The modern definition of organic chemistry is the chemistry of carbon compounds. What is so special about carbon that a whole branch of chemistry is devoted to its compounds? Unlike most other elements, carbon forms strong bonds to other carbon atoms and to a wide variety of other elements. Chains and rings of carbon atoms can be built up to form an endless variety of molecules. It is this diversity of carbon compounds that provides the basis for life on Earth. Living creatures are composed largely of complex organic compounds that serve structural, chemical, or genetic functions.

The term organic literally means “derived from living organisms.” Originally, the science of organic chemistry was the study of compounds extracted from living organisms and their natural products. Compounds such as sugar, urea, starch, waxes, and plant oils were considered “organic,” and people accepted Vitalism, the belief that natural products needed a “vital force” to create them. Organic chemistry, then, was the study of compounds having the vital force. Inorganic chemistry was the study of gases, rocks, and minerals, and the compounds that could be made from them.

In the nineteenth century, experiments showed that organic compounds could be synthesized from inorganic compounds. In 1828, the German chemist Friedrich Wöhler converted ammonium cyanate, made from ammonia and cyanic acid, to urea simply by heating it in the absence of oxygen.

\[
\text{NH}_4^+\text{OCN} \xrightarrow{\text{heat}} \text{H}_2\text{N}^+\text{C}^-\text{NH}_2
\]


Urea had always come from living organisms and was presumed to contain the vital force, yet ammonium cyanate is inorganic and thus lacks the vital force. Some chemists claimed that a trace of vital force from Wöhler’s hands must have contaminated the reaction, but most recognized the possibility of synthesizing organic compounds from inorganics. Many other syntheses were carried out, and the vital force theory was eventually discarded.

Since Vitalism was disproved in the early nineteenth century, you’d think it would be extinct by now. And you’d be wrong! Vitalism lives on today in the minds of those who believe that “natural” (plant-derived) vitamins, flavor compounds, etc. are somehow different and more healthful than the identical “artificial” (synthesized) compounds.
Chapter 1: Introduction and Review

As chemists, we know that plant-derived compounds and the synthesized compounds are identical. Assuming they are pure, the only way to tell them apart is through \(^{14}C\) dating: Compounds synthesized from petrochemicals have a lower content of radioactive \(^{14}C\) and appear old because their \(^{14}C\) has decayed over time. Plant-derived compounds are recently synthesized from CO\(_2\) in the air. They have a higher content of radioactive \(^{14}C\). Some large chemical suppliers provide isotope ratio analyses to show that their “naturals” have high \(^{14}C\) content and are plant-derived. Such a sophisticated analysis lends a high-tech flavor to this twenty-first-century form of Vitalism.

Even though organic compounds do not need a vital force, they are still distinguished from inorganic compounds. The distinctive feature of organic compounds is that they all contain one or more carbon atoms. Still, not all carbon compounds are organic; substances such as diamond, graphite, carbon dioxide, ammonium cyanate, and sodium carbonate are derived from minerals and have typical inorganic properties. Most of the millions of carbon compounds are classified as organic, however.

We ourselves are composed largely of organic molecules, and we are nourished by the organic compounds in our food. The proteins in our skin, the lipids in our cell membranes, the glycogen in our livers, and the DNA in the nuclei of our cells are all organic compounds. Our bodies are also regulated and defended by complex organic compounds.

Four examples of organic compounds in living organisms. Tobacco contains nicotine, an addictive alkaloid. Rose hips contain vitamin C, essential for preventing scurvy. The red dye carmine comes from cochineal insects, shown on prickly pear cactus. Opium poppies contain morphine, a pain-relieving, addictive alkaloid.

Chemists have learned to synthesize or simulate many of these complex molecules. The synthetic products serve as drugs, medicines, plastics, pesticides, paints, and fibers. Many of the most important advances in medicine are actually advances in organic chemistry. New synthetic drugs are developed to combat disease, and new polymers are molded to replace failing organs. Organic chemistry has gone full circle. It began as the study of compounds derived from “organs,” and now it gives us the drugs and materials we need to save or replace those organs.
Before we begin our study of organic chemistry, we must review some basic principles. Many of these concepts of atomic and molecular structure are crucial to your understanding of the structure and bonding of organic compounds.

1-2A Structure of the Atom

Atoms are made up of protons, neutrons, and electrons. Protons are positively charged and are found together with (uncharged) neutrons in the nucleus. Electrons, which have a negative charge that is equal in magnitude to the positive charge on the proton, occupy the space surrounding the nucleus (Figure 1-1). Protons and neutrons have similar masses, about 1800 times the mass of an electron. Almost all the atom’s mass is in the nucleus, but it is the electrons that take part in chemical bonding and reactions.

Each element is distinguished by the number of protons in the nucleus (the atomic number). The number of neutrons is usually similar to the number of protons, although the number of neutrons may vary. Atoms with the same number of protons but different numbers of neutrons are called isotopes. For example, the most common kind of carbon atom has six protons and six neutrons in its nucleus. Its mass number (the sum of the protons and neutrons) is 12, and we write its symbol as \( ^{12}\text{C} \). About 1% of carbon atoms have seven neutrons; the mass number is 13, written \( ^{13}\text{C} \). A very small fraction of carbon atoms have eight neutrons and a mass number of 14. The \( ^{14}\text{C} \) isotope is radioactive, with a half-life (the time it takes for half of the nuclei to decay) of 57,300 years. The predictable decay of \( ^{14}\text{C} \) is used to determine the age of organic materials up to about 50,000 years old.

1-2B Electronic Structure of the Atom

An element’s chemical properties are determined by the number of protons in the nucleus and the corresponding number of electrons around the nucleus. The electrons form bonds and determine the structure of the resulting molecules. Because they are small and light, electrons show properties of both particles and waves; in many ways, the electrons in atoms and molecules behave more like waves than like particles.

Electrons that are bound to nuclei are found in orbitals. The Heisenberg uncertainty principle states that we can never determine exactly where the electron is; nevertheless, we can determine the electron density, the probability of finding the electron in a particular part of the orbital. An orbital, then, is an allowed energy state for an electron, with an associated probability function that defines the distribution of electron density in space.

Atomic orbitals are grouped into different “shells” at different distances from the nucleus. Each shell is identified by a principal quantum number \( n \), with \( n = 1 \) for the lowest-energy shell closest to the nucleus. As \( n \) increases, the shells are farther from the nucleus, higher in energy, and can hold more electrons. Most of the common elements in organic compounds are found in the first two rows of the periodic table, indicating that their electrons are found in the first two electron shells. The first shell \( (n = 1) \) can hold two electrons, and the second shell \( (n = 2) \) can hold eight.

The first electron shell contains just the 1\( s \) orbital. All \( s \) orbitals are spherically symmetrical, meaning that they are nondirectional. The electron density is only a function of the distance from the nucleus. The electron density of the 1\( s \) orbital is graphed in Figure 1-2. Notice how the electron density is highest at the nucleus and falls off exponentially with increasing distance from the nucleus. The 1\( s \) orbital might be imagined as a cotton boll, with the cottonseed at the middle representing the nucleus. The density of the cotton is highest nearest the seed, and it becomes less dense at greater distances from this “nucleus.”

The second electron shell consists of the 2\( s \) and 2\( p \) orbitals. The 2\( s \) orbital is spherically symmetrical like the 1\( s \) orbital, but its electron density is not a simple exponential function. The 2\( s \) orbital has a smaller amount of electron density close to the nucleus.
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Most of the electron density is farther away, beyond a region of zero electron density called a node. Because most of the 2s electron density is farther from the nucleus than that of the 1s, the 2s orbital is higher in energy. Figure 1-3 shows a graph of the 2s orbital.

In addition to the 2s orbital, the second shell also contains three 2p atomic orbitals, one oriented in each of the three spatial directions. These orbitals are called the 2pz, the 2py, and the 2px, according to their direction along the x, y, or z axis. The 2p orbitals are slightly higher in energy than the 2s, because the average location of the electron in a 2p orbital is farther from the nucleus. Each p orbital consists of two lobes, one on either side of the nucleus, with a nodal plane at the nucleus. The nodal plane is a flat (planar) region of space, including the nucleus, with zero electron density. The three 2p orbitals differ only in their spatial orientation, so they have identical energies. Orbitals with identical energies are called degenerate orbitals. Figure 1-4 shows the shapes of the three degenerate 2p atomic orbitals.
The Pauli exclusion principle tells us that each orbital can hold a maximum of 2 electrons, provided that their spins are paired. The first shell (one 1s orbital) can accommodate 2 electrons. The second shell (one 2s orbital and three 2p orbitals) can accommodate 8 electrons, and the third shell (one 3s orbital, three 3p orbitals, and five 3d orbitals) can accommodate 18 electrons.

**1-2C Electronic Configurations of Atoms**

*Aufbau* means “building up” in German, and the *aufbau principle* tells us how to build up the electronic configuration of an atom’s ground (most stable) state. Starting with the lowest-energy orbital, we fill the orbitals in order until we have added the proper number of electrons. Table 1-1 shows the ground-state electronic configurations of the elements in the first two rows of the periodic table.

**TABLE 1-1  Electronic Configurations of the Elements of the First and Second Rows**

<table>
<thead>
<tr>
<th>Element</th>
<th>Configuration</th>
<th>Valence Electrons</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1s(^1)</td>
<td>1</td>
</tr>
<tr>
<td>He</td>
<td>1s(^2)</td>
<td>2</td>
</tr>
<tr>
<td>Li</td>
<td>1s(^2)2s(^1)</td>
<td>1</td>
</tr>
<tr>
<td>Be</td>
<td>1s(^2)2s(^2)</td>
<td>2</td>
</tr>
<tr>
<td>B</td>
<td>1s(^2)2s(^2)2p(^1)</td>
<td>3</td>
</tr>
<tr>
<td>C</td>
<td>1s(^2)2s(^2)2p(^3)</td>
<td>4</td>
</tr>
<tr>
<td>N</td>
<td>1s(^2)2s(^2)2p(^4)</td>
<td>5</td>
</tr>
<tr>
<td>O</td>
<td>1s(^2)2s(^2)2p(^6)</td>
<td>6</td>
</tr>
<tr>
<td>F</td>
<td>1s(^2)2s(^2)2p(^5)</td>
<td>7</td>
</tr>
<tr>
<td>Ne</td>
<td>1s(^2)2s(^2)2p(^6)2p(^2)</td>
<td>8</td>
</tr>
</tbody>
</table>

**Relative orbital energies**

- \(-2p_x\)
- \(-2p_y\)
- \(-2p_z\)

energy: \(-2s\)

- \(-1s\)
Lithium carbonate, a salt of lithium, is a mood-stabilizing agent used to treat the psychiatric disorder known as mania. Mania is characterized by behaviors such as elated mood, feelings of greatness, racing thoughts, and an inability to sleep. We don’t know how lithium carbonate helps to stabilize these patients’ moods.

Two additional concepts are illustrated in Table 1-1. The valence electrons are those electrons that are in the outermost shell. Carbon has four valence electrons, nitrogen has five, and oxygen has six. Helium has two valence electrons, and neon has eight, corresponding to a filled first shell and second shell, respectively. In general (for the representative elements), the column or group number of the periodic table corresponds to the number of valence electrons (Figure 1-5). Hydrogen and lithium have one valence electron, and they are both in the first column (group IA) of the periodic table. Carbon has four valence electrons, and it is in group IVA of the periodic table.

Notice in Table 1-1 that carbon’s third and fourth valence electrons are not paired; they occupy separate orbitals. Although the Pauli exclusion principle says that two electrons can occupy the same orbital, the electrons repel each other, and pairing requires additional energy. Hund’s rule states that when there are two or more orbitals of the same energy, electrons will go into different orbitals rather than pair up in the same orbital. The first 2p electron (boron) goes into one 2p orbital, the second (carbon) goes into a different orbital, and the third (nitrogen) occupies the last 2p orbital. The fourth, fifth, and sixth 2p electrons must pair up with the first three electrons.

