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Organic Chemistry

Chapter 5

Acid-Base Theory

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Chapter Outline

Objectives

✓ Be familiar with the Arrhenius, Brønsted-Lowry, and Lewis
   theories of acids and bases

✓ Recognize the orbitals that are involved in an acid-base reaction

✓ Know the relationship between acid strength and the value of pK_a

✓ Understand the relationship between polarizability and the
   hardness or softness of an acid or base

✓ Predict the stability of a chemical bond using the hard-soft acid
   base theory

✓ Recognize whether an organic functional group is an acid or a base

✓ Predict the relative acid or base strength of two organic compounds

✓ Understand how the presence of a particular functional group
   affects the acid or base strength of another functional group

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I hope no body will offer to dispute whether an *Acid* has points or
no, seeing every ones experience does demonstrate it, they need but to
taste an *Acid* to be satisfied of it, for it pricks the tongue like anything
keen, and finely cut … An *Alkali* is a terrestrous and solid matter, whose
pores are figured after such a manner that the *Acid* points entering them
do strike and divide whatsoever opposes their motion.

> —Nicholas Lemery
> "A Course in Chymistry"
> London (1686)

*A*s you work with chemical reactions in organic
chemistry, you will find that you can classify nearly all
of them as acid-base reactions. The key to understanding organic
chemical reactions is knowledge of acids and bases. When considering
a reaction, you need to ask three questions: Where's the acid? Where's
the base? How can the acid react with the base? The goal for this
chapter is to introduce you to ways that answer these questions.

Whether a molecule acts as an acid or a base in a chemical
reaction largely depends on its characteristics. There are three

significant molecular characteristics that affect acidity and basicity. The most important is the compound's primary functional group. A second factor is the inductive effect caused by the presence of additional functional groups. A third is the delocalization, or resonance effects, of the electrons in a molecule.

Showing Charges on Atoms

When you learned to write ions in your introductory chemistry course, you learned to put the charges after the formula of the ion. For example, you wrote the hydroxide ion as $OH^{\ominus}$. In organic chemistry it is important to know *which* atom in an ion bears the charge. For example, the oxygen in the hydroxide ion has the negative charge. In this book the hydroxide ion is written as $^{\ominus}OH$ to remind you that the oxygen has the negative charge. Other examples of familiar ions written in this manner are $^{\oplus}NH_4$, $^{\ominus}CH_3$, and $NO_3^{\ominus}$. For these three ions, you know immediately that the charges are on N, C, and O respectively.

5.1 Acids and Bases

Three major definitions of acids and bases have influenced the thinking of chemists. In 1884, Svante Arrhenius formulated the first of these definitions. Then, in 1923, independently of each other, Johannes N. Brønsted and Thomas M. Lowry developed the second. The third definition grew from Gilbert Newton Lewis's theory of covalent bonding, which he proposed in 1916.

The first definition, proposed by Svante Arrhenius in his doctoral dissertation, was so revolutionary that he was almost denied his Ph.D. However, in 1903, he received the Nobel Prize in chemistry for his theory. His theory states that a stable ionic compound that is soluble in water will break down, or dissociate, into its component ions. This dissociation, or ionization, of a compound in water, leads to Arrhenius' definition of an acid and a base. An acid is a substance that, when added to water, increases the concentration of hydronium ions, $H_3O^{\oplus}$. Because Arrhenius regarded acid-base reactions as occurring only in water, he frequently called the hydronium ion a hydrogen ion, $H^{\oplus}$. An $H^{\oplus}$ ion is a proton, or a hydrogen that is electron-deficient. Thus, a base is a substance that, when added to water, increases the concentration of hydroxide ions, $^{\ominus}OH$. The following statements summarize his definition.

An Arrhenius acid is a source of $H^{\oplus}$ ion.
An Arrhenius base is a source of $^{\ominus}OH$ ion.

The Arrhenius acid-base theory provided a good start toward understanding acid-base chemistry, but it proved much too limited in its scope.
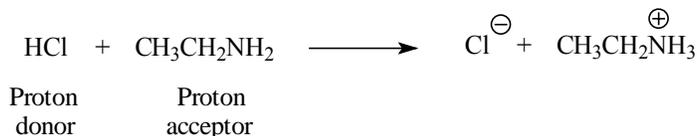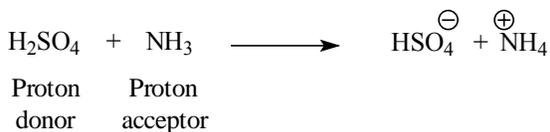
Brønsted and Lowry developed a more general acid-base definition than that of Arrhenius. Although they considered reactions other than those that take place in aqueous solutions, they still said acids were molecules that donate a hydrogen ion—such as HCl and H_2SO_4. However, they broadened the definition of bases to include any compound that accepts a proton. The basis of their acid-base definition is that in a reaction a proton transfers between reactants. Thus, acids involving a transfer of $H^\oplus$ ions are sometimes called proton acids. According to the Brønsted-Lowry definition, an acid is any molecule or ion that donates a proton to another molecule or ion, and a base is any molecule or ion that receives that proton. The following statements briefly summarize the Brønsted-Lowry definition.

A Brønsted-Lowry acid is a proton donor.
A Brønsted-Lowry base is a proton acceptor.

An example of the Brønsted-Lowry definition is the reaction between hydrogen chloride and sodium hydroxide:

$$HCl \ + \ NaOH \ \longrightarrow \ NaCl \ + \ H_2O$$

Proton   Proton
donor   acceptor
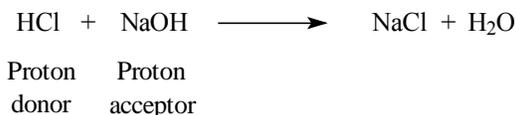
In this reaction, HCl is the acid because it is the source of protons, or hydrogen ions; NaOH is a base because the hydroxide ion is the proton acceptor. The following reactions further illustrate the Brønsted-Lowry acid-base definition.

$$H_2SO_4 \ + \ NH_3 \ \longrightarrow \ HSO_4^\ominus \ + \ \overset{\oplus}{N}H_4$$

Proton   Proton
donor   acceptor

$$HCl \ + \ CH_3CH_2NH_2 \ \longrightarrow \ Cl^\ominus \ + \ CH_3CH_2\overset{\oplus}{N}H_3$$

Proton   Proton
donor   acceptor

$$H_2SO_4 \; + \quad CH_2{=}C\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\big|}} \quad \rightleftharpoons \quad HSO_4^{\ominus} \; + \; CH_3{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C^{\oplus}}}}}$$

Proton   Proton
donor   acceptor
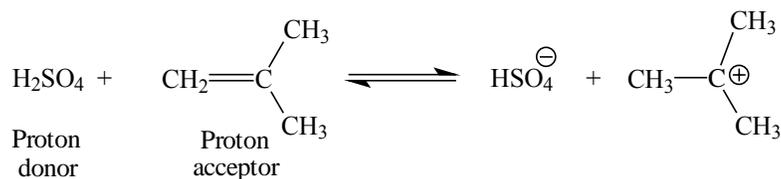
When an acid and a base react with each other, the reactants and products are in equilibrium with each other. Note the two-way arrows. They indicate that this is an equilibrium reaction. That is, the reactants on the left side of the equation are reacting and forming product, and the products on the right side are *also* reacting and forming the starting reactants. Chemists call the acid and base on the right side of the equation the **conjugate acid** and **conjugate base**. The reaction below is labeled to show the conjugate acid and conjugate base.

A conjugate acid-base pair consists of the acid and base products that result from an acid-base reaction.

$$H_2SO_4 \; + \; NH_3 \quad \longrightarrow \quad HSO_4^{\ominus} \; + \; \overset{\oplus}{N}H_4$$

Acid   Base   Conjugate Conjugate
                            base   acid

The hydrogen sulfate $(HSO_4{}^{\ominus})$ anion is also called the bisulfate ion.
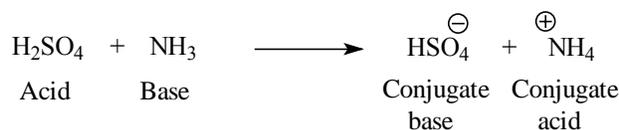
A hydrogen of sulfuric acid (H_2SO_4) is the acid, and the nitrogen of ammonia (NH_3) is the base. They react to form the hydrogen sulfate anion ($HSO_4{}^{\ominus}$) and the ammonium ion ($NH_4{}^{\oplus}$). The ammonium ion is the conjugate acid of ammonia. The bisulfate ion is the conjugate base of the sulfuric acid.

Like Brønsted and Lowry, G. N. Lewis defined acids and bases in a broader scheme than Arrhenius did. Lewis noted that there are a number of reactions that look like acid-base reactions but do not involve the transfer of a proton. Instead, they involve the interaction of a pair of nonbonding electrons. From that observation, he defined an acid as a molecule that forms a covalent bond by accepting a pair of electrons and a base as a molecule that forms a covalent bond by donating a pair of electrons. Below is a simplified statement of the Lewis definition of acids and bases.

A Lewis acid is an electron-pair acceptor.
A Lewis base is an electron-pair donor.

Reconciling the Acid-Base Theories

To prevent confusion over the terms *acceptor* and *donor*, stop and look at the three definitions of acids and bases. Keep in mind that although all three definitions consider the same concept, they do so from different viewpoints. Arrhenius and Brønsted-Lowry look at acids and bases from the viewpoint of

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> proton transfers. Lewis looks at them from the viewpoint of electron pairs. The two viewpoints mesh when you remember that a proton is a positive hydrogen ion that has no electron, and is thus capable of accepting a pair of electrons.

