



2

Polar Covalent Bonds; Acids and Bases

Organic KNOWLEDGE TOOLS

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We saw in the last chapter how covalent bonds between atoms are described, and we looked at the valence bond model, which uses hybrid orbitals to account for the observed shapes of organic molecules. Before going on to a systematic study of organic chemistry, however, we still need to review a few fundamental topics. In particular, we need to look more closely at how electrons are distributed in covalent bonds and at some of the consequences that arise when the electrons in a bond are not shared equally between atoms.

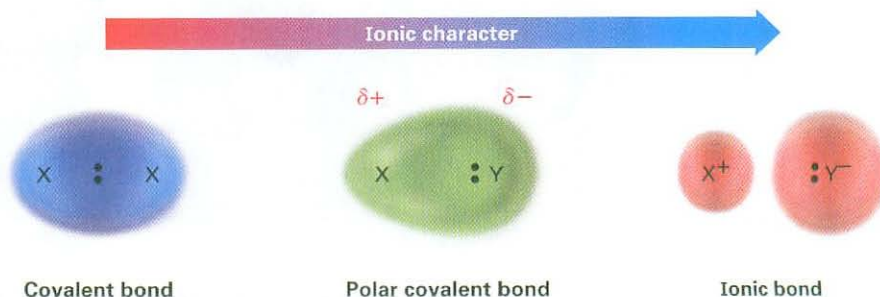
WHY THIS CHAPTER?

Understanding organic chemistry means knowing not just what happens but also why and how it happens. In this chapter, we'll look some of the basic ways chemists use to describe and account for chemical reactivity, thereby providing a foundation for understanding the specific reactions discussed in subsequent chapters.

2.1 Polar Covalent Bonds: Electronegativity

Up to this point, we've treated chemical bonds as either ionic or covalent. The bond in sodium chloride, for instance, is ionic. Sodium transfers an electron to chlorine to give Na^+ and Cl^- ions, which are held together in the solid by electrostatic attractions. The C–C bond in ethane, however, is covalent. The two bonding electrons are shared equally by the two equivalent carbon atoms, resulting in a symmetrical electron distribution in the bond. Most bonds, however, are neither fully ionic nor fully covalent but are somewhere between the two extremes. Such bonds are called **polar covalent bonds**, meaning that the bonding electrons are attracted more strongly by one atom than the other so that the electron distribution between atoms is not symmetrical (Figure 2.1).

Figure 2.1 The continuum in bonding from covalent to ionic is a result of an unequal distribution of bonding electrons between atoms. The symbol δ (lowercase Greek delta) means *partial charge*, either partial positive ($\delta+$) for the electron-poor atom or partial negative ($\delta-$) for the electron-rich atom.



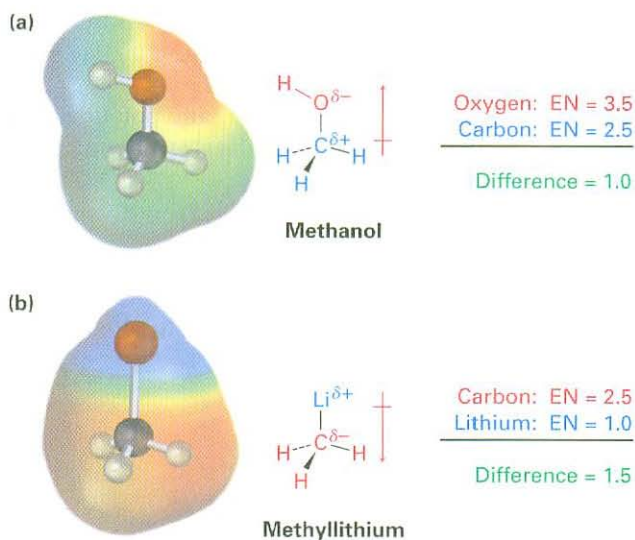
Bond polarity is due to differences in **electronegativity (EN)**, the intrinsic ability of an atom to attract the shared electrons in a covalent bond. As shown in Figure 2.2, electronegativities are based on an arbitrary scale, with fluorine being the most electronegative (EN = 4.0) and cesium, the least (EN = 0.7). Metals on the left side of the periodic table attract electrons weakly and have lower electronegativities, whereas the halogens and other reactive nonmetals on the right side of the periodic table attract electrons strongly and have higher electronegativities. Carbon, the most important element in organic compounds, has an electronegativity value of 2.5.

Figure 2.2 Electronegativity values and trends. Electronegativity generally increases from left to right across the periodic table and decreases from top to bottom. The values are on an arbitrary scale, with F = 4.0 and Cs = 0.7. Elements in orange are the most electronegative, those in yellow are medium, and those in green are the least electronegative.

H																	He
2.1																	
Li	Be											B	C	N	O	F	Ne
1.0	1.6											2.0	2.5	3.0	3.5	4.0	
Na	Mg											Al	Si	P	S	Cl	Ar
0.9	1.2											1.5	1.8	2.1	2.5	3.0	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
0.8	1.0	1.3	1.5	1.6	1.6	1.5	1.8	1.9	1.9	1.9	1.6	1.6	1.8	2.0	2.4	2.8	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
0.8	1.0	1.2	1.4	1.6	1.8	1.9	2.2	2.2	2.2	1.9	1.7	1.7	1.8	1.9	2.1	2.5	
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
0.7	0.9	1.0	1.3	1.5	1.7	1.9	2.2	2.2	2.2	2.4	1.9	1.8	1.9	1.9	2.0	2.1	

As a loose guide, bonds between atoms whose electronegativities differ by less than 0.5 are nonpolar covalent, bonds between atoms whose electronegativities differ by 0.5 to 2 are polar covalent, and bonds between atoms whose electronegativities differ by more than 2 are largely ionic. Carbon–hydrogen bonds, for example, are relatively nonpolar because carbon (EN = 2.5) and hydrogen (EN = 2.1) have similar electronegativities. Bonds between carbon and *more* electronegative elements such as oxygen (EN = 3.5) and nitrogen (EN = 3.0), by contrast, are polarized so that the bonding electrons are drawn away from carbon toward the electronegative atom. This leaves carbon with a partial positive charge, denoted by $\delta+$, and the electronegative atom with a partial negative charge, $\delta-$. An example is the C–O bond in methanol, CH_3OH (Figure 2.3a). Bonds between carbon and *less* electronegative elements are polarized so that carbon bears a partial negative charge and the other atom bears a partial positive charge. An example is methyllithium, CH_3Li (Figure 2.3b).

Figure 2.3 (a) Methanol, CH_3OH , has a polar covalent C–O bond, and (b) methyllithium, CH_3Li , has a polar covalent C–Li bond. The computer-generated representations, called electrostatic potential maps, use color to show calculated charge distributions, ranging from red (electron-rich; δ^-) to blue (electron-poor; δ^+).



Note in the representations of methanol and methyllithium in Figure 2.3 that a crossed arrow $\text{---} \rightarrow$ is used to indicate the direction of bond polarity. By convention, *electrons are displaced in the direction of the arrow*. The tail of the arrow (which looks like a plus sign) is electron-poor (δ^+), and the head of the arrow is electron-rich (δ^-).

Note also in Figure 2.3 that calculated charge distributions in molecules can be displayed visually using so-called electrostatic potential maps, which use color to indicate electron-rich (red; δ^-) and electron-poor (blue; δ^+) regions. In methanol, oxygen carries a partial negative charge and is colored red, while the carbon and hydrogen atoms carry partial positive charges and are colored blue-green. In methyllithium, lithium carries a partial positive charge (blue), while carbon and the hydrogen atoms carry partial negative charges (red). Electrostatic potential maps are useful because they show at a glance the electron-rich and electron-poor atoms in molecules. We'll make frequent use of these maps throughout the text and will see numerous examples of how electronic structure correlates with chemical reactivity.

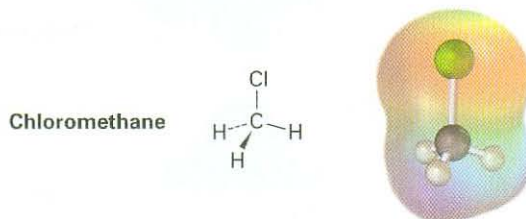
When speaking of an atom's ability to polarize a bond, we often use the term *inductive effect*. An **inductive effect** is simply the shifting of electrons in a σ bond in response to the electronegativity of nearby atoms. Metals, such as lithium and magnesium, inductively donate electrons, whereas reactive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

Problem 2.1 Which element in each of the following pairs is more electronegative?
(a) Li or H (b) B or Br (c) Cl or I (d) C or H

Problem 2.2 Use the δ^+/δ^- convention to show the direction of expected polarity for each of the bonds indicated.
(a) $\text{H}_3\text{C}-\text{Cl}$ (b) $\text{H}_3\text{C}-\text{NH}_2$ (c) $\text{H}_2\text{N}-\text{H}$
(d) $\text{H}_3\text{C}-\text{SH}$ (e) $\text{H}_3\text{C}-\text{MgBr}$ (f) $\text{H}_3\text{C}-\text{F}$

Problem 2.3 Use the electronegativity values shown in Figure 2.2 to rank the following bonds from least polar to most polar: $\text{H}_3\text{C}-\text{Li}$, $\text{H}_3\text{C}-\text{K}$, $\text{H}_3\text{C}-\text{F}$, $\text{H}_3\text{C}-\text{MgBr}$, $\text{H}_3\text{C}-\text{OH}$.

Problem 2.4 Look at the following electrostatic potential map of chloromethane, and tell the direction of polarization of the C-Cl bond:



2.2 Polar Covalent Bonds: Dipole Moments

Just as individual bonds are often polar, molecules as a whole are often polar also. Molecular polarity results from the vector summation of all individual bond polarities and lone-pair contributions in the molecule. As a practical matter, strongly polar substances are often soluble in polar solvents like water, whereas nonpolar substances are insoluble in water.

Net molecular polarity is measured by a quantity called the *dipole moment* and can be thought of in the following way: assume that there is a center of mass of all positive charges (nuclei) in a molecule and a center of mass of all negative charges (electrons). If these two centers don't coincide, then the molecule has a net polarity.

The **dipole moment**, μ (Greek mu), is defined as the magnitude of the charge Q at either end of the molecular dipole times the distance r between the charges, $\mu = Q \times r$. Dipole moments are expressed in *debyes* (D), where $1 \text{ D} = 3.336 \times 10^{-30} \text{ coulomb meter (C} \cdot \text{m)}$ in SI units. For example, the unit charge on an electron is $1.60 \times 10^{-19} \text{ C}$. Thus, if one positive charge and one negative charge were separated by 100 pm (a bit less than the length of a typical covalent bond), the dipole moment would be $1.60 \times 10^{-29} \text{ C} \cdot \text{m}$, or 4.80 D.

$$\mu = Q \times r$$

$$\mu = (1.60 \times 10^{-19} \text{ C})(100 \times 10^{-12} \text{ m}) \left(\frac{1 \text{ D}}{3.336 \times 10^{-30} \text{ C} \cdot \text{m}} \right) = 4.80 \text{ D}$$

It's relatively easy to measure dipole moments in the laboratory, and values for some common substances are given in Table 2.1. Of the compounds shown in the table, sodium chloride has the largest dipole moment (9.00 D) because it is ionic. Even small molecules like water ($\mu = 1.85 \text{ D}$), methanol (CH_3OH ; $\mu = 1.70 \text{ D}$), and ammonia ($\mu = 1.47 \text{ D}$) have substantial dipole moments, however, both because they contain strongly electronegative atoms (oxygen and nitrogen) and because all three molecules have lone-pair electrons. The lone-pair electrons on oxygen and nitrogen atom stick out into space away from

the positively charged nuclei, giving rise to a considerable charge separation and making a large contribution to the dipole moment.