**PROBLEM 1-1**
Write the electronic configurations of the third-row elements shown in the partial periodic table in Figure 1-5.

In 1915, G. N. Lewis proposed several new theories describing how atoms bond together to form molecules. One of these theories states that a filled shell of electrons is especially stable, and atoms transfer or share electrons in such a way as to attain a filled shell of electrons. A filled shell of electrons is simply the electron configuration of a noble gas, such as He, Ne, or Ar. This principle has come to be called the octet rule because a filled shell implies eight valence electrons for the elements in the second row of the periodic table.

**1-3A Ionic Bonding**
There are two ways that atoms can interact to attain noble-gas configurations. Sometimes atoms attain noble-gas configurations by transferring electrons from one atom to another. For example, lithium has one electron more than the helium configuration, and fluorine has one electron less than the neon configuration. Lithium easily loses its valence electron, and fluorine easily gains one.
A transfer of one electron gives each of these two elements a noble-gas configuration. The resulting ions have opposite charges, and they attract each other to form an ionic bond. Ionic bonding usually results in the formation of a large crystal lattice rather than individual molecules. Ionic bonding is common in inorganic compounds but relatively uncommon in organic compounds.

**1-3B Covalent Bonding**

Covalent bonding, in which electrons are shared rather than transferred, is the most common type of bonding in organic compounds. Hydrogen, for example, needs a second electron to achieve the noble-gas configuration of helium. If two hydrogen atoms come together and form a bond, they “share” their two electrons, and each atom has two electrons in its valence shell.

\[
\text{H}^- + \text{H}^- \rightarrow \text{H}_2 \text{H} \quad \text{each H shares two electrons (He configuration)}
\]

We will study covalent bonding in more detail in Chapter 2.

One way to symbolize the bonding in a covalent molecule is to use Lewis structures. In a Lewis structure, each valence electron is symbolized by a dot. A bonding pair of electrons is symbolized by a pair of dots or by a dash (—). We try to arrange all the atoms so they have their appropriate noble-gas configurations: two electrons for hydrogen, and octets for the second-row elements.

Consider the Lewis structure of methane (CH₄).

\[
\begin{array}{c}
\text{H} \\
\text{H} \text{–} \text{C} \text{–} \text{H} \\
\text{H}
\end{array}
\]

methane

Carbon contributes four valence electrons, and each hydrogen contributes one, to give a total of eight electrons. All eight electrons surround carbon to give it an octet, and each hydrogen atom shares two of the electrons.

The Lewis structure for ethane (C₂H₆) is more complex.

\[
\begin{array}{c}
\text{H} \\
\text{H} \text{–} \text{C} \text{–} \text{C} \text{–} \text{H} \\
\text{H} \\
\text{H}
\end{array}
\]

ethane

Once again, we have computed the total number of valence electrons (14) and distributed them so that each carbon atom is surrounded by 8 and each hydrogen by 2. The only possible structure for ethane is the one shown, with the two carbon atoms sharing a pair of electrons and each hydrogen atom sharing a pair with one of the carbons. The ethane structure shows the most important characteristic of carbon—its ability to form strong carbon–carbon bonds.
Valence-shell electrons that are not shared between two atoms are called **nonbonding electrons**. A pair of nonbonding electrons is often called a **lone pair**. Oxygen atoms, nitrogen atoms, and the halogens (F, Cl, Br, I) usually have nonbonding electrons in their stable compounds. These lone pairs of nonbonding electrons help to determine the reactivity of their parent compounds. The following Lewis structures show one lone pair of electrons on the nitrogen atom of methylamine and two lone pairs on the oxygen atom of ethanol. Halogen atoms usually have three lone pairs, as shown in the structure of chloromethane.

A correct Lewis structure should show any lone pairs. Organic chemists often draw structures that omit most or all of the lone pairs. These are not true Lewis structures because you must imagine the correct number of nonbonding electrons.

**PROBLEM 1-2**

draw Lewis structures for the following compounds.

(a) ammonia, NH₃  
(b) water, H₂O  
(c) hydronium ion, H₃O⁺  
(d) propane, C₃H₈  
(e) ethylamine, CH₃CH₂NH₂  
(f) dimethyl ether, CH₃OCH₃  
(g) fluoroethane, CH₂CH₂F  
(h) 2-propanol, CH₃CH(OH)CH₃  
(i) borane, BH₃  
(j) boron trifluoride, BF₃

Explain what is unusual about the bonding in compounds in parts (i) and (j).

**1-5 Multiple Bonding**

In drawing Lewis structures in Section 1-4, we placed just one pair of electrons between any two atoms. The sharing of one pair between two atoms is called a **single bond**. Many molecules have adjacent atoms sharing two or even three electron pairs.

The sharing of two pairs is called a **double bond**, and the sharing of three pairs is called a **triple bond**. Ethylene (C₂H₄) is an organic compound with a double bond. When we draw a Lewis structure for ethylene, the only way to show both carbon atoms with octets is to draw them sharing two pairs of electrons. The following examples show organic compounds with double bonds. In each case, four electrons (two pairs) are shared between two atoms to give them octets. A double dash (═) symbolizes a double bond.

Acetylene, in combination with oxygen, burns with an intense flame that has diverse applications. It can be used for welding parts of a bridge underwater and for repairing an oil pipeline in Siberia.
1-6 Electronegativity and Bond Polarity

SUMMARY  Common Bonding Patterns (Uncharged)

<table>
<thead>
<tr>
<th></th>
<th>carbon</th>
<th>nitrogen</th>
<th>oxygen</th>
<th>hydrogen</th>
<th>halogens</th>
</tr>
</thead>
<tbody>
<tr>
<td>valence</td>
<td>4</td>
<td>3</td>
<td>2</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>lone pairs</td>
<td>0</td>
<td>1</td>
<td>2</td>
<td>0</td>
<td>3</td>
</tr>
</tbody>
</table>

PROBLEM 1-3

Write Lewis structures for the following molecular formulas.

(a) N\textsubscript{2}  (b) HCN  (c) HONO
(d) CO\textsubscript{2}  (e) H\textsubscript{2}C\textsubscript{2}H\textsubscript{2}N  (f) HCO\textsubscript{2}H
(g) C\textsubscript{2}H\textsubscript{4}Cl  (h) HNNH  (i) C\textsubscript{3}H\textsubscript{5}
(j) C\textsubscript{3}H\textsubscript{2}(two double bonds)  (k) C\textsubscript{3}H\textsubscript{4}(one triple bond)

PROBLEM 1-4

Circle any lone pairs (pairs of nonbonding electrons) in the structures you drew for Problem 1-3.

A bond with the electrons shared equally between the two atoms is called a **nonpolar covalent bond**. The bond in H\textsubscript{2} and the C—C bond in ethane are nonpolar covalent bonds. In most bonds between two different elements, the bonding electrons are attracted more strongly to one of the two nuclei. An unequally shared pair of bonding electrons is called a **polar covalent bond**.

PROBLEM-SOLVING Hint

These "usual numbers of bonds" might be single bonds, or they might be combined into double and triple bonds. For example, three bonds to nitrogen might be three single bonds, one single bond and one double bond, or one triple bond (\(N≡N\)). In working problems, consider all possibilities.
Figure 1-6
Bond polarity. Chloromethane contains a polar carbon–chlorine bond with a partial negative charge on chlorine and a partial positive charge on carbon. The electrostatic potential map shows a red region (electron-rich) around the partial negative charge and a blue region (electron-poor) around the partial positive charge. Other colors show intermediate values of electrostatic potential.

Figure 1-6 also shows an electrostatic potential map (EPM) for chloromethane, using color to represent the calculated charge distribution in a molecule. Red shows electron-rich regions, and blue shows electron-poor regions. Orange, yellow, and green show intermediate levels of electrostatic potential. In chloromethane, the red region shows the partial negative charge on chlorine, and the blue region shows the partial positive charges on carbon and the hydrogen atoms.

We often use electronegativities as a guide in predicting whether a given bond will be polar and the direction of its dipole moment. The Pauling electronegativity scale, most commonly used by organic chemists, is based on bonding properties, and it is useful for predicting the polarity of covalent bonds. Elements with higher electronegativities generally have more attraction for the bonding electrons. Therefore, in a bond between two different atoms, the atom with the higher electronegativity is the negative end of the dipole. Figure 1-7 shows Pauling electronegativities for some of the important elements in organic compounds.

Notice that the electronegativities increase from left to right across the periodic table. Nitrogen, oxygen, and the halogens are all more electronegative than carbon; sodium, lithium, and magnesium are less electronegative. Hydrogen’s electronegativity is similar to that of carbon, so we usually consider C—H bonds to be nonpolar. We will consider the polarity of bonds and molecules in more detail in Section 2-9.

PROBLEM 1-5
Use electronegativities to predict the direction of the dipole moments of the following bonds.

(a) C—Cl  (b) C—O  (c) C—N  (d) C—S  (e) C—B
(f) N—Cl  (g) N—O  (h) N—S  (i) N—B  (j) B—Cl

Figure 1-7
The Pauling electronegativities of some of the elements found in organic compounds.
In polar bonds, the partial charges (\(\delta^+\) and \(\delta^-\)) on the bonded atoms are real. **Formal charges** provide a method for keeping track of electrons, but they may or may not correspond to real charges. In most cases, if the Lewis structure shows that an atom has a formal charge, it actually bears at least part of that charge. The concept of formal charge helps us determine which atoms bear most of the charge in a charged molecule, and it also helps us to see charged atoms in molecules that are neutral overall.

To calculate formal charges, count how many electrons contribute to the charge of each atom and compare that number with the number of valence electrons in the free, neutral atom (given by the group number in the periodic table). The electrons that contribute to an atom’s charge are:

1. **all** its unshared (nonbonding) electrons; plus
2. half the (bonding) electrons it shares with other atoms, or one electron of each bonding pair.

The formal charge of a given atom can be calculated by the formula:

\[
\text{formal charge (FC)} = \text{[group number]} - \text{[nonbonding electrons]} - \frac{1}{2}\text{[shared electrons]}
\]

### SOLVED PROBLEM 1-1

Compute the formal charge (FC) on each atom in the following structures.

(a) Methane (CH\(_4\))

\[
\text{H-H-C-H}
\]

**SOLUTION**

Each of the hydrogen atoms in methane has one bonding pair of electrons (two shared electrons). Half of two shared electrons is one electron, and one valence electron is what hydrogen needs to be neutral. Hydrogen atoms with one bond are formally neutral: FC = \(1 - 0 - 1 = 0\).

The carbon atom has four bonding pairs of electrons (eight electrons). Half of eight shared electrons is four electrons, and four electrons are what carbon (group IVA) needs to be neutral. Carbon is formally neutral whenever it has four bonds: FC = \(4 - 0 - \frac{1}{2}(8) = 0\).

(b) The hydronium ion, H\(_3\)O\(^+\)

\[
\text{H-H-O-H}
\]

**SOLUTION**

In drawing the Lewis structure for this ion, we use eight electrons: six from oxygen plus three from the hydrogens, minus one because the ion has a positive charge. Each hydrogen has one bond and is formally neutral. Oxygen is surrounded by an octet, with six bonding electrons and two nonbonding electrons. Half the bonding electrons plus all the nonbonding electrons contribute to its charge: \(\frac{3}{2} + 2 = 5\); but oxygen (group VIA) needs six valence electrons to be neutral. Consequently, the oxygen atom has a formal charge of +1: FC = \(6 - 2 - \frac{1}{2}(6) = +1\).

(c) H\(_3\)N=BH\(_3\)

\[
\text{H-H-H}\quad \text{H:N:B:H}\quad \text{H-H}
\]

**Boron has four bonds, eight bonding electrons**

**Nitrogen has four bonds, eight bonding electrons**
Chapter 1: Introduction and Review

**SOLUTION**
This is a neutral compound where the individual atoms are formally charged. The Lewis structure shows that both nitrogen and boron have four shared bonding pairs of electrons. Both boron and nitrogen have \( \frac{5}{2} = 4 \) electrons contributing to their charges. Nitrogen (group V) needs five valence electrons to be neutral, so it bears a formal charge of +1. Boron (group III) needs only three valence electrons to be neutral, so it bears a formal charge of -1.

