An Introduction to the Study of Organic Chemistry

The first two chapters of the text cover a variety of topics that you need to get started with your study of organic chemistry.

Chapter 1 reviews the topics from general chemistry that will be important to your study of organic chemistry. The chapter starts with a description of the structure of atoms and then proceeds to a description of the structure of molecules. Molecular orbital theory is introduced. Acid–base chemistry, which is central to understanding many organic reactions, is reviewed. You will see how the structure of a molecule affects its acidity and how the acidity of a solution affects molecular structure.

To discuss organic compounds, you must be able to name them and visualize their structures when you read or hear their names. In **Chapter 2**, you will learn how to name five different classes of organic compounds. This will give you a good understanding of the basic rules followed in naming compounds. Because the compounds examined in the chapter are either the reactants or the products of many of the reactions presented in the next 10 chapters, you will have the opportunity to review the nomenclature of these compounds as you proceed through those chapters. The structures and physical properties of these compounds will be compared and contrasted, which makes learning about them a little easier than if each compound were presented separately. Because organic chemistry is a study of compounds that contain carbon, the last part of Chapter 2 discusses the spatial arrangement of the atoms in both chains and rings of carbon atoms.

Chapter 1
Electronic Structure and Bonding
• Acids and Bases

Chapter 2
An Introduction to Organic Compounds: Nomenclature, Physical Properties, and Representation of Structure

1 Electronic Structure and Bonding • Acids and Bases

Ethane

Ethene

Ethyne

Jöns Jakob Berzelius (1779–1848) *not only coined the terms "organic" and "inorganic," but also invented the system of chemical symbols still used today. He published the first list of accurate atomic weights and proposed the idea that atoms carry an electric charge. He purified or discovered the elements cerium, selenium, silicon, thorium, titanium, and zirconium.*

German chemist **Friedrich Wöhler (1800–1882)** *began his professional life as a physician and later became a professor of chemistry at the University of Göttingen. Wöhler codiscovered the fact that two different chemicals could have the same molecular formula. He also developed methods of purifying aluminum—at the time, the most expensive metal on Earth—and beryllium.*
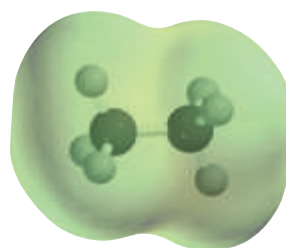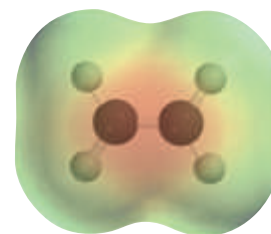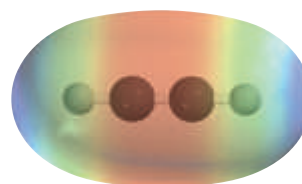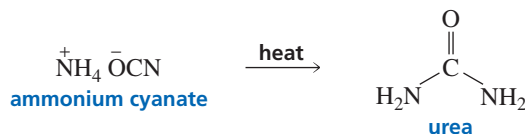
T o stay alive, early humans must have been able to tell the difference between two kinds of materials in their world. "You can live on roots and berries," they might have said, "but you can't live on dirt. You can stay warm by burning tree branches, but you can't burn rocks."

By the eighteenth century, scientists thought they had grasped the nature of that difference, and in 1807, Jöns Jakob Berzelius gave names to the two kinds of materials. Compounds derived from living organisms were believed to contain an unmeasurable vital force—the essence of life. These he called "organic." Compounds derived from minerals—those lacking that vital force—were "inorganic."

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

$$\overset{+}{N}H_4 \ \overset{-}{O}CN \xrightarrow{\text{heat}} \underset{\text{urea}}{H_2N \overset{\overset{\textstyle O}{\|}}{\underset{}{C}} NH_2}$$

$$\underset{\text{ammonium cyanate}}{}$$

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

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

make life possible—proteins, enzymes, vitamins, lipids, carbohydrates, and nucleic acids—contain carbon, so the chemical reactions that take place in living systems, including our own bodies, are organic reactions. Most of the compounds found in nature—those we rely on for food, medicine, clothing (cotton, wool, silk), and energy (natural gas, petroleum)—are organic as well. Important organic compounds are not, however, limited to the ones we find in nature. Chemists have learned to synthesize millions of organic compounds never found in nature, including synthetic fabrics, plastics, synthetic rubber, medicines, and even things like photographic film and Super glue. Many of these synthetic compounds prevent shortages of naturally occurring products. For example, it has been estimated that if synthetic materials were not available for clothing, all of the arable land in the United States would have to be used for the production of cotton and wool just to provide enough material to clothe us. Currently, there are about 16 million known organic compounds, and many more are possible.

What makes carbon so special? Why are there so many carbon-containing compounds? The answer lies in carbon's position in the periodic table. Carbon is in the center of the second row of elements. The atoms to the left of carbon have a tendency to give up electrons, whereas the atoms to the right have a tendency to accept electrons (Section 1.3).

