14 Acids and Bases

Contents

This grass pink orchid thrives in the acidic soil of a bog meadow at Illinois Beach State Park.

In this chapter we reencounter two very important classes of compounds, acids and bases. We will explore their interactions and apply the fundamentals of chemical equilibria discussed in Chapter 13 to systems involving proton-transfer reactions.

Acid–base chemistry is important in a wide variety of everyday applications. There are complex systems in our bodies that carefully control the acidity of our blood, since even small deviations may lead to serious illness and death. The same sensitivity exists in other life forms. If you have ever had tropical fish or goldfish, you know how important it is to monitor and control the acidity of the water in the aquarium.

Acids and bases are also important in industry. For example, the vast quantity of sulfuric acid manufactured in the United States each year is needed to produce fertilizers, polymers, steel, and many other materials.

The influence of acids on living things has assumed special importance in the United States, Canada, and Europe in recent years as a result of the phenomenon of acid rain (see the Chemical Impact in Chapter 5). This problem is complex and has diplomatic and economic overtones that make it all the more difficult to solve.

14.1 The Nature of Acids and Bases

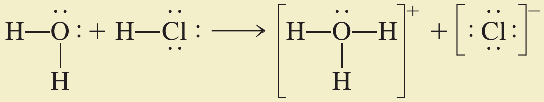
Don't taste chemicals!

Acids and bases were first discussed in Section 4.2.

Acids were first recognized as a class of substances that taste sour. Vinegar tastes sour because it is a dilute solution of acetic acid; citric acid is responsible for the sour taste of a lemon. Bases, sometimes called *alkalis,* are characterized by their bitter taste and slippery feel. Commercial preparations for unclogging drains are highly basic.

The first person to recognize the essential nature of acids and bases was Svante Arrhenius. Based on his experiments with electrolytes, Arrhenius postulated that *acids produce hydrogen ions in aqueous solution, while bases produce hydroxide ions.* At the time, the **Arrhenius concept** of acids and bases was a major step forward in quantifying acid–base chemistry, but this concept is limited because it applies only to aqueous solutions and allows for only one kind of base—the hydroxide ion. A more general definition of acids and bases was suggested by the Danish chemist Johannes Brønsted (1879–1947) and the English chemist Thomas Lowry (1874–1936). In terms of the **Brønsted–Lowry model,** *an acid is a proton (H^+) donor, and a base is a proton acceptor.* For example, when gaseous HCl dissolves in water, each HCl molecule donates a proton to a water molecule and so qualifies as a Brønsted–Lowry acid. The molecule that accepts the proton, in this case water, is a Brønsted–Lowry base.

To understand how water can act as a base, we need to remember that the oxygen of the water molecule has two unshared electron pairs, either of which can form a covalent bond with an H^+ ion. When gaseous HCl dissolves, the following reaction occurs:



$$\mathrm{H{-}}\underset{\substack{|\\ \mathrm{H}}}{\ddot{\mathrm{O}}}{:} + \mathrm{H{-}}\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}{:} \longrightarrow \left[\mathrm{H{-}}\underset{\substack{|\\ \mathrm{H}}}{\ddot{\mathrm{O}}}\mathrm{{-}H}\right]^{+} + \left[:\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}:\right]^{-}$$

Note that the proton is transferred from the HCl molecule to the water molecule to form H_3O^+, which is called the **hydronium ion.** This reaction is represented in Fig. 14.1 using molecular models.

Common household substances that contain acids and bases. Vinegar is a dilute solution of acetic acid. Drain cleaners contain strong bases such as sodium hydroxide.

The general reaction that occurs when an acid is dissolved in water can best be represented as

Recall that (*aq*) means the substance is hydrated.

$$\underset{\text{Acid}}{HA(aq)} + \underset{\text{Base}}{H_2O(l)} \rightleftharpoons \underset{\substack{\text{Conjugate}\\ \text{acid}}}{H_3O^+(aq)} + \underset{\substack{\text{Conjugate}\\ \text{base}}}{A^-(aq)} \qquad (14.1)$$

This representation emphasizes the significant role of the polar water molecule in pulling the proton from the acid. Note that the **conjugate base** is everything that remains of the acid molecule after a proton is lost. The **conjugate acid** is formed when the proton is transferred to the base. A **conjugate acid–base pair** consists of two substances related to each other by the donating and accepting of a single proton. In Equation (14.1) there are two conjugate acid–base pairs: HA and A^- and H_2O and H_3O^+. This reaction is represented by molecular models in Fig. 14.2.

It is important to note that Equation (14.1) really represents *a competition for the proton between the two bases H_2O and A^-*. If H_2O is a much stronger base than A^-, that is, if H_2O has a much greater affinity for H^+ than does A^-, the equilibrium position will be far to the right; most of the acid dissolved will be in the ionized form. Conversely, if A^- is a much stronger base than H_2O, the equilibrium position will lie far to the left. In this case most of the acid dissolved will be present at equilibrium as HA.

Visualization: Acid Ionization Equilibrium

The equilibrium expression for the reaction given in Equation (14.1) is

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} = \frac{[H^+][A^-]}{[HA]} \qquad (14.2)$$

where K_a is called the **acid dissociation constant.** Both $H_3O^+(aq)$ and $H^+(aq)$ are commonly used to represent the hydrated proton. In this book we will often use simply H^+, but you should remember that it is hydrated in aqueous solutions.

In this chapter we will always represent an acid as simply dissociating. This does not mean we are using the Arrhenius model for acids. Since water does not affect the equilibrium position, it is simply easier to leave it out of the acid dissociation reaction.

In Chapter 13 we saw that the concentration of a pure solid or a pure liquid is always omitted from the equilibrium expression. In a dilute solution we can assume that the

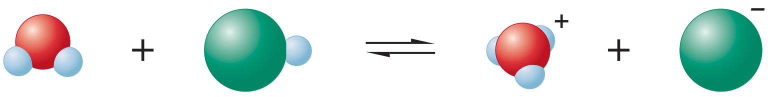


FIGURE 14.1
The reaction of HCl and H_2O.

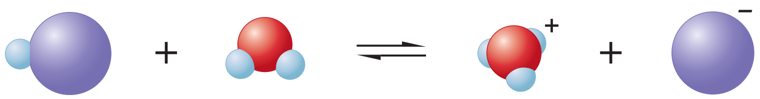


FIGURE 14.2
The reaction of an acid HA with water to form H_3O^+ and a conjugate base A^-.

concentration of liquid water remains essentially constant when an acid is dissolved. Thus the term $[H_2O]$ is not included in Equation (14.2), and the equilibrium expression for K_a has the same form as that for the simple dissociation into ions:

$$\mathrm{HA}(aq) \rightleftharpoons \mathrm{H}^+(aq) + \mathrm{A}^-(aq)$$

You should not forget, however, that water plays an important role in causing the acid to ionize.

Note that K_a is the equilibrium constant for the reaction in which a proton is removed from HA to form the conjugate base A^-. We use K_a to represent *only* this type of reaction. Knowing this, you can write the K_a expression for any acid, even one that is totally unfamiliar to you. As you do Sample Exercise 14.1, focus on the definition of the reaction corresponding to K_a.

Sample Exercise 14.1 Acid Dissociation (Ionization) Reactions

Write the simple dissociation (ionization) reaction (omitting water) for each of the following acids.

a. Hydrochloric acid (HCl)
b. Acetic acid ($HC_2H_3O_2$)
c. The ammonium ion (NH_4^+)
d. The anilinium ion ($C_6H_5NH_3^+$)
e. The hydrated aluminum(III) ion $[Al(H_2O)_6]^{3+}$

Solution

a. $\mathrm{HCl}(aq) \rightleftharpoons \mathrm{H}^+(aq) + \mathrm{Cl}^-(aq)$
b. $\mathrm{HC_2H_3O_2}(aq) \rightleftharpoons \mathrm{H}^+(aq) + \mathrm{C_2H_3O_2}^-(aq)$
c. $\mathrm{NH_4}^+(aq) \rightleftharpoons \mathrm{H}^+(aq) + \mathrm{NH_3}(aq)$
d. $\mathrm{C_6H_5NH_3}^+(aq) \rightleftharpoons \mathrm{H}^+(aq) + \mathrm{C_6H_5NH_2}(aq)$
e. Although this formula looks complicated, writing the reaction is simple if you concentrate on the meaning of K_a. Removing a proton, which can come only from one of the water molecules, leaves one OH^- and five H_2O molecules attached to the Al^{3+} ion. So the reaction is

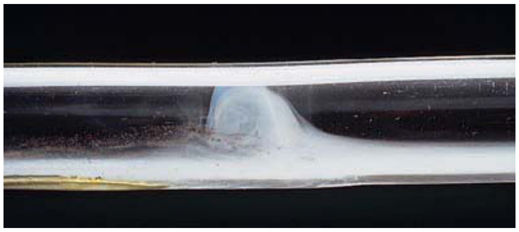
$$\mathrm{Al(H_2O)_6}^{3+}(aq) \rightleftharpoons \mathrm{H}^+(aq) + \mathrm{Al(H_2O)_5OH}^{2+}(aq)$$

See Exercises 14.27 and 14.28.

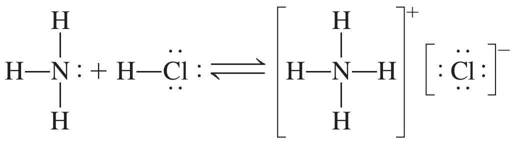
The Brønsted–Lowry model is not limited to aqueous solutions; it can be extended to reactions in the gas phase. For example, we discussed the reaction between gaseous hydrogen chloride and ammonia when we studied diffusion (Section 5.7):

$$\mathrm{NH_3}(g) + \mathrm{HCl}(g) \rightleftharpoons \mathrm{NH_4Cl}(s)$$

In this reaction, a proton is donated by the hydrogen chloride to the ammonia, as shown by these Lewis structures:



When $HCl(g)$ and $NH_3(g)$ meet in a tube, a white ring of $NH_4Cl(s)$ forms.



$$\mathrm{H{-}\overset{\displaystyle H}{\underset{\displaystyle H}{N}}{:}} + \mathrm{H{-}\ddot{\underset{\cdot\cdot}{Cl}}{:}} \rightleftharpoons \left[\mathrm{H{-}\overset{\displaystyle H}{\underset{\displaystyle H}{N}}{-}H}\right]^+ \left[:\ddot{\underset{\cdot\cdot}{Cl}}:\right]^-$$

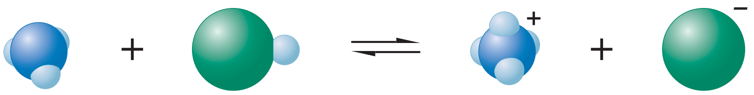


FIGURE 14.3
The reaction of NH_3 with HCl to form NH_4^+ and Cl^-.

Note that this is not considered an acid–base reaction according to the Arrhenius concept. Figure 14.3 shows a molecular representation of this reaction.

14.2 Acid Strength

The strength of an acid is defined by the equilibrium position of its dissociation (ionization) reaction:

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

A strong acid has a weak conjugate base.

A **strong acid** is one for which *this equilibrium lies far to the right.* This means that almost all the original HA is dissociated (ionized) at equilibrium [see Fig. 14.4(a)]. There is an important connection between the strength of an acid and that of its conjugate base. *A strong acid yields a weak conjugate base*—one that has a low affinity for a proton. A strong acid also can be described as an acid whose conjugate base is a much weaker base than water (see Fig. 14.5). In this case the water molecules win the competition for the H^+ ions.

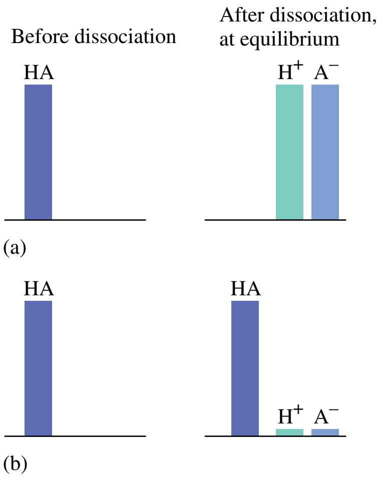


FIGURE 14.4
Graphic representation of the behavior of acids of different strengths in aqueous solution. (a) A strong acid. (b) A weak acid.

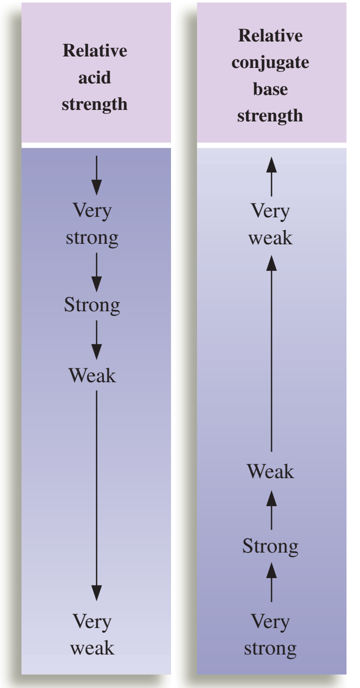


FIGURE 14.5
The relationship of acid strength and conjugate base strength for the reaction

$$\underset{\text{Acid}}{HA(aq)} + H_2O(l) \rightleftharpoons H_3O^+(aq) + \underset{\text{Conjugate base}}{A^-(aq)}$$

$\ll$ means much less than.
$\gg$ means much greater than.

TABLE 14.1 Various Ways to Describe Acid Strength

Property	Strong Acid	Weak Acid
K_a value	K_a is large	K_a is small
Position of the dissociation (ionization) equilibrium	Far to the right	Far to the left
Equilibrium concentration of H^+ compared with original concentration of HA	$[H^+] \approx [HA]_0$	$[H^+] \ll [HA]_0$
Strength of conjugate base compared with that of water	A^- much weaker base than H_2O	A^- much stronger base than H_2O

Conversely, a **weak acid** is one for which *the equilibrium lies far to the left.* Most of the acid originally placed in the solution is still present as HA at equilibrium. That is, a weak acid dissociates only to a very small extent in aqueous solution [see Fig. 14.4(b)]. In contrast to a strong acid, a weak acid has a conjugate base that is a much stronger base than water. In this case a water molecule is not very successful in pulling an H^+ ion from the conjugate base. *The weaker the acid, the stronger its conjugate base.*

Perchloric acid can explode if handled improperly.

The various ways of describing the strength of an acid are summarized in Table 14.1. Strong and weak acids are represented pictorially in Fig. 14.6.

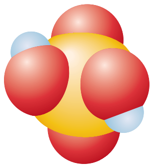
The common strong acids are sulfuric acid [$H_2SO_4(aq)$], hydrochloric acid [$HCl(aq)$], nitric acid [$HNO_3(aq)$], and perchloric acid [$HClO_4(aq)$]. Sulfuric acid is actually a **diprotic acid,** an acid having two acidic protons. The acid H_2SO_4 is a strong acid, virtually 100% dissociated (ionized) in water:

$$H_2SO_4(aq) \longrightarrow H^+(aq) + HSO_4^-(aq)$$

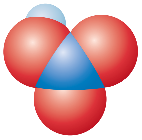
The HSO_4^- ion, however, is a weak acid:

$$HSO_4^-(aq) \rightleftharpoons H^+(aq) + SO_4^{2-}(aq)$$

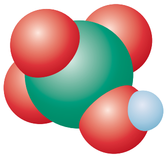
Most acids are **oxyacids,** in which the acidic proton is attached to an oxygen atom. The strong acids mentioned above, except hydrochloric acid, are typical examples. Many common weak acids, such as phosphoric acid (H_3PO_4), nitrous acid (HNO_2), and



Sulfuric acid
(H_2SO_4)



Nitric acid
(HNO_3)



Perchloric acid
($HClO_4$)

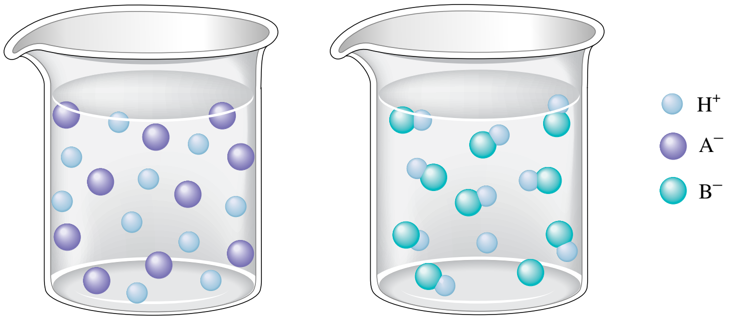
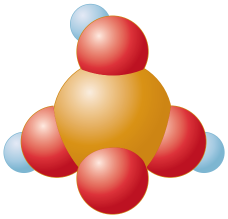
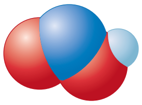


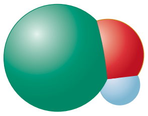
FIGURE 14.6
(a) A strong acid HA is completely ionized in water. (b) A weak acid HB exists mostly as undissociated HB molecules in water. Note that the water molecules are not shown in this figure.



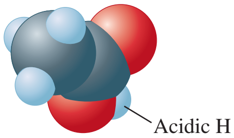
Phosphoric acid (H_3PO_4)



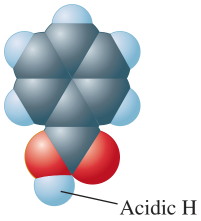
Nitrous acid (HNO_2)



Hypochlorous acid (HOCl)



Acetic acid (CH_3CO_2H)



Benzoic acid ($C_6H_5CO_2H$)

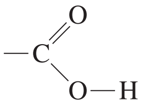
TABLE 14.2 Values of K_a for Some Common Monoprotic Acids

Formula	Name	Value of K_a*
HSO_4^-	Hydrogen sulfate ion	1.2×10^{-2}
$HClO_2$	Chlorous acid	1.2×10^{-2}
$HC_2H_2ClO_2$	Monochloracetic acid	1.35×10^{-3}
HF	Hydrofluoric acid	7.2×10^{-4}
HNO_2	Nitrous acid	4.0×10^{-4}
$HC_2H_3O_2$	Acetic acid	1.8×10^{-5}
$[Al(H_2O)_6]^{3+}$	Hydrated aluminum(III) ion	1.4×10^{-5}
HOCl	Hypochlorous acid	3.5×10^{-8}
HCN	Hydrocyanic acid	6.2×10^{-10}
NH_4^+	Ammonium ion	5.6×10^{-10}
HOC_6H_5	Phenol	1.6×10^{-10}

↑ Increasing acid strength

*The units of K_a are customarily omitted.

hypochlorous acid (HOCl), are also oxyacids. **Organic acids,** those with a carbon atom backbone, commonly contain the **carboxyl group:**



Acids of this type are usually weak. Examples are acetic acid (CH_3COOH), often written $HC_2H_3O_2$, and benzoic acid (C_6H_5COOH). Note that the remainder of the hydrogens in these molecules are not acidic—they do not form H^+ in water.

There are some important acids in which the acidic proton is attached to an atom other than oxygen. The most significant of these are the hydrohalic acids HX, where X represents a halogen atom.

Table 14.2 contains a list of common **monoprotic acids** (those having *one* acidic proton) and their K_a values. Note that the strong acids are not listed. When a strong acid molecule such as HCl, for example, is placed in water, the position of the dissociation equilibrium

$$HCl(aq) + H_2O(l) \rightleftharpoons H^+(aq) + Cl^-(aq)$$

lies so far to the right that [HCl] cannot be measured accurately. This prevents an accurate calculation of K_a:

$$K_a = \frac{[H^+][Cl^-]}{[HCl]}$$

Very small and highly uncertain

Appendix 5.1 contains a table of K_a values.

Sample Exercise 14.2

Relative Base Strength

Using Table 14.2, arrange the following species according to their strengths as bases: H_2O, F^-, Cl^-, NO_2^-, and CN^-.

Solution

Remember that water is a stronger base than the conjugate base of a strong acid but a weaker base than the conjugate base of a weak acid. This leads to the following order:

$$Cl^- < H_2O < \text{conjugate bases of weak acids}$$

Weakest bases ⟶ Strongest bases

We can order the remaining conjugate bases by recognizing that the strength of an acid is *inversely related* to the strength of its conjugate base. Since from Table 14.2 we have

$$K_a \text{ for HF} > K_a \text{ for } HNO_2 > K_a \text{ for HCN}$$

the base strengths increase as follows:

$$F^- < NO_2^- < CN^-$$

The combined order of increasing base strength is

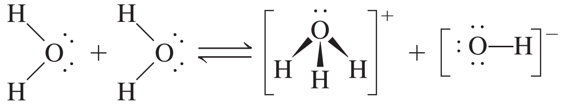
$$Cl^- < H_2O < F^- < NO_2^- < CN^-$$

See Exercises 14.33 through 14.36.

Water as an Acid and a Base

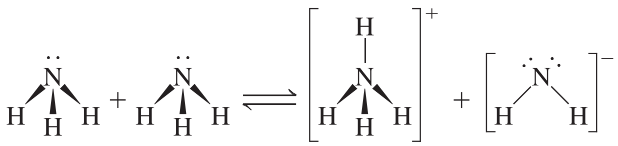
A substance is said to be **amphoteric** if it can behave either as an acid or as a base. Water is the most common **amphoteric substance.** We can see this clearly in the **autoionization** of water, which involves the transfer of a proton from one water molecule to another to produce a hydroxide ion and a hydronium ion:

$$\underset{\text{acid(1)}}{H_2O} + \underset{\text{base(1)}}{H_2O} \rightleftharpoons \underset{\text{acid(2)}}{H_3O^+} + \underset{\text{base(2)}}{OH^-}$$



In this reaction, also illustrated in Fig. 14.7, one water molecule acts as an acid by furnishing a proton, and the other acts as a base by accepting the proton.

Autoionization can occur in other liquids besides water. For example, in liquid ammonia the autoionization reaction is



The autoionization reaction for water

$$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

leads to the equilibrium expression

$$K_w = [H_3O^+][OH^-] = [H^+][OH^-]$$

where K_w, called the **ion-product constant** (or the **dissociation constant** for water), always refers to the autoionization of water.

Experiment shows that at 25°C in pure water,

$$[H^+] = [OH^-] = 1.0 \times 10^{-7} M$$

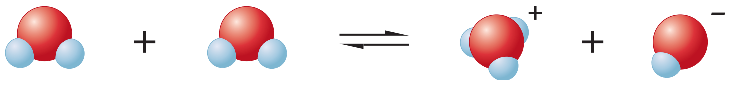
which means that at 25°C

$$K_w = [H^+][OH^-]$$
$$= 1.0 \times 10^{-14}$$

$$K_w = [H^+][OH^-] = (1.0 \times 10^{-7})(1.0 \times 10^{-7})$$
$$= 1.0 \times 10^{-14}$$

FIGURE 14.7

Two water molecules react to form H_3O^+ and OH^-.



It is important to recognize the meaning of K_w. In any aqueous solution at 25°C, *no matter what it contains,* the product of $[H^+]$ and $[OH^-]$ must always equal 1.0×10^{-14}. There are three possible situations:

1. A neutral solution, where $[H^+] = [OH^-]$.
2. An acidic solution, where $[H^+] > [OH^-]$.
3. A basic solution, where $[OH^-] > [H^+]$.

In each case, however, at 25°C,

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$$

Sample Exercise 14.3

Calculating $[H^+]$ and $[OH^-]$

Calculate $[H^+]$ or $[OH^-]$ as required for each of the following solutions at 25°C, and state whether the solution is neutral, acidic, or basic.

a. $1.0 \times 10^{-5}\ M\ OH^-$
b. $1.0 \times 10^{-7}\ M\ OH^-$
c. $10.0\ M\ H^+$

Solution

a. $K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$. Since $[OH^-]$ is $1.0 \times 10^{-5}\ M$, solving for $[H^+]$ gives

$$[H^+] = \frac{1.0 \times 10^{-14}}{[OH^-]} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-5}} = 1.0 \times 10^{-9}\ M$$

Since $[OH^-] > [H^+]$, the solution is basic.

b. As in part a, solving for $[H^+]$ gives

$$[H^+] = \frac{1.0 \times 10^{-14}}{[OH^-]} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-7}} = 1.0 \times 10^{-7}\ M$$

Since $[H^+] = [OH^-]$, the solution is neutral.

c. Solving for $[OH^-]$ gives

$$[OH^-] = \frac{1.0 \times 10^{-14}}{[H^+]} = \frac{1.0 \times 10^{-14}}{10.0} = 1.0 \times 10^{-15}\ M$$

Since $[H^+] > [OH^-]$, the solution is acidic.

