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 humans 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.

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.

The AbioCor® self-contained artificial heart, which is used to sustain patients who are waiting for a heart transplant. The outer shell is polycarbonate, and the valves and inner bladder are polyurethane. Both of these durable substances are synthetic organic compounds.

1-2 Principles of Atomic Structure

Before we begin our study of organic chemistry, we must review some basic principles. 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 1-2). 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}C. About 1% of carbon atoms have seven neutrons; the mass number is 13, written ^{13}C. A very small fraction of carbon atoms have eight neutrons and a mass number of 14. The ^{14}C isotope is radioactive, with a half-life (the time it takes for half of the nuclei to decay) of 5730 years. The predictable decay of ^{14}C is used to determine the age of organic materials up to about 50,000 years old.

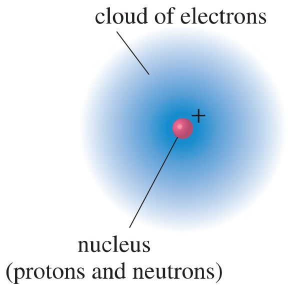


FIGURE 1-2
Basic atomic structure. An atom has a dense, positively charged nucleus surrounded by a cloud of electrons.

1-2B Electron Shells and Orbitals

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.** Orbitals are mathematical descriptions that chemists use to explain and predict the properties of atoms and molecules. 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.

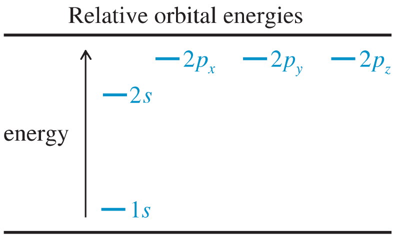
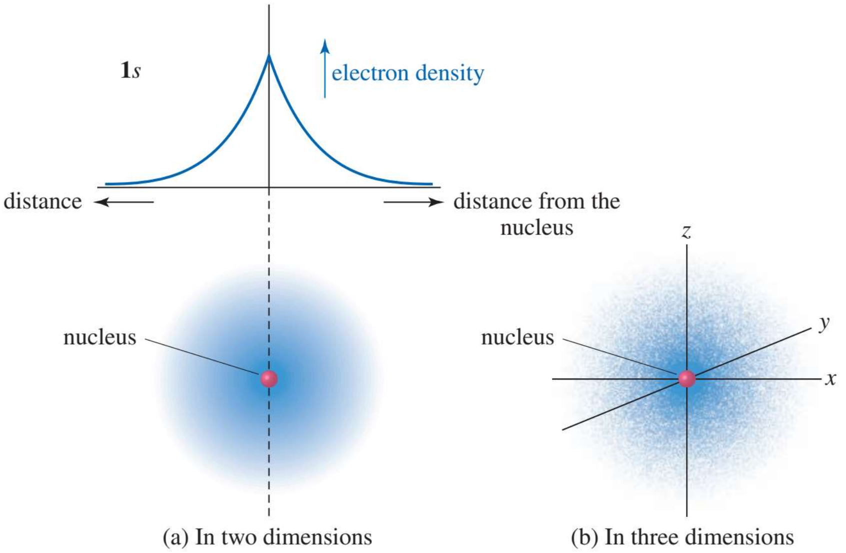


FIGURE 1-3
Graph and diagram of the 1*s* atomic orbital. The electron density is highest at the nucleus and drops off exponentially with increasing distance from the nucleus in any direction.



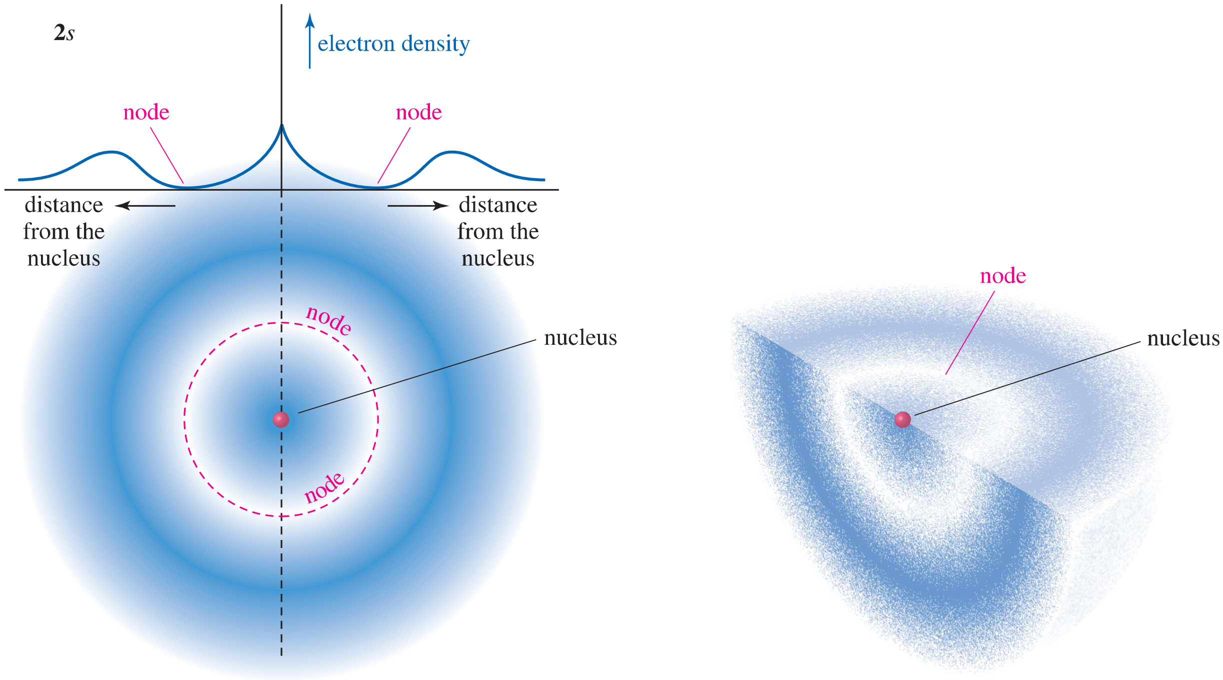
Atomic orbitals are grouped into different "shells" at different distances from the nucleus. Each shell is identified by a principal quantum number n, with $n = 1$ for the lowest-energy shell closest to the nucleus. As n increases, the shells are farther from the nucleus, are higher in energy, and can 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 1-3. 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. Most of the electron density is farther away, beyond a region of zero electron density called a **node.** Because most of the 2*s* electron density is farther from the nucleus than that of the 1*s*, the 2*s* orbital is higher in energy. Figure 1-4 shows a graph of the 2*s* orbital.

In addition to the 2*s* orbital, the second shell also contains three 2*p* atomic orbitals, one oriented in each of the three spatial directions. These orbitals are called the $2p_x$, the $2p_y$, and the $2p_z$, according to their direction along the x, y, or z axis. The 2*p* orbitals are slightly higher in energy than the 2*s*, because the average location of the electron in a 2*p* 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 2*p* orbitals differ only in their spatial orientation, so they have identical energies. Orbitals with identical energies are called **degenerate orbitals.** Figure 1-5 shows the shapes of the three degenerate 2*p* atomic orbitals.

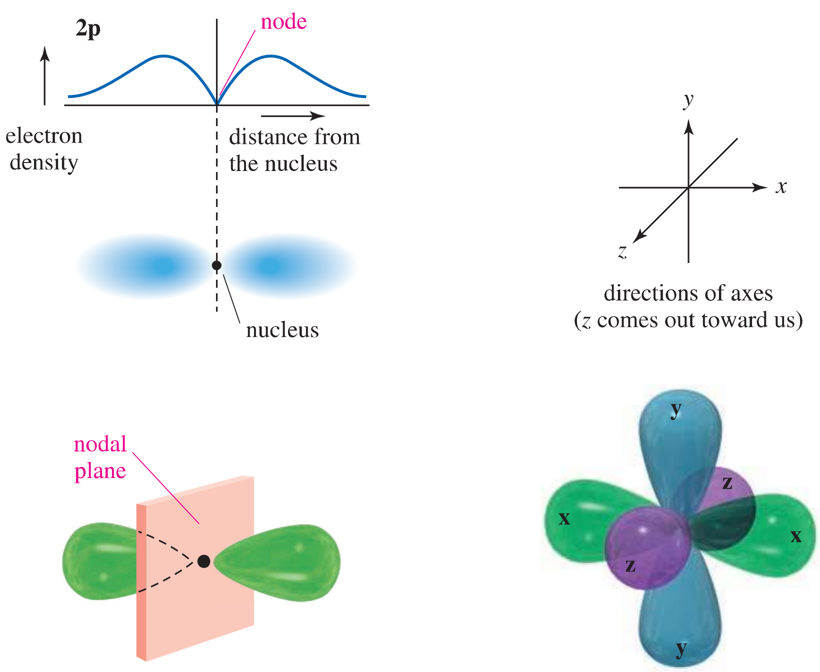
The *Pauli exclusion principle* tells us that each orbital can hold a maximum of two electrons, provided that their spins are paired. The first shell (one 1*s* orbital) can accommodate two electrons. The second shell (one 2*s* orbital and three 2*p* orbitals) can accommodate eight electrons, and the third shell (one 3*s* orbital, three 3*p* orbitals, and five 3*d* orbitals) can accommodate 18 electrons.



(a) In two dimensions

(b) In three dimensions (cutaway)

FIGURE 1-4
Graph and diagram of the 2*s* atomic orbital. The 2*s* orbital has a small region of high electron density close to the nucleus, but most of the electron density is farther from the nucleus, beyond a node, or region of zero electron density.



the $2p_x$ orbital

the $2p_x$, $2p_y$, and $2p_z$ orbitals superimposed at 90° angles

FIGURE 1-5
The 2*p* orbitals. Three 2*p* orbitals are oriented at right angles to each other. Each is labeled according to its orientation along the *x*, *y*, or *z* axis.

Application: Drugs

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.

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.

Two additional concepts are illustrated in Table 1-1. The **valence electrons** are those electrons in the outermost shell. Carbon has four valence electrons, nitrogen has five, and oxygen has six. Helium has a filled first shell with two valence electrons, and neon has has a filled second shell with eight valence electrons (ten electrons total). In general (for the representative elements), the column or group number of the periodic table corresponds to the number of valence electrons (Figure 1-6). Hydrogen and lithium have one valence electron, and they are both in the first column (group 1A) of the periodic table. Carbon has four valence electrons, and it is in group 4A 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 go into *different* orbitals rather than pair up in the same orbital. The first $2p$ electron (boron) goes into one $2p$ orbital, the second $2p$ electron (carbon) goes into a different orbital, and the third $2p$ electron (nitrogen) occupies the last $2p$ orbital. The fourth, fifth, and sixth $2p$ electrons must pair up with the first three electrons.

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

Element	Configuration	Valence Electrons
H	$1s^1$	1
He	$1s^2$	2
Li	$1s^2 2s^1$	1
Be	$1s^2 2s^2$	2
B	$1s^2 2s^2 2p_x^1$	3
C	$1s^2 2s^2 2p_x^1 2p_y^1$	4
N	$1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$	5
O	$1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$	6
F	$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$	7
Ne	$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2$	8

FIGURE 1-6
First three rows of the periodic table. The organization of the periodic table results from the filling of atomic orbitals in order of increasing energy. For these representative elements, the number of the column corresponds to the number of valence electrons.

Partial periodic table

1A	2A	3A	4A	5A	6A	7A	noble gases 8A
H							He
Li	Be	B	C	N	O	F	Ne
Na	Mg	Al	Si	P	S	Cl	Ar

PROBLEM 1-1

(a) Nitrogen has relatively stable isotopes (half-life greater than 1 second) of mass numbers 13, 14, 15, 16, and 17. (All except ^{14}N and ^{15}N are radioactive.) Calculate how many protons and neutrons are in each of these isotopes of nitrogen.

(b) Write the electronic configurations of the third-row elements shown in the partial periodic table in Figure 1-6.

1-3 Bond Formation: The Octet Rule

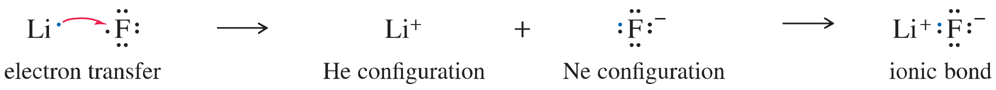
In 1915, G. N. Lewis proposed several new theories describing how atoms bond together to form molecules. One of these theories states that a filled shell of electrons is especially stable, and *atoms transfer or share electrons in such a way as to attain a filled shell of electrons*. A filled shell of 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. Elements in the third and higher rows (such as Al, Si, P, S, Cl, and above) can have an "expanded octet" of more than eight electrons because they have low-lying *d* orbitals available.

PROBLEM-SOLVING HINT

When we speak of a molecule having "all octets satisfied," we mean that all the second-row elements have octets. Hydrogen atoms have just two electrons (the He configuration) in their filled valence shell.

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.

$$\mathrm{H}\cdot \; + \; \mathrm{H}\cdot \;\longrightarrow\; \underset{\text{covalent bond}}{\mathrm{H}:\mathrm{H}} \qquad \text{each H shares two electrons (He configuration)}$$

We will study covalent bonding in more detail later in this chapter.