Nitrogen: \[ \text{FC} = 5 - 0 - \frac{1}{2}(8) = +1 \]
Boron: \[ \text{FC} = 3 - 0 - \frac{1}{2}(8) = -1 \]

(d) \([H_2CNH_2]^+\)

**SOLUTION**
In this structure, both carbon and nitrogen have four shared pairs of bonding electrons. With four bonds, carbon is formally neutral; however, nitrogen is in group V, and it bears a formal positive charge: \( \text{FC} = 5 - 0 - 4 = +1 \).

This compound might also be drawn with the following Lewis structure:

In this structure, the carbon atom has three bonds with six bonding electrons. We calculate that \( \frac{6}{2} = 3 \) electrons, so carbon is one short of the four needed to be formally neutral:

\[ \text{FC} = 4 - 0 - \frac{1}{2}(6) = +1 \]

Nitrogen has six bonding electrons and two nonbonding electrons. We calculate that \( \frac{8}{2} + 2 = 5 \), so the nitrogen is uncharged in this second structure:

\[ \text{FC} = 5 - 2 - \frac{1}{2}(6) = 0 \]

The significance of these two Lewis structures is discussed in Section 1-9.

Most organic compounds contain only a few common elements, usually with complete octets of electrons. The summary table on the facing page shows the most commonly occurring bonding structures, using dashes to represent bonding pairs of electrons. Use the rules for calculating formal charges to verify the charges shown on these structures. A good understanding of the structures shown here will help you to draw organic compounds and their ions quickly and correctly.

1-8

**Ionic Structures**
Some organic compounds contain ionic bonds. For example, the structure of methylammonium chloride \((\text{CH}_3\text{NH}_3\text{Cl})\) cannot be drawn using just covalent bonds. That would require nitrogen to have five bonds, implying ten electrons in its valence shell. The correct structure shows the chloride ion ionically bonded to the rest of the structure.

\[ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{N}^+ \quad \text{H} \quad \text{H} \quad \text{H} \quad :\text{Cl}^- \]

\[ \text{methylnhommonium chloride} \]

\[ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{N}^- \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{Cl}^- \]

\[ \text{too many electrons around nitrogen} \]

\[ \text{cannot be drawn covalently} \]
Some molecules can be drawn either covalently or ionically. For example, sodium acetate (NaOCOCH₃) may be drawn with either a covalent bond or an ionic bond between sodium and oxygen. Because sodium generally forms ionic bonds with oxygen (as in NaOH), the ionically bonded structure is usually preferred. In general, bonds between atoms with very large electronegativity differences (about 2 or more) are usually drawn as ionic.

Some molecules can be drawn either covalently or ionically. For example, sodium acetate (NaOCOCH₃) may be drawn with either a covalent bond or an ionic bond between sodium and oxygen. Because sodium generally forms ionic bonds with oxygen (as in NaOH), the ionically bonded structure is usually preferred. In general, bonds between atoms with very large electronegativity differences (about 2 or more) are usually drawn as ionic.

\[
\text{Na}^+ \quad \begin{array}{c}
\ddots \\
\end{array} 
\text{O} \quad \begin{array}{c}
\ddots \\
\end{array} 
\text{C} \quad \begin{array}{c}
\ddots \\
\end{array} 
\text{C} \quad \begin{array}{c}
\ddots \\
\end{array} 
\text{H}
\]

more common

\[
\text{Na}^+ \quad \begin{array}{c}
\ddots \\
\end{array} 
\text{O} \quad \begin{array}{c}
\ddots \\
\end{array} 
\text{C} \quad \begin{array}{c}
\ddots \\
\end{array} 
\text{C} \quad \begin{array}{c}
\ddots \\
\end{array} 
\text{H}
\]

less common

PROBLEM 1-6

Draw Lewis structures for the following compounds and ions, showing appropriate formal charges.

(a) \([\text{CH}_3\text{OH}]^+\)  
(b) \(\text{NH}_4\text{Cl}\)  
(c) \((\text{CH}_3)_2\text{NH}_2\text{Cl}\)  
(d) \(\text{NaOCH}_3\)  
(e) \(\text{CH}_3\)  
(f) \(\text{CH}_3\)  
(g) \(\text{NaBH}_4\)  
(h) \(\text{NaBH}_3\text{CN}\)  
(i) \((\text{CH}_3)_2\text{O} \rightleftharpoons \text{BF}_3\)  
(j) \([\text{HONH}_3]^+\)  
(k) \(\text{KOC(CH}_3)_3\)  
(l) \([\text{H}_2\text{C} \equiv \text{OH}]^+\)

1-9A Resonance Hybrids

Some compounds’ structures are not adequately represented by a single Lewis structure. When two or more valence-bond structures are possible, differing only in the placement of electrons, the molecule will usually show characteristics of both structures. The different structures are called resonance structures or resonance forms because they are not different compounds, just different ways of drawing the same compound. The actual molecule is said to be a resonance hybrid of its resonance forms. In Solved Problem 1-1(d) we saw that the ion \([\text{H}_2\text{CNH}_2]^+\) might be represented by either of the following resonance forms:

\[
\begin{array}{c}
\text{H} \\
\text{H} \\
\text{C} \\
\text{N} \\
\text{H} \\
\text{H}
\end{array} \quad \leftrightarrow \quad \begin{array}{c}
\text{H} \\
\text{H} \\
\text{C} \\
\equiv \\
\text{N} \\
\text{H}
\end{array}
\]

resonance forms of a resonance hybrid

\[
\begin{array}{c}
\text{H} \\
\text{H} \\
\text{C} \\
\equiv \\
\text{N} \\
\text{H}
\end{array}
\]

combined representation
The actual structure of this ion is a resonance hybrid of the two structures. In the actual molecule, the positive charge is **delocalized** (spread out) over both the carbon atom and the nitrogen atom. In the left resonance form, the positive charge is on carbon, but carbon does not have an octet. Nitrogen’s nonbonding electrons can move into the bond (as indicated by the red arrow) to give the second structure with a double bond a positive charge on nitrogen and an octet on carbon. The combined representation attempts to combine the two resonance forms into a single picture with the charge shared by carbon and nitrogen.

Spreading the positive charge over two atoms makes the ion more stable than it would be if the entire charge were localized only on the carbon or only on the nitrogen. We call this a **resonance-stabilized** cation. Resonance is most important when it allows a charge to be delocalized over two or more atoms, as in this example.

Resonance stabilization plays a crucial role in organic chemistry, especially in the chemistry of compounds having double bonds. We will use the concept of resonance frequently throughout this course. For example, the acidity of acetic acid (following) is enhanced by resonance effects. When acetic acid loses a proton, the resulting acetate ion has a negative charge delocalized over both of the oxygen atoms. Each oxygen atom bears half of the negative charge, and this delocalization stabilizes the ion. Each of the carbon–oxygen bonds is halfway between a single bond and a double bond, and they are said to have a bond order of $1 \frac{1}{2}$.

We use a single double-headed arrow between resonance forms (and often enclose them in brackets) to indicate that the actual structure is a hybrid of the Lewis structures we have drawn. By contrast, an equilibrium is represented by two arrows in opposite directions.

Some uncharged molecules actually have resonance-stabilized structures with equal positive and negative formal charges. We can draw two Lewis structures for nitromethane ($\text{CH}_3\text{NO}_2$), but both of them have a formal positive charge on nitrogen and a negative charge on one of the oxygens. Thus, nitromethane has a positive charge on the nitrogen atom and a negative charge spread equally over the two oxygen atoms. The $\text{N} \equiv \text{O}$ bonds are midway between single and double bonds, as indicated in the combined representation:

![Resonance forms](image1)

Remember that individual resonance forms do not exist. The molecule does not “resonate” between these structures. It is a hybrid with some characteristics of both. An analogy is a mule, which is a hybrid of a horse and a donkey. The mule does not “resonate” between looking like a horse and looking like a donkey; it looks like a mule all the time, with the broad back of the horse and the long ears of the donkey.

### 1-9B Major and Minor Resonance Contributors

Two or more correct Lewis structures for the same compound may or may not represent electron distributions of equal energy. Although separate resonance forms do not
exist, we can estimate their relative energies as if they did exist. More stable resonance forms are closer representations of the real molecule than less stable ones. The two resonance forms shown earlier for the acetate ion have similar bonding, and they are of identical energy. The same is true for the two resonance forms of nitromethane. The following resonance forms are bonded differently, however.

These structures are not equal in estimated energy. The first structure has the positive charge on nitrogen. The second has the positive charge on carbon, and the carbon atom does not have an octet. The first structure is more stable because it has an additional bond and all the atoms have octets. Many stable ions have a positive charge on a nitrogen atom with four bonds (see Summary Table, page 13). We call the more stable resonance form the major contributor, and the less stable form is the minor contributor. The structure of the actual compound resembles the major contributor more than it does the minor contributor.

Many organic molecules have major and minor resonance contributors. Formaldehyde (H₂C═O) can be written with a negative charge on oxygen, balanced by a positive charge on carbon. This polar resonance form is higher in estimated energy than the double-bonded structure because it has charge separation, fewer bonds, and a positively charged carbon atom without an octet. The charge-separated structure is only a minor contributor, but it helps to explain why the formaldehyde C═O bond is very polar, with a partial positive charge on carbon and a partial negative charge on oxygen. The electrostatic potential map (EPM) also shows an electron-rich region (red) around oxygen and an electron-poor region (blue) around carbon in formaldehyde.

In drawing resonance forms, we try to draw structures that are as low in energy as possible. The best candidates are those that have the maximum number of octets and the maximum number of bonds. Also, we look for structures with the minimum amount of charge separation.

Only electrons can be delocalized. Unlike electrons, nuclei cannot be delocalized. They must remain in the same places, with the same bond distances and angles, in all the resonance contributors. The following general rules will help us to draw realistic resonance structures:

1. All the resonance structures must be valid Lewis structures for the compound.
2. Only the placement of the electrons may be shifted from one structure to another. (Electrons in double bonds and lone pairs are the ones that are most commonly shifted.) Nuclei cannot be moved, and the bond angles must remain the same.
PROBLEM-SOLVING Hint
Resonance forms can be compared using the following criteria, beginning with the most important:
1. As many octets as possible
2. As many bonds as possible
3. Any negative charges on electronegative atoms
4. As little charge separation as possible

3. The number of unpaired electrons (if any) must remain the same. Most stable compounds have no unpaired electrons, and all the electrons must remain paired in all the resonance structures.
4. The major resonance contributor is the one with the lowest energy. Good contributors generally have all octets satisfied, as many bonds as possible, and as little charge separation as possible. Negative charges are more stable on more electronegative atoms, such as O, N, and S.
5. Resonance stabilization is most important when it serves to delocalize a charge over two or more atoms.

SOLVED PROBLEM 1-2
For each of the following compounds, draw the important resonance forms. Indicate which structures are major and minor contributors or whether they would have the same energy.