Visualization: Self-Ionization of Water

See Exercises 14.37 and 14.38.

Since K_w is an equilibrium constant, it varies with temperature. The effect of temperature is considered in Sample Exercise 14.4.

Sample Exercise 14.4

Autoionization of Water

At 60°C, the value of K_w is 1×10^{-13}.

a. Using Le Châtelier's principle, predict whether the reaction

$$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

is exothermic or endothermic.

b. Calculate $[H^+]$ and $[OH^-]$ in a neutral solution at 60°C.

Solution

a. K_w *increases* from 1×10^{-14} at 25°C to 1×10^{-13} at 60°C. Le Châtelier's principle states that if a system at equilibrium is heated, it will adjust to consume energy. Since the value of K_w increases with temperature, we must think of energy as a reactant, and so the process must be endothermic.

b. At 60°C,

$$[\mathrm{H}^+][\mathrm{OH}^-] = 1 \times 10^{-13}$$

For a neutral solution,

$$[\mathrm{H}^+] = [\mathrm{OH}^-] = \sqrt{1 \times 10^{-13}} = 3 \times 10^{-7}\,M$$

See Exercise 14.39.

Visualization: The pH Scale

14.3 The pH Scale

The pH scale is a compact way to represent solution acidity.

Appendix 1.2 has a review of logs.

Because $[\mathrm{H}^+]$ in an aqueous solution is typically quite small, the **pH scale** provides a convenient way to represent solution acidity. The pH is a log scale based on 10, where

$$\mathrm{pH} = -\log[\mathrm{H}^+]$$

Thus for a solution where

$$[\mathrm{H}^+] = 1.0 \times 10^{-7}\,M$$
$$\mathrm{pH} = -(-7.00) = 7.00$$

At this point we need to discuss significant figures for logarithms. The rule is that *the number of decimal places in the log is equal to the number of significant figures in the original number.* Thus

$$[\mathrm{H}^+] = \overset{\text{2 significant figures}}{1.0} \times 10^{-9}\,M$$
$$\mathrm{pH} = \underset{\text{2 decimal places}}{9.00}$$

Similar log scales are used for representing other quantities; for example,

$$\mathrm{pOH} = -\log[\mathrm{OH}^-]$$
$$\mathrm{p}K = -\log K$$

Since pH is a log scale based on 10, *the pH changes by 1 for every power of 10 change in* $[\mathrm{H}^+]$. For example, a solution of pH 3 has an H^+ concentration 10 times that of a solution of pH 4 and 100 times that of a solution of pH 5. Also note that because pH is defined as $-\log[\mathrm{H}^+]$, *the pH decreases as* $[\mathrm{H}^+]$ *increases.* The pH scale and the pH values for several common substances are shown in Fig. 14.8.

The pH of a solution is usually measured using a pH meter, an electronic device with a probe that can be inserted into a solution of unknown pH. The probe contains an acidic aqueous solution enclosed by a special glass membrane that allows migration of H^+ ions. If the unknown solution has a different pH from the solution in the probe, an electric potential results, which is registered on the meter (see Fig. 14.9).

Sample Exercise 14.5

Calculating pH and pOH

The pH meter is discussed more fully in Section 17.4.

Calculate pH and pOH for each of the following solutions at 25°C.

a. $1.0 \times 10^{-3}\,M\ \mathrm{OH}^-$

b. $1.0\,M\ \mathrm{OH}^+$

CHEMICAL IMPACT

Arnold Beckman, Man of Science

Arnold Beckman died at age 104 in May 2004. Beckman's leadership of science and business spans virtually the entire twentieth century. He was born in 1900 in Cullom, Illinois, a town of 500 people that had no electricity or telephones. Beckman says, "In Cullom we were forced to improvise. I think it was a good thing."

The son of a blacksmith, Beckman had his interest in science awakened at age nine. At that time, in the attic of his house he discovered *J. Dorman Steele's Fourteen Weeks in Chemistry,* a book containing instructions for doing chemistry experiments. Beckman became so fascinated with chemistry that his father built him a small "chemistry shed" in the back yard for his tenth birthday.

Beckman's interest in chemistry was fostered by his high school teachers, and he eventually attended the University of Illinois, Urbana–Champaign. He graduated with a bachelor's degree in chemical engineering in 1922 and stayed one more year to get a master's degree. He then went to Caltech, where he earned a Ph.D. and became a faculty member.

Arnold Beckman.

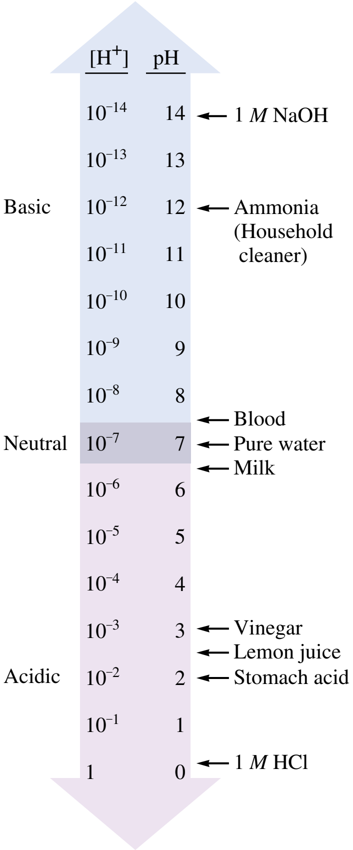


FIGURE 14.8
The pH scale and pH values of some common substances.

Solution

a.

$$[\mathrm{H}^+] = \frac{K_\mathrm{w}}{[\mathrm{OH}^-]} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-3}} = 1.0 \times 10^{-11}\ M$$

$$\mathrm{pH} = -\log[\mathrm{H}^+] = -\log(1.0 \times 10^{-11}) = 11.00$$

$$\mathrm{pOH} = -\log[\mathrm{OH}^-] = -\log(1.0 \times 10^{-3}) = 3.00$$

b.

$$[\mathrm{OH}^-] = \frac{K_\mathrm{w}}{[\mathrm{H}^+]} = \frac{1.0 \times 10^{-14}}{1.0} = 1.0 \times 10^{-14}\ M$$

$$\mathrm{pH} = -\log[\mathrm{H}^+] = -\log(1.0) = 0.00$$

$$\mathrm{pOH} = -\log[\mathrm{OH}^-] = -\log(1.0 \times 10^{-14}) = 14.00$$

See Exercise 14.41.

It is useful to consider the log form of the expression

$$K_\mathrm{w} = [\mathrm{H}^+][\mathrm{OH}^-]$$

FIGURE 14.9
pH meters are used to measure acidity.

Beckman was always known for his inventiveness. As a youth he designed a pressurized fuel system for his Model T Ford to overcome problems with its normal gravity feed fuel system—you had to *back* it up steep hills to keep it from starving for fuel. In 1927 he applied for his first patent: a buzzer to alert drivers that they were speeding.

In 1935 Beckman invented something that would cause a revolution in scientific instrumentation. A college friend who worked in a laboratory in the California citrus industry needed an accurate, convenient way to measure the acidity of orange juice. In response, Beckman invented the pH meter, which he initially called the acidimeter. This compact, sturdy device was an immediate hit. It signaled a new era in scientific instrumentation. In fact, business was so good that Beckman left Caltech to head his own company.

Over the years Beckman invented many other devices, including an improved potentiometer and an instrument for measuring the light absorbed by molecules. At age 65 he retired as president of Beckman Instruments (headquartered in Fullerton, California). After a merger the company became Beckman Coulter; it had sales of more than $2 billion in 2003.

After stepping down as president of Beckman Instruments, Beckman began a new career—donating his wealth for the improvement of science. In 1984 he and Mabel, his wife of 58 years, donated $40 million to his alma mater—the University of Illinois—to fund the Beckman Institute. The Beckmans have also funded many other research institutes, including one at Caltech, and formed a foundation that currently gives $20 million each year to various scientific endeavors.

Arnold Beckman was a man known for his incredible creativity but even more he was recognized as a man of absolute integrity. Mr. Beckman has important words for us: "Whatever you do, be enthusiastic about it."

Note: You can see Arnold Beckman's biography at the Chemical Heritage Foundation Web site (http;//www.chemheritage.org).

That is,

$$\log K_w = \log[H^+] + \log[OH^-]$$

or

$$-\log K_w = -\log[H^+] - \log[OH^-]$$

Thus

$$pK_w = pH + pOH \tag{14.3}$$

Since $K_w = 1.0 \times 10^{-14}$,

$$pK_w = -\log(1.0 \times 10^{-14}) = 14.00$$

Thus, for *any* aqueous solution at 25°C, pH and pOH add up to 14.00:

$$pH + pOH = 14.00 \tag{14.4}$$

Sample Exercise 14.6 Calculating pH

The pH of a sample of human blood was measured to be 7.41 at 25°C. Calculate pOH, $[H^+]$, and $[OH^-]$ for the sample.

Solution

Since pH + pOH = 14.00,

$$pOH = 14.00 - pH = 14.00 - 7.41 = 6.59$$

To find $[H^+]$ we must go back to the definition of pH:

$$pH = -\log[H^+]$$

Thus

$$7.41 = -\log[H^+] \quad \text{or} \quad \log[H^+] = -7.41$$

We need to know the *antilog* of −7.41. As shown in Appendix 1.2, taking the antilog is the same as exponentiation; that is,

antilog$(n) = \log^{-1}(n)$

$$\text{antilog}(n) = 10^n$$

Since $\text{pH} = -\log[\text{H}^+]$,

$$-\text{pH} = \log[\text{H}^+]$$

and $[\text{H}^+]$ can be calculated by taking the antilog of −pH:

$$[\text{H}^+] = \text{antilog}(-\text{pH})$$

In the present case,

$$[\text{H}^+] = \text{antilog}(-\text{pH}) = \text{antilog}(-7.41) = 10^{-7.41} = 3.9 \times 10^{-8}$$

Similarly, $[\text{OH}^-] = \text{antilog}(-\text{pOH})$, and

$$[\text{OH}^-] = \text{antilog}(-6.59) = 10^{-6.59} = 2.6 \times 10^{-7}\ M$$

See Exercises 14.42 through 14.46.

Now that we have considered all the fundamental definitions relevant to acid–base solutions, we can proceed to a quantitative description of the equilibria present in these solutions. The main reason that acid–base problems sometimes seem difficult is that a typical aqueous solution contains many components, so the problems tend to be complicated. However, you can deal with these problems successfully if you use the following general strategies:

- *Think chemistry.* Focus on the solution components and their reactions. It will almost always be possible to choose one reaction that is the most important.
- *Be systematic.* Acid–base problems require a step-by-step approach.
- *Be flexible.* Although all acid–base problems are similar in many ways, important differences do occur. Treat each problem as a separate entity. Do not try to force a given problem into matching any you have solved before. Look for both the similarities and the differences.
- *Be patient.* The complete solution to a complicated problem cannot be seen immediately in all its detail. Pick the problem apart into its workable steps.
- *Be confident.* Look within the problem for the solution, and let the problem guide you. Assume that you can think it out. Do not rely on memorizing solutions to problems. In fact, memorizing solutions is usually detrimental because you tend to try to force a new problem to be the same as one you have seen before. *Understand and think; don't just memorize.*

14.4 Calculating the pH of Strong Acid Solutions

Common Strong Acids
$HCl(aq)$
$HNO_3(aq)$
$H_2SO_4(aq)$
$HClO_4(aq)$

When we deal with acid–base equilibria, *we must focus on the solution components and their chemistry.* For example, what species are present in a 1.0 *M* solution of HCl? Since hydrochloric acid is a strong acid, we assume that it is completely dissociated. Thus, although the label on the bottle says 1.0 *M* HCl, the solution contains virtually no HCl molecules. Typically, container labels indicate the substance(s) used to make up the solution but do not necessarily describe the solution components after dissolution. Thus a 1.0 *M* HCl solution contains H^+ and Cl^- ions rather than HCl molecules.

The next step in dealing with aqueous solutions is to determine which components are significant and which can be ignored. We need to focus on the **major species,** those solution components present in relatively large amounts. In 1.0 *M* HCl, for example, the major species are H^+, Cl^-, and H_2O. Since this is a very acidic solution, OH^- is present only in tiny amounts and is classified as a minor species. In attacking acid–base problems, the importance of *writing the major species in the solution* as the first step cannot be overemphasized. *This single step is the key to solving these problems successfully.*

Always write the major species present in the solution.

To illustrate the main ideas involved, let us calculate the pH of 1.0 *M* HCl. We first list the major species: H^+, Cl^-, and H_2O. Since we want to calculate the pH, we will focus on those major species that can furnish H^+. Obviously, we must consider H^+ from the dissociation of HCl. However, H_2O also furnishes H^+ by autoionization, which is often represented by the simple dissociation reaction

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

The H^+ from the strong acid drives the equilibrium $H_2O \rightleftharpoons H^+ + OH^-$ to the left.

However, is autoionization an important source of H^+ ions? In pure water at 25°C, $[H^+]$ is 10^{-7} *M*. In 1.0 *M* HCl solution, the water will produce even less than 10^{-27} *M* H^+, since by Le Châtelier's principle the H^+ from the dissociated HCl will drive the position of the water equilibrium to the left. Thus the amount of H^+ contributed by water is negligible compared with the 1.0 *M* H^+ from the dissociation of HCl. Therefore, we can say that $[H^+]$ in the solution is 1.0 *M*. The pH is then

$$pH = -\log[H^+] = -\log(1.0) = 0$$

Sample Exercise 14.7

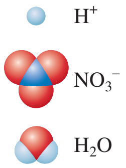
pH of Strong Acids

In pure water, only 10^{-7} *M* H^+ is produced.

a. Calculate the pH of 0.10 *M* HNO_3.
b. Calculate the pH of 1.0×10^{-10} *M* HCl.

Solution

Major Species



a. Since HNO_3 is a strong acid, the major species in solution are

$$H^+, \quad NO_3^-, \quad \text{and} \quad H_2O$$

The concentration of HNO_3 is virtually zero, since the acid completely dissociates in water. Also, $[OH^-]$ will be very small because the H^+ ions from the acid will drive the equilibrium

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

to the left. That is, this is an acidic solution where $[H^+] \gg [OH^-]$, so $[OH^-] \ll 10^{-7}$ *M*. The sources of H^+ are

1. H^+ from HNO_3 (0.10 *M*)
2. H^+ from H_2O

The number of H^+ ions contributed by the autoionization of water will be very small compared with the 0.10 *M* contributed by the HNO_3 and can be neglected. Since the dissolved HNO_3 is the only important source of H^+ ions in this solution,

$$[H^+] = 0.10\ M \quad \text{and} \quad pH = -\log(0.10) = 1.00$$

b. Normally, in an aqueous solution of HCl the major species are H^+, Cl^-, and H_2O. However, in this case the amount of HCl in solution is so small that it has no effect; the only major species is H_2O. Thus the pH will be that of pure water, or pH = 7.00.

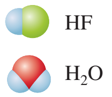
See Exercises 14.47 and 14.48.

14.5 Calculating the pH of Weak Acid Solutions

Since a weak acid dissolved in water can be viewed as a prototype of almost any equilibrium occurring in aqueous solution, we will proceed carefully and systematically. Although some of the procedures we develop here may seem unnecessary, they will become essential as the problems become more complicated. We will develop the necessary strategies by calculating the pH of a 1.00 *M* solution of HF ($K_a = 7.2 \times 10^{-4}$).

First, *always* write the major species present in the solution.

Major Species



The first step, as always, is to *write the major species in the solution.* From its small K_a value, we know that hydrofluoric acid is a weak acid and will be dissociated only to a slight extent. Thus, when we write the major species, the hydrofluoric acid will be represented in its dominant form, as HF. The major species in solution are HF and H_2O.

The next step (since this is a pH problem) is to decide which of the major species can furnish H^+ ions. Actually, both major species can do so:

$$HF(aq) \rightleftharpoons H^+(aq) + F^-(aq) \qquad K_a = 7.2 \times 10^{-4}$$
$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq) \qquad K_w = 1.0 \times 10^{-14}$$

In aqueous solutions, however, typically one source of H^+ can be singled out as dominant. By comparing K_a for HF with K_w for H_2O, we see that hydrofluoric acid, although weak, is still a much stronger acid than water. Thus we will assume that hydrofluoric acid will be the dominant source of H^+. We will ignore the tiny contribution by water.

Therefore, it is the dissociation of HF that will determine the equilibrium concentration of H^+ and hence the pH:

$$HF(aq) \rightleftharpoons H^+(aq) + F^-(aq)$$

The equilibrium expression is

$$K_a = 7.2 \times 10^{-4} = \frac{[H^+][F^-]}{[HF]}$$

To solve the equilibrium problem, we follow the procedures developed in Chapter 13 for gas-phase equilibria. First, we list the initial concentrations, the *concentrations before the reaction of interest has proceeded to equilibrium.* Before any HF dissociates, the concentrations of the species in the equilibrium are

$$[HF]_0 = 1.00\,M \quad [F^-]_0 = 0 \quad [H^+]_0 = 10^{-7}\,M \approx 0$$

(Note that the zero value for $[H^+]_0$ is an approximation, since we are neglecting the H^+ ions from the autoionization of water.)

The next step is to determine the change required to reach equilibrium. Since some HF will dissociate to come to equilibrium (but this amount is presently unknown), we let x be the change in the concentration of HF that is required to achieve equilibrium. That is, we assume that x mol/L HF will dissociate to produce x mol/L H^+ and x mol/L F^- as the system adjusts to its equilibrium position. Now the equilibrium concentrations can be defined in terms of x:

$$[HF] = [HF]_0 - x = 1.00 - x$$
$$[F^-] = [F^-]_0 + x = 0 + x = x$$
$$[H^+] = [H^+]_0 + x \approx 0 + x = x$$

Substituting these equilibrium concentrations into the equilibrium expression gives

$$K_a = 7.2 \times 10^{-4} = \frac{[H^+][F^-]}{[HF]} = \frac{(x)(x)}{1.00 - x}$$

This expression produces a quadratic equation that can be solved using the quadratic formula, as for the gas-phase systems in Chapter 13. However, since K_a for HF is so small, HF will dissociate only slightly, and x is expected to be small. This will allow us to simplify the calculation. If x is very small compared to 1.00, the term in the denominator can be approximated as follows:

$$1.00 - x \approx 1.00$$

The equilibrium expression then becomes

$$7.2 \times 10^{-4} = \frac{(x)(x)}{1.00 - x} \approx \frac{(x)(x)}{1.00}$$

which yields

$$x^2 \approx (7.2 \times 10^{-4})(1.00) = 7.2 \times 10^{-4}$$
$$x \approx \sqrt{7.2 \times 10^{-4}} = 2.7 \times 10^{-2}$$

The validity of an approximation should always be checked.

How valid is the approximation that [HF] = 1.00 *M*? Because this question will arise often in connection with acid–base equilibrium calculations, we will consider it carefully. *The validity of the approximation depends on how much accuracy we demand for the calculated value of $[H^+]$.* Typically, the K_a values for acids are known to an accuracy of only about ± 5%. It is reasonable therefore to apply this figure when determining the validity of the approximation

$$[HA]_0 - x \approx [HA]_0$$

We will use the following test. First, we calculate the value of x by making the approximation

$$K_a = \frac{x^2}{[HA]_0 - x} \approx \frac{x^2}{[HA]_0}$$

where $$x^2 \approx K_a[HA]_0 \quad \text{and} \quad x \approx \sqrt{K_a[HA]_0}$$

We then compare the sizes of x and $[HA]_0$. If the expression

$$\frac{x}{[HA]_0} \times 100\%$$

is less than or equal to 5%, the value of x is small enough that the approximation

$$[HA]_0 - x \approx [HA]_0$$

will be considered valid.

In our example,

$$x = 2.7 \times 10^{-2} \text{ mol/L}$$
$$[HA]_0 = [HF]_0 = 1.00 \text{ mol/L}$$

and $$\frac{x}{[HA]_0} \times 100 = \frac{2.7 \times 10^{-2}}{1.00} \times 100\% = 2.7\%$$

The approximation we made is considered valid, and the value of x calculated using that approximation is acceptable. Thus

$$x = [H^+] = 2.7 \times 10^{-2}\,M \quad \text{and} \quad \text{pH} = -\log(2.7 \times 10^{-2}) = 1.57$$

This problem illustrates all the important steps for solving a typical equilibrium problem involving a weak acid. These steps are summarized as follows:

Solving Weak Acid Equilibrium Problems

1. **List the major species in the solution.**
2. **Choose the species that can produce H^+, and write balanced equations for the reactions producing H^+.**
3. **Using the values of the equilibrium constants for the reactions you have written, decide which equilibrium will dominate in producing H^+.**
4. **Write the equilibrium expression for the dominant equilibrium.**

The K_a values for various weak acids are given in Table 14.2 and in Appendix 5.1.

5 List the initial concentrations of the species participating in the dominant equilibrium.

6 Define the change needed to achieve equilibrium; that is, define *x*.

7 Write the equilibrium concentrations in terms of *x*.

8 Substitute the equilibrium concentrations into the equilibrium expression.

9 Solve for *x* the "easy" way, that is, by assuming that $[HA]_0 - x \approx [HA]_0$.

10 Use the 5% rule to verify whether the approximation is valid.

11 Calculate $[H^+]$ and pH.

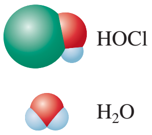
We use this systematic approach in Sample Exercise 14.8.

Sample Exercise 14.8

The pH of Weak Acids

The hypochlorite ion (OCl^-) is a strong oxidizing agent often found in household bleaches and disinfectants. It is also the active ingredient that forms when swimming pool water is treated with chlorine. In addition to its oxidizing abilities, the hypochlorite ion has a relatively high affinity for protons (it is a much stronger base than Cl^-, for example) and forms the weakly acidic hypochlorous acid (HOCl, $K_a = 3.5 \times 10^{-8}$). Calculate the pH of a 0.100 *M* aqueous solution of hypochlorous acid.

Major Species



Solution

1 We list the major species. Since HOCl is a weak acid and remains mostly undissociated, the major species in a 0.100 *M* HOCl solution are

$$\text{HOCl} \quad \text{and} \quad H_2O$$

2 Both species can produce H^+:

$$\begin{aligned} HOCl(aq) &\rightleftharpoons H^+(aq) + OCl^-(aq) \qquad K_a = 3.5 \times 10^{-8} \\ H_2O(l) &\rightleftharpoons H^+(aq) + OH^-(aq) \qquad K_w = 1.0 \times 10^{-14} \end{aligned}$$

3 Since HOCl is a significantly stronger acid than H_2O, it will dominate in the production of H^+.

Swimming pool water must be frequently tested for pH and chlorine content.

4 We therefore use the following equilibrium expression:

$$K_a = 3.5 \times 10^{-8} = \frac{[H^+][OCl^-]}{[HOCl]}$$

5 The initial concentrations appropriate for this equilibrium are

$$\begin{aligned} [HOCl]_0 &= 0.100\ M \\ [OCl^-]_0 &= 0 \\ [H^+]_0 &\approx 0 \qquad \text{(We neglect the contribution from } H_2O.) \end{aligned}$$

6 Since the system will reach equilibrium by the dissociation of HOCl, let *x* be the amount of HOCl (in mol/L) that dissociates in reaching equilibrium.