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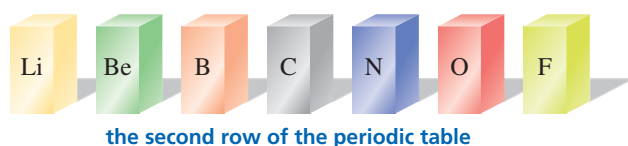
Because carbon is in the middle, it neither readily gives up nor readily accepts electrons. Instead, it shares electrons. Carbon can share electrons with several different kinds of atoms, and it can also share electrons with other carbon atoms. Consequently, carbon is able to form millions of stable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

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

1.1   The Structure of an Atom

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

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

The **atomic number** of an atom equals the number of protons in its nucleus. The atomic number is also the number of electrons that surround the nucleus of a neutral atom. For example, the atomic number of carbon is 6, which means that a neutral carbon atom has six protons and six electrons. Because the number of protons in an atom does not change, the atomic number of a particular element is always the same—all carbon atoms have an atomic number of 6.

The **mass number** of an atom is the *sum* of its protons and neutrons. Not all carbon atoms have the same mass number, because, even though they all have the same number of protons, they do not all have the same number of neutrons. For example, 98.89% of naturally occurring carbon atoms have six neutrons—giving them a mass number of 12—and 1.11% have seven neutrons—giving them a mass number of 13. These two different kinds of carbon atoms (^{12}C and ^{13}C) are called isotopes. **Isotopes** have the same atomic number (i.e., the same number of protons), but different mass numbers because they have different numbers of neutrons. The chemical properties of isotopes of a given element are nearly identical.

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

The **atomic weight** of a naturally occurring element is the average weighted mass of its atoms. Because an *atomic mass unit (amu)* is defined as exactly $1/12$ of the mass of ^{12}C, the atomic mass of ^{12}C is 12.0000 amu; the atomic mass of ^{13}C is 13.0034 amu. Therefore, the atomic weight of carbon is 12.011 amu $(0.9889 \times 12.0000 + 0.0111 \times 13.0034 = 12.011)$. The **molecular weight** is the sum of the atomic weights of all the atoms in the molecule.

PROBLEM 1◆

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

1.2 The Distribution of Electrons in an Atom

Electrons are moving continuously. Like anything that moves, electrons have kinetic energy, and this energy is what counters the attractive force of the positively charged protons that would otherwise pull the negatively charged electrons into the nucleus. For a long time, electrons were perceived to be particles—infinitesimal "planets" orbiting the nucleus of an atom. In 1924, however, a French physicist named Louis de Broglie showed that electrons also have wavelike properties. He did this by combining a formula developed by Einstein that relates mass and energy with a formula developed by Planck relating frequency and energy. The realization that electrons have wavelike properties spurred physicists to propose a mathematical concept known as quantum mechanics.

Quantum mechanics uses the same mathematical equations that describe the wave motion of a guitar string to characterize the motion of an electron around a nucleus. The version of quantum mechanics most useful to chemists was proposed by Erwin Schrödinger in 1926. According to Schrödinger, the behavior of each electron in an atom or a molecule can be described by a **wave equation**. The solutions to the Schrödinger equation are called **wave functions** or **orbitals**. They tell us the *energy* of the electron and the *volume of space* around the nucleus where an electron is most likely to be found.

According to quantum mechanics, the electrons in an atom can be thought of as occupying a set of concentric shells that surround the nucleus. The first shell is the one

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

ALBERT EINSTEIN

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

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

closest to the nucleus. The second shell lies farther from the nucleus, and even farther out lie the third and higher numbered shells. Each shell contains subshells known as **atomic orbitals**. Each atomic orbital has a characteristic shape and energy and occupies a characteristic volume of space, which is predicted by the Schrödinger equation. An important point to remember is that *the closer the atomic orbital is to the nucleus, the lower is its energy.*

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

The first shell consists of only an *s* atomic orbital; the second shell consists of *s* and *p* atomic orbitals; the third shell consists of *s*, *p*, and *d* atomic orbitals; and the fourth and higher shells consist of *s*, *p*, *d*, and *f* atomic orbitals (Table 1.1).