(a) \([\text{CH}_3\text{OCH}_2]^+\)

SOLUTION

\[
\begin{align*}
\text{minor contributor} & \quad \leftrightarrow \quad \text{major contributor} \\
\text{The first (minor) structure has a carbon atom with only six electrons around it. The second (major) structure has octets on all atoms and an additional bond.}
\end{align*}
\]

(b) \(\text{H}^+\text{C}==\text{O}\)

SOLUTION

\[
\begin{align*}
\text{minor contributor} & \quad \leftrightarrow \quad \text{major contributor} \\
\text{Both of these structures have octets on oxygen and both carbon atoms, and they have the same number of bonds. The first structure has the negative charge on carbon; the second has it on oxygen. Oxygen is the more electronegative element, so the second structure is the major contributor.}
\end{align*}
\]

(c) \(\text{H}_2\text{SO}_4\)

SOLUTION

\[
\begin{align*}
\text{The first structure, with more bonds and less charge separation, is possible because sulfur is a third-row element with accessible } d \text{orbitals, giving it an expandable valence. For example, SF}_6\text{ is a stable compound with 12 electrons around sulfur. Theoretical calculations suggest that the last structure, with octets on all atoms, may be the major resonance contributor, however. We cannot always predict the major contributor of a resonance hybrid.}
\end{align*}
\]
**PROBLEM 1-7**

Draw the important resonance forms for the following molecules and ions.
(a) \( \text{CO}_3^{2-} \)  
(b) \( \text{NO}_3^- \)  
(c) \( \text{NO}_2^- \)  
(d) \( \text{H}_2\text{C}═\text{CH}—\text{CH}_2^+ \)  
(e) \( \text{H}_2\text{C}═\text{CH}—\text{CH}_2^- \)  
(f) \( \text{SO}_4^{2-} \)  
(g) \( \text{[CH}_3\text{C(OCH}_3)_2]^+ \)

**PROBLEM 1-8**

For each of the following compounds, draw the important resonance forms. Indicate which structures are major and minor contributors or whether they have the same energy.
(a) \( \text{[H}_2\text{CNO}_2]^- \)  
(b) \( \text{H}_2\text{C}═\text{CH}—\text{NO}_2 \)  
(c) \( \text{[H}_2\text{COH}]^+ \)  
(d) \( \text{H}_2\text{CNN} \)  
(e) \( \text{[H}_2\text{CCN}]^- \)  
(f) \( \text{H}_2\text{N}—\text{CH}═\text{CH}—\text{NH}_2 \)  
(g) \( \text{H}—\text{C}═\text{CH}—\text{C}═\text{H} \)  
(h) \( \text{H}—\text{C}—\text{NH}_2 \)

Several kinds of formulas are used by organic chemists to represent organic compounds. Some of these formulas involve a shorthand notation that requires some explanation. **Structural formulas** actually show which atoms are bonded to which.

There are two types of structural formulas, complete Lewis structures and condensed structural formulas. In addition, there are several ways of drawing condensed structural formulas. As we have seen, a Lewis structure symbolizes a bonding pair of electrons as a pair of dots or as a dash (——). Lone pairs of electrons are shown as pairs of dots.

### 1-10A Condensed Structural Formulas

Condensed structural formulas (Table 1-2) are written without showing all the individual bonds. In a condensed structure, each central atom is shown together with the atoms that are bonded to it. The atoms bonded to a central atom are often listed after the central atom (as in \( \text{CH}_3\text{CH}_3 \), rather than \( \text{H}_2\text{C}—\text{CH}_3 \)) even if that is not their actual bonding order. In many cases, if there are two or more identical groups, parentheses and a subscript may be used to represent all the identical groups. Nonbonding electrons are rarely shown in condensed structural formulas.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Lewis Structure</th>
<th>Condensed Structural Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethane</td>
<td>( \text{H}—\text{C}—\text{C}—\text{H} )</td>
<td>( \text{CH}_3\text{CH}_3 )</td>
</tr>
<tr>
<td>Isobutane</td>
<td>( \text{H}—\text{C}—\text{C}—\text{C}—\text{H} )</td>
<td>( (\text{CH}_3)_2\text{CH} )</td>
</tr>
<tr>
<td>( n )-hexane</td>
<td>( \text{H}—\text{C}—\text{C}—\text{C}—\text{C}—\text{C}—\text{H} )</td>
<td>( \text{CH}_3(\text{CH}_3)_2\text{CH} )</td>
</tr>
</tbody>
</table>

(Continued)
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TABLE 1-3  Condensed Structural Formulas for Double and Triple Bonds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Lewis Structure</th>
<th>Condensed Structural Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-butene</td>
<td>H—C—C=CH—H</td>
<td>CH₃CHCHCH₃ or CH₃CH=CHCH₃</td>
</tr>
<tr>
<td>acetonitrile</td>
<td>H—C=CH=O</td>
<td>CH₃CN or CH₃C≡N</td>
</tr>
<tr>
<td>acetaldehyde</td>
<td>H—C=CH</td>
<td>CH₃CHO or CH₃CH</td>
</tr>
<tr>
<td>acetone</td>
<td>H—C=CH=O</td>
<td>CH₃COCH₃ or CH₃CCH₃</td>
</tr>
<tr>
<td>acetic acid</td>
<td>H—C=CH=O</td>
<td>CH₃COOH or CH₃C—OH</td>
</tr>
</tbody>
</table>

When a condensed structural formula is written for a compound containing double or triple bonds, the multiple bonds are often drawn as they would be in a Lewis structure. Table 1-3 shows examples of condensed structural formulas containing multiple bonds. Notice that the —CHO group of an aldehyde and the —COOH group of a carboxylic acid are actually bonded differently from what the condensed notation suggests.
As you can see from Tables 1-2 and 1-3, the distinction between a complete Lewis structural formula and a condensed structural formula can be blurry. Chemists often draw formulas with some parts condensed and other parts completely drawn out. You should work with these different types of formulas so that you understand what all of them mean.

**PROBLEM 1-9**

Draw complete Lewis structures for the following condensed structural formulas.
(a) \( \text{CH}_3(\text{CH}_2)_3\text{CH}((\text{CH}_3)_2 \)
(b) \( (\text{CH}_3)_2\text{CHCl} \)
(c) \( \text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3 \)
(d) \( \text{CH}_3\text{CHO} \)
(e) \( \text{CH}_3\text{COCN} \)
(f) \( (\text{CH}_3)_2\text{COOH} \)
(g) \( (\text{CH}_3\text{CH}_2)_2\text{CO} \)

**1-10B Line–Angle Formulas**

Another kind of shorthand used for organic structures is the line-angle formula, sometimes called a skeletal structure or a stick figure. Line–angle formulas are often used for cyclic compounds and occasionally for noncyclic ones. In a stick figure, bonds are represented by lines, and carbon atoms are assumed to be present wherever two lines meet or a line begins or ends. Nitrogen, oxygen, and halogen atoms are shown, but hydrogen atoms are not usually drawn unless they are bonded to an atom that is drawn. Each carbon atom is assumed to have enough hydrogen atoms to give it a total of four bonds. Nonbonding electrons are rarely shown. Table 1-4 shows some examples of line-angle drawings.

**TABLE 1-4 Examples of Line–Angle Drawings**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Condensed Structure</th>
<th>Line–Angle Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>hexane</td>
<td>( \text{CH}_3(\text{CH}_2)_3\text{CH}_3 )</td>
<td><img src="image" alt="Hexane Line-Angle" /></td>
</tr>
<tr>
<td>2-hexene</td>
<td>( \text{CH}_3\text{CH}==\text{CHCH}_2\text{CH}_2\text{CH}_3 )</td>
<td><img src="image" alt="2-Hexene Line-Angle" /></td>
</tr>
<tr>
<td>3-hexanol</td>
<td>( \text{CH}_3\text{CH}_2\text{CH(OH)}\text{CH}_2\text{CH}_2\text{CH}_3 )</td>
<td><img src="image" alt="3-Hexanol Line-Angle" /></td>
</tr>
<tr>
<td>2-cyclohexenone</td>
<td><img src="image" alt="2-Cyclohexenone Line-Angle" /></td>
<td></td>
</tr>
<tr>
<td>2-methylcyclohexanol</td>
<td><img src="image" alt="2-Methylcyclohexanol Line-Angle" /></td>
<td></td>
</tr>
<tr>
<td>nicotinic acid</td>
<td><img src="image" alt="Nicotinic Acid Line-Angle" /></td>
<td></td>
</tr>
<tr>
<td>(a vitamin, also called niacin)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
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PROBLEM 1-10
Give Lewis structures corresponding to the following line–angle structures.

(a) \(\text{N}\) \(\text{H}\)
(b) \(\text{O}\)
(c) \(\text{N}\) \(\text{H}\)
(d) \(\text{OH}\)
(e) \(\text{CHO}\)
(f) \(\text{O}\)
(g) \(\text{O}\)
(h) \(\text{O}\)

PROBLEM 1-11
Draw condensed structural formulas corresponding to the following line–angle structures.

(a) \(\text{O}\)
(b) \(\text{OH}\)
(c) \(\text{OH}\)
(d) \(\text{O}\)

1-11
Molecular Formulas and Empirical Formulas

Before we can write possible structural formulas for a compound, we need to know its molecular formula. The molecular formula simply gives the number of atoms of each element in one molecule of the compound. For example, the molecular formula for 1-butanol is \(\text{C}_4\text{H}_{10}\text{O}\).

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \\
\text{1-butanol, molecular formula } \text{C}_4\text{H}_{10}\text{O}
\]

Calculation of the Empirical Formula Molecular formulas can be determined by a two-step process. The first step is the determination of an empirical formula, simply the relative ratios of the elements present. Suppose, for example, that an unknown compound was found by quantitative elemental analysis to contain 40.0% carbon and 6.67% hydrogen. The remainder of the weight (53.3%) is assumed to be oxygen. To convert these numbers to an empirical formula, we can follow a simple procedure.

1. Assume the sample contains 100 g, so the percent value gives the number of grams of each element. Divide the number of grams of each element by the atomic weight to get the number of moles of that atom in the 100-g sample.

2. Divide each of these numbers of moles by the smallest one. This step should give recognizable ratios.

For the unknown compound, we do the following computations:

\[
\begin{align*}
\frac{40.0 \text{ g C}}{12.0 \text{ g/mol}} &= 3.33 \text{ mol C}; & \frac{3.33 \text{ mol}}{3.33 \text{ mol}} &= 1 \\
\frac{6.67 \text{ g H}}{1.01 \text{ g/mol}} &= 6.60 \text{ mol H}; & \frac{6.60 \text{ mol}}{3.33 \text{ mol}} &= 1.98 \approx 2 \\
\frac{53.3 \text{ g O}}{16.0 \text{ g/mol}} &= 3.33 \text{ mol O}; & \frac{3.33 \text{ mol}}{3.33 \text{ mol}} &= 1
\end{align*}
\]

The first computation divides the number of grams of carbon by 12, the number of grams of hydrogen by 1, and the number of grams of oxygen by 16. We
compare these numbers by dividing them by the smallest number, 3.33. The final result is a ratio of one carbon to two hydrogens to one oxygen. This result gives the empirical formula $C_1H_2O_1$ or $CH_2O$, which simply shows the ratios of the elements. The molecular formula can be any multiple of this empirical formula, because any multiple also has the same ratio of elements. Possible molecular formulas are $CH_2O$, $C_2H_4O_2$, $C_3H_6O_3$, $C_4H_8O_4$, etc.

**Calculation of the Molecular Formula** How do we know the correct molecular formula? We can choose the right multiple of the empirical formula if we know the molecular weight. Molecular weights can be determined by methods that relate the freezing-point depression or boiling-point elevation of a solvent to the molal concentration of the unknown. If the compound is volatile, we can convert it to a gas and use its volume to determine the number of moles according to the gas law. Newer methods include mass spectrometry, which we will cover in Chapter 11.

For our example (empirical formula $CH_2O$), let’s assume that the molecular weight is determined to be about 60. The weight of one CH$_2$O unit is 30, so our unknown compound must contain twice this many atoms. The molecular formula must be $C_2H_4O_2$. The compound might be acetic acid.

In Chapters 12, 13, and 15 we will use spectroscopic techniques to determine the complete structure for a compound once we know its molecular formula.

**PROBLEM 1-12**

Compute the empirical and molecular formulas for each of the following elemental analyses.
In each case, propose at least one structure that fits the molecular formula.

<table>
<thead>
<tr>
<th>C</th>
<th>H</th>
<th>N</th>
<th>Cl</th>
<th>MW</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) 40.0%</td>
<td>6.67%</td>
<td>0</td>
<td>0</td>
<td>90</td>
</tr>
<tr>
<td>(b) 32.0%</td>
<td>6.67%</td>
<td>18.7%</td>
<td>0</td>
<td>75</td>
</tr>
<tr>
<td>(c) 37.2%</td>
<td>7.75%</td>
<td>0</td>
<td>55.0%</td>
<td>64</td>
</tr>
<tr>
<td>(d) 38.4%</td>
<td>4.80%</td>
<td>0</td>
<td>56.8%</td>
<td>125</td>
</tr>
</tbody>
</table>

**PROBLEM-SOLVING Hint**

If an elemental analysis does not add up to 100%, the missing percentage is assumed to be oxygen.

