16.6 WEAK ACIDS
We learn that the ionization of a weak acid in water is an equilibrium process with an equilibrium constant K_a that can be used to calculate the pH of a weak acid solution.

16.7 WEAK BASES
We learn that the ionization of a weak base in water is an equilibrium process with equilibrium constant K_b that can be used to calculate the pH of a weak base solution.

16.8 RELATIONSHIP BETWEEN K_a AND K_b
We see that the relationship $K_a \times K_b = K_w$ means that the stronger an acid, the weaker its conjugate base.

16.9 ACID–BASE PROPERTIES OF SALT SOLUTIONS
We explore the fact that the ions of a soluble ionic compound can serve as Brønsted–Lowry acids or bases.

16.10 ACID–BASE BEHAVIOR AND CHEMICAL STRUCTURE
We explore the relationship between chemical structure and acid–base behavior.

16.11 LEWIS ACIDS AND BASES
Finally, we learn that a Lewis acid is an *electron-pair* acceptor and a Lewis base is an *electron-pair donor*.

ACID–BASE EQUILIBRIA

TASTE IS ONE OF THE five senses we use to experience the world around us. Receptors on the tongue are sensitive to chemical stimuli that lead to five basic taste sensations: sweet, sour, salty, bitter, and umami (from the Japanese word for "delicious" and triggered by the amino acid glutamic acid). The sensation of sour is a response to the presence of acids, and we associate a sour taste with certain fruits and vegetables because they contain acids. For example, lemons, limes, and grapefruits contain citric acid ($H_3C_6H_5O_7$), and green apples and grapes contain malic acid ($H_2C_4H_4O_5$). The vegetable rhubarb is among the sourest of foods, so sour that eating a fresh stalk of rhubarb is sure to elicit a pucker on the first bite. The sour taste comes from the high acid content of the stalks. One of several acids found in rhubarb is oxalic acid, ($H_2C_2O_4$) (▶ **FIGURE 16.1**), which in large doses can be lethal. The oxalic acid content in the leaves is much higher than in the stalks, so much so that the leaves are considered toxic.*

Acids and bases are important in numerous chemical processes that occur around us—from industrial processes to biological ones, from reactions in the laboratory to those in our environment. The time required for a metal object immersed in water to corrode, the ability of an aquatic environment to support fish and plant life, the fate of

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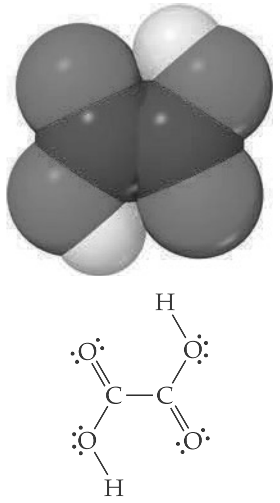
*It is estimated that a 150-lb person would need to eat approximately 5 kg of rhubarb leaves to receive a lethal dose, although much smaller quantities would probably make you sick.

pollutants washed out of the air by rain, and even the rates of reactions that maintain our lives all critically depend on the acidity or basicity of solutions.

We have encountered acids and bases many times in earlier discussions. For example, a portion of Chapter 4 focused on their reactions. In this chapter we reexamine acids and bases, taking a closer look at how they are identified and characterized. In doing so, we consider their behavior both in terms of their structure and bonding and in terms of the chemical equilibria in which they participate.



▲ **FIGURE 16.1** **Oxalic acid, $H_2C_2O_4$.**

16.1 ACIDS AND BASES: A BRIEF REVIEW

From the earliest days of experimental chemistry, scientists have recognized acids and bases by their characteristic properties. Acids have a sour taste and cause certain dyes to change color, whereas bases have a bitter taste and feel slippery (soap is a good example). Use of the term *base* comes from the old English meaning of the word, "to bring low." (We still use the word *debase* in this sense, meaning to lower the value of something.) When a base is added to an acid, the base "lowers" the amount of acid. Indeed, when acids and bases are mixed in certain proportions, their characteristic properties disappear altogether. ∞ (Section 4.3)

By 1830 it was evident that all acids contain hydrogen but not all hydrogen-containing substances are acids. During the 1880s, the Swedish chemist Svante Arrhenius (1859–1927) defined acids as substances that produce H^+ ions in water and bases as substances that produce OH^- ions in water. Over time the Arrhenius concept of acids and bases came to be stated in the following way:

- An *acid* is a substance that, when dissolved in water, increases the concentration of H^+ ions.
- A *base* is a substance that, when dissolved in water, increases the concentration of OH^- ions.

Hydrogen chloride is an Arrhenius acid. Hydrogen chloride gas is highly soluble in water because of its chemical reaction with water, which produces hydrated H^+ and Cl^- ions:

$$\mathrm{HCl}(g) \xrightarrow{\mathrm{H_2O}} \mathrm{H^+}(aq) + \mathrm{Cl^-}(aq) \qquad [16.1]$$

The aqueous solution of HCl is known as hydrochloric acid. Concentrated hydrochloric acid is about 37% HCl by mass and is 12 *M* in HCl.

Sodium hydroxide is an Arrhenius base. Because NaOH is an ionic compound, it dissociates into Na^+ and OH^- ions when it dissolves in water, thereby releasing OH^- ions into the solution.

GIVE IT SOME THOUGHT

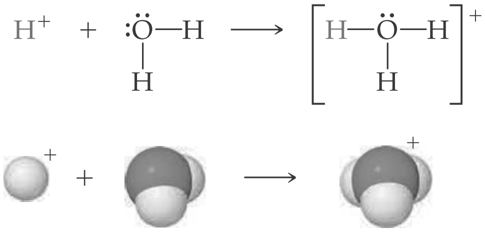
What two ions are central to the Arrhenius definitions of acids and bases?

16.2 BRØNSTED–LOWRY ACIDS AND BASES

The Arrhenius concept of acids and bases, while useful, has limitations. For one thing, it is restricted to aqueous solutions. In 1923 the Danish chemist Johannes Brønsted (1879–1947) and the English chemist Thomas Lowry (1874–1936) independently proposed a more general definition of acids and bases. Their concept is based on the fact that *acid–base reactions involve the transfer of H^+ ions from one substance to another*.

