

simply memorizing them. We'll consider some of the organic chemistry that is industrially important. Finally, we'll examine some of the beautiful applications of organic chemistry in biology, such as how nature does organic chemistry and how the biological world has inspired a great deal of the research in organic chemistry.

1.2 CLASSICAL THEORIES OF CHEMICAL BONDING

To understand organic chemistry, it is necessary to have some understanding of the **chemical bond**—the forces that hold atoms together within molecules. First, we'll review some of the older, or "classical," ideas of chemical bonding—ideas that, despite their age, remain useful today. Then, in the last part of this chapter, we'll consider more modern ways of describing the chemical bond.

A. Electrons in Atoms

Chemistry happens because of the behavior of electrons in atoms and molecules. The basis of this behavior is the arrangement of electrons within atoms, an arrangement suggested by the periodic table. Consequently, let's first review the organization of the periodic table (see page facing inside back cover). The shaded elements are of greatest importance in organic chemistry; knowing their atomic numbers and relative positions will be valuable later on. For the moment, however, consider the following details of the periodic table because they were important in the development of the concepts of bonding.

A neutral atom of each element contains a number of both protons and electrons equal to its atomic number. The periodic aspect of the table—its organization into groups of elements with similar chemical properties—led to the idea that electrons reside in layers, or *shells*, about the nucleus. The outermost shell of electrons in an atom is called its **valence shell**, and the electrons in this shell are called **valence electrons**. *The number of valence electrons for any neutral atom in an A group of the periodic table (except helium) equals its group number.* Thus, lithium, sodium, and potassium (Group 1A) have one valence electron, whereas carbon (Group 4A) has four, the halogens (Group 7A) have seven, and the noble gases (except helium) have eight. Helium has two valence electrons.

Walter Kossel (1888–1956) noted in 1916 that when atoms form ions they tend to gain or lose valence electrons so as to have the same number of electrons as the noble gas of closest atomic number. Thus, potassium, with one valence electron (and 19 total electrons), tends to lose an electron to become K^+ , the potassium ion, which has the same number of electrons (18) as the nearest noble gas (argon). Chlorine, with seven valence electrons (and 17 total electrons) tends to accept an electron to become the 18-electron chloride ion, Cl^- , which also has the same number of electrons as argon. Because the noble gases have an octet of electrons (that is, eight electrons) in their valence shells, the tendency of atoms to gain or lose valence electrons to form ions with the noble-gas configuration has been called the **octet rule**.

B. The Ionic Bond

A chemical compound in which the component atoms exist as ions is called an **ionic compound**. Potassium chloride, KCl , is a common ionic compound. The electronic configurations of the potassium and chloride ions obey the octet rule.

The structure of crystalline KCl is shown in Fig. 1.1 on p. 4. In the KCl structure, which is typical of many ionic compounds, each positive ion is surrounded by negative ions, and each negative ion is surrounded by positive ions. The crystal structure is stabilized by an interaction between ions of opposite charge. Such a stabilizing interaction between opposite charges is

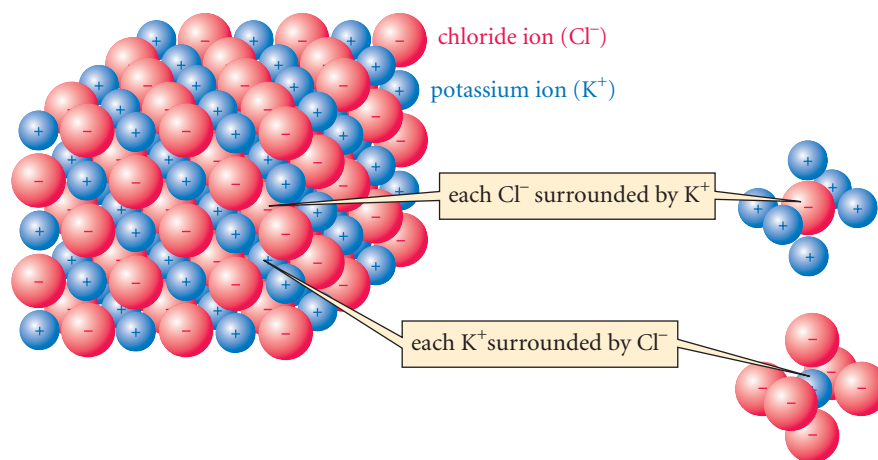


Figure 1.1 Crystal structure of KCl. The potassium and chlorine are present in this substance as K^+ and Cl^- ions, respectively. The ionic bond between the potassium ions and chloride ions is an electrostatic attraction. Each positive ion is surrounded by negative ions, and each negative ion is surrounded by positive ions. Thus, the attraction between ions in the ionic bond is the same in all directions.