7 The equilibrium concentrations in terms of *x* are

$$\begin{aligned} [HOCl] &= [HOCl]_0 - x = 0.100 - x \\ [OCl^-] &= [OCl^-]_0 + x = 0 + x = x \\ [H^+] &= [H^+]_0 + x \approx 0 + x = x \end{aligned}$$

8 Substituting these concentrations into the equilibrium expression gives

$$K_a = 3.5 \times 10^{-8} = \frac{(x)(x)}{0.100 - x}$$

➥ **9** Since K_a is so small, we can expect a small value for x. Thus we make the approximation $[HA]_0 - x \approx [HA]_0$, or $0.100 - x \approx 0.100$, which leads to the expression

$$K_a = 3.5 \times 10^{-8} = \frac{x^2}{0.100 - x} \approx \frac{x^2}{0.100}$$

Solving for x gives

$$x = 5.9 \times 10^{-5}$$

➥ **10** The approximation $0.100 - x \approx 0.100$ must be validated. To do this, we compare x to $[HOCl]_0$:

$$\frac{x}{[HA]_0} \times 100 = \frac{x}{[HOCl]_0} \times 100 = \frac{5.9 \times 10^{-5}}{0.100} \times 100 = 0.059\%$$

Since this value is much less than 5%, the approximation is considered valid.

➥ **11** We calculate $[H^+]$ and pH:

$$[H^+] = x = 5.9 \times 10^{-5}\,M \qquad \text{and} \qquad \text{pH} = 4.23$$

See Exercises 14.53 through 14.55.

The pH of a Mixture of Weak Acids

The same systematic approach applies to all solution equilibria.

Sometimes a solution contains two weak acids of very different strengths. This case is considered in Sample Exercise 14.9. Note that the steps are again followed (though not labeled).

Sample Exercise 14.9

The pH of Weak Acid Mixtures

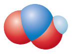
Calculate the pH of a solution that contains 1.00 M HCN ($K_a = 6.2 \times 10^{-10}$) and 5.00 M HNO_2 ($K_a = 4.0 \times 10^{-4}$). Also calculate the concentration of cyanide ion (CN^-) in this solution at equilibrium.

Solution

Since HCN and HNO_2 are both weak acids and are largely undissociated, the major species in the solution are

Major Species

HCN



HNO_2

H_2O

HCN, HNO_2, and H_2O

All three of these components produce H^+:

$$\begin{aligned} HCN(aq) &\rightleftharpoons H^+(aq) + CN^-(aq) & K_a &= 6.2 \times 10^{-10} \\ HNO_2(aq) &\rightleftharpoons H^+(aq) + NO_2^-(aq) & K_a &= 4.0 \times 10^{-4} \\ H_2O(l) &\rightleftharpoons H^+(aq) + OH^-(aq) & K_w &= 1.0 \times 10^{-14} \end{aligned}$$

A mixture of three acids might lead to a very complicated problem. However, the situation is greatly simplified by the fact that even though HNO_2 is a weak acid, it is much stronger than the other two acids present (as revealed by the K values). Thus HNO_2 can be assumed to be the dominant producer of H^+, and we will focus on the equilibrium expression

$$K_a = 4.0 \times 10^{-4} = \frac{[H^+][NO_2^-]}{[HNO_2]}$$

The initial concentrations, the definition of x, and the equilibrium concentrations are as follows:

Initial Concentration (mol/L)		**Equilibrium Concentration (mol/L)**
$[HNO_2]_0 = 5.00$	$\xrightarrow[\text{dissociates}]{x \text{ mol/L } HNO_2}$	$[HNO_2] = 5.00 - x$
$[NO_2^-]_0 = 0$		$[NO_2^-] = x$
$[H^+]_0 \approx 0$		$[H^+] = x$

It is convenient to represent these concentrations in the following shorthand form (called an ICE table):

To avoid clutter we do not show the units of concentration in the ICE tables. All terms have units of mol/L.

	$HNO_2(aq)$	$\rightleftharpoons$	$H^-(aq)$	$+$	$NO_2^-(aq)$
Initial:	5.00		0		0
Change:	$-x$		$+x$		$+x$
Equilibrium:	$5.00 - x$		x		x

Substituting the equilibrium concentrations in the equilibrium expression and making the approximation that $5.00 - x = 5.00$ give

$$K_a = 4.0 \times 10^{-4} = \frac{(x)(x)}{5.00 - x} \approx \frac{x^2}{5.00}$$

We solve for x:

$$x = 4.5 \times 10^{-2}$$

Using the 5% rule, we show that the approximation is valid:

$$\frac{x}{[HNO_2]_0} \times 100 = \frac{4.5 \times 10^{-2}}{5.00} \times 100 = 0.90\%$$

Therefore,

$$[H^+] = x = 4.5 \times 10^{-2}\ M \quad \text{and} \quad \text{pH} = 1.35$$

We also want to calculate the equilibrium concentration of cyanide ion in this solution. The CN^- ions in this solution come from the dissociation of HCN:

$$HCN(aq) \rightleftharpoons H^+(aq) + CN^-(aq)$$

Although the position of this equilibrium lies far to the left and does not contribute *significantly* to $[H^+]$, HCN is the *only source* of CN^-. Thus we must consider the extent of the dissociation of HCN to calculate $[CN^-]$. The equilibrium expression for the preceding reaction is

$$K_a = 6.2 \times 10^{-10} = \frac{[H^+][CN^-]}{[HCN]}$$

We know $[H^+]$ for this solution from the results of the first part of the problem. It is important to understand that *there is only one kind of H^+ in this solution.* It does not matter from which acid the H^+ ions originate. The equilibrium $[H^+]$ we need to insert into the HCN equilibrium expression is $4.5 \times 10^{-2}\ M$, even though the H^+ was contributed almost entirely from the dissociation of HNO_2. What is [HCN] at equilibrium? We know $[HCN]_0 = 1.00\ M$, and since K_a for HCN is so small, a negligible amount of HCN will dissociate. Thus

$$[HCN] = [HCN]_0 - \text{amount of HCN dissociated} \approx [HCN]_0 = 1.00\ M$$

Since $[H^+]$ and [HCN] are known, we can find $[CN^-]$ from the equilibrium expression:

$$K_a = 6.2 \times 10^{-10} = \frac{[H^+][CN^-]}{[HCN]} = \frac{(4.5 \times 10^{-2})[CN^-]}{1.00}$$

$$[CN^-] = \frac{(6.2 \times 10^{-10})(1.00)}{4.5 \times 10^{-2}} = 1.4 \times 10^{-8}\ M$$

Note the significance of this result. Since $[CN^-] = 1.4 \times 10^{-8}\ M$ and HCN is the only source of CN^-, this means that only 1.4×10^{-8} mol/L of HCN dissociated. This is a very small amount compared with the initial concentration of HCN, which is exactly what we would expect from its very small K_a value, and $[HCN] = 1.00\ M$ as assumed.

See Exercises 14.61 and 14.62.

Percent Dissociation

Percent dissociation is also known as *percent ionization.*

It is often useful to specify the amount of weak acid that has dissociated in achieving equilibrium in an aqueous solution. The **percent dissociation** is defined as follows:

$$\text{Percent dissociation} = \frac{\text{amount dissociated (mol/L)}}{\text{initial concentration (mol/L)}} \times 100\% \qquad (14.5)$$

For example, we found earlier that in a 1.00 M solution of HF, $[H^+] = 2.7 \times 10^{-2} M$. To reach equilibrium, 2.7×10^{-2} mol/L of the original 1.00 M HF dissociates, so

$$\text{Percent dissociation} = \frac{2.7 \times 10^{-2}\ \text{mol/L}}{1.00\ \text{mol/L}} \times 100\% = 2.7\%$$

For a given weak acid, the percent dissociation increases as the acid becomes more dilute. For example, the percent dissociation of acetic acid ($HC_2H_3O_2$, $K_a = 1.8 \times 10^{-5}$) is significantly greater in a 0.10 M solution than in a 1.0 M solution, as demonstrated in Sample Exercise 14.10.

Sample Exercise 14.10

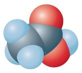
Calculating Percent Dissociation

Calculate the percent dissociation of acetic acid ($K_a = 1.8 \times 10^{-5}$) in each of the following solutions.

a. 1.00 M $HC_2H_3O_2$
b. 0.100 M $HC_2H_3O_2$

Solution

Major Species



$HC_2H_3O_2$

H_2O

a. Since acetic acid is a weak acid, the major species in this solution are $HC_2H_3O_2$ and H_2O. Both species are weak acids, but acetic acid is a much stronger acid than water. Thus the dominant equilibrium will be

$$HC_2H_3O_2(aq) \rightleftharpoons H^+(aq) + C_2H_3O_2^-(aq)$$

and the equilibrium expression is

$$K_a = 1.8 \times 10^{-5} = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]}$$

The initial concentrations, definition of x, and equilibrium concentrations are:

	$HC_2H_3O_2(aq)$	$\rightleftharpoons$	$H^+(aq)$	+	$C_2H_3O_2^-(aq)$
Initial:	1.00		0		0
Change:	$-x$		x		x
Equilibrium:	$1.00 - x$		x		x

An acetic acid solution, which is a weak electrolyte, contains only a few ions and does not conduct as much current as a strong electrolyte. The bulb is only dimly lit.

Inserting the equilibrium concentrations into the equilibrium expression and making the usual approximation that x is small compared with $[HA]_0$ give

$$K_a = 1.8 \times 10^{-5} = \frac{[H^+][C_2H_3O_2{}^-]}{[HC_2H_3O_2]} = \frac{(x)(x)}{1.00 - x} \approx \frac{x^2}{1.00}$$

Thus

$$x^2 \approx 1.8 \times 10^{-5} \quad \text{and} \quad x \approx 4.2 \times 10^{-3}$$

The approximation $1.00 - x \approx 1.00$ is valid by the 5% rule (check this yourself), so

$$[H^+] = x = 4.2 \times 10^{-3}\,M$$

The percent dissociation is

$$\frac{[H^+]}{[HC_2H_3O_2]_0} \times 100 = \frac{4.2 \times 10^{-3}}{1.00} \times 100\% = 0.42\%$$

b. This is a similar problem, except that in this case $[HC_2H_3O_2] = 0.100\,M$. Analysis of the problem leads to the expression

$$K_a = 1.8 \times 10^{-5} = \frac{[H^+][C_2H_3O_2{}^-]}{[HC_2H_3O_2]} = \frac{(x)(x)}{0.100 - x} \approx \frac{x^2}{0.100}$$

Thus $x = [H^+] = 1.3 \times 10^{-3}\,M$

and $\text{Percent dissociation} = \dfrac{1.3 \times 10^{-3}}{0.10} \times 100\% = 1.3\%$

See Exercises 14.63 and 14.64.

The more dilute the weak acid solution, the greater is the percent dissociation.

The results in Sample Exercise 14.10 show two important facts. The concentration of H^+ ion at equilibrium is smaller in the 0.10 M acetic acid solution than in the 1.0 M acetic acid solution, as we would expect. However, the percent dissociation is significantly greater in the 0.10 M solution than in the 1.0 M solution. This is a general result. *For solutions of any weak acid HA, $[H^+]$ decreases as $[HA]_0$ decreases, but the percent dissociation increases as $[HA]_0$ decreases.* This phenomenon can be explained as follows.

Consider the weak acid HA with the initial concentration $[HA]_0$, where at equilibrium

$$[HA] = [HA]_0 - x \approx [HA]_0$$
$$[H^+] = [A^-] = x$$

Thus

$$K_a = \frac{[H^+][A^-]}{[HA]} \approx \frac{(x)(x)}{[HA]_0}$$

Now suppose enough water is added suddenly to dilute the solution by a factor of 10. The new concentrations before any adjustment occurs are

$$[A^-]_{\text{new}} = [H^+]_{\text{new}} = \frac{x}{10}$$

$$[HA]_{\text{new}} = \frac{[HA]_0}{10}$$

and Q, the reaction quotient, is

$$Q = \frac{\left(\dfrac{x}{10}\right)\left(\dfrac{x}{10}\right)}{\dfrac{[HA]_0}{10}} = \frac{1(x)(x)}{10[HA]_0} = \frac{1}{10}K_a$$

Since Q is less than K_a, the system must adjust to the right to reach the new equilibrium position. Thus the percent dissociation increases when the acid is diluted. This behavior

CHEMICAL IMPACT

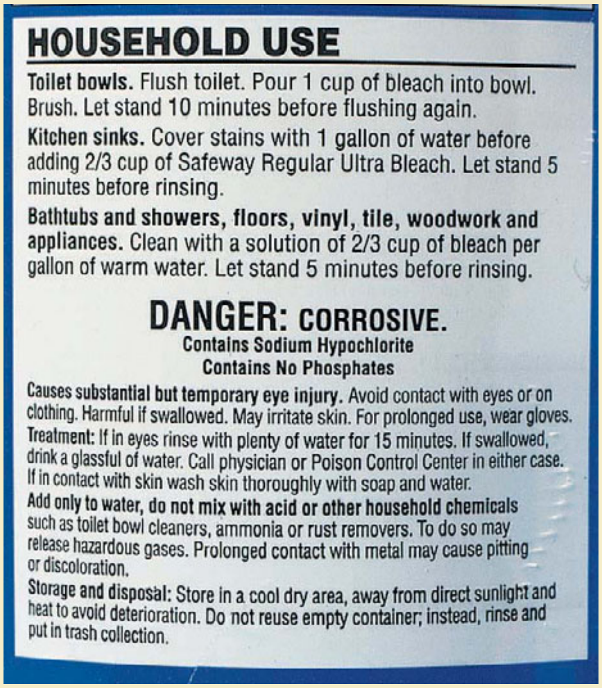
Household Chemistry

Common household bleach is an aqueous solution containing approximately 5% sodium hypochlorite, a potent oxidizing agent that can react with and decolorize chemicals that cause stains. Bleaching solutions are manufactured by dissolving chlorine gas in a sodium hydroxide solution to give the reaction

$$Cl_2(g) + 2OH^-(aq) \rightleftharpoons OCl^-(aq) + Cl^-(aq) + H_2O(l)$$

As long as the pH of this solution is maintained above 8, the OCl^- ion is the predominant chlorine-containing species. However, if the solution is made acidic (the $[OH^-]$ lowered), elemental chlorine (Cl_2) is favored, and since Cl_2 is much less soluble in water than is sodium hypochlorite, Cl_2 gas is suddenly evolved from the solution. This is why labels on bottles of bleach carry warnings about mixing the bleach with other cleaning solutions. For example, toilet bowl cleaners usually contain acids such as H_3PO_4 or HSO_4^- and have pH values around 2. Mixing toilet bowl cleaner with bleach can lead to a very dangerous evolution of chlorine gas.

In addition, if bleach is mixed with a cleaning agent containing ammonia, the chlorine and ammonia can react to produce chloramines, such as NH_2Cl, $NHCl_2$, and NCl_3. These compounds produce acrid fumes that can cause respiratory distress.



HOUSEHOLD USE

Toilet bowls. Flush toilet. Pour 1 cup of bleach into bowl. Brush. Let stand 10 minutes before flushing again.

Kitchen sinks. Cover stains with 1 gallon of water before adding 2/3 cup of Safeway Regular Ultra Bleach. Let stand 5 minutes before rinsing.

Bathtubs and showers, floors, vinyl, tile, woodwork and appliances. Clean with a solution of 2/3 cup of bleach per gallon of warm water. Let stand 5 minutes before rinsing.

DANGER: CORROSIVE.

Contains Sodium Hypochlorite

Contains No Phosphates

Causes substantial but temporary eye injury. Avoid contact with eyes or on clothing. Harmful if swallowed. May irritate skin. For prolonged use, wear gloves.

Treatment: If in eyes rinse with plenty of water for 15 minutes. If swallowed, drink a glassful of water. Call physician or Poison Control Center in either case. If in contact with skin wash skin thoroughly with soap and water.

Add only to water, do not mix with acid or other household chemicals such as toilet bowl cleaners, ammonia or rust removers. To do so may release hazardous gases. Prolonged contact with metal may cause pitting or discoloration.

Storage and disposal: Store in a cool dry area, away from direct sunlight and heat to avoid deterioration. Do not reuse empty container; instead, rinse and put in trash collection.

The label on this bleach bottle warns of the hazards of mixing cleaning solutions.

is summarized in Fig. 14.10. In Sample Exercise 14.11 we see how the percent dissociation can be used to calculate the K_a value for a weak acid.

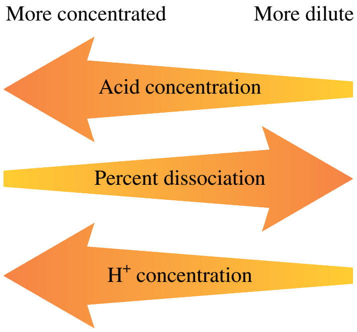


FIGURE 14.10
The effect of dilution on the percent dissociation and $[H^+]$ of a weak acid solution.

Sample Exercise 14.11

Calculating K_a from Percent Dissociation

Lactic acid ($HC_3H_5O_3$) is a waste product that accumulates in muscle tissue during exertion, leading to pain and a feeling of fatigue. In a 0.100 *M* aqueous solution, lactic acid is 3.7% dissociated. Calculate the value of K_a for this acid.

Solution

From the small value for the percent dissociation, it is clear that $HC_3H_5O_3$ is a weak acid. Thus the major species in the solution are the undissociated acid and water:

$$HC_3H_5O_3 \quad \text{and} \quad H_2O$$

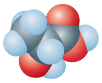
However, even though $HC_3H_5O_3$ is a weak acid, it is a much stronger acid than water and will be the dominant source of H^+ in the solution. The dissociation reaction is

$$HC_3H_5O_3(aq) \rightleftharpoons H^+(aq) + C_3H_5O_3^-(aq)$$

and the equilibrium expression is

$$K_a = \frac{[H^+][C_3H_5O_3^-]}{[HC_3H_5O_3]}$$

Major Species


$HC_3H_5O_3$


H_2O

The initial and equilibrium concentrations are as follows:

Initial Concentration (mol/L)		Equilibrium Concentration (mol/L)
$[HC_3H_5O_3]_0 = 0.10$	$\xrightarrow[\text{dissociates}]{x \text{ mol/L } HC_3H_5O_3}$	$[HC_3H_5O_3] = 0.10 - x$
$[C_3H_5O_3^-]_0 = 0$		$[C_3H_5O_3^-] = x$
$[H^+]_0 \approx 0$		$[H^+] = x$

The change needed to reach equilibrium can be obtained from the percent dissociation and Equation (14.5). For this acid,

$$\text{Percent dissociation} = 3.7\% = \frac{x}{[HC_3H_5O_3]_0} \times 100\% = \frac{x}{0.10} \times 100\%$$

and

$$x = \frac{3.7}{100}(0.10) = 3.7 \times 10^{-3} \text{ mol/L}$$

Now we can calculate the equilibrium concentrations:

$$[HC_3H_5O_3] = 0.10 - x = 0.10\,M \qquad \text{(to the correct number of significant figures)}$$
$$[C_3H_5O_3^-] = [H^+] = x = 3.7 \times 10^{-3}\,M$$

These concentrations can now be used to calculate the value of K_a for lactic acid:

$$K_a = \frac{[H^+][C_3H_5O_3^-]}{[HC_3H_5O_3]} = \frac{(3.7 \times 10^{-3})(3.7 \times 10^{-3})}{0.10} = 1.4 \times 10^{-4}$$

See Exercises 14.65 and 14.66.

Strenuous exercise causes a buildup of lactic acid in muscle tissues.

14.6 Bases

According to the Arrhenius concept, a base is a substance that produces OH^- ions in aqueous solution. According to the Brønsted–Lowry model, a base is a proton acceptor. The bases sodium hydroxide (NaOH) and potassium hydroxide (KOH) fulfill both criteria. They contain OH^- ions in the solid lattice and, behaving as strong electrolytes, dissociate completely when dissolved in aqueous solution:

In a basic solution at 25°C, pH > 7.

$$NaOH(s) \longrightarrow Na^+(aq) + OH^-(aq)$$

leaving virtually no undissociated NaOH. Thus a 1.0 M NaOH solution really contains 1.0 M Na^+ and 1.0 M OH^-. Because of their complete dissociation, NaOH and KOH are called **strong bases** in the same sense as we defined strong acids.

Visualization: Limewater and Carbon Dioxide

All the hydroxides of the Group 1A elements (LiOH, NaOH, KOH, RbOH, and CsOH) are strong bases, but only NaOH and KOH are common laboratory reagents, because the lithium, rubidium, and cesium compounds are expensive. The alkaline earth (Group 2A) hydroxides—$Ca(OH)_2$, $Ba(OH)_2$, and $Sr(OH)_2$—are also strong bases. For these compounds, two moles of hydroxide ion are produced for every mole of metal hydroxide dissolved in aqueous solution.

The alkaline earth hydroxides are not very soluble and are used only when the solubility factor is not important. In fact, the low solubility of these bases can sometimes be an advantage. For example, many antacids are suspensions of metal hydroxides, such as aluminum hydroxide and magnesium hydroxide. The low solubility of these compounds prevents a large hydroxide ion concentration that would harm the tissues of the mouth, esophagus, and stomach. Yet these suspensions furnish plenty of

Drug Facts

Active ingredients (in each tsp=5 mL) **Purpose**

Aluminum hydroxide

(equiv. to dried gel, USP) 200 mg....................Antacid

Magnesium hydroxide 200 mg....................Antacid

Simethicone 20 mg....................Antigas

Uses relieves ■ heartburn ■ sour stomach ■ gas ■ acid indigestion ■ upset stomach due to these symptoms

Warnings

Ask a doctor before use if you have kidney disease

Ask a doctor or pharmacist before use if you are presently taking a prescription drug. Antacids may interact with certain prescription drugs.

When using this product do not exceed 24 tsp (120 mL) in a 24-hour period or use the maximum dosage for more than 2 weeks

Stop use and ask a doctor if symptoms last for more than 2 weeks

If pregnant or breast-feeding, ask a health professional before use.

Keep out of reach of children.

Directions ■ shake well before use ■ take 2-4 tsp (10-20 mL) between meals and at bedtime

Inactive ingredients butylparaben, carboxymethylcellulose sodium, FD&C red #40, flavor, hydroxypropyl methylcellulose, microcrystalline cellulose, propylparaben, purified water, saccharin sodium, sorbitol

Questions or comments? 1-800-842-7886

Store at room temperature tightly closed.

An antacid containing aluminum and magnesium hydroxides.

hydroxide ion to react with the stomach acid, since the salts dissolve as this reaction proceeds.

Calcium hydroxide, $Ca(OH)_2$, often called **slaked lime,** is widely used in industry because it is inexpensive and plentiful. For example, slaked lime is used in scrubbing stack gases to remove sulfur dioxide from the exhaust of power plants and factories. In the scrubbing process a suspension of slaked lime is sprayed into the stack gases to react with sulfur dioxide gas according to the following steps:

$$SO_2(g) + H_2O(l) \rightleftharpoons H_2SO_3(aq)$$
$$Ca(OH)_2(aq) + H_2SO_3(aq) \rightleftharpoons CaSO_3(s) + 2H_2O(l)$$

Calcium carbonate is also used in scrubbing, as discussed in Section 5.10.

Slaked lime is also widely used in water treatment plants for softening hard water, which involves the removal of ions, such as Ca^{2+} and Mg^{2+}, that hamper the action of detergents. The softening method most often employed in water treatment plants is the **lime–soda process,** in which *lime* (CaO) and *soda ash* (Na_2CO_3) are added to the water. As we will see in more detail later in this chapter, the CO_3^{2-} ion reacts with water to produce the HCO_3^- ion. When the lime is added to the water, it forms slaked lime, that is,

$$CaO(s) + H_2O(l) \longrightarrow Ca(OH)_2(aq)$$

which then reacts with the HCO_3^- ion from the added soda ash and the Ca^{2+} ion in the hard water to produce calcium carbonate:

$$Ca(OH)_2(aq) + \underset{\substack{\nearrow \\ \text{From hard water}}}{Ca^{2+}}(aq) + 2HCO_3^-(aq) \longrightarrow 2CaCO_3(s) + 2H_2O(l)$$

Thus, for every mole of $Ca(OH)_2$ consumed, 1 mole of Ca^{2+} is removed from the hard water, thereby softening it. Some hard water naturally contains bicarbonate ions. In this case, no soda ash is needed—simply adding the lime produces the softening.