The H^+ Ion in Water

We might at first imagine that ionization of HCl in water produces just H^+ and Cl^-. A hydrogen ion is no more than a bare proton, however, and would interact strongly with any source of electron density, such as the nonbonding electron pairs on the oxygen atoms of water molecules. For example, the interaction of a proton with water forms the **hydronium ion**, $H_3O^+(aq)$:



$$H^+ + :\ddot{O}(H)-H \longrightarrow [H-\ddot{O}(H)-H]^+ \quad [16.2]$$

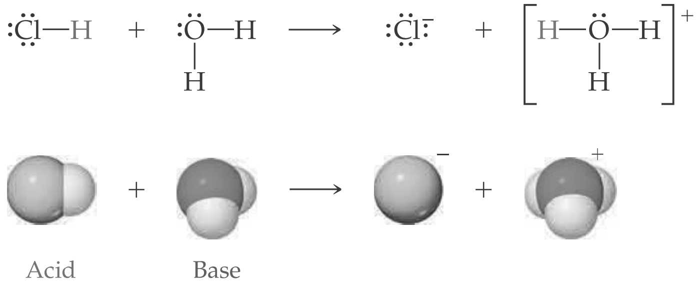
The behavior of H^+ ions in liquid water is complex because hydronium ions are not the only polyatomic ions that form when H^+ interacts with water molecules. The H_3O^+ ion can form hydrogen bonds to additional H_2O molecules to generate such ions as $H_5O_2^+$ and $H_9O_4^+$ (▶ **FIGURE 16.2**)

Chemists use the notations $H^+(aq)$ and $H_3O^+(aq)$ interchangeably to represent the hydrated proton responsible for the characteristic properties of aqueous solutions of acids. We often use the notation $H^+(aq)$ for simplicity and convenience, as we did in Chapter 4 and Equation 16.1. The notation $H_3O^+(aq)$, however, more closely represents reality.

Proton-Transfer Reactions

In the reaction that occurs when HCl dissolves in water, the HCl molecule transfers an H^+ ion (a proton) to a water molecule. Thus, we can represent the reaction as occurring between an HCl molecule and a water molecule to form hydronium and chloride ions:

$$HCl(g) + H_2O(l) \longrightarrow Cl^-(aq) + H_3O^+(aq)$$



$$:\ddot{\underset{..}{Cl}}-H + :\ddot{O}(H)-H \longrightarrow :\ddot{\underset{..}{Cl}}:^- + [H-\ddot{O}(H)-H]^+ \quad [16.3]$$

The polar H_2O molecule promotes the ionization of acids in water solution by accepting a proton to form H_3O^+.

Brønsted and Lowry proposed definitions of acids and bases in terms of their ability to transfer protons:

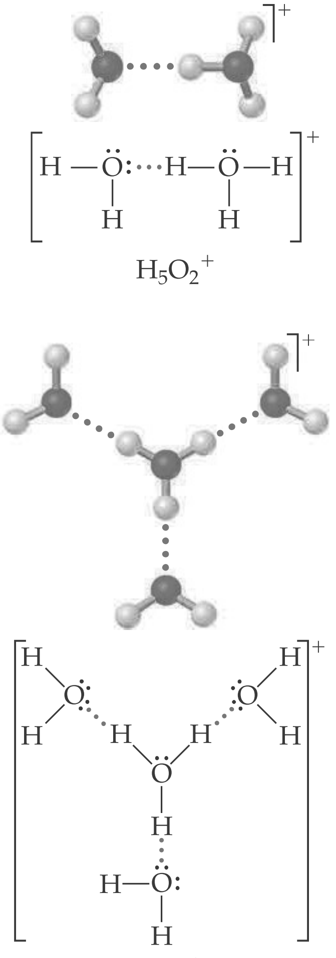
- An *acid* is a substance (molecule or ion) that donates a proton to another substance.
- A *base* is a substance that accepts a proton.

Thus, when HCl dissolves in water (Equation 16.3), HCl acts as a **Brønsted–Lowry acid** (it donates a proton to H_2O), and H_2O acts as a **Brønsted–Lowry base** (it accepts a proton from HCl).

Because the emphasis in the Brønsted–Lowry concept is on proton transfer, the concept also applies to reactions that do not occur in aqueous solution. In the reaction

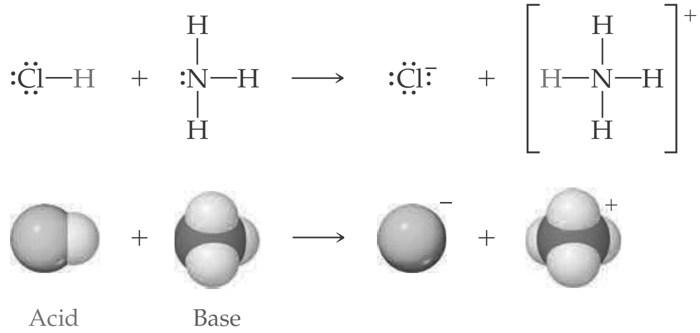
GO FIGURE

Which type of intermolecular force do the dotted lines in this figure represent?



▲ **FIGURE 16.2 Ball-and-stick models and Lewis structures for two hydrated hydronium ions.**

between gas phase HCl and NH_3, for example, a proton is transferred from the acid HCl to the base NH_3:



$$\mathrm{H{-}Cl} + \mathrm{NH_3} \longrightarrow \mathrm{Cl^-} + \left[\mathrm{NH_4}\right]^+ \qquad [16.4]$$

The hazy film that forms on the windows of general chemistry laboratories and on glassware in the laboratory is largely solid NH_4Cl formed by the gas-phase reaction between HCl and NH_3.

Let's consider another example that compares the relationship between the Arrhenius and Brønsted–Lowry definitions of acids and bases—an aqueous solution of ammonia, in which we have the equilibrium:

$$\underset{\text{Base}}{\mathrm{NH_3}(aq)} + \underset{\text{Acid}}{\mathrm{H_2O}(l)} \rightleftharpoons \mathrm{NH_4}^+(aq) + \mathrm{OH}^-(aq) \qquad [16.5]$$

Ammonia is a Brønsted–Lowry base because it accepts a proton from H_2O. Ammonia is also an Arrhenius base because adding it to water leads to an increase in the concentration of $OH^-(aq)$.

An acid and a base always work together to transfer a proton. In other words, a substance can function as an acid only if another substance simultaneously behaves as a base. To be a Brønsted–Lowry acid, a molecule or ion must have a hydrogen atom it can lose as an H^+ ion. To be a Brønsted–Lowry base, a molecule or ion must have a nonbonding pair of electrons it can use to bind the H^+ ion.