The properties and reactions of acids and bases are central to our study of organic chemistry. We need to consider exactly what is meant by the terms **acid** and **base**. Most people would agree that $H_2SO_4$ is an acid and NaOH is a base. Is BF$_3$ an acid or a base? Is ethylene (H$_2$C=CH$_2$) an acid or a base? To answer these questions, we need to understand the three different definitions of acids and bases: the Arrhenius definition, the Bronsted–Lowry definition, and the Lewis definition.

Acidic compounds were first classified on the basis of their sour taste. The Latin terms *acidus* (sour) and *acetum* (vinegar) gave rise to our modern terms **acid** and **acetic acid**. Alkaline compounds (bases) were substances that neutralize acids, such as limestone and plant ashes (*al kalai* in Arabic).

The **Arrhenius** theory, developed at the end of the nineteenth century, defined acids as *substances that dissociate in water to give $H_3O^+$ ions*. The stronger acids, such as sulfuric acid ($H_2SO_4$), were assumed to dissociate to a greater degree than weaker acids, such as acetic acid ($CH_3COOH$).

$$H_2SO_4 + H_2O \rightleftharpoons H_3O^+ + HSO_4^-$$

$$CH_3-C-OH + H_2O \rightleftharpoons H_3O^+ + CH_3-C-O^-$$
According to the Arrhenius definition, bases are substances that dissociate in water to give hydroxide ions. Strong bases, such as NaOH, were assumed to dissociate more completely than weaker, sparingly soluble bases such as Mg(OH)$_2$.

\[
\begin{align*}
\text{NaOH} & \rightarrow \text{Na}^+ + \text{OH}^- \\
\text{Mg(OH)}_2 & \rightarrow \text{Mg}^{2+} + 2\text{OH}^-
\end{align*}
\]

The acidity or basicity of an aqueous (water) solution is measured by the concentration of H$_3$O$^+$. This value also implies the concentration of OH$^-$ because these two concentrations are related by the water ion-product constant:

\[K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.00 \times 10^{-14} \text{ (at 24°C)}\]

In a neutral solution, the concentrations of H$_3$O$^+$ and OH$^-$ are equal.

\[ [\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.00 \times 10^{-7} \text{ M in a neutral solution} \]

Acidic and basic solutions are defined by an excess of H$_3$O$^+$ or OH$^-$. 

- acidic: $[\text{H}_3\text{O}^+ > 10^{-7} \text{ M and } [\text{OH}^- ] < 10^{-7} \text{ M}$
- basic: $[\text{H}_3\text{O}^+ ] < 10^{-7} \text{ M and } [\text{OH}^- ] > 10^{-7} \text{ M}$

Because these concentrations can span a wide range of values, the acidity or basicity of a solution is usually measured on a logarithmic scale. The pH is defined as the negative logarithm (base 10) of the H$_3$O$^+$ concentration.

\[ \text{pH} = -\log_{10}[\text{H}_3\text{O}^+] \]

A neutral solution has a pH of 7, an acidic solution has a pH less than 7, and a basic solution has a pH greater than 7.

**Problem 1-13**

Calculate the pH of the following solutions.

(a) 5.00 g of HBr in 100 mL of aqueous solution

(b) 1.50 g of NaOH in 50 mL of aqueous solution

The Arrhenius definition was an important contribution to understanding many acids and bases, but it does not explain why a compound such as ammonia (NH$_3$) neutralizes acids, even though it has no hydroxide ion in its molecular formula. In Section 1-13 we discuss a more versatile theory of acids and bases that will include ammonia and a wider variety of organic acids and bases.

**1-13 Brønsted–Lowry Acids and Bases**

In 1923, Brønsted and Lowry defined acids and bases on the basis of the transfer of protons. A Brønsted–Lowry acid is any species that can donate a proton, and a Brønsted–Lowry base is any species that can accept a proton. These definitions also include all the Arrhenius acids and bases because compounds that dissociate to give H$_3$O$^+$ are proton donors, and compounds that dissociate to give OH$^-$ are proton acceptors. (Hydroxide ion accepts a proton to form H$_2$O.)

In addition to Arrhenius acids and bases, the Brønsted–Lowry definition includes bases that have no hydroxide ions, yet can accept protons. Consider the
following examples of acids donating protons to bases. NaOH is a base under either the Arrhenius or Brønsted–Lowry definition. The other three are Brønsted–Lowry bases but not Arrhenius bases, because they have no hydroxide ions.

\[
\begin{align*}
\text{HCl} & \quad \text{proton donor} \quad + \quad \text{NaOH} \quad \text{proton acceptor} \quad \rightarrow \quad \text{NaCl} \quad + \quad \text{HOH} \\
\text{H}_2\text{SO}_4 & \quad \text{proton donor} \quad + \quad \text{NH}_3 \quad \text{proton acceptor} \quad \rightarrow \quad \text{HSO}_4^- \quad + \quad \text{H}-\text{NH}_3 \\
\text{HCl} & \quad \text{proton donor} \quad + \quad \text{CH}_3\text{C}=\text{C}+\text{CH}_3 \quad \text{proton acceptor} \quad \rightarrow \quad \text{Cl}^- \quad + \quad \text{CH}_3\text{C}=\text{C}+\text{CH}_3 \\
\text{HNO}_3 & \quad \text{proton donor} \quad + \quad \text{NH}_3 \quad \text{proton acceptor} \quad \rightarrow \quad \text{NO}_3^- \quad + \quad \text{NH}_4^+ \\
\end{align*}
\]

When a base accepts a proton, it becomes an acid capable of returning that proton. When an acid donates its proton, it becomes a base capable of accepting that proton back. One of the most important principles of the Brønsted–Lowry definition is this concept of **conjugate acids and bases**. For example, \(\text{NH}_4^+\) and \(\text{NH}_3\) are a conjugate acid–base pair. \(\text{NH}_3\) is the base; when it accepts a proton, it is transformed into its conjugate acid, \(\text{NH}_4^+\). Many compounds (water, for instance) can react either as an acid or as a base. Here are some additional examples of conjugate acid–base pairs.

\[
\begin{align*}
\text{H}_2\text{SO}_4 \quad \text{acid} \quad + \quad \text{H}_2\text{O} \quad \text{base} \quad \rightarrow \quad \text{HSO}_4^- \quad + \quad \text{H}_2\text{O}^+ \\
\text{H}_2\text{O} \quad \text{acid} \quad + \quad \text{NH}_3 \quad \text{base} \quad \rightarrow \quad ^{-}\text{OH} \quad + \quad \text{NH}_4^+ \\
\text{O} \quad \text{acid} \quad + \quad \text{CH}_3\text{O}^- \quad \text{base} \quad \rightarrow \quad \text{O} \quad + \quad \text{CH}_3\text{O}^- \\
\end{align*}
\]

**1-13A Acid Strength**

The strength of a Brønsted–Lowry acid is expressed as it is in the Arrhenius definition, by the extent of its ionization in water. The general reaction of an acid (HA) with water is the following:

\[
\text{HA} \quad + \quad \text{H}_2\text{O} \quad \xrightarrow{K_a} \quad \text{H}_3\text{O}^+ \quad + \quad \text{A}^- \\
\text{acid} \quad \text{base} \quad \text{conjugate acid–base pair} \\
K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \]
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$K_a$ is called the **acid-dissociation constant**, and its value indicates the relative strength of the acid. The stronger the acid, the more it dissociates, giving a larger value of $K_a$. Acid-dissociation constants vary over a wide range. Strong acids are almost completely ionized in water, and their dissociation constants are greater than 1. Most organic acids are weak acids, with values less than 1. Many organic compounds are extremely weak acids; for example, methane and ethane are essentially nonacidic, with $K_a$ values less than $10^{-30}$.

Because they span such a wide range, acid-dissociation constants are often expressed on a logarithmic scale. The $pK_a$ of an acid is defined just like the pH of a solution: as the negative logarithm (base 10) of $K_a$.

$$pK_a = -\log_{10} K_a$$

**SOLVED PROBLEM 1-3**

Calculate $K_a$ and $pK_a$ for water.

**SOLUTION**

The equilibrium that defines $K_a$ for water is

$$\begin{align*}
H_2O & \quad \rightleftharpoons \quad H_3O^+ + OH^- \\
\text{acid (HA)} & \quad \text{solvent} & \quad \text{conjugate base (A^-)}
\end{align*}$$

Water serves as both the acid and the solvent in this dissociation. The equilibrium expression is

$$K_a = \frac{[H_3O^+][OH^-]}{[H_2O]}$$

We already know that $[H_3O^+] = 1.00 \times 10^{-14}$, the ion-product constant for water.

The concentration of $H_2O$ in water is simply the number of moles of water in 1 L (about 1 kg).

$$\frac{1000 \text{ g/L}}{18 \text{ g/mol}} = 55.6 \text{ mol/L}$$

Substitution gives

$$K_a = \frac{[H_3O^+][OH^-]}{[H_2O]} = \frac{1.00 \times 10^{-14}}{55.6} = 1.8 \times 10^{-16} \text{ M}$$

The logarithm of $1.8 \times 10^{-16}$ is $-15.7$, so the $pK_a$ of water is 15.7.

**PROBLEM-SOLVING Hint**

In most cases, the $pK_a$ of an acid corresponds to the pH where the acid is about half dissociated. At a lower (more acidic) pH, the acid is mostly undissociated; at a higher (more basic) pH, the acid is mostly dissociated.

**PROBLEM 1-14**

Ammonia appears in Table 1-5 both as an acid and as a conjugate base.

(a) Explain how ammonia can act as both an acid and a base. Which of these roles does it commonly fill in aqueous solutions?

(b) Show how water can serve as both an acid and a base.

(c) Show how methanol ($\text{CH}_3\text{OH}$) can serve as both an acid and a base. Write an equation for the reaction of methanol with sulfuric acid.

**1-13B Base Strength**

The strength of an acid is inversely related to the strength of its conjugate base. For an acid (HA) to be strong, its conjugate base (A\(^-\)) must be stable in its anionic form;
otherwise, HA would not easily lose its proton. Therefore, the conjugate base of a strong acid must be a weak base. On the other hand, if an acid is weak, its conjugate is a strong base.

\[
\text{HCl} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{Cl}^-
\]

\[
\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{CH}_3\text{O}^-
\]

In the reaction of an acid with a base, the equilibrium generally favors the weaker acid and base. For example, in the preceding reactions, \(\text{H}_3\text{O}^+\) is a weaker acid than HCl but a stronger acid than CH\(_3\)OH. It also follows that H\(_2\)O is a stronger base than Cl\(^-\) but a weaker base than CH\(_3\)O\(^-\).
The strength of a base is measured much like the strength of an acid, by using the equilibrium constant of the hydrolysis reaction.

\[\text{A}^- + \text{H}_2\text{O} \rightleftharpoons \text{HA} + \cdot\text{OH} \]

The equilibrium constant \((K_b)\) for this reaction is called the base-dissociation constant for the base. Because this constant spans a wide range of values, it is often given in logarithmic form. The negative logarithm (base 10) of \(K_b\) is defined as \(pK_b\).

\[K_b = \frac{[\text{HA}][\cdot\text{OH}]}{[\text{A}^-]} \quad pK_b = -\log_{10} K_b\]

When we multiply \(K_a\) by \(K_b\), we can see how the acidity of an acid is related to the basicity of its conjugate base.

\[(K_a)(K_b) = \left(\frac{[\text{H}_2\text{O}^+][\text{A}^-]}{[\text{HA}]}ight) \cdot \left(\frac{[\text{HA}][\cdot\text{OH}]}{[\text{A}^-]}\right) = \frac{[\text{H}_2\text{O}^+][\cdot\text{OH}]}{[\text{H}_3\text{O}^+] [\cdot\text{OH}]} = 1.0 \times 10^{-14}\]

water ion-product constant

\[(K_a)(K_b) = 10^{-14}\]

Logarithmically,

\[pK_a + pK_b = -\log 10^{-14} = 14\]

The product of \(K_a\) and \(K_b\) must always equal the ion-product constant of water, \(10^{-14}\). If the value of \(K_a\) is large, the value of \(K_b\) must be small; that is, the stronger an acid, the weaker its conjugate base. Similarly, a small value of \(K_a\) (weak acid) implies a large value of \(K_b\) (strong base).