called an **electrostatic attraction**. An electrostatic attraction that holds ions together, as in crystalline KCl, is called an **ionic bond**. Thus, the crystal structure of KCl is maintained by *ionic bonds* between potassium ions and chloride ions. The ionic bond is the same in all directions; that is, a positive ion has the same attraction for each of its neighboring negative ions, and a negative ion has the same attraction for each of its neighboring positive ions.

When an ionic compound such as KCl dissolves in water, it dissociates into free ions (each surrounded by water). (We'll consider this process further in Sec. 8.4.) Each potassium ion moves around in solution more or less independently of each chloride ion. The conduction of electricity by KCl solutions shows that the ions are present. Thus, the ionic bond is broken when KCl dissolves in water.

To summarize, the ionic bond

1. is an electrostatic attraction between ions;
2. is the same in all directions—that is, it has no preferred orientation in space; and
3. is broken when an ionic compound dissolves in water.

PROBLEMS*

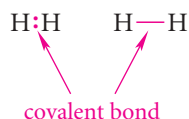
- 1.1 How many valence electrons are found in each of the following species?
(a) Na (b) Ca (c) O^{2-} (d) Br^+
- 1.2 When two different species have the same number of electrons, they are said to be *isoelectronic*. Name the species that satisfies each of the following criteria:
(a) the singly charged negative ion isoelectronic with neon
(b) the singly charged positive ion isoelectronic with neon
(c) the dipositive ion isoelectronic with argon
(d) the neon species that is isoelectronic with neutral fluorine

* The solutions to problems or problem parts labeled with boldface blue numbers or letters can be found in the *Study Guide and Solutions Manual* supplement.

C. The Covalent Bond

Many compounds contain bonds that are very different from the ionic bond in KCl. Neither these compounds nor their solutions conduct electricity. This observation indicates that these compounds are *not* ionic. How are the bonding forces that hold atoms together in such compounds different from those in KCl? In 1916, G. N. Lewis (1875–1946), an American physical chemist, proposed an electronic model for bonding in nonionic compounds. According to this model, the chemical bond in a nonionic compound is a **covalent bond**, which consists of an electron pair that is *shared* between bonded atoms. Let's examine some of the ideas associated with the covalent bond.

Lewis Structures One of the simplest examples of a covalent bond is the bond between the two hydrogen atoms in the hydrogen molecule.

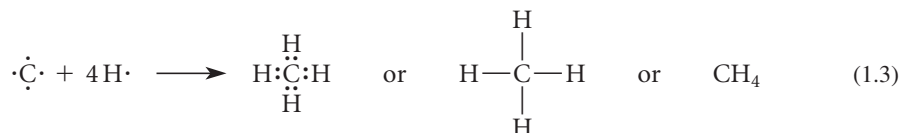


The symbols “:” and “—” are both used to denote an electron pair. A *shared electron pair is the essence of the covalent bond*. Molecular structures that use this notation for the electron-pair bond are called **Lewis structures**. In the hydrogen molecule, an electron-pair bond holds the two hydrogen atoms together. Conceptually, the bond can be envisioned to come from the pairing of the valence electrons of two hydrogen atoms:



Both electrons in the covalent bond are shared equally between the hydrogen atoms. Even though electrons are mutually repulsive, bonding occurs because the electron of each hydrogen atom is attracted to both hydrogen nuclei (protons) simultaneously.

An example of a covalent bond between two different atoms is provided by methane (CH_4), the simplest stable organic molecule. We can form methane conceptually by pairing each of the four carbon valence electrons with a hydrogen valence electron to make four C—H electron-pair bonds.



In the previous examples, all valence electrons of the bonded atoms are shared. In some covalent compounds, such as water (H_2O), however, some valence electrons remain unshared. In the water molecule, oxygen has six valence electrons. Two of these combine with hydrogens to make two O—H covalent bonds; four of the oxygen valence electrons are left over. These are represented in the Lewis structure of water as electron pairs on the oxygen. In general, unshared valence electrons in Lewis structures are depicted as paired dots and referred to as **unshared pairs**.