Solved Exercise 5.1

The following compounds can act either as a Brønsted-Lowry acid or a Lewis acid. Show the reactive site in each compound and the structure of the conjugate base that results from a reaction with base $A^{\ominus}$. Determine whether the compound is a Brønsted-Lowry acid or a Lewis acid.
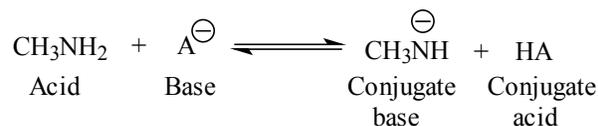
a) CH_3OH

Solution
Both the oxygen and the carbon have full valence shells and both have at least one hydrogen as a source of protons. However, oxygen is much more electronegative than carbon, so a negative charge on oxygen is more stable than a negative charge on carbon. Thus, the O—H bond is the reactive site and a stronger Brønsted-Lowry acid than is the C—H bond.

$$CH_3OH \;+\; A^{\ominus} \;\rightleftharpoons\; CH_3O^{\ominus} \;+\; HA$$
Acid   Base   Conjugate   Conjugate
   base   acid
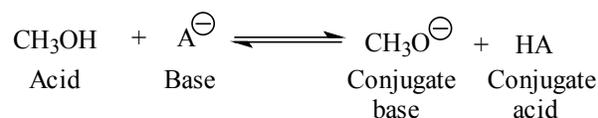
b) CH_3NH_2

Solution
Nitrogen is much more electronegative than carbon, so a negative charge on nitrogen is more stable than a negative charge on carbon. Thus, the N—H bond is a stronger Brønsted-Lowry acid than is the C—H bond.

$$CH_3NH_2 \;+\; A^{\ominus} \;\rightleftharpoons\; CH_3\overset{\ominus}{N}H \;+\; HA$$
Acid   Base   Conjugate   Conjugate
                        base   acid
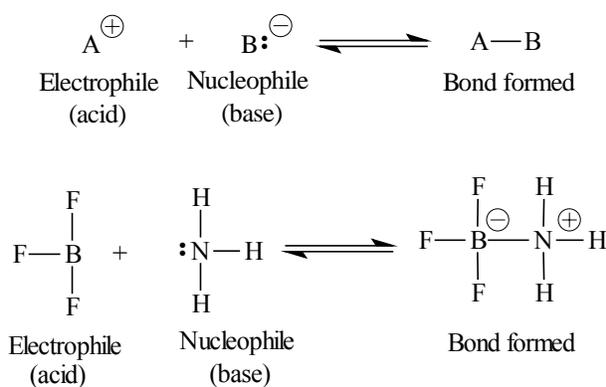
c) CH_3BH_2

Solution
Because boron is electron deficient with only six electrons in its valence shell, it will react before any bonds to hydrogen are broken. Thus, the boron is the reactive site, and it acts as a Lewis acid.

$$CH_3BH_2 \;+\; A^{\ominus} \;\rightleftharpoons\; CH_3\overset{H}{\underset{H}{\overset{|}{\underset{|}{B}}}}{}^{\ominus}\!\!-A$$
Acid   Base
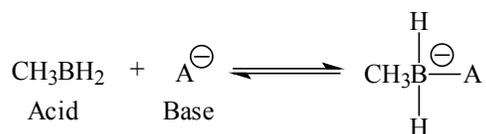
In the formation of a new chemical bond, an electrophile accepts electrons, and a nucleophile donates electrons.

Because a Lewis acid accepts a pair of electrons, chemists call it an **electrophile**, from the Greek meaning "lover of electrons." They call the base a **nucleophile**, or "lover of nuclei," because it donates the electrons to a nucleus with an empty orbital. In a chemical reaction, a nucleophile seeks a nucleus, or a positive charge, and an electrophile seeks electrons, or a negative charge. Fundamental to organic chemistry is the fact that nearly all the reactions that you will study are reactions of an acid with a base or, more commonly, of an electrophile with a nucleophile.

$$A^{\oplus} \quad + \quad B{:}^{\ominus} \quad \rightleftharpoons \quad A\!-\!B$$

Electrophile   Nucleophile   Bond formed
(acid)   (base)

Electrophile   Nucleophile   Bond formed
(acid)   (base)

Curved arrows are introduced in Section 1.13, page 000.

Chemists use a curved arrow ( ) to show electron movement. A curved arrow points from the electron-rich reactant, the base or nucleophile, toward the electron-poor reactant, the acid or electrophile. Rewriting the previous two reactions using a curved arrow shows the movement of electrons. In each reaction, a pair of nonbonding electrons from a nucleophile reacts with an electrophile to form a bond.
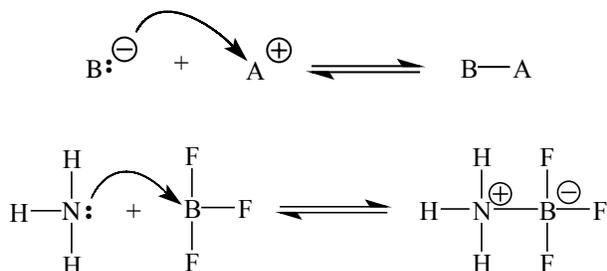
Exercise 5.1

Use curved arrows to write the acid-base reaction of a hydrogen ion with a hydroxide ion.

Acids and Bases versus Electrophiles and Nucleophiles

In organic chemistry, the terms *acid* and *electrophile* are formally synonymous, but informally, they have evolved different shades of meaning. The term *acid* has come to mean a proton donor and the term *electrophile* has come to mean an electron pair acceptor. Similarly, the term *base* has come to mean a proton acceptor, and the term *nucleophile* has come to mean an electron pair donor. However, from time to time, the dividing line between the two sets of terms becomes fuzzy. For example, chemists may call the same group of atoms a base or a nucleophile depending on the chemical environment of that group. Probably the most useful generalization is that the difference between a base and a nucleophile is in how they react. In organic reactions, a base generally reacts with a proton, and a nucleophile generally reacts with a positively charged or electron-deficient carbon. An electron-deficient carbon is a carbon with an unfilled octet in its valence shell.

All chemical reactions involve orbital interactions. The orbital description of a reaction can help you understand how chemical reactions occur. As you study the various reactions presented in this book, think about the orbitals involved in the reactions. Figure 5.1 is a molecular orbital picture of ammonia reacting with boron trifluoride to form a new bond. Ammonia is a base with a pair of nonbonding electrons. The nitrogen of ammonia is sp^3 hybridized. Boron trifluoride is an acid with an incomplete octet of electrons. The boron is sp^2 hybridized with an empty *p* orbital. The reaction occurs when an sp^3 orbital of ammonia overlaps with the empty *p* orbital of boron trifluoride. In the process, the boron becomes sp^3 hybridized. With this overlap the two molecules form a new bond.
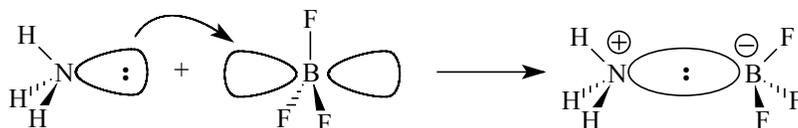

Figure 5.1. The orbitals involved in the acid-base reaction of NH_3 and BF_3.

Exercise 5.2

Show the orbitals involved in the acid-base reaction of a hydrogen ion with a hydroxide ion.

Being able to identify an acid or base is important. Of equal importance is the ability to recognize how the structure of that acid or base affects its strength. The rest of this chapter is devoted to helping you acquire the tools to do so. With these tools, you can predict the outcome of chemical reactions. Much of the rest of the material in this book depends on your ability to recognize acids and bases and their relative strengths.

5.2 Acid and Base Strength

The strength of a Brønsted-Lowry acid or base depends on the extent to which it ionizes in water. Although there are numerous solvents besides water, chemists discuss acid and base strength in relation to water because they use it so widely as a solvent. Chemists use the **autoionization** of pure water to determine the values for the concentrations of acidic and basic solutions. Autoionization is the reaction of two molecules of water with each other to give a hydronium ion, $H_3O^{\oplus}$, and a hydroxide ion, $^{\ominus}OH$.

$$H_2O + H_2O \rightleftharpoons H_3O^{\oplus} + {}^{\ominus}OH$$

For this reaction, the amount of autoionization is extremely slight—at 25°C, it is 10^{-7} M (moles/liter). The concentrations of $H_3O^{\oplus}$ and $^{\ominus}OH$ are equal; that is, both measure 10^{-7} M. Chemists call this a neutral solution. If you add a compound that is more acidic than water, you increase the concentration of $H_3O^{\oplus}$ ions and make the solution acidic. If you add a compound that is more basic than water, you increase the concentration of $^{\ominus}OH$ ions and make the solution basic.

The product of the $H_3O^{\oplus}$ and $^{\ominus}OH$ concentrations in water is equal to 10^{-14} and is a constant, K_w. Chemists define K_w with the following equation.

$$K_w = [H_3O^{\oplus}][^{\ominus}OH] = 1.00 \times 10^{-14}$$

When performing a concentration calculation, replace the chemical species listed within the brackets, [$^{\ominus}OH$], for example, with that species' molar concentration.

Because the concentrations of $H_3O^{\oplus}$ and $^{\ominus}OH$ are equal in a neutral solution, you can easily calculate the concentration of both:

$$[H_3O^{\oplus}] = [^{\ominus}OH] = 1.00 \times 10^{-7} \text{ M}$$

Because the product of the two concentrations is a constant, K_w, when one concentration increases, the other must decrease. For example, if you add $^{\ominus}OH$ ions to water the concentration of the $H_3O^{\oplus}$ decreases by whatever amount is necessary for the product of the two concentrations to still equal 10^{-14}.
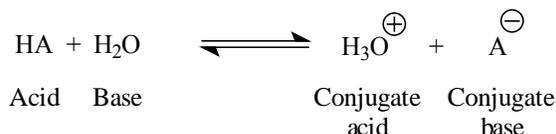
Because the hydronium ion concentrations can span a very wide range of values, from greater than 1 M down to less than 10^{-14} M, chemists measure the concentration of $H_3O^{\oplus}$ on a logarithmic scale called pH. The pH values give the hydronium ion concentration of a solution. Therefore, measuring the pH of a solution is a means of quantifying the acidity of that solution. Chemists define this

measurement as the negative logarithm (base 10) of the $H_3O^{\oplus}$ concentration, represented by the following equation:

$$pH = -\log_{10}[H_3O^{\oplus}]$$

For simplicity, this book will normally refer to the $H_3O^{\oplus}$ ion as the $H^{\oplus}$ ion from now on. If an equation shows the $H^{\oplus}$ ion present in aqueous solution, remember that it is actually the $H_3O^{\oplus}$ ion.

This equation shows the general reaction of an acid in water:

$$HA \; + \; H_2O \quad \rightleftharpoons \quad H_3O^{\oplus} \; + \; A^{\ominus}$$

| Acid | Base | | Conjugate acid | Conjugate base |

Note that this reaction is an equilibrium. Most acid-base reactions are equilibrium reactions because the reactants only partly ionize. Strong acids and bases ionize completely in water. Weak acids and bases ionize only partly in water. An acidic, aqueous solution is any solution with a concentration of hydrogen ions greater than 10^{-7} M. Similarly, a basic solution is any solution with a concentration of hydroxide ions greater than 10^{-7} M.

To determine the relative strength of an acid or a base, you need to find out how much the acid or the base ionizes, or dissociates, in water at equilibrium. The equilibrium constant, K_e, gives this information and is defined as follows:

$$K_e = \frac{[H_3O^{\oplus}][A^{\ominus}]}{[HA][H_2O]}$$

However, because water is the solvent and its concentration is essentially constant, a more meaningful value for acid ionization comes from multiplying the equilibrium constant by the water concentration:

$$K_a = K_e[H_2O] = \frac{[H_3O^{\oplus}][A^{\ominus}]}{[HA]}$$

An acid dissociation constant expression is the equilibrium expression without the solvent concentration.