Each shell contains one *s* atomic orbital. The second and higher shells—in addition to their *s* orbital—each contain three *degenerate p* atomic orbitals. **Degenerate orbitals** are orbitals that have the same energy. The third and higher shells—in

Table 1.1 Distribution of Electrons in the First Four Shells That Surround the Nucleus				
	First shell	**Second shell**	**Third shell**	**Fourth shell**
Atomic orbitals	*s*	*s*, *p*	*s*, *p*, *d*	*s*, *p*, *d*, *f*
Number of atomic orbitals	1	1, 3	1, 3, 5	1, 3, 5, 7
Maximum number of electrons	2	8	18	32

MAX KARL ERNST LUDWIG PLANCK

Max Planck (1858–1947) was born in Germany, the son of a professor of civil law. He was a professor at the Universities of Munich (1880–1889) and Berlin (1889–1926). Two of his daughters died in childbirth, and one of his sons was killed in action in World War I. In 1918, Planck received the Nobel Prize in physics for his development of quantum theory. He became president of the Kaiser Wilhelm Society of Berlin—later renamed the Max Planck Society—in 1930. Planck felt that it was his duty to remain in Germany during the Nazi era, but he never supported the Nazi regime. He unsuccessfully interceded with Hitler on behalf of his Jewish colleagues and, as a consequence, was forced to resign from the presidency of the Kaiser Wilhelm Society in 1937. A second son was accused of taking part in the plot to kill Hitler and was executed. Planck lost his home to Allied bombings. He was rescued by Allied forces during the final days of the war.

addition to their s and p orbitals—also contain five degenerate d atomic orbitals, and the fourth and higher shells also contain seven degenerate f atomic orbitals. Because a maximum of two electrons can coexist in an atomic orbital (see the Pauli exclusion principle, below), the first shell, with only one atomic orbital, can contain no more than two electrons. The second shell, with four atomic orbitals—one s and three p— can have a total of eight electrons. Eighteen electrons can occupy the nine atomic orbitals—one s, three p, and five d—of the third shell, and 32 electrons can occupy the 16 atomic orbitals of the fourth shell. In studying organic chemistry, we will be concerned primarily with atoms that have electrons only in the first and second shells.

The **ground-state electronic configuration** of an atom describes the orbitals occupied by the atom's electrons when they are all in the available orbitals with the lowest energy. If energy is applied to an atom in the ground state, one or more electrons can jump into a higher energy orbital. The atom then would be in an **excited-state electronic configuration**. The ground-state electronic configurations of the 11 smallest atoms are shown in Table 1.2. (Each arrow—whether pointing up or down—represents one electron.) The following principles are used to determine which orbitals electrons occupy:

1. The **aufbau principle** (*aufbau* is German for "building up") tells us the first thing we need to know to be able to assign electrons to the various atomic orbitals. According to this principle, an electron always goes into the available orbital with the lowest energy. The relative energies of the atomic orbitals are as follows:

   $1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p <$
   $6s < 4f < 5d < 6p < 7s < 5f$
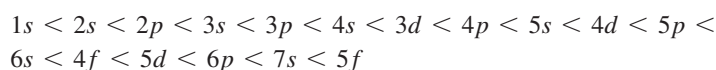
   Because a $1s$ atomic orbital is closer to the nucleus, it is lower in energy than a $2s$ atomic orbital, which is lower in energy—and is closer to the nucleus—than a $3s$ atomic orbital. Comparing atomic orbitals in the same shell, we see that an s atomic orbital is lower in energy than a p atomic orbital, and a p atomic orbital is lower in energy than a d atomic orbital.

2. The **Pauli exclusion principle** states that (a) no more than two electrons can occupy each atomic orbital, and (b) the two electrons must be of opposite spin. It is called an exclusion principle because it states that only so many electrons can occupy any particular shell. Notice in Table 1.2 that spin in one direction is designated by an upward-pointing arrow, and spin in the opposite direction by a downward-pointing arrow.

As a teenager, Austrian **Wolfgang Pauli (1900–1958)** *wrote articles on relativity that caught the attention of Albert Einstein. Pauli went on to teach physics at the University of Hamburg and at the Zurich Institute of Technology. When World War II broke out, he immigrated to the United States, where he joined the Institute for Advanced Study at Princeton.*

TABLE 1.2 The Ground-State Electronic Configurations of the Smallest Atoms								
Atom	Name of element	Atomic number	$1s$	$2s$	$2p_x$	$2p_y$	$2p_z$	$3s$
H	Hydrogen	1	↑					
He	Helium	2	↑↓					
Li	Lithium	3	↑↓	↑				
Be	Beryllium	4	↑↓	↑↓				
B	Boron	5	↑↓	↑↓	↑			
C	Carbon	6	↑↓	↑↓	↑	↑		
N	Nitrogen	7	↑↓	↑↓	↑	↑	↑	
O	Oxygen	8	↑↓	↑↓	↑↓	↑	↑	
F	Fluorine	9	↑↓	↑↓	↑↓	↑↓	↑	
Ne	Neon	10	↑↓	↑↓	↑↓	↑↓	↑↓	
Na	Sodium	11	↑↓	↑↓	↑↓	↑↓	↑↓	↑

From these first two rules, we can assign electrons to atomic orbitals for atoms that contain one, two, three, four, or five electrons. The single electron of a hydrogen atom occupies a $1s$ atomic orbital, the second electron of a helium atom fills the $1s$ atomic orbital, the third electron of a lithium atom occupies a $2s$ atomic orbital, the fourth electron of a beryllium atom fills the $2s$ atomic orbital, and the fifth electron of a boron atom occupies one of the $2p$ atomic orbitals. (The subscripts x, y, and z distinguish the three $2p$ atomic orbitals.) Because the three p orbitals are degenerate, the electron can be put into any one of them. Before we can continue to larger atoms—those containing six or more electrons—we need Hund's rule:

3. **Hund's rule** states that when there are degenerate orbitals—two or more orbitals with the same energy—an electron will occupy an empty orbital before it will pair up with another electron. In this way, electron repulsion is minimized. The sixth electron of a carbon atom, therefore, goes into an empty $2p$ atomic orbital, rather than pairing up with the electron already occupying a $2p$ atomic orbital. (See Table 1.2.) The seventh electron of a nitrogen atom goes into an empty $2p$ atomic orbital, and the eighth electron of an oxygen atom pairs up with an electron occupying a $2p$ atomic orbital rather than going into a higher energy $3s$ orbital.

Using these three rules, the locations of the electrons in the remaining elements can be assigned.

Tutorial:
Electrons in orbitals

Friedrich Hermann Hund (1896–1997) *was born in Germany. He was a professor of physics at several German universities, the last being the University of Göttingen. He spent a year as a visiting professor at Harvard University. In February 1996, the University of Göttingen held a symposium to honor Hund on his 100th birthday.*

PROBLEM 2◆

Potassium has an atomic number of 19 and one unpaired electron. What orbital does the unpaired electron occupy?

PROBLEM 3◆

Write electronic configurations for chlorine (atomic number 17), bromine (atomic number 35), and iodine (atomic number 53).

1.3   Ionic, Covalent, and Polar Bonds

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

Lithium (Li) has a single electron in its $2s$ atomic orbital. If it loses this electron, the lithium atom ends up with a filled outer shell—a stable configuration. Removing an electron from an atom takes energy—called the **ionization energy**. Lithium has a relatively low ionization energy—the drive to achieve a filled outer shell with no electrons of higher energy causes it to lose an electron relatively easily. Sodium (Na) has a single electron in its $3s$ atomic orbital. Consequently, sodium also has a relatively low ionization energy because, when it loses an electron, it is left with an outer shell of eight electrons. Elements (such as lithium and sodium) that have low ionization energies are said to be **electropositive**—they readily lose an electron and thereby become positively charged. The elements in the first column of the periodic table are all electropositive—each readily loses an electron because each has a single electron in its outermost shell.

Electrons in inner shells (those below the outermost shell) are called **core electrons**. Core electrons do not participate in chemical bonding. Electrons in the outermost shell are called **valence electrons**, and the outermost shell is called the valence shell. Carbon, for example, has two core electrons and four valence electrons (Table 1.2).

Lithium and sodium each have one valence electron. Elements in the same column of the periodic table have the same number of valence electrons, and because the number of valence electrons is the major factor determining an element's chemical properties, elements in the same column of the periodic table have similar chemical properties. Thus, the chemical behavior of an element depends on its electronic configuration.

PROBLEM 4

Compare the ground-state electronic configurations of the following atoms, and check the relative positions of the atoms in Table 1.3 on p. 10.

a. carbon and silicon
b. oxygen and sulfur
c. fluorine and bromine
d. magnesium and calcium

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

$$Li\cdot \longrightarrow Li^+ + e^-$$

$$Na\cdot \longrightarrow Na^+ + e^-$$

Fluorine has seven valence electrons (Table 1.2). Consequently, it readily acquires an electron in order to have an outer shell of eight electrons. When an atom acquires an electron, energy is released. Elements in the same column as fluorine (e.g., chlorine, bromine, and iodine) also need only one electron to have an outer shell of eight, so they, too, readily acquire an electron. Elements that readily acquire an electron are said to be **electronegative**—they acquire an electron easily and thereby become negatively charged.

$$:\ddot{F}\cdot + e^- \longrightarrow :\ddot{F}:^-$$

$$:\ddot{C}l\cdot + e^- \longrightarrow :\ddot{C}l:^-$$
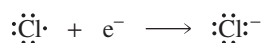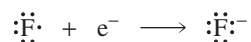
Ionic Bonds

Because sodium gives up an electron easily and chlorine acquires an electron readily, when sodium metal and chlorine gas are mixed, each sodium atom transfers an electron to a chlorine atom, and crystalline sodium chloride (table salt) is formed as a result. The positively charged sodium ions and negatively charged chloride ions are independent species held together by the attraction of opposite charges (Figure 1.1). A **bond** is an attractive force between two atoms. Attractive forces between opposite charges are called **electrostatic attractions**. A **bond** that is the result of only electrostatic attractions is called an ionic bond. Thus, an **ionic bond** is formed when there is a *transfer of electrons*, causing one atom to become a positively charged ion and the other to become a negatively charged ion.
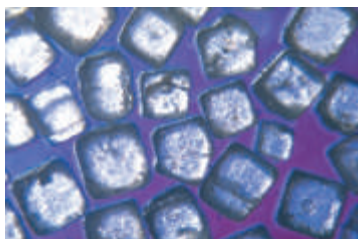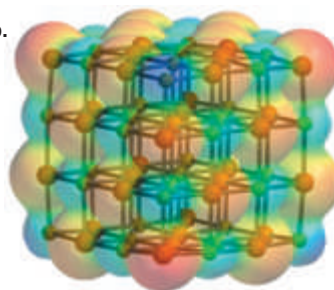
3-D Molecule:
Sodium chloride lattice