The stronger an acid, the weaker its conjugate base.

The weaker an acid, the stronger its conjugate base.

Acid–base reactions favor the weaker acid and the weaker base.

**Problem-Solving Hint**

An acid will donate a proton to the conjugate base of any weaker acid (smaller \(K_a\) or higher \(pK_a\)).

**Problem 1-15 (Partially Solved)**

Write equations for the following acid–base reactions. Use the information in Table 1-5 to predict whether the equilibrium will favor the reactants or the products.

(a) HCOOH + ?CN  
(b) CH$_3$COO$^-$ + CH$_3$OH  
(c) CH$_3$OH + NaNH$_2$  
(d) NaOCH$_3$ + HCN  
(e) HCl + H$_2$O  
(f) H$_3$O$^+$ + CH$_3$O$^-$

**Solution to (A)**

Cyanide is the conjugate base of HCN. It can accept a proton from formic acid:

\[
\begin{align*}
\text{H--C--N} : \quad &\text{H--C--N} : \\
\text{stronger acid} &\text{stronger base}
\end{align*}
\]

\[
\begin{align*}
\text{H--C--N} : \quad &\text{H--C--N} : \\
\text{stronger acid} &\text{stronger base}
\end{align*}
\]

Reading from Table 1-5, formic acid \((pK_a = 3.76)\) is a stronger acid than HCN \((pK_a = 9.22)\), and cyanide is a stronger base than formate. The products (weaker acid and base) are favored.
SOLVED PROBLEM 1-4

Each of the following compounds can act as an acid. Show the reaction of each compound with a general base (A⁻), and show the Lewis structure of the conjugate base that results.

(a) CH₃CH₂OH  (b) CH₃NH₂  (c) CH₃COOH

SOLUTION

(a) Ethanol (CH₃CH₂OH) can lose the O—H proton to give a conjugate base that is an organic analogue of hydroxide ion.

```
CH₃CH₂OH + A⁻ ⇌ CH₃CH₂O⁻ + HA
```

(C—H protons are much less acidic than O—H protons because carbon is less electronegative than oxygen, and the negative charge is therefore less stable on carbon.)

(b) Methylamine (CH₃NH₂) is a very weak acid. A very strong base can abstract a proton to give a powerful conjugate base.

```
CH₃NH₂ + A⁻ ⇌ CH₃N⁻ + HA
```

(c) Acetic acid (CH₃COOH) is a moderately strong acid, giving the resonance-stabilized acetate ion as its conjugate base.

```
CH₃COOH + A⁻ ⇌ CH₃COO⁻ + HA
```

SOLVED PROBLEM 1-5

Each of the compounds in Solved Problem 1-4 can also react as a base. Show the reaction of each compound with a general acid (HA), and show the Lewis structure of the conjugate acid that results.

SOLUTION

(a) Ethanol can undergo protonation on its oxygen atom. Notice that one of the lone pairs of the oxygen forms the new O—H bond.

```
CH₃CH₂OH + HA ⇌ CH₃CH₂O⁻ + H⁺
```

(b) The nitrogen atom of methylamine has a pair of electrons that can bond to a proton.

```
CH₃NH₂ + HA ⇌ CH₃NH⁺ + H⁺
```

(c) Acetic acid has nonbonding electrons on both of its oxygen atoms. Either of these oxygen atoms might become protonated, but protonation of the double-bonded oxygen is favored because protonation of this oxygen gives a symmetrical, resonance-stabilized conjugate acid.

```
CH₃COOH + HA ⇌ CH₃COO⁻ + H⁺
```
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PROBLEM 1-16
Solved Problem 1-5(c) showed protonation of the double-bonded oxygen in acetic acid. Show the product of protonation on the other (—OH) oxygen. Explain why protonation of the double-bonded oxygen is favored.

PROBLEM 1-17
(a) Rank ethanol, methylamine, and acetic acid in decreasing order of acidity.
(b) Rank ethanol, methylamine (pK₆ 3.36), and ethoxide ion (CH₃CH₂O⁻) in decreasing order of basicity. In each case, explain your ranking.

1-13C Structural Effects on Acidity
How can we look at a structure and predict whether a compound will be a strong acid, a weak acid, or not an acid at all? To be a Brønsted–Lowry acid (HA), a compound must contain a hydrogen atom that can be lost as a proton. A strong acid must have a stable conjugate base (A⁻) after losing the proton.

The stability of the conjugate base is a good guide to acidity. More stable anions tend to be weaker bases, and their conjugate acids tend to be stronger acids. Some of the factors that affect the stability of conjugate bases are electronegativity, size, and resonance.

Electronegativity A more electronegative element bears a negative charge more easily, giving a more stable conjugate base and a stronger acid. Electronegativities increase from left to right in the periodic table:

<table>
<thead>
<tr>
<th>Electronegativity</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stability</td>
<td>CH₃</td>
<td>NH₂</td>
<td>OH</td>
<td>F</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acidity</td>
<td>H—CH₃</td>
<td>H—NH₂</td>
<td>H—OH</td>
<td>H—F</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Basicity</td>
<td>CH₃</td>
<td>NH₂</td>
<td>OH</td>
<td>F</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Size The negative charge of an anion is more stable if it is spread over a larger region of space. Within a column of the periodic table, acidity increases down the column, as the size of the elements increases.

<table>
<thead>
<tr>
<th>Acidity</th>
<th>H—F</th>
<th>H—Cl</th>
<th>H—Br</th>
<th>H—I</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basicity</td>
<td>F⁻</td>
<td>Cl⁻</td>
<td>Br⁻</td>
<td>I⁻</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Size increases</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>acidity increases</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
**Resonance Stabilization** The negative charge of a conjugate base may be delocalized over two or more atoms by resonance. Depending on how electronegative those atoms are, and how many share the charge, resonance delocalization is often the dominant effect helping to stabilize an anion. Consider the following conjugate bases.

<table>
<thead>
<tr>
<th>Conjugate Base</th>
<th>Acid</th>
<th>pK_a</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃CH₂O⁻</td>
<td>CH₃CH₂OH</td>
<td>15.9</td>
</tr>
<tr>
<td>acetate ion</td>
<td>ethanol</td>
<td>(weak acid)</td>
</tr>
<tr>
<td>CH₃C≡C=O⁻</td>
<td>CH₃C≡OH</td>
<td>4.74</td>
</tr>
<tr>
<td>acetic acid</td>
<td>(moderate acid)</td>
<td></td>
</tr>
<tr>
<td>CH₃S=O⁻</td>
<td>CH₃SOH</td>
<td>−1.2</td>
</tr>
<tr>
<td>methanesulfonate ion</td>
<td>methanesulfonic acid</td>
<td>(strong acid)</td>
</tr>
</tbody>
</table>

Ethoxide ion is the strongest of these three bases. Ethoxide has a negative charge localized on one oxygen atom; acetate ion has the negative charge shared by two oxygen atoms; and the methanesulfonate ion has the negative charge spread over three oxygen atoms. The pKₐ values of the conjugate acids of these anions show that acids are stronger if they deprotonate to give resonance-stabilized conjugate bases.

**PROBLEM 1-18**
Write equations for the following acid–base reactions. Label the conjugate acids and bases, and show any resonance stabilization. Predict whether the equilibrium favors the reactants or products.
(a) CH₃CH₂OH + CH₃NH⁻
(b) CH₃CH₂COOH + CH₃NHCH₃
(c) CH₃OH + H₂SO₄
(d) NaOH + H₂S
(e) CH₃NH₃⁺ + CH₃O⁻
(f) CH₃O⁻ + CH₃COOH
(g) CH₃SO₃⁻ + CH₃COOH

The Bronsted–Lowry definition of acids and bases depends on the transfer of a proton from the acid to the base. The base uses a pair of nonbonding electrons to form a bond to the proton. G. N. Lewis reasoned that this kind of reaction does not need a proton. Instead, a base could use its lone pair of electrons to bond to some other electron-deficient atom. In effect, we can look at an acid–base reaction from the viewpoint of the bonds that are formed and broken rather than a proton that is transferred. The following reaction shows the proton transfer, with emphasis on the bonds being broken and formed. Organic chemists routinely use curved arrows to show the movement of the participating electrons.

Levens bases are species with nonbonding electrons that can be donated to form new bonds. Lewis acids are species that can accept these electron pairs to form new bonds. Since a Lewis acid accepts a pair of electrons, it is called an
Some of the terms associated with acids and bases have evolved specific meanings in organic chemistry. When organic chemists use the term base, they usually mean a proton acceptor (a Brønsted–Lowry base). Similarly, the term acid usually means a proton donor (a Brønsted–Lowry acid). When the acid–base reaction involves formation of a bond to some other element (especially carbon), organic chemists refer to the electron donor as a nucleophile (Lewis base) and the electron acceptor as an electrophile (Lewis acid).

The Lewis acid–base definitions include reactions having nothing to do with protons. Following are some examples of Lewis acid–base reactions. Notice that the common Brønsted–Lowry acids and bases also fall under the Lewis definition, with a proton serving as the electrophile. Curved arrows (red) are used to show the movement of electrons, generally from the nucleophile to the electrophile.

PROBLEM-SOLVING

A nucleophile donates electrons. An electrophile accepts electrons. Acidic protons may serve as electron acceptors.

The following illustration shows electrostatic potential maps for the preceding examples. The electron-rich (red) region of NH₃ attacks the electron-poor (blue) region of BF₃. The product shows high electron density on the boron atom and its three fluorine atoms and low electron density on nitrogen and its three hydrogen atoms.
The curved-arrow formalism is used to show the flow of an electron pair from the electron donor to the electron acceptor. The movement of each pair of electrons involved in making or breaking bonds is indicated by its own separate arrow, as shown in the preceding set of reactions. In this book, these curved arrows are always printed in red. In the preceding reaction of \( \text{CH}_3\text{O}^- + \text{CH}_3\text{Cl} \), one curved arrow shows the lone pair on oxygen forming a bond to carbon. Another curved arrow shows that the \( \text{C}—\text{Cl} \) bonding pair detaches from carbon and becomes a lone pair on the \( \text{Cl}^- \) product.

\[
\text{CH}_3\underbrace{\text{O}^-} \quad \text{H}\quad \text{C}\quad \text{Cl}: \quad \rightarrow \quad \text{CH}_3\underbrace{\text{O}^-}\text{C}—\text{H} + \text{Cl}^-.
\]

The curved-arrow formalism is universally used for keeping track of the flow of electrons in reactions. We have also used this device (in Section 1-9, for example) to keep track of electrons in resonance structures as we imagined their “flow” in going from one resonance structure to another. Remember that electrons do not “flow” in resonance structures; they are simply delocalized. Still, the curved-arrow formalism helps our minds flow from one resonance structure to another. We will find ourselves constantly using these (red) curved arrows to keep track of electrons, both as reactants change to products and as we imagine additional resonance structures of a hybrid.

**PROBLEM 1-19 (PARTIALLY SOLVED)**

In the following acid–base reactions,
1. determine which species are acting as electrophiles (acids) and which are acting as nucleophiles (bases).
2. use the curved-arrow formalism to show the movement of electron pairs in these reactions, as well as the imaginary movement in the resonance hybrids of the products.
3. indicate which reactions are best termed Brønsted–Lowry acid–base reactions.