Chemists call K_a the **acid dissociation constant**. The value of K_a specifies the strength of the acid. The stronger the acid, the larger the amount of dissociation and the larger the concentration of $H_3O^{\oplus}$ ions. Thus, the stronger the acid, the larger the value of K_a. Strong acids completely dissociate in water and have large dissociation constants. Most organic compounds are weak acids and have dissociation constants in the range from 10^{-2} to 10^{-60}.

Because acids have such a large range of values for their dissociation constants, chemists often convert those values to a logarithmic scale, similar to pH. The following equation defines this scale:

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

Solved Exercise 5.2

Calculate the value of K_a and pK_a for water.

Solution
Below is the autoionization equation for water

$$H_2O + H_2O \rightleftharpoons H_3O^{\oplus} + {}^{\ominus}OH$$

and the K_a expression for water.

$$K_a = \frac{[H_3O^{\oplus}][{}^{\ominus}OH]}{[H_2O]}$$

The numerator of the K_a expression is the same as the expression for K_w:

$$K_w = [H_3O^{\oplus}][{}^{\ominus}OH] = 1.00 \times 10^{-14}$$

So, you can substitute 1.00×10^{-14} for the numerator of the K_a expression. The $[H_2O]$ is the number of moles per liter of water and is calculated as follows.

$$[H_2O] = \frac{\text{Wt of 1 L of } H_2O}{\text{molecular weight of } H_2O} = \frac{1000 \text{ g/L}}{18 \text{ g/mol}} = 55.6 \text{ mol/L}$$

Substitute the values in the K_a expression and calculate:

$$K_a = \frac{[H_3O^{\oplus}][{}^{\ominus}OH]}{[H_2O]} = \frac{K_w}{[H_2O]} = \frac{1.00 \times 10^{-14}}{55.6} = 1.8 \times 10^{-16}$$

The value of pK_a for water is 15.7.

Strong acids generally have pK_a values around 0 or below, and most neutral organic acids have pK_a values greater than 2. Table 5.1 gives some values for a sampling of acids. A more complete listing is found in Appendix A. The pK_a values given are relative to water. Values higher than 18 and lower than –5 are estimates. Many of the values here and in the appendix will be useful to you as you learn organic chemistry. Mark the location of Appendix A for quick access.

Figure 5.2 is a graphical summary of pK_a values for some important categories of acids. It gives you an overview of the acid strengths of a variety of types of compounds.
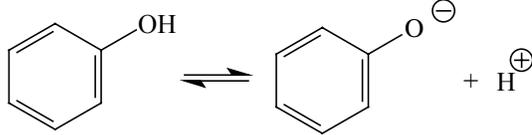
Acid Dissociation Reaction	pK_a
$CH_4 \rightleftharpoons {}^{\ominus}CH_3 + H^{\oplus}$	49
$CH_2{=}CH_2 \rightleftharpoons CH_2{=}\overset{\ominus}{C}H + H^{\oplus}$	44
$NH_3 \rightleftharpoons {}^{\ominus}NH_2 + H^{\oplus}$	36
$CH_2{=}CHCH_3 \rightleftharpoons CH_2{=}CH\overset{\ominus}{C}H_2 + H^{\oplus}$	35
$HC{\equiv}CH \rightleftharpoons HC{\equiv}C^{\ominus} + H^{\oplus}$	26
$H_2O \rightleftharpoons {}^{\ominus}OH + H^{\oplus}$	15.7
$CH_3OH \rightleftharpoons CH_3O^{\ominus} + H^{\oplus}$	15.1
	10.0
$H_2S \rightleftharpoons {}^{\ominus}SH + H^{\oplus}$	7.0
$CH_3\overset{O}{\overset{\|}{C}}OH \rightleftharpoons CH_3\overset{O}{\overset{\|}{C}}O^{\ominus} + H^{\oplus}$	4.8
$HF \rightleftharpoons F^{\ominus} + H^{\oplus}$	3.2
$HNO_3 \rightleftharpoons NO_3{}^{\ominus} + H^{\oplus}$	−1.4
$H_3O^{\oplus} \rightleftharpoons H_2O + H^{\oplus}$	−1.7
$H_2SO_4 \rightleftharpoons HSO_4{}^{\ominus} + H^{\oplus}$	−5.2
$HCl \rightleftharpoons Cl^{\ominus} + H^{\oplus}$	−7.0
$HBr \rightleftharpoons Br^{\ominus} + H^{\oplus}$	−9.0
$HI \rightleftharpoons I^{\ominus} + H^{\oplus}$	−10

Table 5.1. Some pK_a values for various acids. See Appendix A for a more complete list of pK_a values.
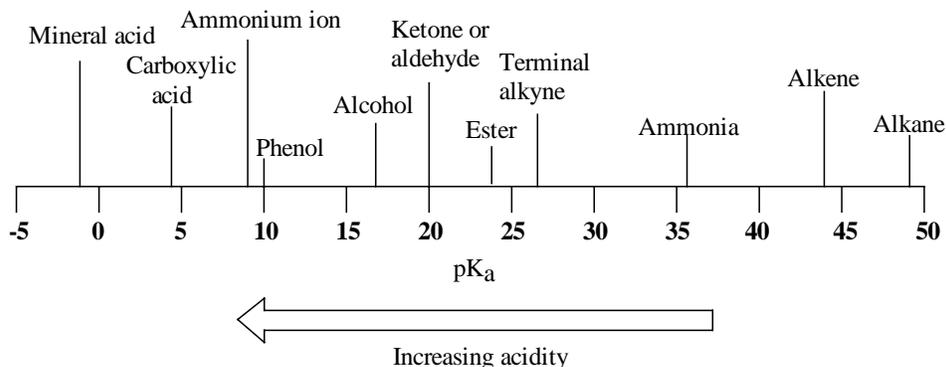

Figure 5.2. A graphical representation of pK_a values for some important categories of Brønsted-Lowry acids. Note that the value indicated for a functional group shows the most typical pK_a value for members of that group. For ketones, aldehydes, and esters, the pK_a is for the hydrogen on the carbon adjacent, or α, to the C=O double bond.

Exercise 5.3

Using the pK_a value given with each acid, calculate the pH of its aqueous solution.

a) 0.1 M CH_3COOH (pK_a = 4.8)   b) 0.1 M H_2S (pK_a = 7.0)
c) 0.1 M CH_3CH_2SH (pK_a = 10.6)   d) 0.1 M HCOOH (pK_a = 3.7)

Sample Solution

c) The pK_a is 10.6. The dissociation reaction is:

$$CH_3CH_2SH \rightleftharpoons CH_3CH_2S^{\ominus} + H^{\oplus}$$

Assume that the concentration of the acid is unchanged. You can make this assumption with less than 1% error if the pK_a is greater than 4 and the acid has one acidic proton. Use the K_a equation:
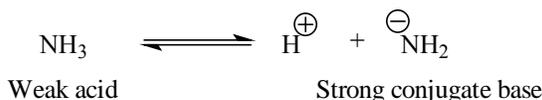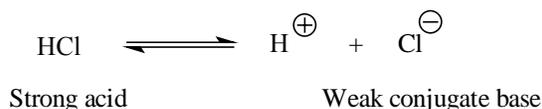
$$K_a = \frac{[H^{\oplus}][CH_3CH_2S^{\ominus}]}{[CH_3CH_2SH]}$$

Because you know the K_a of CH_3CH_2SH and since the concentrations of $H^{\oplus}$ and $CH_3CH_2S^{\ominus}$ are equal, the equation becomes:

$$10^{-10.6} = \frac{x^2}{10^{-1}}$$

Solve for x. The result is a value of $10^{-5.8}$, or a pH of 5.8.

A strong acid always reacts to form a weak conjugate base, and a weak acid always reacts to form a strong conjugate base. This relationship exists because the stronger the Brønsted-Lowry acid, the more willing it is to give up a proton thus forming a more stable conjugate base. A more stable conjugate base is less willing to accept a proton. The following examples illustrate this relationship.

$$\text{HCl} \rightleftharpoons \text{H}^{\oplus} + \text{Cl}^{\ominus}$$

Strong acid   Weak conjugate base

$$\text{NH}_3 \rightleftharpoons \text{H}^{\oplus} + {}^{\ominus}\text{NH}_2$$

Weak acid   Strong conjugate base

The first reaction, the dissociation of HCl, may be familiar from your introductory chemistry course. At equilibrium, the right side is favored. The dissociation of NH_3, however, is very unlikely to occur because the amide ion ($^{\ominus}NH_2$) is a very strong base. Thus, at equilibrium, the left side is favored.

Stability

Frequently, as you read and study chemistry, you will see the term *stable*. Chemists use this word in a comparative sense, saying that one chemical species is more stable than another chemical species. Seldom, if ever, do they use it in an absolute sense. Usually, when chemists compare one chemical species with another, the two have some similarities. In the previous example, the similarity is that both $Cl^{\ominus}$ and $^{\ominus}NH_2$ are bases. Experience shows that $Cl^{\ominus}$ is less reactive than $^{\ominus}NH_2$, so $Cl^{\ominus}$ is more stable.

The relationship between a base and its conjugate acid is similar to that of an acid and its conjugate base. Strong bases react to form weak conjugate acids, and weak bases react to form strong conjugate acids. The reasons for base strength are the opposite of the reasons for acid strength. For a Brønsted-Lowry base, the stronger the base, the *more* willing it is to accept a proton. For a Lewis base, the stronger the base, the *more* willing it is to give up electron pairs.

$$\overset{\ominus}{C}H_3 \quad + \quad \overset{\oplus}{H} \quad \rightleftharpoons \quad CH_4$$

Strong base   Weak conjugate acid

$$NO_3^{\ominus} \quad + \quad \overset{\oplus}{H} \quad \rightleftharpoons \quad HNO_3$$

Weak base   Strong conjugate acid
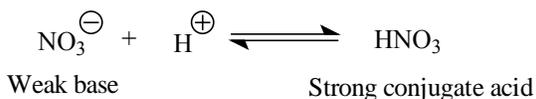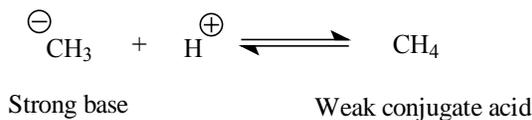
The reactants and products are usually in equilibrium in these reactions.