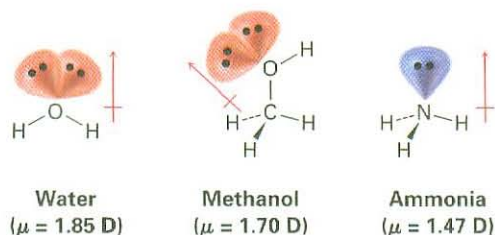

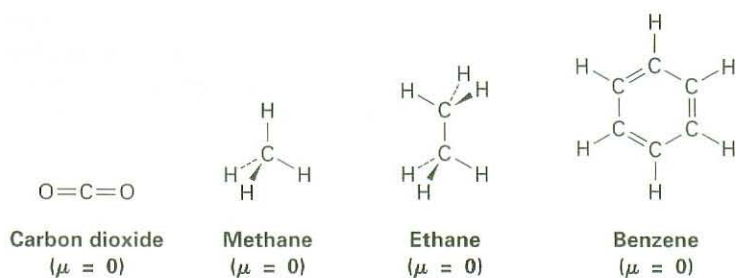


Table 2.1 Dipole Moments of Some Compounds

Compound	Dipole moment (D)	Compound	Dipole moment (D)
NaCl	9.00	NH ₃	1.47
CH ₂ O	2.33	CH ₃ NH ₂	1.31
CH ₃ Cl	1.87	CO ₂	0
H ₂ O	1.85	CH ₄	0
CH ₃ OH	1.70	CH ₃ CH ₃	0
CH ₃ CO ₂ H	1.70		0
CH ₃ SH	1.52	Benzene	

In contrast with water, methanol, ammonia, and other substances in Table 2.1, carbon dioxide, methane, ethane, and benzene have zero dipole moments. Because of the symmetrical structures of these molecules, the individual bond polarities and lone-pair contributions exactly cancel.



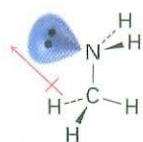
WORKED EXAMPLE 2.1

Predicting the Direction of a Dipole Moment

Make a three-dimensional drawing of methylamine, CH₃NH₂, a substance responsible for the odor of rotting fish, and show the direction of its dipole moment ($\mu = 1.31$).

Strategy Look for any lone-pair electrons, and identify any atom with an electronegativity substantially different from that of carbon. (Usually, this means O, N, F, Cl, or Br.) Electron density will be displaced in the general direction of the electronegative atoms and the lone pairs.

Solution Methylamine contains an electronegative nitrogen atom with two lone-pair electrons. The dipole moment thus points generally from $-\text{CH}_3$ toward $-\text{NH}_2$.



Methylamine
($\mu = 1.31$)

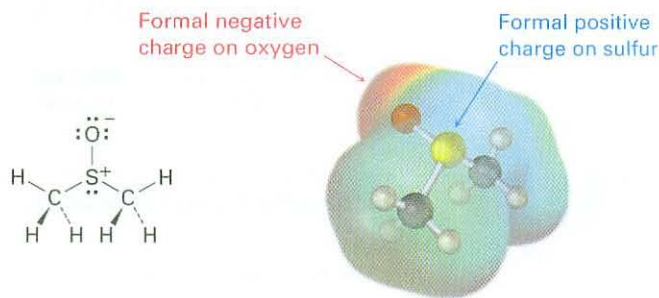
Problem 2.5 Ethylene glycol, $\text{HOCH}_2\text{CH}_2\text{OH}$, has zero dipole moment even though carbon-oxygen bonds are strongly polarized. Explain.

Problem 2.6 Make three-dimensional drawings of the following molecules, and predict whether each has a dipole moment. If you expect a dipole moment, show its direction.

- (a) $\text{H}_2\text{C}=\text{CH}_2$ (b) CHCl_3 (c) CH_2Cl_2 (d) $\text{H}_2\text{C}=\text{CCl}_2$

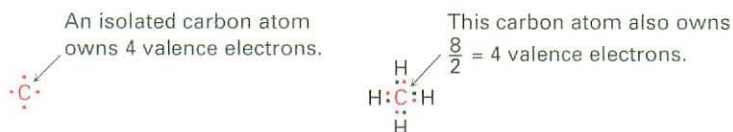
2.3 Formal Charges

Closely related to the ideas of bond polarity and dipole moment is the concept of assigning *formal charges* to specific atoms within a molecule, particularly atoms that have an apparently “abnormal” number of bonds. Look at dimethyl sulfoxide (CH_3SOCH_3), for instance, a solvent commonly used for preserving biological cell lines at low temperatures. The sulfur atom in dimethyl sulfoxide has three bonds rather than the usual two and has a formal positive charge. The oxygen atom, by contrast, has one bond rather than the usual two and has a formal negative charge. Note that an electrostatic potential map of dimethyl sulfoxide shows the oxygen as negative (red) and the sulfur as relatively positive (blue), in accord with the formal charges.

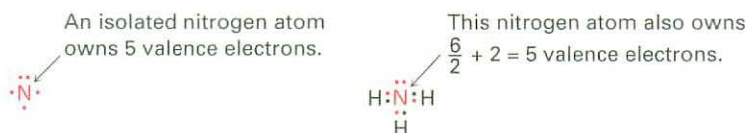


Dimethyl sulfoxide

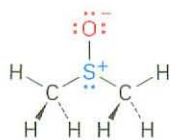
Formal charges, as the name suggests, are a formalism and don't imply the presence of actual ionic charges in a molecule. Instead, they're a device for electron "bookkeeping" and can be thought of in the following way: a typical covalent bond is formed when each atom donates one electron. Although the bonding electrons are shared by both atoms, each atom can still be considered to "own" one electron for bookkeeping purposes. In methane, for instance, the carbon atom owns one electron in each of the four C–H bonds, for a total of four. Because a neutral, isolated carbon atom has four valence electrons, and because the carbon atom in methane still owns four, the methane carbon atom is neutral and has no formal charge.



The same is true for the nitrogen atom in ammonia, which has three covalent N–H bonds and two nonbonding electrons (a lone pair). Atomic nitrogen has five valence electrons, and the ammonia nitrogen also has five—one in each of three shared N–H bonds plus two in the lone pair. Thus, the nitrogen atom in ammonia has no formal charge.



The situation is different in dimethyl sulfoxide. Atomic sulfur has six valence electrons, but the dimethyl sulfoxide sulfur owns only *five*—one in each of the two S–C single bonds, one in the S–O single bond, and two in a lone pair. Thus, the sulfur atom has formally lost an electron and therefore has a positive charge. A similar calculation for the oxygen atom shows that it has formally gained an electron and has a negative charge. Atomic oxygen has six valence electrons, but the oxygen in dimethyl sulfoxide has seven—one in the O–S bond and two in each of three lone pairs.



For sulfur:

Sulfur valence electrons = 6
 Sulfur bonding electrons = 6
 Sulfur nonbonding electrons = 2

$$\text{Formal charge} = 6 - 6/2 - 2 = +1$$

For oxygen:

Oxygen valence electrons = 6
 Oxygen bonding electrons = 2
 Oxygen nonbonding electrons = 6

$$\text{Formal charge} = 6 - 2/2 - 6 = -1$$

To express the calculations in a general way, the **formal charge** on an atom is equal to the number of valence electrons in a neutral, isolated atom minus the number of electrons owned by that atom in a molecule. The number of electrons in the bonded atom, in turn, is equal to half the number of bonding electrons plus the nonbonding, lone-pair electrons.

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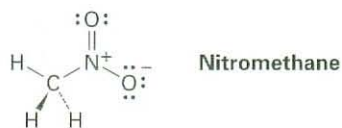
$$\begin{aligned} \text{Formal charge} &= \left(\begin{array}{c} \text{Number of} \\ \text{valence electrons} \\ \text{in free atom} \end{array} \right) - \left(\begin{array}{c} \text{Number of} \\ \text{valence electrons} \\ \text{in bonded atom} \end{array} \right) \\ &= \left(\begin{array}{c} \text{Number of} \\ \text{valence electrons} \\ \text{in free atom} \end{array} \right) - \left(\frac{\text{Number of} \\ \text{bonding electrons}}{2} \right) - \left(\begin{array}{c} \text{Number of} \\ \text{nonbonding} \\ \text{electrons} \end{array} \right) \end{aligned}$$

A summary of commonly encountered formal charges and the bonding situations in which they occur is given in Table 2.2. Although only a bookkeeping device, formal charges often give clues about chemical reactivity, so it's helpful to be able to identify and calculate them correctly.

Table 2.2 A Summary of Common Formal Charges

Atom	C			N		O		S		P
Structure										
Valence electrons	4	4	4	5	5	6	6	6	6	5
Number of bonds	3	3	3	4	2	3	1	3	1	4
Number of nonbonding electrons	1	0	2	0	4	2	6	2	6	0
Formal charge	0	+1	-1	+1	-1	+1	-1	+1	-1	+1

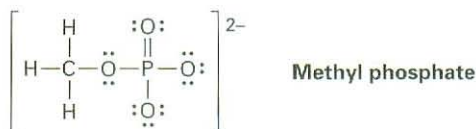
Problem 2.7 Nitromethane has the structure indicated. Explain why it must have formal charges on N and O.



Problem 2.8 Calculate formal charges for the nonhydrogen atoms in the following molecules:

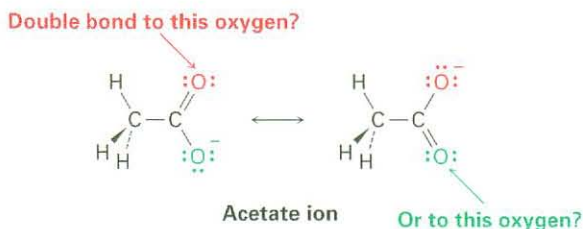
- (a) Diazomethane, $\text{H}_2\text{C}=\text{N}=\ddot{\text{N}}:$ (b) Acetonitrile oxide, $\text{H}_3\text{C}-\text{C}\equiv\text{N}-\ddot{\text{O}}:$
 (c) Methyl isocyanide, $\text{H}_3\text{C}-\text{N}\equiv\text{C}:$

Problem 2.9 Organic phosphate groups occur commonly in biological molecules. Calculate formal charges on the four O atoms in the methyl phosphate dianion.

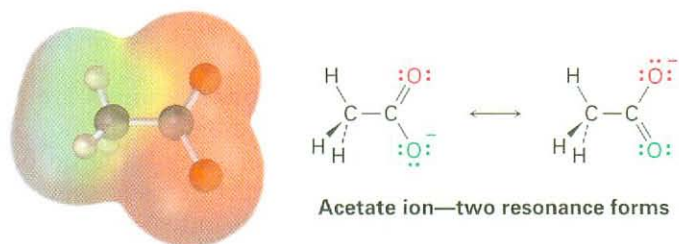


2.4 Resonance

Most substances can be represented without difficulty by the Kekulé line-bond structures we've been using up to this point, but an interesting problem sometimes arises. Look at the acetate ion, for instance. When we draw a line-bond structure for acetate, we need to show a double bond to one oxygen and a single bond to the other. But which oxygen is which? Should we draw a double bond to the "top" oxygen and a single bond to the "bottom" oxygen or vice versa?



Although the two oxygen atoms in the acetate ion appear different in line-bond structures, experiments show that they are equivalent. Both carbon–oxygen bonds, for example, are 127 pm in length, midway between the length of a typical C–O bond (135 pm) and a typical C=O bond (120 pm). In other words, *neither* of the two structures for acetate is correct by itself. The true structure is intermediate between the two, and an electrostatic potential map shows that both oxygen atoms share the negative charge and have equal electron densities (red).

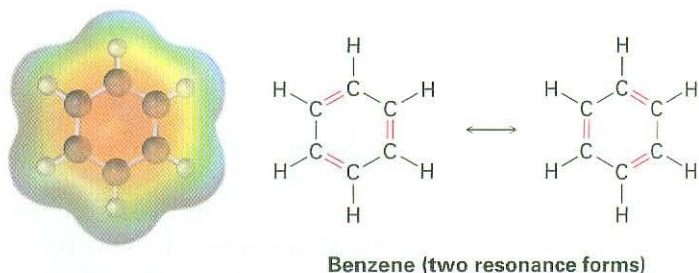


The two individual line-bond structures for acetate are called **resonance forms**, and their special resonance relationship is indicated by the double-headed arrow between them. *The only difference between resonance forms is the placement of the π and nonbonding valence electrons.* The atoms themselves occupy exactly the same place in both resonance forms, the connections between atoms are the same, and the three-dimensional shapes of the resonance forms are the same.

A good way to think about resonance forms is to realize that a substance like the acetate ion is no different from any other. Acetate doesn't jump back and forth between two resonance forms, spending part of the time looking like one and part of the time looking like the other. Rather, acetate has a single

unchanging structure that is a **resonance hybrid** of the two individual forms and has characteristics of both. The only “problem” with acetate is that we can’t draw it accurately using a familiar line-bond structure. Line-bond structures just don’t work well for resonance hybrids. The difficulty, however, lies with the *representation* of acetate on paper, not with acetate itself.

Resonance is an extremely useful concept that we’ll return to on numerous occasions throughout the rest of this book. We’ll see in Chapter 15, for instance, that the six carbon–carbon bonds in so-called *aromatic* compounds, such as benzene, are equivalent and that benzene is best represented as a hybrid of two resonance forms. Although an individual resonance form seems to imply that benzene has alternating single and double bonds, neither form is correct by itself. The true benzene structure is a hybrid of the two individual forms, and all six carbon–carbon bonds are equivalent. This symmetrical distribution of electrons around the molecule is evident in an electrostatic potential map.