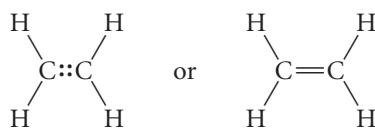
Although we often write water as $\text{H}-\text{O}-\text{H}$, or even H_2O , it is a good habit to indicate all unshared pairs with paired dots until you remember instinctively that they are there.

The foregoing examples illustrate an important point: *The sum of all shared and unshared valence electrons around each atom in many stable covalent compounds is eight (two for the*

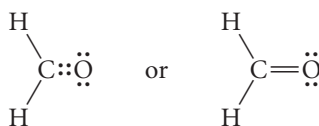
hydrogen atom). This is the **octet rule** for covalent bonding, and *it will prove to be extremely important for understanding chemical reactivity*. It is reminiscent of the octet rule for ion formation (Sec. 1.2A), except that in ionic compounds, valence electrons belong completely to a particular ion. In covalent compounds, shared electrons are counted twice, once for each of the sharing partner atoms.

Notice how the covalent compounds we've just considered follow the octet rule. In the structure of methane (Eq. 1.3), four shared pairs surround the carbon atom—that is, eight shared electrons, an octet. Each hydrogen shares two electrons, the “octet rule” number for hydrogen. Similarly, the oxygen of the water molecule has four shared electrons and two unshared pairs for a total of eight, and again the hydrogens have two shared electrons.

Two atoms in covalent compounds may be connected by more than one covalent bond. The following compounds are common examples:



ethylene



formaldehyde

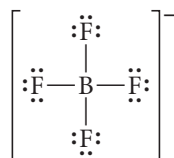


acetylene

Ethylene and formaldehyde each contain a **double bond**—a bond consisting of two electron pairs. Acetylene contains a **triple bond**—a bond involving three electron pairs.

Covalent bonds are especially important in organic chemistry because *all organic molecules contain covalent bonds*.

Formal Charge The Lewis structures considered in the previous discussion are those of neutral molecules. However, many familiar ionic species, such as $[\text{SO}_4]^{2-}$, $[\text{NH}_4]^+$, and $[\text{BF}_4]^-$, also contain covalent bonds. Consider the tetrafluoroborate anion, which contains covalent B—F bonds:



tetrafluoroborate ion

Because the ion bears a negative charge, one or more of the atoms within the ion must be charged—but which one(s)? The rigorous answer is that the charge is shared by all of the atoms. However, chemists have adopted a useful and important procedure for electronic book-keeping that assigns a charge to specific atoms. The charge on each atom thus assigned is called its **formal charge**. The sum of the formal charges on the individual atoms must equal the total charge on the ion.

Computation of formal charge on an atom involves dividing the total number of valence electrons between the atom and its bonding partners. Each atom receives *all* of its unshared electrons and *half* of its bonding electrons. To assign a formal charge to an atom, then, use the following procedure:

1. Write down the *group number* of the atom from its column heading in the periodic table. This is equal to the number of valence electrons in the *neutral atom*.
2. Determine the *valence electron count* for the atom by adding the number of unshared valence electrons on the atom to the number of covalent bonds to the atom. Counting the covalent bonds in effect adds *half* the bonding electrons—one electron for each bond.
3. Subtract the valence electron count from the group number. The result is the formal charge.

This procedure is illustrated in Study Problem 1.1.

Study Problem 1.1

Assign a formal charge to each of the atoms in the tetrafluoroborate ion, $[\text{BF}_4]^-$, which has the structure shown above.

Solution Let's first apply the procedure outlined above to fluorine:

Group number of fluorine: 7

Valence-electron count: 7

(Unshared pairs contribute 6 electrons; the covalent bond contributes 1 electron.)

Formal charge on fluorine: Group number – Valence-electron count = $7 - 7 = 0$

Because all fluorine atoms in $[\text{BF}_4]^-$ are equivalent, they all must have the same formal charge—zero. It follows that the boron must bear the formal negative charge. Let's compute it to be sure.