An extremely important concept in predicting the outcome of a reaction is that *the position of equilibrium is on the side of the weaker member of the acid-conjugate base (or base-conjugate acid) pair*. A strong acid or base is more reactive than a weak acid or base.
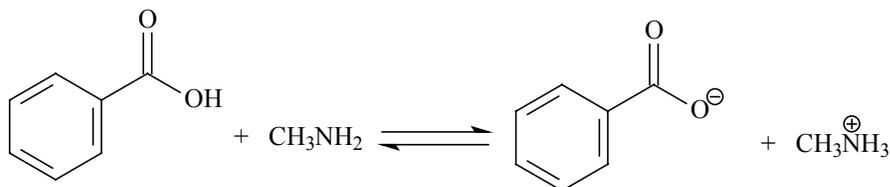

Exercise 5.4

For each of the following reactions identify the acid, base, conjugate acid, and conjugate base. Then, using the pK_a values from Appendix A, predict whether the position of equilibrium will favor the starting materials or the products.
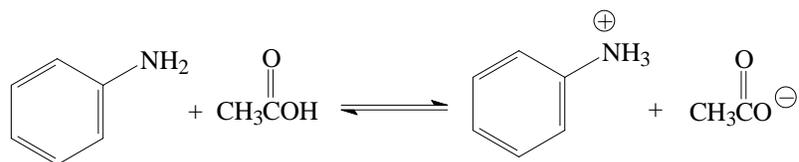
a)

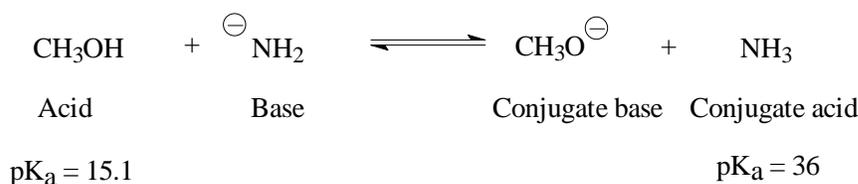$$CH_3OH \quad + \quad \overset{\ominus}{N}H_2 \quad \rightleftharpoons \quad CH_3O^{\ominus} \quad + \quad NH_3$$

b)

c)

d)

e)

Solution

a)

$$CH_3OH \quad + \quad {}^{\ominus}NH_2 \quad \rightleftharpoons \quad CH_3O^{\ominus} \quad + \quad NH_3$$

Acid   Base   Conjugate base   Conjugate acid

$pK_a = 15.1$ $pK_a = 36$

The conjugate acid is much weaker than the acid. Thus, the products are favored.

5.3 Hard and Soft Acids and Bases

The ease with which an acid-base reaction occurs depends on the strength of both the acid and the base. Strong acids and bases are generally more reactive than weak acids and bases. However, the direction of the reaction and the stability of the products often depend on another quality—the **hardness** or **softness** of the acid and base. Although chemists have not created a quantitative measure to describe the qualities that makes an acid or base hard or soft, they do describe them qualitatively. As you look at the following list of characteristics that describe hard and soft acids and bases, remember that an acid has an empty orbital and an unfilled valence shell, and a base has in its valence shell a pair of nonbonding electrons that is available for donation.

Hardness or softness is a qualitative measure of the reactivity of acids and bases. Hard or soft is independent of strength or weakness of acids and bases.

Charge density is the volume of space occupied by a charge. A large ion has a lower charge density than a small ion does.

Polarizability means the ability of an atom to have a distorted distribution of electrons.

Soft Acids. For soft acids, the electron-pair acceptor atoms are large, have a low positive **charge density**, and contain unshared pairs of electrons in their valence shells. The unshared pairs of electrons are in the *p* or *d* orbitals. Also, soft acids have a high **polarizability** and a low electronegativity. In organic chemistry, the soft acids usually include only the halogens, phosphorus, and sulfur compounds.

Hard Acids. For hard acids, the acceptor atoms are small, have a high positive charge density, and contain no unshared pairs of electrons in their valence shells. They have a low polarizability and a high electronegativity. The hydrogen ion is a good example of a hard acid.

Soft Bases. For soft bases, the donor atoms hold their valence electrons loosely. They have high polarizability, low negative charge density, and low electronegativity. Common soft bases are the cyanide ($^{\ominus}$CN) and iodide (I$^{\ominus}$) ions.

Hard Bases. For hard bases, the donor atoms are small, have a high negative charge density, and hold their valence electrons tightly. They have a low polarizability and a high electronegativity. The hydroxide ion is a good example of a hard base.

To visualize a polarizable atom, imagine that an atom is a large floppy ball and you are holding it cupped in both hands. The ball tends to be spherical, but, as you shift one hand higher than the other, it easily deforms. If you raise your left hand a little, the portion of the ball in your right hand becomes larger. Then, if you raise your right hand a little, the portion of the ball in your left hand becomes larger. A polarizable atom shifts its electron density from one part of the atom to another: at one instant, one portion of the atom has the higher electron density; then the next instant, another portion has the higher electron density.

Bond Polarity Versus Polarizability

Bond polarity differs from polarizability. In a polar bond, the more electronegative atom of the bonded pair pulls the bonding electrons toward itself. A polarizable atom or group can momentarily shift electron density from one portion of the atom or group to another.

For the concepts of hardness or softness of acids and bases to be of value to you, you must be able to differentiate between them. To do this, your most useful tool is the periodic table. A general rule is that hardness goes to softness moving from the top to the bottom on the periodic table because the size of the atoms increases with increasing numbers of electrons. A larger acid or base has a lower charge density and is more polarizable. For example, base softness in Group VII A on the periodic table decreases in this order: I$^{\ominus}$ > Br$^{\ominus}$ > Cl$^{\ominus}$ > F$^{\ominus}$. Also, the elements on the left side tend to be acids, and elements on the right side tend to be bases. In this way, chemists approximately rank acids and bases in order of hardness or softness. Base softness within a period on the periodic table decreases in order of increasing electronegativity; for example, $^{\ominus}$CH$_3$ > $^{\ominus}$NH$_2$ > $^{\ominus}$OH > F$^{\ominus}$.

Hardness and softness are difficult to quantify. Rather than relying specifically on these types of sequences, chemists divide acids and bases into three groups: (1) hard acids or bases, (2) soft acids or

bases, and (3) borderline acids or bases. Table 5.2 lists a few examples of each category.

Acids	Type	Bases
$H^{\oplus}$, $Li^{\oplus}$, $^{\oplus}CH_3$, $Na^{\oplus}$, $K^{\oplus}$, $Mg^{2\oplus}$, $Ca^{2\oplus}$, $Al^{3\oplus}$, BF_3, $AlCl_3$, $RCO^{\oplus}$, CO_2	*Hard*	H_2O, $^{\ominus}OH$, $F^{\ominus}$, $Cl^{\ominus}$, $^{\ominus}CH_3$, $^{\ominus}NH_2$, $RCOO^{\ominus}$, $CO_3{}^{2\ominus}$, ROH, $RO^{\ominus}$, NH_3, RNH_2
$Fe^{2\oplus}$, $Zn^{2\oplus}$, $Sn^{2\oplus}$, $Sb^{3\oplus}$, BR_3, SO_2, $R_3C^{\oplus}$, $NO^{\oplus}$	*Borderline*	$C_6H_5NH_2$, $N_3{}^{\ominus}$, $Br^{\ominus}$, $NO_2{}^{\ominus}$, $R^{\ominus}$
$Cu^{\oplus}$, $Ag^{\oplus}$, $Hg^{2\oplus}$, BH_3, I_2, Br_2, $:CH_2$ (carbenes)	*Soft*	$RS^{\ominus}$, $I^{\ominus}$, $^{\ominus}CN$, RCN, CO, C_6H_6, $^{\ominus}SH$, $H^{\ominus}$

Table 5.2. Some examples of hard and soft acids and bases. (R represents an alkyl group.)

H$^{\oplus}$ is a hard acid because it has no electrons and has a high positive charge density. The H$^{\ominus}$ ion is a soft base because it has a pair of electrons and only one proton, so it holds the electrons rather loosely. Thus, it is quite polarizable and soft.

Exercise 5.5

Classify each of the following chemical species as a hard, soft, or borderline acid or base.

a) $(CH_3)_3B$ b) $CH_3CH_2O^{\ominus}$ c) $(CH_3)_3Al$
d) AsH_3 e) $FeCl_3$ f) CH_3OH
g) $(CH_3)_3C^{\oplus}$ h) $(CH_3)_3C^{\ominus}$ i) $^{\ominus}SeH$
j) $(CH_3)_3N$ k) CH_3NH_2 l) $SnCl_2$

Sample solution

b) Oxygen is small and nonpolarizable and has a high electronegativity. Therefore, it is a hard base, making the alkoxide ion a hard base.

The HSAB principle is the preference for hard bases to form bonds with hard acids and soft bases to form bonds with soft acids.

Chapter 12, which begins on page 000, presents an application of the HSAB principle.

An important rule concerning acid-base reactions is that hard acids prefer to bond with hard bases, and soft acids prefer to bond with soft bases. This rule, often called the **HSAB Principle**, has nothing to do with acid or base strength, but merely states that a bond between a particular acid and a particular base has extra stability if both are either hard or soft. The HSAB Principle also helps to predict the outcome of an acid-base reaction. For example, the acyl group (RCO$^{\oplus}$) is a hard Lewis acid and forms stable combinations with hard Lewis bases such as $^{\ominus}NH_2$, $RO^{\ominus}$, and $Cl^{\ominus}$. In contrast, it forms

marginally stable or even unstable compounds with soft Lewis bases such as $RS^\ominus$ and $I^\ominus$.


Exercise 5.6

According to the HSAB Principle, which of the following chemical compounds would you expect to be stable (or only moderately reactive) and which would you expect to be unstable (or very reactive)?

a) AlI_3 b) CH_3COSH c) NaH
d) $Mg(SH)_2$ e) $Hg(OH)_2$ f) CH_3Cl
g) AgF   h) $CuCH_3$ i) CuI
j) $HgCO_3$ k) CsOH   l) KCH_3

Sample solution

a) From Table 5.2, note that $Al^{3\oplus}$ is a hard acid, and $I^\ominus$ is a soft base. Thus, AlI_3 is either unstable or highly reactive.