Some substances can act as an acid in one reaction and as a base in another. For example, H_2O is a Brønsted–Lowry base in Equation 16.3 and a Brønsted–Lowry acid in Equation 16.5. A substance capable of acting as either an acid or a base is called **amphiprotic**. An amphiprotic substance acts as a base when combined with something more strongly acidic than itself and as an acid when combined with something more strongly basic than itself.

GIVE IT SOME THOUGHT

In the forward reaction of this equilibrium, which substance acts as the Brønsted–Lowry base?

$$\mathrm{H_2S}(aq) + \mathrm{CH_3NH_2}(aq) \rightleftharpoons \mathrm{HS^-}(aq) + \mathrm{CH_3NH_3}^+(aq)$$

Conjugate Acid–Base Pairs

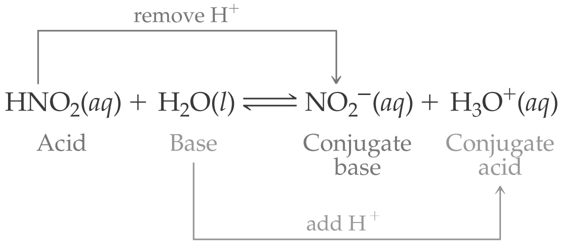
In any acid–base equilibrium, both the forward reaction (to the right) and the reverse reaction (to the left) involve proton transfer. For example, consider the reaction of an acid HX with water:

$$\mathrm{HX}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{X}^-(aq) + \mathrm{H_3O}^+(aq) \qquad [16.6]$$

In the forward reaction, HX donates a proton to H_2O. Therefore, HX is the Brønsted–Lowry acid and H_2O is the Brønsted–Lowry base. In the reverse reaction, the H_3O^+ ion donates a proton to the X^- ion, so H_3O^+ is the acid and X^- is the base. When the acid HX donates a proton, it leaves behind a substance, X^-, that can act as a base. Likewise, when H_2O acts as a base, it generates H_3O^+, which can act as an acid.

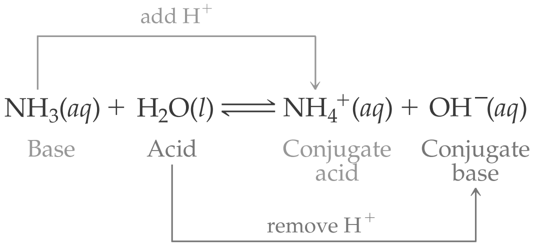
An acid and a base such as HX and X^- that differ only in the presence or absence of a proton are called a **conjugate acid–base pair**.* Every acid has a **conjugate base**, formed by removing a proton from the acid. For example, OH^- is the conjugate base of H_2O, and X^- is the conjugate base of HX. Every base has a **conjugate acid**, formed by adding a proton to the base. Thus, H_3O^+ is the conjugate acid of H_2O, and HX is the conjugate acid of X^-.

In any acid–base (proton-transfer) reaction, we can identify two sets of conjugate acid–base pairs. For example, consider the reaction between nitrous acid and water:



$$HNO_2(aq) + H_2O(l) \rightleftharpoons NO_2^-(aq) + H_3O^+(aq) \qquad [16.7]$$

Likewise, for the reaction between NH_3 and H_2O (Equation 16.5), we have



$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \qquad [16.8]$$

SAMPLE EXERCISE 16.1 Identifying Conjugate Acids and Bases

(**a**) What is the conjugate base of $HClO_4$, H_2S, PH_4^+, HCO_3^-? (**b**) What is the conjugate acid of CN^-, SO_4^{2-}, H_2O, HCO_3^-?

SOLUTION

Analyze We are asked to give the conjugate base for several acids and the conjugate acid for several bases.

Plan The conjugate base of a substance is simply the parent substance minus one proton, and the conjugate acid of a substance is the parent substance plus one proton.

Solve
(**a**) $HClO_4$ less one proton H^+ is ClO_4^-. The other conjugate bases are HS^-, PH_3, and CO_3^{2-}.
(**b**) CN^- plus one proton H^+ is HCN. The other conjugate acids are HSO_4^-, H_3O^+, and H_2CO_3. Notice that the hydrogen carbonate ion (HCO_3^-) is amphiprotic. It can act as either an acid or a base.

PRACTICE EXERCISE

Write the formula for the conjugate acid of each of the following: HSO_3^-, F^-, PO_4^{3-}, CO.

Answers: H_2SO_3, HF, HPO_4^{2-}, HCO^+

Once you become proficient at identifying conjugate acid–base pairs it is not difficult to write equations for reactions involving Brønsted–Lowry acids and bases (proton-transfer reactions).

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*The word *conjugate* means "joined together as a pair."

SAMPLE EXERCISE 16.2 **Writing Equations for Proton-Transfer Reactions**

The hydrogen sulfite ion (HSO_3^-) is amphiprotic. Write an equation for the reaction of HSO_3^- with water (**a**) in which the ion acts as an acid and (**b**) in which the ion acts as a base. In both cases identify the conjugate acid–base pairs.

SOLUTION

Analyze and Plan We are asked to write two equations representing reactions between HSO_3^- and water, one in which HSO_3^- should donate a proton to water, thereby acting as a Brønsted–Lowry acid, and one in which HSO_3^- should accept a proton from water, thereby acting as a base. We are also asked to identify the conjugate pairs in each equation.

Solve

(**a**)

$$HSO_3^-(aq) + H_2O(l) \rightleftharpoons SO_3^{2-}(aq) + H_3O^+(aq)$$

The conjugate pairs in this equation are HSO_3^- (acid) and SO_3^{2-} (conjugate base), and H_2O (base) and H_3O^+ (conjugate acid).

(**b**)

$$HSO_3^-(aq) + H_2O(l) \rightleftharpoons H_2SO_3(aq) + OH^-(aq)$$

The conjugate pairs in this equation are H_2O (acid) and OH^- (conjugate base), and HSO_3^- (base) and H_2SO_3 (conjugate acid).

PRACTICE EXERCISE

When lithium oxide (Li_2O) is dissolved in water, the solution turns basic from the reaction of the oxide ion (O^{2-}) with water. Write the equation for this reaction and identify the conjugate acid–base pairs.

Answer: $O^{2-}(aq) + H_2O(l) \longrightarrow OH^-(aq) + OH^-(aq)$. The OH^- is both the conjugate acid of O^{2-} and the conjugate base of H_2O.