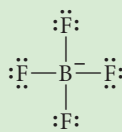
Group number of boron: 3

Valence-electron count: 4

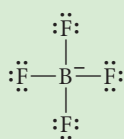
(Four covalent bonds contribute 1 electron each.)

Formal charge on boron: Group number – Valence-electron count = $3 - 4 = -1$

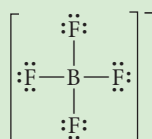
Because the formal charge of boron is -1 , the structure of $[\text{BF}_4]^-$ is written with the minus charge assigned to boron:



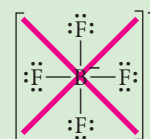
When indicating charge on a compound, we can show the formal charges on each atom, or we can show the formal charge on the ion as a whole, *but we should not show both*.



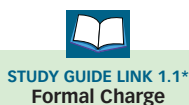
formal charge



overall charge



don't show both



* Study Guide Links are short discussions in the *Study Guide and Solutions Manual* supplement that provide extra hints or shortcuts that can help you master the material more easily.

Rules for Writing Lewis Structures The previous two sections can be summarized in the following rules for writing Lewis structures.

1. Hydrogen can share no more than two electrons.
2. The sum of all bonding electrons and unshared pairs for atoms in the second period of the periodic table—the row beginning with lithium—is never greater than eight (octet rule). These atoms may, however, have fewer than eight electrons.
3. In some cases, atoms below the second period of the periodic table may have more than eight electrons. However, rule 2 should also be followed for these cases until exceptions are discussed later in the text.
4. Nonvalence electrons are not shown in Lewis structures.
5. The formal charge on each atom is computed by the procedure illustrated in Study Problem 1.1 and, if not equal to zero, is indicated with a plus or minus sign on the appropriate atom(s).

Here's something very important to notice: There are two types of electron counting. When we want to know whether an atom has a complete octet, we count all unshared valence electrons and *all bonding electrons* (rule 2 in the previous list). When we want to determine formal charge, we count all unshared valence electrons and *half of the bonding electrons*.

Study Problem 1.2

Draw a Lewis structure for the covalent compound methanol, CH_4O . Assume that the octet rule is obeyed, and that none of the atoms have formal charges.

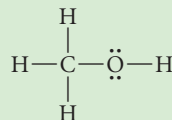
Solution For carbon to be *both neutral and consistent* with the octet rule, it must have four covalent bonds:



There is also only one way each for oxygen and hydrogen to have a formal charge of zero and simultaneously not violate the octet rule:



If we connect the carbon and the oxygen, and fill in the remaining bonds with hydrogens, we obtain a structure that meets all the criteria in the problem:



correct structure of methanol

PROBLEMS

1.3 Draw a Lewis structure for each of the following species. Show all unshared pairs and the formal charges, if any. Assume that bonding follows the octet rule in all cases.

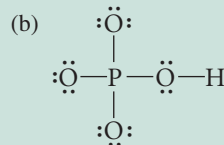
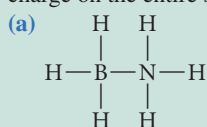
- (a) HCCl_3 (b) NH_3 (c) $[\text{NH}_4]^+$ (d) $[\text{H}_3\text{O}]^+$

ammonia

ammonium ion

1.4 Write two reasonable structures corresponding to the formula $\text{C}_2\text{H}_6\text{O}$. Assume that all bonding adheres to the octet rule, and that no atom bears a formal charge.

- 1.5 Draw a Lewis structure for acetonitrile, C_2H_3N , assuming that all bonding obeys the octet rule, and that no atom bears a formal charge. Acetonitrile contains a carbon–nitrogen triple bond.
- 1.6 Compute the formal charges on each atom of the following structures. In each case, what is the charge on the entire structure?



D. The Polar Covalent Bond

In many covalent bonds the electrons are not shared equally between two bonded atoms. Consider, for example, the covalent compound hydrogen chloride, HCl. (Although HCl dissolves in water to form H_3O^+ and Cl^- ions, in the gaseous state pure HCl is a covalent compound.) The electrons in the H—Cl covalent bond are *unevenly* distributed between the two atoms; they are polarized, or “pulled,” toward the chlorine and away from the hydrogen. A bond in which electrons are shared unevenly is called a **polar bond**. The H—Cl bond is an example of a polar bond.