        Perhaps the most important application of the HSAB Principle is in determining whether a particular compound will act as a base or as a nucleophile. Generally, a soft base is a good nucleophile, and a hard base is a better base. Chapters 12 through 14 show this rule of thumb in action. The statement was made earlier that a nucleophile generally reacts with a positive or partially positive carbon, and a base generally reacts with a positive or partially positive hydrogen. This statement is a simplified form of the HSAB principle: $H^\oplus$ is a much harder acid than $C^\oplus$, so it tends to react with a harder base than $C^\oplus$ does. For example, chlorocyclohexane reacts with a hydroxide ion to remove a proton from the carbon adjacent to the carbon bearing the chlorine. This reaction forms a double bond.
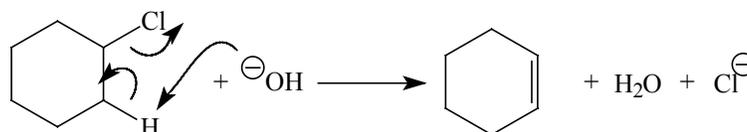
On the other hand, chlorocyclohexane reacts with cyanide ion ($^\ominus CN$) to form a product containing a nitrile group.
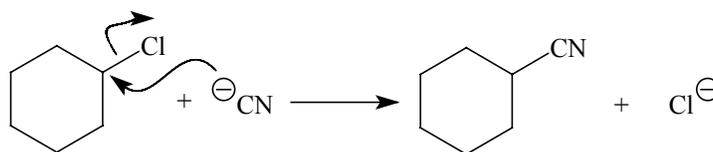
The difference between these two reactions is that the hydroxide ion is a hard base, whereas the cyanide ion is a soft base. The hydroxide ion removes a proton; the cyanide ion reacts with the carbon bearing the chlorine to displace the chlorine.
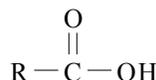

Curved Arrows

A word of further explanation about curved arrows is appropriate here. As noted previously, curved arrows show the flow of electrons in reactions. As you look at the reaction of hydroxide ion with chlorocyclohexane, start following the arrows at the hydroxide ion. The first arrow points toward a hydrogen on the ring, forming a new H—OH bond. Simultaneously, the electrons in the C—H bond form a double bond, ejecting the chloride ion with its pair of electrons. In the second reaction, the cyanide ion reacts with the carbon bearing the chlorine to form a new C—C bond. At the same time the chloride ion leaves with its pair of electrons.

Thus far, this chapter has presented acids and bases in a broad sense. It covered the different theories of acidity and basicity and how to estimate their relative strengths. It also showed how acids and bases react with each other. Section 5.4 applies these concepts specifically to organic acids and bases.

5.4 Organic Acids and Bases

Organic acids and bases have acidic or basic functional groups and a carbon backbone.

Section 5.4 moves from the broad spectrum of acids and bases in all areas of chemistry to the narrower topic of the organic acids and bases. **Organic acids** and **organic bases** are acids and bases that contain a carbon skeleton. Within these categories are a number of classes of neutral proton acids and bases (that is, uncharged acids and bases.) The first part of this section examines the three main types of neutral organic proton acids to see why they are acids and why they have widely different acid strengths. The second part looks at the two main types of neutral organic bases. The last part looks at positively charged carbon acids and negatively charged carbon bases.

Three main types of neutral organic Brønsted-Lowry acids are carboxylic acids, phenols, and alcohols. Each of these three functional groups has an —OH group. Each is acidic because of the electronegativity difference between the oxygen and the hydrogen involved in the O—H bond. The differences in acid strength of the three functional groups are due to the differences in stability of the conjugate base. The most acidic of the three groups are the carboxylic acids. Carboxylic acids are characterized by the presence of the carboxyl group:

$$R - \overset{\overset{\displaystyle O}{\|}}{C} - OH$$

Carboxylic acids are among the most acidic of the neutral organic acids, but they are rather weak acids. For example, the pK_a of acetic acid, a common carboxylic acid, is 4.8, indicating that only a small portion of the molecules of acetic acid ionize in an aqueous solution. In contrast, mineral acids, such as HCl, with a pK_a of –7.0, and HNO_3, with a pK_a of –5.2, completely ionize in aqueous solutions. Although carboxylic acids are weaker than mineral acids, they are the strongest of the neutral organic acids that you will study.

$$\underset{\displaystyle R-\overset{\textstyle O}{\overset{\textstyle \|}{C}}-O-H}{} \quad \rightleftharpoons \quad R-\overset{\textstyle O}{\overset{\textstyle \|}{C}}-O^{\ominus} \;+\; H^{\oplus}$$

The reason for the relative strength of the carboxylic acids is the conjugate base is resonance-stabilized, which makes it a weak base.

Carboxylate ion resonance
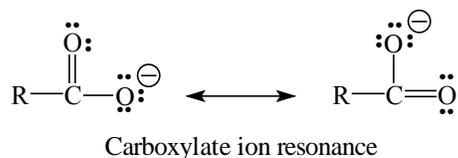
In the carboxylate ion the negative charge spreads over the two oxygen atoms as a resonance hybrid. This reduces the energy of the anion and makes the carboxylic acid more acidic.

Another way of visualizing the reason for the acid strength of carboxylic acids is to look at the molecular orbital system of the carboxylate ion. The carboxylate ion includes three *p* orbitals that contain a total of four electrons. The overlap of these three *p* orbitals results in a **three-centered π molecular orbital system**.

A three-centered π molecular orbital system is a π molecular orbital that includes three atoms. More examples are discussed in Chapter 16.

$$O-C-O$$
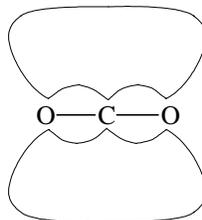
The carbon is joined to each oxygen atom by the equivalent of ½ of a π bond. Each oxygen atom bears ½ of the negative charge.

$$R—C\overset{\displaystyle O^{½\ominus}}{\underset{\displaystyle O^{½\ominus}}{}}$$
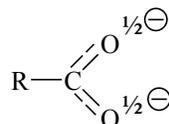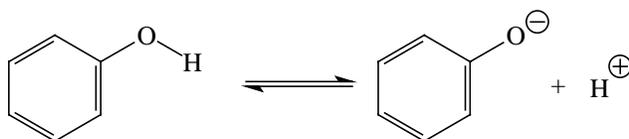
The second main type of neutral organic acids are the phenols. Phenols are much less acidic than carboxylic acids. An —OH group attached to an aromatic ring is characteristic of phenols:
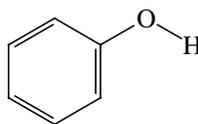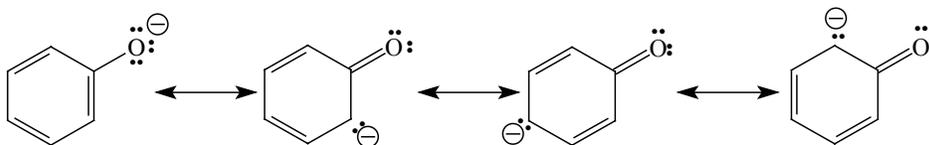
Phenol

Phenol has a pK_a of 10.0 in aqueous media, indicating that in water only a very small portion of it ionizes.

Phenols are moderately strong organic acids because their conjugate bases are resonance-stabilized. The aromatic ring is involved in resonance, which stabilizes the negative charge.

However, this stabilization is less significant than it is for carboxylic acids for two reasons: the resonance stabilization of the phenolate ion disrupts the aromaticity of the aromatic ring, and the resonance stabilization places a negative charge on the carbon atoms, which, when compared to oxygen, are not very electronegative.

The third type of neutral organic acids are alcohols. An —OH group attached to an alkyl group characterizes an alcohol:

$$R\!-\!O\!-\!H$$
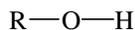
Alcohols are much less acidic than phenols. In fact, most alcohols have an acid strength slightly lower than that of water.

$$R\!-\!O\!-\!H \;\rightleftharpoons\; R\!-\!O^{\ominus} \;+\; H^{\oplus}$$

A typical alcohol has a pK_a of 15 to 18 in aqueous media, indicating only a very small amount of ionization. Alcohols have such a low acidity because there is no resonance stabilization of the conjugate base.

This section discusses only two of the many types of neutral organic bases: amines and ethers. The primary characteristic of neutral organic bases is they contain one or more pairs of nonbonding electrons. These pairs of electrons are available to donate to a Lewis acid or to accept a proton when the base is acting as a Brønsted-Lowry base. The more available the pair of electrons, often called a lone pair, the stronger the base. Any molecule with a lone pair of electrons can act as a base.

The most common of the organic bases are the amines. Amines are derivatives of ammonia (NH_3) and most are weak bases in aqueous media.

$$H_2O \;+\; CH_3NH_2 \;\rightleftharpoons\; CH_3\overset{\oplus}{N}H_3 \;+\; {}^{\ominus}OH$$

Methyl amine   Methyl ammonium ion
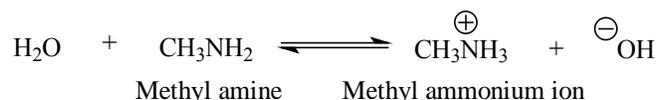
The pK_a of methyl ammonium ion is 10.6 meaning that the methyl ammonium ion is a relatively weak acid. Thus, methylamine is a moderately strong base.

Amines are stronger bases than other neutral organic bases because the nonbonding pair of electrons on the nitrogen is more available than nonbonding pairs of electrons on other neutral organic bases. The atoms that are found in these other neutral organic bases are oxygen, sulfur, or the halogens. Nitrogen holds its electrons less tightly than these other atoms, so its compounds are the stronger bases. Figure 5.3 illustrates the structure of an amine.
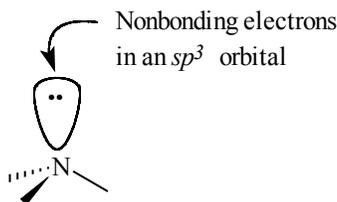
Nonbonding electrons
in an sp^3 orbital

Figure 5.3. Structure of the amine nitrogen.

Ethers, the second type of neutral organic bases, have the general structure ROR′. Ethers are weak bases in aqueous media. In fact, they are so weak that they do not appreciably protonate, or accept a proton, even in 1 M HCl. The pK_a of the conjugate acid of ethyl ether is –3.8. A pK_a of this magnitude indicates that water is a better base than is an ether.

A complex is a type of molecule in which one of the atoms either donates or receives both electrons involved in the bond between that atom and an adjacent atom.

In nonaqueous media, ethers are good Lewis bases, forming stable **complexes** with Lewis acids. The ability to form stable complexes is extremely important in organic reactions. For example, in organic synthesis, chemists widely use the complex of BH_3 with the cyclic ether tetrahydrofuran:

A carbocation is a positively charged carbon atom. The carbon atom normally is sp2 *hybridized.*

The third category of organic acids and bases discussed in this section are the positively charged acids and the negatively charged bases. Positively charged acids are electron-deficient. That is, they are organic acids that contain a carbon without an octet of electrons. The most significant electron-deficient organic acid is the **carbocation** (formerly called a carbonium ion). Carbocations are very reactive reaction intermediates, so chemists seldom observe them directly. A carbocation is a Lewis acid because, without a full octet of electrons, it is electron-deficient and "needs" electrons. As a result of this need for electrons, it reacts with the first available Lewis base—although it prefers a hard one because it is a hard acid. As Figure 5.4 shows, the positively charged carbon forms three sp^2 hybridized bonds in a plane with an empty *p* orbital perpendicular to that plane. Chapter 12 examines nucleophilic substitution reactions that involve carbocations.