Figure 1.1 ▶
(a) Crystalline sodium chloride.
(b) The electron-rich chloride ions are red and the electron-poor sodium ions are blue. Each chloride ion is surrounded by six sodium ions, and each sodium ion is surrounded by six chloride ions. Ingore the "bonds" holding the balls together; they are there only to keep the model from falling apart.
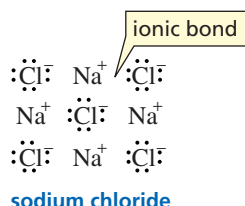
a.

b.

ionic bond

:$\ddot{\text{C}}\text{l}$:⁻ Na⁺ :$\ddot{\text{C}}\text{l}$:⁻

Na⁺ :$\ddot{\text{C}}\text{l}$:⁻ Na⁺

:$\ddot{\text{C}}\text{l}$:⁻ Na⁺ :$\ddot{\text{C}}\text{l}$:⁻

sodium chloride

Sodium chloride is an example of an ionic compound. **Ionic compounds** are formed when an element on the left side of the periodic table (an electropositive element) transfers one or more electrons to an element on the right side of the periodic table (an electronegative element).

Covalent Bonds

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

a covalent bond

:$\ddot{\text{F}}$· + ·$\ddot{\text{F}}$: $\longrightarrow$:$\ddot{\text{F}}$:$\ddot{\text{F}}$:
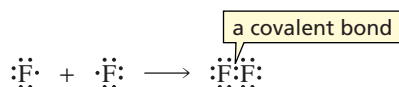
Two hydrogen atoms can form a covalent bond by sharing electrons. As a result of covalent bonding, each hydrogen acquires a stable, filled outer shell (with two electrons).
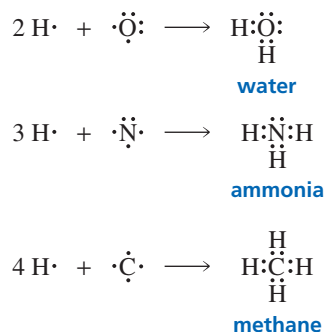
H· + ·H $\longrightarrow$ H:H

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

H· + ·$\ddot{\text{C}}\text{l}$: $\longrightarrow$ H:$\ddot{\text{C}}\text{l}$:
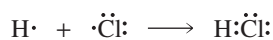
A hydrogen atom can achieve a completely empty shell by losing an electron. Loss of its sole electron results in a positively charged **hydrogen ion**. A positively charged hydrogen ion is called a **proton** because when a hydrogen atom loses its valence electron, only the hydrogen nucleus—which consists of a single proton—remains. A hydrogen atom can achieve a filled outer shell by gaining an electron, thereby forming a negatively charged hydrogen ion, called a **hydride ion**.

H· $\longrightarrow$ H⁺ + e⁻

a hydrogen atom   **a proton**

H· + e⁻ $\longrightarrow$ H:⁻

a hydrogen atom   **a hydride ion**
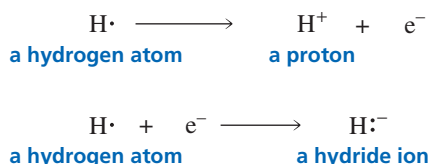
Because oxygen has six valence electrons, it needs to form two covalent bonds to achieve an outer shell of eight electrons. Nitrogen, with five valence electrons, must form three covalent bonds, and carbon, with four valence electrons, must form four covalent bonds to achieve a filled outer shell. Notice that all the atoms in water, ammonia, and methane have filled outer shells.
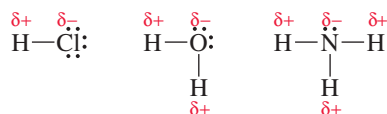
2 H· + ·$\ddot{\text{O}}$: $\longrightarrow$ H:$\ddot{\text{O}}$:
                                            H

water

3 H· + ·$\ddot{\text{N}}$· $\longrightarrow$ H:$\ddot{\text{N}}$:H
                                            H

ammonia

                                            H
4 H· + ·$\dot{\text{C}}$· $\longrightarrow$ H:$\overset{..}{\text{C}}$:H
                                            H

methane

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

Polar Covalent Bonds

In the F—F and H—H covalent bonds shown previously, the atoms that share the bonding electrons are identical. Therefore, they share the electrons equally; that is, each electron spends as much time in the vicinity of one atom as in the other. An even (nonpolar) distribution of charge results. Such a bond is called a **nonpolar covalent bond**.