Relative Strengths of Acids and Bases

Some acids are better proton donors than others, and some bases are better proton acceptors than others. If we arrange acids in order of their ability to donate a proton, we find that the more easily a substance gives up a proton, the less easily its conjugate base accepts a proton. Similarly, the more easily a base accepts a proton, the less easily its conjugate acid gives up a proton. In other words, *the stronger an acid*, *the weaker its conjugate base*, and *the stronger a base*, *the weaker its conjugate acid*. Thus, if we know something about the strength of an acid (its ability to donate protons), we also know something about the strength of its conjugate base (its ability to accept protons).

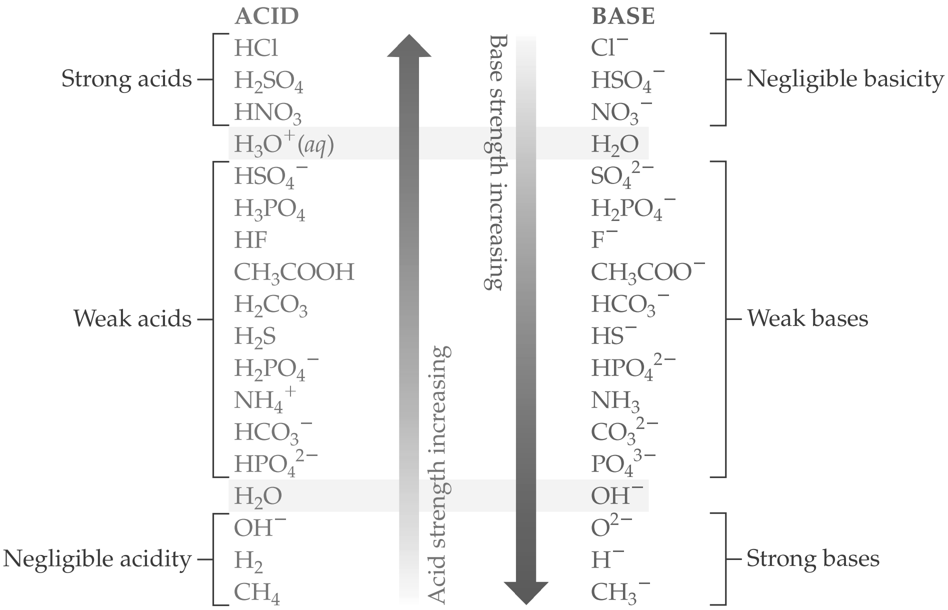
The inverse relationship between the strengths of acids and their conjugate bases is illustrated in ▶ **FIGURE 16.3**. Here we have grouped acids and bases into three broad categories based on their behavior in water:

1. A *strong acid* completely transfers its protons to water, leaving no undissociated molecules in solution. ∞ (Section 4.3) Its conjugate base has a negligible tendency to be protonated (to accept protons) in aqueous solution. (*The conjugate base of a strong acid shows negligible basicity*.)
2. A *weak acid* only partially dissociates in aqueous solution and therefore exists in the solution as a mixture of the acid and its conjugate base. The conjugate base of a weak acid shows a slight ability to remove protons from water. (*The conjugate base of a weak acid is a weak base*.)
3. A substance with *negligible acidity* contains hydrogen but does not demonstrate any acidic behavior in water. Its conjugate base is a strong base, reacting completely with water, abstracting protons to form OH^- ions. (*The conjugate base of a substance with negligible acidity is a strong base*.)

The ions $H^+(aq)$ and $OH^-(aq)$ are, respectively, the strongest possible acid and strongest possible base that can exist at equilibrium in aqueous solution. Stronger acids react with water to produce $H^+(aq)$ ions, and stronger bases react with water to produce $OH^-(aq)$ ions. This effect is known as the *leveling effect*.

GO FIGURE

If O^{2-} ions are added to water, what reaction, if any, occurs?



▲ **FIGURE 16.3 Relative strengths of select conjugate acid–base pairs.** The two members of each pair are listed opposite each other in the two columns.

GIVE IT SOME THOUGHT

Given that $HClO_4$ is a strong acid, how would you classify the basicity of ClO_4^-?

We can think of proton-transfer reactions as being governed by the relative abilities of two bases to abstract protons. For example, consider the proton transfer that occurs when an acid HX dissolves in water:

$$HX(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + X^-(aq) \qquad [16.9]$$

If H_2O (the base in the forward reaction) is a stronger base than X^- (the conjugate base of HX), H_2O abstracts the proton from HX to produce H_3O^+ and X^-. As a result, the equilibrium lies to the right. This describes the behavior of a strong acid in water. For example, when HCl dissolves in water, the solution consists almost entirely of H_3O^+ and Cl^- ions with a negligible concentration of HCl molecules:

$$HCl(g) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq) \qquad [16.10]$$

H_2O is a stronger base than Cl^- (Figure 16.3), so H_2O acquires the proton to become the hydronium ion.

When X^- is a stronger base than H_2O, the equilibrium lies to the left. This situation occurs when HX is a weak acid. For example, an aqueous solution of acetic acid consists mainly of CH_3COOH molecules with only a relatively few H_3O^+ and CH_3COO^- ions:

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq) \qquad [16.11]$$

The CH_3COO^- ion is a stronger base than H_2O (Figure 16.3) and therefore abstracts the proton from H_3O^+.

From these examples, we conclude that *in every acid–base reaction, equilibrium favors transfer of the proton from the stronger acid to the stronger base to form the weaker acid and the weaker base.*

SAMPLE EXERCISE 16.3 **Predicting the Position of a Proton-Transfer Equilibrium**

For the following proton-transfer reaction use Figure 16.3 to predict whether the equilibrium lies to the left ($K_c < 1$) or to the right ($K_c > 1$):

$$HSO_4^-(aq) + CO_3^{2-}(aq) \rightleftharpoons SO_4^{2-}(aq) + HCO_3^-(aq)$$

SOLUTION

Analyze We are asked to predict whether an equilibrium lies to the right, favoring products, or to the left, favoring reactants.

Plan This is a proton-transfer reaction, and the position of the equilibrium will favor the proton going to the stronger of two bases. The two bases in the equation are CO_3^{2-}, the base in the forward reaction, and SO_4^{2-}, the conjugate base of HSO_4^-. We can find the relative positions of these two bases in Figure 16.3 to determine which is the stronger base.