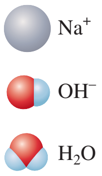
Calculating the pH of a strong base solution is relatively simple, as illustrated in Sample Exercise 14.12.

Sample Exercise 14.12

The pH of Strong Bases

Calculate the pH of a $5.0 \times 10^{-2}\,M$ NaOH solution.

Major Species



Solution

The major species in this solution are

$$\underbrace{Na^+,\ OH^-,}_{\text{From NaOH}}\ \text{and}\ H_2O$$

Although autoionization of water also produces OH^- ions, the pH will be dominated by the OH^- ions from the dissolved NaOH. Thus, in the solution,

$$[OH^-] = 5.0 \times 10^{-2}\,M$$

and the concentration of H^+ can be calculated from K_w:

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{5.0 \times 10^{-2}} = 2.0 - 10^{-13}\,M$$
$$pH = 12.70$$

Note that this is a basic solution for which

$$[OH^-] > [H^+] \quad \text{and} \quad pH > 7$$

The added OH^- from the salt has shifted the water autoionization equilibrium

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

to the left, significantly lowering $[H^+]$ compared with that in pure water.

See Exercises 14.77 through 14.80.

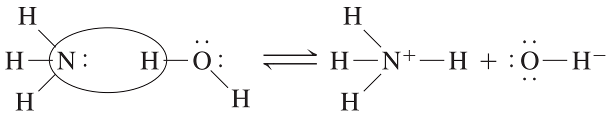
A base does not have to contain hydroxide ion.

Many types of proton acceptors (bases) do not contain the hydroxide ion. However, when dissolved in water, these substances increase the concentration of hydroxide ion because of their reaction with water. For example, ammonia reacts with water as follows:

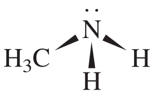
$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

The ammonia molecule accepts a proton and thus functions as a base. Water is the acid in this reaction. Note that even though the base ammonia contains no hydroxide ion, it still increases the concentration of hydroxide ion to yield a basic solution.

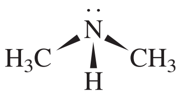
Bases such as ammonia typically have at least one unshared pair of electrons that is capable of forming a bond with a proton. The reaction of an ammonia molecule with a water molecule can be represented as follows:



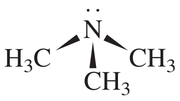
There are many bases like ammonia that produce hydroxide ion by reaction with water. In most of these bases, the lone pair is located on a nitrogen atom. Some examples are



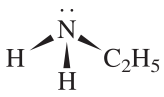
Methylamine



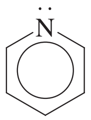
Dimethylamine



Trimethylamine

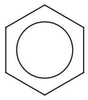


Ethylamine



Pyridine

Note that the first four bases can be thought of as substituted ammonia molecules with hydrogen atoms replaced by methyl (CH_3) or ethyl (C_2H_5) groups. The pyridine molecule is like benzene



except that a nitrogen atom replaces one of the carbon atoms in the ring. The general reaction between a base B and water is given by

$$\underset{\text{Base}}{B(aq)} + \underset{\text{Acid}}{H_2O(l)} \rightleftharpoons \underset{\substack{\text{Conjugate}\\\text{acid}}}{BH^+(aq)} + \underset{\substack{\text{Conjugate}\\\text{base}}}{OH^-(aq)} \qquad (14.6)$$

The equilibrium constant for this general reaction is

Appendix 5.3 contains a table of K_b values.

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

where K_b *always refers to the reaction of a base with water to form the conjugate acid and the hydroxide ion.*

Bases of the type represented by B in Equation (14.6) compete with OH^-, a very strong base, for the H^+ ion. Thus their K_b values tend to be small (for example, for ammonia, $K_b = 1.8 \times 10^{-5}$), and they are called **weak bases.** The values of K_b for some common weak bases are listed in Table 14.3.

TABLE 14.3 Values of K_b for Some Common Weak Bases

Name	Formula	Conjugate Acid	K_b
Ammonia	NH_3	NH_4^+	1.8×10^{-5}
Methylamine	CH_3NH_2	$CH_3NH_3^+$	4.38×10^{-4}
Ethylamine	$C_2H_5NH_2$	$C_2H_5NH_3^+$	5.6×10^{-4}
Aniline	$C_6H_5NH_2$	$C_6H_5NH_3^+$	3.8×10^{-10}
Pyridine	C_5H_5N	$C_5H_5NH^+$	1.7×10^{-9}

Visualization: Brønsted–Lowry Reaction

Typically, pH calculations for solutions of weak bases are very similar to those for weak acids, as illustrated by Sample Exercises 14.13 and 14.14.

Sample Exercise 14.13 The pH of Weak Bases I

Calculate the pH for a 15.0 *M* solution of NH_3 ($K_b = 1.8 \times 10^{-5}$).

Solution

Since ammonia is a weak base, as can be seen from its small K_b value, most of the dissolved NH_3 will remain as NH_3. Thus the major species in solution are

Major Species


NH_3


H_2O

NH_3 and H_2O

Both these substances can produce OH^- according to the reactions

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \qquad K_b = 1.8 \times 10^{-5}$$

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq) \qquad K_w = 1.0 \times 10^{-14}$$

However, the contribution from water can be neglected, since $K_b \gg K_w$. The equilibrium for NH_3 will dominate, and the equilibrium expression to be used is

$$K_b = 1.8 \times 10^{-5} = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

The appropriate concentrations are

Refer to the steps for solving weak acid equilibrium problems. Use the same systematic approach for weak base equilibrium problems.

Initial Concentration (mol/L)		Equilibrium Concentration (mol/L)
$[NH_3]_0 = 15.0$	$\xrightarrow[\text{H}_2\text{O to reach equilibrium}]{x \text{ mol/L NH}_3 \text{ reacts with}}$	$[NH_3] = 15.0 - x$
$[NH_4^+]_0 = 0$		$[NH_4^+] = x$
$[OH^-]_0 \approx 0$		$[OH^-] = x$

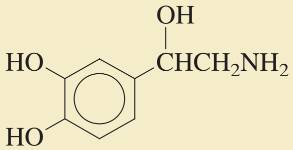
In terms of an ICE table, these concentrations are:

	$NH_3(aq)$	+	$H_2O(l)$	$\rightleftharpoons$	$NH_4^+(aq)$	+	$OH^-(aq)$
Initial:	15.0		—		0		0
Change:	$-x$		—		$+x$		$+x$
Equilibrium:	$15.0 - x$		—		x		x

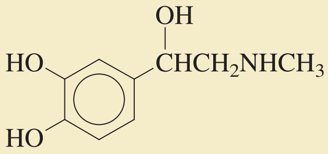
CHEMICAL IMPACT

Amines

We have seen that many bases have nitrogen atoms with one lone pair and can be viewed as substituted ammonia molecules, with the general formula $R_xNH_{(3-x)}$. Compounds of this type are called **amines.** Amines are widely distributed in animals and plants, and complex amines often serve as messengers or regulators. For example, in the human nervous system, there are two amine stimulants, *norepinephrine* and *adrenaline.*

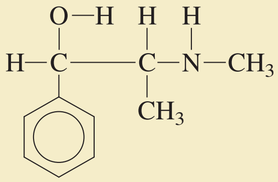


Norepinephrine

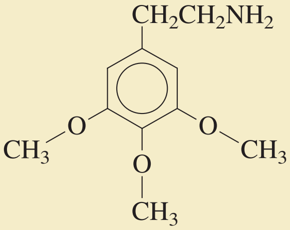


Adrenaline

Ephedrine, widely used as a decongestant, was a known drug in China over 2000 years ago. Indians in Mexico and the Southwest have used the hallucinogen *mescaline,* extracted from the peyote cactus, for centuries.



Ephedrine



Mescaline

Substituting the equilibrium concentrations into the equilibrium expression and making the usual approximation gives

$$K_b = 1.8 \times 10^{-5} = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{(x)(x)}{15.0 - x} \approx \frac{x^2}{15.0}$$

Thus $$x \approx 1.6 \times 10^{-2}$$

The 5% rule validates the approximation (check it yourself), so

$$[OH^-] = 1.6 \times 10^{-2}\ M$$

Since we know that K_w must be satisfied for this solution, we can calculate $[H^+]$ as follows:

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{1.6 \times 10^{-2}} = 6.3 \times 10^{-13}\ M$$

Therefore, $$pH = -\log(6.3 \times 10^{-13}) = 12.20$$

See Exercises 14.83 and 14.84.

Sample Exercise 14.13 illustrates how a typical weak base equilibrium problem should be solved. Note two additional important points:

A table of K_b values for bases is also given in Appendix 5.3.

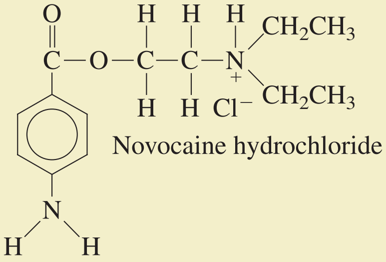
1. We calculated $[H^+]$ from K_w and then calculated the pH, but another method is available. The pOH could have been calculated from $[OH^-]$ and then used in Equation (14.3):

$$pK_w = 14.00 = pH + pOH$$
$$pH = 14.00 - pOH$$

Many other drugs, such as codeine and quinine, are amines, but they are usually not used in their pure amine forms. Instead, they are treated with an acid to become acid salts. An example of an acid salt is ammonium chloride, obtained by the reaction

$$NH_3 + HCl \longrightarrow NH_4Cl$$

Amines also can be protonated in this way. The resulting acid salt, written as AHCl (where A represents the amine), contains AH^+ and Cl^-. In general, the acid salts are more stable and more soluble in water than the parent amines. For instance, the parent amine of the well-known local anesthetic *novocaine* is insoluble in water, whereas the acid salt is much more soluble.



Novocaine hydrochloride

Peyote cactus growing on a rock.

2. In a 15.0 *M* NH_3 solution, the equilibrium concentrations of NH_4^+ and OH^- are each 1.6×10^{-2} *M*. Only a small percentage,

$$\frac{1.6 \times 10^{-2}}{15.0} \times 100\% = 0.11\%$$

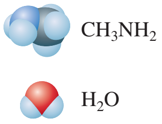
of the ammonia reacts with water. Bottles containing 15.0 *M* NH_3 solution are often labeled 15.0 *M* NH_4OH, but as you can see from these results, 15.0 *M* NH_3 is actually a much more accurate description of the solution contents.

Sample Exercise 14.14 The pH of Weak Bases II

Calculate the pH of a 1.0 *M* solution of methylamine ($K_b = 4.38 \times 10^{-4}$).

Solution

Major Species



Since methylamine (CH_3NH_2) is a weak base, the major species in solution are

$$CH_3NH_2 \quad \text{and} \quad H_2O$$

Both are bases; however, water can be neglected as a source of OH^-, so the dominant equilibrium is

$$CH_3NH_2(aq) + H_2O(l) \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq)$$

and

$$K_b = 4.38 \times 10^{-4} = \frac{[CH_3NH_3^+][OH^-]}{[CH_3NH_2]}$$

The ICE table is:

	$CH_3NH_2(aq)$	$+$	$H_2O(l)$	$\rightleftharpoons$	$CH_3NH_3^+(aq)$	$+$	$OH^-(aq)$
Initial:	1.0		—		0		0
Change:	$-x$		—		$+x$		$+x$
Equilibrium:	$1.0 - x$		—		x		x

Substituting the equilibrium concentrations in the equilibrium expression and making the usual approximation give

$$K_b = 4.38 \times 10^{-4} = \frac{[CH_3NH_3^+][OH^-]}{[CH_3NH_2]} = \frac{(x)(x)}{1.0 - x} \approx \frac{x^2}{1.0}$$

and

$$x \approx 2.1 \times 10^{-2}$$

The approximation is valid by the 5% rule, so

$$[OH^-] = x = 2.1 \times 10^{-2}\,M$$
$$\text{pOH} = 1.68$$
$$\text{pH} = 14.00 - 1.68 = 12.32$$

See Exercises 14.85 and 14.86.

14.7 Polyprotic Acids

Some important acids, such as sulfuric acid (H_2SO_4) and phosphoric acid (H_3PO_4), can furnish more than one proton and are called **polyprotic acids.** A polyprotic acid always dissociates in a *stepwise* manner, one proton at a time. For example, the diprotic (two-proton) acid carbonic acid (H_2CO_3), which is so important in maintaining a constant pH in human blood, dissociates in the following steps:

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq) \qquad K_{a_1} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = 4.3 \times 10^{-7}$$

$$HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq) \qquad K_{a_2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = 5.6 \times 10^{-11}$$

The successive K_a values for the dissociation equilibria are designated K_{a_1} and K_{a_2}. Note that the conjugate base HCO_3^- of the first dissociation equilibrium becomes the acid in the second step.

Carbonic acid is formed when carbon dioxide gas is dissolved in water. In fact, the first dissociation step for carbonic acid is best represented by the reaction

$$CO_2(aq) + H_2O(l) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

since relatively little H_2CO_3 actually exists in solution. However, it is convenient to consider CO_2 in water as H_2CO_3 so that we can treat such solutions using the familiar dissociation reactions for weak acids.

Phosphoric acid is a **triprotic acid** (three protons) that dissociates in the following steps:

$$H_3PO_4(aq) \rightleftharpoons H^+(aq) + H_2PO_4^-(aq) \qquad K_{a_1} = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]} = 7.5 \times 10^{-3}$$

$$H_2PO_4^-(aq) \rightleftharpoons H^+(aq) + HPO_4^{2-}(aq) \qquad K_{a_2} = \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]} = 6.2 \times 10^{-8}$$

$$HPO_4^{2-}(aq) \rightleftharpoons H^+(aq) + PO_4^{3-}(aq) \qquad K_{a_3} = \frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]} = 4.8 \times 10^{-13}$$

TABLE 14.4 Stepwise Dissociation Constants for Several Common Polyprotic Acids

Name	Formula	K_{a_1}	K_{a_2}	K_{a_3}
Phosphoric acid	H_3PO_4	7.5×10^{-3}	6.2×10^{-8}	4.8×10^{-13}
Arsenic acid	H_3AsO_4	5×10^{-3}	8×10^{-8}	6×10^{-10}
Carbonic acid	H_2CO_3	4.3×10^{-7}	5.6×10^{-11}	
Sulfuric acid	H_2SO_4	Large	1.2×10^{-2}	
Sulfurous acid	H_2SO_3	1.5×10^{-2}	1.0×10^{-7}	
Hydrosulfuric acid*	H_2S	1.0×10^{-7}	$\sim 10^{-19}$	
Oxalic acid	$H_2C_2O_4$	6.5×10^{-2}	6.1×10^{-5}	
Ascorbic acid (vitamin C)	$H_2C_6H_6O_6$	7.9×10^{-5}	1.6×10^{-12}	

*The K_{a_2} value for H_2S is very uncertain. Because it is so small, the K_{a_2} value is very difficult to measure accurately.

For a typical weak polyprotic acid,

$$K_{a_1} > K_{a_2} > K_{a_3}$$

A table of K_a values for polyprotic acids is also given in Appendix 5.2.

That is, the acid involved in each step of the dissociation is successively weaker, as shown by the stepwise dissociation constants given in Table 14.4. These values indicate that the loss of a second or third proton occurs less readily than loss of the first proton. This is not surprising; as the negative charge on the acid increases, it becomes more difficult to remove the positively charged proton.

Although we might expect the pH calculations for solutions of polyprotic acids to be complicated, the most common cases are surprisingly straightforward. To illustrate, we will consider a typical case, phosphoric acid, and a unique case, sulfuric acid.

Phosphoric Acid

Phosphoric acid is typical of most polyprotic acids in that the successive K_a values are very different. For example, the ratios of successive K_a values (from Table 14.4) are

$$\frac{K_{a_1}}{K_{a_2}} = \frac{7.5 \times 10^{-3}}{6.2 \times 10^{-8}} = 1.2 \times 10^{5}$$

$$\frac{K_{a_2}}{K_{a_3}} = \frac{6.2 \times 10^{-8}}{4.8 \times 10^{-13}} = 1.3 \times 10^{5}$$

Thus the relative acid strengths are

$$H_3PO_4 \gg H_2PO_4^{-} \gg HPO_4^{2-}$$

For a typical polyprotic acid in water, only the first dissociation step is important in determining the pH.

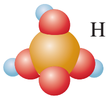
This means that in a solution prepared by dissolving H_3PO_4 in water, *only the first dissociation step makes an important contribution to [H^+].* This greatly simplifies the pH calculations for phosphoric acid solutions, as is illustrated in Sample Exercise 14.15.

Sample Exercise 14.15 The pH of a Polyprotic Acid

Calculate the pH of a 5.0 M H_3PO_4 solution and the equilibrium concentrations of the species H_3PO_4, $H_2PO_4^{-}$, HPO_4^{2-}, and PO_4^{3-}.

Solution

Major Species



The major species in solution are

$$H_3PO_4 \quad \text{and} \quad H_2O$$

None of the dissociation products of H_3PO_4 is written, since the K_a values are all so small that they will be minor species. The dominant equilibrium is the dissociation of H_3PO_4:

$$H_3PO_4(aq) \rightleftharpoons H^+(aq) + H_2PO_4^-(aq)$$

where $$K_{a_1} = 7.5 \times 10^{-3} = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]}$$

The ICE table is:

	$H_3PO_4(aq)$	$\rightleftharpoons$	$H^+(aq)$	$+$	$H_2PO_4^-(aq)$
Initial:	5.0		0		0
Change:	$-x$		$+x$		$+x$
Equilibrium:	$5.0 - x$		x		x

Substituting the equilibrium concentrations into the expression for K_{a_1} and making the usual approximation give

$$K_{a_1} = 7.5 \times 10^{-3} = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]} = \frac{(x)(x)}{5.0 - x} \approx \frac{x^2}{5.0}$$

Thus $$x \approx 1.9 \times 10^{-1}$$

Since 1.9×10^{-1} is less than 5% of 5.0, the approximation is acceptable, and

$$[H^+] = x = 0.19\ M$$
$$\text{pH} = 0.72$$

So far we have determined that

$$[H^+] = [H_2PO_4^-] = 0.19\ M$$

and $$[H_3PO_4] = 5.0 - x = 4.8\ M$$

The concentration of HPO_4^{2-} can be obtained by using the expression for K_{a_2}:

$$K_{a_2} = 6.2 \times 10^{-8} = \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]}$$

where $$[H^+] = [H_2PO_4^-] = 0.19\ M$$

Thus $$[HPO_4^{2-}] = K_{a_2} = 6.2 \times 10^{-8}\ M$$

To calculate $[PO_4^{3-}]$, we use the expression for K_{a_3} and the values of $[H^+]$ and $[HPO_4^{2-}]$ calculated previously:

$$K_{a_3} = \frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]} = 4.8 \times 10^{-13} = \frac{0.19[PO_4^{3-}]}{(6.2 \times 10^{-8})}$$

$$[PO_4^{3-}] = \frac{(4.8 \times 10^{-13})(6.2 \times 10^{-8})}{0.19} = 1.6 \times 10^{-19}\ M$$

These results show that the second and third dissociation steps do not make an important contribution to $[H^+]$. This is apparent from the fact that $[HPO_4^{2-}]$ is 6.2×10^{-8} M, which means that only 6.2×10^{-8} mol/L $H_2PO_4^-$ has dissociated. The value of $[PO_4^{3-}]$ shows that the dissociation of HPO_4^{2-} is even smaller. We must, however, use the second and third dissociation steps to calculate $[HPO_4^{2-}]$ and $[PO_4^{3-}]$, since these steps are the only sources of these ions.

See Exercises 14.95 and 14.96.

Sulfuric Acid

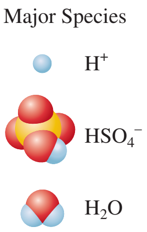
Sulfuric acid is unique among the common acids in that it is *a strong acid in its first dissociation step and a weak acid in its second step:*

$$H_2SO_4(aq) \longrightarrow H^+(aq) + HSO_4^-(aq) \quad K_{a_1} \text{ is very large}$$
$$HSO_4^-(aq) \rightleftharpoons H^+(aq) + SO_4^{2-}(aq) \quad K_{a_2} = 1.2 \times 10^{-2}$$

Sample Exercise 14.16 illustrates how to calculate the pH for sulfuric acid solutions.

Sample Exercise 14.16 The pH of Sulfuric Acid

Calculate the pH of a 1.0 M H_2SO_4 solution.



Solution

The major species in the solution are

$$H^+, HSO_4^-, \quad \text{and} \quad H_2O$$

where the first two ions are produced by the complete first dissociation step of H_2SO_4. The concentration of H^+ in this solution will be at least 1.0 M, since this amount is produced by the first dissociation step of H_2SO_4. We must now answer this question: Does the HSO_4^- ion dissociate enough to produce a significant contribution to the concentration of H^+? This question can be answered by calculating the equilibrium concentrations for the dissociation reactions of HSO_4^-:

$$HSO_4^-(aq) \rightleftharpoons H^+(aq) + SO_4^{2-}(aq)$$

where

$$K_{a_2} = 1.2 \times 10^{-2} = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]}$$

A bottle of sulfuric acid.

The ICE table is:

	$HSO_4^-(aq)$	$\rightleftharpoons$	$H^+(aq)$	+	$SO_4^{2-}(aq)$
Initial:	1.0		1.0		0
Change:	$-x$		$+x$		$+x$
Equilibrium:	$1.0 - x$		$1.0 + x$		x

Note that $[H^+]_0$ is not equal to zero, as it usually is for a weak acid, because the first dissociation step has already occurred. Substituting the equilibrium concentrations into the expression for K_{a_2} and making the usual approximation give

$$K_{a_2} = 1.2 \times 10^{-2} = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]} = \frac{(1.0 + x)(x)}{1.0 - x} \approx \frac{(1.0)(x)}{(1.0)}$$

Thus $$x \approx 1.2 \times 10^{-2}$$

Since 1.2×10^{-2} is 1.2% of 1.0, the approximation is valid according to the 5% rule. Note that x is not equal to $[H^+]$ in this case. Instead,

$$[H^+] = 1.0\,M + x = 1.0\,M + (1.2 \times 10^{-2})\,M$$
$$= 1.0\,M \quad \text{(to the correct number of significant figures)}$$

Thus the dissociation of HSO_4^- does not make a significant contribution to the concentration of H^+, and

$$[H^+] = 1.0\,M \quad \text{and} \quad pH = 0.00$$

See Exercise 14.97.

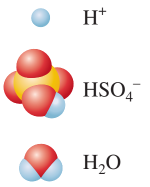
Only in dilute H_2SO_4 solutions does the second dissociation step contribute significantly to $[H^+]$.

Sample Exercise 14.16 illustrates the most common case for sulfuric acid in which only the first dissociation makes an important contribution to the concentration of H^+. In solutions more dilute than 1.0 *M* (for example, 0.10 *M* H_2SO_4), the dissociation of HSO_4^- is important, and solving the problem requires use of the quadratic formula, as shown in Sample Exercise 14.17.

Sample Exercise 14.17 The pH of Sulfuric Acid

Calculate the pH of a 1.00×10^{-2} *M* H_2SO_4 solution.