In contrast, the bonding electrons in hydrogen chloride, water, and ammonia are more attracted to one atom than another because the atoms that share the electrons in these molecules are different and have different electronegativities. **Electronegativity** is the tendency of an atom to pull bonding electrons toward itself. The bonding electrons in hydrogen chloride, water, and ammonia molecules are more attracted to the atom with the greater electronegativity. This results in a polar distribution of charge. A **polar covalent bond** is a covalent bond between atoms of different electronegativities. The electronegativities of some of the elements are shown in Table 1.3. Notice that electronegativity increases as you go from left to right across a row of the periodic table or up any of the columns.

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

$$
\overset{\delta+}{H}-\overset{\delta-}{\underset{}{\ddot{C}l}}:
\qquad
\overset{\delta+}{H}-\overset{\delta-}{\underset{\underset{\delta+}{H}}{\ddot{O}}}:
\qquad
\overset{\delta+}{H}-\overset{\delta-}{\underset{\underset{\delta+}{H}}{N}}-\overset{\delta+}{H}
$$

The direction of bond polarity can be indicated with an arrow. By convention, the arrow points in the direction in which the electrons are pulled, so the head of the arrow is at the negative end of the bond; a short perpendicular line near the tail of the arrow marks the positive end of the bond.

$$
H-\ddot{C}l:
$$

TABLE 1.3 The Electronegativities of Selected Elements[a]

IA	IIA	IB	IIB	IIIA	IVA	VA	VIA	VIIA
H 2.1								
Li 1.0	Be 1.5			B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2			Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0							Br 2.8
								I 2.5

increasing electronegativity →

increasing electronegativity ↑

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

You can think of ionic bonds and nonpolar covalent bonds as being at the opposite ends of a continuum of bond types. An ionic bond involves no sharing of electrons. A nonpolar covalent bond involves equal sharing. Polar covalent bonds fall somewhere in between, and the greater the difference in electronegativity between the atoms forming the bond, the closer the bond is to the ionic end of the continuum. C—H bonds are relatively nonpolar, because carbon and hydrogen have similar electronegativities (electronegativity difference = 0.4; see Table 1.3). N—H bonds are relatively polar (electronegativity difference = 0.9), but not as polar as O—H bonds (electronegativity difference = 1.4). The bond between sodium and chloride ions is closer to the ionic end of the continuum (electronegativity difference = 2.1), but sodium chloride is not as ionic as potassium fluoride (electronegativity difference = 3.2).

continuum of bond types

ionic bond	polar covalent bond	nonpolar covalent bond
K^+F^- Na^+Cl^-	O—H N—H	C—H, C—C
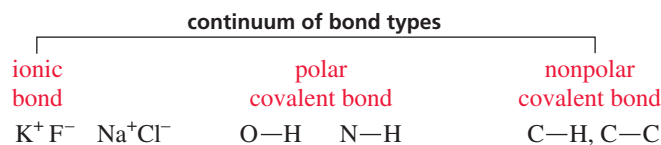
Tutorial:
Electronegativity differences
and bond types

PROBLEM 5◆

Which of the following has

a. the most polar bond?   b. the least polar bond?

   NaI   LiBr Cl_2 KCl

Understanding bond polarity is critical to understanding how organic reactions occur, because a central rule that governs the reactivity of organic compounds is that *electron-rich atoms or molecules are attracted to electron-deficient atoms or molecules*. **Electrostatic potential maps** (often simply called potential maps) are models that show how charge is distributed in the molecule under the map. Therefore, these maps show the kind of electrostatic attraction an atom or molecule has for another atom or molecule, so you can use them to predict chemical reactions. The potential maps for LiH, H_2, and HF are shown below.

LiH   **H₂**   **HF**
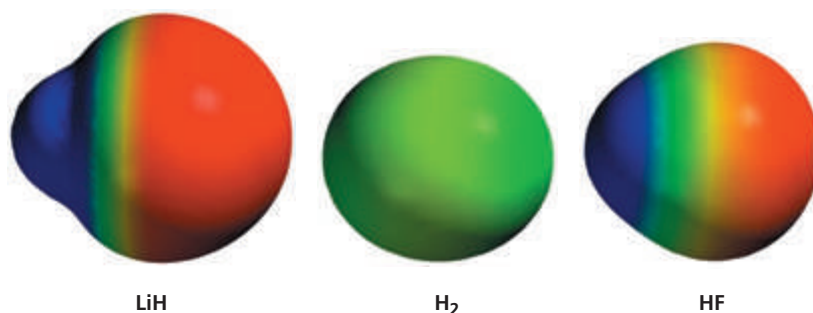
The colors on a potential map indicate the degree to which a molecule or an atom in a molecule attracts charged particles. Red—signifying the most negative electrostatic potential—is used for regions that attract positively charged molecules most strongly, and blue is used for areas with the most positive electrostatic potential—that is, regions that attract negatively charged molecules most strongly. Other colors indicate intermediate levels of attraction.

red   <   **orange**   <   **yellow**   <   **green**   <   **blue**

**most negative
electrostatic potential**   **most positive
electrostatic potential**

The colors on a potential map can also be used to estimate charge distribution. For example, the potential map for LiH indicates that the hydrogen atom is more negatively charged than the lithium atom. By comparing the three maps, we can tell that the hydrogen in LiH is more negatively charged than a hydrogen in H_2, and the hydrogen in HF is more positively charged than a hydrogen in H_2.