2.5 Rules for Resonance Forms

When first dealing with resonance forms, it’s useful to have a set of guidelines that describe how to draw and interpret them.

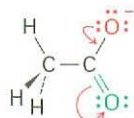
Rule 1 **Individual resonance forms are imaginary, not real.** The real structure is a composite, or resonance hybrid, of the different forms. Species such as the acetate ion and benzene are no different from any other. They have single, unchanging structures, and they do not switch back and forth between resonance forms. The only difference between these and other substances is in the way they must be represented on paper.

Rule 2 **Resonance forms differ only in the placement of their π or nonbonding electrons.** Neither the position nor the hybridization of any atom changes from one resonance form to another. In the acetate ion, for example, the carbon atom is sp^2 -hybridized and the oxygen atoms remain in exactly the same place in both resonance forms. Only the positions of the π electrons in the C=O bond and the lone-pair electrons on oxygen differ from one form to another. This movement of electrons from one resonance structure to another can be indicated by using curved arrows. *A curved arrow always indicates the movement of electrons, not the movement of atoms.* An arrow shows that a pair of electrons moves *from* the atom or bond at the tail of the arrow *to* the atom or bond at the head of the arrow.

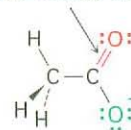
Key IDEAS

Test your knowledge of Key Ideas by using resources in ThomsonNOW or by answering end-of-chapter problems marked with ▲.

The red curved arrow indicates that a lone pair of electrons moves from the top oxygen atom to become part of a C=O bond.



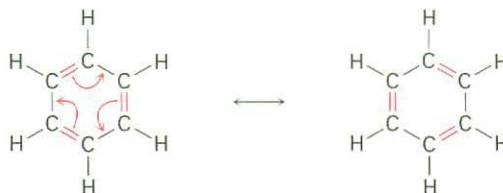
The new resonance form has a double bond here...



Simultaneously, two electrons from the C=O bond move onto the bottom oxygen atom to become a lone pair.

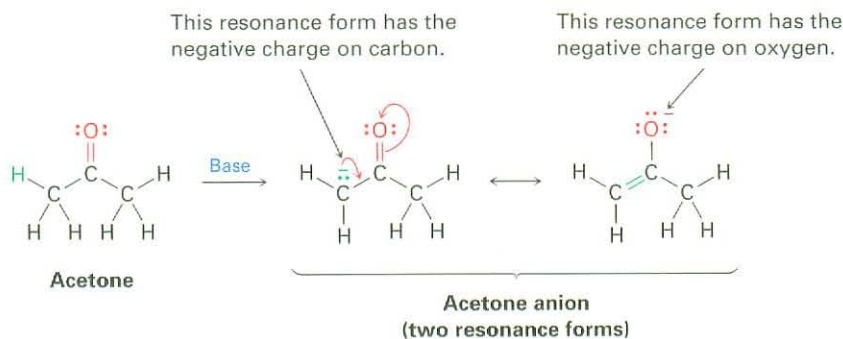
and has a lone pair of electrons here.

The situation with benzene is similar to that with acetate. The π electrons in the double bonds move, as shown with curved arrows, but the carbon and hydrogen atoms remain in place.



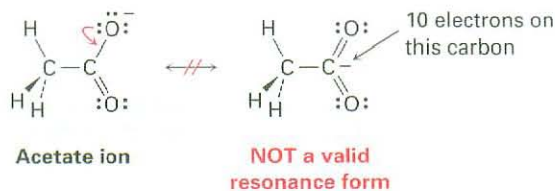
Rule 3 Different resonance forms of a substance don't have to be equivalent.

For example, we'll see in Chapter 22 that a compound such as acetone, which contains a C=O bond, can be converted into its anion by reaction with a strong base. The resultant anion has two resonance forms. One form contains a carbon–oxygen double bond and has a negative charge on *carbon*; the other contains a carbon–carbon double bond and has a negative charge on *oxygen*. Even though the two resonance forms aren't equivalent, both contribute to the overall resonance hybrid.



When two resonance forms are nonequivalent, the actual structure of the resonance hybrid is closer to the more stable form than to the less stable form. Thus, we might expect the true structure of the acetone anion to be closer to the resonance form that places the negative charge on an electronegative oxygen atom than to the form that places the charge on a carbon atom.

Rule 4 Resonance forms obey normal rules of valency. A resonance form is like any other structure: the octet rule still applies to main-group atoms. For example, one of the following structures for the acetate ion is not a valid resonance form because the carbon atom has five bonds and ten valence electrons:

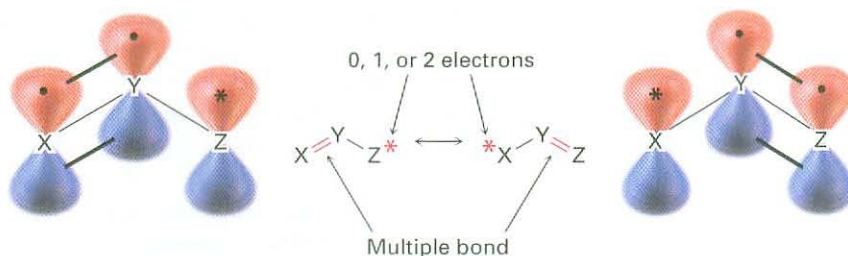


Rule 5 The resonance hybrid is more stable than any individual resonance form. In other words, resonance leads to stability. Generally speaking, the larger the number of resonance forms, the more stable a substance is because electrons are spread out over a larger part of the molecule and are closer to more nuclei. We'll see in Chapter 15, for instance, that a benzene ring is more stable because of resonance than might otherwise be expected.

2.6 Drawing Resonance Forms

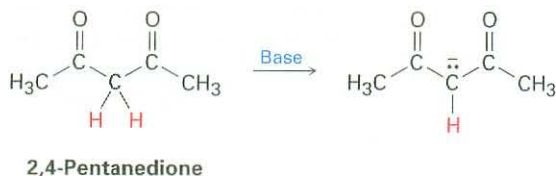
ThomsonNOW Click *Organic Interactive* to use an online palette to practice drawing resonance forms.

Look back at the resonance forms of the acetate ion and the acetone anion shown in the previous section. The pattern seen there is a common one that leads to a useful technique for drawing resonance forms. In general, any three-atom grouping with a *p* orbital on each atom has two resonance forms.

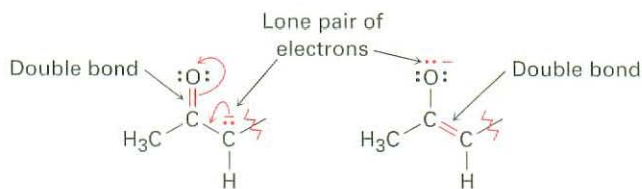


The atoms X, Y, and Z in the general structure might be C, N, O, P, or S, and the asterisk (*) might mean that the *p* orbital on atom Z is vacant, that it contains a single electron, or that it contains a lone pair of electrons. The two resonance forms differ simply by an exchange in position of the multiple bond and the asterisk from one end to the other.

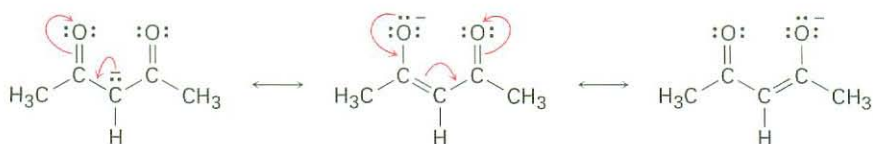
By learning to recognize such three-atom groupings within larger structures, resonance forms can be systematically generated. Look, for instance, at the anion produced when H^+ is removed from 2,4-pentanedione by reaction with a base. How many resonance structures does the resultant anion have?



The 2,4-pentanedione anion has a lone pair of electrons and a formal negative charge on the central carbon atom, next to a C=O bond on the left. The $\text{O}=\text{C}-\text{C}^-$ grouping is a typical one for which two resonance structures can be drawn.



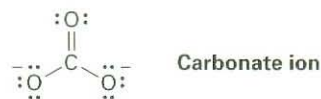
Just as there is a C=O bond to the left of the lone pair, there is a second C=O bond to the right. Thus, we can draw a total of three resonance structures for the 2,4-pentanedione anion.



WORKED EXAMPLE 2.2

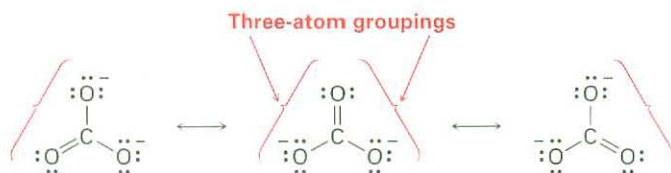
Drawing Resonance Forms for an Anion

Draw three resonance forms for the carbonate ion, CO_3^{2-} .



Strategy Look for one or more three-atom groupings that contain a multiple bond next to an atom with a p orbital. Then exchange the positions of the multiple bond and the electrons in the p orbital. In the carbonate ion, each of the singly bonded oxygen atoms with its lone pairs and negative charge is next to the C=O bond, giving the grouping $\text{O}=\text{C}-\text{O}^-$.

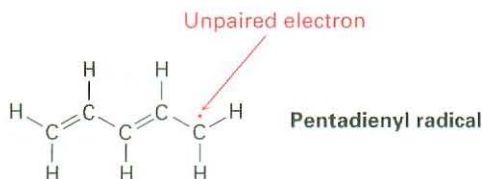
Solution Exchanging the position of the double bond and an electron lone pair in each grouping generates three resonance structures.



WORKED EXAMPLE 2.3

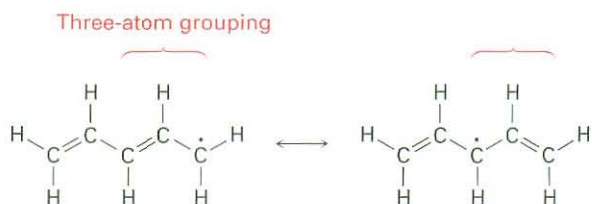
Drawing Resonance Forms for a Radical

Draw three resonance forms for the pentadienyl radical. A *radical* is a substance that contains a single, unpaired electron in one of its orbitals, denoted by a dot (\cdot).

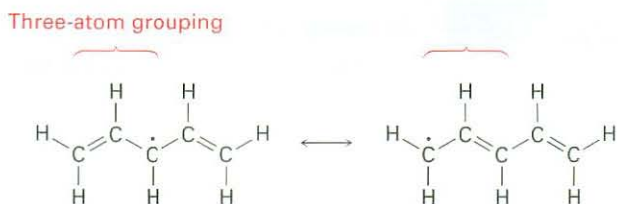


Strategy Find the three-atom groupings that contain a multiple bond next to a p orbital.

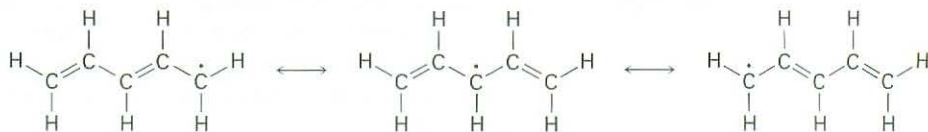
Solution The unpaired electron is on a carbon atom next to a $C=C$ bond, giving a typical three-atom grouping that has two resonance forms.



In the second resonance form, the unpaired electron is next to another double bond, giving another three-atom grouping and leading to another resonance form.



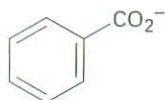
Thus, the three resonance forms for the pentadienyl radical are:



Problem 2.10

Draw the indicated number of resonance forms for each of the following species:

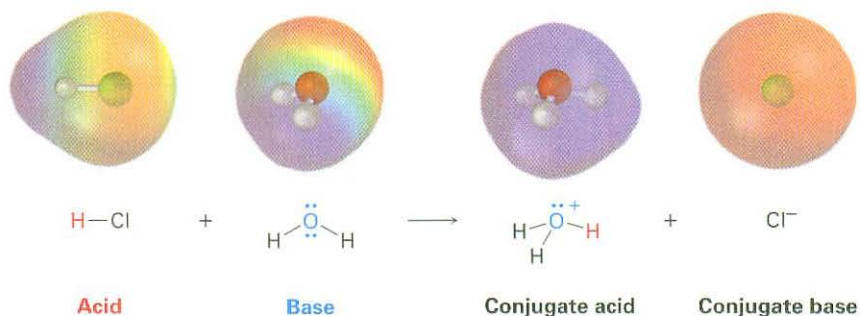
- The methyl phosphate anion, $\text{CH}_3\text{OPO}_3^{2-}$ (3)
- The nitrate anion, NO_3^- (3)
- The allyl cation, $\text{H}_2\text{C}=\text{CH}-\text{CH}_2^+$ (2)
- The benzoate anion (4)



2.7 Acids and Bases: The Brønsted–Lowry Definition

A further important concept related to electronegativity and polarity is that of *acidity* and *basicity*. We'll see, in fact, that much of the chemistry of organic molecules can be explained by their acid–base behavior. You may recall from a course in general chemistry that there are two frequently used definitions of acidity: the *Brønsted–Lowry definition* and the *Lewis definition*. We'll look at the Brønsted–Lowry definition in this and the next three sections and then discuss the Lewis definition in Section 2.11.