Solve The CO_3^{2-} ion appears lower in the right-hand column in Figure 16.3 and is therefore a stronger base than SO_4^{2-}. CO_3^{2-}, therefore, will get the proton preferentially to become HCO_3^-, while SO_4^{2-} will remain mostly unprotonated. The resulting equilibrium lies to the right, favoring products (that is, $K_c > 1$):

$$\underset{\text{Acid}}{HSO_4^-(aq)} + \underset{\text{Base}}{CO_3^{2-}(aq)} \rightleftharpoons \underset{\text{Conjugate base}}{SO_4^{2-}(aq)} + \underset{\text{Conjugate acid}}{HCO_3^-(aq)} \qquad K_c > 1$$

Comment Of the two acids HSO_4^- and HCO_3^-, the stronger one (HSO_4^-) gives up a proton more readily, and the weaker one (HCO_3^-) tends to retain its proton. Thus, the equilibrium favors the direction in which the proton moves from the stronger acid and becomes bonded to the stronger base.

PRACTICE EXERCISE

For each reaction, use Figure 16.3 to predict whether the equilibrium lies to the left or to the right:

(**a**) $HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons H_2PO_4^-(aq) + OH^-(aq)$

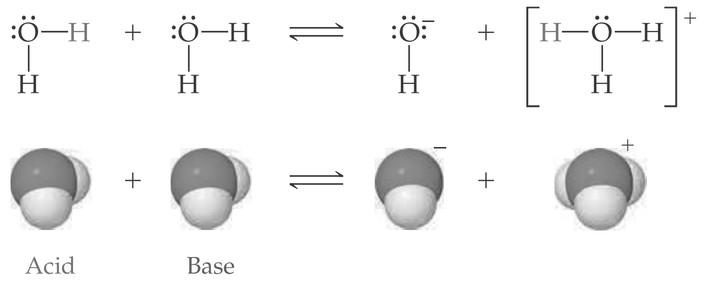
(**b**) $NH_4^+(aq) + OH^-(aq) \rightleftharpoons NH_3(aq) + H_2O(l)$

Answers: (**a**) left, (**b**) right

16.3 THE AUTOIONIZATION OF WATER

One of the most important chemical properties of water is its ability to act as either a Brønsted-Lowry acid or a Brønsted-Lowry base. In the presence of an acid, it acts as a proton acceptor; in the presence of a base, it acts as a proton donor. In fact, one water molecule can donate a proton to another water molecule:

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



[16.12]

We call this process the **autoionization** of water.

Because the forward and reverse reactions in Equation 16.12 are extremely rapid no water molecule remains ionized for long. At room temperature only about two out of every 10^9 water molecules are ionized at any given instant. Thus, pure water consists almost entirely of H_2O molecules and is an extremely poor conductor of electricity. Nevertheless, the autoionization of water is very important, as we will soon see.

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

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

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

▲ **FIGURE 16.4 Relative concentrations of H^+ and OH^- in aqueous solutions at 25 °C.**

The Ion Product of Water

The equilibrium-constant expression for the autoionization of water is

$$K_c = [H_3O^+][OH^-] \qquad [16.13]$$

The term $[H_2O]$ is excluded from the equilibrium-constant expression because we exclude the concentrations of pure solids and liquids. (Section 15.4) Because this expression refers specifically to the autoionization of water, we use the symbol K_w to denote the equilibrium constant, which we call the **ion-product constant** for water. At 25 °C, K_w equals 1.0×10^{-14}. Thus, we have

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \quad (\text{at } 25\ ^\circ\text{C}) \qquad [16.14]$$

Because we use $H^+(aq)$ and $H_3O^+(aq)$ interchangeably to represent the hydrated proton, the autoionization reaction for water can also be written as

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq) \qquad [16.15]$$

Likewise, the expression for K_w can be written in terms of either H_3O^+ or H^+, and K_w has the same value in either case:

$$K_w = [H_3O^+][OH^-] = [H^+][OH^-] = 1.0 \times 10^{-14} \quad (\text{at } 25\ ^\circ\text{C}) \qquad [16.16]$$

This equilibrium-constant expression and the value of K_w at 25 °C are extremely important, and you should commit them to memory.

A solution in which $[H^+] = [OH^-]$ is said to be *neutral*. In most solutions, however, the H^+ and OH^- concentrations are not equal. As the concentration of one of these ions increases, the concentration of the other must decrease, so that the product of their concentrations always equals 1.0×10^{-14} (▲ **FIGURE 16.4**).

SAMPLE EXERCISE 16.4 Calculating $[H^+]$ for Pure Water

Calculate the values of $[H^+]$ and $[OH^-]$ in a neutral solution at 25 °C.

SOLUTION

Analyze We are asked to determine the concentrations of H^+ and OH^- ions in a neutral solution at 25 °C.

Plan We will use Equation 16.16 and the fact that, by definition, $[H^+] = [OH^-]$ in a neutral solution.

Solve We will represent the concentration of H^+ and OH^- in neutral solution with x. This gives

$$[H^+][OH^-] = (x)(x) = 1.0 \times 10^{-14}$$
$$x^2 = 1.0 \times 10^{-14}$$
$$x = 1.0 \times 10^{-7}\,M = [H^+] = [OH^-]$$

In an acid solution $[H^+]$ is greater than $1.0 \times 10^{-7}\,M$; in a basic solution $[H^+]$ is less than $1.0 \times 10^{-7}\,M$.

PRACTICE EXERCISE

Indicate whether solutions with each of the following ion concentrations are neutral, acidic, or basic: (**a**) $[H^+] = 4 \times 10^{-9}\ M$; (**b**) $[OH^-] = 1 \times 10^{-7}\ M$; (**c**) $[OH^-] = 7 \times 10^{-13}\ M$.

Answers: (**a**) basic, (**b**) neutral, (**c**) acidic

What makes Equation 16.16 particularly useful is that it is applicable both to pure water and to any aqueous solution. Although the equilibrium between $H^+(aq)$ and $OH^-(aq)$ as well as other ionic equilibria are affected somewhat by the presence of additional ions in solution, it is customary to ignore these ionic effects except in work requiring exceptional accuracy. Thus, Equation 16.16 is taken to be valid for any dilute aqueous solution and can be used to calculate either $[H^+]$ (if $[OH^-]$ is known) or $[OH^-]$ (if $[H^+]$ is known).

SAMPLE EXERCISE 16.5 Calculating $[H^+]$ from $[OH^-]$

Calculate the concentration of $H^+(aq)$ in (**a**) a solution in which $[OH^-]$ is 0.010 *M*, (**b**) a solution in which $[OH^-]$ is $1.8 \times 10^{-9}\ M$. *Note:* In this problem and all that follow, we assume, unless stated otherwise, that the temperature is 25 °C.

SOLUTION

Analyze We are asked to calculate the $[H^+]$ concentration in an aqueous solution where the hydroxide concentration is known.