Empty *p* orbital
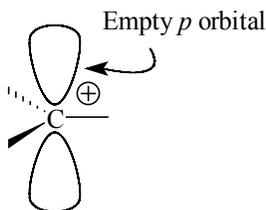
Figure 5.4. The structure of a carbocation.

The negatively charged organic base discussed in this section is the **carbanion.** A carbanion has bonds to three other atoms and one pair of nonbonding electrons. The structure of a carbanion is much like the structure of an amine (See Figure 5.5). Because carbon is not very electronegative, it holds these nonbonding electrons loosely. Thus, a carbanion is a strong base. (Chapters 19 and 20 cover carbanion reactions extensively.)
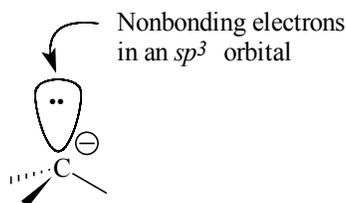
Carbanions have a negatively charged carbon and are structurally similar to amines.

Nonbonding electrons in an sp^3 orbital

Figure 5.5. Carbanion structure.

Now that you have seen the various types of organic acids and bases, Section 5.5 examines the factors that modify the strength of the specific acids and bases.

5.5 Relative Acidity and Basicity

Each functional group has its own specific and measurable acidity or basicity. When you look at the groups involved in a chemical reaction, however, the values of their absolute strengths are of much less concern than their relative strengths. By knowing the relative strengths of the acids and bases on both sides of a reaction, you can accurately predict the direction of the equilibrium of that reaction. The direction of the equilibrium of a reaction moves from the stronger reactants toward the weaker reactants.

Because understanding acid-base concepts is the basis of organic chemistry, it is important that you be able to determine the relative acidity or basicity of various elements and groups. To do so, you must consider several factors. These factors include resonance, inductive forces, and electronegativity, topics covered in Chapter 1 and the HSAB Principle covered in this chapter.

Brønsted-Lowry Acid Strength
The strength of a Brønsted-Lowry acid depends on how much the acid dissociates to form protons and on the strength of the conjugate base that the acid forms. Among two or more Brønsted-Lowry acids in a reaction, the one that reacts to form the most stable, or weakest, conjugate base is the one that most readily releases a proton ($H^{\oplus}$) and is therefore the stronger acid. The strength of a Lewis acid depends on how strongly the acid attracts a pair of electrons. The strength of most bases, either

> Brønsted-Lowry or Lewis bases depends on the availability of a pair of nonbonding electrons. The more loosely the base holds that pair of electrons, the stronger it is.

A helpful tool for predicting acid and base strength is the periodic table. By understanding the trends among the elements listed there, you can predict the relative acid and base strengths of the various functional groups. Also, you can predict the direction of a particular reaction and the stability of the products.

Consider the relative acid strengths of the Brønsted-Lowry hydrogen halide acids, HF, HCl, HBr, and HI. These four compounds differ only in the halogen bonded to the hydrogen. Their general ionization equation is:

$$HX \rightleftharpoons H^{\oplus} + X^{\ominus}$$

This equation shows that the acid strength of each of these hydrogen halides is a measure of the ease of ionization of the H—X bond (X = a halogen). The stronger the bond, the weaker the acid. Understanding how to determine which H—X bond is stronger will allow you to predict the relative strength of each acid.

Determining which H—X bond is stronger requires consideration of the differences among the various halogens. Two significant differences between fluorine (F), the element at the top of the periodic table in the halogen family, and iodine (I), an element near the bottom are: F is more electronegative than I thus allowing F to hold its electrons more tightly. Also F is much smaller than I because F has fewer electrons. Being larger, I is more polarizable and therefore softer than F. The higher electronegativity of F would seem to result in a more stable ion, whereas, the softness of I means that the bond between I and the hard H is weaker than the bond between the hard F and the hard H. These predictions are obviously true as shown by the pK_a of the two acids: HF has a pK_a of 3.2, whereas HI is much stronger with a pK_a of –10.

Because a Brønsted-Lowry acid donates a proton ($H^{\oplus}$) to a base, the point of comparison for the relative strengths of the various acids is the atom, or group of atoms, to which the proton is attached. This atom or group of atoms bears the charge in the conjugate base. *The more stable the conjugate base, the higher the acid strength of the Brønsted-Lowry acid.* For example, HF with a pK_a of 3.2 is a much stronger acid than CH_4 with a pK_a of 49. This occurs because the F is more electronegative than C so F holds its electrons more tightly than C. Thus, the F anion is a weaker base than a C anion. Because F is a weaker base, it can donate a proton more readily than can C. Within a period on the periodic table, Brønsted-Lowry acidity increases from left to right: for example, $CH_4 < NH_3 < H_2O < HF$.

Compare the relative strengths of Lewis acids (MX_n) by looking at the positions of the elements represented by the X on the periodic table. Remember that a Lewis acid is an electron-pair acceptor. For Lewis acids, acid strength decreases going down the periodic table (for example, $BCl_3 > AlCl_3 > GaCl_3$.) This decrease in acid strength occurs because as the size of the atom represented by M increases, the attraction between the incoming electron pair and the nucleus weakens.


Brønsted-Lowry vs. Lewis Acid Strength

Note that Lewis acidity *decreases,* but Brønsted-Lowry acidity *increases* when going down the periodic table. These apparently opposite characteristics are not a contradiction. When measuring Lewis acidity, chemists compare the actual acid—the electron-deficient atom. For Brønsted-Lowry acidity, they do not compare the acidic atom because, in each case, it is the same—the proton. To determine the acidity of a Brønsted-Lowry acid, chemists look at how readily the acid gives up the proton. For example, when comparing the acidity of HF and HI, they compare only the relative ease with which $F^{\ominus}$ and $I^{\ominus}$ give up a proton. In this pair, the $F^{\ominus}$ ion is a hard base and forms a better bond with a hard $H^{\oplus}$ ion than does the soft $I^{\ominus}$ ion. Thus, HI is a stronger acid than HF.

Another factor to consider when comparing Lewis acids is the number of electron pairs required for the acid to fill its outer shell with electrons. Acids that require only one pair to complete that shell are stronger than those that require two. Adding one electron pair gives the electron-deficient atom a formal charge of –1; adding a second pair gives a formal charge of –2. Bringing in the second pair requires more energy because of the negative charge already present.
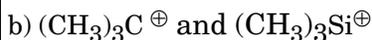
Solved Exercise 5.3

Determine whether the following pairs of acids are Lewis or Brønsted-Lowry acids and which one of the pair is the stronger acid. Justify your choice.
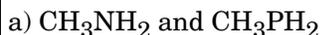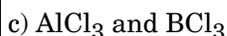
a) CH_3NH_2 and CH_3PH_2

Solution
CH_3NH_2 and CH_3PH_2 are Brønsted-Lowry acids. CH_3PH_2 is stronger because P is softer than N, so the P—H bond is weaker than the N—H bond.

b) $(CH_3)_3C^{\oplus}$ and $(CH_3)_3Si^{\oplus}$

Solution
$(CH_3)_3C^{\oplus}$ and $(CH_3)_3Si^{\oplus}$ are Lewis acids. $(CH_3)_3C^{\oplus}$ is stronger because C is more electronegative than Si, so C "needs" the electrons more.

c) $AlCl_3$ and BCl_3

Solution
$AlCl_3$ and BCl_3 are Lewis acids. BCl_3 is stronger because B is more electronegative than Al, so B "needs" the electrons more.

Exercise 5.7

Determine whether the following pairs of acids are Lewis or Brønsted-Lowry acids and which one of the pair is the stronger acid. Justify your choice.

a) CH_3SH and CH_3OH b) NH_3 and PH_3
c) H_2Se and H_2S d) AlH_3 and BH_3
e) $CH_3^{\oplus}$ and $SiH_3^{\oplus}$ f) HBr and HCl
g) HNO_3 and H_2SO_4 h) $NH_4^{\oplus}$ and $PH_4^{\oplus}$

Sample Solution

c) H_2Se and H_2S are Brønsted-Lowry acids. Because S and Se are both members of Group VIA on the periodic table, you must consider the softness of these atoms. Selenium is a softer base than sulfur and will more easily release a proton, so H_2Se is a stronger acid than H_2S.

The most important factor when determining the relative basicity of a set of compounds is the electronegativity of the element in each compound that contains a nonbonded pair of electrons. Basicity decreases for atoms with a pair of nonbonded electrons moving from left to right across the periodic table. Thus, $^{\ominus}CH_3$ is a stronger base than $F^{\ominus}$. Brønsted-Lowry basicity increases from the bottom to the top of the periodic table. Thus, the $F^{\ominus}$ ion is a stronger base than the $I^{\ominus}$ ion.
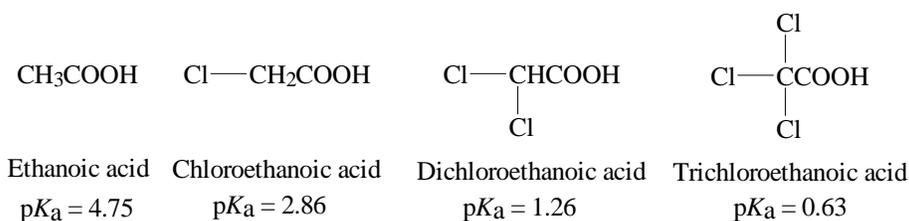
5.6 Substituent Effects on Acidity and Basicity

For more on the inductive effect see Section 1.11, page 000.