A **Brønsted–Lowry acid** is a substance that donates a proton (H^+), and a **Brønsted–Lowry base** is a substance that accepts a proton. (The name *proton* is often used as a synonym for hydrogen ion, H^+ , because loss of the valence electron from a neutral hydrogen atom leaves only the hydrogen nucleus—a proton.) When gaseous hydrogen chloride dissolves in water, for example, a polar HCl molecule acts as an acid and donates a proton, while a water molecule acts as a base and accepts the proton, yielding hydronium ion (H_3O^+) and chloride ion (Cl^-).

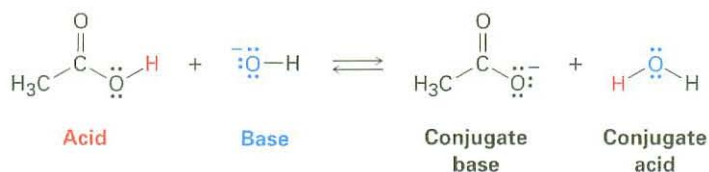


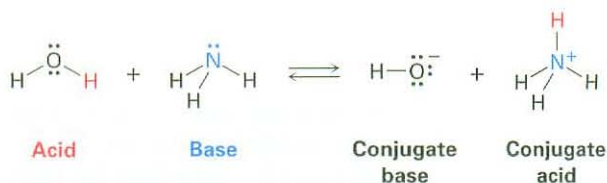
Hydronium ion, the product that results when the base H_2O gains a proton, is called the **conjugate acid** of the base, and chloride ion, the product that results when the acid HCl loses a proton, is called the **conjugate base** of the acid. Other common mineral acids such as H_2SO_4 and HNO_3 behave similarly, as do organic acids such as acetic acid, $\text{CH}_3\text{CO}_2\text{H}$.

In a general sense,



For example:



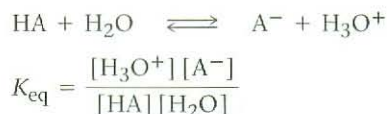


Notice that water can act *either* as an acid or as a base, depending on the circumstances. In its reaction with HCl, water is a base that accepts a proton to give the hydronium ion, H_3O^+ . In its reaction with amide ion, NH_2^- , however, water is an acid that donates a proton to give ammonia, NH_3 , and hydroxide ion, HO^- .

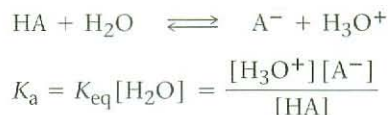
Problem 2.11 Nitric acid (HNO_3) reacts with ammonia (NH_3) to yield ammonium nitrate. Write the reaction, and identify the acid, the base, the conjugate acid product, and the conjugate base product.

2.8 Acid and Base Strength

Acids differ in their ability to donate H^+ . Stronger acids such as HCl react almost completely with water, whereas weaker acids such as acetic acid ($\text{CH}_3\text{CO}_2\text{H}$) react only slightly. The exact strength of a given acid, HA, in water solution is described using the equilibrium constant K_{eq} for the acid-dissociation equilibrium. Remember from general chemistry that brackets $[\]$ around a substance mean that the concentration of the enclosed species is given in moles per liter, M.



In the dilute aqueous solution normally used for measuring acidity, the concentration of water, $[\text{H}_2\text{O}]$, remains nearly constant at approximately 55.4 M at 25 °C. We can therefore rewrite the equilibrium expression using a new quantity called the **acidity constant**, K_{a} . The acidity constant for any acid HA is simply the equilibrium constant for the acid dissociation multiplied by the molar concentration of pure water.



Stronger acids have their equilibria toward the right and thus have larger acidity constants, whereas weaker acids have their equilibria toward the left and have smaller acidity constants. The range of K_{a} values for different acids is enormous, running from about 10^{15} for the strongest acids to about 10^{-60} for the

weakest. The common inorganic acids such as H_2SO_4 , HNO_3 , and HCl have K_a 's in the range of 10^2 to 10^9 , while organic acids generally have K_a 's in the range of 10^{-5} to 10^{-15} . As you gain more experience, you'll develop a rough feeling for which acids are "strong" and which are "weak" (always remembering that the terms are relative).

For convenience, acid strengths are normally expressed using $\text{p}K_a$ values rather than K_a values, where the $\text{p}K_a$ is the negative common logarithm of the K_a .

$$\text{p}K_a = -\log K_a$$

A stronger acid (larger K_a) has a smaller $\text{p}K_a$, and a weaker acid (smaller K_a) has a larger $\text{p}K_a$. Table 2.3 lists the $\text{p}K_a$'s of some common acids in order of their strength. A more comprehensive table is given in Appendix B.

Table 2.3 Relative Strengths of Some Common Acids and Their Conjugate Bases

	Acid	Name	$\text{p}K_a$	Conjugate base	Name	
<p>Weaker acid</p> <p>Stronger acid</p>	$\text{CH}_3\text{CH}_2\text{OH}$	Ethanol	16.00	$\text{CH}_3\text{CH}_2\text{O}^-$	Ethoxide ion	<p>Stronger base</p> <p>Weaker base</p>
	H_2O	Water	15.74	HO^-	Hydroxide ion	
	HCN	Hydrocyanic acid	9.31	CN^-	Cyanide ion	
	H_2PO_4^-	Dihydrogen phosphate ion	7.21	HPO_4^{2-}	Hydrogen phosphate ion	
	$\text{CH}_3\text{CO}_2\text{H}$	Acetic acid	4.76	CH_3CO_2^-	Acetate ion	
	H_3PO_4	Phosphoric acid	2.16	H_2PO_4^-	Dihydrogen phosphate ion	
	HNO_3	Nitric acid	-1.3	NO_3^-	Nitrate ion	
	HCl	Hydrochloric acid	-7.0	Cl^-	Chloride ion	

Notice that the $\text{p}K_a$ value shown in Table 2.3 for water is 15.74, which results from the following calculation: the K_a for any acid in water is the equilibrium constant K_{eq} for the acid dissociation multiplied by 55.4, the molar concentration of pure water. For the acid dissociation of water, we have



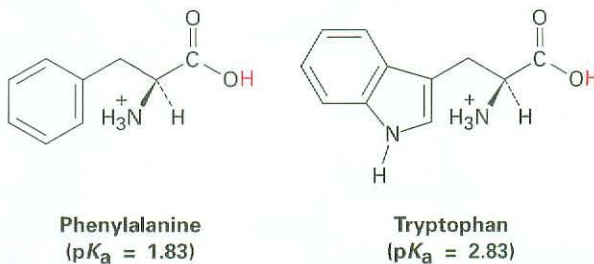
$$K_{\text{eq}} = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2} \quad \text{and} \quad K_a = K_{\text{eq}} \times [\text{H}_2\text{O}] = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$$

The numerator in this expression, $[\text{H}_3\text{O}^+][\text{OH}^-]$, is the so-called ion-product constant for water, $K_w = 1.00 \times 10^{-14}$, and the denominator is $[\text{H}_2\text{O}] = 55.4 \text{ M}$ at 25 °C. Thus, we have

$$K_a = \frac{1.0 \times 10^{-14}}{55.4} = 1.8 \times 10^{-16} \quad \text{and} \quad \text{p}K_a = 15.74$$

Notice also in Table 2.3 that there is an inverse relationship between the acid strength of an acid and the base strength of its conjugate base. That is, a *strong* acid has a *weak* conjugate base, and a *weak* acid has a *strong* conjugate base. To understand this relationship, think about what happens to the acidic hydrogen in an acid–base reaction. A strong acid is one that loses an H^+ easily, meaning that its conjugate base holds on to the H^+ weakly and is therefore a weak base. A weak acid is one that loses an H^+ with difficulty, meaning that its conjugate base holds on to the H^+ strongly and is therefore a strong base. HCl , for instance, is a strong acid, meaning that Cl^- holds on to the H^+ weakly and is thus a weak base. Water, on the other hand, is a weak acid, meaning that OH^- holds on to the H^+ strongly and is a strong base.

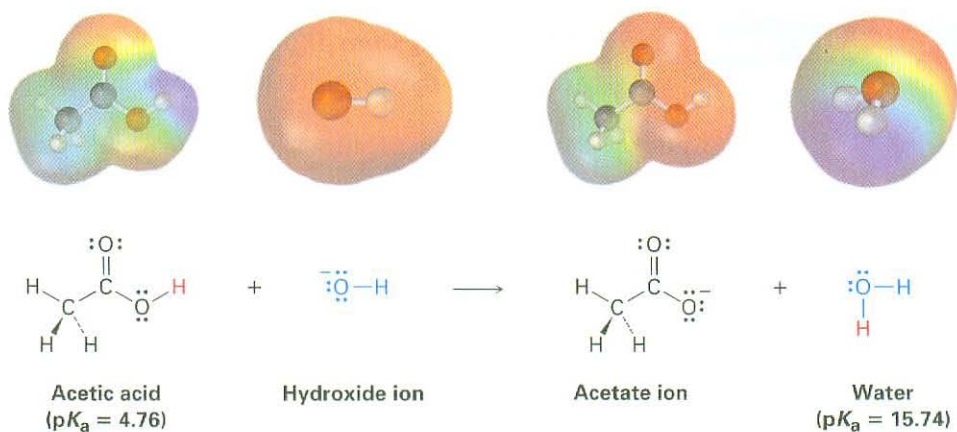
Problem 2.12 The amino acid phenylalanine has $\text{p}K_a = 1.83$, and tryptophan has $\text{p}K_a = 2.83$. Which is the stronger acid?



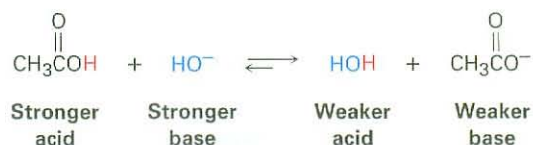
Problem 2.13 Amide ion, H_2N^- , is a much stronger base than hydroxide ion, HO^- . Which is the stronger acid, NH_3 or H_2O ? Explain.

2.9 Predicting Acid–Base Reactions from $\text{p}K_a$ Values

Compilations of $\text{p}K_a$ values like those in Table 2.2 and Appendix B are useful for predicting whether a given acid–base reaction will take place because H^+ will always go *from* the stronger acid *to* the stronger base. That is, an acid will donate a proton to the conjugate base of a weaker acid, and the conjugate base of a weaker acid will remove the proton from a stronger acid. For example, since water ($\text{p}K_a = 15.74$) is a weaker acid than acetic acid ($\text{p}K_a = 4.76$), hydroxide ion holds a proton more tightly than acetate ion does. Hydroxide ion will therefore react with acetic acid, $\text{CH}_3\text{CO}_2\text{H}$, to yield acetate ion and H_2O .



Another way to predict acid–base reactivity is to remember that the product conjugate acid in an acid–base reaction must be weaker and less reactive than the starting acid and the product conjugate base must be weaker and less reactive than the starting base. In the reaction of acetic acid with hydroxide ion, for example, the product conjugate acid (H_2O) is weaker than the starting acid ($\text{CH}_3\text{CO}_2\text{H}$) and the product conjugate base (CH_3CO_2^-) is weaker than the starting base (OH^-).



WORKED EXAMPLE 2.4

Predicting Acid Strengths from pK_a Values

Water has $pK_a = 15.74$, and acetylene has $pK_a = 25$. Which is the stronger acid? Does hydroxide ion react with acetylene?



Strategy In comparing two acids, the one with the lower pK_a is stronger. Thus, water is a stronger acid than acetylene and gives up H^+ more easily.