How can we determine whether a bond is polar? Think of the two atoms at each end of the bond as if they were engaging in a tug-of-war for the bonding electrons. *The tendency of an atom to attract electrons to itself in a covalent bond is indicated by its electronegativity.* The electronegativities of a few elements that are important in organic chemistry are shown in Table 1.1. Notice the trends in this table. Electronegativity increases to the top and to the right of the table. The more an atom attracts electrons, the more **electronegative** it is. Fluorine is the most electronegative element. Electronegativity decreases to the bottom and to the left of the periodic table. The less an atom attracts electrons, the more **electropositive** it is. Of the common stable elements, cesium is the most electropositive.

Increasing electronegativity

TABLE 1.1 Average Pauling Electronegativities of Some Main-Group Elements

			H 2.20				
Li 0.98	Be 1.57	B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	
Na 0.93	Mg 1.31	Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16	
K 0.82	Ca 1.00				Se 2.55	Br 2.96	
Rb 0.82						I 2.66	
Cs 0.79							

Increasing electropositivity

Increasing electronegativity

Increasing electropositivity

If two bonded atoms have equal electronegativities, then the bonding electrons are shared equally. But if two bonded atoms have considerably different electronegativities, then the electrons are unequally shared, and the bond is polar. (We might think of a polar covalent bond as a covalent bond that is trying to become ionic!) Thus, *a polar bond is a bond between atoms with significantly different electronegativities.*

Sometimes we indicate the polarity of a bond in the following way:



In this notation, the delta (δ) is read as “partially” or “somewhat,” so that the hydrogen atom of HCl is “partially positive,” and the chlorine atom is “partially negative.”

Another more graphical way that we’ll use to show polarities is the *electrostatic potential map*. An **electrostatic potential map (EPM)** of a molecule starts with a map of the total electron density. This is a picture of the spatial distribution of the electrons in the molecule that comes from molecular orbital theory, which we’ll learn about in Sec. 1.8. Think of this as a picture of “where the electrons are.” The EPM is a map of total electron density that has been color-coded for regions of local positive and negative charge. Areas of greater negative charge are colored red, and areas of greater positive charge are colored blue. Areas of neutrality are colored green.

local positive charge

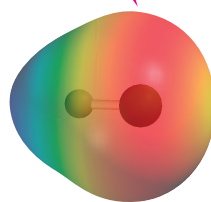


local negative charge

This is called a “potential map” because it represents the interaction of a test positive charge with the molecule at various points in the molecule. When the test positive charge encounters negative charge in the molecule, an attractive potential energy occurs; this is color-coded red. When the test positive charge encounters positive charge, a repulsive potential energy results, and this is color-coded blue.

The EPM of H—Cl shows the red region over the Cl and the blue region over the H, as we expect from the greater electronegativity of Cl versus H. In contrast, the EPM of dihydrogen shows the same color on both hydrogens because the two atoms share the electrons equally. The green color indicates that neither hydrogen atom bears a net charge.

electrons pulled towards Cl



hydrogen chloride (H—Cl)



dihydrogen (H—H)

How can bond polarity be measured experimentally? The uneven electron distribution in a compound containing covalent bonds is measured by a quantity called the **dipole moment**, which is abbreviated with the Greek letter μ (mu). The dipole moment is commonly given in derived units called *debyes*, abbreviated D, and named for the physical chemist Peter Debye (1884–1966), who won the 1936 Nobel Prize in Chemistry. For example, the HCl molecule has a dipole moment of 1.08 D, whereas dihydrogen (H_2), which has a uniform electron distribution, has a dipole moment of zero.



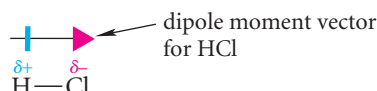
Further Exploration 1.1*
Dipole Moments

* *Further Explorations* are brief sections in the *Study Guide and Solutions Manual* supplement that cover the subject in greater depth.