Plan We can use the equilibrium-constant expression for the autoionization of water and the value of K_w to solve for each unknown concentration.

Solve

(**a**) Using Equation 16.16, we have

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

$$[H^+] = \frac{(1.0 \times 10^{-14})}{[OH^-]} = \frac{1.0 \times 10^{-14}}{0.010} = 1.0 \times 10^{-12}\ M$$

This solution is basic because $[OH^-] > [H^+]$

(**b**) In this instance

$$[H^+] = \frac{(1.0 \times 10^{-14})}{[OH^-]} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-9}} = 5.6 \times 10^{-6}\ M$$

This solution is acidic because $[H^+] > [OH^-]$

PRACTICE EXERCISE

Calculate the concentration of $OH^-(aq)$ in a solution in which (**a**) $[H^+] = 2 \times 10^{-6}\ M$; (**b**) $[H^+] = [OH^-]$; (**c**) $[H^+] = 100 \times [OH^-]$.

Answers: (**a**) $5 \times 10^{-9}\ M$, (**b**) $1.0 \times 10^{-7}\ M$, (**c**) $1.0 \times 10^{-8}\ M$

16.4 THE pH SCALE

The molar concentration of $H^+(aq)$ in an aqueous solution is usually very small. For convenience, we therefore usually express $[H^+]$ in terms of **pH**, which is the negative logarithm in base 10 of $[H^+]$:*

$$pH = -\log[H^+] \qquad [16.17]$$

If you need to review the use of logarithms, see Appendix A.

We can use Equation 16.17 to calculate the pH of a neutral solution at 25 °C (that is, one in which $[H^+] = 1.0 \times 10^{-7}\ M$):

$$pH = -\log(1.0 \times 10^{-7}) = -(-7.00) = 7.00$$

The pH of a neutral solution is 7.00 at 25 °C. Notice that the pH is reported with two decimal places. We do so because only the numbers to the right of the decimal point are the significant

---

*Because $[H^+]$ and $[H_3O^+]$ are used interchangeably, you might see pH defined as $-\log[H_3O^+]$.

TABLE 16.1 • Relationships among (H^+), (OH^-), and pH at 25 °C

Solution Type	$[H^+]$ (M)	$[OH^-]$ (M)	pH
Acidic	$>1.0 \times 10^{-7}$	$<1.0 \times 10^{-7}$	<7.00
Neutral	1.0×10^{-7}	1.0×10^{-7}	7.00
Basic	$<1.0 \times 10^{-7}$	$>1.0 \times 10^{-7}$	>7.00

figures in a logarithm. Because our original value for the concentration (1.0×10^{-7} M) has two significant figures, the corresponding pH has two decimal places (7.00).

What happens to the pH of a solution as we make the solution more and more acidic, so that $[H^+]$ increases? Because of the negative sign in the logarithm term of Equation 16.17, *the pH decreases as* $[H^+]$ *increases*. For example, the pH of a neutral solution ($[H^+] = 1.0 \times 10^{-7}$ M) is 7.00, but when we add sufficient acid to make $[H^+] = 1.0 \times 10^{-3}$ M the pH is

$$\text{pH} = -\log(1.0 \times 10^{-3}) = -(-3.00) = 3.00$$

At 25 °C the pH of an acidic solution is less than 7.00.

We can also calculate the pH of a basic solution, one in which $[OH^-] > 1.0 \times 10^{-7}$ M. Suppose $[OH^-] = 2.0 \times 10^{-3}$ M. We can use Equation 16.16 to calculate $[H^+]$ for this solution and Equation 16.17 to calculate the pH:

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{2.0 \times 10^{-3}} = 5.0 \times 10^{-12}\ M$$

$$\text{pH} = -\log(5.0 \times 10^{-12}) = 11.30$$

At 25 °C the pH of a basic solution is greater than 7.00. The relationships among $[H^+]$, $[OH^-]$, and pH are summarized in ▲ **TABLE 16.1**.

GIVE IT SOME THOUGHT

Is it possible for a solution to have a negative pH? If so, would that pH signify a basic or acidic solution?

You might think that when $[H^+]$ is very small, as is often the case, it would be unimportant. Nothing is further from the truth. If $[H^+]$ is part of a kinetic rate law, for example, changing its concentration changes the rate. ∞ (Section 14.3) Thus, if the rate law is first order in $[H^+]$, doubling the H^+ concentration doubles the rate even if the change is merely from 1×10^{-7} M to 2×10^{-7} M. In biological systems, many reactions involve proton transfers and have rates that depend on $[H^+]$. Because the speeds of these reactions are crucial, the pH of biological fluids must be maintained within narrow limits. For example, human blood has a normal pH range of 7.35 to 7.45. Illness and even death can result if the pH varies much from this narrow range.

SAMPLE EXERCISE 16.6 Calculating pH from $[H^+]$

Calculate the pH values for the two solutions of Sample Exercise 16.5.

SOLUTION

Analyze We are asked to determine the pH of aqueous solutions for which we have already calculated $[H^+]$.

Plan We can calculate pH using its defining equation, Equation 16.17.

Solve

(a) In the first instance we found $[H^+]$ to be 1.0×10^{-12} M, so that

$$\text{pH} = -\log(1.0 \times 10^{-12}) = -(-12.00) = 12.00$$

Because 1.0×10^{-12} has two significant figures, the pH has two decimal places, 12.00.

(**b**) For the second solution, $[H^+] = 5.6 \times 10^{-6}\, M$. Before performing the calculation, it is helpful to estimate the pH. To do so, we note that $[H^+]$ lies between 1×10^{-6} and 1×10^{-5}. Thus, we expect the pH to lie between 6.0 and 5.0. We use Equation 16.17 to calculate the pH:

$$\text{pH} = -\log(5.6 \times 10^{-6}) = 5.25$$

Check After calculating a pH, it is useful to compare it to your estimate. In this case the pH, as we predicted, falls between 6 and 5. Had the calculated pH and the estimate not agreed, we should have reconsidered our calculation or estimate or both.

PRACTICE EXERCISE

(**a**) In a sample of lemon juice, $[H^+] = 3.8 \times 10^{-4}\, M$. What is the pH? (**b**) A commonly available window-cleaning solution has $[OH^-] = 1.9 \times 10^{-6}\, M$. What is the pH?