Solution Because water is a stronger acid and gives up H^+ more easily than acetylene does, the HO^- ion must have less affinity for H^+ than the $\text{HC}\equiv\text{C}:^-$ ion has. In other words, the anion of acetylene is a stronger base than hydroxide ion, and the reaction will not proceed as written.

WORKED EXAMPLE 2.5**Calculating K_a from pK_a**

According to the data in Table 2.3, acetic acid has $pK_a = 4.76$. What is its K_a ?

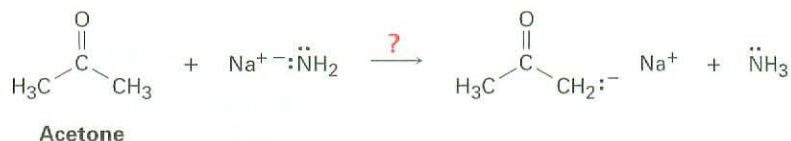
Strategy Since pK_a is the negative logarithm of K_a , it's necessary to use a calculator with an ANTILOG or INV LOG function. Enter the value of the pK_a (4.76), change the sign (-4.76), and then find the antilog (1.74×10^{-5}).

Solution $K_a = 1.74 \times 10^{-5}$.

Problem 2.14 Will either of the following reactions take place as written, according to the data in Table 2.3?



Problem 2.15 Ammonia, NH_3 , has $pK_a \approx 36$, and acetone has pK_a 19. Will the following reaction take place?



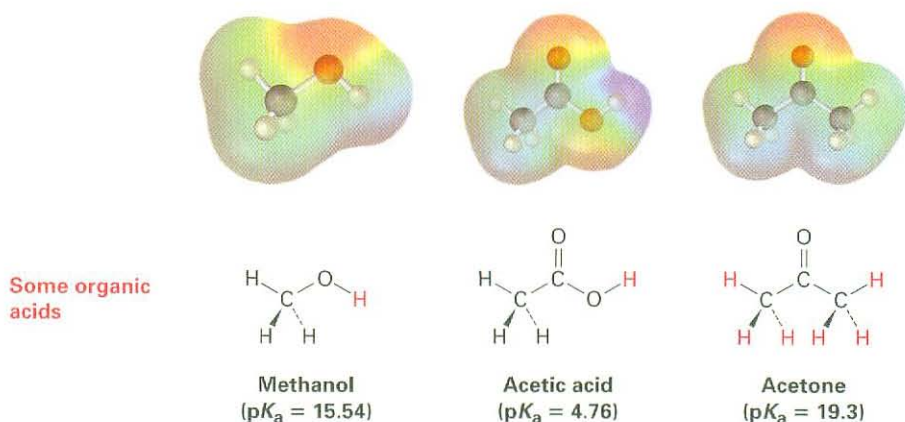
Problem 2.16 What is the K_a of HCN if its $pK_a = 9.31$?

2.10 Organic Acids and Organic Bases

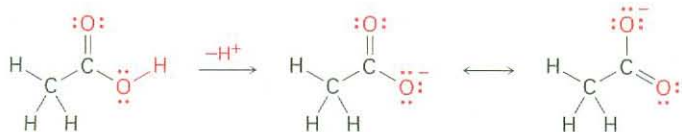
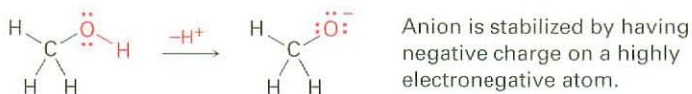
Many of the reactions we'll be seeing in future chapters involve organic acids and organic bases. Although it's too early to go into the details of these processes now, you might keep the following generalities in mind as your study progresses.

Organic Acids

Organic acids are characterized by the presence of a positively polarized hydrogen atom (blue in electrostatic potential maps) and are of two main kinds: those acids such as methanol and acetic acid that contain a hydrogen atom bonded to an electronegative oxygen atom (O-H) and those such as acetone (Section 2.5) that contain a hydrogen atom bonded to a carbon atom next to a C=O bond (O=C-C-H).

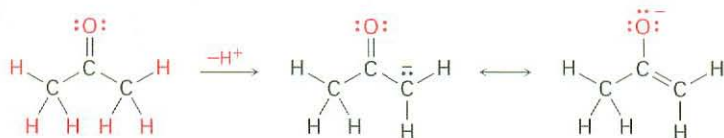


Methanol contains an O–H bond and is a weak acid; acetic acid also contains an O–H bond and is a somewhat stronger acid. In both cases, acidity is due to the fact that the conjugate base resulting from loss of H^+ is stabilized by having its negative charge on a strongly electronegative oxygen atom. In addition, the conjugate base of acetic acid is stabilized by resonance (Sections 2.4 and 2.5).



Anion is stabilized both by having negative charge on a highly electronegative atom and by resonance.

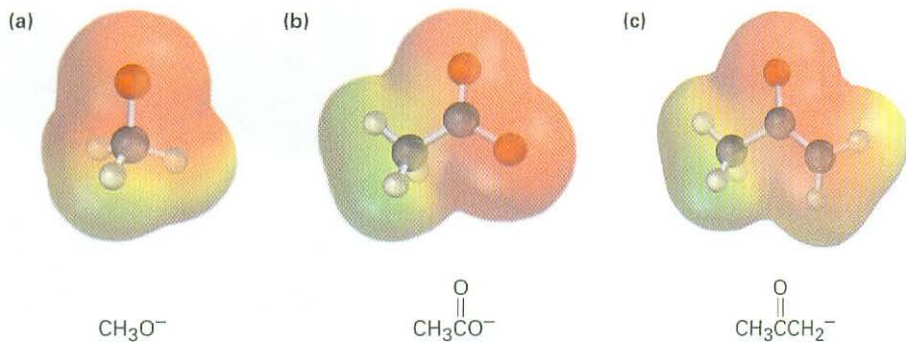
The acidity of acetone and other compounds with C=O bonds is due to the fact that the conjugate base resulting from loss of H^+ is stabilized by resonance. In addition, one of the resonance forms stabilizes the negative charge by placing it on an electronegative oxygen atom.



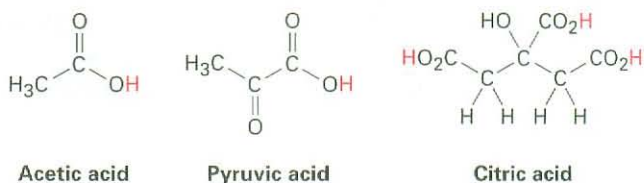
Anion is stabilized both by resonance and by having negative charge on a highly electronegative atom.

Electrostatic potential maps of the conjugate bases from methanol, acetic acid, and acetone are shown in Figure 2.4. As you might expect, all three show a substantial amount of negative charge (red) on oxygen.

Figure 2.4 Electrostatic potential maps of the conjugate bases of (a) methanol, (b) acetic acid, and (c) acetone. The electronegative oxygen atoms stabilize the negative charge in all three.

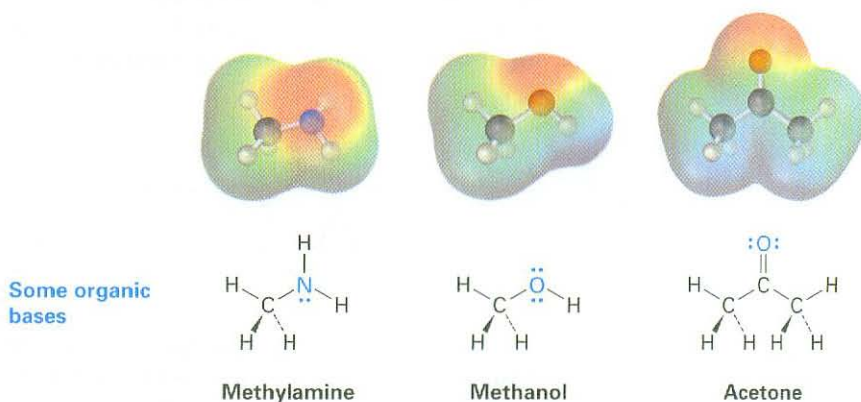


Compounds called *carboxylic acids*, which contain the $-\text{CO}_2\text{H}$ grouping, occur abundantly in all living organisms and are involved in almost all metabolic pathways. Acetic acid, pyruvic acid, and citric acid are examples.



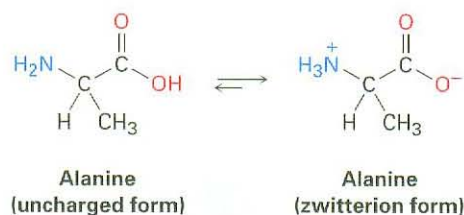
Organic Bases

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



We'll see in Chapter 26 that substances called *amino acids*, so-named because they are both amines ($-\text{NH}_2$) and carboxylic acids ($-\text{CO}_2\text{H}$), are the building

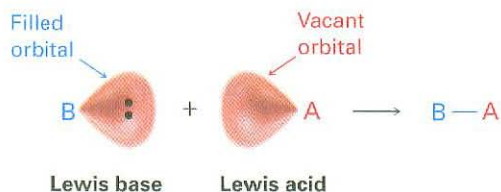
blocks from which the proteins present in all living organisms arise. Twenty different amino acids go into making up proteins; alanine is an example.



Interestingly, alanine and other amino acids exist primarily in a doubly charged form called a *zwitterion* rather than in the uncharged form. The zwitterion form arises because amino acids have both acidic and basic sites within the same molecule and therefore undergo an *internal* acid–base reaction.

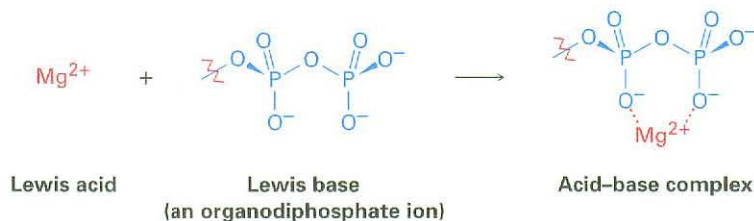
2.11 Acids and Bases: The Lewis Definition

The *Lewis definition* of acids and bases is broader and more encompassing than the Brønsted–Lowry definition because it's not limited to substances that donate or accept just protons. A **Lewis acid** is a substance that *accepts an electron pair*, and a **Lewis base** is a substance that *donates an electron pair*. The donated electron pair is shared between the acid and the base in a covalent bond.



Lewis Acids and the Curved Arrow Formalism

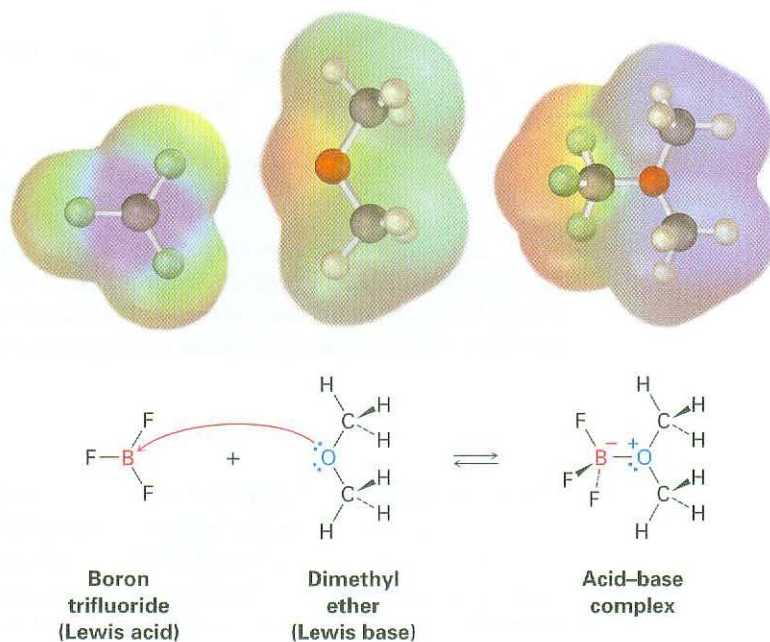
The fact that a Lewis acid is able to accept an electron pair means that it must have either a vacant, low-energy orbital or a polar bond to hydrogen so that it can donate H⁺ (which has an empty 1s orbital). Thus, the Lewis definition of acidity includes many species in addition to H⁺. For example, various metal cations, such as Mg²⁺, are Lewis acids because they accept a pair of electrons when they form a bond to a base. We'll also see in later chapters that certain metabolic reactions begin with an acid–base reaction between Mg²⁺ as a Lewis acid and an organic diphosphate or triphosphate ion as the Lewis base.