Various atoms or groups, when bonded to an acid or base, affect the acidity or basicity of that particular compound. As you recall from Chapter 1 chemists call this effect the inductive effect. For acids, if the substituent stabilizes the conjugate base, so that the ion forms more readily, it has increased the acidity of the acid; thus, making it stronger. Conversely, if the substituent destabilizes the conjugate base, so that the ion forms less readily, it has decreased the acidity of the acid. Because of its electronegativity, the substituent either draws the electrons toward itself or donates them to the acid functional group. For example, if the **α carbon** of a carboxylic acid has one or more strongly electron-withdrawing groups, the inductive effect is
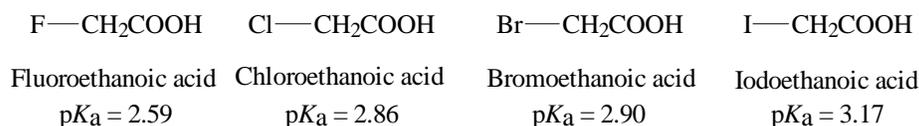
An α carbon is the carbon adjacent to a functional group.
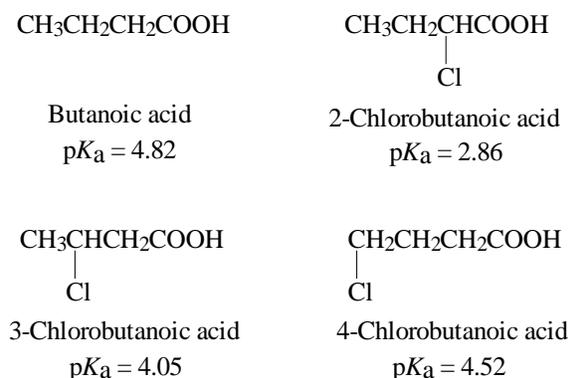
larger than without those groups. Compare ethanoic acid (commonly called acetic acid) with the chloroethanoic acids.

CH_3COOH $Cl—CH_2COOH$ $Cl—CHCOOH$ with Cl below $Cl—CCOOH$ with Cl above and Cl below

Ethanoic acid   Chloroethanoic acid   Dichloroethanoic acid   Trichloroethanoic acid
$pK_a = 4.75$ $pK_a = 2.86$ $pK_a = 1.26$ $pK_a = 0.63$

The effect on the acidity of each one is proportional to the number of substituents involved. The inductive effect is also proportional to the electronegativity of the substituent. The more electronegative the substituent, the lower the pK_a of the acid.

$F—CH_2COOH$ $Cl—CH_2COOH$ $Br—CH_2COOH$ $I—CH_2COOH$

Fluoroethanoic acid   Chloroethanoic acid   Bromoethanoic acid   Iodoethanoic acid
$pK_a = 2.59$ $pK_a = 2.86$ $pK_a = 2.90$ $pK_a = 3.17$

A final comparison illustrates how the effect diminishes with distance from the carboxyl functional group. The pK_a of the acid increases as the distance between the substituent and the carboxylic acid group increases.

$CH_3CH_2CH_2COOH$ $CH_3CH_2CHCOOH$ with Cl

Butanoic acid   2-Chlorobutanoic acid
$pK_a = 4.82$ $pK_a = 2.86$

CH_3CHCH_2COOH with Cl $CH_2CH_2CH_2COOH$ with Cl

3-Chlorobutanoic acid   4-Chlorobutanoic acid
$pK_a = 4.05$ $pK_a = 4.52$

Exercise 5.8

Consider the following pairs of Brønsted-Lowry acids. Which member of each pair is the stronger acid? Why?

a) $CH_3O—CH_2—OH$ and $F—CH_2—OH$
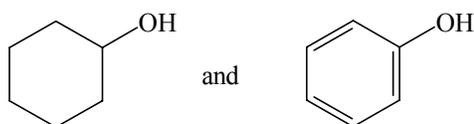b) $CH_3S—CH_2—COOH$ and $CH_3O—CH_2—COOH$
c) Cl_3CH and I_3CH

d) CH$_3$SH and CH$_3$OH

e)

and
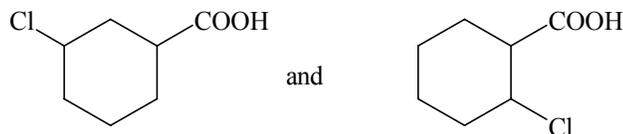
f) CH$_3$CH$_2$NH$_2$ and CH$_3$CH$_2$PH$_2$

g)

and

Sample Solution

d) To determine the difference in acidity between methanethiol and methanol, you must look at the difference in the hardness of the conjugate bases. The methoxide ion (CH$_3$O$^\ominus$) is a harder base than the thiomethoxide ion (CH$_3$S$^\ominus$). The hydrogen ion is a hard acid. As a result, the bond between the hard base, the methoxide ion, and the hydrogen ion is stronger than the bond between the thiomethoxide ion and the hydrogen ion. Therefore, methanethiol is the stronger acid.

With bases, hybridization is an important factor in the effect of substituents. For example, because ammonia and the amines are proton acceptors, any structural feature that reduces the availability of the nonbonding electrons on nitrogen also reduces the basicity of the compound. Consider the relative acidities of the pyridinium ion and the piperidinium ion:
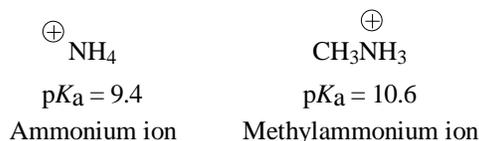

Pyridinium ion
pK_a = 5.2

Piperidinium ion
pK_a = 11.1
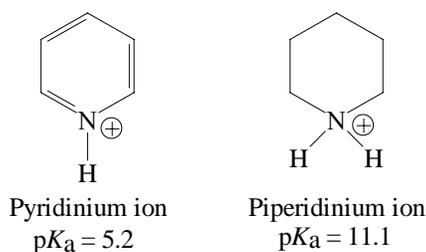
This large difference in pK_a is due to hybridization—in pyridine, the nitrogen is sp^2 hybridized; in piperidine, it is sp^3 hybridized. Orbitals with more *s* character hold the nonbonding pair of electrons closer to the nucleus and, because the nitrogen in pyridine has more *s* character than the nitrogen in piperidine, the electrons are less available for donation to a hydrogen ion.

This effect is even more pronounced with an *sp* hybridized nitrogen. For example, protonated acetonitrile has a pK_a of –10. This value indicates that protonated acetonitrile is a rather strong acid making acetonitrile a rather weak base.

$$CH_3C\equiv\overset{\oplus}{N}\!-\!H$$
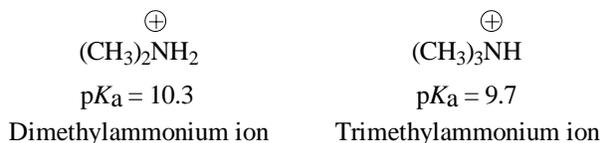
pK_a = –10
Protonated acetonitrile
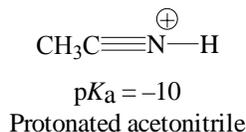
A factor of less importance is the inductive effect of alkyl groups bonded to the nitrogen of amines. Alkyl groups donate electrons to cations and thus can help stabilize a positive charge on nitrogen. This effect is seen in the relative acidities of the conjugate acids ammonium and methylammonium ions:

$$\overset{\oplus}{N}H_4 \qquad\qquad CH_3\overset{\oplus}{N}H_3$$

pK_a = 9.4   pK_a = 10.6
Ammonium ion   Methylammonium ion

Steric crowding is where a reactive site is difficult to reach because of the alkyl groups surrounding it.

The simple alkylamines are stronger bases than ammonia. Following the above line of reasoning you might expect that secondary amines would be even stronger bases and tertiary amines would be the strongest bases of all the amines. However, the effect of the solvent on the cation adds a complication. As the number of alkyl groups increases, so does the **steric crowding** around nitrogen. This crowding decreases the number of water molecules that can be involved in stabilizing the ion. As a result, trimethylamine is actually *less* basic than either dimethylamine or methylamine.

$$(CH_3)_2\overset{\oplus}{N}H_2 \qquad\qquad (CH_3)_3\overset{\oplus}{N}H$$

pK_a = 10.3   pK_a = 9.7
Dimethylammonium ion   Trimethylammonium ion

Exercise 5.9

Consider the following pairs of bases. Which member of each pair is the stronger Brønsted-Lowry base. Why?

    a) LiOH and LiSH
    b) $(CH_3)_3N$ and $(CH_3)_3P$
    c) CH_3OCH_3 and CH_3SCH_3
    d) $^{\ominus}CH_3$ and $^{\ominus}SiH_3$

e) CH_3OCH_3 and $ClCH_2OCH_3$
f) $Cl_3C^{\ominus}$ and $I_3C^{\ominus}$
g) $CH_3O^{\ominus}$ and $CH_3S^{\ominus}$

Sample Solution

c) Because sulfur is softer than oxygen, it forms a weaker bond with hydrogen. Thus, dimethyl ether is the stronger base.

Key Ideas from Chapter 5

❑   According to the Brønsted-Lowry definition of acids and bases, an acid is a proton donor and a base is a proton acceptor.

❑   Acid strength is related to the stability of the acid's conjugate base. The stronger the acid, the more stable is its conjugate base.

❑   A measure of acid strength is the value of the acid dissociation constant, K_a.

❑   According to the Lewis definition of acids and bases, an acid is an electron-pair acceptor and a base is an electron-pair donor.

❑   Lewis acids and bases can be classified as either hard or soft. The HSAB Principle states that hard acids prefer to bond with hard bases and soft acids prefer to bond with soft bases.

❑   The character of the acidic or basic functional group, as well as the inductive effect of any adjacent functional group, affects acid or base strength.

Supplementary Exercises

5.10 Arrange the following Brønsted-Lowry acids in order of increasing acidity. Justify your choices.

$$^{\oplus}NH_4 \quad H_2SO_4 \quad NH_3 \quad CH_3OH \quad CH_3COOH \quad CH_3SH$$
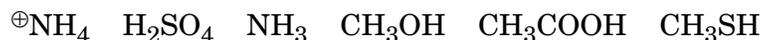
5.11 Rank the following compounds in order of increasing Brønsted-Lowry basicity. Justify your choices.

$$NH_3 \quad CH_3O^{\ominus} \quad {}^{\ominus}OH \quad {}^{\ominus}NH_2 \quad Cl^{\ominus} \quad CH_3S^{\ominus} \quad CH_3COO^{\ominus}$$

5.12 The pK_a of acetic acid is 4.8 and the K_a of benzoic acid is 6.3 x 10^{-5}. Calculate the K_a of acetic acid and the pK_a of benzoic acid. Which is the stronger Brønsted-Lowry acid?

5.13 For each of the following compounds, identify the most acidic proton for reaction with a hydroxide ion ($^{\ominus}$OH). What factors are important to the stabilization of the conjugate base ion?

　a)　　HOCH$_2$COOH　　　　　　b)　　HOCH$_2$CH$_2$SH
　c)　　CH$_3$CH$_2$NO$_2$　　　　　　d)

　e)

　f)
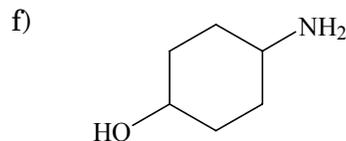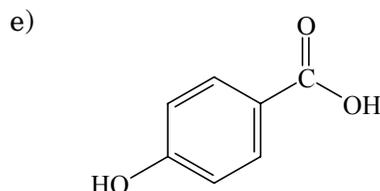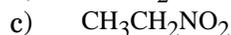
5.14　4.71 Grams of phenol were dissolved in water. Enough water was added to bring the volume to 500 mL and the pH was adjusted to 11.0. What is the concentration of the phenolate ion (the conjugate base of phenol)?