Major Species



Solution

The major species in solution are

$$H^+, \quad HSO_4^-, \quad \text{and} \quad H_2O$$

Proceeding as in Sample Exercise 14.16, we consider the dissociation of HSO_4^-, which leads to the following ICE table:

	$HSO_4^-(aq)$	$\rightleftharpoons$	$H^+(aq)$	+	$SO_4^{2-}(aq)$
Initial:	0.0100		0.0100 From dissociation of H_2SO_4		0
Change:	$-x$		$+x$		$+x$
Equilibrium:	$0.0100 - x$		$0.0100 + x$		x

Substituting the equilibrium concentrations into the expression for K_{a_2} gives

$$1.2 \times 10^{-2} = K_{a_2} = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]} = \frac{(0.0100 + x)(x)}{(0.0100 - x)}$$

If we make the usual approximation, then $0.0100 + x \approx 0.0100$ and $0.0100 - x \approx 0.0100$, and we have

$$1.2 \times 10^{-2} = \frac{(0.0100 + x)(x)}{(0.0100 - x)} \approx \frac{(0.0100)x}{(0.0100)}$$

The calculated value of x is

$$x = 1.2 \times 10^{-2} = 0.012$$

This value is larger than 0.010, clearly a ridiculous result. Thus we cannot make the usual approximation and must instead solve the quadratic equation. The expression

$$1.2 \times 10^{-2} = \frac{(0.0100 + x)(x)}{(0.0100 - x)}$$

leads to

$$(1.2 \times 10^{-2})(0.0100 - x) = (0.0100 + x)(x)$$
$$(1.2 \times 10^{-4}) - (1.2 \times 10^{-2})x = (1.0 \times 10^{-2})x + x^2$$
$$x^2 + (2.2 \times 10^{-2})x - (1.2 \times 10^{-4}) = 0$$

This equation can be solved using the quadratic formula

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

where $a = 1$, $b = 2.2 \times 10^{-2}$, and $c = -1.2 \times 10^{-4}$. Use of the quadratic formula gives one negative root (which cannot be correct) and one positive root,

$$x = 4.5 \times 10^{-3}$$

Thus $[H^+] = 0.0100 + x = 0.0100 + 0.0045 = 0.0145$

and $pH = 1.84$

Note that in this case the second dissociation step produces about half as many H^+ ions as the initial step does.

This problem also can be solved by successive approximations, a method illustrated in Appendix 1.4.

See Exercise 14.98.

Characteristics of Weak Polyprotic Acids

1. Typically, successive K_a values are so much smaller than the first value that only the first dissociation step makes a significant contribution to the equilibrium concentration of H^+. This means that the calculation of the pH for a solution of a typical weak polyprotic acid is identical to that for a solution of a weak monoprotic acid.
2. Sulfuric acid is unique in being a strong acid in its first dissociation step and a weak acid in its second step. For relatively concentrated solutions of sulfuric acid (1.0 *M* or higher), the large concentration of H^+ from the first dissociation step represses the second step, which can be neglected as a contributor of H^+ ions. For dilute solutions of sulfuric acid, the second step does make a significant contribution, and the quadratic equation must be used to obtain the total H^+ concentration.

14.8 Acid–Base Properties of Salts

Salt is simply another name for *ionic compound.* When a salt dissolves in water, we assume that it breaks up into its ions, which move about independently, at least in dilute solutions. Under certain conditions, these ions can behave as acids or bases. In this section we explore such reactions.

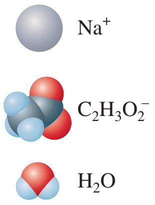
Salts That Produce Neutral Solutions

Recall that the conjugate base of a strong acid has virtually no affinity for protons in water. This is why strong acids completely dissociate in aqueous solution. Thus, when anions such as Cl^- and NO_3^- are placed in water, they do not combine with H^+ and have no effect on the pH. Cations such as K^+ and Na^+ from strong bases have no affinity for H^+, nor can they produce H^+, so they too have no effect on the pH of an aqueous solution. *Salts that consist of the cations of strong bases and the anions of strong acids have no effect on* $[H^+]$ *when dissolved in water.* This means that aqueous solutions of salts such as KCl, NaCl, $NaNO_3$, and KNO_3 are neutral (have a pH of 7).

The salt of a strong acid and a strong base gives a neutral solution.

Salts That Produce Basic Solutions

Major Species



In an aqueous solution of sodium acetate ($NaC_2H_3O_2$), the major species are

$$Na^+, \quad C_2H_3O_2^-, \quad \text{and} \quad H_2O$$

What are the acid–base properties of each component? The Na^+ ion has neither acid nor base properties. The $C_2H_3O_2^-$ ion is the conjugate base of acetic acid, a weak acid. This means that $C_2H_3O_2^-$ has a significant affinity for a proton and is a base. Finally, water is a weakly amphoteric substance.

The pH of this solution will be determined by the $C_2H_3O_2^-$ ion. Since $C_2H_3O_2^-$ is a base, it will react with the best proton donor available. In this case, water is the *only* source of protons, and the reaction between the acetate ion and water is

$$C_2H_3O_2^-(aq) + H_2O(l) \rightleftharpoons HC_2H_3O_2(aq) + OH^-(aq) \qquad (14.7)$$

Note that this reaction, which yields a base solution, involves a *base reacting with water to produce hydroxide ion and a conjugate acid.* We have defined K_b as the equilibrium constant for such a reaction. In this case,

$$K_b = \frac{[HC_2H_3O_2][OH^-]}{[C_2H_3O_2^-]}$$

The value of K_a for acetic acid is well known (1.8×10^{-5}). But how can we obtain the K_b value for the acetate ion? The answer lies in the relationships among K_a, K_b, and K_w. Note that when the expression for K_a for acetic acid is multiplied by the expression for K_b for the acetate ion, the result is K_w:

$$K_a \times K_b = \frac{[H^+]\cancel{[C_2H_3O_2^-]}}{\cancel{[HC_2H_3O_2]}} \times \frac{\cancel{[HC_2H_3O_2]}[OH^-]}{\cancel{[C_2H_3O_2^-]}} = [H^+][OH^-] = K_w$$

This is a very important result. For any weak acid and its conjugate base,

$$K_a \times K_b = K_w$$

Thus, when either K_a or K_b is known, the other can be calculated. For the acetate ion,

$$K_b = \frac{K_w}{K_a\ (\text{for } HC_2H_3O_2)} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

This is the K_b value for the reaction described by Equation (14.7). Note that it is obtained from the K_a value of the parent weak acid, in this case acetic acid. The sodium acetate solution is an example of an important general case. *For any salt whose cation has neutral properties (such as Na^+ or K^+) and whose anion is the conjugate base of a weak acid, the aqueous solution will be basic.* The K_b value for the anion can be obtained from the relationship $K_b = K_w/K_a$. Equilibrium calculations of this type are illustrated in Sample Exercise 14.18.

A basic solution is formed if the anion of the salt is the conjugate base of a weak acid.

Sample Exercise 14.18

Salts as Weak Bases

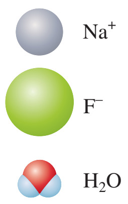
Calculate the pH of a 0.30 *M* NaF solution. The K_a value for HF is 7.2×10^{-4}.

Solution

The major species in solution are

$$Na^+, F^-, \quad \text{and} \quad H_2O$$

Major Species



Since HF is a weak acid, the F^- ion must have a significant affinity for protons, and the dominant reaction will be

$$F^-(aq) + H_2O(l) \rightleftharpoons HF(aq) + OH^-(aq)$$

which yields the K_b expression

$$K_b = \frac{[HF][OH^-]}{[F^-]}$$

The value of K_b can be calculated from K_w and the K_a value for HF:

$$K_b = \frac{K_w}{K_a\ (\text{for HF})} = \frac{1.0 \times 10^{-14}}{7.2 \times 10^{-4}} = 1.4 \times 10^{-11}$$

The corresponding ICE table is:

	$F^-(aq)$	$+$	$H_2O(l)$	$\rightleftharpoons$	$HF(aq)$	$+$	$OH^-(aq)$
Initial:	0.30		—		0		≈ 0
Change:	$-x$		—		$+x$		$+x$
Equilibrium:	$0.30 - x$		—		x		x

Thus

$$K_b = 1.4 \times 10^{-11} = \frac{[HF][OH^-]}{[F^-]} = \frac{(x)(x)}{0.30 - x} \approx \frac{x^2}{0.30}$$

and

$$x \approx 2.0 \times 10^{-6}$$

The approximation is valid by the 5% rule, so

$$[OH^-] = x = 2.0 \times 10^{-6}\,M$$

$$\mathrm{pOH} = 5.69$$

$$\mathrm{pH} = 14.00 - 5.69 = 8.31$$

As expected, the solution is basic.

See Exercise 14.103.

Base Strength in Aqueous Solutions

To emphasize the concept of base strength, let us consider the basic properties of the cyanide ion. One relevant reaction is the dissociation of hydrocyanic acid in water:

$$HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CN^-(aq) \qquad K_a = 6.2 \times 10^{-10}$$

Since HCN is such a weak acid, CN^- appears to be a *strong* base, showing a very high affinity for H^+ *compared to* H_2O, with which it is competing. However, we also need to look at the reaction in which cyanide ion reacts with water:

$$CN^-(aq) + H_2O(l) \rightleftharpoons HCN(aq) + OH^-(aq)$$

where

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{6.2 \times 10^{-10}} = 1.6 \times 10^{-5}$$

In this reaction CN^- appears to be a weak base; the K_b value is only 1.6×10^{-5}. What accounts for this apparent difference in base strength? The key idea is that in the reaction of CN^- with H_2O, *CN^- is competing with OH^- for H^+, instead of competing with H_2O,* as it does in the HCN dissociation reaction. These equilibria show the following relative base strengths:

$$OH^- > CN^- > H_2O$$

Similar arguments can be made for other "weak" bases, such as ammonia, the acetate ion, the fluoride ion, and so on.

Salts That Produce Acidic Solutions

Some salts produce acidic solutions when dissolved in water. For example, when solid NH_4Cl is dissolved in water, NH_4^+ and Cl^- ions are present, with NH_4^+ behaving as a weak acid:

$$NH_4^+(aq) \rightleftharpoons NH_3(aq) + H^+(aq)$$

The Cl^- ion, having virtually no affinity for H^+ in water, does not affect the pH of the solution.

In general, *salts in which the anion is not a base and the cation is the conjugate acid of a weak base produce acidic solutions.*

Sample Exercise 14.19 Salts as Weak Acids I

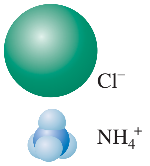
Calculate the pH of a 0.10 M NH_4Cl solution. The K_b value for NH_3 is 1.8×10^{-5}.

Solution

The major species in solution are

$$NH_4^+, \quad Cl^-, \quad \text{and} \quad H_2O$$

Major Species



Note that both NH_4^+ and H_2O can produce H^+. The dissociation reaction for the NH_4^+ ion is

$$NH_4^+(aq) \rightleftharpoons NH_3(aq) + H^+(aq)$$

for which

$$K_a = \frac{[NH_3][H^+]}{[NH_4^+]}$$

Note that although the K_b value for NH_3 is given, the reaction corresponding to K_b is not appropriate here, since NH_3 is not a major species in the solution. Instead, the given value of K_b is used to calculate K_a for NH_4^+ from the relationship

$$K_a \times K_b = K_w$$

Thus

$$K_a\,(\text{for } NH_4^+) = \frac{K_w}{K_b\,(\text{for } NH_3)} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

Although NH_4^+ is a very weak acid, as indicated by its K_a value, it is stronger than H_2O and will dominate in the production of H^+. Thus we will focus on the dissociation reaction of NH_4^+ to calculate the pH in this solution.

We solve the weak acid problem in the usual way:

	$NH_4^+(aq)$	$\rightleftharpoons$	$H^+(aq)$	+	$NH_3(aq)$
Initial:	0.10		≈ 0		0
Change:	$-x$		$+x$		$+x$
Equilibrium:	$0.10 - x$		x		x

Thus

$$5.6 \times 10^{-10} = K_a = \frac{[H^+][NH_3]}{[NH_4^+]} = \frac{(x)(x)}{0.10 - x} \approx \frac{x^2}{0.10}$$

$$x \approx 7.5 \times 10^{-6}$$

The approximation is valid by the 5% rule, so

$$[H^+] = x = 7.5 \times 10^{-6}\,M \qquad \text{and} \qquad pH = 5.13$$

See Exercise 14.104.

A second type of salt that produces an acidic solution is one that contains a *highly charged metal ion.* For example, when solid aluminum chloride ($AlCl_3$) is dissolved in water, the resulting solution is significantly acidic. Although the Al^{3+} ion is not itself a Brønsted–Lowry acid, the hydrated ion $Al(H_2O)_6^{3+}$ formed in water is a weak acid:

$$Al(H_2O)_6^{3+}(aq) \rightleftharpoons Al(OH)(H_2O)_5^{2+}(aq) + H^+(aq)$$

The high charge on the metal ion polarizes the O—H bonds in the attached water molecules, making the hydrogens in these water molecules more acidic than those in free water molecules. Typically, the higher the charge on the metal ion, the stronger the acidity of the hydrated ion.

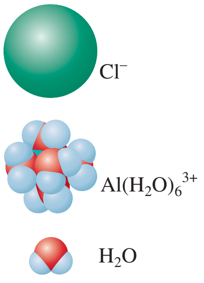
Section 14.9 contains a further discussion of the acidity of hydrated ions.

Sample Exercise 14.20 Salts as Weak Acids II

Calculate the pH of a 0.010 *M* $AlCl_3$ solution. The K_a value for $Al(H_2O)_6^{3+}$ is 1.4×10^{-5}.

Solution

Major Species



The major species in solution are

$$Al(H_2O)_6^{3+}, \quad Cl^-, \quad \text{and} \quad H_2O$$

Since the $Al(H_2O)_6^{3+}$ ion is a stronger acid than water, the dominant equilibrium is

$$Al(H_2O)_6^{3+}(aq) \rightleftharpoons Al(OH)(H_2O)_5^{2+}(aq) + H^+(aq)$$

and

$$1.4 \times 10^{-5} = K_a = \frac{[Al(OH)(H_2O)_5^{2+}][H^+]}{[Al(H_2O)_6^{3+}]}$$

This is a typical weak acid problem, which we can solve with the usual procedure:

	$Al(H_2O)_6^{3+}(aq)$	$\rightleftharpoons$	$Al(OH)(H_2O)_5^{2+}(aq)$	+	$H^+(aq)$
Initial:	0.010		0		≈0
Change:	$-x$		$+x$		$+x$
Equilibrium:	$0.010 - x$		x		x

Thus

$$1.4 \times 10^{-5} = K_a = \frac{[Al(OH)(H_2O)_5^{2+}][H^+]}{[Al(H_2O)_6^{3+}]} = \frac{(x)(x)}{0.010 - x} \approx \frac{x^2}{0.010}$$

$$x \approx 3.7 \times 10^{-4}$$

Since the approximation is valid by the 5% rule,

$$[H^+] = x = 3.7 \times 10^{-4}\ M \quad \text{and} \quad pH = 3.43$$

See Exercises 14.109 and 14.110.

So far we have considered salts in which only one of the ions has acidic or basic properties. For many salts, such as ammonium acetate ($NH_4C_2H_3O_2$), both ions can affect the pH of the aqueous solution. Because the equilibrium calculations for these cases can be quite complicated, we will consider only the qualitative aspects of such problems. We can predict whether the solution will be basic, acidic, or neutral by comparing the K_a value for the acidic ion with the K_b value for the basic ion. If the K_a value for the acidic ion is larger than the K_b value for the basic ion, the solution will be acidic. If the K_b value is larger than the K_a value, the solution will be basic. Equal K_a and K_b values mean a neutral solution. These facts are summarized in Table 14.5.

TABLE 14.5 Qualitative Prediction of pH for Solutions of Salts for Which Both Cation and Anion Have Acidic or Basic Properties

$K_a > K_b$	pH < 7 (acidic)
$K_b > K_a$	pH > 7 (basic)
$K_a = K_b$	pH = 7 (neutral)

Sample Exercise 14.21 The Acid–Base Properties of Salts

Predict whether an aqueous solution of each of the following salts will be acidic, basic, or neutral.

a. $NH_4C_2H_3O_2$ **b.** NH_4CN **c.** $Al_2(SO_4)_3$

Solution

a. The ions in solution are NH_4^+ and $C_2H_3O_2^-$. As we mentioned previously, K_a for NH_4^+ is 5.6×10^{-10} and K_b for $C_2H_3O_2^-$ is 5.6×10^{-10}. Thus K_a for NH_4^+ is equal to K_b for $C_2H_3O_2^-$, and the solution will be neutral (pH = 7).

b. The solution will contain NH_4^+ and CN^- ions. The K_a value for NH_4^+ is 5.6×10^{-10} and

$$K_b(\text{for CN}^-) = \frac{K_w}{K_a\,(\text{for HCN})} = 1.6 \times 10^{-5}$$

Since K_b for CN^- is much larger than K_a for NH_4^+, CN^- is a much stronger base than NH_4^+ is an acid. This solution will be basic.

c. The solution will contain $Al(H_2O)_6^{3+}$ and SO_4^{2-} ions. The K_a value for $Al(H_2O)_6^{3+}$ is 1.4×10^{-5}, as given in Sample Exercise 14.20. We must calculate K_b for SO_4^{2-}. The HSO_4^- ion is the conjugate acid of SO_4^{2-}, and its K_a value is K_{a_2} for sulfuric acid, or 1.2×10^{-2}. Therefore,

$$K_b\,(\text{for SO}_4^{\,2-}) = \frac{K_w}{K_{a_2}\,(\text{for sulfuric acid})} = \frac{1.0 \times 10^{-14}}{1.2 \times 10^{-2}} = 8.3 \times 10^{-13}$$

This solution will be acidic, since K_a for $Al(H_2O)_6^{3+}$ is much greater than K_b for SO_4^{2-}.

See Exercises 14.111 and 14.112.

The acid–base properties of aqueous solutions of various salts are summarized in Table 14.6.

TABLE 14.6 Acid–Base Properties of Various Types of Salts

Type of Salt	Examples	Comment	pH of Solution
Cation is from strong base; anion is from strong acid	KCl, KNO_3, NaCl, $NaNO_3$	Neither acts as an acid or a base	Neutral
Cation is from strong base; anion is from weak acid	$NaC_2H_3O_2$, KCN, NaF	Anion acts as a base; cation has no effect on pH	Basic
Cation is conjugate acid of weak base; anion is from strong acid	NH_4Cl, NH_4NO_3	Cation acts as acid; anion has no effect on pH	Acidic
Cation is conjugate acid of weak base; anion is conjugate base of weak acid	$NH_4C_2H_3O_2$, NH_4CN	Cation acts as an acid; anion acts as a base	Acidic if $K_a > K_b$, basic if $K_b > K_a$, neutral if $K_a = K_b$
Cation is highly charged metal ion; anion is from strong acid	$Al(NO_3)_3$, $FeCl_3$	Hydrated cation acts as an acid; anion has no effect on pH	Acidic

14.9 The Effect of Structure on Acid–Base Properties

Further aspects of acid strengths are discussed in Section 20.7.

TABLE 14.7 Bond Strengths and Acid Strengths for Hydrogen Halides

H—X Bond	Bond Strength (kJ/mol)	Acid Strength in Water
H—F	565	Weak
H—Cl	427	Strong
H—Br	363	Strong
H—I	295	Strong

We have seen that when a substance is dissolved in water, it produces an acidic solution if it can donate protons and produces a basic solution if it can accept protons. What structural properties of a molecule cause it to behave as an acid or as a base?

Any molecule containing a hydrogen atom is potentially an acid. However, many such molecules show no acidic properties. For example, molecules containing C—H bonds, such as chloroform ($CHCl_3$) and nitromethane (CH_3NO_2), do not produce acidic aqueous solutions because a C—H bond is both strong and nonpolar and thus there is no tendency to donate protons. On the other hand, although the H—Cl bond in gaseous hydrogen chloride is slightly stronger than a C—H bond, it is much more polar, and this molecule readily dissociates when dissolved in water.

Thus there are two main factors that determine whether a molecule containing an X—H bond will behave as a Brønsted–Lowry acid: the strength of the bond and the polarity of the bond.

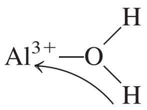
To explore these factors let's consider the relative acid strengths of the hydrogen halides. The bond polarities vary as shown

$$\underset{\substack{\uparrow \\ \text{Most polar}}}{\text{H—F}} > \text{H—Cl} > \text{H—Br} > \underset{\substack{\uparrow \\ \text{Least polar}}}{\text{H—I}}$$

because electronegativity decreases going down the group. Based on the high polarity of the H—F bond, we might expect hydrogen fluoride to be a very strong acid. In fact, among HX molecules, HF is the only weak acid ($K_a = 7.2 \times 10^{-4}$) when dissolved in water. The H—F bond is unusually strong, as shown in Table 14.7, and thus is difficult to break. This contributes significantly to the reluctance of the HF molecules to dissociate in water.

Another important class of acids are the oxyacids, which as we saw in Section 14.2 characteristically contain the grouping H—O—X. Several series of oxyacids are listed with their K_a values in Table 14.8. Note from these data that for a given series the acid strength increases with an increase in the number of oxygen atoms attached to the central atom. For example, in the series containing chlorine and a varying number of oxygen atoms, HOCl is a weak acid, but the acid strength is successively greater as the number of oxygen atoms increases. This happens because the very electronegative oxygen atoms are able to draw electrons away from the chlorine atom and the O—H bond, as shown in Fig. 14.11. The net effect is to both polarize and weaken the O—H bond; this effect becomes more important as the number of attached oxygen atoms increases. This means that a proton is most readily produced by the molecule with the largest number of attached oxygen atoms ($HClO_4$).

This type of behavior is also observed for hydrated metal ions. Earlier in this chapter we saw that highly charged metal ions such as Al^{3+} produce acidic solutions. The acidity of the water molecules attached to the metal ion is increased by the attraction of electrons to the positive metal ion:



The greater the charge on the metal ion, the more acidic the hydrated ion becomes.

For acids containing the H—O—X grouping, the greater the ability of X to draw electrons toward itself, the greater the acidity of the molecule. Since the electronegativity of X reflects its ability to attract the electrons involved in bonding, we might expect acid strength to depend on the electronegativity of X. In fact, there is an excellent correlation between the electronegativity of X and the acid strength for oxyacids, as shown in Table 14.9.

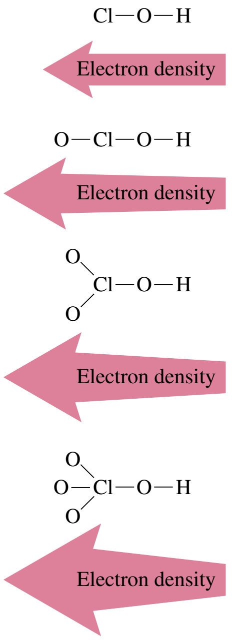


FIGURE 14.11
The effect of the number of attached oxygens on the O—H bond in a series of chlorine oxyacids. As the number of oxygen atoms attached to the chlorine atom increases, they become more effective at withdrawing electron density from the O—H bond, thereby weakening and polarizing it. This increases the tendency for the molecule to produce a proton, and so its acid strength increases.

TABLE 14.8 Several Series of Oxyacids and Their K_a Values

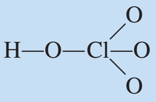
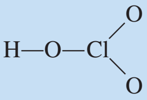
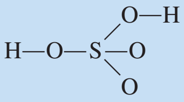
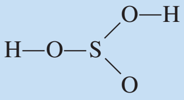
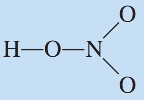
Oxyacid	Structure	K_a Value
$HClO_4$		Large (~10^7)
$HClO_3$		~1
$HClO_2$	H—O—Cl—O	1.2×10^{-2}
HClO	H—O—Cl	3.5×10^{-8}
H_2SO_4		Large
H_2SO_3		1.5×10^{-2}
HNO_3		Large
HNO_2	H—O—N—O	4.0×10^{-4}

TABLE 14.9 Comparison of Electronegativity of X and K_a Value for a Series of Oxyacids

Acid	X	Electronegativity of X	K_a for Acid
HOCl	Cl	3.0	4×10^{-8}
HOBr	Br	2.8	2×10^{-9}
HOI	I	2.5	2×10^{-11}
$HOCH_3$	CH_3	2.3 (for carbon in CH_3)	$\sim 10^{-15}$

14.10 Acid–Base Properties of Oxides

We have just seen that molecules containing the grouping H—O—X can behave as acids and that the acid strength depends on the electron-withdrawing ability of X. But substances with this grouping also can behave as bases if the hydroxide ion instead of a proton is produced. What determines which behavior will occur? The answer lies mainly in the nature of the O—X bond. If X has a relatively high electronegativity, the O—X bond will be covalent and strong. When the compound containing the H—O—X grouping is dissolved in water, the O—X bond will remain intact. It will be the polar and relatively weak H—O bond that will tend to break, releasing a proton. On the other hand, if X has

A compound containing the H—O—X group will produce an acidic solution in water if the O—X bond is strong and covalent. If the O—X bond is ionic, the compound will produce a basic solution in water.

a very low electronegativity, the O—X bond will be ionic and subject to being broken in polar water. Examples are the ionic substances NaOH and KOH that dissolve in water to give the metal cation and the hydroxide ion.

We can use these principles to explain the acid–base behavior of oxides when they are dissolved in water. For example, when a covalent oxide such as sulfur trioxide is dissolved in water, an acidic solution results because sulfuric acid is formed:

$$SO_3(g) + H_2O(l) \longrightarrow H_2SO_4(aq)$$

The structure of H_2SO_4 is shown in the margin. In this case, the strong, covalent O—S bonds remain intact and the H—O bonds break to produce protons. Other common covalent oxides that react with water to form acidic solutions are sulfur dioxide, carbon dioxide, and nitrogen dioxide, as shown by the following reactions:

$$SO_2(g) + H_2O(l) \longrightarrow H_2SO_3(aq)$$
$$CO_2(g) + H_2O(l) \longrightarrow H_2CO_3(aq)$$
$$2NO_2(g) + H_2O(l) \longrightarrow HNO_3(aq) + HNO_2(aq)$$

Thus, when a covalent oxide dissolves in water, an acidic solution forms. These oxides are called **acidic oxides.**

On the other hand, when an ionic oxide dissolves in water, a basic solution results, as shown by the following reactions:

$$CaO(s) + H_2O(l) \longrightarrow Ca(OH)_2(aq)$$
$$K_2O(s) + H_2O(l) \longrightarrow 2KOH(aq)$$

These reactions can be explained by recognizing that the oxide ion has a high affinity for protons and reacts with water to produce hydroxide ions:

$$O^{2-}(aq) + H_2O(l) \longrightarrow 2OH^-(aq)$$

Thus the most ionic oxides, such as those of the Group 1A and 2A metals, produce basic solutions when they are dissolved in water. As a result, these oxides are called **basic oxides.**

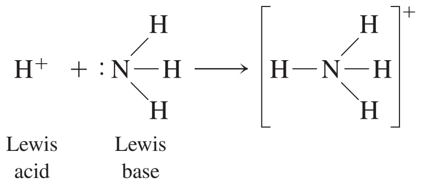
14.11 The Lewis Acid–Base Model

We have seen that the first successful conceptualization of acid–base behavior was proposed by Arrhenius. This useful but limited model was replaced by the more general Brønsted–Lowry model. An even more general model for acid–base behavior was suggested by G. N. Lewis in the early 1920s. A **Lewis acid** is an *electron-pair acceptor,* and a **Lewis base** is an *electron-pair donor.* Another way of saying this is that a Lewis acid has an empty atomic orbital that it can use to accept (share) an electron pair from a molecule that has a lone pair of electrons (Lewis base). The three models for acids and bases are summarized in Table 14.10.

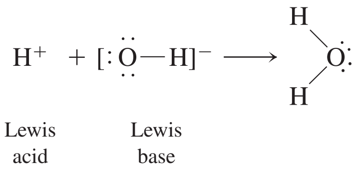
TABLE 14.10 Three Models for Acids and Bases

Model	Definition of Acid	Definition of Base
Arrhenius	H^+ producer	OH^- producer
Brønsted–Lowry	H^+ donor	H^+ acceptor
Lewis	Electron-pair acceptor	Electron-pair donor

Note that Brønsted–Lowry acid–base reactions (proton donor–proton acceptor reactions) are encompassed by the Lewis model. For example, the reaction between a proton and an ammonia molecule, that is,

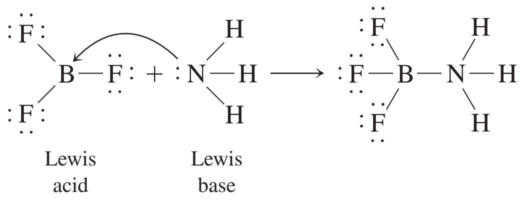


can be represented as a reaction between an electron-pair acceptor (H^+) and an electron-pair donor (NH_3). The same holds true for a reaction between a proton and a hydroxide ion:



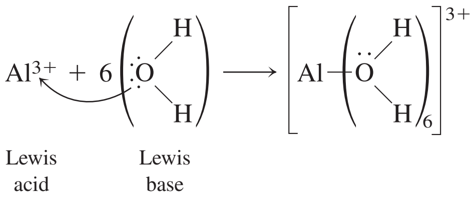
The Lewis model encompasses the Brønsted–Lowry model, but the reverse is not true.

The real value of the Lewis model for acids and bases is that it covers many reactions that do not involve Brønsted–Lowry acids. For example, consider the gas-phase reaction between boron trifluoride and ammonia.



Here the electron-deficient BF_3 molecule (there are only six electrons around the boron) completes its octet by reacting with NH_3, which has a lone pair of electrons. (see Fig. 14.12.) In fact, as mentioned in Chapter 8, the electron deficiency of boron trifluoride makes it very reactive toward any electron-pair donor. That is, it is a strong Lewis acid.

The hydration of a metal ion, such as Al^{3+}, also can be viewed as a Lewis acid–base reaction:



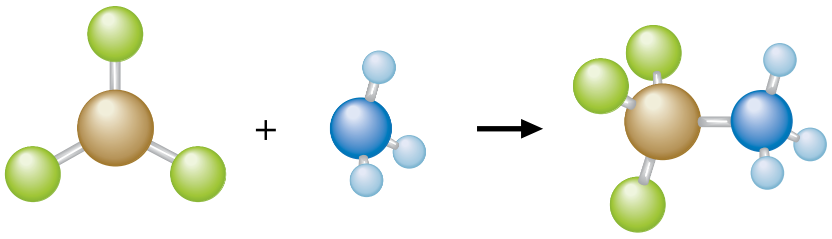


FIGURE 14.12
Reaction of BF_3 with NH_3.

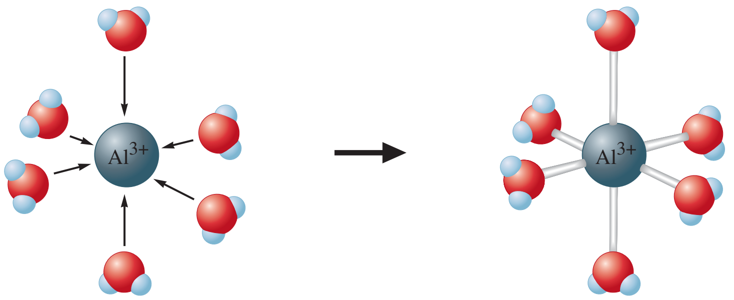
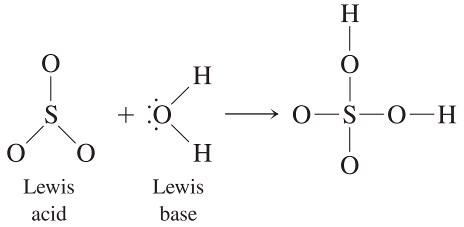


FIGURE 14.13
The $Al(H_2O)_6^{3+}$ ion.

Here the Al^{3+} ion accepts one electron pair from each of six water molecules to form $Al(H_2O)_6^{3+}$ (see Fig. 14.13).

In addition, the reaction between a covalent oxide and water to form a Brønsted–Lowry acid can be defined as a Lewis acid–base reaction. An example is the reaction between sulfur trioxide and water:



Note that as the water molecule attaches to sulfur trioxide, a proton shift occurs to form sulfuric acid.

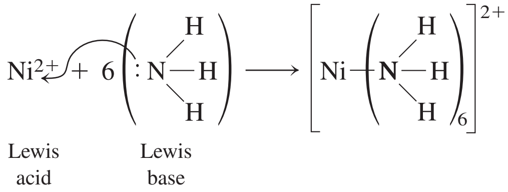
Sample Exercise 14.22 Lewis Acids and Bases

For each reaction, identify the Lewis acid and base.

a. $Ni^{2+}(aq) + 6NH_3(aq) \longrightarrow Ni(NH_3)_6^{2+}(aq)$
b. $H^+(aq) + H_2O(aq) \rightleftharpoons H_3O^+(aq)$

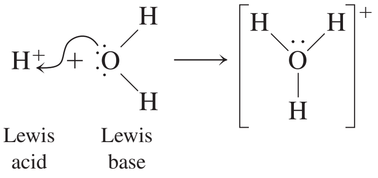
Solution

a. Each NH_3 molecule donates an electron pair to the Ni^{2+} ion:



The nickel(II) ion is the Lewis acid, and ammonia is the Lewis base.

b. The proton is the Lewis acid and the water molecule is the Lewis base:



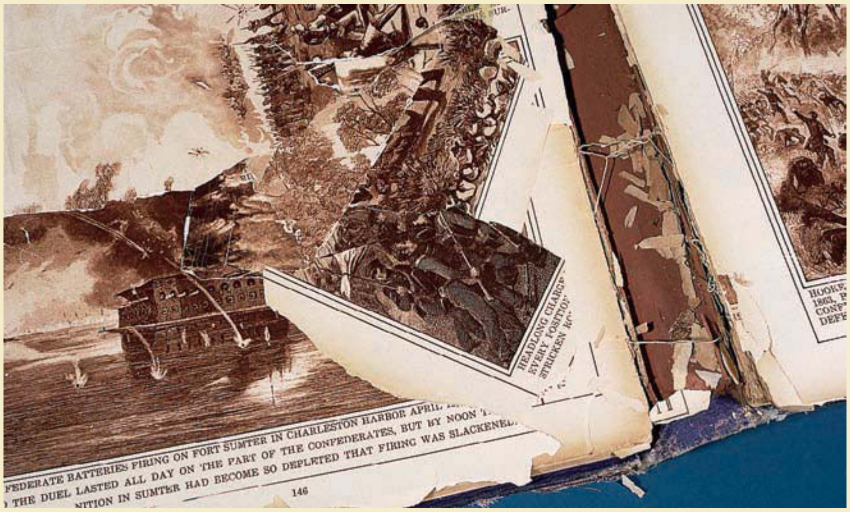
See Exercises 14.119 and 14.120.

CHEMICAL IMPACT

Self-Destructing Paper

The New York City Public Library has 88 miles of bookshelves, and on 36 miles of these shelves the books are quietly disintegrating between their covers. In fact, an estimated 40% of the books in the major research collections in the United States will soon be too fragile to handle.

The problem results from the acidic paper widely used in printing books in the past century. Ironically, books from the eighteenth, seventeenth, sixteenth, and even fifteenth century are in much better shape. Gutenberg Bibles contain paper that is in remarkably good condition. In those days, paper was made by hand from linen or rags, but in the nineteenth century, the demand for cheap paper skyrocketed. Paper manufacturers found that paper could be made economically, by machine, using wood pulp. To size the paper (that is, fill in microscopic holes to lower absorption of moisture and prevent seeping or spreading of inks), alum [$Al_2(SO_4)_3$] was added in large amounts. Because the hydrated aluminum ion [$Al(H_2O)_6^{3+}$] is an acid ($K_a \approx 10^{-5}$), paper manufactured using alum is quite acidic.



A book ravaged by the decomposition of acidic paper.

14.12 Strategy for Solving Acid–Base Problems: A Summary

In this chapter we have encountered many different situations involving aqueous solutions of acids and bases, and in the next chapter we will encounter still more. In solving for the equilibrium concentrations in these aqueous solutions, it is tempting to create a pigeonhole for each possible situation and to memorize the procedures necessary to deal with that particular case. This approach is just not practical and usually leads to frustration: Too many pigeonholes are required—there seems to be an infinite number of cases. But you can handle any case successfully by taking a systematic, patient, and thoughtful approach. When analyzing an acid–base equilibrium problem, do *not* ask yourself how a memorized solution can be used to solve the problem. Instead, ask this question: *What are the major species in the solution and what is their chemical behavior?*

The most important part of doing a complicated acid–base equilibrium problem is the analysis you do at the beginning of a problem.

What major species are present?

Does a reaction occur that can be assumed to go to completion?

What equilibrium dominates the solution?

Let the problem guide you. Be patient.

The following steps outline a general strategy for solving problems involving acid–base equilibria.

Over time this acidity causes the paper fibers to disintegrate; the pages of books fall apart when they are used.

One could transfer the contents of the threatened books to microfilm, but that would be a very slow and expensive process. Can the books be chemically treated to neutralize the acid and stop the deterioration? Yes. In fact, you know enough chemistry at this point to design the treatment patented in 1936 by Otto Schierholz. He dipped individual pages in solutions of alkaline earth bicarbonate salts [$Mg(HCO_3)_2$, $Ca(HCO_3)_2$, and so on]. The HCO_3^- ions present in these solutions react with the H^+ in the paper to give CO_2 and H_2O. This treatment works well and is used today to preserve especially important works, but it is slow and labor-intensive.

It would be much more economical if large numbers of books could be treated at one time without disturbing the bindings. However, soaking entire books in an aqueous solution is out of the question. A logical question then is: Are there gaseous bases that could be used to neutralize the acid? Certainly; the organic amines (general formula, RNH_2) are bases, and those with low molar masses are gases under normal conditions. Experiments in which books were treated using ammonia, butylamine ($CH_3CH_2CH_2CH_2NH_2$), and other amines have shown that the method works, but only for a short time. The amines do enter the paper and neutralize the acid, but being volatile, they gradually evaporate, leaving the paper in its original acidic condition.

A much more effective treatment involves diethylzinc [$(CH_3CH_2)_2Zn$], which boils at 117°C and 1 atm. Diethylzinc (DEZ) reacts with oxygen or water to produce ZnO as follows:

$$(CH_3CH_2)_2Zn(g) + 7O_2(g) \longrightarrow ZnO(s) + 4CO_2(g) + 5H_2O(g)$$

$$(CH_3CH_2)_2Zn(g) + H_2O(g) \longrightarrow ZnO(s) + 2CH_3CH_3(g)$$

The solid zinc oxide produced in these reactions is deposited among the paper fibers, and being a basic oxide, it neutralizes the acid present as shown in the equation

$$ZnO + 2H^+ \longrightarrow Zn^{2+} + H_2O$$

One major problem is that DEZ ignites spontaneously on contact with air. Therefore, this treatment must be carried out in a chamber filled mainly with $N_2(g)$, where the amount of O_2 present can be rigorously controlled. The pressure in the chamber must be maintained well below one atmosphere both to lower the boiling point of DEZ and to remove excess moisture from the book's pages. Several major DEZ fires have slowed its implementation as a book preservative. However, the Library of Congress has designed a new DEZ treatment plant that includes a chamber large enough for approximately 9000 books to be treated at one time.

Solving Acid–Base Problems

➥ 1 **List the major species in solution.**

➥ 2 **Look for reactions that can be assumed to go to completion—for example, a strong acid dissociating or H^+ reacting with OH^-.**

➥ 3 **For a reaction that can be assumed to go to completion:**
  a. **Determine the concentration of the products.**
  b. **Write down the major species in solution after the reaction.**

➥ 4 **Look at each major component of the solution and decide if it is an acid or a base.**

➥ 5 **Pick the equilibrium that will control the pH. Use known values of the dissociation constants for the various species to help decide on the dominant equilibrium.**
  a. **Write the equation for the reaction and the equilibrium expression.**
  b. **Compute the initial concentrations (assuming the dominant equilibrium has not yet occurred, that is, no acid dissociation, and so on).**
  c. **Define *x*.**
  d. **Compute the equilibrium concentrations in terms of *x*.**
  e. **Substitute the concentrations into the equilibrium expression, and solve for *x*.**
  f. **Check the validity of the approximation.**
  g. **Calculate the pH and other concentrations as required.**

Although these steps may seem somewhat cumbersome, especially for simpler problems, they will become increasingly helpful as the aqueous solutions become more complicated. If you develop the habit of approaching acid–base problems systematically, the more complex cases will be much easier to manage.

Key Terms

Section 14.1

Arrhenius concept
Brønsted–Lowry model
hydronium ion
conjugate base
conjugate acid
conjugate acid–base pair
acid dissociation constant

Section 14.2

strong acid
weak acid
diprotic acid
oxyacids
organic acids
carboxyl group
monoprotic acids
amphoteric substance
autoionization
ion-product (dissociation) constant

Section 14.3

pH scale

Section 14.4

major species

Section 14.5

percent dissociation

Section 14.6

strong bases
slaked lime
lime–soda process
weak bases
amine

Section 14.7

polyprotic acid
triprotic acid

Section 14.8

salt

Section 14.10

acidic oxides
basic oxides

Section 14.11

Lewis acid
Lewis base

For Review

Models for acids and bases

- Arrhenius model
  - Acids produce H^+ in solution
  - Bases produce OH^- in solution
- Brønsted–Lowry model
  - An acid is a proton donor
  - A base is a proton acceptor
  - In this model an acid molecule reacts with a water molecule, which behaves as a base:

$$\underset{\text{Acid}}{HA(aq)} + \underset{\text{Base}}{H_2O(l)} \rightleftharpoons \underset{\substack{\text{Conjugate}\\ \text{acid}}}{H_3O^+(aq)} + \underset{\substack{\text{Conjugate}\\ \text{base}}}{A^-(aq)}$$

  to form a new acid (conjugate acid) and a new base (conjugate base).

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

Acid–base equilibrium

- The equilibrium constant for an acid dissociating (ionizing) in water is called K_a
- The K_a expression is

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

which is often simplified as

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

  - $[H_2O]$ is never included because it is assumed to be constant

Acid strength

- A strong acid has a very large K_a value
  - The acid completely dissociates (ionizes) in water
  - The dissociation (ionization) equilibrium position lies all the way to the right
  - Strong acids have very weak conjugate bases
  - The common strong acids are nitric acid $[HNO_3(aq)]$, hydrochloric acid $[HCl(aq)]$, sulfuric acid $[H_2SO(aq)]$ and perchloric acid $[HClO_4(aq)]$
- A weak acid has a small K_a value
  - The acid dissociates (ionizes) to only a slight extent
  - The dissociation (ionization) equilibrium position lies far to the left
  - Weak acids have relatively strong conjugate bases
  - Percent dissociation of a weak acid

$$\%\ \text{dissociation} = \frac{\text{amount dissociated (mol/L)}}{\text{initial concentration (mol/L)}} \times 100\%$$

    - The smaller the percent dissociation, the weaker the acid
    - Dilution of a weak acid increases its percent dissociation

Autoionization of water

- Water is an amphoteric substance: it behaves as both an acid and a base
- Water reacts with itself in an acid–base reaction

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

which leads to the equilibrium expression

$$K_w = [H_3O^+][OH^-] \quad \text{or} \quad [H^+][OH^-] = K_w$$

  - K_w is the ion-product constant for water
  - At 25°C in pure water $[H^+] = [OH^-] = 1.0 \times 10^{-7}$, so $K_w = 1.0 \times 10^{-14}$
- Acidic solution: $[H^+] > [OH^-]$
- Basic solution: $[OH^-] > [H^+]$
- Neutral solution: $[H^+] = [OH^-]$

The pH scale

- $pH = -\log [H^+]$
- Since pH is a log scale, the pH changes by 1 for every 10-fold change in $[H^+]$
- The log scale is also used for $[OH^-]$ and for K_a values

$$pOH = -\log[OH^-]$$

$$pK_a = -\log K_a$$

Bases

- Strong bases are hydroxide salts, such as NaOH and KOH
- Weak bases react with water to produce OH^-

$$B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq)$$

  - The equilibrium constant for this reaction is called K_b where

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

  - In water a base B is always competing with OH^- for a proton (H^+), so K_b values tend to be very small, thus making B a weak base (compared to OH^-)

Polyprotic acids

- A polyprotic acid has more than one acidic proton
- Polyprotic acids dissociate one proton at a time
  - Each step has a characteristic K_a value
  - Typically for a weak polyprotic acid, $K_{a_1} > K_{a_2} > K_{a_3}$
- Sulfuric acid is unique
  - It is a strong acid in the first dissociation step (K_{a_1} is very large)
  - It is a weak acid in the second step

Acid–base properties of salts

- Can produce acidic, basic, or neutral solutions
- Salts that contain:
  - Cations of strong bases and anions of strong acids produce neutral solutions
  - Cations of strong bases and anions of weak acids produce basic solutions
  - Cations of weak bases and anions of strong acids produce acidic solutions
- Acidic solutions are produced by salts containing a highly charged metal cation—for example, Al^{3+} and Fe^{3+}

Effect of structure on acid–base properties

- Many substances that function as acids or bases contain the H—O—X grouping
  - Molecules in which the O—X bond is strong and covalent tend to behave as acids
    - As X becomes more electronegative, the acid becomes stronger
  - When the O—X bond is ionic, the substance behaves as a base, releasing OH^- ions in water

REVIEW QUESTIONS

1. Define each of the following:
   a. Arrhenius acid
   b. Brønsted–Lowry acid
   c. Lewis acid

   Which of the definitions is most general? Write reactions to justify your answer.
2. Define or illustrate the meaning of the following terms:
   a. K_a reaction
   b. K_a equilibrium constant
   c. K_b reaction
   d. K_b equilibrium constant
   e. conjugate acid–base pair
3. Define or illustrate the meaning of the following terms:
   a. amphoteric
   b. K_w reaction
   c. K_w equilibrium constant
   d. pH
   e. pOH
   f. pK_w

   Give the conditions for a neutral solution at 25°C, in terms of $[H^+]$, pH, and the relationship between $[H^+]$ and $[OH^-]$. Do the same for an acidic solution and for a basic solution. As a solution becomes more acidic, what happens to pH, pOH, $[H^+]$, and $[OH^-]$? As a solution becomes more basic, what happens to pH, pOH, $[H^+]$, and $[OH^-]$?
4. How is acid strength related to the value of K_a? What is the difference between strong acids versus weak acids (see Table 14.1)? As the strength of an acid increases, what happens to the strength of the conjugate base? How is base strength related to the value of K_b? As the strength of a base increases, what happens to the strength of the conjugate acid?
5. Two strategies are followed when solving for the pH of an acid in water. What is the strategy for calculating the pH of a strong acid in water? What major assumptions are made when solving strong acid problems? The best way to recognize strong acids is to memorize them. List the six common strong acids (the two not listed in the text are HBr and HI).

   Most acids, by contrast, are weak acids. When solving for the pH of a weak acid in water, you must have the K_a value. List two places in this text that provide K_a values for weak acids. You can utilize these tables to help you recognize weak acids. What is the strategy for calculating the pH of a weak acid in water? What assumptions are generally made? What is the 5% rule? If the 5% rule fails, how do you calculate the pH of a weak acid in water?
6. Two strategies are also followed when solving for the pH of a base in water. What is the strategy for calculating the pH of a strong base in water? List the strong bases mentioned in the text that should be committed to memory. Why is calculating the pH of $Ca(OH)_2$ solutions a little more difficult than calculating the pH of NaOH solutions?

   Most bases are weak bases. The presence of what element most commonly results in basic properties for an organic compound? What is present on this element in compounds that allows it to accept a proton?

   Table 14.3 and Appendix 5 of the text list K_b values for some weak bases. What strategy is used to solve for the pH of a weak base in water? What assumptions are made when solving for the pH of weak base solutions? If the 5% rule fails, how do you calculate the pH of a weak base in water?

7. Table 14.4 lists the stepwise K_a values for some polyprotic acids. What is the difference between a monoprotic acid, a diprotic acid, and a triprotic acid? Most polyprotic acids are weak acids; the major exception is H_2SO_4. To solve for the pH of a solution of H_2SO_4, you must solve a strong acid problem as well as a weak acid problem. Explain. Write out the reactions that refer to K_{a_1} and K_{a_2} for H_2SO_4.

   For H_3PO_4, $K_{a_1} = 7.5 \times 10^{-3}$, $K_{a_2} = 6.2 \times 10^{-8}$, and $K_{a_3} = 4.8 \times 10^{-13}$. Write out the reactions that refer to the K_{a_1}, K_{a_2}, and K_{a_3} equilibrium constants. What are the three acids in a solution of H_3PO_4? Which acid is strongest? What are the three conjugate bases in a solution of H_3PO_4? Which conjugate base is strongest? Summarize the strategy for calculating the pH of a polyprotic acid in water.

8. For conjugate acid–base pairs, how are K_a and K_b related? Consider the reaction of acetic acid in water

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons CH_3CO_2^-(aq) + H_3O^+(aq)$$

   where $K_a = 1.8 \times 10^{-5}$.
   a. Which two bases are competing for the proton?
   b. Which is the stronger base?
   c. In light of your answer to part b, why do we classify the acetate ion ($CH_3CO_2^-$) as a weak base? Use an appropriate reaction to justify your answer.

   In general, as base strength increases, conjugate acid strength decreases. Explain why the conjugate acid of the weak base NH_3 is a weak acid.

   To summarize, the conjugate base of a weak acid is a weak base and the conjugate acid of a weak base is a weak acid (weak gives you weak). Assuming K_a for a monoprotic strong acid is 1×10^6, calculate K_b for the conjugate base of this strong acid. Why do conjugate bases of strong acids have no basic properties in water? List the conjugate bases of the six common strong acids. To tie it all together, some instructors have students think of Li^+, K^+, Rb^+, Cs^+, Ca^{2+}, Sr^{2+}, and Ba^{2+} as the conjugate acids of the strong bases LiOH, KOH, RbOH, CsOH, $Ca(OH)_2$, $Sr(OH)_2$, and $Ba(OH)_2$. Although not technically correct, the conjugate acid strength of these cations is similar to the conjugate base strength of the strong acids. That is, these cations have no acidic properties in water; similarly, the conjugate bases of strong acids have no basic properties (strong gives you worthless). Fill in the blanks with the correct response. The conjugate base of a weak acid is a ____________ base. The conjugate acid of a weak base is a ____________ acid. The conjugate base of a strong acid is a ____________ base. The conjugate acid of a strong base is a ____________ acid. (*Hint:* Weak gives you weak and strong gives you worthless.)

9. What is a salt? List some anions that behave as weak bases in water. List some anions that have no basic properties in water. List some cations that behave as weak acids in water. List some cations that have no acidic properties in water. Using these lists, give some formulas for salts that have only weak base properties in water. What strategy would you use to solve for the pH of these basic salt solutions? Identify some salts that have only weak acid properties in water. What strategy would you use to solve for the pH of these acidic salt solutions? Identify some salts that have no acidic or basic properties in water (produce neutral solutions). When a salt contains both a weak acid ion and a weak base ion, how do you predict whether the solution pH is acidic, basic, or neutral?

10. For oxyacids, how does acid strength depend on
    a. the strength of the bond to the acidic hydrogen atom?
    b. the electronegativity of the element bonded to the oxygen atom that bears the acidic hydrogen?
    c. the number of oxygen atoms?

    How does the strength of a conjugate base depend on these factors?

    What type of solution forms when a nonmetal oxide dissolves in water? Give an example of such an oxide. What type of solution forms when a metal oxide dissolves in water? Give an example of such an oxide.

Active Learning Questions

These questions are designed to be used by groups of students in class. The questions allow students to explore their understanding of concepts through discussion and peer teaching. The real value of these questions is the learning that occurs while students talk to each other about chemical concepts.

1. Consider two beakers of pure water at different temperatures. How do their pH values compare? Which is more acidic? more basic? Explain.

2. Differentiate between the terms *strength* and *concentration* as they apply to acids and bases. When is HCl strong? Weak? Concentrated? Dilute? Answer the same questions for ammonia. Is the conjugate base of a weak acid a strong base?

3. Sketch two graphs: (a) percent dissociation for weak acid HA versus the initial concentration of HA ($[HA]_0$) and (b) H^+ concentration versus $[HA]_0$. Explain both.

4. Consider a solution prepared by mixing a weak acid HA and HCl. What are the major species? Explain what is occurring in solution. How would you calculate the pH? What if you added NaA to this solution? Then added NaOH?

5. Explain why salts can be acidic, basic, or neutral, and show examples. Do this without specific numbers.

6. Consider two separate aqueous solutions: one of a weak acid HA and one of HCl. Assuming you started with 10 molecules of each:

- **a.** Draw a picture of what each solution looks like at equilibrium.
- **b.** What are the major species in each beaker?
- **c.** From your pictures, calculate the K_a values of each acid.
- **d.** Order the following from the strongest to the weakest base: H_2O, A^-, Cl^-. Explain your order.

7. You are asked to calculate the H^+ concentration in a solution of NaOH(*aq*). Because sodium hydroxide is a base, can we say there is no H^+, since having H^+ would imply that the solution is acidic?

8. Consider a solution prepared by mixing a weak acid HA, HCl, and NaA. Which of the following statements best describes what happens?

- **a.** The H^+ from the HCl reacts completely with the A^- from the NaA. Then the HA dissociates somewhat.
- **b.** The H^+ from the HCl reacts somewhat with the A^- from the NaA to make HA, while the HA is dissociating. Eventually you have equal amounts of everything.
- **c.** The H^+ from the HCl reacts somewhat with the A^- from the NaA to make HA while the HA is dissociating. Eventually all the reactions have equal rates.
- **d.** The H^+ from the HCl reacts completely with the A^- from the NaA. Then the HA dissociates somewhat until "too much" H^+ and A^- are formed, so the H^+ and A^- react to form HA, and so on. Eventually equilibrium is reached.

Justify your choice, and for choices you did not pick, explain what is wrong with them.

9. Consider a solution formed by mixing 100.0 mL of 0.10 *M* HA ($K_a = 1.0 \times 10^{-6}$), 100.00 mL of 0.10 *M* NaA, and 100.0 mL of 0.10 *M* HCl. In calculating the pH for the final solution, you would make some assumptions about the order in which various reactions occur to simplify the calculations. State these assumptions. Does it matter whether the reactions actually occur in the assumed order? Explain.

10. A certain sodium compound is dissolved in water to liberate Na^+ ions and a certain negative ion. What evidence would you look for to determine whether the anion is behaving as an acid or a base? How could you tell whether the anion is a strong base? Explain how the anion could behave simultaneously as an acid and a base.

11. Acids and bases can be thought of as chemical opposites (acids are proton donors, and bases are proton acceptors). Therefore, one might think that $K_a = 1/K_b$. Why isn't this the case? What is the relationship between K_a and K_b? Prove it with a derivation.

12. Consider two solutions of the salts NaX(*aq*) and NaY(*aq*) at equal concentrations. What would you need to know to determine which solution has the higher pH? Explain how you would decide (perhaps even provide a sample calculation).

13. What is meant by *pH*? True or false: A strong acid solution always has a lower pH than a weak acid solution. Explain.

14. Why is the pH of water at 25°C equal to 7.00?

15. Can the pH of a solution be negative? Explain.

A blue question or exercise number indicates that the answer to that question or exercise appears at the back of this book and a solution appears in the *Solutions Guide.*

Questions

16. Why is H_3O^+ the strongest acid and OH^- the strongest base that can exist in significant amounts in aqueous solutions?

17. How many significant figures are there in the numbers: 10.78, 6.78, 0.78? If these were pH values, to how many significant figures can you express the $[H^+]$? Explain any discrepancies between your answers to the two questions.

18. In terms of orbitals and electron arrangements, what must be present for a molecule or an ion to act as a Lewis acid? What must be present for a molecule or an ion to act as a Lewis base?

19. Give three example solutions that fit each of the following descriptions.

- **a.** A strong electrolyte solution that is very acidic.
- **b.** A strong electrolyte solution that is slightly acidic.
- **c.** A strong electrolyte solution that is very basic.
- **d.** A strong electrolyte solution that is slightly basic.
- **e.** A strong electrolyte solution that is neutral.

20. Derive an expression for the relationship between pK_a and pK_b for a conjugate acid–base pair. ($pK = -\log K$.)

21. Consider the following statements. Write out an example reaction and K expression that is associated with each statement.

- **a.** The autoionization of water.
- **b.** An acid reacts with water to produce the conjugate base of the acid and the hydronium ion.
- **c.** A base reacts with water to produce the conjugate acid of the base and the hydroxide ion.

22. Which of the following statements is(are) true? Correct the false statements.

- **a.** When a base is dissolved in water, the lowest possible pH of the solution is 7.0.
- **b.** When an acid is dissolved in water, the lowest possible pH is 0.
- **c.** A strong acid solution will have a lower pH than a weak acid solution.
- **d.** A 0.0010 M $Ba(OH)_2$ solution has a pOH that is twice the pOH value of a 0.0010 M KOH solution.

23. Consider the following mathematical expressions.

- **a.** $[H^+] = [HA]_o$
- **b.** $[H^+] = (K_a \times [HA]_o)^{1/2}$
- **c.** $[OH^-] = 2[B]_o$
- **d.** $[OH^-] = (K_b \times [B]_o)^{1/2}$

For each expression, give three solutions where the mathematical expression would give a good approximation for the $[H^+]$ or $[OH^-]$. $[Ha_o]$ and $[B]$ represent initial concentrations of an acid or a base.

24. Consider a 0.10 M H_2CO_3 solution and a 0.10 M H_2SO_4 solution. Without doing any detailed calculations, choose one of the following statements that best describes the $[H^+]$ of each solution and explain your answer.

- **a.** The $[H^+]$ is less than 0.10 M.
- **b.** The $[H^+]$ is 0.10 M.
- **c.** The $[H^+]$ is between 0.10 M and 0.20 M.
- **d.** The $[H^+]$ is 0.20 M.

25. Of the hydrogen halides, only HF is a weak acid. Give a possible explanation.

26. Explain why the following are done, both of which are related to acid/base chemistry.

- **a.** Power plants burning coal with high sulfur content use scrubbers to help eliminate sulfur emissions.
- **b.** A gardener mixes lime (CaO) into the soil of his garden.

Exercises

In this section similar exercises are paired.

Nature of Acids and Bases

27. Write balanced equations that describe the following reactions.

- **a.** the dissociation of perchloric acid in water
- **b.** the dissociation of propanoic acid ($CH_3CH_2CO_2H$) in water
- **c.** the dissociation of ammonium ion in water

28. Write the dissociation reaction and the corresponding K_a equilibrium expression for each of the following acids in water.

- **a.** HCN
- **b.** HOC_6H_5
- **c.** $C_6H_5NH_3^+$

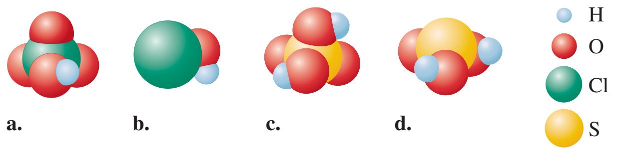
29. For each of the following aqueous reactions, identify the acid, the base, the conjugate base, and the conjugate acid.

- **a.** $H_2O + H_2CO_3 \rightleftharpoons H_3O^+ + HCO_3^-$
- **b.** $C_5H_5NH^+ + H_2O \rightleftharpoons C_5H_5N + H_3O^+$
- **c.** $HCO_3^- + C_5H_5NH^+ \rightleftharpoons H_2CO_3 + C_5H_5N$

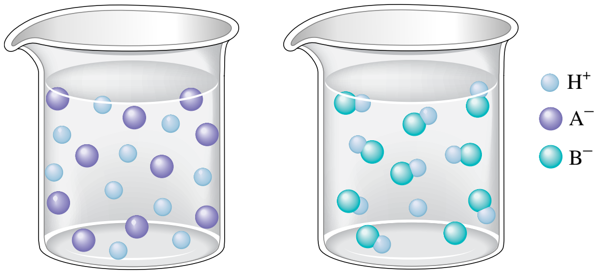
30. For each of the following aqueous reactions, identify the acid, the base, the conjugate base, and the conjugate acid.

- **a.** $Al(H_2O)_6^{3+} + H_2O \rightleftharpoons H_3O^+ + Al(H_2O)_5(OH)^{2+}$
- **b.** $H_2O + HONH_3^+ \rightleftharpoons HONH_2 + H_3O^+$
- **c.** $HOCl + C_6H_5NH_2 \rightleftharpoons OCl^- + C_6H_5NH_3^+$

31. Classify each of the following as a strong acid or a weak acid.



32. Consider the following illustrations:



Which beaker best illustrates what happens when the following acids are dissolved in water?

a. HNO_2 **d.** HF
b. HNO_3 **e.** $HC_2H_3O_2$
c. HCl

33. Use Table 14.2 to order the following from the strongest to the weakest acid.

$HClO_2$, H_2O, NH_4^+, $HClO_4$

34. Use Table 14.2 to order the following from the strongest to the weakest base.

ClO_2^-, H_2O, NH_3, ClO_4^-

35. You may need Table 14.2 to answer the following questions.
a. Which is the stronger acid, HCl or H_2O?
b. Which is the stronger acid, H_2O or HNO_2?
c. Which is the stronger acid, HCN or HOC_6H_5?

36. You may need Table 14.2 to answer the following questions.
a. Which is the stronger base, Cl^- or H_2O?
b. Which is the stronger base, H_2O or NO_2^-?
c. Which is the stronger base, CN^- or $OC_6H_5^-$?

Autoionization of Water and the pH Scale

37. Calculate the $[OH^-]$ of each of the following solutions at 25°C. Identify each solution as neutral, acidic, or basic.
a. $[H^+] = 1.0 \times 10^{-7}\ M$ **c.** $[H^+] = 12\ M$
b. $[H^+] = 8.3 \times 10^{-16}\ M$ **d.** $[H^+] = 5.4 \times 10^{-5}\ M$

38. Calculate the $[H^+]$ of each of the following solutions at 25°C. Identify each solution as neutral, acidic, or basic.
a. $[OH^-] = 1.5\ M$ **c.** $[OH^-] = 1.0 \times 10^{-7}\ M$
b. $[OH^-] = 3.6 \times 10^{-15}\ M$ **d.** $[OH^-] = 7.3 \times 10^{-4}\ M$

39. Values of K_w as a function of temperature are as follows:

Temperature (°C)	K_w
0	1.14×10^{-15}
25	1.00×10^{-14}
35	2.09×10^{-14}
40.	2.92×10^{-14}
50.	5.47×10^{-14}

a. Is the autoionization of water exothermic or endothermic?
b. Calculate $[H^+]$ and $[OH^-]$ in a neutral solution at 50.°C.

40. At 40°C the value of K_w is 2.92×10^{-14}.
a. Calculate the $[H^+]$ and $[OH^-]$ in pure water at 40°C.
b. What is the pH of pure water at 40°C?
c. If the hydroxide ion concentration in a solution is 0.10 M, what is the pH at 40°C?

41. Calculate the pH and pOH of the solutions in Exercises 37 and 38.

42. Calculate $[H^+]$ and $[OH^-]$ for each solution at 25°C. Identify each solution as neutral, acidic, or basic.
a. pH = 7.40 (the normal pH of blood)
b. pH = 15.3
c. pH = −1.0
d. pH = 3.20
e. pOH = 5.0
f. pOH = 9.60

43. Fill in the missing information in the following table.

	pH	pOH	$[H^+]$	$[OH^-]$	Acidic, Basic, or Neutral?
Solution a	6.88	____	____	____	____
Solution b	____	____	____	$8.4 \times 10^{-14}\ M$	____
Solution c	____	3.11	____	____	____
Solution d	____	____	$1.0 \times 10^{-7}\ M$	____	____

44. Fill in the missing information in the following table.

	pH	pOH	$[H^+]$	$[OH^-]$	Acidic, Basic, or Neutral?
Solution a	9.63	____	____	____	____
Solution b	____	____	____	$3.9 \times 10^{-6}\ M$	____
Solution c	____	____	$0.027\ M$	____	____
Solution d	____	12.2	____	____	____

45. The pH of a sample of gastric juice in a person's stomach is 2.1. Calculate the pOH, $[H^+]$, and $[OH^-]$ for this sample. Is gastric juice acidic or basic?

46. The pOH of a sample of baking soda dissolved in water is 5.74 at 25°C. Calculate the pH, $[H^+]$, and $[OH^-]$ for this sample. Is the solution acidic or basic?

Solutions of Acids

47. What are the major species present in 0.250 M solutions of each of the following acids? Calculate the pH of each of these solutions.
a. $HClO_4$ **b.** HNO_3

48. Calculate the pH of each of the following solutions of a strong acid in water.
a. 0.10 M HCl **c.** $1.0 \times 10^{-11}\ M$ HCl
b. 5.0 M HCl

49. A solution is prepared by adding 50.0 mL of 0.050 M HCl to 150.0 mL of 0.10 M HNO_3. Calculate the concentrations of all species in this solution.

50. A solution is prepared by mixing 90.0 mL of 5.00 M HCl and 30.0 mL of 8.00 M HNO_3. Water is then added until the final volume is 1.00 L. Calculate $[H^+]$, $[OH^-]$, and the pH for this solution.

51. How would you prepare 1600 mL of a pH = 1.50 solution using concentrated (12 *M*) HCl?

52. What mass of HNO_3 is present in 250.0 mL of a nitric acid solution having a pH = 5.10?

53. What are the major species present in 0.250 *M* solutions of each of the following acids? Calculate the pH of each of these solutions.

a. HNO_2 **b.** CH_3CO_2H ($HC_2H_3O_2$)

54. What are the major species present in 0.250 *M* solutions of each of the following acids? Calculate the pH of each of these solutions.

a. HOC_6H_5 **b.** HCN

55. A 0.0560-g sample of acetic acid is added to enough water to make 50.00 mL of solution. Calculate $[H^+]$, $[CH_3COO^-]$, $[CH_3COOH]$, and the pH at equilibrium. K_a for acetic acid is 1.8×10^{-5}.

56. For propanoic acid ($HC_3H_5O_2$, $K_a = 1.3 \times 10^{-5}$), determine the concentration of all species present, the pH, and the percent dissociation of a 0.100 *M* solution.

57. Calculate the concentration of all species present and the pH of a 0.020 *M* HF solution.

58. Calculate the pH of a 0.20 *M* solution of iodic acid (HIO_3, $K_a = 0.17$).

59. Monochloroacetic acid, $HC_2H_2ClO_2$, is a skin irritant that is used in "chemical peels" intended to remove the top layer of dead skin from the face and ultimately improve the complexion. The value of K_a for monochloroacetic acid is 1.35×10^{-3}. Calculate the pH of a 0.10 *M* solution of monochloroacetic acid.

60. A typical aspirin tablet contains 325 mg of acetylsalicylic acid, $HC_9H_7O_4$. Calculate the pH of a solution that is prepared by dissolving two aspirin tablets in one cup (237 mL) of solution. Assume the aspirin tablets are pure acetylsalicylic acid, $K_a = 3.3 \times 10^{-4}$.

61. Calculate the pH of each of the following.

a. a solution containing 0.10 *M* HCl and 0.10 *M* HOCl

b. a solution containing 0.050 *M* HNO_3 and 0.50 *M* $HC_2H_3O_2$.

62. Calculate the pH of a solution that contains 1.0 *M* HF and 1.0 *M* HOC_6H_5. Also calculate the concentration of $OC_6H_5^-$ in this solution at equilibrium.

63. Calculate the percent dissociation of the acid in each of the following solutions.

a. 0.50 *M* acetic acid

b. 0.050 *M* acetic acid

c. 0.0050 *M* acetic acid

d. Use Le Châtelier's principle to explain why percent dissociation increases as the concentration of a weak acid decreases.

e. Even though the percent dissociation increases from solutions a to c, the $[H^+]$ decreases. Explain.

64. Using the K_a values in Table 14.2, calculate the percent dissociation in a 0.20 *M* solution of each of the following acids.

a. nitric acid (HNO_3)

b. nitrous acid (HNO_2)

c. phenol (HOC_6H_5)

d. How is percent dissociation of an acid related to the K_a value for the acid (assuming equal initial concentrations of acids)?

65. A 0.15 *M* solution of a weak acid is 3.0% dissociated. Calculate K_a.

66. An acid HX is 25% dissociated in water. If the equilibrium concentration of HX is 0.30 *M*, calculate the K_a value for HX.

67. The pH of a 1.00×10^{-2} *M* solution of cyanic acid (HOCN) is 2.77 at 25°C. Calculate K_a for HOCN from this result.

68. Trichloroacetic acid (CCl_3CO_2H) is a corrosive acid that is used to precipitate proteins. The pH of a 0.050 *M* solution of trichloroacetic acid is the same as the pH of a 0.040 *M* $HClO_4$ solution. Calculate K_a for trichloroacetic acid.

69. A solution of formic acid (HCOOH, $K_a = 1.8 \times 10^{-4}$) has a pH of 2.70. Calculate the initial concentration of formic acid in this solution.

70. One mole of a weak acid HA was dissolved in 2.0 L of solution. After the system had come to equilibrium, the concentration of HA was found to be 0.45 *M*. Calculate K_a for HA.

Solutions of Bases

71. Write the reaction and the corresponding K_b equilibrium expression for each of the following substances acting as bases in water.

a. NH_3 **b.** C_5H_5N

72. Write the reaction and the corresponding K_b equilibrium expression for each of the following substances acting as bases in water.

a. aniline, $C_6H_5NH_2$ **b.** dimethylamine, $(CH_3)_2NH$

73. Use Table 14.3 to help order the following bases from strongest to weakest.

$$NO_3^-, \quad H_2O, \quad NH_3, \quad C_5H_5N$$

74. Use Table 14.3 to help order the following acids from strongest to weakest.

$$HNO_3, \quad H_2O, \quad NH_4^+, \quad C_5H_5NH^+$$

75. Use Table 14.3 to help answer the following questions.

a. Which is the stronger base, ClO_4^- or $C_6H_5NH_2$?

b. Which is the stronger base, H_2O or $C_6H_5NH_2$?

c. Which is the stronger base, OH^- or $C_6H_5NH_2$?

d. Which is the stronger base, $C_6H_5NH_2$ or CH_3NH_2?

76. Use Table 14.3 to help answer the following questions.

a. Which is the stronger acid, $HClO_4$ or $C_6H_5NH_3^+$?

b. Which is the stronger acid, H_2O or $C_6H_5NH_3^+$?

c. Which is the stronger acid, $C_6H_5NH_3^+$ or $CH_3NH_3^+$?

77. Calculate the pH of the following solutions.

a. 0.10 *M* NaOH

b. 1.0×10^{-10} *M* NaOH

c. 2.0 *M* NaOH

78. Calculate $[OH^-]$, pOH, and pH for each of the following.

a. 0.00040 *M* $Ca(OH)_2$

b. a solution containing 25 g of KOH per liter

c. a solution containing 150.0 g of NaOH per liter

79. What are the major species present in 0.015 *M* solutions of each of the following bases?
a. KOH **b.** $Ba(OH)_2$
What is $[OH^-]$ and the pH of each of these solutions?

80. What are the major species present in the following mixtures of bases?
a. 0.050 *M* NaOH and 0.050 *M* LiOH
b. 0.0010 *M* $Ca(OH)_2$ and 0.020 *M* RbOH
What is $[OH^-]$ and the pH of each of these solutions?

81. What mass of KOH is necessary to prepare 800.0 mL of a solution having a pH = 11.56?

82. Calculate the concentration of an aqueous $Sr(OH)_2$ that has pH = 10.50.

83. What are the major species present in a 0.150 *M* NH_3 solution? Calculate the $[OH^-]$ and the pH of this solution.

84. For the reaction of hydrazine (N_2H_4) in water,

$$H_2NNH_2(aq) + H_2O(l) \rightleftharpoons H_2NNH_3^+(aq) + OH^-(aq)$$

K_b is 3.0×10^{-6}. Calculate the concentrations of all species and the pH of a 2.0 *M* solution of hydrazine in water.

85. Calculate $[OH^-]$, $[H^+]$, and the pH of 0.20 *M* solutions of each of the following amines.
a. triethylamine $[(C_2H_5)_3N, K_b = 4.0 \times 10^{-4}]$
b. hydroxylamine ($HONH_2$, $K_b = 1.1 \times 10^{-8}$)

86. Calculate $[OH^-]$, $[H^+]$, and the pH of 0.20 *M* solutions of each of the following amines (the K_b values are found in Table 14.3).
a. aniline **b.** methylamine

87. Calculate the pH of a 0.20 *M* $C_2H_5NH_2$ solution ($K_b = 5.6 \times 10^{-4}$).

88. Calculate the pH of a 0.050 *M* $(C_2H_5)_2NH$ solution ($K_b = 1.3 \times 10^{-3}$).

89. Calculate the percent ionization in each of the following solutions.
a. 0.10 *M* NH_3 **b.** 0.010 *M* NH_3

90. Calculate the percentage of pyridine (C_5H_5N) that forms pyridinium ion, $C_5H_5NH^+$, in a 0.10 *M* aqueous solution of pyridine ($K_b = 1.7 \times 10^{-9}$).

91. Codeine ($C_{18}H_{21}NO_3$) is a derivative of morphine that is used as an analgesic, narcotic, or antitussive. It was once commonly used in cough syrups but is now available only by prescription because of its addictive properties. If the pH of a 1.7×10^{-3} *M* solution of codeine is 9.59, calculate K_b.

92. Calculate the mass of $HONH_2$ required to dissolve in enough water to make 250.0 mL of solution having a pH of 10.00. ($K_b = 1.1 \times 10^{-8}$.)

Polyprotic Acids

93. Write out the stepwise K_a reactions for the diprotic acid H_2SO_3.

94. Write out the stepwise K_a reactions for citric acid ($H_3C_6H_5O_7$), a triprotic acid.

95. Using the K_a values in Table 14.4 and only the first dissociation step, calculate the pH of 0.10 *M* solutions of each of the following polyprotic acids.
a. H_3PO_4 **b.** H_2CO_3

96. Arsenic acid (H_3AsO_4) is a triprotic acid with $K_{a_1} = 5 \times 10^{-3}$, $K_{a_2} = 8 \times 10^{-8}$, and $K_{a_3} = 6 \times 10^{-10}$. Calculate $[H^+]$, $[OH^-]$, $[H_3AsO_4]$, $[H_2AsO_4^-]$, $[HAsO_4^{2-}]$, and $[AsO_4^{3-}]$ in a 0.20 *M* arsenic acid solution.

97. Calculate the pH of a 2.0 *M* H_2SO_4 solution.

98. Calculate the pH of a 5.0×10^{-3} *M* solution of H_2SO_4.

Acid–Base Properties of Salts

99. Arrange the following 0.10 *M* solutions in order of most acidic to most basic.

KOH, KCl, KCN, NH_4Cl, HCl

100. Arrange the following 0.10 *M* solutions in order from most acidic to most basic. See Appendix 5 for K_a and K_b values.

$CaBr_2$, KNO_2, $HClO_4$, HNO_2, $HONH_3ClO_4$

101. Given that the K_a value for acetic acid is 1.8×10^{-5} and the K_a value for hypochlorous acid is 3.5×10^{-8}, which is the stronger base, OCl^- or $C_2H_3O_2^-$?

102. The K_b values for ammonia and methylamine are 1.8×10^{-5} and 4.4×10^{-4}, respectively. Which is the stronger acid, NH_4^+ or $CH_3NH_3^+$?

103. Sodium azide (NaN_3) is sometimes added to water to kill bacteria. Calculate the concentration of all species in a 0.010 *M* solution of NaN_3. The K_a value for hydrazoic acid (HN_3) is 1.9×10^{-5}.

104. Calculate the concentrations of all species present in a 0.25 *M* solution of ethylammonium chloride ($C_2H_5NH_3Cl$).

105. Calculate the pH of each of the following solutions.
a. 0.10 *M* CH_3NH_3Cl **b.** 0.050 *M* NaCN

106. Calculate the pH of each of the following solutions.
a. 0.12 *M* KNO_2 **c.** 0.40 *M* NH_4ClO_4
b. 0.45 *M* NaOCl

107. An unknown salt is either NaCN, $NaC_2H_3O_2$, NaF, NaCl, or NaOCl. When 0.100 mol of the salt is dissolved in 1.00 L of solution, the pH of the solution is 8.07. What is the identity of the salt?

108. Consider a solution of an unknown salt having the general formula BHCl, where B is one of the weak bases in Table 14.3. A 0.10 *M* solution of the unknown salt has a pH of 5.82. What is the actual formula of the salt?

109. Calculate the pH of a 0.050 *M* $Al(NO_3)_3$ solution. The K_a value for $Al(H_2O)_6^{3+}$ is 1.4×10^{-5}.

110. Calculate the pH of a 0.10 *M* $CoCl_3$ solution. The K_a value for $Co(H_2O)_6^{3+}$ is 1.0×10^{-5}.

111. Are solutions of the following salts acidic, basic, or neutral? For those that are not neutral, write balanced chemical equations for the reactions causing the solution to be acidic or basic. The relevant K_a and K_b values are found in Tables 14.2 and 14.3.
a. $NaNO_3$ **c.** $C_5H_5NHClO_4$ **e.** KOCl
b. $NaNO_2$ **d.** NH_4NO_2 **f.** NH_4OCl

112. Are solutions of the following salts acidic, basic, or neutral? For those that are not neutral, write balanced equations for the reactions causing the solution to be acidic or basic. The relevant K_a and K_b values are found in Tables 14.2 and 14.3.

a. KCl
b. $NH_4C_2H_3O_2$
c. CH_3NH_3Cl
d. KF
e. NH_4F
f. CH_3NH_3CN

Relationships Between Structure and Strengths of Acids and Bases

113. Place the species in each of the following groups in order of increasing acid strength. Explain the order you chose for each group.

a. HIO_3, $HBrO_3$
b. HNO_2, HNO_3
c. HOCl, HOI
d. H_3PO_4, H_3PO_3

114. Place the species in each of the following groups in order of increasing base strength. Give your reasoning in each case.

a. IO_3^-, BrO_3^-
b. NO_2^-, NO_3^-
c. OCl^-, OI^-

115. Place the species in each of the following groups in order of increasing acid strength.

a. H_2O, H_2S, H_2Se (bond energies: H—O, 467 kJ/mol; H—S, 363 kJ/mol; H—Se, 276 kJ/mol)
b. CH_3CO_2H, FCH_2CO_2H, F_2CHCO_2H, F_3CCO_2H
c. NH_4^+, $HONH_3^+$
d. NH_4^+, PH_4^+(bond energies: N—H, 391 kJ/mol; P—H, 322 kJ/mol)

Give reasons for the orders you chose.

116. Using your results from Exercise 115, place the species in each of the following groups in order of increasing base strength.

a. OH^-, SH^-, SeH^-
b. NH_3, PH_3
c. NH_3, $HONH_2$

117. Will the following oxides give acidic, basic, or neutral solutions when dissolved in water? Write reactions to justify your answers.

a. CaO
b. SO_2
c. Cl_2O

118. Will the following oxides give acidic, basic, or neutral solutions when dissolved in water? Write reactions to justify your answers.

a. Li_2O
b. CO_2
c. SrO

Lewis Acids and Bases

119. Identify the Lewis acid and the Lewis base in each of the following reactions.

a. $B(OH)_3(aq) + H_2O(l) \rightleftharpoons B(OH)_4^-(aq) + H^+(aq)$
b. $Ag^+(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq)$
c. $BF_3(g) + F^-(aq) \rightleftharpoons BF_4^-(aq)$

120. Identify the Lewis acid and the Lewis base in each of the following reactions.

a. $Fe^{3+}(aq) + 6H_2O(l) \rightleftharpoons Fe(H_2O)_6^{3+}(aq)$
b. $H_2O(l) + CN^-(aq) \rightleftharpoons HCN(aq) + OH^-(aq)$
c. $HgI_2(s) + 2I^-(aq) \rightleftharpoons HgI_4^{2-}(aq)$

121. Aluminum hydroxide is an amphoteric substance. It can act as either a Brønsted–Lowry base or a Lewis acid. Write a reaction showing $Al(OH)_3$ acting as a base toward H^+ and as an acid toward OH^-.

122. Zinc hydroxide is an amphoteric substance. Write equations that describe $Zn(OH)_2$ acting as a Brønsted–Lowry base toward H^+ and as a Lewis acid toward OH^-.

123. Would you expect Fe^{3+} or Fe^{2+} to be the stronger Lewis acid? Explain.

124. Use the Lewis acid–base model to explain the following reaction.

$$CO_2(g) + H_2O(l) \longrightarrow H_2CO_3(aq)$$

Additional Exercises

125. A 10.0-mL sample of an HCl solution has a pH of 2.000. What volume of water must be added to change the pH to 4.000?

126. Which of the following represent conjugate acid–base pairs? For those pairs that are not conjugates, write the correct conjugate acid or base for each species in the pair.

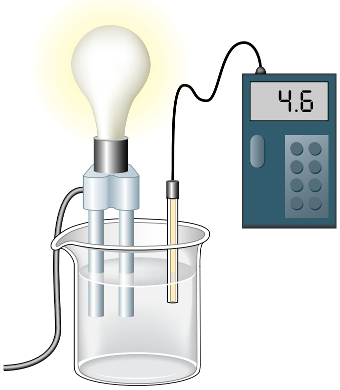
a. H_2O, OH^-
b. H_2SO_4, SO_4^{2-}
c. H_3PO_4, $H_2PO_4^-$
d. $HC_2H_3O_2$, $C_2H_3O_2^-$

127. A solution is made by adding 50.0 mL of 0.200 *M* acetic acid ($K_a = 1.8 \times 10^{-5}$) to 50.0 mL of 1.00×10^{-3} *M* HCl.

a. Calculate the pH of the solution.
b. Calculate the acetate ion concentration.

128. You have 100.0 g of saccharin, a sugar substitute, and you want to prepare a pH = 5.75 solution. What volume of solution can be prepared? For saccharin, $HC_7H_4NSO_3$, $pK_a = 11.70$ ($pK_a = -\log K_a$).

129. A solution is tested for pH and conductivity as pictured below:



The solution contains one of the following substances: HCl, NaOH, NH_4Cl, HCN, NH_3, HF, or NaCN. If the solute concentration is about 1.0 *M*, what is the identity of the solute?

130. A 0.25-g sample of lime (CaO) is dissolved in enough water to make 1500 mL of solution. Calculate the pH of the solution.

131. At 25°C, a saturated solution of benzoic acid ($K_a = 6.4 \times 10^{-5}$) has a pH of 2.80. Calculate the water solubility of benzoic acid in moles per liter.

132. Calculate the pH and $[S^{2-}]$ in a 0.10 *M* H_2S solution. Assume $K_{a_1} = 1.0 \times 10^{-7}$; $K_{a_2} = 1.0 \times 10^{-19}$.

133. A typical vitamin C tablet (containing pure ascorbic acid, $H_2C_6H_6O_6$) weighs 500. mg. One vitamin C tablet is dissolved in enough water to make 200.0 mL of solution. Calculate the pH of this solution. Ascorbic acid is a diprotic acid.

134. Calculate the pH of an aqueous solution containing 1.0×10^{-2} *M* HCl, 1.0×10^{-2} *M* H_2SO_4, and 1.0×10^{-2} *M* HCN.

135. Acrylic acid ($CH_2{=}CHCO_2H$) is a precursor for many important plastics. K_a for acrylic acid is 5.6×10^{-5}.

a. Calculate the pH of a 0.10 *M* solution of acrylic acid.

b. Calculate the percent dissociation of a 0.10 *M* solution of acrylic acid.

c. Calculate the pH of a 0.050 *M* solution of sodium acrylate ($NaC_3H_3O_2$).

136. A 0.20 *M* sodium chlorobenzoate ($NaC_7H_4ClO_2$) solution has a pH of 8.65. Calculate the pH of a 0.20 *M* chlorobenzoic acid ($HC_7H_4ClO_2$) solution.

137. The equilibrium constant K_a for the reaction

$$Fe(H_2O)_6^{3+}(aq) + H_2O(l) \rightleftharpoons Fe(H_2O)_5(OH)^{2+}(aq) + H_3O^+(aq)$$

is 6.0×10^{-3}.

a. Calculate the pH of a 0.10 *M* solution of $Fe(H_2O)_6^{3+}$.

b. Will a 1.0 *M* solution of iron(II) nitrate have a higher or lower pH than a 1.0 *M* solution of iron(III) nitrate? Explain.

138. Rank the following 0.10 *M* solutions in order of increasing pH.

a. HI, HF, NaF, NaI

b. NH_4Br, HBr, KBr, NH_3

c. $C_6H_5NH_3NO_3$, $NaNO_3$, NaOH, HOC_6H_5, KOC_6H_5, $C_6H_5NH_2$, HNO_3

139. Is an aqueous solution of $NaHSO_4$ acidic, basic, or neutral? What reaction occurs with water? Calculate the pH of a 0.10 *M* solution of $NaHSO_4$.

140. Calculate $[CO_3^{2-}]$ in a 0.010 *M* solution of CO_2 in water (H_2CO_3). If all the CO_3^{2-} in this solution comes from the reaction

$$HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq)$$

what percentage of the H^+ ions in the solution is a result of the dissociation of HCO_3^-? When acid is added to a solution of sodium hydrogen carbonate ($NaHCO_3$), vigorous bubbling occurs. How is this reaction related to the existence of carbonic acid (H_2CO_3) molecules in aqueous solution?

141. Hemoglobin (abbreviated Hb) is a protein that is responsible for the transport of oxygen in the blood of mammals. Each hemoglobin molecule contains four iron atoms that are the binding sites for O_2 molecules. The oxygen binding is pH dependent. The relevant equilibrium reaction is

$$HbH_4^{4+}(aq) + 4O_2(g) \rightleftharpoons Hb(O_2)_4(aq) + 4H^+(aq)$$

Use Le Châtelier's principle to answer the following.

a. What form of hemoglobin, HbH_4^{4+} or $Hb(O_2)_4$, is favored in the lungs? What form is favored in the cells?

b. When a person hyperventilates, the concentration of CO_2 in the blood is decreased. How does this affect the oxygen-binding equilibrium? How does breathing into a paper bag help to counteract this effect?

c. When a person has suffered a cardiac arrest, injection of a sodium bicarbonate solution is given. Why is this necessary?

142. Calculate the value for the equilibrium constant for each of the following aqueous reactions.

a. $NH_3 + H_3O^+ \rightleftharpoons NH_4^+ + H_2O$

b. $NO_2^- + H_3O^+ \rightleftharpoons HNO_2 + H_2O$

c. $NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O$

d. $HNO_2 + OH^- \rightleftharpoons H_2O + NO_2^-$

143. Students are often surprised to learn that organic acids, such as acetic acid, contain —OH groups. Actually, all oxyacids contain hydroxyl groups. Sulfuric acid, usually written as H_2SO_4, has the structural formula $SO_2(OH)_2$, where S is the central atom. Identify the acids whose structural formulas are shown below. Why do they behave as acids, while NaOH and KOH are bases?

a. $SO(OH)_2$ **b.** $ClO_2(OH)$ **c.** $HPO(OH)_2$

Challenge Problems

144. The pH of 1.0×10^{-8} *M* hydrochloric acid is not 8.00. The correct pH can be calculated by considering the relationship between the molarities of the three principal ions in the solution (H^+, Cl^-, and OH^-). These molarities can be calculated from algebraic equations that can be derived from the considerations given below.

a. The solution is electrically neutral.

b. The hydrochloric acid can be assumed to be 100% ionized.

c. The product of the molarities of the hydronium ions and the hydroxide ions must equal K_w.

Calculate the pH of a 1.0×10^{-8} HCl solution.

145. Calculate the pH of a 1.0×10^{-7} *M* solution of NaOH in water.

146. Calculate $[OH^-]$ in a 3.0×10^{-7} *M* solution of $Ca(OH)_2$.

147. Consider 50.0 mL of a solution of weak acid HA = $K_a(1.00 \times 10^{-6})$, which has a pH of 4.000. What volume of water must be added to make the pH = 5.000?

148. Making use of the assumptions we ordinarily make in calculating the pH of an aqueous solution of a weak acid, calculate the pH of a 1.0×10^{-6} *M* solution of hypobromous acid (HBrO, $K_a = 2 \times 10^{-9}$). What is wrong with your answer? Why is it wrong? Without trying to solve the problem, tell what has to be included to solve the problem correctly.

149. Calculate the pH of a 0.200 *M* solution of C_5H_5NHF. *Hint:* C_5H_5NHF is a salt composed of $C_5H_5NH^+$ and F^- ions. The principal equilibrium in this solution is the best acid reacting with the best base; the reaction for the principal equilibrium is

$$C_5H_5NH^+(aq) + F^-(aq) \rightleftharpoons C_5H_5N(aq) + HF(aq) \quad K = 8.2 \times 10^{-3}$$

150. Determine the pH of a 0.50 *M* solution of NH_4OCl. See Exercise 149.

151. Calculate $[OH^-]$ in a solution obtained by adding 0.0100 mol of solid NaOH to 1.00 L of 15.0 *M* NH_3.

152. What mass of NaOH(*s*) must be added to 1.0 L of 0.050 *M* NH_3 to ensure that the percent ionization of NH_3 is no greater than 0.0010%? Assume no volume change on addition of NaOH.

153. A certain acid, HA, has a vapor density of 5.11 g/L when in the gas phase at a temperature of 25°C and a pressure of 1.00 atm. When 1.50 g of this acid is dissolved in enough water to make 100.0 mL of solution, the pH is found to be 1.80. Calculate K_a for the acid.

154. Calculate the mass of sodium hydroxide that must be added to 1.00 L of 1.00 *M* $HC_2H_3O_2$ to double the pH of the solution (assume that the NaOH does not change the volume of the solution).

155. Consider the species PO_4^{3-}, HPO_4^{2-}, and $H_2PO_4^-$. Each ion can act as a base in water. Determine the K_b value for each of these species. Which species is the strongest base?

156. Calculate the pH of a 0.10 *M* solution of sodium phosphate. See Exercise 155.

157. Will 0.10 *M* solutions of the following salts be acidic, basic, or neutral? See Appendix 5 for K_a values.

- **a.** ammonium bicarbonate
- **b.** sodium dihydrogen phosphate
- **c.** sodium hydrogen phosphate
- **d.** ammonium dihydrogen phosphate
- **e.** ammonium formate

158. **a.** The principal equilibrium in a solution of $NaHCO_3$ is

$$HCO_3^-(aq) + HCO_3^-(aq) \rightleftharpoons H_2CO_3(aq) + CO_3^{2-}(aq)$$

Calculate the value of the equilibrium constant for this reaction.

b. At equilibrium, what is the relationship between $[H_2CO_3]$ and $[CO_3^{2-}]$?

c. Using the equilibrium

$$H_2CO_3(aq) \rightleftharpoons 2H^+(aq) + CO_3^{2-}(aq)$$

derive an expression for the pH of the solution in terms of K_{a_1} and K_{a_2} using the result from part b.

d. What is the pH of a solution of $NaHCO_3$?

159. A 0.100-g sample of the weak acid HA (molar mass = 100.0 g/mol) is dissolved in 500.0 g of water. The freezing point of the resulting solution is −0.0056°C. Calculate the value of K_a for this acid. Assume molarity equals molarity in this solution.

160. A sample containing 0.0500 mol of $Fe_2(SO_4)_3$ is dissolved in enough water to make 1.00 L of solution. This solution contains hydrated SO_4^{2-} and $Fe(H_2O)_6^{3+}$ ions. The latter behaves as an acid:

$$Fe(H_2O)_6^{3+}(aq) \rightleftharpoons Fe(H_2O)_5OH^{2+}(aq) + H^+(aq)$$

a. Calculate the expected osmotic pressure of this solution at 25°C if the above dissociation is negligible.

b. The actual osmotic pressure of the solution is 6.73 atm at 25°C. Calculate K_a for the dissociation reaction of $Fe(H_2O)_6^{3+}$. (To do this calculation, you must assume that none of the ions goes through the semipermeable membrane. Actually, this is not a great assumption for the tiny H^+ ion.)

Integrative Problems

These problems require the integration of multiple concepts to find the solutions.

161. A 2.14-g sample of sodium hypoiodite is dissolved in water to make 1.25 L of solution. The solution pH is 11.32. What is K_b for the hypoiodite ion?

162. Isocyanic acid (HNCO) can be prepared by heating sodium cyanate in the presence of solid oxalic acid according to the equation

$$2NaOCN(s) + H_2C_2O_4(s) \longrightarrow 2HNCO(l) + Na_2C_2O_4(s)$$

Upon isolating pure HNCO(*l*), an aqueous solution of HNCO can be prepared by dissolving the liquid HNCO in water. What is the pH of a 100.-mL solution of HNCO prepared from the reaction of 10.0 g each of NaOCN and $H_2C_2O_4$, assuming all of the HNCO produced is dissolved in solution? (K_a of HNCO = 1.2×10^{-4}.)

163. Papaverine hydrochloride (abbreviated $papH^+Cl^-$; molar mass = 378.85 g/mol) is a drug that belongs to a group of medicines called vasodilators, which cause blood vessels to expand, thereby increasing blood flow. This drug is the conjugate acid of the weak base papaverine (abbreviated pap; $K_b = 8.33 \times 10^{-9}$ at 35.0°C). Calculate the pH of a 30.0 mg/mL aqueous dose of $papH^+Cl^-$ prepared at 35.0°C. K_w at 35.0°C is 2.1×10^{-14}.

Marathon Problems*

These problems are designed to incorporate several concepts and techniques into one situation. Marathon Problems can be used in class by groups of students to help facilitate problem-solving skills.

164. Captain Kirk, of the Starship *Enterprise,* has been told by his superiors that only a chemist can be trusted with the combination to the safe containing the dilithium crystals that power the ship. The combination is the pH of solution A, described below, followed by the pH of solution C. (Example: If the pH of solution A is 3.47 and that of solution C is 8.15, then the combination to the safe is 3-47-8-15.) The chemist must determine the combination using only the information below (all solutions are at 25°C):

Solution A is 50.0 mL of a 0.100 *M* solution of the weak monoprotic acid HX.

Solution B is a 0.0500 *M* solution of the salt NaX. It has a pH of 10.02.

Solution C is made by adding 15.0 mL of 0.250 *M* KOH to solution A.

What is the combination to the safe?

165. For the following, mix equal volumes of one solution from Group I with one solution from Group II to achieve the indicated pH. Calculate the pH of each solution.

Group I: 0.20 *M* NH_4Cl, 0.20 *M* HCl, 0.20 *M* $C_6H_5NH_3Cl$, 0.20 *M* $(C_2H_5)_3NHCl$

Group II: 0.20 *M* KOI, 0.20 *M* NaCN, 0.20 *M* KOCl, 0.20 *M* $NaNO_2$

- **a.** the solution with the lowest pH
- **b.** the solution with the highest pH
- **c.** the solution with the pH closest to 7.00

Get help understanding core concepts and visualizing molecular-level interactions, and practice problem solving, by visiting the Online Study Center at **college.hmco.com/PIC/zumdahl7e.**

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