In the same way, compounds of group 3A elements, such as BF₃ and AlCl₃, are Lewis acids because they have unfilled valence orbitals and can accept electron

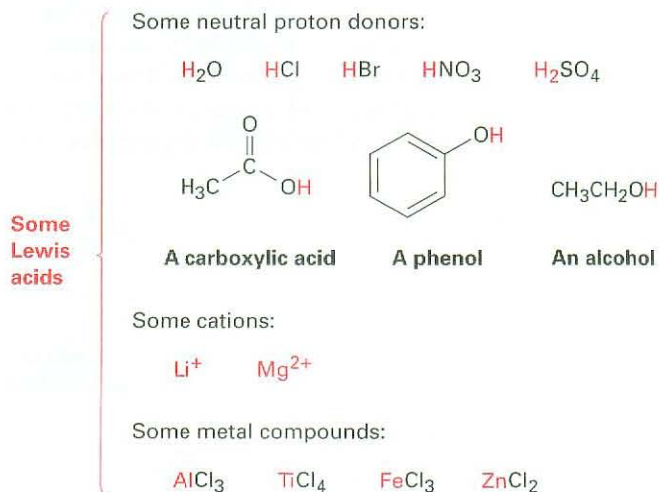
pairs from Lewis bases, as shown in Figure 2.5. Similarly, many transition-metal compounds, such as TiCl_4 , FeCl_3 , ZnCl_2 , and SnCl_4 , are Lewis acids.

Active Figure 2.5 The reaction of boron trifluoride, a Lewis acid, with dimethyl ether, a Lewis base. The Lewis acid accepts a pair of electrons, and the Lewis base donates a pair of nonbonding electrons. Note how the movement of electrons *from* the Lewis base *to* the Lewis acid is indicated by a curved arrow. Note also how, in electrostatic potential maps, the boron becomes more negative (red) after reaction because it has gained electrons and the oxygen atom becomes more positive (blue) because it has donated electrons. Sign in at www.thomsonedu.com to see a simulation based on this figure and to take a short quiz.



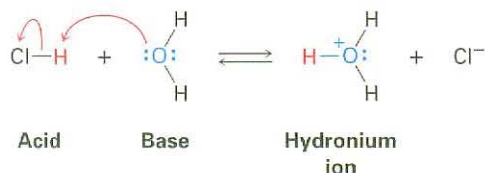
Look closely at the acid–base reaction in Figure 2.5, and note how it is shown. Dimethyl ether, the Lewis base, donates an electron pair to a vacant valence orbital of the boron atom in BF_3 , a Lewis acid. The direction of electron-pair flow from the base to acid is shown using curved arrows, just as the direction of electron flow in going from one resonance structure to another was shown using curved arrows in Section 2.5. A curved arrow always means that a pair of electrons moves from the atom at the tail of the arrow to the atom at the head of the arrow. We'll use this curved-arrow notation throughout the remainder of this text to indicate electron flow during reactions.

Some further examples of Lewis acids follow:

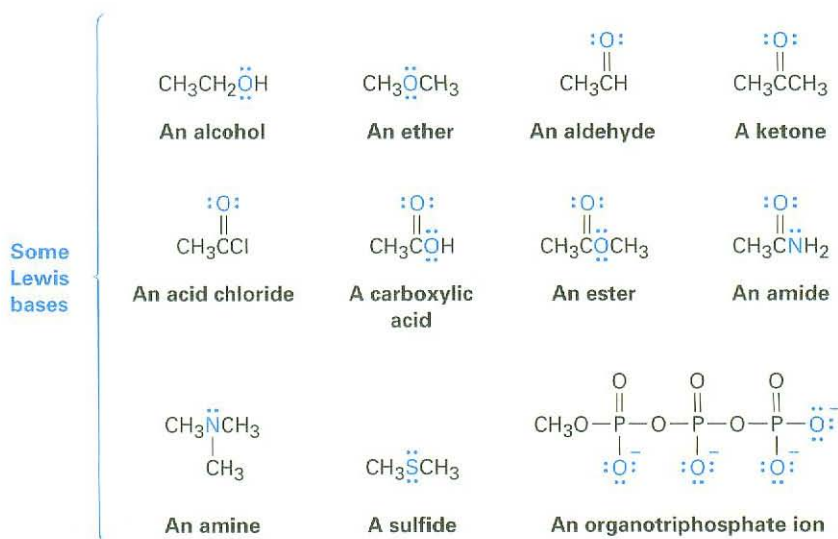


Lewis Bases

The Lewis definition of a base as a compound with a pair of nonbonding electrons that it can use to bond to a Lewis acid is similar to the Brønsted–Lowry definition. Thus, H_2O , with its two pairs of nonbonding electrons on oxygen, acts as a Lewis base by donating an electron pair to an H^+ in forming the hydronium ion, H_3O^+ .



In a more general sense, most oxygen- and nitrogen-containing organic compounds can act as Lewis bases because they have lone pairs of electrons. A divalent oxygen compound has two lone pairs of electrons, and a trivalent nitrogen compound has one lone pair. Note in the following examples that some compounds can act as both acids and bases, just as water can. Alcohols and carboxylic acids, for instance, act as acids when they donate an H^+ but as bases when their oxygen atom accepts an H^+ .



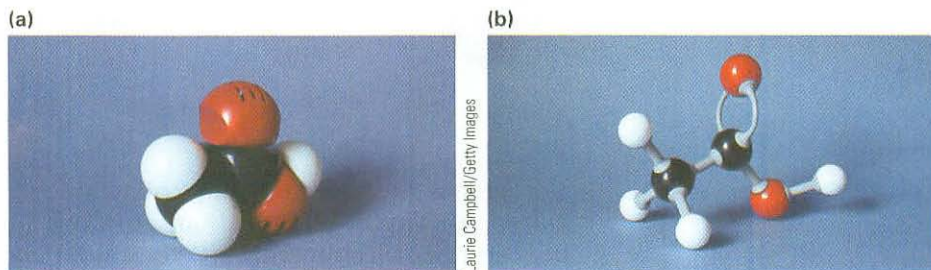
Notice in the list of Lewis bases just given that some compounds, such as carboxylic acids, esters, and amides, have more than one atom with a lone pair of electrons and can therefore react at more than one site. Acetic acid, for example, can be protonated either on the doubly bonded oxygen atom or on the singly bonded oxygen atom. Reaction normally occurs only once in such instances, and the more stable of the two possible protonation products is formed. For acetic acid, protonation by reaction with sulfuric acid occurs on

2.12 Molecular Models

Because organic chemistry is a three-dimensional science, molecular shape is often critical in determining the chemistry a compound undergoes, both in the laboratory and in living organisms. Learning to visualize molecular shapes is therefore an important skill to develop. One helpful technique, particularly when dealing with large biomolecules, is to use one of the many computer programs that are available for rotating and manipulating molecules on the screen. Another technique is to use molecular models. With practice, you can learn to see many spatial relationships even when viewing two-dimensional drawings, but there's no substitute for building a molecular model and turning it in your hands to get different perspectives.

Many kinds of models are available, some at relatively modest cost, and it's a good idea to have access to a set of models while studying this book. *Space-filling models* are better for examining the crowding within a molecule, but *ball-and-stick models* are generally the least expensive and most durable for student use. Figure 2.6 shows two kinds of models of acetic acid, $\text{CH}_3\text{CO}_2\text{H}$.

Figure 2.6 Molecular models of acetic acid, $\text{CH}_3\text{CO}_2\text{H}$. (a) Space-filling; (b) ball-and-stick.

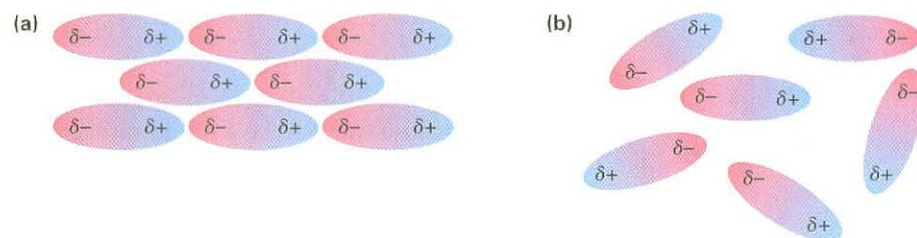


2.13 Noncovalent Interactions

When thinking about chemical reactivity, chemists usually focus their attention on bonds, the covalent interactions between atoms *within* individual molecules. Also important, however, particularly in large biomolecules like proteins and nucleic acids, are a variety of interactions *between* molecules that strongly affect molecular properties. Collectively called either *intermolecular forces*, *van der Waals forces*, or **noncovalent interactions**, they are of several different types: dipole–dipole forces, dispersion forces, and hydrogen bonds.

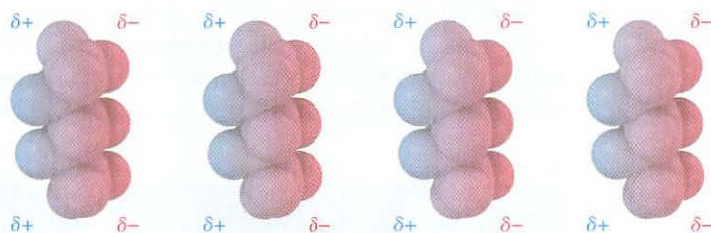
Dipole–dipole forces occur between polar molecules as a result of electrostatic interactions among dipoles. The forces can be either attractive or repulsive depending on the orientation of the molecules—attractive when unlike charges are together and repulsive when like charges are together. The attractive geometry is lower in energy and therefore predominates (Figure 2.7).

Figure 2.7 Dipole–dipole forces cause polar molecules (a) to attract one another when they orient with unlike charges together but (b) to repel one another when they orient with like charges together.

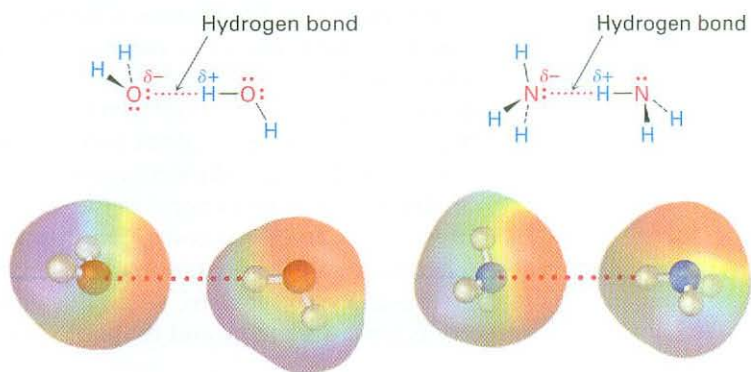


Dispersion forces occur between all neighboring molecules and arise because the electron distribution within molecules is constantly changing. Although uniform on a time-averaged basis, the electron distribution even in nonpolar molecules is likely to be nonuniform at any given instant. One side of a molecule may, by chance, have a slight excess of electrons relative to the opposite side, giving the molecule a temporary dipole. This temporary dipole in one molecule causes a nearby molecule to adopt a temporarily opposite dipole, with the result that a tiny attraction is induced between the two (Figure 2.8). Temporary molecular dipoles have *only* a fleeting existence and are constantly changing, but their cumulative effect is often strong enough to cause a substance to be liquid or solid rather than gaseous.

Figure 2.8 Attractive dispersion forces in nonpolar molecules are caused by temporary dipoles, as shown in these models of pentane, C_5H_{12} .

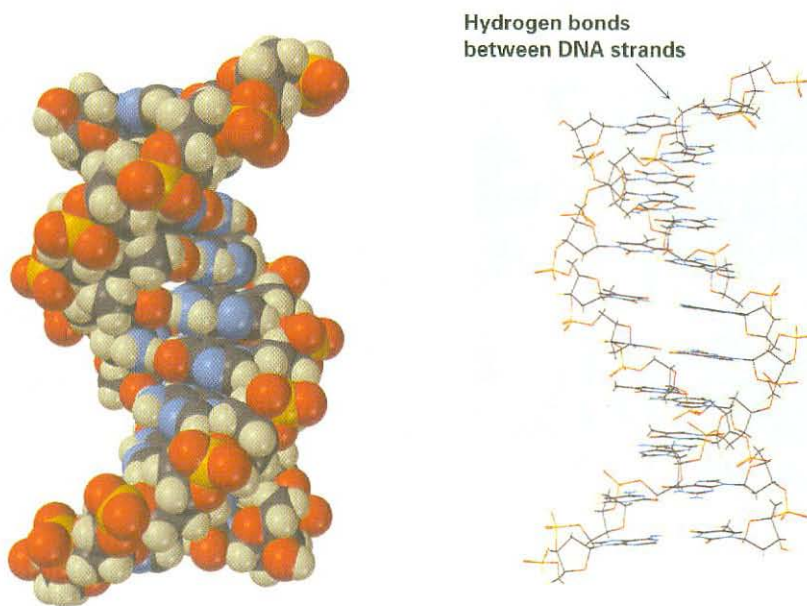


Perhaps the most important noncovalent interaction in biological molecules is the **hydrogen bond**, an attractive interaction between a hydrogen bonded to an electronegative O or N atom and an unshared electron pair on another O or N atom. In essence, a hydrogen bond is a strong dipole-dipole interaction involving polarized O–H and N–H bonds. Electrostatic potential maps of water and ammonia clearly show the positively polarized hydrogens (blue) and the negatively polarized oxygens and nitrogens (red).