5.15 For each of the following compounds, identify the most basic atom for reaction with a proton (H$^{\oplus}$). What factors are important to the stabilization of the resulting cation?

　a)　　CH$_3$OCH$_2$CH$_2$N(CH$_3$)$_2$　　　b)　　CH$_3$OCH$_2$CH$_2$SCH$_3$
　c)　　　　　　　　　　　　　　　　　　d)

　e)
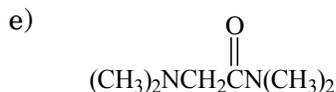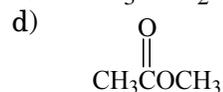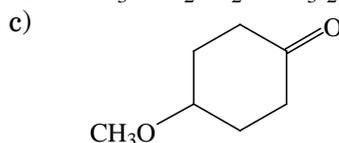
5.16 Is a proton a Lewis acid, a Brønsted-Lowry acid, or both? Explain.

5.17 At a pH of 5.0, the amino acid glycine (H$_2$NCH$_2$COOH) exists in aqueous solution as an internal salt in which both the positive and negative ions are in the same molecule (a zwitterion). a) Suggest a

structure for the zwitterion of glycine. b) What is the structure at pH 1.0? At pH 10.0?

5.18 Predict the products of the following acid-base reactions. Indicate the side favored by the equilibrium.

a)
$$HCl + CH_3COO^{\ominus} \rightleftharpoons$$

b)
$$(CH_3)_2NH + {}^{\ominus}OH \rightleftharpoons$$

c)
$$CH_3COOH + CH_3O^{\ominus} \rightleftharpoons$$

d)
$$H_2SO_4 + (CH_3)_3N \rightleftharpoons$$

e)
$$NH_3 + H_2O \rightleftharpoons$$

f)
$$H_2SO_4 + CH_3OCH_3 \rightleftharpoons$$

**5.19** Draw resonance structures for aniline $(C_6H_5NH_2)$ and its conjugate acid. Account for the fact that aniline is a weaker base than methylamine (CH_3NH_2).

5.20 An acid with more than one acidic proton has a different pK_a for each proton. For example, phosphoric acid (H_3PO_4) has the following pK_a values: $pK_{a1} = 2.1$, $pK_{a2} = 7.2$, and $pK_{a3} = 12.7$. Account for the large differences in these pK_a values.

5.21 Predict whether CH_3CH_2OH is more acidic or less acidic than CF_3CH_2OH. Explain.

5.22 For each of the following reactions identify the acid, base, conjugate acid, and conjugate base. Then, using the pK_a values from Appendix A, predict whether the position of equilibrium will favor the starting materials or the products. (Hint: You may not find all the compounds in these reactions in Appendix A. However, they will be similar to compounds that are found there. Reason by analogy to come up with the correct results.)

a)

b)

c)

d)
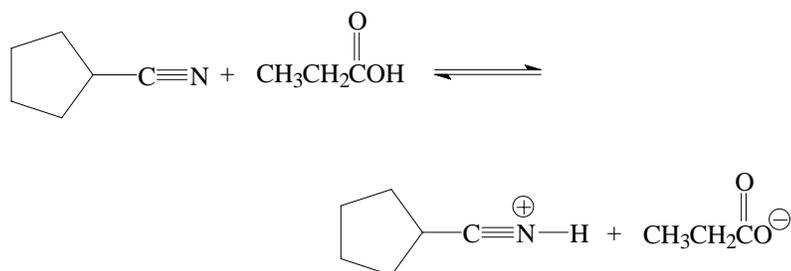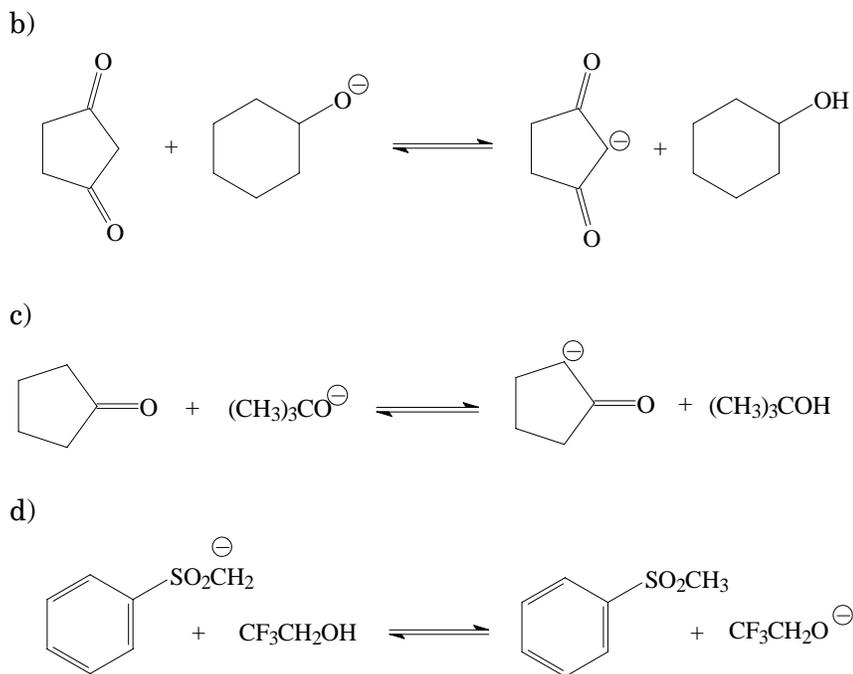
5.23 When chemists dissolve strong acids or strong bases in water, they observe a phenomenon known as the leveling effect. Because of the leveling effect they cannot measure differences in acidity for strong acids such as HCl (pK_a = −7) and H_2SO_4 (pK_a = −5.2) in water. They appear to have the same acidity. The same situation occurs with strong bases in water. a) Considering the leveling effect what is the strongest acid that can exist in water? b) What is the strongest base?

5.24 A mixture of aniline, benzoic acid, ethylene glycol, and naphthalene was shaken with equal volumes of aqueous sodium hydroxide and ethyl ether. The two layers were separated to give ether layer **A** and water layer **B**. Solution **A** was then extracted with an equal volume of dilute hydrochloric acid, and the layers were separated to give ether layer **C** and aqueous layer **D**. Solution **B** was made acidic with sulfuric acid, and the resulting solution extracted with an equal volume of ether. The layers were separated to give ether layer **E** and aqueous layer **F**. The procedure separated the four compounds. Show the distribution of the compounds in each of the layers **A** through **F**. (Hint: You will need to look up the structures and water solubilities of these four compounds in a chemical handbook. Consult Appendix A for pKa values. You may need to estimate some of these pKa values.)
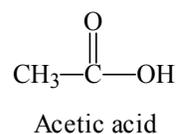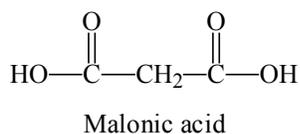
5.25 Measures of acidity and basicity are relative values depending on the medium in which they are measured. For example, acetic acid is an acid when water is the solvent, but it acts as a base when 100% sulfuric acid is the solvent. Explain.

5.26 The pK_a of the conjugate acid of diphenylamine, $(C_6H_5)_2NH$, is 0.75. Is diphenylamine a strong or a weak base? Explain.

5.27 Guanidine protonates (has a hydrogen ion react with an electron pair) on any of its three nitrogen atoms. However, one is much more basic than the others and tends to protonate first. Draw resonance structures for the products of the protonation of each of the nitrogens. Which is the most stable; and thus, tends to protonate first? Justify your choice.

$$\overset{\displaystyle \ddot{N}H}{\underset{\displaystyle CH_3\overset{..}{N}HC\overset{..}{N}H_2}{\|}}$$

Guanidine
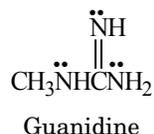
5.28 Malonic acid has two carboxylic acid groups and consequently undergoes two ionization reactions. The pK_a for the first ionization reaction is 2.9; the pK_a for the second is 5.7. For comparison, the pK_a for acetic acid is 4.8.

$$HO-\overset{\displaystyle O}{\overset{\|}{C}}-CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-OH \qquad\qquad CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-OH$$

Malonic acid   Acetic acid

a) Show the first and second ionization reactions of malonic acid. Identify each with the appropriate pK_a value using pK_{a1} and pK_{a2}.

b) Why is the first pK_a of malonic acid lower than the pK_a of acetic acid, but the second pK_a higher than the pK_a of acetic acid?

c) Consider a series of dicarboxylic acids with the following general structure:

$$HO-\overset{\displaystyle O}{\overset{\|}{C}}-(CH_2)_n-\overset{\displaystyle O}{\overset{\|}{C}}-OH$$
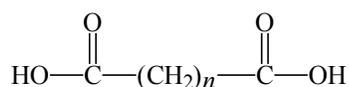
How would you expect the difference between the first and second pK_a value to change as n increases? Briefly explain.

5.29 Ammonia is a weak acid with a pK_a of 35. Ammonia's conjugate base $^{\ominus}NH_2$, called the amide ion, is readily available as alkali metal compounds; for example, $LiNH_2$. Calculate the pH of 0.1 mole of lithium amide dissolved in 1 L of water. Calculate the pH of 0.1 mole of NaOH in 1 L of water. The solutions should have similar pH values. Why?

5.30 Acetylsalicylic acid (aspirin) has a pK_a of 3.5. The digestive fluids in the stomach have a pH of 2. The blood has a pH of 7. a) What is the predominant form (ionized or unionized) of aspirin in the stomach? b) What is the predominant form in the blood? c) What does this suggest about the passage of materials from the digestive tract to the bloodstream?
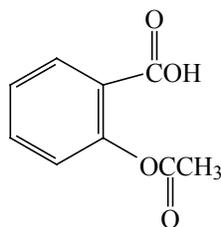
Aspirin

5.31 Diethyl propanedioate has a pK_a= 9.0; diethylbutanedioate has a pK_a = 21. Explain.
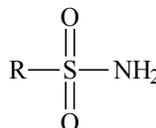

Diethyl propanedioate   Diethyl butanedioate

5.32 The hydrogen on the nitrogen of sulfonamides is quite acidic. Explain this observation. (Hint: Remember sulfur can have an expanded octet by placing electrons in the 3d orbital.)

A sulfonamide