The dipole moment is defined by the following equation:

$$\boldsymbol{\mu} = q\mathbf{r} \quad (1.4)$$

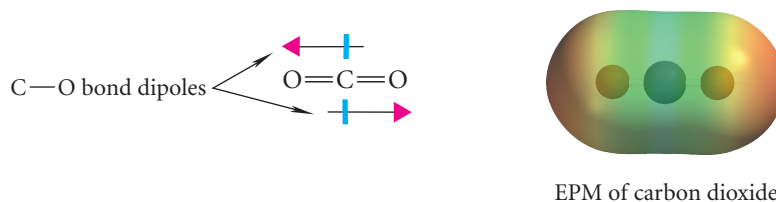
In this equation, q is the magnitude of the separated charge and \mathbf{r} is a vector from the site of the positive charge to the site of the negative charge. For a simple molecule like HCl, the magnitude of the vector \mathbf{r} is merely the length of the HCl bond, and it is oriented from the H (the positive end of the dipole) to the Cl (the negative end). The dipole moment is a *vector quantity*, and $\boldsymbol{\mu}$ and \mathbf{r} have the same direction—from the positive to the negative end of the dipole. As a result, the dipole moment vector for the HCl molecule is oriented along the H—Cl bond from the H to the Cl:



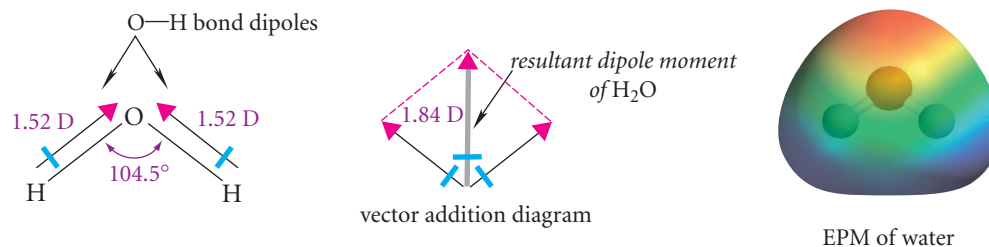
Notice that the magnitude of the dipole moment is affected not only by the *amount* of charge that is separated (q) but also by *how far* the charges are separated (\mathbf{r}). Consequently, a molecule in which a relatively small amount of charge is separated by a large distance can have a dipole moment as great as one in which a large amount of charge is separated by a small distance.

Molecules that have permanent dipole moments are called **polar molecules**. HCl is a polar molecule, whereas H_2 is a nonpolar molecule. Some molecules contain several polar bonds. Each polar bond has associated with it a dipole moment contribution, called a **bond dipole**. The net dipole moment of such a polar molecule is the vector sum of its bond dipoles. (Because HCl has only one bond, its dipole moment is equal to the H—Cl bond dipole.) Dipole moments of typical polar organic molecules are in the 1–3 D range.

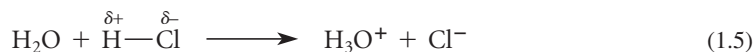
The vectorial aspect of bond dipoles can be illustrated in a relatively simple way with the carbon dioxide molecule, CO_2 :



Because the CO_2 molecule is *linear*, the C—O bond dipoles are oriented in opposite directions. Because they have equal magnitudes, they *exactly cancel*. (Two vectors of equal magnitude oriented in opposite directions always cancel.) Consequently, CO_2 is a nonpolar molecule, *even though it has polar bonds*. In contrast, if a molecule contains several bond dipoles that do not cancel, the various bond dipoles add vectorially to give the overall resultant dipole moment. For example, in the water molecule, which has a bond angle of 104.5° , the O—H bond dipoles add vectorially to give a resultant dipole moment of 1.84 D, which bisects the bond angle. The EPM of water shows the charge distribution suggested by the dipole vectors—a concentration of negative charge on oxygen and positive charge on hydrogen.

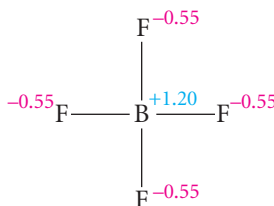


Polarity is an important concept because the polarity of a molecule can significantly influence its chemical and physical properties. For example, a molecule's polarity may give some indication of how it reacts chemically. Returning to the HCl molecule, we know that HCl in water dissociates to its ions in a manner suggested by its bond polarity.



We'll find many similar examples in organic chemistry in which bond polarity provides a clue to chemical reactivity.

