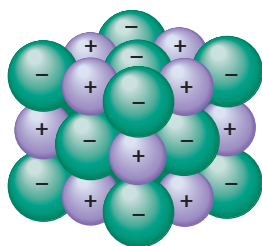
EXAMPLE 1.1

Write an equation for the reaction of magnesium (Mg) with fluorine (F) atoms.



Solution Magnesium has two valence electrons. Since each fluorine atom can accept only one electron (from the magnesium) to complete its valence shell, two fluorine atoms are needed to react with one magnesium atom.

PROBLEM 1.1 Write an equation for the reaction of sodium atoms (Na) with chlorine atoms (Cl).



■ Figure 1.1

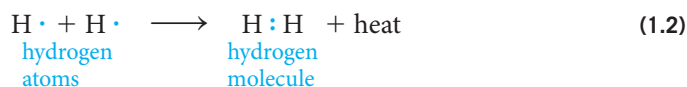
Sodium chloride, NaCl, is an ionic crystal. The purple spheres represent sodium ions, Na⁺, and the green spheres are chloride ions, Cl[−]. Each ion is surrounded by six oppositely charged ions, except for those ions that are at the surface of the crystal.

The product of eq. 1.1 is sodium chloride, an ionic compound made up of equal numbers of sodium and chloride ions. In general, ionic compounds form when strongly electropositive atoms and strongly electronegative atoms interact. The ions in a crystal of an ionic substance are held together by the attractive force between their opposite charges, as shown in Figure 1.1 for a sodium chloride crystal.

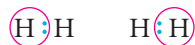
In a sense, the ionic bond is not really a bond at all. Being oppositely charged, the ions attract one another like the opposite poles of a magnet. In the crystal, the ions are packed in a definite arrangement, but we cannot say that any particular ion is bonded or connected to any other particular ion. And, of course, when the substance is dissolved, the ions separate and are able to move about in solution relatively freely.

*The curved arrow in eq. 1.1 shows the movement of one electron from the valence shell of the sodium atom to the valence shell of the chlorine atom. The use of curved arrows to show the movement of electrons is explained in greater detail in Section 1.13.

equal electronegativities, the electron pairs are shared equally. The hydrogen molecule is an example.

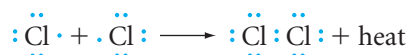


Each hydrogen atom can be considered to have filled its first electron shell by the sharing process. That is, each atom is considered to “own” all of the electrons it shares with the other atom, as shown by the loops in these structures.



EXAMPLE 1.4

Write an equation similar to eq. 1.2 for the formation of a chlorine molecule from two chlorine atoms.



Solution One electron pair is shared by the two chlorine atoms. In that way, each chlorine completes its valence shell with eight electrons (three unshared pairs and one shared pair).

PROBLEM 1.6 Write an equation similar to eq. 1.2 for the formation of a fluorine molecule from two fluorine atoms.

Bond energy (BE) is the energy necessary to break a mole of covalent bonds. The amount of energy depends on the type of bond broken.

The **bond length** is the average distance between two covalently bonded atoms.

When two hydrogen atoms combine to form a molecule, heat is liberated. Conversely, this same amount of heat (energy) has to be supplied to a hydrogen molecule to break it apart into atoms. To break apart 1 mole (2 g) of hydrogen molecules into atoms requires 104 kcal (or 435 kJ*) of heat, quite a lot of energy. This energy is called the **bond energy**, or **BE**, and is different for bonds between different atoms (see Table A in the Appendix).

The H—H bond is a very strong bond. The main reason for this is that the shared electron pair is attracted to *both* hydrogen nuclei, whereas in a hydrogen atom, the valence electron is associated with only one nucleus. But other forces in the hydrogen molecule tend to counterbalance the attraction between the electron pair and the nuclei. These forces are the repulsion between the two like-charged nuclei and the repulsion between the two like-charged electrons. A balance is struck between the attractive and the repulsive forces. The hydrogen atoms neither fly apart nor do they fuse together. Instead, they remain connected, or bonded, and vibrate about some equilibrium distance, which we call the **bond length**. For a hydrogen molecule, the bond length (that is, the average distance between the two hydrogen nuclei) is 0.74 Å.** The length of a covalent bond depends on the atoms that are bonded and the number of electron pairs shared between the atoms. Bond lengths for some typical covalent bonds are given in Table B in the Appendix.

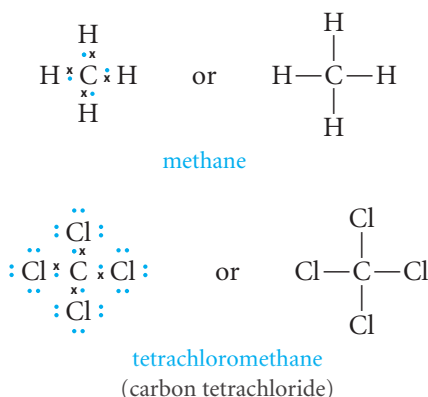
*Although most organic chemists use the kilocalorie as the unit of heat energy, the currently used international unit is the kilojoule; 1 kcal = 4.184 kJ. In this text, the kilocalorie will be used. If your instructor prefers to use kJ, multiply kcal \times 4.184 (or \times 4 for a rough estimate) to convert to kJ.

**Å, or angstrom unit, is 10^{-8} cm, so the H—H bond length is 0.74×10^{-8} cm. Although the angstrom is commonly used by organic chemists, another unit often used for bond lengths is the picometer (pm; 1 Å = 100 pm). To convert the H—H bond length from Å to pm, multiply 0.74×100 . The H—H bond length is 74 pm. In this text, the angstrom will be used as the unit for bond lengths.

1.3 Carbon and the Covalent Bond

Now let us look at carbon and its bonding. We represent atomic carbon by the symbol $\cdot\dot{\text{C}}\cdot$ where the letter C stands for the kernel (the nucleus plus the two 1s electrons) and the dots represent the valence electrons.

With four valence electrons, the valence shell of carbon is half filled (or half empty). Carbon atoms have neither a strong tendency to lose all their electrons (and become C^{4+}) nor a strong tendency to gain four electrons (and become C^{4-}). Being in the middle of the periodic table, *carbon is neither strongly electropositive nor strongly electronegative*. Instead, it usually forms covalent bonds with other atoms by sharing electrons. For example, carbon combines with four hydrogen atoms (each of which supplies one valence electron) by sharing four electron pairs.* The substance formed is known as methane. Carbon can also share electron pairs with four chlorine atoms, forming tetrachloromethane.**



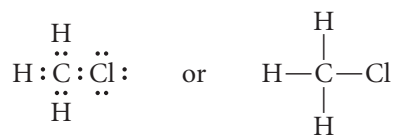
By sharing electron pairs, the atoms complete their valence shells. In both examples, carbon has eight valence electrons around it. In methane, each hydrogen atom completes its valence shell with two electrons, and in tetrachloromethane, each chlorine atom fills its valence shell with eight electrons. In this way, all valence shells are filled and the compounds are quite stable.

The shared electron pair is called a covalent bond because it bonds or links the atoms by its attraction to both nuclei. The single bond is usually represented by a dash, or a single line, as shown in the structures above for methane and tetrachloromethane.

EXAMPLE 1.5

Draw the structure for chloromethane (also called methyl chloride), CH_3Cl .

Solution



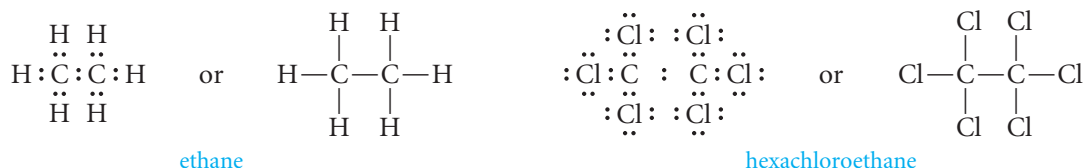
PROBLEM 1.7 Draw the structures for dichloromethane (also called methylene chloride), CH_2Cl_2 , and trichloromethane (chloroform), CHCl_3 .

*To designate electrons from different atoms, the symbols \cdot and \times are often used. But the electrons are, of course, identical.

**Tetrachloromethane is the systematic name, and carbon tetrachloride is the common name. We discuss how to name organic compounds later.

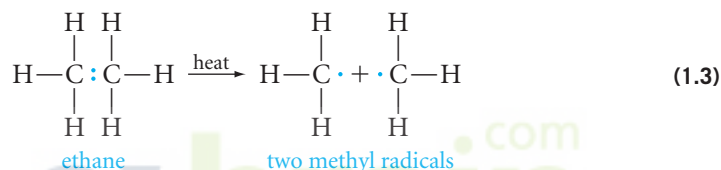
1.4 Carbon–Carbon Single Bonds

The unique property of carbon atoms—that is, the property that makes it possible for millions of organic compounds to exist—is their ability to share electrons not only with different elements but also with other carbon atoms. For example, two carbon atoms may be bonded to one another, and each of these carbon atoms may be linked to other atoms. In ethane and hexachloroethane, each carbon is connected to the other carbon *and* to three hydrogen atoms or three chlorine atoms. Although they have two carbon atoms instead of one, these compounds have chemical properties similar to those of methane and tetrachloromethane, respectively.



The carbon–carbon bond in ethane, like the hydrogen–hydrogen bond in a hydrogen molecule, is a purely covalent bond, with the electrons being shared *equally* between the two identical carbon atoms. As with the hydrogen molecule, heat is required to break the carbon–carbon bond of ethane to give two CH_3 fragments (called methyl radicals). A **radical** is a molecular fragment with an odd number of unshared electrons.

A **radical** is a molecular fragment with an odd number of unshared electrons.



However, less heat is required to break the carbon–carbon bond in ethane than is required to break the hydrogen–hydrogen bond in a hydrogen molecule. The actual amount is 88 kcal (or 368 kJ) per mole of ethane. The carbon–carbon bond in ethane is longer (1.54 Å) than the hydrogen–hydrogen bond (0.74 Å) and also somewhat weaker. Breaking carbon–carbon bonds by heat, as represented in eq. 1.3, is the first step in the *cracking* of petroleum, an important process in the manufacture of gasoline (see “A Word About Petroleum, Gasoline, and Octane Number” on pages 102–103).

EXAMPLE 1.6

What do you expect the length of a C—H bond (as in methane or ethane) to be?

Solution It should measure somewhere between the H—H bond length in a hydrogen molecule (0.74 Å) and the C—C bond length in ethane (1.54 Å). The actual value is about 1.09 Å, close to the average of the H—H and C—C bond lengths.

PROBLEM 1.8 The Cl—Cl bond length is 1.98 Å. Which bond will be longer, the C—C bond in ethane or the C—Cl bond in chloromethane?

Catenation is the ability of an element to form chains of its own atoms through covalent bonding.

1.5 Polar Covalent Bonds

A **polar covalent bond** is a covalent bond in which the electron pair is not shared equally between the two atoms.

[illegible]

You can usually rely on the periodic table to determine which end of a polar covalent bond is more negative and which end is more positive. As we proceed from left to right across the table within a given period, the elements become *more* electronegative, owing to increasing atomic number or charge on the nucleus. The increasing nuclear charge attracts valence electrons more strongly. As we proceed from the top to the bottom of the table within a given group (down a column), the elements become *less* electronegative because the valence electrons are shielded from the nucleus by an increasing number of inner-shell electrons. From these generalizations, we can safely predict that the atom on the right in each of the following bonds will be negative with respect to the atom on the left:



The carbon–hydrogen bond, which is so common in organic compounds, requires special mention. Carbon and hydrogen have nearly identical electronegativities, so the C—H bond is almost purely covalent. The electronegativities of some common elements are listed in Table 1.4.

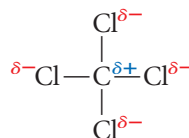
Table 1.4 ■ Electronegativities of Some Common Elements

Group

I	II	III	IV	V	VI	VII
H 2.2						
Li 1.0	Be 1.6	B 2.0	C 2.5	N 3.0	O 3.4	F 4.0
Na 0.9	Mg 1.3	Al 1.6	Si 1.9	P 2.2	S 2.6	Cl 3.2
K 0.8	Ca 1.0					Br 3.0
						I 2.7

 < 1.0 1.0–1.4 1.5–1.9 2.0–2.4 2.5–2.9 3.0–3.4**EXAMPLE 1.7**

Indicate any bond polarization in the structure of tetrachloromethane.

Solution

Chlorine is more electronegative than carbon. The electrons in each C—Cl bond are therefore displaced toward the chlorine.

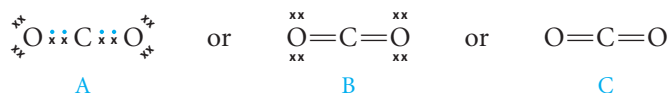
PROBLEM 1.10 Predict the polarity of the N—Cl bond and of the S—O bond.

PROBLEM 1.11 Draw the structure of the refrigerant dichlorodifluoromethane, CCl₂F₂ (CFC-12), and indicate the polarity of the bonds. (The C atom is the central atom.)

PROBLEM 1.12 Draw the formula for methanol, CH₃OH, and (where appropriate) indicate the bond polarity with an arrow, \longleftrightarrow . (The C atom is bonded to three H atoms and the O atom.)

1.6 Multiple Covalent Bonds

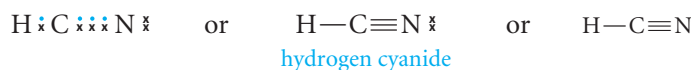
To complete their valence shells, atoms may sometimes share more than one electron pair. Carbon dioxide, CO_2 , is an example. The carbon atom has four valence electrons, and each oxygen has six valence electrons. A structure that allows each atom to complete its valence shell with eight electrons is



In structure A, the dots represent the electrons from carbon, and the x's are the electrons from the oxygens. Structure B shows the bonds' and oxygens' unshared electrons, and structure C shows only the covalent bonds. Two electron pairs are shared between carbon and oxygen. Consequently, the bond is called a **double bond**. Each oxygen atom also has two pairs of **nonbonding electrons**, or **unshared electron pairs**. The loops in the following structures show that each atom in carbon dioxide has a complete valence shell of eight electrons:



Hydrogen cyanide, HCN , is an example of a simple compound with a **triple bond**, a bond in which three electron pairs are shared.



In a **double bond**, two electron pairs are shared between two atoms.

Nonbonding electrons, or **unshared electron pairs**, reside on one atom.

In a **triple bond**, three electron pairs are shared between two atoms.

PROBLEM 1.13 Show with loops how each atom in hydrogen cyanide completes its valence shell.

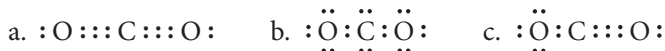
EXAMPLE 1.8

Determine what, if anything, is wrong with the following electron arrangement for carbon dioxide:



Solution The formula contains the correct total number of valence electrons (16), and each oxygen is surrounded by 8 valence electrons, which is correct. However, what is wrong is that the carbon atom has 10 valence electrons, 2 more than is allowable.

PROBLEM 1.14 Show what is wrong with each of the following electron arrangements for carbon dioxide:

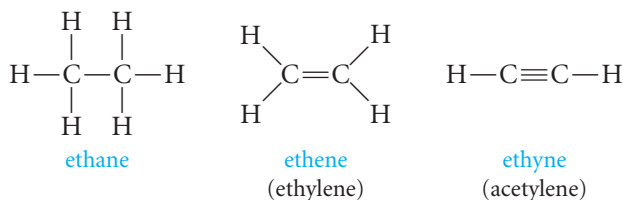


PROBLEM 1.15 Methanal (formaldehyde) has the formula H_2CO . Draw a structure that shows how the valence electrons are arranged.

PROBLEM 1.16 Draw an electron-dot structure for carbon monoxide, CO .

Hydrocarbons are compounds composed of just hydrogen and carbon atoms.

Carbon atoms can be connected to one another by double bonds or triple bonds, as well as by single bonds. Thus, there are three **hydrocarbons** (compounds with just carbon and hydrogen atoms) that have two carbon atoms per molecule: ethane, ethene, and ethyne.

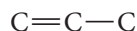


They differ in that the carbon–carbon bond is single, double, or triple, respectively. They also differ in the number of hydrogens. As we will see later, these compounds have different chemical reactivities because of the different types of bonds between the carbon atoms.

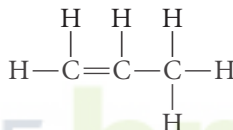
EXAMPLE 1.9

Draw the structure for C_3H_6 having one carbon–carbon double bond.

Solution First, draw the three carbons with one double bond.



Then add the hydrogens in such a way that each carbon has eight electrons around it (or in such a way that each carbon has four bonds).



PROBLEM 1.17 Draw three different structures that have the formula C_4H_8 and have one carbon–carbon double bond.

1.7 Valence

The **valence** of an element is the number of bonds that an atom of the element can form.

The **valence** of an element is simply the number of bonds that an atom of the element can form. The number is usually equal to the *number of electrons needed to fill the valence shell*. Table 1.5 gives the common valences of several elements. Notice the difference between the number of valence electrons and the valence. Oxygen, for example, has six valence electrons but a valence of only 2. The *sum* of the two numbers is equal to the number of electrons in the filled shell.

The valences in Table 1.5 apply whether the bonds are single, double, or triple. For example, carbon has four bonds in each of the structures we have written so far: methane, tetrachloromethane, ethane, ethene, ethyne, carbon dioxide, and so on. These common valences are worth remembering, because they will help you to write correct structures.

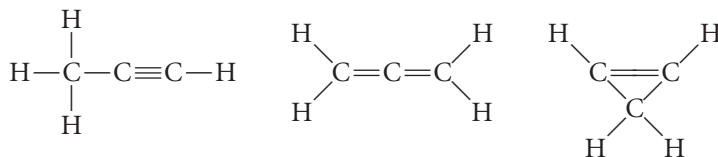
Table 1.5 ■ Valences of Common Elements

Element	H ·	· $\dot{\text{C}}$ ·	· $\dot{\text{N}}$ ·	· $\ddot{\text{O}}$ ·	· $\ddot{\text{F}}$ ·	· $\ddot{\text{Cl}}$ ·
Valence	1	4	3	2	1	1

EXAMPLE 1.10

Using dashes for bonds, draw a structure for C_3H_4 that has the proper valence of 1 for each hydrogen and 4 for each carbon.

Solution There are three possibilities:



A compound that corresponds to each of these three different arrangements of the atoms is known.

PROBLEM 1.18 Use dashes for bonds and use the valences given in Table 1.5 to write a structure for each of the following:

- a. CH_3F b. CH_5N

PROBLEM 1.19 Does C_2H_5 represent a stable molecule?

In Example 1.10, we saw that three carbon atoms and four hydrogen atoms can be connected to one another in three different ways, each of which satisfies the valences of both kinds of atoms. Let us take a closer look at this phenomenon.

1.8 Isomerism

The **molecular formula** of a substance tells us the numbers of different atoms present, but a **structural formula** tells us how those atoms are arranged. For example, H_2O is the molecular formula for water. It tells us that each water molecule contains two hydrogen atoms and one oxygen atom. But the structural formula $H-O-H$ tells us

The **molecular formula** of a substance gives the number of different atoms present; the **structural formula** indicates how those atoms are arranged.

A CLOSER LOOK AT... Green Chemistry

Conduct research on the Internet to find more information on green chemistry and to answer the following questions.

Green Chemistry

1. What is green chemistry?
2. What are the 12 principles of green chemistry?
3. What is the Pollution Prevention Act of 1990?
4. What are some organizations involved in promoting green chemistry? How are these organizations promoting green chemistry?

Hangers Cleaners

1. How does Hangers Cleaners make use of carbon dioxide?
2. What are the advantages of using CO_2 over traditional dry cleaning solvents? Explain why you think so.

Ionic Liquids and Their Uses

1. What are some of the advantages of using ionic liquids as solvents in chemical reactions?
2. What environmental problems posed by traditional solvents are avoided by using ionic liquids?

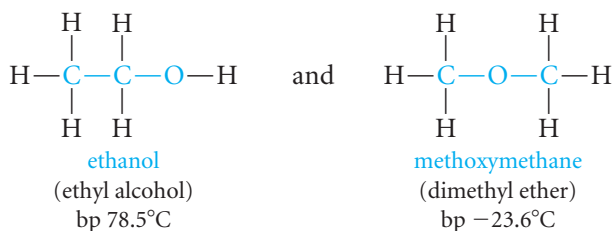
Isomers are molecules with the same number and kinds of atoms but different arrangements of the atoms. **Structural** (or **constitutional**) **isomers** have the same molecular formula but different structural formulas.

more than that. The structural formula gives us the connectivity between atoms and tells us that the hydrogens are connected to the oxygen (and not to each other).

It is sometimes possible to arrange the same atoms in more than one way and still satisfy their valences. Molecules that have the same kinds and numbers of atoms but different arrangements are called **isomers**, a term that comes from the Greek (*isos*, equal, and *meros*, part). **Structural** (or **constitutional**) **isomers** are compounds that have the same molecular formula, but different structural formulas. Let us look at a particular pair of isomers.

Two very different chemical substances are known, each with the molecular formula C_2H_6O . One of these substances is a colorless liquid that boils at 78.5°C , whereas the other is a colorless gas at ordinary temperatures (boiling point (bp) -23.6°C). The only possible explanation is that the atoms must be arranged differently in the molecules of each substance and that these arrangements are somehow responsible for the fact that one substance is a liquid and the other is a gas.

For the molecular formula C_2H_6O , two (and only two) structural formulas are possible that satisfy the valence requirement of 4 for carbon, 2 for oxygen, and 1 for hydrogen. They are:



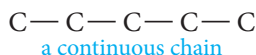
In one formula, the two carbons are connected to one another by a single covalent bond; in the other formula, each carbon is connected to the oxygen. When we complete the valences by adding hydrogens, each arrangement requires six hydrogens. Many kinds of experimental evidence verify these structural assignments. We leave for later chapters (Chapters 7 and 8) an explanation of why these arrangements of atoms produce substances that are so different from one another.

Ethanol and methoxymethane are structural isomers. They have the same molecular formula but different structural formulas. Ethanol and methoxymethane differ in physical and chemical properties as a consequence of their different molecular structures. In general, structural isomers are different compounds. They differ in physical and chemical properties as a consequence of their different molecular structures.

PROBLEM 1.20 Draw structural formulas for the three possible isomers of C_3H_8O .

1.9 Writing Structural Formulas

You will be writing structural formulas throughout this course. Perhaps a few hints about how to do so will be helpful. Let's look at another case of isomerism. Suppose we want to write out all possible structural formulas that correspond to the molecular formula C_5H_{12} . We begin by writing all five carbons in a **continuous chain**.

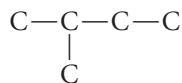


This chain uses up one valence for each of the end carbons and two valences for the carbons in the middle of the chain. Each end carbon therefore has three valences

In a **continuous chain**, atoms are bonded one after another.

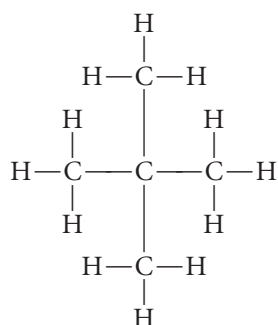
$$\begin{array}{ccccccc} & \text{H} & & \text{H} & & \text{H} & & \text{H} & & \text{H} \\ & | & & | & & | & & | & & | \\ \text{H} & - \text{C} & - & \text{C} & - & \text{C} & - & \text{C} & - & \text{C} & - \text{H} \\ & | & & | & & | & & | & & | \\ & \text{H} & & \text{H} & & \text{H} & & \text{H} & & \text{H} \end{array}$$

In a **branched chain**, some atoms form branches from the longest continuous chain.

[illegible]
$$\begin{array}{ccc} \text{C}-\text{C}-\text{C}-\text{C} & \text{C}-\text{C}-\text{C}-\text{C} & \text{C}-\text{C}-\text{C}-\text{C} \\ | & & | \\ \text{C} & & \text{C} \end{array}$$
$$\begin{array}{c} \text{C} \\ | \\ \text{C}-\text{C}-\text{C} \\ | \\ \text{C} \end{array}$$

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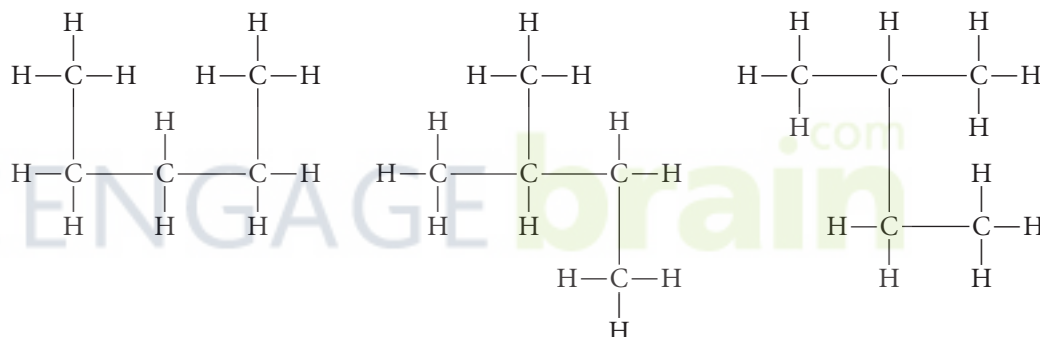
If we fill in the hydrogens, we see that the middle carbon has no hydrogens attached to it.



2,2-dimethylpropane, bp 10°C
(neopentane)

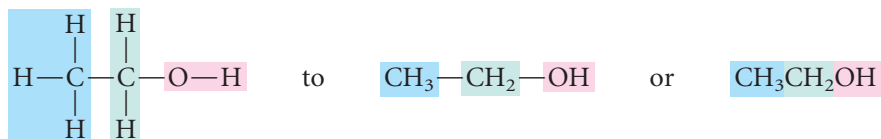
So we can draw three (and only three) different structural formulas that correspond to the molecular formula C_5H_{12} , and in fact, we find that only three different chemical substances with this formula exist. They are commonly called *n*-pentane (*n* for normal, with an unbranched carbon chain), isopentane, and neopentane.

PROBLEM 1.21 To which isomer of C_5H_{12} does each of the following structural formulas correspond?

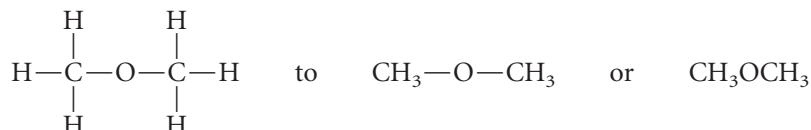


1.10 Abbreviated Structural Formulas

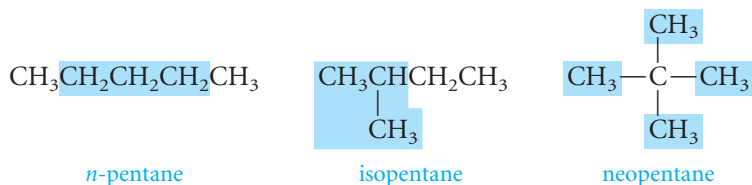
Structural formulas like the ones we have written so far are useful, but they are also somewhat cumbersome. They take up a lot of space and are tiresome to write out. Consequently, we often take some shortcuts that still convey the meaning of structural formulas. For example, we may abbreviate the structural formula of ethanol (ethyl alcohol) from:



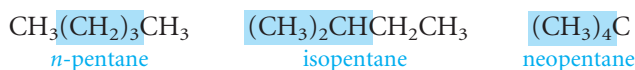
Each formula clearly represents ethanol rather than its isomer methoxymethane (dimethyl ether), which can be represented by any of the following structures:



The structural formulas for the three pentanes can be abbreviated in a similar fashion.



Sometimes these formulas are abbreviated even further. For example, they can be printed on a single line in the following ways:

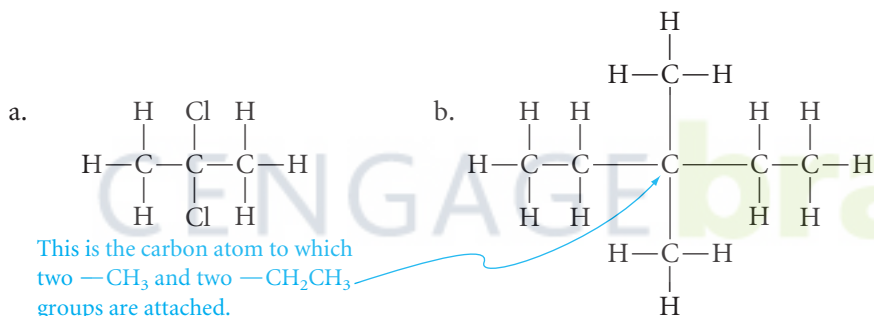


EXAMPLE 1.11

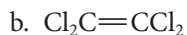
Write a structural formula that shows all bonds for each of the following:



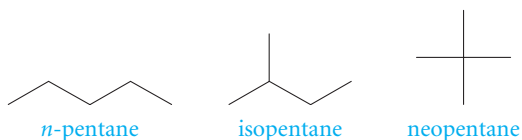
Solution



PROBLEM 1.22 Write a structural formula that shows all bonds for each of the following:

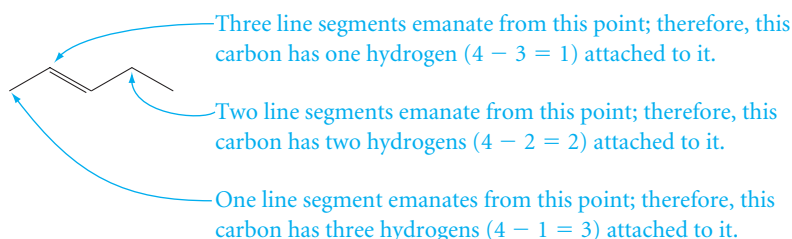


Perhaps the ultimate abbreviation of structures is the use of lines to represent the carbon framework:

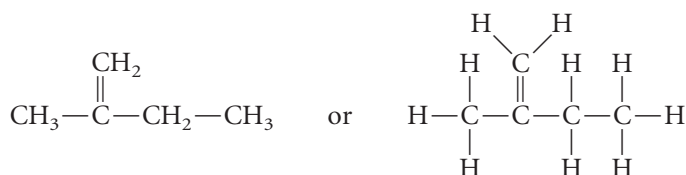


In these formulas, *each line segment is understood to have a carbon atom at each end*. The hydrogens are omitted, but we can quickly find the number of hydrogens on each carbon by subtracting from four (the valence of carbon) the number of line segments that emanates from any point. Multiple bonds are represented by multiple line segments. For example, the hydrocarbon with a chain of five carbon atoms and a double

bond between the second and third carbon atoms (that is, $\text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}_3$) is represented as follows:

**EXAMPLE 1.12**

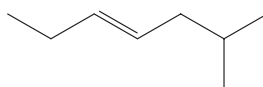
Write a more detailed structural formula for

Solution

PROBLEM 1.23 Write a more detailed structural formula for

EXAMPLE 1.13

Write a line-segment formula for $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}(\text{CH}_3)_2$.

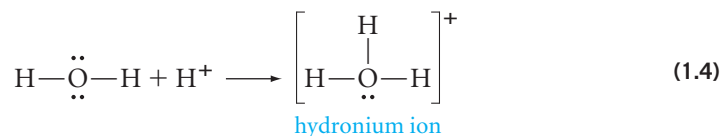
Solution

PROBLEM 1.24 Write a line-segment formula for $(\text{CH}_3)_2\text{C}=\text{CHCH}(\text{CH}_3)_2$.

1.11 Formal Charge

So far, we have considered only molecules whose atoms are neutral. But in some molecules, one or more atoms may be charged, either positively or negatively. Because such charges usually affect the chemical reactions of such molecules, it is important to know how to tell where the charge is located.

Consider the formula for hydronium ion, H_3O^+ , the product of the reaction of a water molecule with a proton.



The structure has eight electrons around the oxygen and two electrons around each hydrogen, so that all valence shells are complete. Note that there are eight valence electrons altogether. Oxygen contributes six, and each hydrogen contributes one, for a total of nine, but the ion has a single positive charge, so one electron must have been given away, leaving eight. Six of these eight electrons are used to form three O—H single bonds, leaving one unshared electron pair on the oxygen.

Although the entire hydronium ion carries a positive charge, we can ask, “Which atom, in a formal sense, bears the charge?” To determine **formal charge**, we consider each atom to “own” *all* of its unshared electrons plus only *half* of its shared electrons (one electron from each covalent bond). We then subtract this total from the number of valence electrons in the neutral atom to get the formal charge. This definition can be expressed in equation form as follows:

$$\text{Formal charge} = \begin{array}{l} \text{number of valence electrons} \\ \text{in the neutral atom} \end{array} - \left(\begin{array}{l} \text{unshared} \\ \text{electrons} \end{array} + \begin{array}{l} \text{half the shared} \\ \text{electrons} \end{array} \right) \quad (1.5)$$

or, in a simplified form,

$$\text{Formal charge} = \begin{array}{l} \text{number of valence electrons} \\ \text{in the neutral atom} \end{array} - (\text{dots} + \text{bonds})$$

Let us apply this definition to the hydronium ion.

For each hydrogen atom:

$$\begin{array}{ll} \text{Number of valence electrons in the neutral atom} & = 1 \\ \text{Number of unshared electrons} & = 0 \\ \text{Half the number of the shared electrons} & = 1 \\ \text{Therefore, the formal charge} & = 1 - (0 + 1) = 0 \end{array}$$

For the oxygen atom:

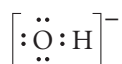
$$\begin{array}{ll} \text{Number of valence electrons in the neutral atom} & = 6 \\ \text{Number of unshared electrons} & = 2 \\ \text{Half the number of the shared electrons} & = 3 \\ \text{Therefore, the formal charge} & = 6 - (2 + 3) = +1 \end{array}$$

Thus, it is the oxygen atom that formally carries the +1 charge in the hydronium ion.

EXAMPLE 1.14

On which atom is the formal charge in the hydroxide ion, OH[−]?

Solution The electron-dot formula is



Oxygen contributes six electrons, hydrogen contributes one, and there is one more for the negative charge, for a total of eight electrons. The formal charge on oxygen is $6 - (6 + 1) = -1$, so the oxygen carries the negative charge. (So instead, you might see hydroxide written as HO[−] to reflect the negative charge on oxygen.) The hydrogen is neutral.

PROBLEM 1.25 Calculate the formal charge on the nitrogen atom in ammonia, NH₃; in the ammonium ion, NH₄⁺; and in the amide ion, NH₂[−].

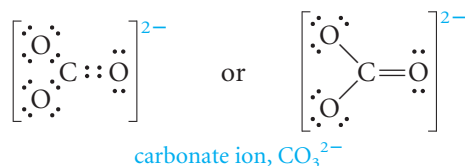
Now let us look at a slightly more complex situation involving electron-dot structures and formal charge.

The **formal charge** on an atom in a covalently bonded molecule or ion is the number of valence electrons in the neutral atom minus the number of covalent bonds to the atom and the number of unshared electrons on the atom.

1.12 Resonance

In electron-dot structures, a pair of dots or a dash represents a bond between just two atoms. But sometimes, an electron pair is involved with more than two atoms in the process of forming bonds. Molecules and ions in which this occurs cannot be adequately represented by a single electron-dot structure. As an example, consider the structure of the carbonate ion, CO_3^{2-} .

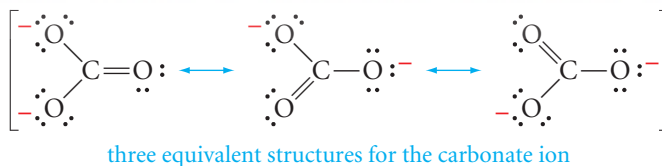
The total number of valence electrons in the carbonate ion is 24 (4 from the carbon, $3 \times 6 = 18$ from the three oxygens, *plus* 2 more electrons that give the ion its negative charge; these 2 electrons presumably have been donated by some metal, perhaps one each from two sodium atoms). An electron-dot structure that completes the valence shell of eight electrons around the carbon and each oxygen is



The structure contains two carbon–oxygen *single* bonds and one carbon–oxygen *double* bond. Application of the definition for formal charge shows that the carbon is formally neutral, each singly bonded oxygen has a formal charge of -1 , and the doubly bonded oxygen is formally neutral.

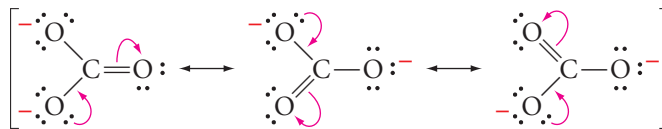
PROBLEM 1.26 Show that the last sentence of the preceding paragraph is correct.

When we wrote the electron-dot structure for the carbonate ion, our choice of which oxygen atom would be doubly bonded to the carbon atom was purely arbitrary. There are in fact *three exactly equivalent* structures that we might write.



In each structure there is one $\text{C}=\text{O}$ bond and there are two $\text{C}-\text{O}$ bonds. These structures have the same arrangement of the atoms. They differ from one another *only* in the arrangement of the electrons.

The three structures for the carbonate ion are redrawn below, with curved arrows to show how electron pairs can be moved to convert one structure to another:



Chemists use curved arrows to keep track of a change in the location of electrons. A detailed explanation of the use of curved arrows is given in Section 1.13.

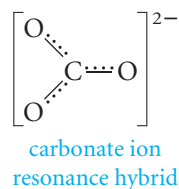
Physical measurements tell us that *none of the foregoing structures accurately describes the real carbonate ion*. For example, although each structure shows two different types of bonds between carbon and oxygen, we find experimentally that *all three carbon–oxygen bond lengths are identical*: 1.31 \AA . This distance is intermediate between the normal $\text{C}=\text{O}$ (1.20 \AA) and $\text{C}-\text{O}$ (1.41 \AA) bond lengths. To explain this fact, we usually say that the real carbonate ion has a structure that is a **resonance hybrid** of the three contributing **resonance structures**. It is as if we could take an average

Resonance structures of a molecule or ion are two or more structures with identical arrangements of the atoms but different arrangements of the electrons. If resonance structures can be written, the true structure of the molecule or ion is a **resonance hybrid** of the contributing resonance structures.

of the three structures. In the real carbonate ion, the two formal negative charges are spread *equally* over the three oxygen atoms, so that each oxygen atom carries two-thirds of a negative charge. It is important to note that the carbonate ion does not physically alternate among three resonance structures but has in fact one structure—a *hybrid* of the three resonance structures.

Whenever we can write two or more structures for a molecule with different arrangements of the electrons but identical arrangements of the atoms, we call these structures *resonance structures*. Resonance is very different from isomerism, for which the atoms themselves are arranged differently. When resonance is possible, the substance is said to have a structure that is a resonance hybrid of the various contributing structures. We use a double-headed arrow (\longleftrightarrow) between contributing structures to distinguish resonance from an equilibrium between different compounds, for which we use \rightleftharpoons .

Each carbon–oxygen bond in the carbonate ion is neither single nor double, but something in between—perhaps a one-and-one-third bond (any particular carbon–oxygen bond is single in two contributing structures and double in one). Sometimes we represent a resonance hybrid with one formula by writing a solid line for each full bond and a dotted line for each partial bond (in the carbonate ion, the dots represent one-third of a bond).



PROBLEM 1.27 Draw the three equivalent contributing resonance structures for the nitrate ion, NO_3^- . What is the formal charge on the nitrogen atom and on each oxygen atom in the individual structures? What is the charge on the oxygens and on the nitrogen in the resonance hybrid structure? Show with curved arrows how the structures can be interconverted.

1.13 1.13 Arrow Formalism

Arrows in chemical drawings have specific meanings. For example, in Section 1.12 we used curved arrows to move electrons to show the relatedness of the three resonance structures of the carbonate ion. Just as it is important to learn the structural representations and names of molecules, it is important to learn the language of arrow formalism in organic chemistry.

- 1. Curved arrows** are used to show how electrons are moved in resonance structures and in reactions. Therefore, curved arrows always start at the initial position of electrons and end at their final position. In the example given below, the arrow that points from the $\text{C}=\text{O}$ bond to the oxygen atom in the structure on the left indicates that the two electrons in one of the covalent bonds between carbon and oxygen are moved onto the oxygen atom:



Note that the carbon atom in the structure on the right now has a formal positive charge, and the oxygen has a formal negative charge. Notice also that when a pair of electrons in a polar covalent bond is moved to one of the bonded atoms, *it is moved to the more electronegative atom*, in this case oxygen. In the following example,

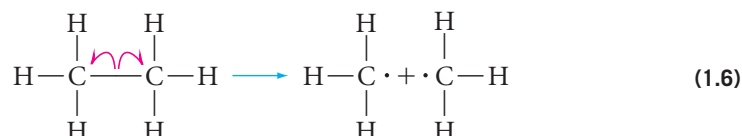
Curved arrows show how electrons are moved in resonance structures and in reactions.

the arrow that points from the unshared pair of electrons on the oxygen atom to a point between the carbon and oxygen atoms in the structure on the left indicates that the unshared pair of electrons on the oxygen atom moves between the oxygen and carbon atoms to form a covalent bond:



Note that both carbon and oxygen have formal charges of 0 in the structure on the right.

A curved arrow with half a head is called a **fishhook**. This kind of arrow is used to indicate the movement of a single electron. In eq. 1.6, two fishhooks are used to show the movement of each of the two electrons in the C—C bond of ethane to a carbon atom, forming two methyl radicals (see eq. 1.3):



Fishhook arrows indicate the movement of only a single electron.

Straight arrows point from reactants to products in chemical reaction equations.

- 2. Straight arrows** point from reactants to products in chemical reaction equations. An example is the straight arrow pointing from ethane to the two methyl radicals in eq. 1.6. Straight arrows with half-heads are commonly used in pairs to indicate that a reaction is *reversible*.



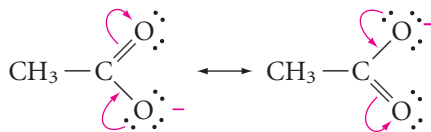
A **double-headed straight arrow** between two structures indicates resonance structures.

A **double-headed straight arrow** (\longleftrightarrow) between two structures indicates that they are resonance structures. Such an arrow does not indicate the occurrence of a chemical reaction. The double-headed arrows between resonance structures (Sec. 1.12) for the C=O bond are shown above.

EXAMPLE 1.15

Using correct arrow formalism, write the contributors to the resonance hybrid structure of the acetate ion, CH_3CO_2^- . Indicate any formal charges.

Solution There are two equivalent resonance structures for the acetate ion. Each one has a formal negative charge on one of the oxygen atoms.



Notice that when one pair of electrons from oxygen is moved to form a covalent bond with carbon, a pair of electrons in a covalent bond between carbon and the other oxygen atom is moved to oxygen. This is necessary to ensure that the carbon atom does not exceed its valence of 4.

PROBLEM 1.28 Using correct arrow formalism, write the contributors to the resonance hybrid of azide ion, a linear ion with three connected nitrogens, N_3^- . Indicate the formal charge on each nitrogen atom.

We will use curved arrows throughout this text as a way of keeping track of electron movement. Several curved-arrow problems are included at the end of this chapter to help you get used to drawing them.

1.14 The Orbital View of Bonding; the Sigma Bond

Although electron-dot structures are often useful, they have some limitations. The Lewis theory of bonding itself has some limitations, especially in explaining the three-dimensional geometries of molecules. For this purpose in particular, we will discuss how another theory of bonding, involving orbitals, is more useful.

The atomic orbitals named in Section 1.1 have definite shapes. The s orbitals are spherical. The electrons that fill an s orbital confine their movement to a spherical region of space around the nucleus. The three p orbitals are dumbbell shaped and mutually perpendicular, oriented along the three coordinate axes, x , y , and z . Figure 1.2 shows the shapes of these orbitals.

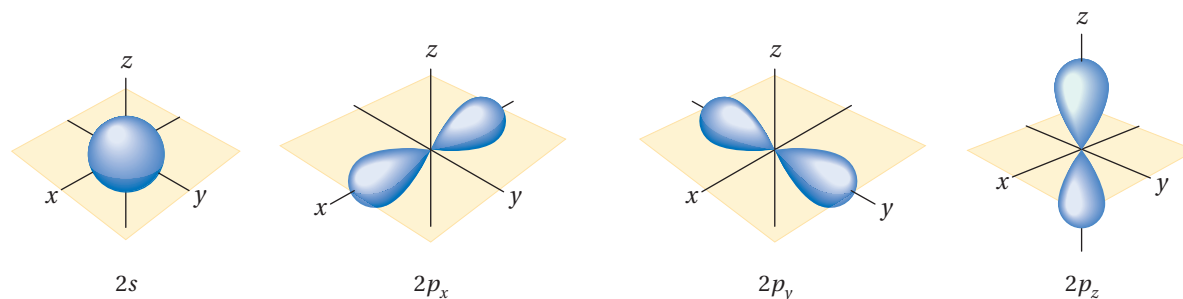


Figure 1.2

The shapes of the s and p orbitals used by the valence electrons of carbon. The nucleus is at the origin of the three coordinate axes.

In the orbital view of bonding, atoms approach each other in such a way that their atomic orbitals can *overlap* to form a bond. For example, if two hydrogen atoms form a hydrogen molecule, their two spherical $1s$ orbitals combine to form a new orbital that encompasses both of the atoms (see Figure 1.3). This orbital contains both valence electrons (one from each hydrogen). Like atomic orbitals, each **molecular orbital** can contain no more than two electrons. In the hydrogen molecule, these electrons mainly occupy the space between the two nuclei.

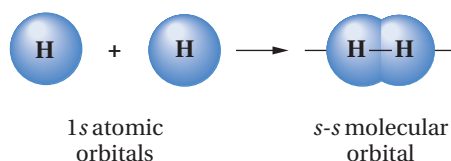


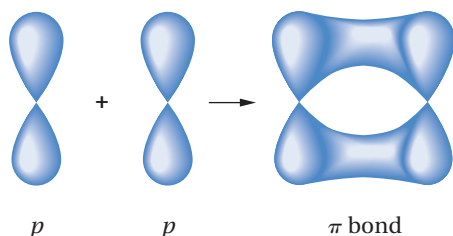
Figure 1.3

The molecular orbital representation of covalent bond formation between two hydrogen atoms.

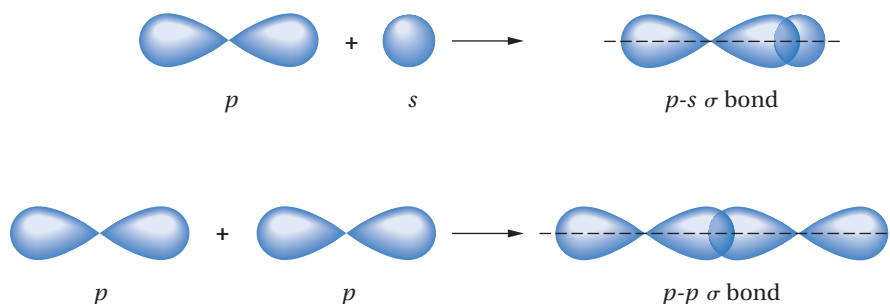
The orbital in the hydrogen molecule is cylindrically symmetric along the H—H internuclear axis. Such orbitals are called **sigma (σ) orbitals**, and the bond is referred to as a **sigma bond**. Sigma bonds may also be formed by the overlap of an s and a p orbital or of two p orbitals, as shown in Figure 1.4.*

A **sigma (σ) orbital** lies along the axis between two bonded atoms; a pair of electrons in a sigma orbital is called a **sigma bond**.

*Two properly aligned p orbitals can also overlap to form another type of bond, called a π (pi) bond. We discuss this type of bond in Chapter 3.



■ Figure 1.4

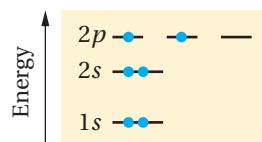
Orbital overlap to form σ bonds.

Let us see how these ideas apply to bonding in carbon compounds.

1.15 Carbon sp^3 Hybrid Orbitals

■ Figure 1.5

Distribution of the six electrons in a carbon atom. Each dot stands for an electron.



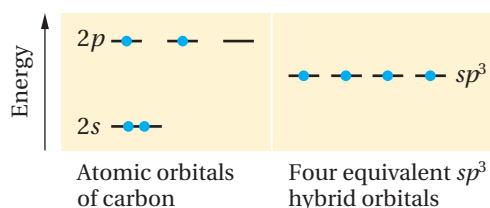
In a carbon atom, the six electrons are arranged as shown in Figure 1.5 (compare with carbon in Table 1.2). The 1s shell is filled, and the four valence electrons are in the 2s orbital and two different 2p orbitals. There are a few things to notice about Figure 1.5. The energy scale at the left represents the energy of electrons in the various orbitals. The farther the electron is from the nucleus, the greater its potential energy, because it takes energy to keep the electron (negatively charged) and the nucleus (positively charged) apart. The 2s orbital has a slightly lower energy than the three 2p orbitals, which have equal energies (they differ from one another only in orientation around the nucleus, as shown in Figure 1.2). The two highest energy electrons are placed in different 2p orbitals rather than in the same orbital, because this keeps them farther apart and thus reduces the repulsion between these like-charged particles. One p orbital is vacant.

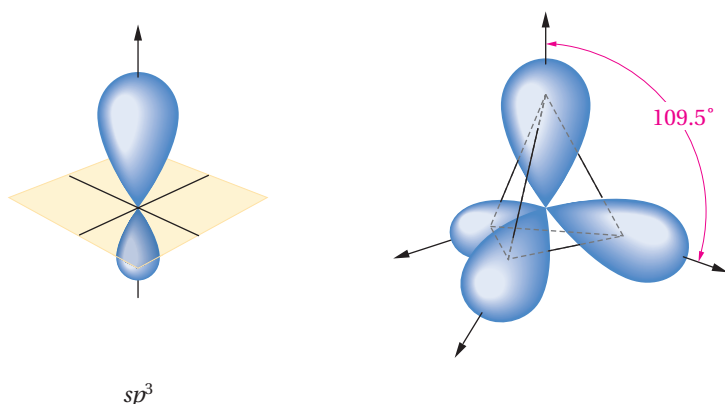
We might get a misleading idea about the bonding of carbon from Figure 1.5. For example, we might think that carbon should form only two bonds (to complete the partially filled 2p orbitals) or perhaps three bonds (if some atom donated two electrons to the empty 2p orbital). But we know from experience that this picture is wrong. Carbon usually forms *four* single bonds, and often these bonds are all equivalent, as in CH_4 or CCl_4 . How can this discrepancy between theory and fact be resolved?

One solution, illustrated in Figure 1.6, is to mix or combine the four atomic orbitals of the valence shell to form four identical hybrid orbitals, each containing one valence electron. In this model, the hybrid orbitals are called sp^3 hybrid orbitals because each one has one part s character and three parts p character. As shown in Figure 1.6, each sp^3 orbital has the same energy: less than that of the 2p orbitals but greater than that of the 2s orbital. The shape of sp^3 orbitals resembles the shape of p orbitals, except that the dumbbell is lopsided, and the electrons are more likely to be found in the lobe that extends out the greater distance from the nucleus, as shown in Figure 1.7. The four sp^3 hybrid orbitals of a single carbon atom are directed toward the corners of a regular tetrahedron, also shown in Figure 1.7. This particular geometry puts each orbital as far from the other three orbitals as it can be and thus minimizes repulsion when the orbitals are filled with electron pairs. The angle between any two of the four bonds formed from sp^3 orbitals is approximately 109.5° , the angle made by lines drawn from the center to the corners of a regular tetrahedron.

■ Figure 1.6

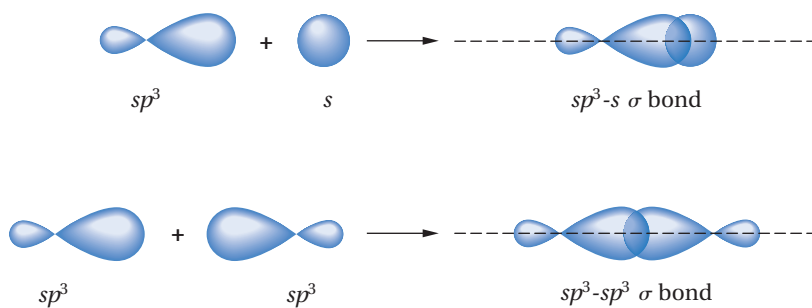
Unhybridized vs. sp^3 hybridized orbitals on carbon. The dots stand for electrons. (Only the electrons in the valence shell are shown; the electrons in the 1s orbital are omitted because they are not involved in bonding.)



**Figure 1.7**

An sp^3 orbital extends mainly in one direction from the nucleus and forms bonds with other atoms in that direction. The four sp^3 orbitals of any particular carbon atom are directed toward the corners of a regular tetrahedron, as shown in the right-hand part of the figure (in this part of the drawing, the small “back” lobes of the orbitals have been omitted for simplification, although they can be important in chemical reactions).

Hybrid orbitals can form sigma bonds by overlap with other hybrid orbitals or with nonhybridized atomic orbitals. Figure 1.8 shows some examples.

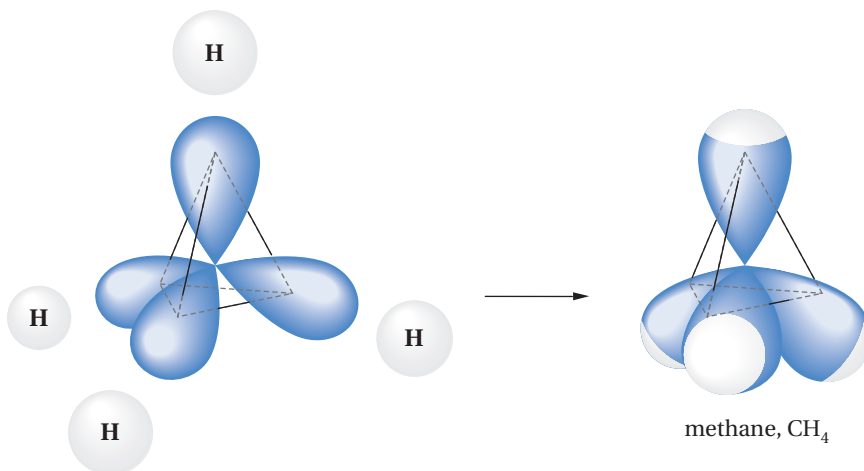
**Figure 1.8**

Examples of sigma (σ) bonds formed from sp^3 hybrid orbitals.

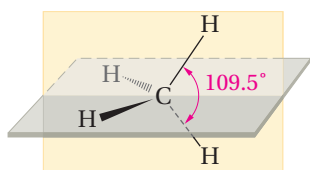
1.16 Tetrahedral Carbon; the Bonding in Methane

We can now describe how a carbon atom combines with four hydrogen atoms to form methane. This process is pictured in Figure 1.9. The carbon atom is joined to each hydrogen atom by a sigma bond, which is formed by the overlap of a carbon sp^3 orbital with a hydrogen $1s$ orbital. The four sigma bonds are directed from the carbon nucleus to the corners of a regular tetrahedron. In this way, the electron pair in any one bond experiences minimum repulsion from the electrons in the other bonds. Each H—C—H **bond angle** is the same, 109.5° . To summarize, in methane, there are four sp^3-s C—H sigma bonds, each directed from the carbon atom to one of the four corners of a regular tetrahedron.

A **bond angle** is the angle made by two covalent bonds to the same atom.

**Figure 1.9**

A molecule of methane, CH_4 , is formed by the overlap of the four sp^3 carbon orbitals with the $1s$ orbitals of four hydrogen atoms. The resulting molecule has the geometry of a regular tetrahedron and contains four sigma bonds of the sp^3-s type.



■ **Figure 1.10**

The carbon and two of the hydrogens in methane form a plane that perpendicularly bisects the plane formed by the carbon and the other two hydrogens.

PROBLEM 1.29 Considering the repulsion that exists between electrons in different bonds, give a reason why a planar geometry for methane would be less stable than the tetrahedral geometry.

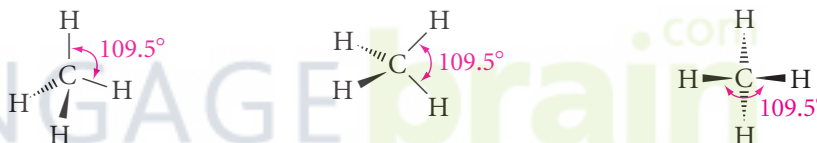
Because the tetrahedral geometry of carbon plays such an important role in organic chemistry, it is a good idea to become familiar with the features of a regular tetrahedron. One feature is that *the center and any two corners of a tetrahedron form a plane that is the perpendicular bisector of a similar plane formed by the center and the other two corners*. In methane, for example, any two hydrogens and the carbon form a plane that perpendicularly bisects the plane formed by the carbon and the other two hydrogens. These planes are illustrated in Figure 1.10.

The geometry of carbon with four single bonds, as in methane, is commonly represented as shown in Figure 1.11a, in which the **solid lines** lie in the plane of the page, the **dashed wedge** goes behind the plane of the paper, and the **solid wedge** extends out of the plane of the paper toward you. Structures drawn in this way are sometimes called **3D** (that is, three-dimensional) **structures**.

Two other 3D representations commonly used are the ball-and-stick model (Figure 1.11b) and the space-filling model (Figure 1.11c). The ball-and-stick model emphasizes the bonds that connect the atoms, while the space-filling model emphasizes the space occupied by the atoms.

In addition, a 3D representation, called an **electrostatic potential map**, is sometimes used to show the distribution of electrons in a molecule (Figure 1.11d). Red indicates partial negative charge (greater electron density), and blue indicates partial positive charge.

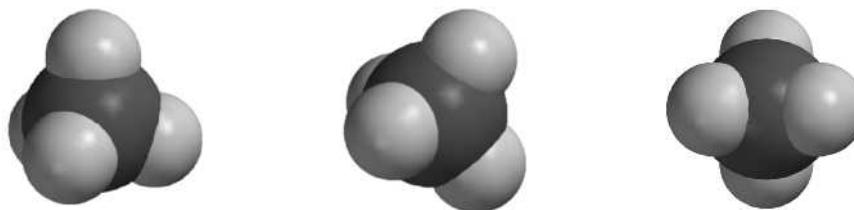
(a) In a **3D structure**, **solid lines** lie in the plane of the page (C and H in C—H lie in the plane). **Dashed wedges** extend behind the plane (H in C—H lies behind the plane). **Solid wedges** project out toward you (H in C—H is in front of the plane).



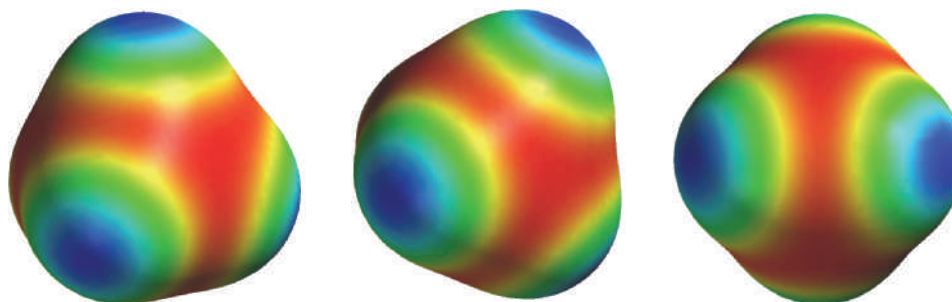
(b) A **ball-and-stick model** of a molecule emphasizes the bonds that connect atoms.



(c) A **space-filling model** emphasizes the space occupied by the atoms.



(d) An **electrostatic potential map** shows the distribution of electrons in a molecule. Red indicates partial negative charge, and blue indicates partial positive charge.



■ **Figure 1.11**

Four representations of methane.

charge (less electron density). This representation is useful for showing whether a molecule is polar or nonpolar (see Sec. 2.7) and can give us insight into the chemical behavior of a molecule, as we will see when we look at the chemistry of functional groups in later chapters.

Now that we have described single covalent bonds and their geometry, we are ready to tackle, in the next chapter, the structure and chemistry of saturated hydrocarbons. But before we do that, we present a brief overview of organic chemistry, so that you can see how the subject will be organized for study.

Because carbon atoms can be linked to one another or to other atoms in so many different ways, the number of possible organic compounds is almost limitless. Literally millions of organic compounds have been characterized, and the number grows daily. How can we hope to study this vast subject systematically? Fortunately, organic compounds can be classified according to their structures into a relatively small number of groups. Structures can be classified both according to the molecular framework (sometimes called the carbon *skeleton*) and according to the groups that are attached to that framework.

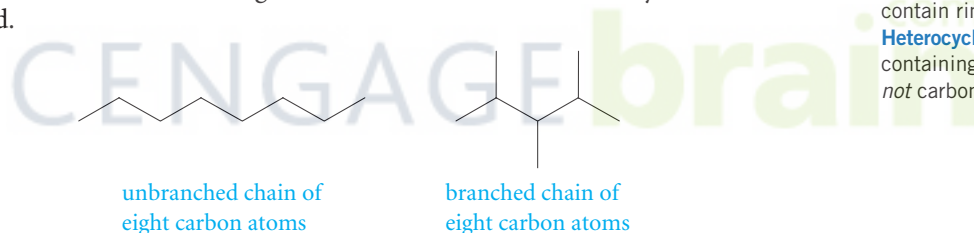
1.17 Classification According to Molecular Framework

The three main classes of molecular frameworks for organic structures are acyclic, carbocyclic, and heterocyclic compounds.

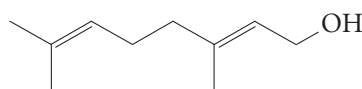
1.17.a Acyclic Compounds

By **acyclic** (pronounced a'-cyclic), we mean *not cyclic*. Acyclic organic molecules have chains of carbon atoms but no rings. As we have seen, the chains may be unbranched or branched.

Acyclic compounds contain no rings. **Carbocyclic compounds** contain rings of carbon atoms. **Heterocyclic compounds** have rings containing at least one atom that is *not* carbon.



Pentane is an example of an acyclic compound with an unbranched carbon chain, whereas isopentane and neopentane are also acyclic but have branched carbon frameworks (Sec. 1.9). Figure 1.12 shows the structures of a few acyclic compounds that occur in nature.



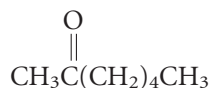
geraniol
(oil of roses)
bp 229–230°C

A branched chain compound used in perfumes



heptane
(petroleum)
bp 98.4°C

A hydrocarbon present in petroleum, used as a standard in testing the octane rating of gasoline



2-heptanone
(oil of cloves)
bp 151.5°C

A colorless liquid with a fruity odor, in part responsible for the “peppery” odor of blue cheese



Foodcollection/Getty Images

■ Figure 1.12

Examples of natural acyclic compounds, their sources (in parentheses), and selected characteristics.

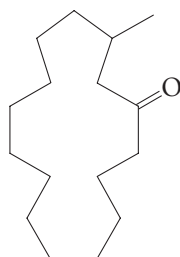
2-Heptanone contributes to the “peppery” odor of blue cheese.

1.17.b Carbocyclic Compounds

Carbocyclic compounds contain rings of carbon atoms. The smallest possible carbocyclic ring has three carbon atoms, but carbon rings come in many sizes and shapes. The rings may have chains of carbon atoms attached to them and may contain multiple bonds. Many compounds with more than one carbocyclic ring are known. Figure 1.13 shows the structures of a few carbocyclic compounds that occur in nature. Five- and six-membered rings are most common, but smaller and larger rings are also found.

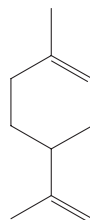
■ **Figure 1.13**

Examples of natural carbocyclic compounds with rings of various sizes and shapes. The source and special features of each structure are indicated below it.



muscone
(musk deer)
bp 327–330°C

A 15-membered ring ketone, used in perfumes



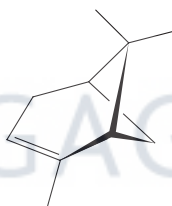
limonene
(citrus fruit oils)
bp 178°C

A ring with two side chains, one of which is branched



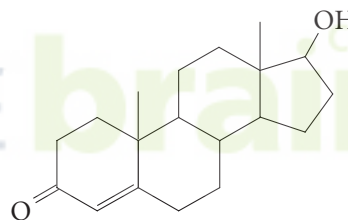
benzene
(petroleum)
mp 5.5°C, bp 80.1°C

A very common ring



α -pinene
(turpentine)
bp 156.2°C

A bicyclic molecule; one would have to break *two* bonds to make it acyclic



testosterone
(testes)
mp 155°C

A male sex hormone in which several rings of common sizes are *fused* together; that is, they share two adjacent carbon atoms



© Dani, Jeske/Animals Animals

Musk deer, source of muscone.

1.17.c Heterocyclic Compounds

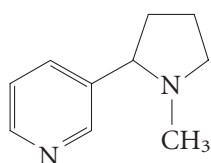
Heterocyclic compounds make up the third and largest class of molecular frameworks for organic compounds. In heterocyclic compounds, at least one atom in the ring must be a heteroatom, an atom that is *not* carbon. The most common heteroatoms are oxygen, nitrogen, and sulfur, but heterocyclics with other elements are also known. More than one heteroatom may be present and, if so, the heteroatoms may be alike or different. Heterocyclic rings come in many sizes, may contain multiple bonds, may have

carbon chains or rings attached to them, and in short may exhibit a great variety of structures. Figure 1.14 shows the structures of a few natural products that contain heterocyclic rings. In these abbreviated structural formulas, the symbols for the heteroatoms are shown, but the carbons are indicated using lines only.

The structures in Figures 1.12 through 1.14 show not only the molecular frameworks, but also various groups of atoms that may be part of or attached to the frameworks. Fortunately, these groups can also be classified in a way that helps simplify the study of organic chemistry.

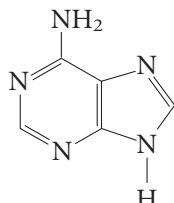


Clover, a source of coumarin.



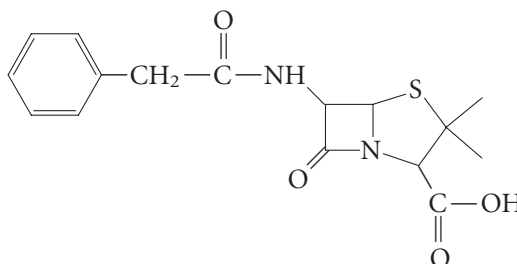
nicotine
bp 246°C

Present in tobacco, nicotine has two heterocyclic rings of different sizes, each containing one nitrogen.



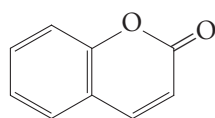
adenine
mp 360–365°C
(decomposes)

One of the four heterocyclic bases of DNA, adenine contains two fused heterocyclic rings, each of which contains two heteroatoms (nitrogen).



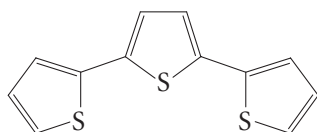
penicillin-G
(amorphous solid)

One of the most widely used antibiotics, penicillin has two heterocyclic rings, the smaller of which is crucial to biological activity.



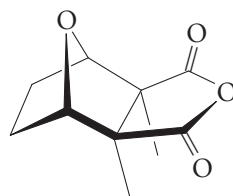
coumarin
mp 71°C

Found in clover and grasses, coumarin produces the pleasant odor of new-mown hay.



α -terthienyl
mp 92–93°C

This compound, with three linked sulfur-containing rings, is present in certain marigold species.



cantharidin
mp 218°C

This compound, an oxygen heterocycle, is the active principle in cantharis (also known as Spanish fly), a material isolated from certain dried beetles of the species *Cantharis vesicatoria* and incorrectly thought by some to increase sexual desire.

■ Figure 1.14

Examples of natural heterocyclic compounds having a variety of heteroatoms and ring sizes.

1.18 Classification According to Functional Group

Functional groups are groups of atoms that have characteristic chemical properties regardless of the molecular framework to which they are attached.

Certain groups of atoms have chemical properties that depend only moderately on the molecular framework to which they are attached. These groups of atoms are called **functional groups**. The hydroxyl group, —OH , is an example of a functional group, and compounds with this group attached to a carbon framework are called alcohols. In most organic reactions, some chemical change occurs at the functional group, but the rest of the molecule keeps its original structure. This maintenance of most of the structural formula throughout a chemical reaction greatly simplifies our study of organic chemistry. It allows us to focus attention on the chemistry of the various functional groups. We can study classes of compounds instead of having to learn the chemistry of each individual compound.

Some of the main functional groups that we will study are listed in Table 1.6, together with a typical compound of each type. Although we will describe these classes of compounds in greater detail in later chapters, it would be a good idea for you to become familiar with their names and structures now. If a particular functional group is mentioned before its chemistry is discussed in detail, and you forget what it is, you can refer to Table 1.6 or to the inside front cover of this book.

PROBLEM 1.30 What functional groups can you find in the following natural products? (Their formulas are given in Figures 1.12, 1.13, and 1.14.)

- a. testosterone b. penicillin-G c. muscone d. α -pinene

Table 1.6 ■ The Main Functional Groups

	Structure	Class of compound	Specific example	Common name of the specific example
<i>A. Functional groups that are a part of the molecular framework</i>		alkane	$\text{CH}_3\text{—CH}_3$	ethane, a component of natural gas
		alkene	$\text{CH}_2\text{=CH}_2$	ethylene, used to make polyethylene
		alkyne	$\text{HC}\equiv\text{CH}$	acetylene, used in welding
		arene		benzene, raw material for polystyrene and phenol
<i>B. Functional groups containing oxygen</i>				
1. With carbon–oxygen single bonds		alcohol	$\text{CH}_3\text{CH}_2\text{OH}$	ethyl alcohol, found in beer, wines, and liquors
		ether	$\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$	diethyl ether, once a common anesthetic

(continued)

Table 1.6 ■ continued

	Structure	Class of compound	Specific example	Common name of the specific example
2. With carbon–oxygen double bonds*	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{H} \end{array}$	aldehyde	$\text{CH}_2=\text{O}$	formaldehyde, used to preserve biological specimens
	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{C}-\text{C}- \\ \quad \quad \end{array}$	ketone	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{CCH}_3 \end{array}$	acetone, a solvent for varnish and rubber cement
3. With single and double carbon–oxygen bonds	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{OH} \end{array}$	carboxylic acid	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{C}-\text{OH} \end{array}$	acetic acid, a component of vinegar
	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{O}-\text{C}- \\ \quad \end{array}$	ester	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{C}-\text{OCH}_2\text{CH}_3 \end{array}$	ethyl acetate, a solvent for nail polish and model airplane glue
C. Functional groups containing nitrogen**	$\begin{array}{c} \\ -\text{C}-\text{NH}_2 \\ \end{array}$	primary amine	$\text{CH}_3\text{CH}_2\text{NH}_2$	ethylamine, smells like ammonia
	$-\text{C}\equiv\text{N}$	nitrile	$\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$	acrylonitrile, raw material for making Orlon
D. Functional group with oxygen and nitrogen	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{NH}_2 \end{array}$	primary amide	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}-\text{C}-\text{NH}_2 \end{array}$	formamide, a softener for paper
E. Functional group with halogen	$-\text{X}$	alkyl or aryl halide	CH_3Cl	methyl chloride, refrigerant and local anesthetic
F. Functional groups containing sulfur†	$\begin{array}{c} \\ -\text{C}-\text{SH} \\ \end{array}$	thiol (also called mercaptan)	CH_3SH	methanethiol, has the odor of rotten cabbage
	$\begin{array}{c} \quad \quad \\ -\text{C}-\text{S}-\text{C}- \\ \quad \quad \end{array}$	thioether (also called sulfide)	$(\text{CH}_2=\text{CHCH}_2)_2\text{S}$	diallyl sulfide, has the odor of garlic

*The $\begin{array}{c} \diagup \\ \text{C}=\text{O} \end{array}$ group, present in several functional groups, is called a **carbonyl group**. The $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{OH} \end{array}$ group of acids is called a **carboxyl group** (a contraction of *carbonyl* and *hydroxyl*).

The $-\text{NH}_2$ group is called an **amino group.

†Thiols and thioethers are the sulfur analogs of alcohols and ethers.

ADDITIONAL PROBLEMS

 Interactive versions of these problems are assignable in OWL.

Valence, Bonding, and Lewis Structures

1.31 Show the number of valence electrons in each of the following atoms. Let the element's symbol represent its kernel, and use dots for the valence electrons.

- | | | |
|-------------|-------------|--------------|
| a. chlorine | b. nitrogen | c. sulfur |
| d. carbon | e. oxygen | f. potassium |

1.32 Use the relative positions of the elements in the periodic table (Table 1.3 or inside back cover) to classify the following substances as ionic or covalent:

- | | | |
|-----------|-------------|-----------|
| a. F_2 | b. SiF_4 | c. CH_4 |
| d. O_2 | e. $CaCl_2$ | f. NaI |
| g. $NaBr$ | h. ClF | |

1.33 When a solution of salt (sodium chloride) in water is treated with a silver nitrate solution, a white precipitate forms immediately. When tetrachloromethane is shaken with aqueous silver nitrate, no such precipitate is produced. Explain these facts in terms of the types of bonds present in the two chlorides.

1.34 For each of the following elements, determine (1) how many valence electrons it has and (2) what its common valence is:

- | | | |
|------|------|------|
| a. N | b. C | c. F |
| d. O | e. P | f. S |

1.35 Write a structural formula for each of the following compounds, using a line to represent each single bond and dots for any unshared electron pairs:

- | | | |
|-------------------|-----------------|-------------|
| a. CH_3OH | b. CH_3CH_2Cl | c. C_3H_8 |
| d. $CH_3CH_2NH_2$ | e. C_2H_5F | f. CH_2O |

1.36 Draw a structural formula for each of the following covalent molecules. Which bonds are polar? Indicate the polarity by proper placement of the symbols $\delta+$ and $\delta-$.

- | | | |
|-----------|-------------|-----------|
| a. BF_3 | b. CH_3F | c. CO_2 |
| d. Cl_2 | e. SF_6 | f. CH_4 |
| g. SO_2 | h. CH_3OH | |

1.37 Consider the X—H bond, in which X is an atom other than H. The H in a polar bond is more acidic (more easily removed) than the H in a nonpolar bond. Considering bond polarity, which hydrogen in acetic acid,

$$\begin{array}{c} O \\ || \\ CH_3C-OH \end{array}$$
do you expect to be most acidic? Write an equation for the reaction between acetic acid and potassium carbonate.

Structural Isomers

1.38 Draw structural formulas for all possible isomers having the following molecular formulas:

- | | | |
|--------------|----------------|-----------------|
| a. C_3H_8 | b. C_3H_7F | c. $C_2H_2Br_2$ |
| d. C_3H_6 | e. C_4H_9Cl | f. $C_3H_6Cl_2$ |
| g. C_3H_8S | h. $C_2H_4F_2$ | |

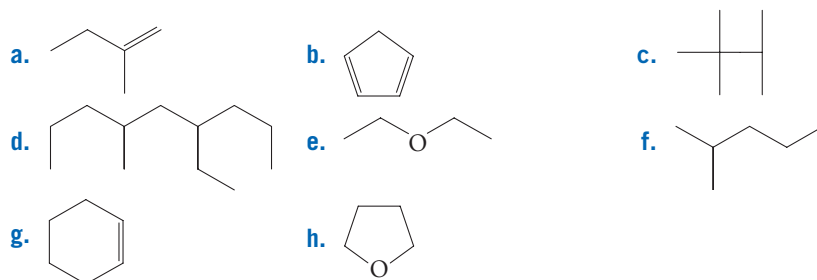
1.39 Draw structural formulas for the five isomers of C_6H_{14} . As you write them out, try to be systematic, starting with a consecutive chain of six carbon atoms.

Structural Formulas

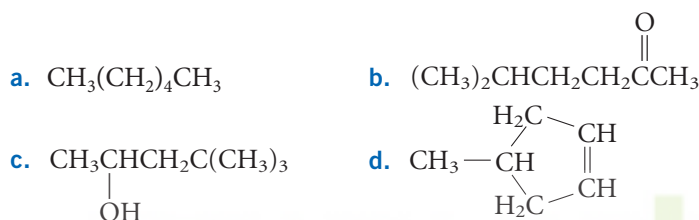
1.40 For each of the following abbreviated structural formulas, write a structural formula that shows all of the bonds:

- a. $\text{CH}_3(\text{CH}_2)_4\text{CH}_3$ b. $(\text{CH}_3)_3\text{CCH}_2\text{CH}_2\text{CH}_3$ c. $(\text{CH}_3\text{CH}_2)_2\text{NH}$
 d. $\text{CH}_3\text{CH}_2\text{SCH}_2\text{CH}_3$ e. $\text{ClCH}_2\text{CH}_2\text{OH}$ f. $(\text{CH}_3\text{CH}_2)_2\text{CHOH}$

1.41 Write structural formulas that correspond to the following abbreviated structures, and show the correct number of hydrogens on each carbon:



1.42 For each of the following abbreviated structural formulas, write a line-segment formula (like those in Problem 1.41).



1.43 An abbreviated formula of 2-heptanone is shown in Figure 1.12.

- a. How many carbons does 2-heptanone have?
 b. What is its molecular formula?
 c. Write a more detailed structural formula for it.

1.44 What is the *molecular formula* for each of the following compounds? Consult Figures 1.13 and 1.14 for the abbreviated structural formulas.

- a. nicotine b. adenine
 c. limonene d. coumarin
 e. benzene

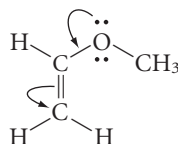
Formal Charge, Resonance, and Curved-Arrow Formalism

1.45 Write electron-dot formulas for the following species. Show where the formal charges, if any, are located.

- a. cyanide ion, CN^- b. nitric acid, HONO_2
 c. dimethyl ether, CH_3OCH_3 d. ammonium ion, NH_4^+
 e. nitrous acid, HONO f. carbon monoxide, CO
 g. boron trifluoride, BF_3 h. hydrogen peroxide, H_2O_2
 i. bicarbonate ion, HCO_3^-

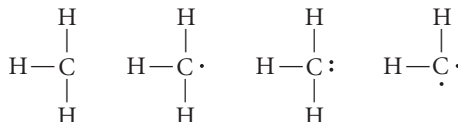
1.46 Draw electron-dot formulas for the two contributors to the resonance hybrid structure of the nitrite ion, NO_2^- . (Each oxygen is connected to the nitrogen.) What is the charge on each oxygen in each contributor and in the hybrid structure? Show by curved arrows how the electron pairs can relocate to interconvert the two structures.

- 1.47** Write the structure obtained when electrons move as indicated by the curved arrows in the following structure:

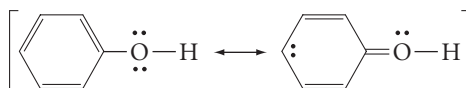


Does each atom in the resulting structure have a complete valence shell of electrons? Locate any formal charges in each structure.

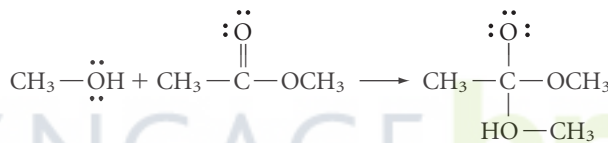
- 1.48** Consider each of the following highly reactive carbon species. What is the formal charge on carbon in each of these structures?



- 1.49** Add curved arrows to the following structures to show how electron pairs must be moved to interconvert the structures, and locate any formal charges.



- 1.50** Add curved arrows to show how electrons must move to form the product from the reactants in the following equation, and locate any formal charges.



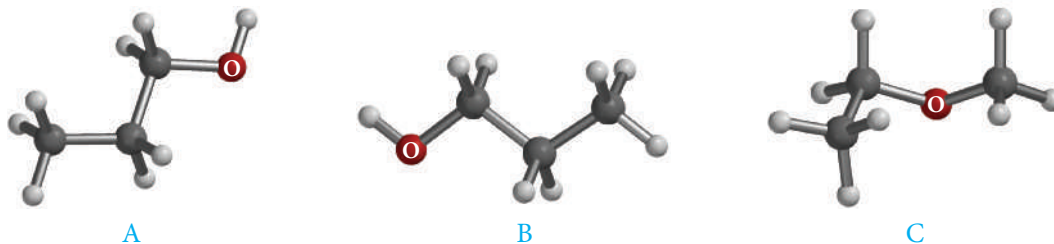
Electronic Structure and Molecular Geometry

- 1.51** Fill in any unshared electron pairs that are missing from the following formulas:



- 1.52** Make a drawing (similar to the right-hand part of Figure 1.6) of the electron distribution that will be expected in nitrogen atoms if the s and p orbitals are hybridized to sp^3 . Based on this model, predict the geometry of the ammonia molecule, NH_3 .
- 1.53** The ammonium ion, NH_4^+ , has a tetrahedral geometry analogous to that of methane. Explain this structure in terms of atomic and molecular orbitals.
- 1.54** Use lines, dashed wedges, and solid wedges to show the geometry of CF_4 and CH_3SH .
- 1.55** Silicon is just below carbon in the periodic table. Predict the geometry of silicon tetrafluoride, SiF_4 .

1.56 Examine the three ball-and-stick models shown below:



- a. Redraw the three structures using solid lines, dashed wedges, and solid wedges (see Figure 1.11).
- b. What is the relationship, identical or isomers, between structures A and B? Between structures A and C?

Classification of Organic Compounds

1.57 Write a structural formula that corresponds to the molecular formula C_3H_6O and is

- a. acyclic
- b. carbocyclic
- c. heterocyclic

1.58 Draw a chemical structure for diacetyl (2,3-butanedione), a diketone (see Table 1.6) with the $C_4H_6O_2$ chemical formula. Diacetyl is used as a flavoring for microwave popcorn, but has been under scrutiny of late as a possible causative agent for bronchiolitis obliterans, often referred to as popcorn lung disease.

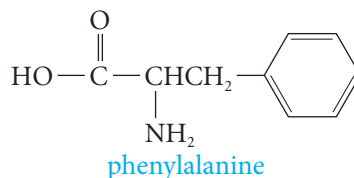
1.59 Divide the following compounds into groups that might be expected to exhibit similar chemical behavior:

- | | | |
|-------------------|-----------------------|-----------------------|
| a. C_4H_{10} | b. CH_3OCH_3 | c. C_3H_7OH |
| d. C_8H_{18} | e. $HOCH_2CH_2CH_2OH$ | f. CH_3NH_2 |
| g. $CH_3CH_2CH_3$ | h. CH_3OH | i. $(CH_3)_2CHNH_2$ |
| j. C_3H_7OH | k. $CH_3CH_2OCH_3$ | l. $H_2NCH_2CH_2NH_2$ |

1.60 Using Table 1.6, write a structural formula for each of the following:

- | | |
|-----------------------------------|-----------------------------|
| a. an alcohol, C_3H_8O | b. an ether, $C_4H_{10}O$ |
| c. an aldehyde, C_3H_6O | d. a ketone, C_3H_6O |
| e. a carboxylic acid, $C_3H_6O_2$ | f. an ester, $C_5H_{10}O_2$ |

1.61 Many organic compounds contain more than one functional group. An example is phenylalanine (shown below), one of the simple building blocks of proteins (Chapter 17).



- a. What functional groups are present in phenylalanine?
- b. Redraw the structure, adding all unshared electron pairs.
- c. What is the molecular formula of phenylalanine?
- d. Draw another structural isomer that has this formula. What functional groups does this isomer have?