Answers: (**a**) 3.42, (**b**) $[H^+] = 5.3 \times 10^{-9}\, M$, so pH = 8.28

pOH and Other "p" Scales

The negative logarithm is a convenient way of expressing the magnitudes of other small quantities. We use the convention that the negative logarithm of a quantity is labeled "p" (quantity). Thus, we can express the concentration of OH^- as pOH:

$$\text{pOH} = -\log[OH^-] \qquad [16.18]$$

Likewise, pK_w equals $-\log K_w$.

By taking the negative logarithm of both sides of the equilibrium-constant expression for water, $K_w = [H^+][OH^-]$, we obtain

$$-\log[H^+] + (-\log[OH^-]) = -\log K_w \qquad [16.19]$$

from which we obtain the useful expression

$$\text{pH} + \text{pOH} = 14.00 \quad (\text{at } 25\ ^\circ\text{C}) \qquad [16.20]$$

The pH and pOH values characteristic of a number of familiar solutions are shown in ▶ **FIGURE 16.5**. Notice that a change in $[H^+]$ by a factor of 10 causes the pH to change by 1. Thus, the concentration of $H^+(aq)$ in a solution of pH 6 is 10 times the $H^+(aq)$ concentration in a solution of pH 7.

GIVE IT SOME THOUGHT

If the pOH for a solution is 3.00, what is the pH? Is the solution acidic or basic?

SAMPLE EXERCISE 16.7 **Calculating $[H^+]$ from pOH**

A sample of freshly pressed apple juice has a pOH of 10.24. Calculate $[H^+]$.

SOLUTION

Analyze We need to calculate $[H^+]$ from pOH.

Plan We will first use Equation 16.20, pH + pOH = 14.00, to calculate pH from pOH. Then we will use Equation 16.17 to determine the concentration of H^+.

Solve From Equation 16.20, we have

$$\text{pH} = 14.00 - \text{pOH}$$
$$\text{pH} = 14.00 - 10.24 = 3.76$$

Next we use Equation 16.17:

$$\text{pH} = -\log[H^+] = 3.76$$

Thus,

$$\log[H^+] = -3.76$$

To find $[H^+]$, we need to determine the *antilogarithm* of −3.76. Scientific calculators have an antilogarithm function (sometimes labeled INV log or 10^x) that allows us to perform the calculation:

$$[H^+] = \text{antilog}(-3.76) = 10^{-3.76} = 1.7 \times 10^{-4}\, M$$

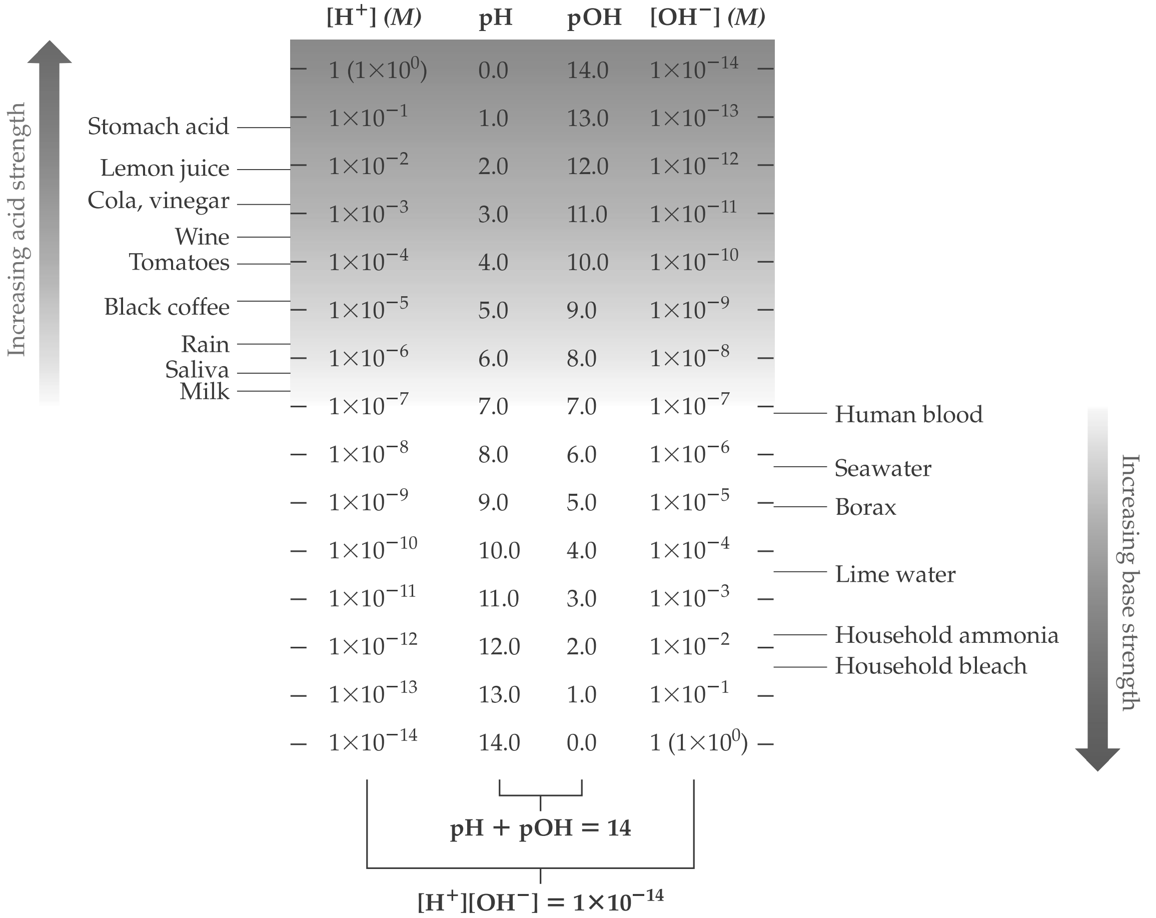
Comment The number of significant figures in $[H^+]$ is two because the number of decimal places in the pH is two.

Check Because the pH is between 3.0 and 4.0, we know that $[H^+]$ will be between 1.0×10^{-3} *M* and 1.0×10^{-4} *M*. Our calculated $[H^+]$ falls within this estimated range.

PRACTICE EXERCISE

A solution formed by dissolving an antacid tablet has a pH of 9.18. Calculate $[OH^-]$.