Hydrogen-bonding has enormous consequences for living organisms. Hydrogen bonds cause water to be a liquid rather than a gas at ordinary temperatures,

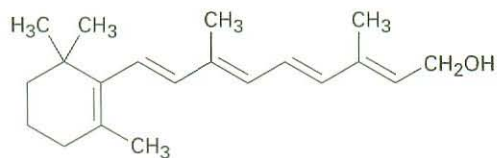
they hold enzymes in the shapes necessary for catalyzing biological reactions, and they cause strands of deoxyribonucleic acid (DNA) to pair up and coil into the double helix that stores genetic information.



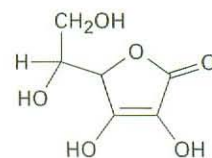
A deoxyribonucleic acid segment

One further point before leaving the subject of noncovalent interactions: chemists frequently use the terms **hydrophilic**, meaning “water-loving,” to describe a substance that dissolves in water and **hydrophobic**, meaning “water-fearing,” to describe a substance that does not dissolve in water. Hydrophilic substances, such as table sugar, usually have a number of ionic charges or polar -OH groups in their structure, so they are strongly attracted to water. Hydrophobic substances, such as vegetable oil, do not have groups that form hydrogen bonds, so their attraction to water is weak.

Problem 2.19 Of the two vitamins A and C, one is hydrophilic and water-soluble while the other is hydrophobic and fat-soluble. Which is which?



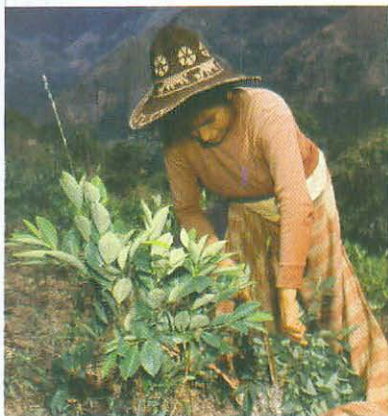
Vitamin A
(retinol)



Vitamin C
(ascorbic acid)

Focus On...

Alkaloids: Naturally Occurring Bases



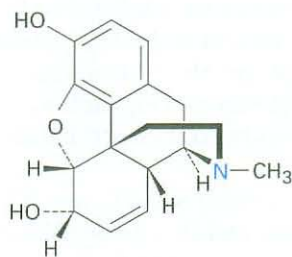
© Gustavo Giliberti/CORBIS SABA

The coca bush *Erythroxylon coca*, native to upland rain forest areas of Colombia, Ecuador, Peru, Bolivia, and western Brazil, is the source of the alkaloid cocaine.

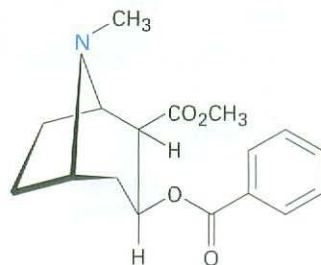
Just as ammonia is a weak base, there are a large number of nitrogen-containing organic compounds called *amines* that are also weak bases. In the early days of organic chemistry, basic amines derived from natural sources were known as *vegetable alkali*, but they are now called *alkaloids*. The study of alkaloids provided much of the impetus for the growth of organic chemistry in the 19th century and remains today an active and fascinating area of research.

Alkaloids vary widely in structure, from the simple to the enormously complex. The odor of rotting fish, for example, is caused largely by methylamine, CH_3NH_2 , a simple relative of ammonia in which one of the NH_3 hydrogens has been replaced by an organic CH_3 group. In fact, the use of lemon juice to mask fish odors is simply an acid–base reaction of the citric acid in lemons with methylamine base in the fish.

Many alkaloids have pronounced biological properties, and a substantial number of the pharmaceutical agents used today are derived from naturally occurring amines. As a few examples, morphine, an analgesic agent, is obtained from the opium poppy *Papaver somniferum*. Cocaine, both an anesthetic and a central nervous system stimulant, is obtained from the coca bush *Erythroxylon coca*, endemic to upland rain forest areas of Colombia, Ecuador, Peru, Bolivia, and western Brazil. Reserpine, a tranquilizer and antihypertensive, comes from powdered roots of the semitropical plant *Rauwolfia serpentina*. Ephedrine, a bronchodilator and decongestant, is obtained from the Chinese plant *Ephedra sinica*.

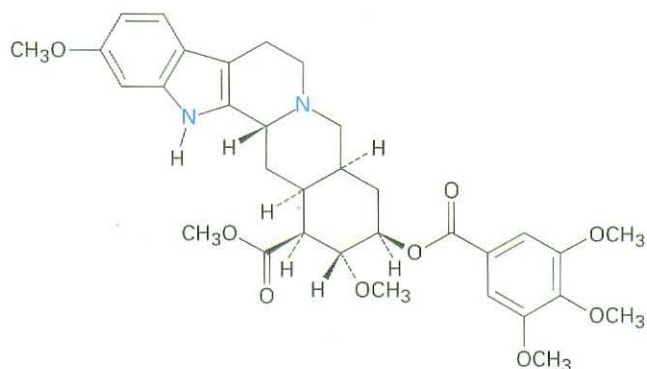


Morphine

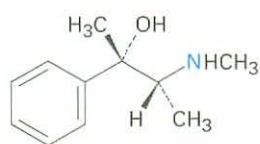


Cocaine

(continued)



Reserpine



Ephedrine

A recent report from the U.S. National Academy of Sciences estimates that less than 1% of all living species have been characterized. Thus, alkaloid chemistry remains today an active area of research, and innumerable substances with potentially useful properties remain to be discovered.

SUMMARY AND KEY WORDS

acidity constant (K_a), 50
 Brønsted–Lowry acid, 49
 Brønsted–Lowry base, 49
 conjugate acid, 49
 conjugate base, 49
 dipole moment (μ), 38
 electronegativity (EN), 36
 formal charge, 41
 hydrogen bond, 62
 hydrophilic, 63
 hydrophobic, 63
 inductive effect, 37
 Lewis acid, 57
 Lewis base, 57
 noncovalent interaction, 61

Organic molecules often have **polar covalent bonds** as a result of unsymmetrical electron sharing caused by differences in the **electronegativity** of atoms. A carbon–oxygen bond is polar, for example, because oxygen attracts the shared electrons more strongly than carbon does. Carbon–hydrogen bonds are relatively nonpolar. Many molecules as a whole are also polar owing to the vector summation of individual polar bonds and electron lone pairs. The polarity of a molecule is measured by its **dipole moment**, μ .

Plus (+) and minus (–) signs are often used to indicate the presence of **formal charges** on atoms in molecules. Assigning formal charges to specific atoms is a bookkeeping technique that makes it possible to keep track of the valence electrons around an atom and offers some clues about chemical reactivity.

Some substances, such as acetate ion and benzene, can't be represented by a single line-bond structure and must be considered as a **resonance hybrid** of two or more structures, neither of which is correct by itself. The only difference between two **resonance forms** is in the location of their π and nonbonding electrons. The nuclei remain in the same places in both structures, and the hybridization of the atoms remains the same.

pK_a , 51
 polar covalent bond, 35
 resonance form, 43
 resonance hybrid, 44

Acidity and basicity are closely related to the ideas of polarity and electronegativity. A **Brønsted–Lowry acid** is a compound that can donate a proton (hydrogen ion, H^+), and a **Brønsted–Lowry base** is a compound that can accept a proton. The strength of a Brønsted–Lowry acid or base is expressed by its **acidity constant**, K_a , or by the negative logarithm of the acidity constant, pK_a . The larger the pK_a , the weaker the acid. More useful is the Lewis definition of acids and bases. A **Lewis acid** is a compound that has a low-energy empty orbital that can accept an electron pair; Mg^{2+} , BF_3 , $AlCl_3$, and H^+ are examples. A **Lewis base** is a compound that can donate an unshared electron pair; NH_3 and H_2O are examples. Most organic molecules that contain oxygen and nitrogen can act as Lewis bases toward sufficiently strong acids.

A variety of **noncovalent interactions** have a significant effect on the properties of large biomolecules. **Hydrogen-bonding**—the attractive interaction between a positively polarized hydrogen atom bonded to an oxygen or nitrogen atom with an unshared electron pair on another O or N atom, is particularly important in giving proteins and nucleic acids their shapes.

EXERCISES

Organic KNOWLEDGE TOOLS

ThomsonNOW Sign in at www.thomsonedu.com to assess your knowledge of this chapter's topics by taking a pre-test. The pre-test will link you to interactive organic chemistry resources based on your score in each concept area.



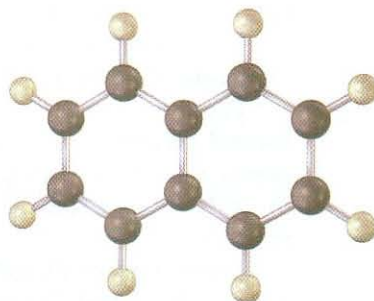
Online homework for this chapter may be assigned in Organic OWL.

- indicates problems assignable in Organic OWL.
- ▲ denotes problems linked to Key Ideas of this chapter and testable in ThomsonNOW.

VISUALIZING CHEMISTRY

(Problems 2.1–2.19 appear within the chapter.)

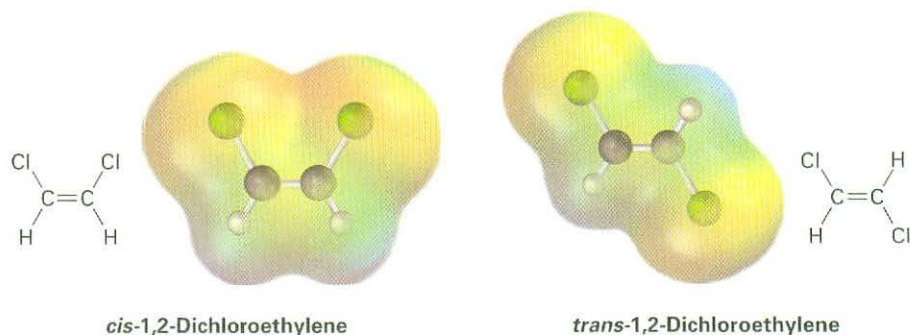
- 2.20** Fill in the multiple bonds in the following model of naphthalene, $C_{10}H_8$ (gray = C, ivory = H). How many resonance structures does naphthalene have?



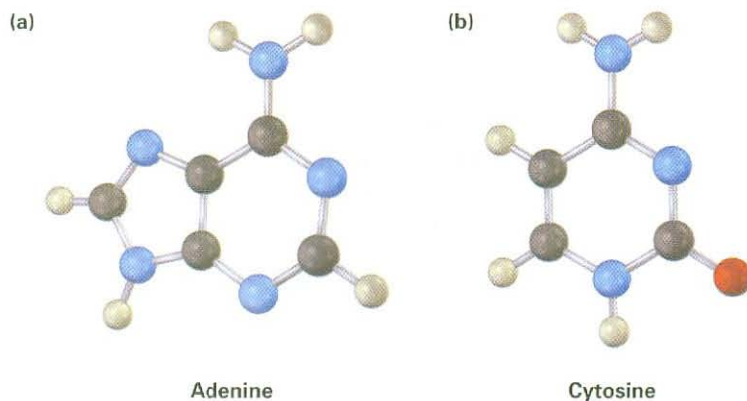
- 2.21 ■ The following model is a representation of ibuprofen, a common over-the-counter pain reliever. Indicate the positions of the multiple bonds, and draw a skeletal structure (gray = C, red = O, ivory = H).



- 2.22 *cis*-1,2-Dichloroethylene and *trans*-dichloroethylene are *isomers*, compounds with the same formula but different chemical structures. Look at the following electrostatic potential maps, and tell whether either compound has a dipole moment.

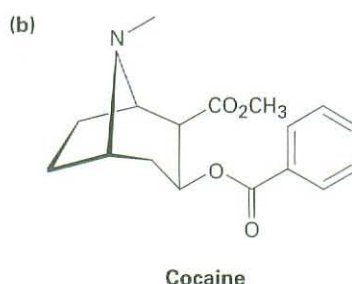
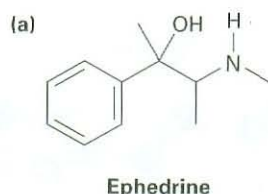


- 2.23 ■ The following molecular models are representations of (a) adenine and (b) cytosine, constituents of DNA. Indicate the positions of multiple bonds and lone pairs for both, and draw skeletal structures (gray = C, red = O, blue = N, ivory = H).



ADDITIONAL PROBLEMS

2.24 Tell the number of hydrogens bonded to each carbon atom in the following substances, and give the molecular formula of each:



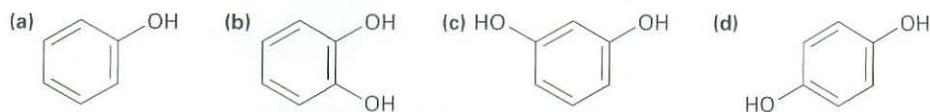
2.25 ■ Identify the most electronegative element in each of the following molecules:

- (a) CH_2FCl (b) $\text{FCH}_2\text{CH}_2\text{CH}_2\text{Br}$
 (c) $\text{HOCH}_2\text{CH}_2\text{NH}_2$ (d) $\text{CH}_3\text{OCH}_2\text{Li}$

2.26 ■ Use the electronegativity table (Figure 2.2) to predict which bond in each of the following sets is more polar, and indicate the direction of bond polarity for each compound.

- (a) $\text{H}_3\text{C}-\text{Cl}$ or $\text{Cl}-\text{Cl}$ (b) $\text{H}_3\text{C}-\text{H}$ or $\text{H}-\text{Cl}$
 (c) $\text{HO}-\text{CH}_3$ or $(\text{CH}_3)_3\text{Si}-\text{CH}_3$ (d) $\text{H}_3\text{C}-\text{Li}$ or $\text{Li}-\text{OH}$

2.27 ■ Which of the following molecules has a dipole moment? Indicate the expected direction of each.



2.28 (a) The $\text{H}-\text{Cl}$ bond length is 136 pm. What would the dipole moment of HCl be if the molecule were 100% ionic, $\text{H}^+ \text{Cl}^-$?

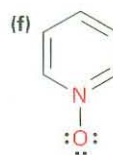
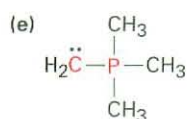
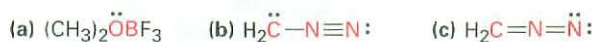
(b) The actual dipole moment of HCl is 1.08 D. What is the percent ionic character of the $\text{H}-\text{Cl}$ bond?

2.29 Phosgene, $\text{Cl}_2\text{C}=\text{O}$, has a smaller dipole moment than formaldehyde, $\text{H}_2\text{C}=\text{O}$, even though it contains electronegative chlorine atoms in place of hydrogen. Explain.

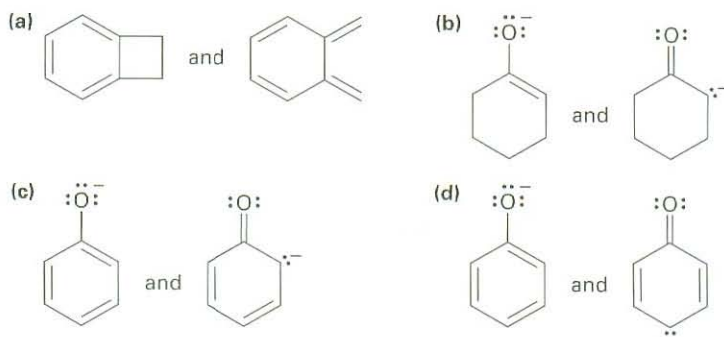
2.30 Fluoromethane (CH_3F , $\mu = 1.81$ D) has a smaller dipole moment than chloromethane (CH_3Cl , $\mu = 1.87$ D) even though fluorine is more electronegative than chlorine. Explain.

2.31 Methanethiol, CH_3SH , has a substantial dipole moment ($\mu = 1.52$) even though carbon and sulfur have identical electronegativities. Explain.

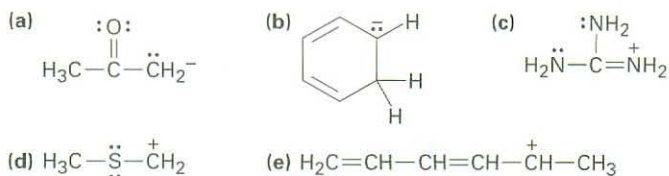
2.32 ■ Calculate the formal charges on the atoms shown in red.



2.33 ■ Which of the following pairs of structures represent resonance forms?



2.34 ■ ▲ Draw as many resonance structures as you can for the following species:

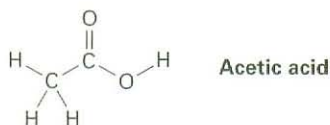


2.35 Cyclobutadiene is a rectangular molecule with two shorter double bonds and two longer single bonds. Why do the following structures *not* represent resonance forms?

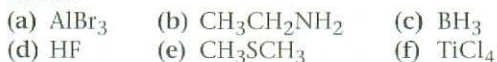


2.36 Alcohols can act either as weak acids or as weak bases, just as water can. Show the reaction of methanol, CH_3OH , with a strong acid such as HCl and with a strong base such as $\text{Na}^+ \text{NH}_2^-$.

2.37 ▲ The O–H hydrogen in acetic acid is much more acidic than any of the C–H hydrogens. Explain this result using resonance structures.

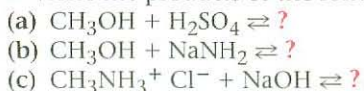


2.38 ■ Which of the following are likely to act as Lewis acids and which as Lewis bases?

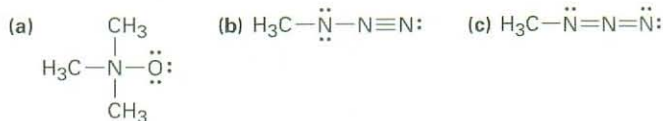


2.39 Draw an electron-dot structure for each of the molecules in Problem 2.38, indicating any unshared electron pairs.

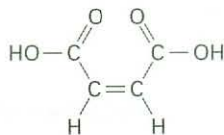
2.40 ■ Write the products of the following acid–base reactions:



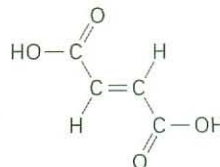
2.41 ■ Assign formal charges to the atoms in each of the following molecules:



2.42 Maleic acid has a dipole moment, but the closely related fumaric acid, a substance involved in the citric acid cycle by which food molecules are metabolized, does not. Explain.

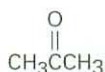
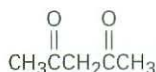
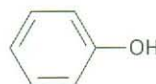


Maleic acid



Fumaric acid

2.43 ■ Rank the following substances in order of increasing acidity:

Acetone
($pK_a = 19.3$)2,4-Pentanedione
($pK_a = 9$)Phenol
($pK_a = 9.9$)Acetic acid
($pK_a = 4.76$)

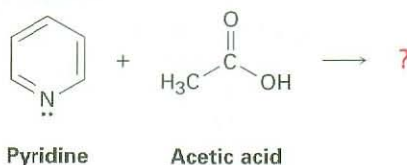
2.44 Which, if any, of the four substances in Problem 2.43 is a strong enough acid to react almost completely with NaOH? (The pK_a of H_2O is 15.74.)

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

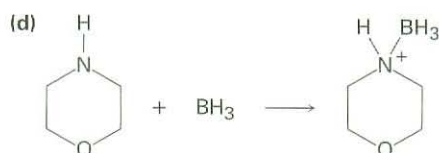
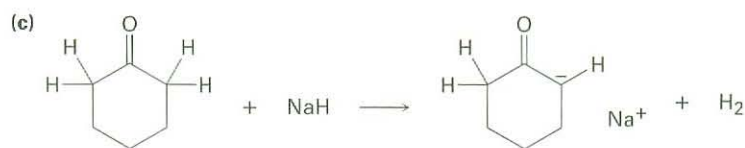
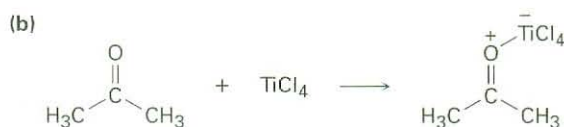
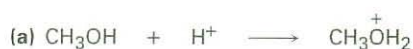
2.46 Is *tert*-butoxide anion a strong enough base to react with water? In other words, can a solution of potassium *tert*-butoxide be prepared in water? The pK_a of *tert*-butyl alcohol is approximately 18.



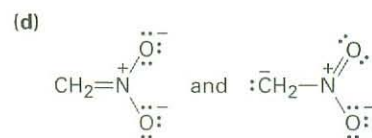
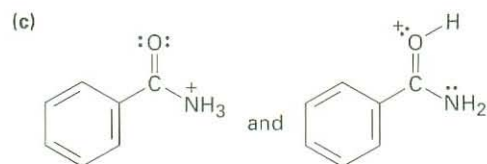
2.47 Predict the structure of the product formed in the reaction of the organic base pyridine with the organic acid acetic acid, and use curved arrows to indicate the direction of electron flow.



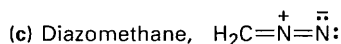
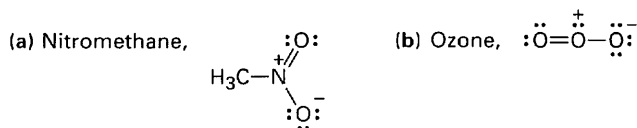
- 2.48 ■ Calculate K_a values from the following pK_a 's:
 (a) Acetone, $pK_a = 19.3$ (b) Formic acid, $pK_a = 3.75$
- 2.49 ■ Calculate pK_a values from the following K_a 's:
 (a) Nitromethane, $K_a = 5.0 \times 10^{-11}$ (b) Acrylic acid, $K_a = 5.6 \times 10^{-5}$
- 2.50 What is the pH of a 0.050 M solution of formic acid, $pK_a = 3.75$?
- 2.51 Sodium bicarbonate, NaHCO_3 , is the sodium salt of carbonic acid (H_2CO_3), $pK_a = 6.37$. Which of the substances shown in Problem 2.43 will react with sodium bicarbonate?
- 2.52 Assume that you have two unlabeled bottles, one of which contains phenol ($pK_a = 9.9$) and one of which contains acetic acid ($pK_a = 4.76$). In light of your answer to Problem 2.51, suggest a simple way to determine what is in each bottle.
- 2.53 ■ Identify the acids and bases in the following reactions:



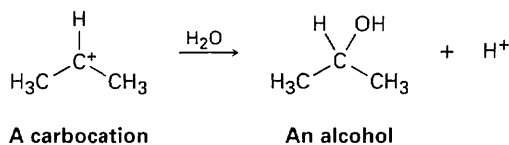
- 2.54 ■ ▲ Which of the following pairs represent resonance structures?



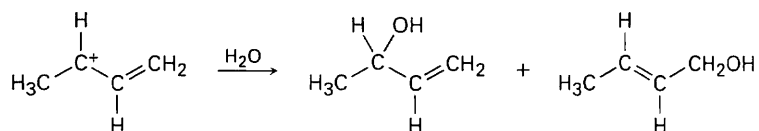
2.55 ▲ Draw as many resonance structures as you can for the following species, adding appropriate formal charges to each:



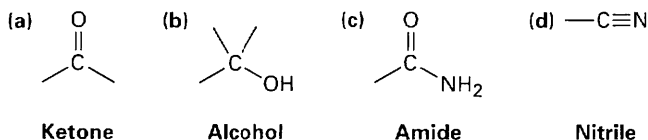
2.56 Carbocations, ions that contain a trivalent, positively charged carbon atom, react with water to give alcohols:



How can you account for the fact that the following carbocation gives a mixture of *two* alcohols on reaction with water?



2.57 We'll see in the next chapter that organic molecules can be classified according to the *functional groups* they contain, where a functional group is a collection of atoms with a characteristic chemical reactivity. Use the electronegativity values given in Figure 2.2 to predict the direction of polarization of the following functional groups.



2.58 Phenol, $\text{C}_6\text{H}_5\text{OH}$, is a stronger acid than methanol, CH_3OH , even though both contain an O–H bond. Draw the structures of the anions resulting from loss of H^+ from phenol and methanol, and use resonance structures to explain the difference in acidity.