A molecule's size and shape are determined by the number of electrons in the molecule and by the way they move. Because a potential map roughly marks the "edge" of the molecule's electron cloud, the map tells us something about the relative size and shape of the molecule. Notice that a given kind of atom can have different sizes in different molecules. The negatively charged hydrogen in LiH is bigger than a neutral hydrogen in H_2, which, in turn, is bigger than the positively charged hydrogen in HF.

PROBLEM 6◆

After examining the potential maps for LiH, HF, and H_2, answer the following questions:

a. Which compounds are polar?

b. Why does LiH have the largest hydrogen?

c. Which compound has the most positively charged hydrogen?

A polar bond has a **dipole**—it has a negative end and a positive end. The size of the dipole is indicated by the dipole moment, which is given the Greek letter μ. The **dipole moment** of a bond is equal to the magnitude of the charge (e) on the atom (either the partial positive charge or the partial negative charge, because they have the same magnitude) times the distance between the two charges (d):

$$\text{dipole moment} = \mu = e \times d$$

A dipole moment is reported in a unit called a **debye (D)** (pronounced de-bye). Because the charge on an electron is 4.80×10^{-10} electrostatic units (esu) and the distance between charges in a polar bond is on the order of 10^{-8} cm, the product of charge and distance is on the order of 10^{-18} esu cm. A dipole moment of 1.5×10^{-18} esu cm can be more simply stated as 1.5 D. The dipole moments of some bonds commonly found in organic compounds are listed in Table 1.4.

In a molecule with only one covalent bond, the dipole moment of the molecule is identical to the dipole moment of the bond. For example, the dipole moment of hydrogen chloride (HCl) is 1.1 D because the dipole moment of the single H—Cl bond is 1.1 D. The dipole moment of a molecule with more than one covalent bond depends on the dipole moments of all the bonds in the molecule and the geometry of the molecule. We will examine the dipole moments of molecules with more than one covalent bond in Section 1.15 after you learn about the geometry of molecules.

Table 1.4	The Dipole Moments of Some Commonly Encountered Bonds		
Bond	**Dipole moment (D)**	**Bond**	**Dipole moment (D)**
H—C	0.4	C—C	0
H—N	1.3	C—N	0.2
H—O	1.5	C—O	0.7
H—F	1.7	C—F	1.6
H—Cl	1.1	C—Cl	1.5
H—Br	0.8	C—Br	1.4
H—I	0.4	C—I	1.2

PROBLEM 7   SOLVED

Determine the partial negative charge on the oxygen atom in a $C\!\!=\!\!O$ bond. The bond length is 1.22 Å* and the bond dipole moment is 2.30 D.

SOLUTION   If there were a full negative charge on the oxygen atom, the dipole moment would be

$$(4.80 \times 10^{-10} \text{ esu})(1.22 \times 10^{-8} \text{ cm}) = 5.86 \times 10^{-18} \text{ esu cm} = 5.86 \text{ D}$$

Knowing that the dipole moment is 2.30 D, we calculate that the partial negative charge on the oxygen atom is about 0.4:

$$\frac{2.30}{5.86} = 0.39$$

PROBLEM 8

Use the symbols $\delta+$ and $\delta-$ to show the direction of polarity of the indicated bond in each of the following compounds (for example, $\overset{\delta+}{H_3C}\!\!-\!\!\overset{\delta-}{OH}$).
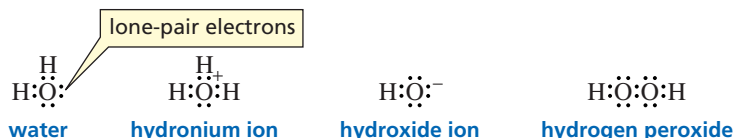
a. $HO\!\!-\!\!H$

b. $F\!\!-\!\!Br$

c. $H_3C\!\!-\!\!NH_2$

d. $H_3C\!\!-\!\!Cl$

e. $HO\!\!-\!\!Br$

f. $H_3C\!\!-\!\!MgBr$

g. $I\!\!-\!\!Cl$

h. $H_2N\!\!-\!\!OH$

1.4   Representation of Structure

Lewis Structures

The chemical symbols we have been using, in which the valence electrons are represented as dots, are called **Lewis structures**. Lewis structures are useful because they show us which atoms are bonded together and tell us whether any atoms possess *lone-pair electrons* or have a *formal charge*.