(a) \( \text{CH}_3\underbrace{\text{C}—\text{H}} + \text{HCl} \rightarrow \text{CH}_3\underbrace{\text{C}—\text{H}}^- + \text{Cl}^- \)

This reaction is a proton transfer from HCl to the \( \text{C}==\text{O} \) group of acetaldehyde. Therefore, it is a Brønsted–Lowry acid–base reaction, with HCl acting as the acid (proton donor) and acetaldehyde acting as the base (proton acceptor). Before drawing any curved arrows, remember that arrows must show the movement of electrons from the electron-pair donor (the base) to the electron-pair acceptor (the acid). An arrow must go from the electrons on acetaldehyde that form the bond to the hydrogen atom, and the bond to chlorine must break, with the chloride ion taking these electrons. Drawing these arrows is easier once we draw good Lewis structures for all the reactants and products.

![Curved Arrow Reaction](image)

The resonance forms of the product show that a pair of electrons can be moved between the oxygen atom and the \( \text{C}==\text{O} \) pi bond. The positive charge is delocalized over the carbon and oxygen atoms, with most of the positive charge on oxygen because all octets are satisfied in that resonance structure.

(b) \( \text{CH}_3\underbrace{\text{C}—\text{H}} + \text{CH}_3\underbrace{\text{O}^-} \rightarrow \text{CH}_3\underbrace{\text{C}—\text{H}}^- + \text{Cl}^- \)

![Curved Arrow Reaction](image)
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In this case, no proton has been transferred, so this is not a Brønsted–Lowry acid–base reaction. Instead, a bond has formed between the C=O carbon atom and the oxygen of the CH₃—O⁻ group. Drawing the Lewis structures helps to show that the CH₃—O⁻ group (the nucleophile in this reaction) donates the electrons to form the new bond to acetaldehyde (the electrophile). This result agrees with our intuition that a negatively charged ion is likely to be electron-rich and therefore an electron donor.

\[
\text{CH}_3-C=O \rightarrow \text{CH}_3-C-H + \text{O}^- \)
\[
\text{electrophile} \quad \text{nucleophile}
\]

Notice that acetaldehyde acts as the nucleophile (Lewis base) in part (a) and as the electrophile (Lewis acid) in part (b). Like most organic compounds, acetaldehyde is both acidic and basic. It acts as a base if we add a strong enough acid to make it donate electrons or accept a proton. It acts as an acid if the base we add is strong enough to donate an electron pair or abstract a proton.

(c) \( \text{BH}_3 + \text{CH}_3-O-\text{CH}_3 \rightarrow \text{CH}_3-O-\text{CH}_3 \)

(d) \( \text{CH}_3-C-H + \cdot \text{OH} \rightarrow \text{CH}_3-C-H \)

(e) \( \text{CH}_3-C-H + \cdot \text{OH} \rightarrow \left[ \begin{array}{c} \text{H} \text{H} \text{H} \text{O} \\ \text{H-C-C-H} \leftrightarrow \text{H-C=O-C-H} \end{array} \right] + \text{H}_2\text{O} \)

(f) \( \text{CH}_3-\text{NH}_2 + \text{CH}_3-\text{Cl} \rightarrow \text{CH}_3-\text{NH}_2-\text{CH}_3 + \cdot \text{Cl}^- \)

Chapter 1
Glossary

Each chapter ends with a glossary that summarizes the most important new terms in the chapter. These glossaries are more than just a dictionary to look up unfamiliar terms as you encounter them (the index serves that purpose). The glossary is one of the tools for reviewing the chapter. You can read carefully through the glossary to see if you understand and remember all the terms and associated chemistry mentioned there. Anything that seems unfamiliar should be reviewed by turning to the page number given in the glossary listing.

**acid-dissociation constant** \( (K_a) \)  The equilibrium constant for the reaction of the acid with water to generate \( \text{H}_3\text{O}^+ \). (p. 23)

\[
\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^- \quad K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \]

The negative logarithm of \( K_a \) is expressed as \( pK_a \):

\[ pK_a = -\log_{10} K_a \]

**acids** and **bases** (pp. 21–32)
(Arrhenius definitions)

- **acid**: dissociates in water to give \( \text{H}_3\text{O}^+ \)
- **base**: dissociates in water to give \( \cdot \text{OH} \)
(Brønsted–Lowry definitions) acid: proton donor
base: proton acceptor
(Lewis definitions) acid: electron-pair acceptor (electrophile)
base: electron-pair donor (nucleophile)

conjugate acid The acid that results from protonation of a base. (p. 23)
conjugate base The base that results from loss of a proton from an acid. (p. 25)
covalent bonding Bonding that occurs by the sharing of electrons in the region between two nuclei. (p. 7)
single bond A covalent bond that involves the sharing of one pair of electrons. (p. 8)
double bond A covalent bond that involves the sharing of two pairs of electrons. (p. 8)
triple bond A covalent bond that involves the sharing of three pairs of electrons. (p. 8)
curved-arrow formalism A method of drawing curved arrows to keep track of electron movement from nucleophile to electrophile (or within a molecule) during the course of a reaction. (p. 31)
degenerate orbitals Orbitals with identical energies. (p. 4)
dipole moment ($\mu$) A measure of the polarity of a bond (or a molecule), proportional to the product of the charge separation times the bond length. (p. 10)
electron density The relative probability of finding an electron in a certain region of space. (p. 3)
electronegativity A measure of an element’s ability to attract electrons. Elements with higher electronegativities attract electrons more strongly. (p. 10)
electrophile An electron-pair acceptor (Lewis acid). (p. 29)
electrostatic potential map (EPM) A computer-calculated molecular representation that uses colors to show the charge distribution in a molecule. In most cases, the EPM uses red to show electron-rich regions (most negative electrostatic potential) and blue to show electron-poor regions (most positive electrostatic potential). The intermediate colors orange, yellow, and green show regions with intermediate electrostatic potentials. (p. 10)
empirical formula The ratios of atoms in a compound. (p. 20) See also molecular formula.
formal charges A method for keeping track of charges, showing what charge would be on an atom in a particular Lewis structure. (p. 11)
Hund’s rule When there are two or more unfilled orbitals of the same energy (degenerate orbitals), the lowest-energy configuration places the electrons in different orbitals (with parallel spins) rather than paired in the same orbital. (p. 6)
ionic bonding Bonding that occurs by the attraction of oppositely charged ions. Ionic bonding usually results in the formation of a large, three-dimensional crystal lattice. (p. 7)
isotopes Atoms with the same number of protons but different numbers of neutrons; atoms of the same element but with different atomic masses. (p. 3)
Lewis acid, Lewis base See acids and bases.
Lewis structure A structural formula that shows all valence electrons, with the bonds symbolized by dashes (—) or by pairs of dots, and nonbonding electrons symbolized by dots. (p. 7)
line–angle formula (skeletal structure, stick figure) A shorthand structural formula with bonds represented by lines. Carbon atoms are implied wherever two lines meet or a line begins or bends. Atoms other than C and H are drawn in, but hydrogen atoms are not shown unless they are on an atom that is drawn. Each carbon atom is assumed to have enough hydrogens to give it four bonds. (p. 19)

![Lewis structure of 2-cyclohexenol](image1)

lone pair A pair of nonbonding electrons. (p. 7)
molecular formula The number of atoms of each element in one molecule of a compound. The empirical formula simply gives the ratios of atoms of the different elements. For example, the molecular formula of glucose is C_{6}H_{12}O_{6}. Its empirical formula is CH_{2}O. Neither the molecular formula nor the empirical formula gives structural information. (p. 20)
node A region in an orbital with zero electron density. (p. 4)
nodal plane A flat (planar) region of space with zero electron density. (p. 4)
nonbonding electrons Valence electrons that are not used for bonding. A pair of nonbonding electrons is often called a lone pair. (p. 7)
nucleophile An electron-pair donor (Lewis base). (p. 29)
octet rule Atoms generally form bonding arrangements that give them filled shells of electrons (noble-gas configurations). For the second-row elements, this configuration has eight valence electrons. (p. 6)

orbital An allowed energy state for an electron bound to a nucleus; the probability function that defines the distribution of electron density in space. The Pauli exclusion principle states that up to two electrons can occupy each orbital if their spins are paired. (p. 3)

organic chemistry New definition: The chemistry of carbon compounds. Old definition: The study of compounds derived from living organisms and their natural products. (p. 1)

polar covalent bond A covalent bond in which electrons are shared unequally. A bond with equal sharing of electrons is called a nonpolar covalent bond. (p. 9)

resonance hybrid A molecule or ion for which two or more valid Lewis structures can be drawn, differing only in the placement of the valence electrons. These Lewis structures are called resonance forms or resonance structures. Individual resonance forms do not exist, but we can estimate their relative energies. The more important (lower-energy) structures are called major contributors, and the less important (higher-energy) structures are called minor contributors. When a charge is spread over two or more atoms by resonance, it is said to be delocalized and the molecule is said to be resonance stabilized. (pp. 13–16)

structural formulas A complete structural formula (such as a Lewis structure) shows all the atoms and bonds in the molecule. A condensed structural formula shows each central atom along with the atoms bonded to it. A line–angle formula (sometimes called a skeletal structure or stick figure) assumes that there is a carbon atom wherever two lines meet or a line begins or ends. See Section 1-10 for examples. (p. 17)

valence The number of bonds an atom usually forms. (p. 9)

valence electrons Those electrons that are in the outermost shell. (p. 6)

Vitalism The belief that syntheses of organic compounds require the presence of a “vital force.” (p. 1)

**Essential Problem-Solving Skills in Chapter I**

1. Draw and interpret Lewis, condensed, and line–angle structural formulas. Show which atoms bear formal charges.
2. Draw resonance forms, and use them to predict stabilities.
3. Calculate empirical and molecular formulas from elemental compositions.
4. Predict relative acidities and basicities based on structure, bonding, and resonance of conjugate acid–base pairs.
5. Calculate, use, and interpret values of $K_a$ and $pK_a$.
6. Identify nucleophiles (Lewis bases) and electrophiles (Lewis acids), and write equations for Lewis acid–base reactions using curved arrows to show the flow of electrons.

**Study Problems**

It’s easy to fool yourself into thinking you understand organic chemistry when you actually do not. As you read through this book, all the facts and ideas may make sense, yet you have not learned to combine and use those facts and ideas. An examination is a painful time to learn that you do not really understand the material.

The best way to learn organic chemistry is to use it. You will certainly need to read and reread all the material in the chapter, but this level of understanding is just the beginning. Problems are provided so you can work with the ideas, applying them to new compounds and new reactions that you have never seen before. By working problems, you force yourself to use the material and fill in the gaps in your understanding. You also increase your level of self-confidence and your ability to do well on exams.

Several kinds of problems are included in each chapter. There are problems within the chapters, providing examples and drill for the material as it is covered. Work these problems as you read through the chapter to ensure your understanding as you go along. Answers to many of these in-chapter problems are found at the back of this book. Study Problems at the end of each chapter give you additional experience using the material, and they force you to think in depth about the ideas. Problems with red stars (*) are more difficult problems that require extra thought and perhaps some extension of the material presented in the chapter. Some of the study problems have short answers in the back of this book, and all of them have detailed answers in the accompanying Solutions Manual.
Taking organic chemistry without working the problems is like skydiving without a parachute. Initially there is a breezy sense of freedom and daring. But then, there is the inevitable jolt that comes at the end for those who went unprepared.

1-20 Define and give an example for each term.

(a) isotopes  (b) orbital  (c) node
(d) degenerate orbitals  (e) valence electrons  (f) ionic bonding
(g) covalent bonding  (h) Lewis structure  (i) nonbonding electrons
(j) single bond  (k) double bond  (l) triple bond
(m) polar bond  (n) formal charges  (o) resonance forms
(p) molecular formula  (q) empirical formula  (r) Brønsted-Lowry acid and base
(s) covalent bonding  (t) Lewis acid and base  (u) electrophile
(v) nucleophile

1-21 Name the element that corresponds to each electronic configuration.

(a) 1s^22s^22p^63s^23p^4  (b) 1s^22s^22p^63s^23p^5  (c) 1s^22s^22p^63s^23p^5

1-22 There is a small portion of the periodic table that you must know to do organic chemistry. Construct this part from memory, using the following steps.