Bond polarity is also useful because it gives us some insight that we can apply to the concept of formal charge. It's important to keep in mind that formal charge is only a bookkeeping device for keeping track of charge. In some cases, formal charge corresponds to the actual charge. For example, the actual negative charge on the hydroxide ion, OH^- , is on the oxygen, because oxygen is much more electronegative than hydrogen. In this case, the locations of the formal charge and actual charge are the same. But in other cases the formal charge does not correspond to the actual charge. For example, in the BF_4^- anion, fluorine is *much* more electronegative than boron (Table 1.1). So, most of the charge should actually be situated on the fluorines. In fact, the *actual* charges on the atoms of the tetrafluoroborate ion are in accord with this intuition:

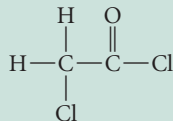


actual charge on the tetrafluoroborate anion

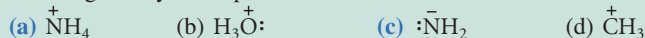
Because the Lewis structure doesn't provide a simple way of showing this distribution, we assign the charge to the boron by the formal-charge rules. An analogy might help. Let's say a big corporation arbitrarily chalks up all of its receipts to its sales department. This is a bookkeeping device. Everyone in the company knows that the receipts are in reality due to a company-wide effort. As long as no one forgets the reality, the administrative convenience of showing receipts in one place makes keeping track of the money a little simpler. Thus, showing formal charge on single atoms makes our handling of Lewis structures much simpler, but applying what we know about bond polarities helps us to see where the charge really resides.

PROBLEMS

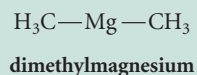
- 1.7 Analyze the polarity of each bond in the following organic compound. Which bond, other than the C—C bond, is the least polar one in the molecule? Which carbon has the most partial positive character?



- 1.8 For which of the following ions does the formal charge give a fairly accurate picture of where the charge really is? Explain in each case.



1.9 Draw an appropriate bond dipole for the carbon–magnesium bond of dimethylmagnesium. Explain your reasoning.



1.3

STRUCTURES OF COVALENT COMPOUNDS

We know the **structure** of a molecule containing covalent bonds when we know its *atomic connectivity* and its *molecular geometry*. **Atomic connectivity** is the specification of how atoms in a molecule are connected. For example, we specify the atomic connectivity within the water molecule when we say that two hydrogens are bonded to an oxygen. **Molecular geometry** is the specification of how far apart the atoms are and how they are situated in space.

Chemists learned about atomic connectivity before they learned about molecular geometry. The concept of covalent compounds as three-dimensional objects emerged in the latter part of the nineteenth century on the basis of indirect chemical and physical evidence. Until the early part of the twentieth century, however, no one knew whether these concepts had any physical reality, because scientists had no techniques for viewing molecules at the atomic level. By the second decade of the twentieth century, investigators could ask two questions: (1) Do organic molecules have specific geometries and, if so, what are they? (2) How can molecular geometry be predicted?

A. Methods for Determining Molecular Geometry

Among the greatest developments of chemical physics in the early twentieth century were the discoveries of ways to deduce the structures of molecules. Such techniques include various types of spectroscopy and mass spectrometry, which we'll consider in Chapters 12–15. As important as these techniques are, they are used primarily to provide information about atomic connectivity. Other physical methods, however, permit the determination of molecular structures that are complete in every detail. Most complete structures today come from three sources: X-ray crystallography, electron diffraction, and microwave spectroscopy.

The arrangement of atoms in the crystalline solid state can be determined by *X-ray crystallography*. This technique, invented in 1915 and subsequently revolutionized by the availability of high-speed computers, uses the fact that X-rays are diffracted from the atoms of a crystal in precise patterns that can be mathematically deciphered to give a molecular structure. In 1930, *electron diffraction* was developed. With this technique, the diffraction of electrons by molecules of gaseous substances can be interpreted in terms of the arrangements of atoms in molecules. Following the development of radar in World War II came *microwave spectroscopy*, in which the absorption of microwave radiation by molecules in the gas phase provides detailed structural information.

Most of the spatial details of molecular structure in this book are derived from gas-phase methods: electron diffraction and microwave spectroscopy. For molecules that are not readily studied in the gas phase, X-ray crystallography is the most important source of structural information. No methods of comparable precision exist for molecules in solution, a fact that is unfortunate because most chemical reactions take place in solution. The consistency of gas-phase and crystal structures suggests, however, that molecular structures in solution probably differ little from those of molecules in the solid or gaseous state.