The Lewis structures for H_2O, H_3O^+, HO^-, and H_2O_2 are shown below.

lone-pair electrons

H:Ö:

water

H:Ö:H
  $+$

hydronium ion

H:Ö:⁻

hydroxide ion

H:Ö:Ö:H

hydrogen peroxide

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

Once the atoms and the electrons are in place, each atom must be examined to see whether a charge should be assigned to it. A positive or a negative charge assigned to an atom is called a *formal charge*; the oxygen atom in the hydronium ion has a formal charge of $+1$, and the oxygen atom in the hydroxide ion has a formal charge of -1. A **formal charge** is the *difference* between the number of valence electrons an atom has when it is not bonded to any other atoms and the number of electrons it "owns" when it is bonded. An atom "owns" all of its lone-pair electrons and half of its bonding (shared) electrons.

**formal charge = number of valence electrons –
(number of lone-pair electrons + 1/2 number of bonding electrons)**

*American chemist **Gilbert Newton Lewis (1875–1946)** was born in Weymouth, Massachusetts, and received a Ph.D. from Harvard in 1899. He was the first person to prepare "heavy water," which has deuterium atoms in place of the usual hydrogen atoms (D_2O versus H_2O). Because heavy water can be used as a moderator of neutrons, it became important in the development of the atomic bomb. Lewis started his career as a professor at the Massachusetts Institute of Technology and joined the faculty at the University of California, Berkeley, in 1912.*

---

* The angstrom (Å) is not a Système International unit. Those who opt to adhere strictly to SI units can convert it into picometers: 1 picometer (pm) $= 10^{-12}$ m; 1 Å $= 10^{-10}$ m $= 100$ pm. Because the angstrom continues to be used by many organic chemists, we will use angstroms in this book.

For example, an oxygen atom has six valence electrons (Table 1.2). In water (H_2O), oxygen "owns" six electrons (four lone-pair electrons and half of the four bonding electrons). Because the number of electrons it "owns" is equal to the number of its valence electrons ($6 - 6 = 0$), the oxygen atom in water has no formal charge. The oxygen atom in the hydronium ion (H_3O^+) "owns" five electrons: two lone-pair electrons plus three (half of six) bonding electrons. Because the number of electrons it "owns" is one less than the number of its valence electrons ($6 - 5 = 1$), its formal charge is $+1$. The oxygen atom in hydroxide ion (HO^-) "owns" seven electrons: six lone-pair electrons plus one (half of two) bonding electron. Because it "owns" one more electron than the number of its valence electrons ($6 - 7 = -1$), its formal charge is -1.

H_3O^+ H_2O HO^-
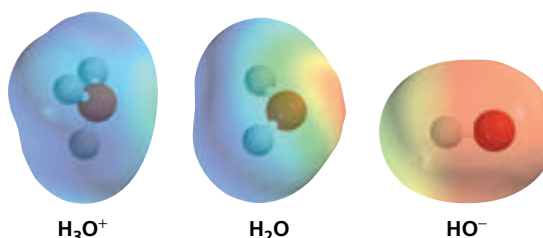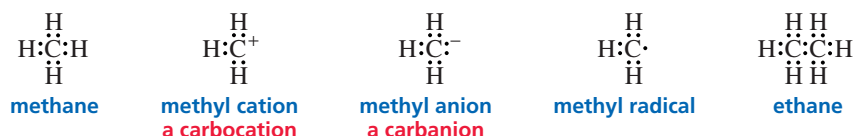

PROBLEM 9◆

A formal charge is a bookkeeping device. It does not necessarily indicate that the atom has greater or less electron density than other atoms in the molecule without formal charges. You can see this by examining the potential maps for H_2O, H_3O^+, and HO^-.

a. Which atom bears the formal negative charge in the hydroxide ion?
b. Which atom is the most negative in the hydroxide ion?
c. Which atom bears the formal positive charge in the hydronium ion?
d. Which atom is the most positive in the hydronium ion?

Knowing that nitrogen has five valence electrons (Table 1.2), convince yourself that the appropriate formal charges have been assigned to the nitrogen atoms in the following Lewis structures:

ammonia   **ammonium ion**   **amide anion**   **hydrazine**

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

methane   **methyl cation**   **methyl anion**   **methyl radical**   **ethane**
              a carbocation   **a carbanion**

A species containing a positively charged carbon atom is called a **carbocation**, and a species containing a negatively charged carbon atom is called a **carbanion**. (Recall that a *cation* is a positively charged ion and an *anion* is a negatively charged ion.) Carbocations were formerly called carbonium ions, so you will see this term in older chemical literature. A species containing an atom with a single unpaired electron is called a **radical** (often called a **free radical**). Hydrogen has one valence electron, and each halogen (F, Cl, Br, I) has seven valence electrons, so the following species have the indicated formal charges: