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Fundamentals of
ORGANIC CHEMISTRY

Seventh Edition

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CHAPTER

1

The enzyme HMG-CoA reductase, shown here as a so-called ribbon model, catalyzes a crucial step in the body's synthesis of cholesterol. Understanding how this enzyme functions has led to the development of drugs credited with saving millions of lives.

Structure and Bonding; Acids and Bases

OWL

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

Organic chemistry is all around us. The reactions and interactions of organic molecules allow us to see, smell, fight, and fear. Organic chemistry provides the molecules that feed us, treat our illnesses, protect our crops, and clean our clothes. Anyone with a curiosity about life and living things must have a basic understanding of organic chemistry.

Historically, the term **organic chemistry** dates to the late 1700s, when it was used to mean the chemistry of compounds found in living organisms. Little was known about chemistry at that time, and the behavior of the "organic" substances isolated from plants and animals seemed different from that of the "inorganic" substances found in minerals. Organic compounds were generally low-melting solids and were usually more difficult to isolate, purify, and work with than high-melting inorganic compounds. By the mid-1800s, however, it was clear that there was no fundamental difference between organic and inorganic compounds. The same principles explain the behaviors of all substances, regardless of origin or complexity. The only distinguishing characteristic of organic chemicals is that *all contain the element carbon* (Figure 1.1).

Figure 1.1 The position of carbon in the periodic table. Other elements commonly found in organic compounds are shown in the colors typically used to represent them.

Group
1A

H	2A											3A	4A	5A	6A	7A	8A He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															

But why is carbon special? Why, of the more than 37 million presently known chemical compounds, do more than 99% of them contain carbon? The answers to these questions come from carbon's electronic structure and its consequent position in the periodic table. As a group 4A element, carbon can share four valence electrons and form four strong covalent bonds. Furthermore, carbon atoms can bond to one another, forming long chains and rings. Carbon, alone of all elements, is able to form an immense diversity of compounds, from the simple methane, with one carbon atom, to the staggeringly complex DNA, which can have more than *100 million* carbons.

Not all carbon compounds are derived from living organisms of course. Modern chemists have developed a remarkably sophisticated ability to design and synthesize new organic compounds in the laboratory—medicines, dyes, polymers, and a host of other substances. Organic chemistry touches the lives of everyone; its study can be a fascinating undertaking.

WHY THIS CHAPTER?

We'll ease into the study of organic chemistry by first reviewing some ideas about atoms, bonds, and molecular geometry that you may recall from your general chemistry course. Much of the material in this chapter is likely to be familiar to you, but some of it may be new and it's a good idea to make sure you understand it before going on.

1.1 Atomic Structure

As you probably know from your general chemistry course, an atom consists of a dense, positively charged *nucleus* surrounded at a relatively large distance by negatively charged *electrons* (Figure 1.2). The nucleus consists of subatomic particles called *neutrons,* which are electrically neutral, and *protons,* which are positively charged. Because an atom is neutral overall, the number of positive protons in the nucleus and the number of negative electrons surrounding the nucleus are the same.

Although extremely small—about 10^{-14} to 10^{-15} meter (m) in diameter—the nucleus nevertheless contains essentially all the mass of the atom. Electrons have negligible mass and circulate around the nucleus at a distance of approximately 10^{-10} m. Thus, the diameter of a typical atom is about

2×10^{-10} m, or 200 picometers (pm), where $1 \text{ pm} = 10^{-12}$ m. To give you an idea of how small this is, a thin pencil line is about 3 million carbon atoms wide. Many organic chemists and biochemists still use the unit *angstrom* (Å) to express atomic distances, where $1 \text{ Å} = 100 \text{ pm} = 10^{-10}$ m, but we'll stay with the SI unit picometer in this book.

Figure 1.2 A schematic view of an atom. The dense, positively charged nucleus contains most of the atom's mass and is surrounded by negatively charged electrons. The three-dimensional view on the right shows calculated electron-density surfaces. Electron density increases steadily toward the nucleus and is 40 times greater at the blue solid surface than at the gray mesh surface.

Nucleus (protons + neutrons)

Volume around nucleus occupied by orbiting electrons
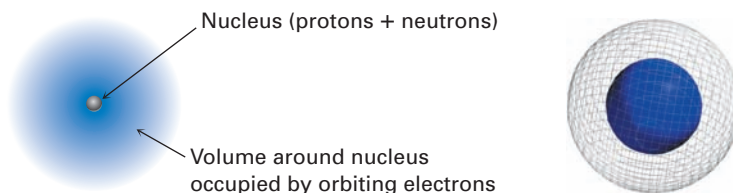
A specific atom is described by its *atomic number (Z),* which gives the number of protons (or electrons) it contains, and its *mass number (A),* which gives the total number of protons plus neutrons in its nucleus. All the atoms of a given element have the same atomic number—1 for hydrogen, 6 for carbon, 15 for phosphorus, and so on—but they can have different mass numbers depending on how many neutrons they contain. Atoms with the same atomic number but different mass numbers are called **isotopes.**

The weighted average mass in atomic mass units (amu) of an element's naturally occurring isotopes is called the element's *atomic mass* (or atomic weight)—1.008 amu for hydrogen, 12.011 amu for carbon, 30.974 amu for phosphorus, and so on. Atomic masses of the elements are given in the periodic table in the back of this book.

What about the electrons? How are they distributed in an atom? According to the *quantum mechanical model* of atomic structure, the behavior of a specific electron in an atom can be described by a mathematical expression called a *wave equation*—the same sort of expression used to describe the motion of waves in a fluid. The solution to a wave equation is a *wave function,* or **orbital,** denoted by the Greek letter psi, ψ. An orbital can be thought of as defining a region of space around the nucleus where the electron can most likely be found.

What do orbitals look like? There are four different kinds of orbitals, denoted *s, p, d,* and *f,* each with a different shape. Of the four, we'll be concerned only with *s* and *p* orbitals because these are the most common in organic and biological chemistry. An *s* orbital is spherical, with the nucleus at its center, while a *p* orbital is dumbbell-shaped and can be oriented in space along any of three mutually perpendicular directions, arbitrarily denoted p_x, p_y, and p_z (Figure 1.3). The two parts, or *lobes,* of a *p* orbital have different algebraic signs ($+$ and $-$) in the wave function and are separated by a region of zero electron density called a *node*.

Figure 1.3 Representations of *s* and *p* orbitals. An *s* orbital is spherical, while a *p* orbital is dumbbell-shaped and can be oriented along any of three mutually perpendicular directions. Each *p* orbital has two lobes separated by a node. The two lobes have different algebraic signs in the corresponding wave function, as indicated by the different colors.

An *s* orbital   A $2p_x$ orbital   A $2p_y$ orbital   A $2p_z$ orbital
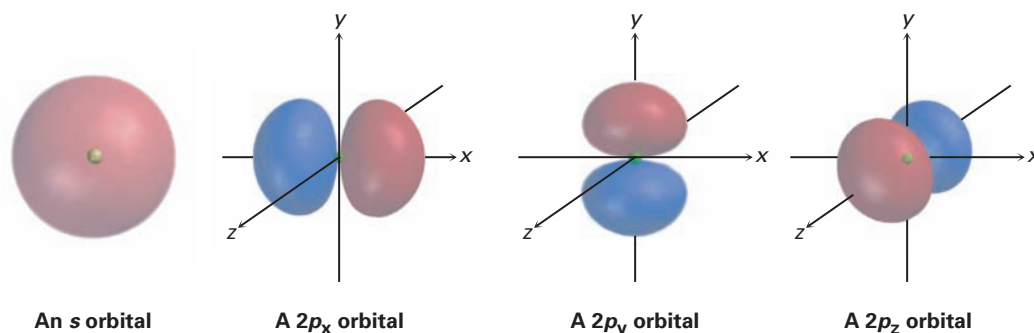
Orbitals are organized into different layers around the nucleus of successively larger size and energy. Different layers, or **electron shells,** contain different numbers and kinds of orbitals, and each orbital can be occupied by 2 electrons. The first shell contains only a single s orbital, denoted 1s, and thus holds only 2 electrons. The second shell contains an s orbital (designated 2s) and three mutually perpendicular p orbitals (each designated 2p) and thus holds a total of 8 electrons. The third shell contains an s orbital (3s), three p orbitals (3p), and five d orbitals (3d), for a total capacity of 18 electrons. These orbital groupings are shown in Figure 1.4.

Figure 1.4 The energy levels of electrons in an atom. The first shell holds a maximum of 2 electrons in one 1s orbital; the second shell holds a maximum of 8 electrons in one 2s and three 2p orbitals; the third shell holds a maximum of 18 electrons in one 3s, three 3p, and five 3d orbitals; and so on. The 2 electrons in each orbital are represented by up and down arrows, ↑↓. Although not shown, the energy level of the 4s orbital falls between 3p and 3d.
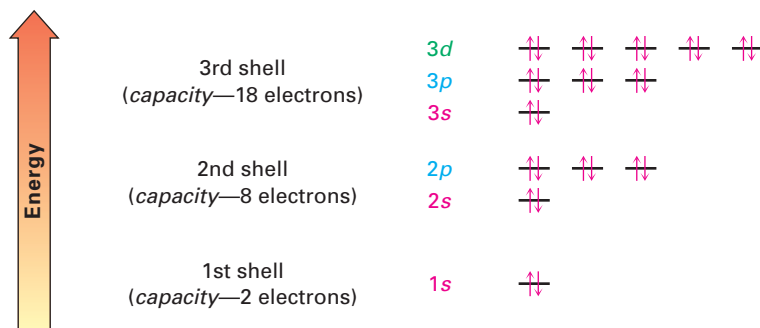
1.2 Atomic Structure: Electron Configurations

The lowest-energy arrangement, or **ground-state electron configuration,** of an atom is a listing of the orbitals that the atom's electrons occupy. We can predict this arrangement by following three rules.

RULE 1   The orbitals of lowest energy are filled first, according to the order 1s → 2s → 2p → 3s → 3p → 4s → 3d, as shown in Figure 1.4.

RULE 2   Only two electrons can occupy an orbital, and they must be of opposite *spin*. (Electrons act in some ways as if they were spinning on an axis, somewhat as the earth spins. This spin can have two orientations, denoted as up ↑ and down ↓.)

RULE 3   If two or more empty orbitals of equal energy are available, one electron occupies each with the spins parallel until all orbitals are half-full.

Some examples of how these rules apply are shown in Table 1.1. Hydrogen, for instance, has only one electron, which must occupy the lowest-energy

Table **1.1**		Ground-State Electron Configuration of Some Elements				
Element	Atomic number	Configuration	Element	Atomic number	Configuration	
Hydrogen	1	1s ⊥	Phosphorus	15	3p ⊥ ⊥ ⊥	
Carbon	6	2p ⊥ ⊥ —			3s ⊥⊥	
		2s ⊥⊥			2p ⊥⊥ ⊥⊥ ⊥⊥	
		1s ⊥⊥			2s ⊥⊥	
					1s ⊥⊥	

orbital. Thus, hydrogen has a $1s$ ground-state electron configuration. Carbon has six electrons and the ground-state electron configuration $1s^2\, 2s^2\, 2p^2$. Note that a superscript is used to represent the number of electrons in a particular orbital.

Worked Example 1.1

Assigning an Electron Configuration to an Element

Give the ground-state electron configuration of nitrogen.

Strategy   Find the atomic number of nitrogen to see how many electrons it has, and then apply the three rules to assign electrons into orbitals according to the energy levels given in Figure 1.4.

Solution   Nitrogen has atomic number 7 and thus has seven electrons. The first two electrons go into the lowest-energy orbital ($1s^2$), the next two go into the second-lowest-energy orbital ($2s^2$), and the remaining three go into the next-lowest-energy orbitals ($2p^3$), with one electron in each. Thus, the configuration of nitrogen is $1s^2\, 2s^2\, 2p^3$.

Problem 1.1   How many electrons does each of the following elements have in its outermost electron shell?

(a) Potassium   **(b)** Calcium   **(c)** Aluminum

Problem 1.2   Give the ground-state electron configuration of the following elements:

(a) Boron   **(b)** Phosphorus   **(c)** Oxygen   **(d)** Argon

1.3 Development of Chemical Bonding Theory

By the mid-1800s, the new science of chemistry was developing rapidly and chemists had begun to probe the forces holding molecules together. In 1858, August Kekulé and Archibald Couper independently proposed that, in all organic compounds, carbon is *tetravalent;* that is, it always forms four bonds when it joins other elements to form chemical compounds. Furthermore, said Kekulé, carbon atoms can bond to one another to form extended chains of linked atoms and chains can double back on themselves to form rings.

Although Kekulé and Couper were correct in describing the tetravalent nature of carbon, chemistry was still viewed in a two-dimensional way until 1874. In that year, Jacobus van't Hoff and Joseph Le Bel added a third dimension to our ideas about organic compounds. They proposed that the four bonds of carbon are not oriented randomly but have specific spatial directions. Van't Hoff went even further and suggested that the four atoms to which carbon is bonded sit at the corners of a regular tetrahedron, with carbon in the center.

A representation of a tetrahedral carbon atom is shown in Figure 1.5. Note the conventions used to show three-dimensionality: solid lines represent bonds in the plane of the page, the heavy wedged line represents a bond coming out of the page toward the viewer, and the dashed line represents a bond receding back behind the page away from the viewer. These representations will be used throughout this text.

Figure 1.5 A representation of van't Hoff's tetrahedral carbon atom. The solid lines represent bonds in the plane of the paper, the heavy wedged line represents a bond coming out of the plane of the page, and the dashed line represents a bond going back behind the plane of the page.

Bond receding into page

Bonds in plane of page

Bond coming out of plane

A regular tetrahedron

A tetrahedral carbon atom
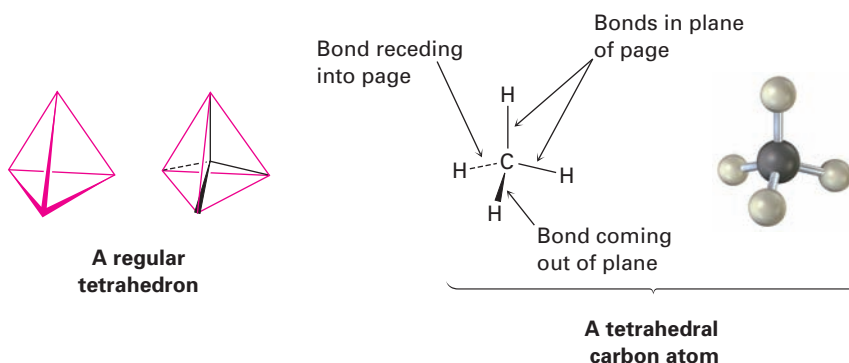
Problem 1.3 Draw a molecule of chloromethane, CH_3Cl, using solid, wedged, and dashed lines to show its tetrahedral geometry.

Problem 1.4 Convert the following molecular model of ethane, C_2H_6, into a structure that uses wedged, normal, and dashed lines to represent three-dimensionality.
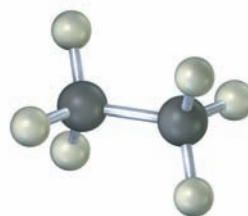
Ethane

1.4 The Nature of Chemical Bonds

Why do atoms bond together, and how can bonds be described electronically? The *why* question is relatively easy to answer: atoms bond together because the compound that results is more stable and lower in energy than the separate atoms. Energy (usually as heat) is always released and flows *out of* the chemical system when a bond forms. Conversely, energy must be put *into* the system to break a bond. Making bonds always releases energy, and breaking bonds always absorbs energy. The *how* question is more difficult. To answer it, we need to know more about the electronic properties of atoms.

We know through observation that eight electrons—an electron *octet*—in an atom's outermost shell, or **valence shell,** impart special stability to the noble-gas elements in group 8A of the periodic table: Ne (2 + 8); Ar (2 + 8 + 8); Kr (2 + 8 + 18 + 8). We also know that the chemistry of main-group elements is governed by their tendency to take on the electron configuration of the nearest noble gas. The alkali metals in group 1A, for example, achieve a noble-gas configuration by losing the single *s* electron from their valence shell to form a cation, while the halogens in group 7A achieve a noble-gas configuration by gaining a *p* electron to fill their valence shell and form an anion. The

resultant ions are held together in compounds like $Na^+ Cl^-$ by an electrostatic attraction that we call an *ionic bond.*

How, though, do elements near the middle of the periodic table form bonds? Look at methane, CH_4, the main constituent of natural gas, for example. The bonding in methane is not ionic because it would take too much energy for carbon ($1s^2 2s^2 2p^2$) to either gain or lose *four* electrons to achieve a noble-gas configuration. As a result, carbon bonds to other atoms, not by gaining or losing electrons, but by *sharing* them. Such a shared-electron bond, first proposed in 1916 by G. N. Lewis, is called a **covalent bond.** The neutral group of atoms held together by covalent bonds is called a **molecule**.

A simple way of indicating the covalent bonds in molecules is to use what are called *Lewis structures,* or **electron-dot structures**, in which the valence-shell electrons of an atom are represented as dots. Thus, hydrogen has one dot representing its $1s$ electron, carbon has four dots ($2s^2 2p^2$), oxygen has six dots ($2s^2 2p^4$), and so on. A stable molecule results whenever a noble-gas configuration is achieved for all the atoms—eight dots (an octet) for main-group atoms or two dots for hydrogen. Simpler still is the use of *Kekulé structures,* or **line-bond structures**, in which a two-electron covalent bond is indicated as a line drawn between atoms.

Electron-dot structures
(Lewis structures)

Line-bond structures
(Kekulé structures)

Methane
(CH_4)

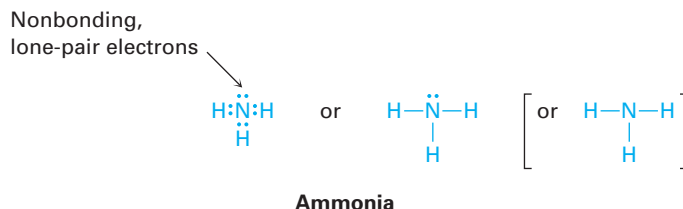Ammonia
(NH_3)

Water
(H_2O)

Methanol
(CH_3OH)
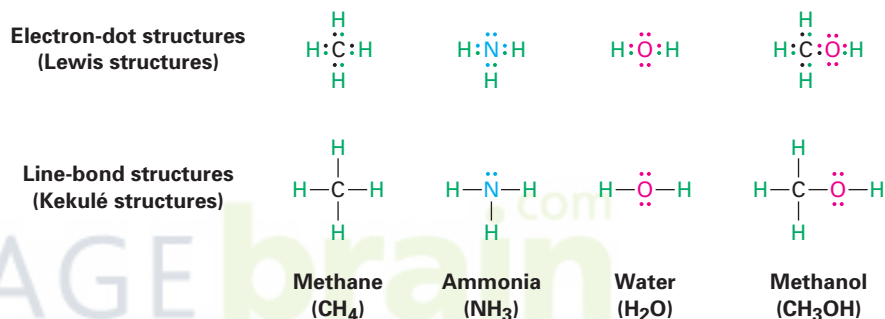
The number of covalent bonds an atom forms depends on how many additional valence electrons it needs to reach a noble-gas configuration. Hydrogen has one valence electron ($1s$) and needs one more to reach the helium configuration ($1s^2$), so it forms one bond. Carbon has four valence electrons ($2s^2 2p^2$) and needs four more to reach the neon configuration ($2s^2 2p^6$), so it forms four bonds. Nitrogen has five valence electrons ($2s^2 2p^3$), needs three more, and forms three bonds; oxygen has six valence electrons ($2s^2 2p^4$), needs two more, and forms two bonds; and the halogens have seven valence electrons, need one more, and form one bond.

One bond   Four bonds   Three bonds   Two bonds   One bond
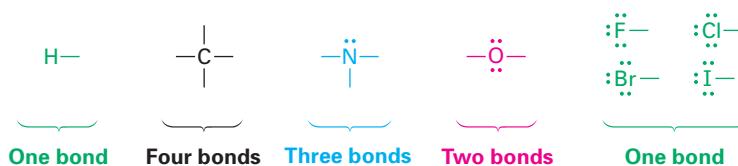
Valence electrons that are not used for bonding are called **lone-pair electrons**, or *nonbonding electrons.* The nitrogen atom in ammonia (NH_3), for instance, shares six valence electrons in three covalent bonds and has its

remaining two valence electrons in a nonbonding lone pair. As a time-saving shorthand, nonbonding electrons are often omitted when drawing line-bond structures, but you still have to keep them in mind since they're often crucial in chemical reactions.

Nonbonding, lone-pair electrons

$$H:\overset{..}{N}:H \quad \text{or} \quad H-\overset{\overset{..}{|}}{\underset{|}{N}}-H \quad \left[\text{or} \quad H-\overset{|}{\underset{|}{N}}-H \right]$$

Ammonia

Worked Example 1.2

Predicting the Number of Bonds Formed by an Atom

How many hydrogen atoms does phosphorus bond to in forming phosphine, $PH_?$?

Strategy   Identify the periodic group of phosphorus, and tell from that how many electrons (bonds) are needed to make an octet.

Solution   Phosphorus is in group 5A of the periodic table and has five valence electrons. It thus needs to share three more electrons to make an octet and therefore bonds to three hydrogen atoms, giving PH_3.

Worked Example 1.3

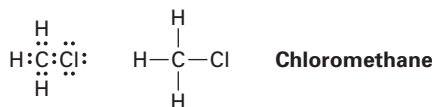**Drawing Electron-Dot and Line-Bond Structures**

Draw both electron-dot and line-bond structures for chloromethane, CH_3Cl.

Strategy   Remember that a bond—that is, a pair of shared electrons—is represented as a line between atoms.

Solution   Hydrogen has one valence electron, carbon has four valence electrons, and chlorine has seven valence electrons. Thus, chloromethane is represented as

$$H:\overset{\overset{..}{H}}{\underset{..}{\underset{H}{C}}}:\overset{..}{\underset{..}{Cl}}: \qquad H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-Cl \qquad \textbf{Chloromethane}$$

Problem 1.5   What are likely formulas for the following molecules?

(a) $CCl_?$ (b) $AlH_?$ (c) $CH_?Cl_2$ (d) $SiF_?$

Problem 1.6   Write both electron-dot and line-bond structures for the following molecules, showing all nonbonded electrons:

(a) $CHCl_3$, chloroform   (b) H_2S, hydrogen sulfide

(c) CH_3NH_2, methylamine

Problem 1.7   Why can't an organic molecule have the formula C_2H_7?

## 1.5 | Forming Covalent Bonds: Valence Bond Theory

How does electron sharing lead to bonding between atoms? According to **valence bond theory**, a covalent bond forms when two atoms approach each other closely and a singly occupied orbital on one atom *overlaps* a singly occupied orbital on the other atom. The electrons are now paired in the overlapping orbitals and are attracted to the nuclei of both atoms, thus bonding the atoms together. In the H_2 molecule, for example, the H–H bond results from the overlap of two singly occupied hydrogen 1s orbitals.
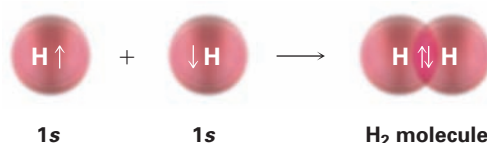
During the bond-forming reaction $2 \; H\cdot \rightarrow H_2$, 436 kJ/mol (104 kcal/mol) of energy is released. Because the product H_2 molecule has 436 kJ/mol less energy than the starting 2 H· atoms, we say that the product is *more stable* than the reactant and that the new H–H bond has a **bond strength** of 436 kJ/mol. In other words, we would have to put 436 kJ/mol of energy *into* the H–H bond to break the H_2 molecule apart into two H atoms. [For convenience, we'll generally give energies in both the SI unit kilojoules (kJ) and the older unit kilocalories (kcal): 1 kJ = 0.2390 kcal; 1 kcal = 4.184 kJ.]

How close are the two nuclei in the H_2 molecule? If they are too close, they will repel each other because both are positively charged, yet if they are too far apart, they won't be able to share the bonding electrons. Thus, there is an optimum distance between nuclei that leads to maximum stability (Figure 1.6). Called the **bond length**, this distance is 74 pm in the H_2 molecule. Every covalent bond has both a characteristic bond strength and bond length.

Figure 1.6 A plot of energy versus internuclear distance for two hydrogen atoms. The distance at the minimum energy point is the bond length.
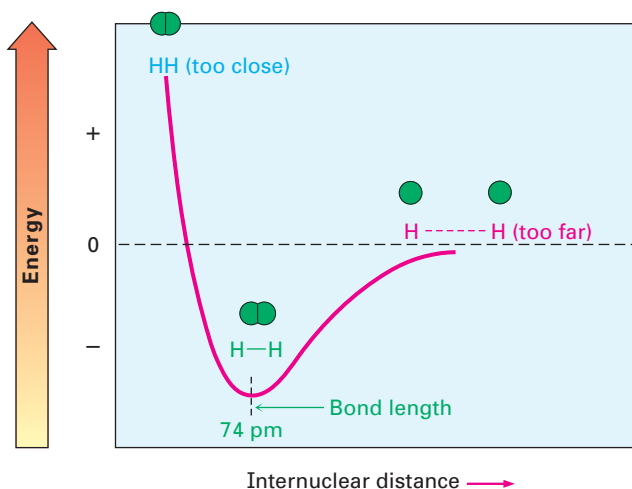
1.6 / sp^3 Hybrid Orbitals and the Structure of Methane

The bonding in the H_2 molecule is fairly straightforward, but the situation is more complicated in organic molecules with tetravalent carbon atoms. Take methane, CH_4, for instance. Carbon has four valence electrons ($2s^2\ 2p^2$) and forms four bonds. Because carbon uses two kinds of orbitals for bonding, $2s$ and $2p$, we might expect methane to have two kinds of C–H bonds. In fact, though, all four C–H bonds in methane are identical and are spatially oriented toward the corners of a regular tetrahedron (Figure 1.5). How can we explain this?

An answer was provided in 1931 by Linus Pauling, who proposed that an s orbital and three p orbitals can combine, or *hybridize*, to form four equivalent atomic orbitals with tetrahedral orientation. Shown in Figure 1.7, these tetrahedrally oriented orbitals are called **sp^3 hybrids**. Note that the superscript 3 in the name sp^3 tells how many of each type of atomic orbital combine to form the hybrid, not how many electrons occupy it.
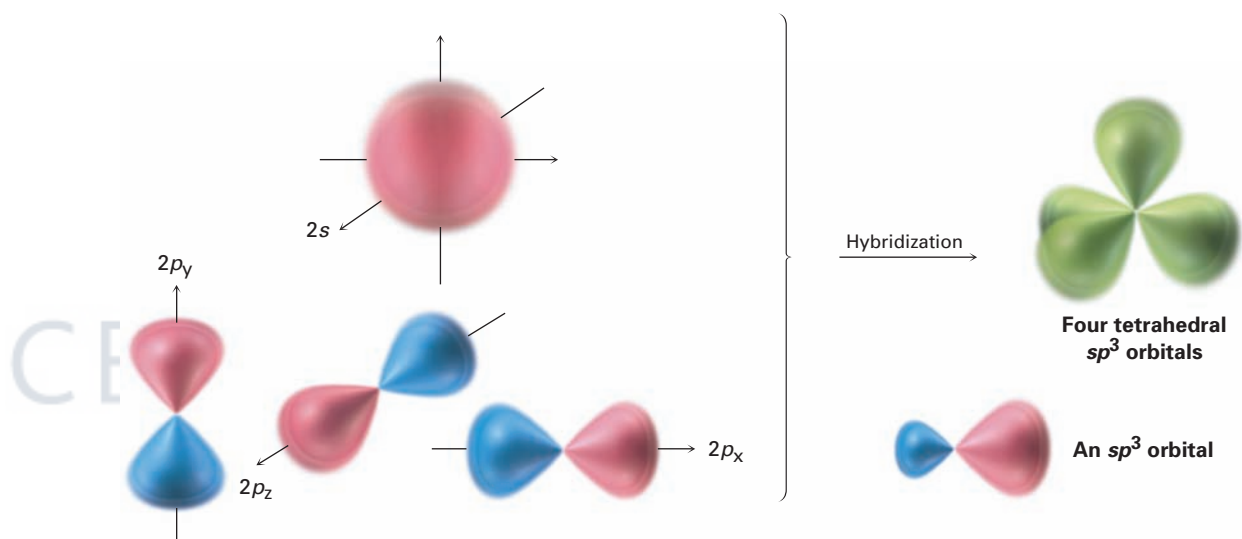

Figure 1.7 Four sp^3 hybrid orbitals (green), oriented to the corners of a regular tetrahedron, are formed by combination of an atomic s orbital (red) and three atomic p orbitals (red/blue). The sp^3 hybrids have two lobes and are unsymmetrical about the nucleus, giving them a directionality and allowing them to form strong bonds when they overlap an orbital from another atom.

The concept of hybridization explains how carbon forms four equivalent tetrahedral bonds but not why it does so. The shape of the hybrid orbital suggests the answer. When an s orbital hybridizes with three p orbitals, the resultant sp^3 hybrid orbitals are unsymmetrical about the nucleus. One of the two lobes is much larger than the other (Figure 1.7) and can therefore overlap better with another orbital when it forms a bond. As a result, sp^3 hybrid orbitals form stronger bonds than do unhybridized s or p orbitals.

The asymmetry of sp^3 orbitals arises because, as noted in Section 1.1, the two lobes of a p orbital have different algebraic signs, $+$ and $-$. Thus, when a p orbital hybridizes with an s orbital, the positive p lobe adds to the s orbital

but the negative p lobe subtracts from the s orbital. The resultant hybrid orbital is therefore unsymmetrical about the nucleus and is strongly oriented in one direction.

When each of the four identical sp^3 hybrid orbitals of a carbon atom overlaps with the $1s$ orbital of a hydrogen atom, four identical C–H bonds are formed and methane results. Each C–H bond in methane has a strength of 439 kJ/mol (105 kcal/mol) and a length of 109 pm. Because the four bonds have a specific geometry, we also can define a property called the **bond angle**. The angle formed by each H—C—H is 109.5°, the so-called tetrahedral angle. Methane thus has the structure shown in Figure 1.8.

Figure 1.8 The structure of methane, showing its 109.5° bond angles.
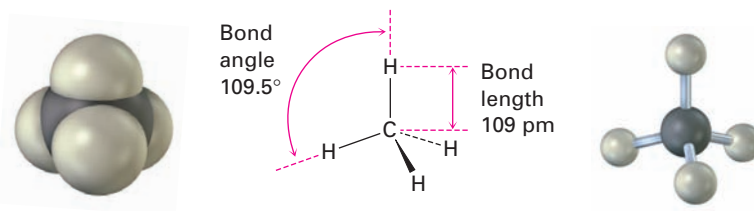
Problem 1.8   Draw a tetrahedral representation of tetrachloromethane, CCl_4, using the standard convention of solid, dashed, and wedged lines.

Problem 1.9   Why do you think a C–H bond (109 pm) is longer than an H–H bond (74 pm)?

# 1.7 *sp3* Hybrid Orbitals and the Structure of Ethane

The same kind of orbital hybridization that accounts for the methane structure also accounts for the bonding together of carbon atoms into chains and rings to make possible many millions of organic compounds. Ethane, C_2H_6, is the simplest molecule containing a carbon–carbon bond.
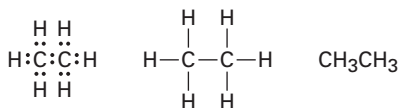
Some representations of ethane

We can picture the ethane molecule by imagining that the two carbon atoms bond to each other by overlap of an sp^3 hybrid orbital from each (Figure 1.9). The remaining three sp^3 hybrid orbitals of each carbon overlap with the $1s$ orbitals of three hydrogens to form the six C–H bonds. The C–H bonds in ethane are similar to those in methane, although a bit weaker—421 kJ/mol (101 kcal/mol) for ethane versus 439 kJ/mol for methane. The C–C bond is 154 pm long and has a strength of 377 kJ/mol (90 kcal/mol). All the bond angles of ethane are near, although not exactly at, the tetrahedral value of 109.5°.

Figure 1.9 The structure of ethane. The carbon–carbon bond is formed by overlap of two carbon sp^3 hybrid orbitals. For clarity, the smaller lobes of the hybrid orbitals are not shown.

sp^3 carbon sp^3 carbon sp^3–sp^3 σ bond
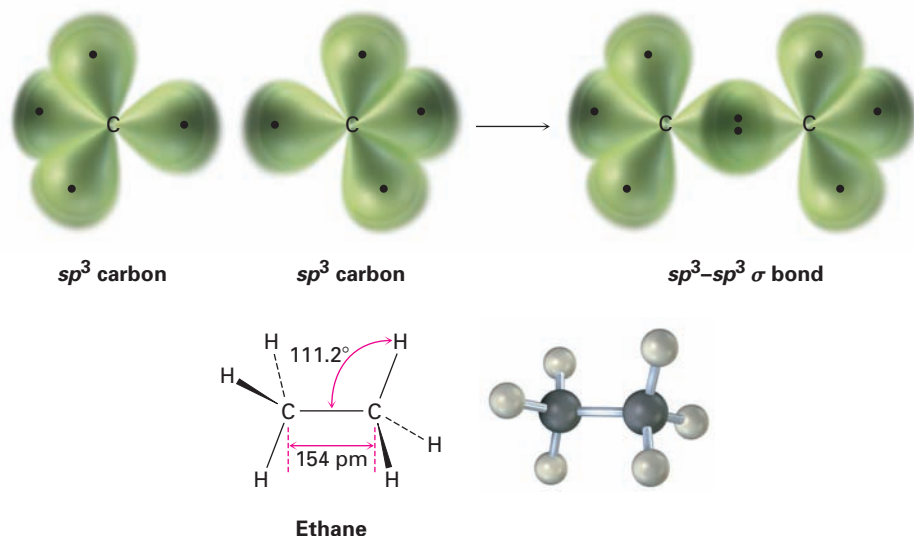
Ethane

Problem 1.10   Draw a line-bond structure for propane, $CH_3CH_2CH_3$. Predict the value of each bond angle, and indicate the overall shape of the molecule.

1.8 Other Kinds of Hybrid Orbitals: sp^2 and sp

The bonds we've seen in methane and ethane are called *single bonds* because they result from the sharing of one electron pair between bonded atoms. It was recognized more than 100 years ago, however, that in some molecules carbon atoms can also form a *double bond* by sharing *two* electron pairs between atoms or a *triple bond* by sharing *three* electron pairs. Ethylene, for instance, has the structure $H_2C=CH_2$ and contains a carbon–carbon double bond, while acetylene has the structure $HC\equiv CH$ and contains a carbon–carbon triple bond. How are multiple bonds described by valence bond theory?

When discussing sp^3 hybrid orbitals in Section 1.6, we said that the $2s$ orbital of carbon combines with all three $2p$ orbitals to form four equivalent sp^3 hybrids. Imagine instead, however, that the $2s$ orbital combines with only one or two of the three available $2p$ orbitals. If the $2s$ orbital combines with only two $2p$ orbitals, three **sp^2 hybrids** result and one unhybridized $2p$ orbital remains unchanged. If the $2s$ orbital combines with only one $2p$ orbital, two **sp hybrids** result and two unhybridized $2p$ orbitals remain unchanged.

Like sp^3 hybrids, sp^2 and sp hybrid orbitals are unsymmetrical about the nucleus and are strongly oriented in a specific direction so they can form strong bonds. In an sp^2-hybridized carbon atom, for instance, the three sp^2 orbitals lie in a plane at angles of 120° to one another, with the remaining p orbital perpendicular to the sp^2 plane (Figure 1.10a). In an sp-hybridized carbon atom, the two sp orbitals are oriented 180° apart, with the remaining two p orbitals perpendicular both to the sp hybrids and to each other (Figure 1.10b).

Figure 1.10 **(a)** An *sp²*-hybridized carbon. The three equivalent *sp²* hybrid orbitals (green) lie in a plane at angles of 120° to one another, and a single unhybridized *p* orbital (red/blue) is perpendicular to the *sp²* plane. **(b)** An *sp*-hybridized carbon atom. The two *sp* hybrid orbitals (green) are oriented 180° away from each other, perpendicular to the two remaining *p* orbitals (red/blue).

Side view

Top view

One *sp* hybrid   Another *sp* hybrid
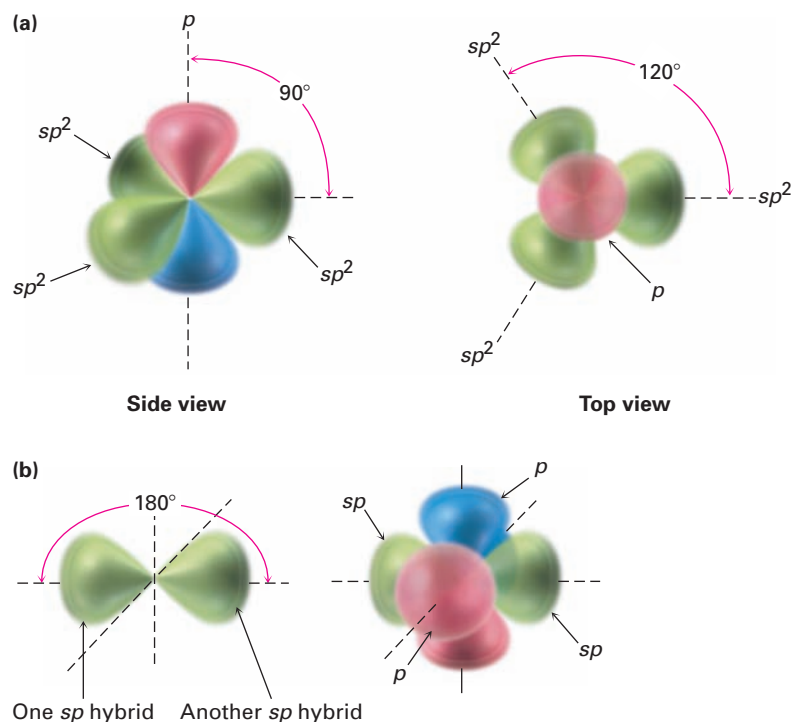
When two sp^2-hybridized carbon atoms approach each other, they form a strong bond by sp^2–sp^2 head-on overlap. At the same time, the unhybridized *p* orbitals interact by *sideways* overlap to form a second bond. Head-on overlap gives what is called a **sigma (σ) bond**, while sideways overlap gives a **pi (π) bond**. The combination of sp^2–sp^2 σ overlap and $2p$–$2p$ π overlap results in the net sharing of two electron pairs and the formation of a carbon–carbon double bond (Figure 1.11). Note that the electrons in a σ bond occupy the region centered between nuclei, while the electrons in a π bond occupy regions on either side of a line drawn between nuclei.

Figure 1.11 The structure of ethylene. Orbital overlap of two *sp²*-hybridized carbons forms a carbon–carbon double bond. One part of the double bond results from σ (head-on) overlap of *sp²* orbitals (green), and the other part results from π (sideways) overlap of unhybridized *p* orbitals (red/blue). The π bond has regions of electron density above and below a line drawn between nuclei.

sp² carbon   *sp²* carbon   Carbon–carbon double bond
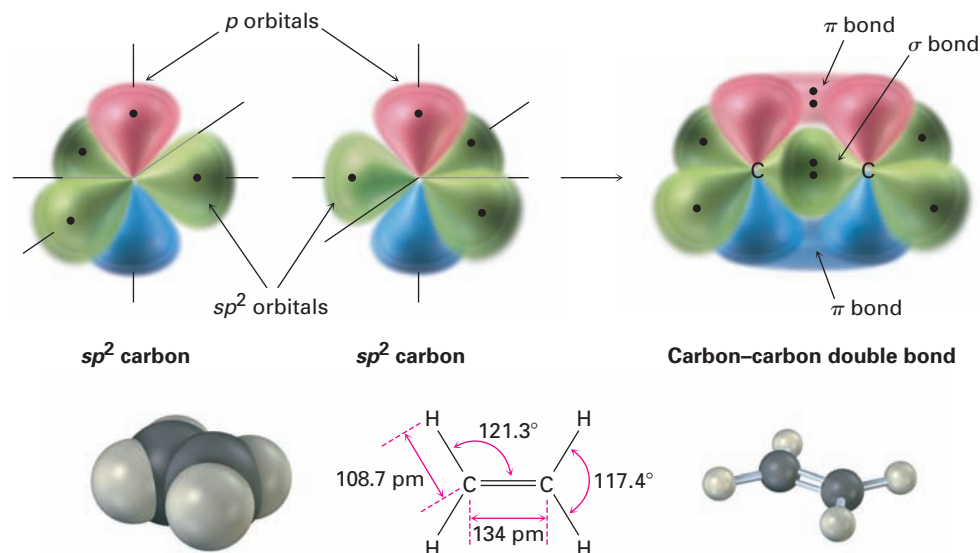
To complete the structure of ethylene, four hydrogen atoms form σ bonds to the remaining four carbon sp^2 orbitals. The resultant ethylene molecule has a planar structure with H–C–H and H–C=C bond angles of approximately 120°. As you might expect, the double bond in ethylene is both shorter and stronger than the single bond in ethane because it has four electrons bonding the nuclei together rather than two. Ethylene has a C=C bond length of 134 pm and a strength of 728 kJ/mol (174 kcal/mol) versus a C–C length of 154 pm and a strength of 377 kJ/mol for ethane. The carbon–carbon double bond is less than twice as strong as a single bond because the sideways overlap in the π part of the double bond is less favorable than the head-on overlap in the σ part.

Just as the C=C double bond in ethylene consists of two parts, a σ part formed by head-on overlap of sp^2 hybrid orbitals and a π part formed by sideways overlap of unhybridized p orbitals, the C≡C triple bond in acetylene consists of three parts. When two sp-hybridized carbon atoms approach each other, sp hybrid orbitals from each overlap head-on to form a strong sp–sp σ bond. At the same time, the p_z orbitals from each carbon form a p_z–p_z π bond by sideways overlap, and the p_y orbitals overlap similarly to form a p_y–p_y π bond. The net effect is the formation of one σ bond and two π bonds— a carbon–carbon triple bond. Each of the remaining sp hybrid orbitals forms a σ bond to hydrogen to complete the acetylene molecule (Figure 1.12).

Figure 1.12 The structure of acetylene. The two sp-hybridized carbon atoms are joined by one sp–sp σ bond and two p–p π bonds.
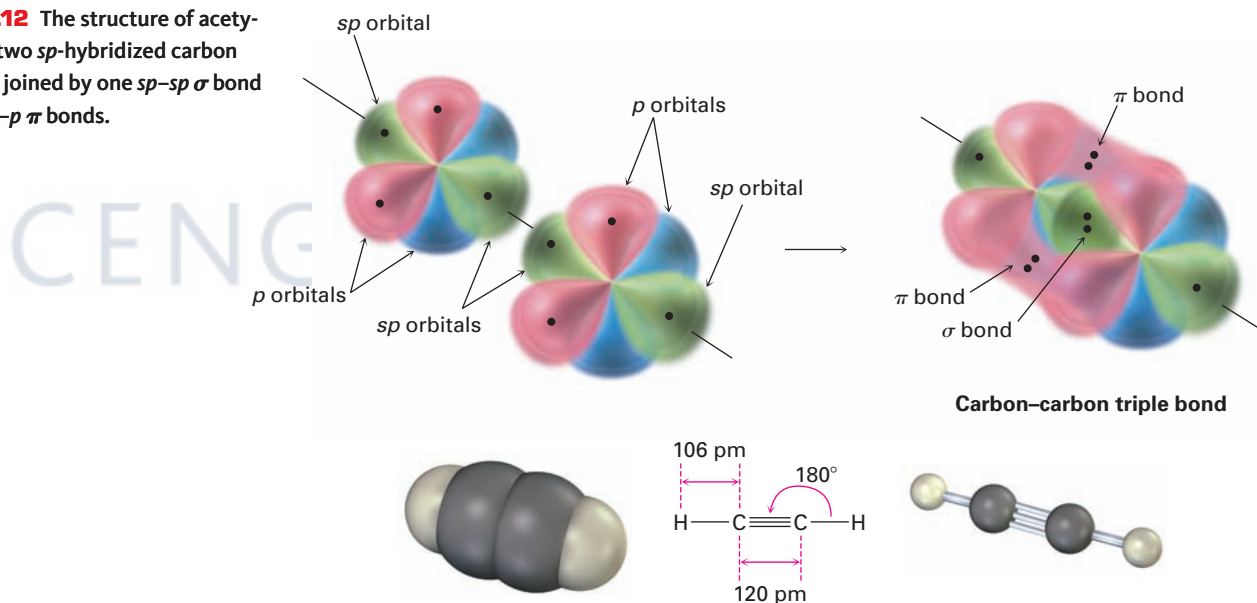
As suggested by sp hybridization, acetylene is a linear molecule with H–C≡C bond angles of 180°. The C≡C bond has a length of 120 pm and a strength of about 965 kJ/mol (231 kcal/mol), making it the shortest and strongest of any carbon–carbon bond.

Worked Example 1.4

Drawing Electron-Dot and Line-Bond Structures

Formaldehyde, CH_2O, contains a carbon–*oxygen* double bond. Draw electron-dot and line-bond structures of formaldehyde, and indicate the hybridization of the carbon atom.

Strategy   We know that hydrogen forms one covalent bond, carbon forms four, and oxygen forms two. Trial and error, combined with intuition, must be used to fit the atoms together.

Solution   There is only one way that two hydrogens, one carbon, and one oxygen can combine:

Electron-dot structure   **Line-bond structure**
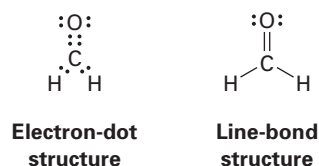
Like the carbon atoms in ethylene, the carbon atom in formaldehyde is sp^2-hybridized.

Problem 1.11   Draw both an electron-dot and a line-bond structure for acetaldehyde, CH_3CHO.

Problem 1.12   Draw a line-bond structure for propene, $CH_3CH=CH_2$. Indicate the hybridization of each carbon, and predict the value of each bond angle.

Problem 1.13   Draw a line-bond structure for propyne, $CH_3C\equiv CH$. Indicate the hybridization of each carbon, and predict a value for each bond angle.

Problem 1.14   Draw a line-bond structure for buta-1,3-diene, $H_2C=CH-CH=CH_2$. Indicate the hybridization of each carbon, and predict a value for each bond angle.

Problem 1.15   Convert the following molecular model of aspirin into a line-bond structure, and identify the hybridization of each carbon atom (gray = C, red = O, ivory = H).
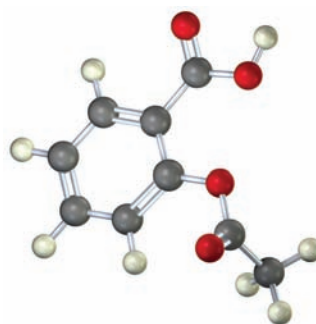
Aspirin (acetylsalicylic acid)

1.9 Polar Covalent Bonds: Electronegativity

Up to this point, we've treated chemical bonds as either ionic or covalent. The bond in sodium chloride, for instance, is ionic. Sodium transfers an electron to chlorine to give Na^+ and Cl^- ions, which are held together in the solid by electrostatic attractions between the unlike charges. The C–C bond in ethane, however, is covalent. The two bonding electrons are shared equally by the two

equivalent carbon atoms, resulting in a symmetrical electron distribution in the bond. Most bonds, however, are neither fully ionic nor fully covalent but are somewhere between the two extremes. Such bonds are called **polar covalent bonds**, meaning that the bonding electrons are attracted more strongly by one atom than the other so that the electron distribution between atoms is not symmetrical (Figure 1.13).

Figure 1.13 The continuum in bonding from covalent to ionic is a result of an unequal distribution of bonding electrons between atoms. The symbol δ (lowercase Greek delta) means *partial* charge, either partial positive ($\delta+$) for the electron-poor atom or partial negative ($\delta-$) for the electron-rich atom.
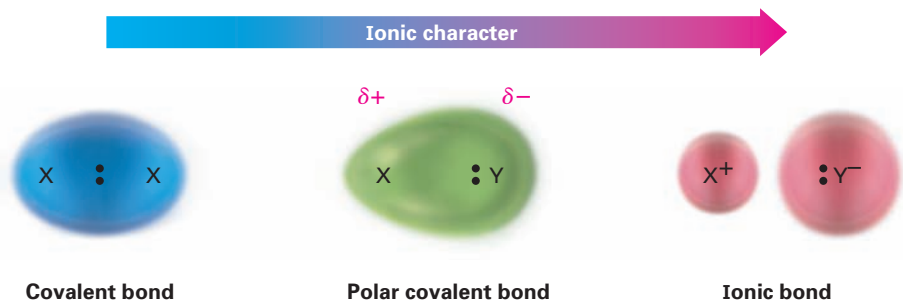
Bond polarity is due to differences in **electronegativity (EN)**, the intrinsic ability of an atom to attract the shared electrons in a covalent bond. As shown in Figure 1.14, electronegativities are based on an arbitrary scale, with fluorine the most electronegative (EN = 4.0) and cesium the least (EN = 0.7). Metals on the left side of the periodic table attract electrons weakly and have lower electronegativities, while oxygen, nitrogen, and halogens on the right side of the periodic table attract electrons strongly and have higher electronegativities. Carbon, the most important element in organic compounds, has an electronegativity value of 2.5.

Figure 1.14 Electronegativity values and trends. Electronegativity generally increases from left to right across the periodic table and decreases from top to bottom. The values are on an arbitrary scale, with F = 4.0 and Cs = 0.7. Elements in orange are the most electronegative, those in yellow are medium, and those in green are the least electronegative.

As a rough guide, a bond between atoms with similar electronegativities is covalent, a bond between atoms whose electronegativities differ by less than 2 units is polar covalent, and a bond between atoms whose electronegativities differ by 2 units or more is largely ionic. A carbon–hydrogen bond, for instance, is relatively nonpolar because carbon and hydrogen have similar electronegativities. A bond between carbon and a *more* electronegative element such as oxygen or chlorine, however, is polar covalent. The electrons in such a bond are drawn away from carbon toward the more electronegative atom, leaving the carbon with a partial positive charge, denoted $\delta+$, and leaving the more electronegative atom with a partial

negative charge, denoted $\delta-$ (δ is the lowercase Greek letter delta). An example is the C–O bond in methanol, CH_3OH (Figure 1.15a).

A bond between carbon and a *less* electronegative element is polarized so that carbon bears a partial negative charge and the other atom bears a partial positive charge. An example is the C–Li bond in methyllithium, CH_3Li (Figure 1.15b).

Figure 1.15 **(a)** Methanol, CH_3OH, has a polar covalent C–O bond, and **(b)** methyllithium, CH_3Li, has a polar covalent C–Li bond. The computer-generated representations, called electrostatic potential maps, use color to show calculated charge distributions, ranging from red (electron-rich; $\delta-$) to blue (electron-poor; $\delta+$).

(a)

Oxygen: EN = 3.5
Carbon: EN = 2.5

Difference = 1.0

Methanol

(b)

Carbon: EN = 2.5
Lithium: EN = 1.0

Difference = 1.5
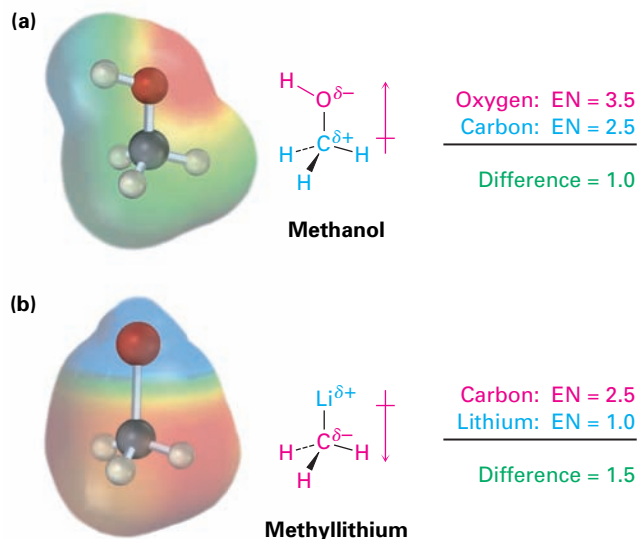
Methyllithium

Note in the representations of methanol and methyllithium in Figure 1.15 that a crossed arrow $\longmapsto$ is used to indicate the direction of bond polarity. By convention, *electrons are displaced in the direction of the arrow*. The tail of the arrow (which looks like a plus sign) is electron-poor ($\delta+$), and the head of the arrow is electron-rich ($\delta-$).

Note also in Figure 1.15 that charge distributions in a molecule can be displayed visually with what are called *electrostatic potential maps,* which use color to indicate electron-rich (red) and electron-poor (blue) regions. In methanol, oxygen carries a partial negative charge and is colored red, while the carbon and hydrogen atoms carry partial positive charges and are colored blue-green. In methyllithium, lithium carries a partial positive charge (blue), while carbon and the hydrogen atoms carry partial negative charges (red). Electrostatic potential maps are useful because they show at a glance the electron-rich and electron-poor atoms in molecules. We'll make frequent use of these maps throughout the text and will see how electronic structure often correlates with chemical reactivity.

When speaking of an atom's ability to polarize a bond, we often use the term *inductive effect*. An **inductive effect** is simply the shifting of electrons in a σ bond in response to the electronegativity of nearby atoms. Metals, such as lithium and magnesium, inductively donate electrons, whereas reactive nonmetals, such as oxygen and nitrogen, inductively withdraw electrons. Inductive effects play a major role in understanding chemical reactivity, and we'll use them many times throughout this text to explain a variety of chemical phenomena.

Worked Example 1.5

Predicting the Polarity of Bonds

Predict the extent and direction of polarization of the O–H bonds in H_2O.

Strategy   Look at the electronegativity table in Figure 1.14 to see which atoms attract electrons more strongly.

Solution   Oxygen (electronegativity = 3.5) is more electronegative than hydrogen (electronegativity = 2.1) according to Figure 1.14, and it therefore attracts electrons more strongly. The difference in electronegativities ($3.5 - 2.1 = 1.4$) implies that an O–H bond is strongly polarized.
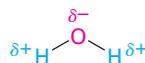
Problem 1.16   Which element in each of the following pairs is more electronegative?
(a) Li or H   **(b)** Be or Br   **(c)** Cl or I

Problem 1.17   Use the $\delta+/\delta-$ convention to indicate the direction of expected polarity for each of the bonds shown:
(a) H_3C—Br   **(b)** H_3C—NH_2 **(c)** H_2N—H
(d) H_3C—SH   **(e)** H_3C—MgBr   **(f)** H_3C—F

Problem 1.18   Order the bonds in the following compounds according to their increasing ionic character: CCl_4, $MgCl_2$, $TiCl_3$, Cl_2O.

Problem 1.19   Look at the following electrostatic potential map of chloromethane, and tell the direction of polarization of the C–Cl bond:

Chloromethane
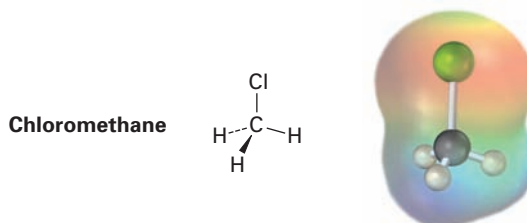
1.10 Acids and Bases: The Brønsted–Lowry Definition

A further important concept related to electronegativity and bond polarity is that of *acidity* and *basicity*. We'll soon see that the acid–base behavior of organic molecules helps explain much of their chemistry. You may recall from a course in general chemistry that two definitions of acidity are frequently used: the *Brønsted–Lowry definition* and the *Lewis definition*. Let's look at the Brønsted–Lowry definition first.

A **Brønsted–Lowry acid** is a substance that donates a hydrogen ion (H^+), and a **Brønsted–Lowry base** is a substance that accepts a hydrogen ion. (The name *proton* is often used as a synonym for H^+ because loss of the valence electron from a neutral hydrogen atom leaves only the hydrogen nucleus—a proton.) When hydrogen chloride gas dissolves in water, for instance, HCl donates a proton and a water molecule accepts the proton, yielding hydronium ion (H_3O^+) and chloride ion (Cl^-). Chloride ion, the product that results when the acid HCl loses a proton, is called the **conjugate base** of the acid, and H_3O^+, the product that results when the base H_2O gains a proton, is called the **conjugate acid** of the base.

H—Cl	+	H—O—H	⟶	H—O⁺—H (H)	+	Cl⁻
Acid		**Base**		**Conjugate acid**		**Conjugate base**
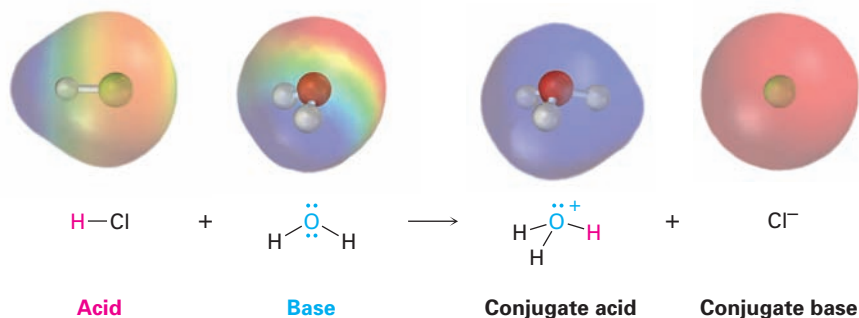
Acids differ in their ability to donate H^+. Stronger acids, such as HCl, react almost completely with water, whereas weaker acids, such as acetic acid (CH_3CO_2H), react only slightly. The exact strength of a given acid HA in water solution can be expressed by its **acidity constant, K_a**. Remember from general chemistry that the concentration of solvent is ignored in the equilibrium expression and that brackets [ ] around a substance refer to the concentration of the enclosed species in moles per liter.

$$HA + H_2O \rightleftharpoons A^- + H_3O^+$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$
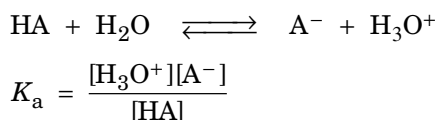
Stronger acids have their equilibria toward the right and thus have larger acidity constants; weaker acids have their equilibria toward the left and have smaller acidity constants. The range of K_a values for different acids is enormous, running from about 10^{15} for the strongest acids to about 10^{-60} for the weakest. The common inorganic acids such as H_2SO_4, HNO_3, and HCl have K_a's in the range 10^2 to 10^9, while many organic acids have K_a's in the range 10^{-5} to 10^{-15}. As you gain more experience, you'll develop a rough feeling for which acids are "strong" and which are "weak" (remembering that the terms are always relative).

Acid strengths are normally given using pK_a values rather than K_a values, where the **pK_a** is the negative common logarithm of the K_a.

$$pK_a = -\log K_a$$

A *stronger acid* (larger K_a) has a *smaller* pK_a, and a *weaker acid* (smaller K_a) has a *larger* pK_a. Table 1.2 lists the pK_a's of some common acids in order of their strength.

Table **1.2**		Relative Strengths of Some Common Acids and Their Conjugate Bases			
	Acid	Name	pK_a	Conjugate base	Name
Weaker acid	CH_3CH_2OH	Ethanol	16.00	$CH_3CH_2O^-$	Ethoxide ion	**Stronger base**
	H_2O	Water	15.74	HO^-	Hydroxide ion	
	HCN	Hydrocyanic acid	9.31	CN^-	Cyanide ion	
	$H_2PO_4^-$	Dihydrogen phosphate ion	7.21	HPO_4^{2-}	Hydrogen phosphate ion	
	CH_3CO_2H	Acetic acid	4.76	$CH_3CO_2^-$	Acetate ion	
	H_3PO_4	Phosphoric acid	2.16	$H_2PO_4^-$	Dihydrogen phosphate ion	
	HNO_3	Nitric acid	−1.3	NO_3^-	Nitrate ion	
Stronger acid	HCl	Hydrochloric acid	−7.0	Cl^-	Chloride ion	**Weaker base**

Notice that the pK_a value shown in Table 1.2 for water is 15.74, which results from the following calculation. Because water is both the acid and the solvent, the equilibrium expression is

$$H_2O + H_2O \rightleftharpoons OH^- + H_3O^+$$
$$\text{(acid)} \quad \text{(solvent)}$$
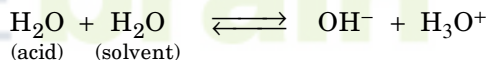
$$K_a = \frac{[H_3O^+][A^-]}{[HA]} = \frac{[H_3O^+][OH^-]}{[H_2O]} = \frac{[1.0 \times 10^{-7}][1.0 \times 10^{-7}]}{[55.4]} = 1.8 \times 10^{-16}$$

$$pK_a = 15.74$$

The numerator in this expression is the so-called ion-product constant for water, $K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}$, and the denominator is the molar concentration of pure water, $[H_2O] = 55.4$ M at 25 °C. The calculation is artificial in that the concentration of "solvent" water is ignored while the concentration of "acid" water is not, but it is nevertheless useful in allowing us to make a comparison of water with other weak acids on a similar footing.

Notice also in Table 1.2 that there is an inverse relationship between the acid strength of an acid and the base strength of its conjugate base. A *strong* acid yields a *weak* conjugate base, and a *weak* acid yields a *strong* conjugate base. To understand this inverse relationship, think about what is happening to the acidic hydrogen in an acid–base reaction: a strong acid is one that loses H^+ easily, meaning that its conjugate base holds the H^+ weakly and is therefore a weak base. A weak acid is one that loses H^+ with difficulty, meaning that its conjugate base *does* hold the proton tightly and is therefore a strong base. The fact that HCl is a strong acid, for example, means that Cl^- does not hold H^+ tightly and is thus a weak base. Water, on the other hand, is a weak acid, meaning that OH^- holds H^+ tightly and is a strong base.

A proton always goes *from* the stronger acid *to* the stronger base in an acid–base reaction. That is, an acid donates a proton to the conjugate base of any acid with a larger pK_a, and the conjugate base of an acid removes a proton from any acid with a smaller pK_a. For example, the data in Table 1.2 indicate that OH^- reacts with acetic acid, CH_3CO_2H, to yield acetate ion, $CH_3CO_2^-$, and H_2O. Because water ($pK_a = 15.74$) is a weaker acid than acetic acid ($pK_a = 4.76$), hydroxide ion holds a proton more tightly than acetate ion does.

| Acetic acid ($pK_a = 4.76$) | Hydroxide ion | Acetate ion | Water ($pK_a = 15.74$) |
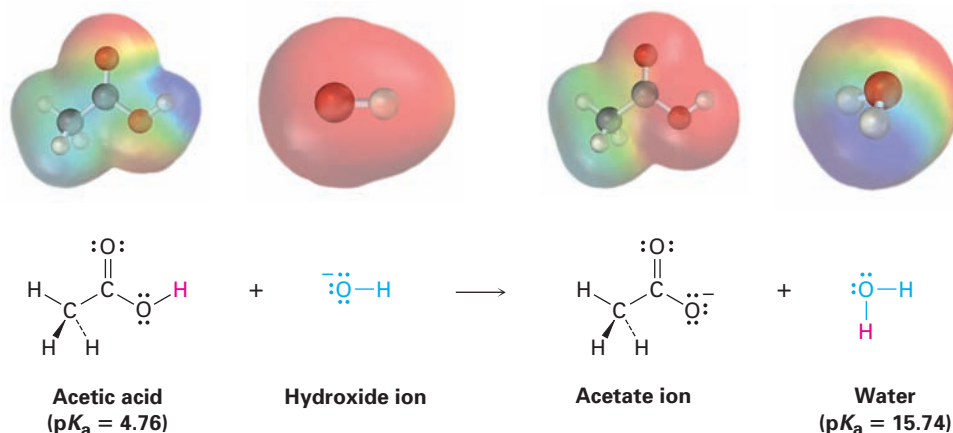
Another way to predict acid–base reactivity is to remember that the product conjugate acid in an acid–base reaction must be weaker and less reactive than the starting acid and that the product conjugate base must be weaker and less reactive than the starting base. In the reaction of acetic acid with hydroxide ion, for example, the product conjugate acid (H_2O) is weaker than the starting acid (CH_3CO_2H) and the product conjugate base ($CH_3CO_2^-$) is weaker than the starting base (OH^-).

$$CH_3COH \;+\; HO^- \;\rightleftharpoons\; HOH \;+\; CH_3CO^-$$

| Stronger acid | Stronger base | Weaker acid | Weaker base |
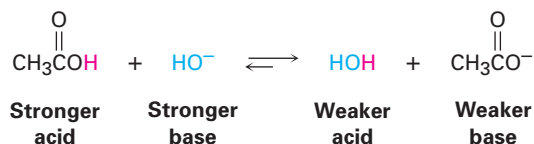
Worked Example 1.6

Predicting Acid–Base Reactions

Water has $pK_a = 15.74$, and acetylene has $pK_a = 25$. Which of the two is more acidic? Will hydroxide ion react with acetylene?

$$H-C\equiv C-H \;+\; OH^- \overset{?}{\longrightarrow} H-C\equiv C\mathbf{:}^- \;+\; H_2O$$
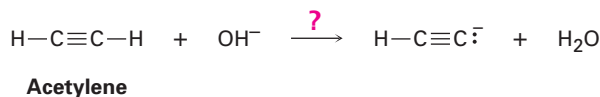
Acetylene

Strategy   In comparing two acids, the one with the smaller pK_a is stronger. Thus, water is a stronger acid than acetylene.

Solution   Because water loses a proton more easily than acetylene, the HO^- ion has less affinity for a proton than the $HC\equiv C\mathbf{:}^-$ ion. In other words, the anion of acetylene is a stronger base than hydroxide ion, and the reaction will not proceed as written.

Worked Example 1.7

Calculating K_a from pK_a

Butanoic acid, the substance responsible for the odor of rancid butter, has pK_a = 4.82. What is its K_a?

Strategy

Since pK_a is the negative logarithm of K_a, it's necessary to use a calculator with an ANTILOG or INV LOG function. Enter the value of the pK_a (4.82), change the sign (–4.82), and then find the antilog (1.5 × 10^{-5}).

Solution

$K_a = 1.5 \times 10^{-5}$

Problem 1.20

Formic acid, HCO_2H, has pK_a = 3.75, and picric acid, $C_6H_3N_3O_7$, has pK_a = 0.38.
(a) What is the K_a of each?
(b) Which is stronger, formic acid or picric acid?

Problem 1.21

Amide ion, H_2N^-, is a stronger base than hydroxide ion, HO^-. Which is the stronger acid, H_2N—H (ammonia) or HO—H (water)? Explain.

Problem 1.22

Is either of the following reactions likely to take place according to the pK_a data in Table 1.2?
(a) $HCN + CH_3CO_2^-\ Na^+ \longrightarrow Na^+\ ^-CN + CH_3CO_2H$
(b) $CH_3CH_2OH + Na^+\ ^-CN \longrightarrow CH_3CH_2O^-\ Na^+ + HCN$

1.11 Organic Acids and Organic Bases

Many of the reactions we'll be seeing in future chapters, including essentially all biological reactions, involve organic acids and organic bases. Organic acids are characterized by the presence of a positively polarized hydrogen atom (blue in electrostatic potential maps) and are of two main kinds: those acids such as methanol and acetic acid that contain a hydrogen atom bonded to an electronegative oxygen atom (O—H) and those such as acetone that contain a hydrogen atom bonded to a carbon atom next to a C=O double bond (O=C—C—H). We'll see the reasons for this behavior in Chapters 8 and 11.

Some organic acids

Methanol
(pK_a = 15.54)

Acetic acid
(pK_a = 4.76)

Acetone
(pK_a = 19.3)
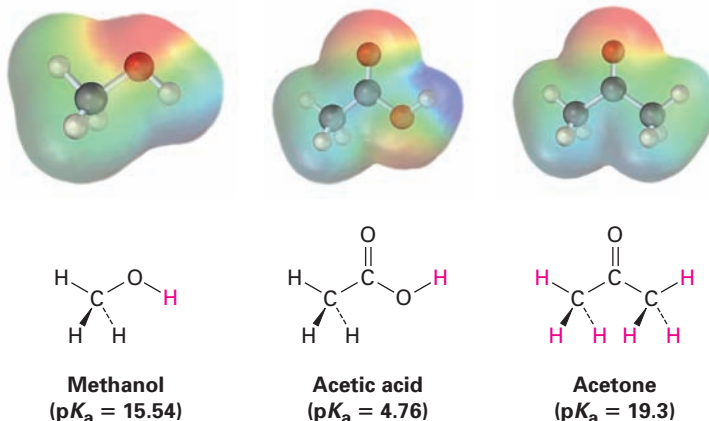
Compounds called *carboxylic acids,* which contain the $-CO_2H$ grouping, are particularly common. They occur abundantly in all living organisms and are involved in almost all metabolic pathways. Acetic acid, pyruvic acid, and citric acid are examples.

Acetic acid   **Pyruvic acid**   **Citric acid**
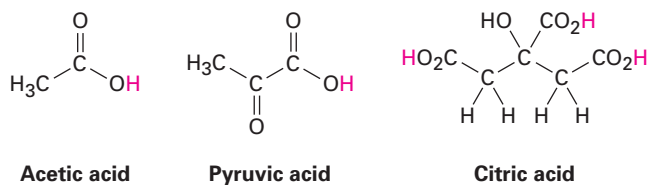
Organic bases are characterized by the presence of an atom (reddish in electrostatic potential maps) with a lone pair of electrons that can bond to H^+. Nitrogen-containing compounds such as methylamine are the most common organic bases, but oxygen-containing compounds can also act as bases when reacting with a sufficiently strong acid. Note that some oxygen-containing compounds can act as both acids and bases depending on the circumstances, just as water can. Methanol and acetone, for instance, act as *acids* when they donate a proton but act as bases when their oxygen atom accepts a proton.

Some organic bases

Methylamine   **Methanol**   **Acetone**
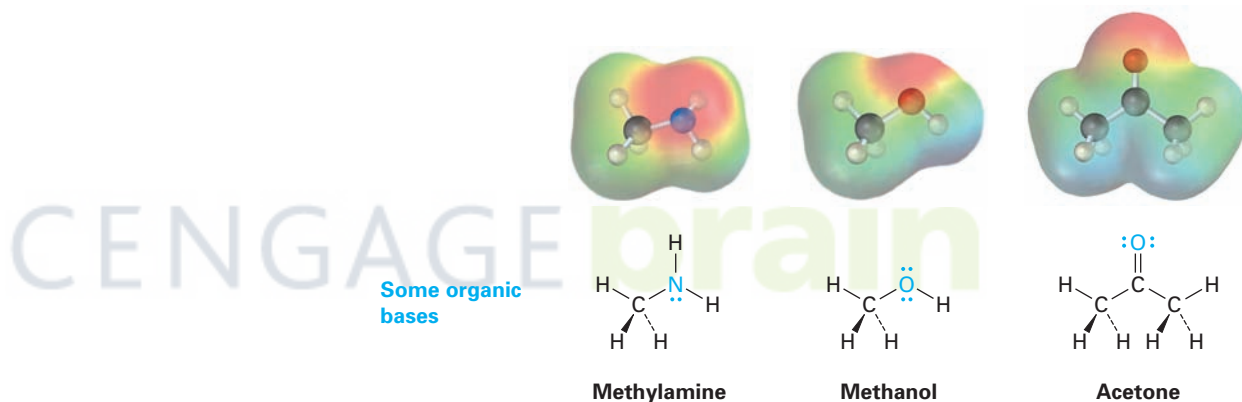
We'll see in Chapter 15 that substances called *amino acids,* so named because they are both amines ($-NH_2$) and carboxylic acids ($-CO_2H$), are the building blocks from which the proteins present in all living organisms are made. Twenty different amino acids go into making up proteins; alanine is an example. Interestingly, alanine and other amino acids exist primarily in a doubly charged form called a *zwitterion* rather than in the uncharged form. The zwitterion form arises because amino acids have both acidic and basic sites within the same molecule and therefore undergo an *internal* acid–base reaction.

Alanine
(uncharged form)   **Alanine**
(zwitterion form)
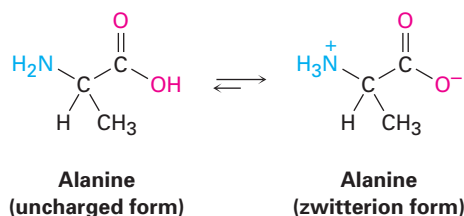
1.12 Acids and Bases: The Lewis Definition

The Lewis definition of acids and bases is broader and more encompassing than the Brønsted–Lowry definition because it's not limited to substances that donate or accept protons. A **Lewis acid** is a substance that *accepts an electron pair,* and a **Lewis base** is a substance that *donates an electron pair.* The donated electron pair is shared between the acid and the base in a covalent bond.
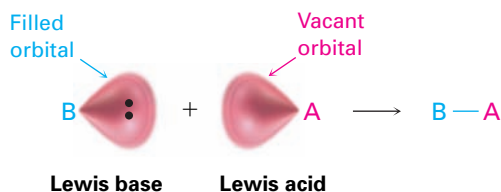
The fact that a Lewis acid is able to accept an electron pair means that it must have either a vacant, low-energy orbital or a polar bond to hydrogen so that it can donate H^+ (which has an empty $1s$ orbital). Thus, the Lewis definition of acidity includes many species in addition to H^+. For example, various metal cations, such as Mg^{2+}, and metal compounds, such as $AlCl_3$, are Lewis acids because they have unfilled valence orbitals and can accept electron pairs from Lewis bases.
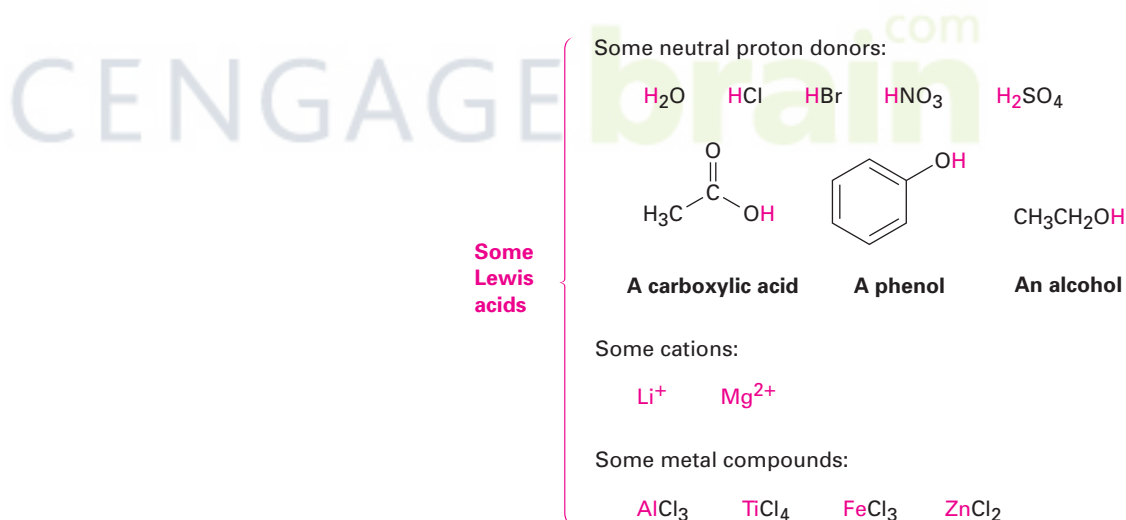
The Lewis definition of a base—a compound with a pair of nonbonding electrons that it can use in bonding to a Lewis acid—is similar to the Brønsted–Lowry definition. Thus, H_2O, with its two pairs of nonbonding electrons on oxygen, acts as a Lewis base by donating an electron pair to an H^+ in forming the hydronium ion, H_3O^+. Similarly, trimethylamine acts as a Lewis base by donating an electron pair on its nitrogen atom to aluminum chloride. In a more

general sense, most oxygen- and nitrogen-containing organic compounds can act as Lewis bases because they have lone pairs of electrons.

Hydrogen chloride (Lewis acid)   **Water (Lewis base)**   **Hydronium ion**

Aluminum trichloride (Lewis acid)   **Trimethylamine (Lewis base)**
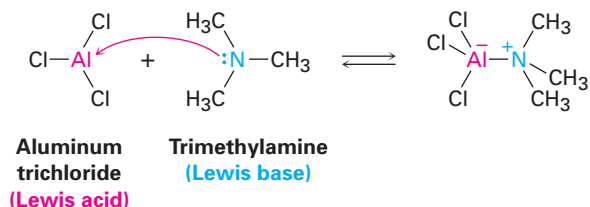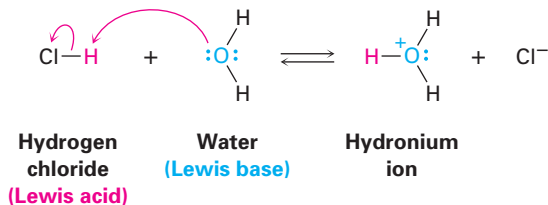
Look closely at the two acid–base reactions just shown. In the first reaction, the Lewis base water uses an electron pair to abstract H^+ from the polar HCl molecule. In the second reaction, the Lewis base trimethylamine donates an electron pair to a vacant valence orbital of an aluminum atom. In both reactions, the direction of electron-pair flow from the electron-rich Lewis base to the electron-poor Lewis acid is shown using curved arrows. *A curved arrow always means that a pair of electrons moves from the atom at the tail of the arrow to the atom at the head of the arrow.* We'll use this curved-arrow notation frequently in the remainder of this text to indicate electron flow during reactions.

Worked Example 1.8

Using Curved Arrows to Show Electron Flow

Using curved arrows, show how acetaldehyde, CH_3CHO, can act as a Lewis base in a reaction with a strong acid, H^+.

Strategy

A Lewis base donates an electron pair to a Lewis acid. We therefore need to locate the electron lone pairs on acetaldehyde and use a curved arrow to show the movement of an electron pair from the oxygen toward a strong acid.

Solution

Acetaldehyde
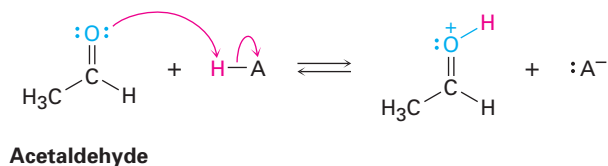
Problem 1.23

Which of the following are likely to act as Lewis acids and which as Lewis bases? Which might act both ways?

(a) CH_3CH_2OH (b) $(CH_3)_2NH$ (c) $MgBr_2$
(d) $(CH_3)_3B$ (e) H_3C^+ (f) $(CH_3)_3P$

Problem 1.24   Show how the species in part **(a)** can act as Lewis bases in their reactions with HCl, and show how the species in part **(b)** can act as Lewis acids in their reaction with OH^-.

(a) CH_3CH_2OH, $(CH_3)_2NH$, $(CH_3)_3P$

(b) H_3C^+, $(CH_3)_3B$, $MgBr_2$

Problem 1.25   Imidazole, which forms part of the structure of the amino acid histidine, can act as both an acid and a base. Look at the electrostatic potential map of imidazole, and identify the most acidic hydrogen atom and the most basic nitrogen atom.
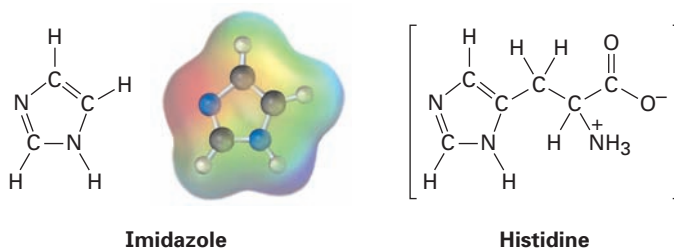
Imidazole   **Histidine**

Organic Foods: Risk versus Benefit

How dangerous is the pesticide being sprayed on this crop?

Contrary to what you may hear in supermarkets or on television, all foods are organic—complex mixtures of organic molecules. Even so, when applied to food, the word *organic* has come to mean an absence of synthetic chemicals, typically pesticides. How concerned should we be about traces of pesticides in the food we eat? Or toxins in the water we drink? Or pollutants in the air we breathe?

Life is not risk-free—we all take many risks each day without even thinking about it. We decide to ride a bike rather than drive, although there is a ten times greater likelihood per mile of dying in a bicycling accident than in a car. We decide to walk down stairs rather than take an elevator, although 7000 people die from falls each year in the United States. Some of us even decide to smoke cigarettes, although it increases our chance of getting cancer by 50%. But what about risks from chemicals like pesticides?

One thing is certain: without pesticides, whether they target weeds (herbicides), insects (insecticides), or molds and fungi (fungicides), crop production would drop significantly and food prices would increase. Take the herbicide atrazine, for instance. In the United States alone,

INTERLUDE

approximately 100 million pounds of atrazine are used each year to kill weeds in corn, sorghum, and sugar cane fields, greatly improving the yields of these crops. Nevertheless, the use of atrazine continues to be a concern because traces persist in the environment. Indeed, heavy atrazine exposure *can* pose health risks to humans and some animals, but the U.S. Environmental Protection Agency (EPA) is unwilling to ban its use because doing so would result in significantly lower crop yields and increased food costs, and because there is no suitable alternative herbicide available.

How can the potential hazards from a chemical like atrazine be determined? Risk evaluation of chemicals is carried out by exposing test animals, usually mice or rats, to the chemical and then monitoring the animals for signs of harm. To limit the expense and time needed, the amounts administered are typically hundreds or thousands of times greater than those a person might normally encounter. The results obtained in animal tests are then distilled into a single number called an LD_{50} *value*, the amount of substance per kilogram body weight that is a lethal dose for 50% of the test animals. For atrazine, the LD_{50} value is between 1 and 4 g/kg depending on the animal species. Aspirin, for comparison, has an LD_{50} of 1.1 g/kg, and Table 1.3 lists values for some other familiar substances. The lower the value, the more toxic the substance. Note, though, that LD_{50} values tell only about the effects of very heavy exposure for a relatively short time. They say nothing about the risks of long-term exposure, such as whether the substance can cause cancer or interfere with development in the unborn.

Table 1.3	Some LD_{50} Values		
Substance	**LD_{50} (g/kg)**	**Substance**	**LD_{50} (g/kg)**
Strychnine	0.005	Chloroform	1.2
Arsenic trioxide	0.015	Iron(II) sulfate	1.5
DDT	0.115	Ethyl alcohol	10.6
Aspirin	1.1	Sodium cyclamate	17

So, should we still use atrazine? All decisions involve tradeoffs, and the answer is rarely obvious. Does the benefit of increased food production outweigh possible health risks of a pesticide? Do the beneficial effects of a new drug outweigh a potentially dangerous side effect in a small number of users? Different people will have different opinions, but an honest evaluation of facts is surely the best way to start. At present, atrazine is approved for continued use in the United States because the EPA believes that the benefits of increased food production outweigh possible health risks. At the same time, though, atrazine use is being phased out in Europe.

Summary and Key Words

The purpose of this chapter has been to get you up to speed—to review some ideas about atoms, bonds, and molecular geometry. As we've seen, **organic chemistry** is the study of carbon compounds. Although a division into inorganic and organic chemistry occurred historically, there is no scientific reason for the division.

An atom is composed of a positively charged nucleus surrounded by negatively charged electrons that occupy specific regions of space called **orbitals**. Different orbitals have different energy levels and shapes. For example, *s* orbitals are spherical and *p* orbitals are dumbbell-shaped.

There are two fundamental kinds of chemical bonds: ionic bonds and **covalent bonds**. The ionic bonds commonly found in inorganic salts result from the electrical attraction of unlike charges. The covalent bonds found in organic molecules result from the sharing of one or more electron pairs between atoms. Electron sharing occurs when two atoms approach and their atomic orbitals overlap. Bonds formed by head-on overlap of atomic orbitals are called **sigma (σ) bonds**, and bonds formed by sideways overlap of *p* orbitals are called **pi (π) bonds**.

In the valence bond description, carbon uses hybrid orbitals to form bonds in organic molecules. When forming only single bonds with tetrahedral geometry, carbon uses four equivalent **sp^3 hybrid orbitals**. When forming double bonds, carbon has three equivalent **sp^2 orbitals** with planar geometry and one unhybridized *p* orbital. When forming triple bonds, carbon has two equivalent **sp orbitals** with linear geometry and two unhybridized *p* orbitals.

Organic molecules often have **polar covalent bonds** because of unsymmetrical electron sharing caused by the **electronegativity** of atoms. A carbon–oxygen bond, for instance, is polar because oxygen attracts the bonding electrons more strongly than carbon does. A carbon–metal bond, by contrast, is polarized in the opposite sense because carbon attracts electrons more strongly than metals do.

A **Brønsted–Lowry acid** is a substance that can donate a proton (hydrogen ion, H^+), and a **Brønsted–Lowry base** is a substance that can accept a proton. The strength of an acid is given by its acidity constant, K_a. A **Lewis acid** is a substance that can accept an electron pair. A **Lewis base** is a substance that can donate an unshared electron pair. Most organic molecules that contain oxygen and nitrogen are Lewis bases.

WORKING PROBLEMS

There is no surer way to learn organic chemistry than by working problems. Although careful reading and rereading of this text are important, reading alone isn't enough. You must also be able to use the information you've read and be able to apply your knowledge in new situations. Working problems gives you practice at doing this.

Each chapter in this book provides many problems of different sorts. The in-chapter problems are placed for immediate reinforcement of ideas just learned; the end-of-chapter problems provide additional practice and are of several types. They begin with a short section called "Visualizing Chemistry," which helps you "see" the microscopic world of molecules and provides

practice for working in three dimensions. After the visualizations are many "Additional Problems" that are grouped according to topic.

As you study organic chemistry, take the time to work the problems. Do the ones you can, and ask for help on the ones you can't. If you're stumped by a particular problem, check the accompanying *Study Guide and Solutions Manual* for an explanation that will help clarify the difficulty. Working problems takes effort, but the payoff in knowledge and understanding is immense.

Exercises

Visualizing Chemistry

(Problems 1.1–1.25 appear within the chapter.)

⊘WL

Interactive versions of these problems are assignable in OWL.

1.26 Convert each of the following molecular models into a line-bond structure, and give the formula of each (gray = C, red = O, blue = N, ivory = H).

(a)

(b)

Coniine (the toxic substance in poison hemlock)
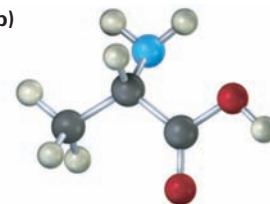
Alanine (an amino acid)

1.27 The following model is a representation of citric acid, a substance in the so-called citric acid cycle by which food molecules are metabolized in the body. Only the connections between atoms are shown; multiple bonds are not indicated. Complete the structure by indicating the positions of multiple bonds and lone-pair electrons (gray = C, red = O, ivory = H).
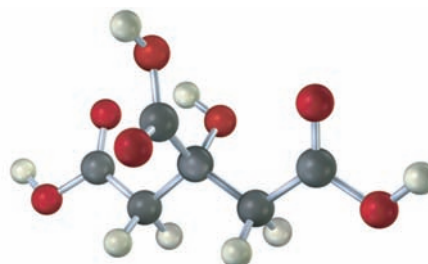
1.28 The following model is that of acetaminophen, a pain reliever sold in drugstores under a variety of names, including Tylenol. Identify the hybridization of each carbon atom in acetaminophen, and tell which atoms have lone pairs of electrons (gray = C, red = O, blue = N, ivory = H).
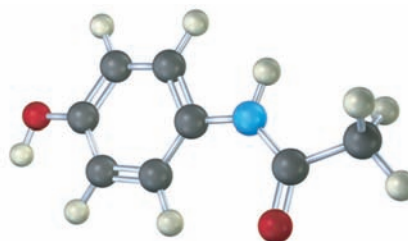
1.29 The following model is that of aspartame, $C_{14}H_{18}N_2O_5$, known commercially under many names, including NutraSweet. Only the connections between atoms are shown; multiple bonds are not indicated. Complete the structure by indicating the positions of multiple bonds (gray = C, red = O, blue = N, ivory = H).
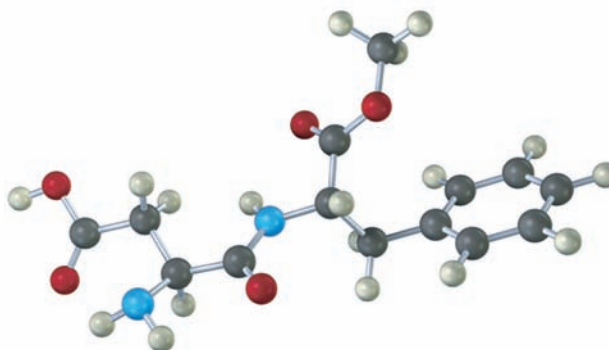
CENGAG

1.30 Electrostatic potential maps of **(a)** acetamide and **(b)** methylamine are shown. Which of the two has the more basic nitrogen atom? Which of the two has the more acidic hydrogen atoms?

(a)
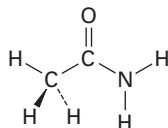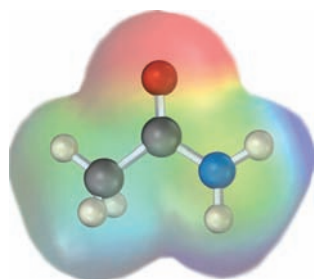
Acetamide

(b)
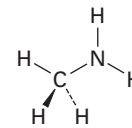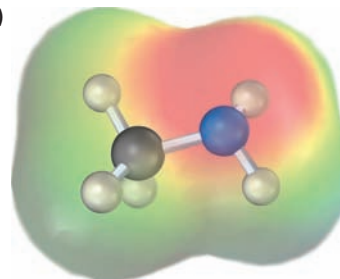
Methylamine

Additional Problems

1.31 How many valence electrons does each of the following atoms have?
(a) Oxygen   (b) Magnesium   (c) Fluorine

1.32 Give the ground-state electron configuration of the following elements. For example, carbon is $1s^2\, 2s^2\, 2p^2$.
(a) Lithium   (b) Sodium   (c) Aluminum   (d) Sulfur

1.33 What are the likely formulas of the following molecules?
(a) $AlCl_?$ (b) $CF_2Cl_?$ (c) $NI_?$ (d) $CH_?O$

1.34 Write an electron-dot structure for acetonitrile, $CH_3C\equiv N$. How many electrons does the nitrogen atom have in its valence shell? How many are used for bonding, and how many are not used for bonding?

1.35 Fill in any unshared electrons that are missing from the following line-bond structures:

(a)
H_3C — S — S — CH_3
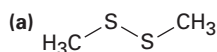
Dimethyl disulfide

(b)
H_3C — C(=O) — NH_2

Acetamide

(c)
H_3C — C(=O) — O^-
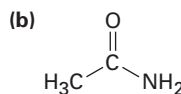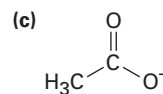
Acetate ion

1.36 Why can't molecules with the following formulas exist?
(a) CH_5 (b) C_2H_6N (c) $C_3H_5Br_2$

1.37 Draw both an electron-dot structure and a line-bond structure for vinyl chloride, C_2H_3Cl, the starting material from which PVC [poly(vinyl chloride)] plastic is made.

1.38 There are two structures with the formula C_4H_{10}. Draw them, and tell how they differ.

1.39 Convert the following line-bond structures into molecular formulas:
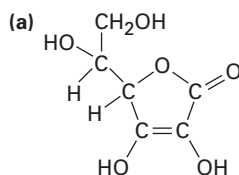
(a) **Vitamin C (ascorbic acid)**
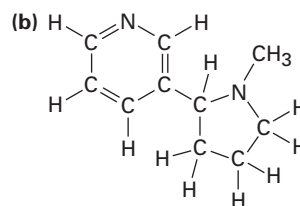
(b) **Nicotine**
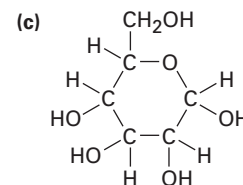
(c) **Glucose**

1.40 Convert the following molecular formulas into line-bond structures:
(a) C_3H_8 (b) C_3H_7Br (two possibilities)
(c) C_3H_6 (two possibilities)   (d) C_2H_6O (two possibilities)

1.41 Draw a three-dimensional representation of the OH-bearing carbon atom in ethanol, CH_3CH_2OH.

1.42 Draw line-bond structures for the following molecules:
  (a) Ethyl methyl ether, C_3H_8O, which contains an oxygen atom bonded to two carbons
  (b) Butane, C_4H_{10}, which contains a chain of four carbon atoms
  (c) Cyclohexene, C_6H_{10}, which contains a ring of six carbon atoms and one carbon–carbon double bond

1.43 Oxaloacetic acid, an important intermediate in food metabolism, has the formula $C_4H_4O_5$ and contains three $C=O$ bonds and two $O-H$ bonds. Propose two possible structures.

ELECTRONEGATIVITY

1.44 Identify the bonds in the following molecules as covalent, polar covalent, or ionic:
  (a) BeF_2 **(b)** SiH_4 **(c)** CBr_4

1.45 Indicate which of the bonds in the following molecules are polar covalent, using the symbols $\delta+$ and $\delta-$.
  (a) Br_2 **(b)** CH_3Cl **(c)** HF **(d)** CH_3CH_2OH

1.46 Sodium methoxide, $NaOCH_3$, contains both ionic and covalent bonds. Indicate which is which.

1.47 Identify the most electronegative element in each of the following molecules:
  (a) CH_2FCl **(b)** $FCH_2CH_2CH_2Br$
  (c) $HOCH_2CH_2NH_2$ **(d)** CH_3OCH_2Li

1.48 Use the electronegativity values in Figure 1.14 to predict which of the indicated bonds in each of the following sets is more polar. Tell the direction of the polarity in each.
  (a) $Cl-CH_3$ or $Cl-Cl$ **(b)** $H-CH_3$ or $H-Cl$
  (c) $HO-CH_3$ or $(CH_3)_3Si-CH_3$

1.49 Use Figure 1.14 to order the following molecules according to increasing positive character of the carbon atom:

$$CH_3F, \quad CH_3OH, \quad CH_3Li, \quad CH_3I, \quad CH_3CH_3, \quad CH_3NH_2$$

1.50 We'll see in the next chapter that organic molecules can be classified according to the *functional groups* they contain, where a functional group is a collection of atoms with a characteristic chemical reactivity. Use the electronegativity values given in Figure 1.14 to predict the polarity of the following functional groups:
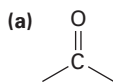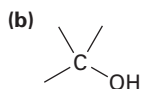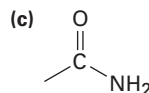
(a) Ketone **(b)** Alcohol **(c)** Amide **(d)** Nitrile

HYBRIDIZATION

1.51 What is the hybridization of each carbon atom in acetonitrile, $CH_3C{\equiv}N$?

1.52 What values do you expect for the indicated bond angles in each of the following molecules, and what kind of hybridization do you expect for the central atom in each?

(a)

$$H_2N-CH_2-\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}-OH$$

(b)

(c)

$$CH_3-\overset{\displaystyle OH}{\overset{\displaystyle |}{C}H}-\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}-OH$$
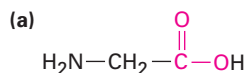
Glycine
(an amino acid)
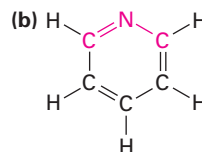
Pyridine
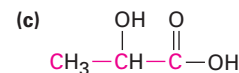
Lactic acid
(in sour milk)

1.53 What kind of hybridization do you expect for each carbon atom in the following molecules?

(a)

(b)
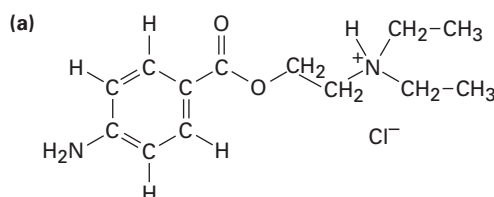
Procaine
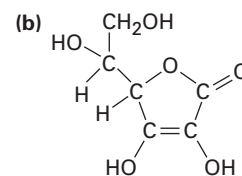
Vitamin C
(ascorbic acid)

1.54 What is the hybridization of each carbon atom in benzene? What shape do you expect benzene to have?

Benzene
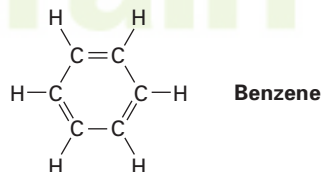
1.55 Propose structures for molecules that meet the following descriptions:
   (a) Contains two sp^2-hybridized carbons and two sp^3-hybridized carbons
   (b) Contains only four carbons, all of which are sp^2-hybridized
   (c) Contains two sp-hybridized carbons and two sp^2-hybridized carbons

ACIDS AND BASES

1.56 Ammonia, $H_2N—H$, has $pK_a \approx 36$, and acetone has $pK_a \approx 19$. Will the following reaction take place? Explain.

Acetone
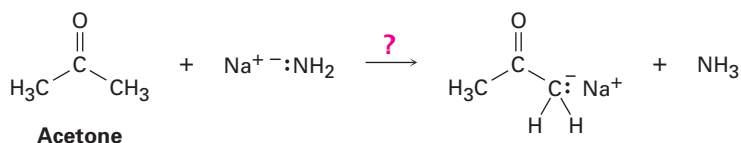
1.57 Which of the following substances are likely to behave as Lewis acids and which as Lewis bases?
(a) $AlBr_3$ (b) $CH_3CH_2NH_2$ (c) HF   (d) CH_3SCH_3

1.58 Is the bicarbonate anion (HCO_3^-) a strong enough base to react with methanol (CH_3OH)? In other words, does the following reaction take place as written? (The pK_a of methanol is 15.5; the pK_a of H_2CO_3 is 6.4.)

$$CH_3OH + HCO_3^- \xrightarrow{?} CH_3O^- + H_2CO_3$$

1.59 Identify the acids and bases in the following reactions:
(a) $CH_3OH + H^+ \longrightarrow CH_3OH_2^+$
(b) $CH_3OH + NH_2^- \longrightarrow CH_3O^- + NH_3$
(c)
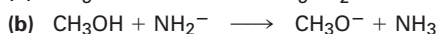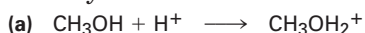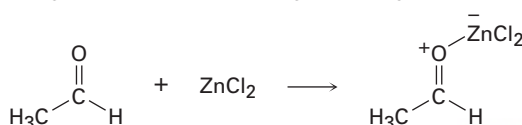
1.60 Rank the following substances in order of increasing acidity:
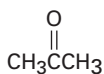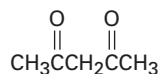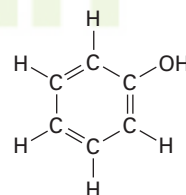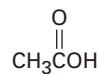
Acetone	Pentane-2,4-dione	Phenol	Acetic acid
(pK_a = 19.3)	(pK_a = 9)	(pK_a = 9.9)	(pK_a = 4.76)

1.61 Which, if any, of the four substances in Problem 1.60 are strong enough acids to react almost completely with NaOH? (The pK_a of H_2O is 15.7.)

1.62 The ammonium ion (NH_4^+, pK_a = 9.25) has a lower pK_a than the methyl-ammonium ion ($CH_3NH_3^+$, pK_a = 10.66). Which is the stronger base, ammonia (NH_3) or methylamine (CH_3NH_2)? Explain.

1.63 Predict the structure of the product formed in the reaction of the organic base pyridine with the organic acid acetic acid, and use curved arrows to indicate the direction of electron flow.

**Pyridine**   **Acetic acid**
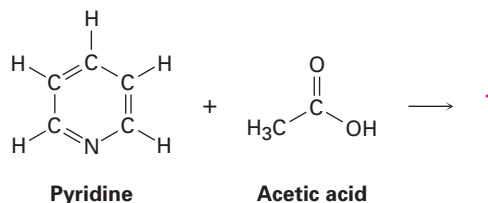
GENERAL PROBLEMS

1.64 Complete the electron-dot structure of caffeine, showing all lone-pair electrons, and identify the hybridization of the indicated atoms.


Caffeine
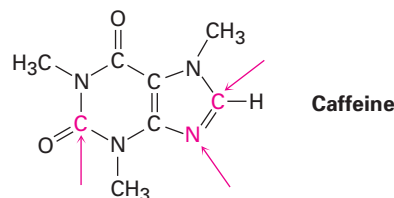
1.65 The ammonium ion, NH_4^+, has a geometry identical to that of methane, CH_4. What kind of hybridization do you think the nitrogen atom has? Explain.

1.66 Why do you suppose no one has ever been able to make cyclopentyne as a stable molecule?

Cyclopentyne
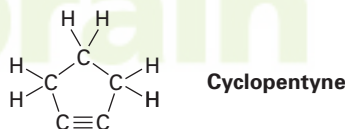
1.67 Draw an orbital picture of allene, $H_2C{=}C{=}CH_2$. What hybridization must the central carbon atom have to form two double bonds? What shape does allene have?

1.68 Draw an electron-dot structure and an orbital picture for carbon dioxide, CO_2. What kind of hybridization does the carbon atom have? What is the relationship between CO_2 and allene (Problem 1.67)?

1.69 Although most stable organic compounds have tetravalent carbon atoms, high-energy species with trivalent carbon atoms also exist. *Carbocations* are one such class of compounds. If the positively charged carbon atom has planar geometry, what hybridization do you think it has? How many valence electrons does the carbon have?
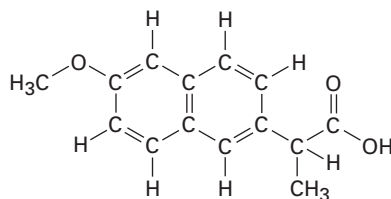

A carbocation
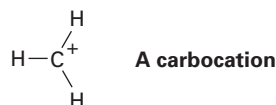
IN THE MEDICINE CABINET   1.70   Nonsteroidal anti-inflammatory drugs, often referred to as NSAIDs, are commonly used to treat minor aches and pains. Four of the most common NSAIDs are:
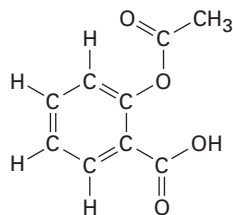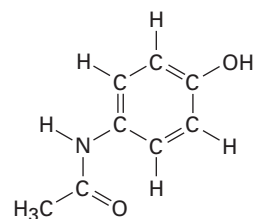
**Acetylsalicylic acid
(aspirin)**
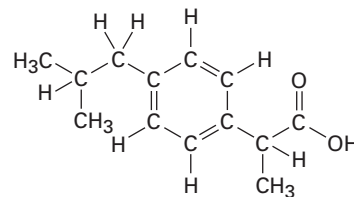
**Ibuprofen
(Advil, Nuprin, Motrin)**

**Naproxen
(Naprosyn, Aleve)**

**Acetaminophen
(Tylenol)**

(a) How many sp^3-hybridized carbons are present in aspirin?
(b) How many sp^2-hybridized carbons are present in naproxen?
(c) What is the molecular formula of acetaminophen?
(d) Aspirin, ibuprofen, and naproxen are all believed to target the same enzyme, cyclooxygenase, which produces substances called prostaglandins, that mediate inflammation. Discuss any similarities in the structures of these drugs.

IN THE FIELD   **1.71** Herbicides that differ greatly in structure also often differ in how they act.
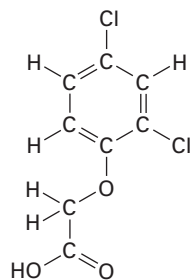
2,4-D
(Hi-Dep or
Weedar 64)

Disrupts growth
regulation signals
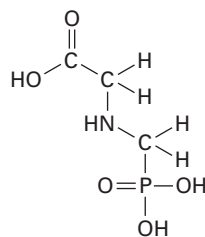
Glyphosate
(Roundup)

Inhibits amino
acid synthesis
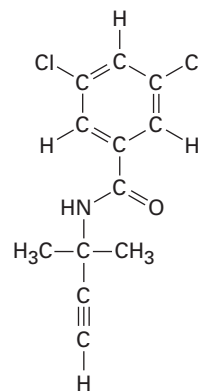
Pronamide
(Propyzamide)

Interferes with
cell division
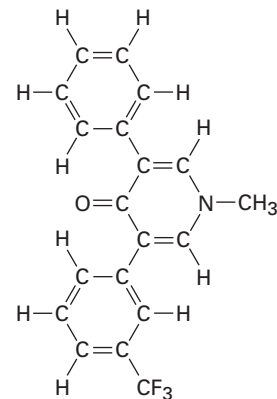
Fluridone
(Sonar)

Inhibits pigment
biosynthesis

(a) How many sp^3-hybridized carbons are present in 2,4-D?
(b) How many sp^2-hybridized carbons are present in Roundup?
(c) How many sp-hybridized carbons are present in pronamide?
(d) What is the molecular formula of fluridone?

APPENDIX C

Answers to Selected In-Chapter Problems

The following answers to in-chapter problems are meant only as a quick check. Full answers and explanations for all problems, both in-chapter and end-of-chapter, are provided in the accompanying *Study Guide and Solutions Manual*.
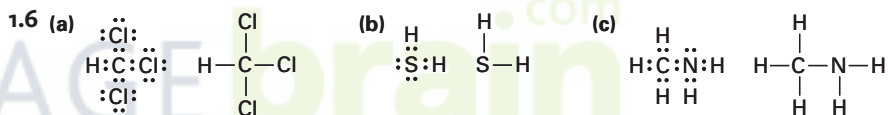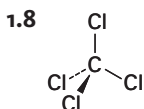
Chapter 1

1.1 (a) 1 (b) 2 (c) 3

1.2 (a) B: $1s^2\, 2s^2\, 2p$ (b) P: $1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^3$
(c) O: $1s^2\, 2s^2\, 2p^4$ (d) Ar: $1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6$

1.3

1.4
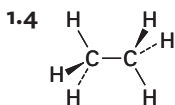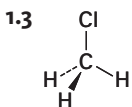
1.5 (a) CCl_4 (b) AlH_3 (c) CH_2Cl_2 (d) SiF_4
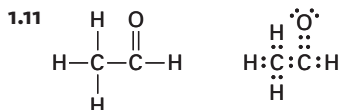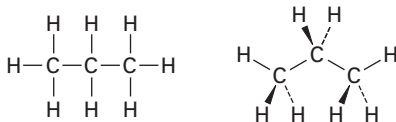
1.6 (a)

(b)

(c)

1.7 C_2H_7 has too many hydrogens for a compound with two carbons.
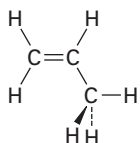
1.8

1.9 A carbon atom is larger than a hydrogen atom.

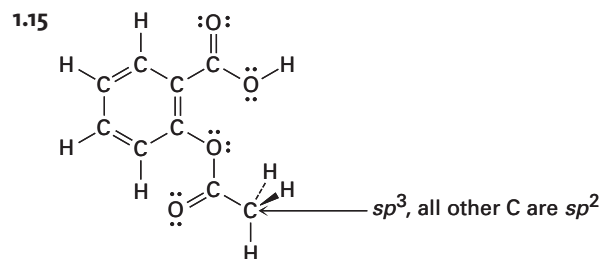**1.10** All bond angles are approximately 109°.

1.11

1.12 The CH_3 carbon is sp^3, the double-bond carbons are sp^2, and the C=C–C bond angle is approximately 120°.

1.13 The CH_3 carbon is sp^3, the triple-bond carbons are sp, and the C≡C–C bond angle is approximately 180°.

1.14 All carbons are sp^2, and all bond angles are approximately 120°.

1.15

sp^3, all other C are sp^2

1.16 (a) H   **(b)** Br   **(c)** Cl

1.17 (a) C is $\delta+$, Br is $\delta-$ **(b)** C is $\delta+$, N is $\delta-$
    (c) H is $\delta+$, N is $\delta-$ **(d)** C is $\delta+$, S is $\delta-$
    (e) Mg is $\delta+$, C is $\delta-$ **(f)** C is $\delta+$, F is $\delta-$

1.18 CCl_4 and Cl_2O < $TiCl_3$ < $MgCl_2$

1.19
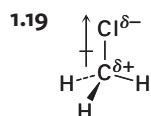
1.20 (a) Formic acid: $K_a = 1.8 \times 10^{-4}$; picric acid: $K_a = 0.42$
    (b) Picric acid is stronger.

1.21 Water is the stronger acid.

1.22 (a) No   **(b)** No

1.23 Lewis acids: (c), (d), (e); Lewis bases: (b), (f); both: (a)

1.24 (a) $CH_3CH_2OH + HCl \longrightarrow CH_3CH_2OH_2^+ Cl^-$;
        $(CH_3)_2NH + HCl \longrightarrow (CH_3)_2NH_2^+ Cl^-$; $(CH_3)_3P + HCl \longrightarrow$
        $(CH_3)_3PH^+ Cl^-$

    (b) $HO^- + CH_3^+ \longrightarrow HO—CH_3$; $HO^- + B(CH_3)_3 \longrightarrow$
        $HO—B(CH_3)_3^-$;
        $HO^- + MgBr_2 \longrightarrow HO—MgBr_2^-$

1.25

Most basic   Most acidic