(a) From memory, make a list of the elements in the first two rows of the periodic table, together with their numbers of valence electrons.
(b) Use this list to construct the first two rows of the periodic table.
(c) Organic compounds often contain sulfur, phosphorus, chlorine, bromine, and iodine. Add these elements to your periodic table.

1-23 For each compound, state whether its bonding is covalent, ionic, or a mixture of covalent and ionic.

(a) NaCl  (b) NaOH  (c) CH_3Li  (d) CH_2Cl_2
(e) NaOCH_3  (f) HCO_2Na  (g) CF_4

1-24 (a) Both and are stable compounds. Draw Lewis structures for these two compounds.
(b) is a known compound, but all attempts to synthesize have failed. Draw Lewis structures for and a hypothetical and explain why is an unlikely structure.

1-25 Draw a Lewis structure for each species.

(a) N_2H_4  (b) N_2H_2  (c) (CH_3)_4NCl  (d) CH_3CN
(e) CH_3CHO  (f) CH_3S(O)CH_3  (g) H_2SO_4  (h) CH_3NCO
(i) CH_3OSO_2CH_3  (j) CH_3C(NH)CH_3  (k) (CH_3)_3CNO

1-26 Draw a Lewis structure for each compound. Include all nonbonding pairs of electrons.

(a) CH_3CHCHCH_3CHCHCOOH  (b) NCCCH_2COCH_2CHO
(c) CH_3CHCH(OH)CH_2CO_2H  (d) CH_3CH(CH_3)CH_2C(CH_2CH_3)_2CHO

1-27 Draw a line-structure formula for each compound in Problem 1-26.

1-28 Draw Lewis structures for

(a) two compounds of formula C_4H_10  (b) two compounds of formula C_2H_2N
(c) three compounds of formula C_3H_8O_2  (d) two compounds of formula C_2H_6O

1-29 Draw a complete structural formula and a condensed structural formula for

(a) three compounds of formula C_3H_6O  (b) five compounds of formula C_2H_4O

1-30 Some of the following molecular formulas correspond to stable compounds. When possible, draw a stable structure for each formula.

\[
\begin{align*}
\text{CH}_2 & \quad \text{CH}_3 & \quad \text{CH}_4 & \quad \text{CH}_5 \\
\text{C}_2\text{H}_2 & \quad \text{C}_2\text{H}_3 & \quad \text{C}_2\text{H}_4 & \quad \text{C}_2\text{H}_5 & \quad \text{C}_2\text{H}_7 \\
\text{C}_3\text{H}_2 & \quad \text{C}_3\text{H}_3 & \quad \text{C}_3\text{H}_4 & \quad \text{C}_3\text{H}_5 & \quad \text{C}_3\text{H}_7 & \quad \text{C}_3\text{H}_8 & \quad \text{C}_3\text{H}_9
\end{align*}
\]

Can you propose a general rule for the numbers of hydrogen atoms in stable hydrocarbons?

1-31 Draw complete Lewis structures, including lone pairs, for the following compounds.

(a) pyridine  (b) pyrrolidine  (c) morpholine
(d) NH_2\-
\begin{align*}
\text{COOH} & \quad \text{\gamma\text{-aminobutyric acid}} \\
& \quad (\text{a neurotransmitter})
\end{align*}
(e) (f) (g) (h)
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1-32 Give the molecular formula of each compound shown in Problem 1-31.

1-33 Compound X, isolated from lanolin (sheep's wool fat), has the pungent aroma of dirty sweatsocks. A careful analysis showed that compound X contains 62.0% carbon and 10.4% hydrogen. No nitrogen or halogen was found.

(a) Compute an empirical formula for compound X.
(b) A molecular weight determination showed that compound X has a molecular weight of approximately 117. Find the molecular formula of compound X.
(c) There are many possible structures that have this molecular formula. Draw complete structural formulas for four of them.

1-34 For each of the following structures,
1. Draw a Lewis structure; fill in any nonbonding electrons.
2. Calculate the formal charge on each atom other than hydrogen. All are electrically neutral except as noted.

1-35 1. From what you remember of electronegativities, show the direction of the dipole moments of the following bonds.
2. In each case, predict whether the dipole moment is relatively large or small.

(a) C—Cl    (b) C—H    (c) C—Li    (d) C—N    (e) C—O
(f) C—B    (g) C—Mg    (h) N—H    (i) O—H    (j) C—Br

1-36 Determine whether the following pairs of structures are actually different compounds or simply resonance forms of the same compounds.

1-37 Draw the important resonance forms to show the delocalization of charges in the following ions.

1-38 (a) Draw the resonance forms for SO₂ (bonded O—S—O).
(b) Draw the resonance forms for ozone (bonded O—O—O).
(c) Sulfur dioxide has one more resonance form than ozone. Explain why this structure is not possible for ozone.
Study Problems

*1-39* The following compound can become protonated on any of the three nitrogen atoms. One of these nitrogens is much more basic than the others, however.

(a) Draw the important resonance forms of the products of protonation on each of the three nitrogen atoms.

(b) Determine which nitrogen atom is the most basic.

\[ \text{CH}_3\text{NH} - \equiv \text{N} \]

1-40 In the following sets of resonance forms, label the major and minor contributors and state which structures would be of equal energy. Add any missing resonance forms.

(a) \[ [\text{CH}_3\equiv\text{N} + \text{H}_2\text{O} : \leftrightarrow \text{CH}_3\equiv\text{N}^+ \text{H}_2\text{O}^-] \]

(b) \[ [\text{CH}_3\equiv\text{N} + \text{H}_2\text{O} : \leftrightarrow \text{CH}_3\equiv\text{N}^+ \text{H}_2\text{O}^-] \]

(c) \[ [\text{CH}_3\equiv\text{N} + \text{H}_2\text{O} : \leftrightarrow \text{CH}_3\equiv\text{N}^+ \text{H}_2\text{O}^-] \]

(d) \[ [\text{CH}_3\equiv\text{N} + \text{H}_2\text{O} : \leftrightarrow \text{CH}_3\equiv\text{N}^+ \text{H}_2\text{O}^-] \]

(e) \[ [\text{CH}_3\equiv\text{N} + \text{H}_2\text{O} : \leftrightarrow \text{CH}_3\equiv\text{N}^+ \text{H}_2\text{O}^-] \]

1-41 For each pair of ions, determine which ion is more stable. Use resonance forms to explain your answers.

(a) \( \text{CH}_3\equiv\text{CH}\equiv\text{CH}_3 \) or \( \text{CH}_3\equiv\text{CH}-\text{OCH}_3 \)

(b) \( \text{CH}_3\equiv\text{CH}\equiv\text{CH}_3 \) or \( \text{CH}_3\equiv\text{CH}-\text{CH}_3 \)

(c) \( \text{CH}_3\equiv\text{CH}_3 \) or \( \text{CH}_3\equiv\text{C} \equiv\text{N} \)

(d) \[ \text{CH}_3\equiv\text{CH}_3 \] or \[ \text{CH}_3\equiv\text{C} \equiv\text{N} \]

(e) \( \text{CH}_3\equiv\text{C} \equiv\text{CH}_3 \) or \( \text{CH}_3\equiv\text{C} \equiv\text{CH}_3 \)

1-42 Rank the following species in order of increasing acidity. Explain your reasons for ordering them as you do.

\[ \text{NH}_3 \quad \text{H}_2\text{SO}_4 \quad \text{CH}_3\text{OH} \quad \text{CH}_3\text{COOH} \]

1-43 Rank the following species in order of increasing basicity. Explain your reasons for ordering them as you do.

\[ \text{CH}_3\text{O}^- \quad \text{H}_2\text{O} \quad \text{CH}_3\text{COO}^- \quad \text{NaOH} \quad \text{HF} \quad \text{NH}_2 \quad \text{HSO}_4^- \]

1-44 The \( K_a \) of phenylacetic acid is \( 5.2 \times 10^{-5} \), and the \( pK_a \) of propionic acid is 4.87.

(a) Calculate the \( pK_a \) of phenylacetic acid and the \( K_a \) of propionic acid.

(b) Which of these is the stronger acid? Calculate how much stronger an acid it is.

(c) Predict whether the following equilibrium will favor the reactants or the products.

\[ \text{CH}_3\text{COO}^- + \text{CH}_3\text{CH}_2\text{COOH} \rightleftharpoons \text{CH}_3\text{COOH} + \text{CH}_3\text{CH}_2\text{COO}^- \]
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1-45 Label the reactants in these acid–base reactions as Lewis acids (electrophiles) or Lewis bases (nucleophiles). Use curved arrows to show the movement of electron pairs in the reactions.

(a) \( \text{CH}_3\text{O}^- + \text{CH}_3\text{Cl} : \rightarrow \text{CH}_3\text{O}^-\text{CH}_3 + :\text{Cl}^- \)

(b) \( \text{CH}_3\text{O}^-\text{CH}_3 + :\text{O}^-\text{H} \rightarrow \text{CH}_3\text{O}^- + \text{CH}_3\text{O}^-\text{H} \)

(c) \( \text{H} - \text{C}^-\text{H} + :\text{NH}_3 \rightarrow \text{H} - \text{C}^-\text{H} - \text{NH}_3 \)

(d) \( \text{CH}_3\text{NH}_2 + \text{CH}_3\text{O}^-\text{H} \rightarrow \text{CH}_3\text{O}^-\text{CH}_3 + :\text{NH}_3^- \)

(e) \( \text{CH}_3\text{C}^-\text{CH}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{CH}_3\text{C}^-\text{CH}_3 + \text{HSO}_4^- \)

(f) \( (\text{CH}_3)_2\text{CCl} + \text{AlCl}_3 \rightarrow (\text{CH}_3)_2\text{C}^+ + :\text{AlCl}_4^- \)

(g) \( \text{CH}_3\text{C}^-\text{CH}_3 + :\text{O}^-\text{H} \rightarrow \text{CH}_3\text{C}^-\text{CH}_2 + \text{H} - :\text{O}^-\text{H} \)

(h) \( \text{CH}_2=\text{CH}_2 + \text{BF}_3 \rightarrow \text{BF}_3 - \text{CH}_2 = \text{CH}_2 \)

(i) \( \text{BF}_3 - \text{CH}_2 = \text{CH}_2 + \text{CH}_2=\text{CH}_2 \rightarrow \text{BF}_3 - \text{CH}_2 = \text{CH}_2 - \text{CH}_2 = \text{CH}_2 \)

1-46 Predict the products of the following acid–base reactions.

(a) \( \text{H}_2\text{SO}_4 + \text{CH}_3\text{COO}^- \rightarrow \)

(b) \( \text{CH}_3\text{COOH} + (\text{CH}_3)_2\text{N}: \rightarrow \)

(c) \( \text{O} \)

(d) \( (\text{CH}_3)_2\text{NH} + :\text{OH} \rightarrow \)

(e) \( \text{H} - \text{O}^-\text{OH} + 2 :\text{OH} \rightarrow \)

(f) \( \text{H}_2\text{O} + \text{NH}_3 \rightarrow \)

(g) \( \text{HCOOH} + \text{CH}_3\text{O}^- \rightarrow \)

1-47 Methyllithium \((\text{CH}_3\text{Li})\) is often used as a base in organic reactions.

(a) Predict the products of the following acid–base reaction.

(b) What is the conjugate acid of \(\text{CH}_3\text{Li}\)? Would you expect \(\text{CH}_3\text{Li}\) to be a strong base or a weak base?

1-48 In 1934, Edward A. Doisy of Washington University extracted 3000 lb of hog ovaries to isolate a few milligrams of pure estradiol, a potent female hormone. Doisy burned 5.00 mg of this precious sample in oxygen and found that 14.54 mg of \(\text{CO}_2\) and 3.97 mg of \(\text{H}_2\text{O}\) were generated.

(a) Determine the empirical formula of estradiol.

(b) The molecular weight of estradiol was later determined to be 272. Determine the molecular formula of estradiol.