Answer: $[OH^-] = 1.5 \times 10^{-5}$



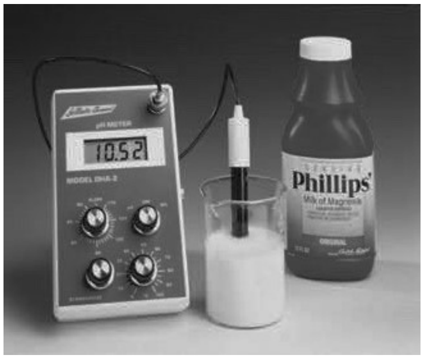
$[H^+]$ (*M*)	pH	pOH	$[OH^-]$ (*M*)
$1\ (1\times10^{0})$	0.0	14.0	1×10^{-14}
1×10^{-1}	1.0	13.0	1×10^{-13}
1×10^{-2}	2.0	12.0	1×10^{-12}
1×10^{-3}	3.0	11.0	1×10^{-11}
1×10^{-4}	4.0	10.0	1×10^{-10}
1×10^{-5}	5.0	9.0	1×10^{-9}
1×10^{-6}	6.0	8.0	1×10^{-8}
1×10^{-7}	7.0	7.0	1×10^{-7}
1×10^{-8}	8.0	6.0	1×10^{-6}
1×10^{-9}	9.0	5.0	1×10^{-5}
1×10^{-10}	10.0	4.0	1×10^{-4}
1×10^{-11}	11.0	3.0	1×10^{-3}
1×10^{-12}	12.0	2.0	1×10^{-2}
1×10^{-13}	13.0	1.0	1×10^{-1}
1×10^{-14}	14.0	0.0	$1\ (1\times10^{0})$

$$\text{pH} + \text{pOH} = 14$$

$$[H^+][OH^-] = 1\times10^{-14}$$

▲ **FIGURE 16.5 Concentrations of H^+ and pH values of some common substances at 25 °C.**

Measuring pH



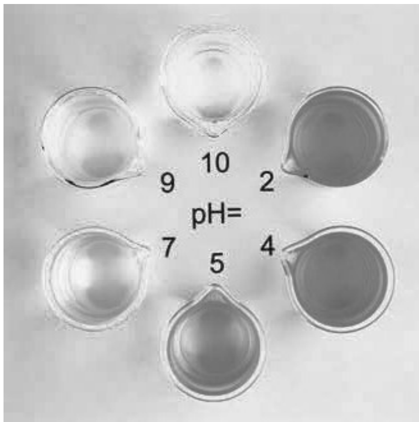
▲ **FIGURE 16.6 A digital pH meter.** The device is a millivoltmeter, and the electrodes immersed in a solution produce a voltage that depends on the pH of the solution.

The pH of a solution can be measured with a *pH meter* (▶ **FIGURE 16.6**). A complete understanding of how this important device works requires a knowledge of electrochemistry, a subject we take up in Chapter 20. In brief, a pH meter consists of a pair of electrodes connected to a meter capable of measuring small voltages, on the order of millivolts. A voltage, which varies with pH, is generated when the electrodes are placed in a solution. This voltage is read by the meter, which is calibrated to give pH.

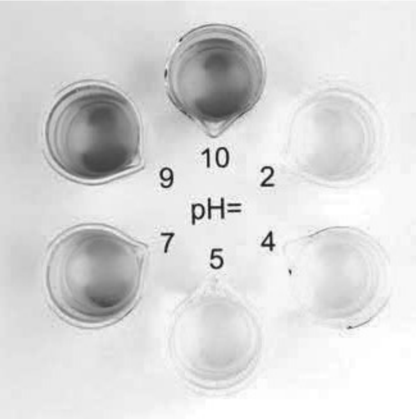
Although less precise, acid–base indicators can be used to measure pH. An acid–base indicator is a colored substance that can exist in either an acid or a base form. The two forms have different colors. Thus, the indicator has one color at lower pH and another at higher pH. If you know the pH at which the indicator turns from one form to the other, you can determine whether a solution has a higher or lower pH than this value. Litmus, for example, changes color in the vicinity of pH 7. The color change, however, is not very sharp. Red litmus indicates a pH of about 5 or lower, and blue litmus indicates a pH of about 8 or higher.

GO FIGURE

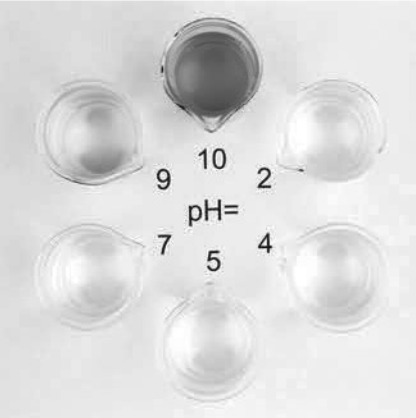
Which of these indicators is best suited to distinguish between a solution that is slightly acidic and one that is slightly basic?



Methyl red



Bromthymol blue

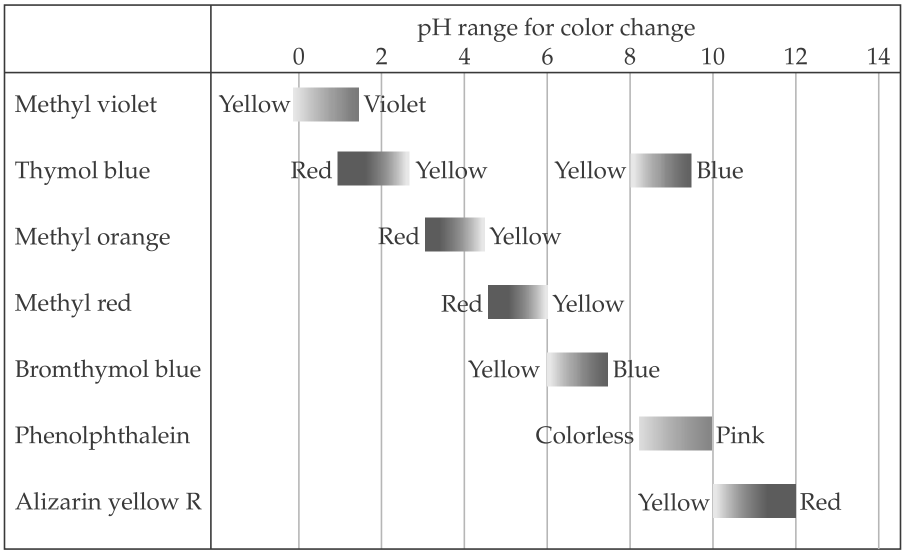


Phenolphthalein

▲ **FIGURE 16.8 Solutions containing three common acid–base indicators at various pH values.**

GO FIGURE

If a colorless solution turns pink when we add phenolphthalein, what can we conclude about the pH of the solution?



▲ **FIGURE 16.7 pH ranges for common acid–base indicators.** Most indicators have a useful range of about 2 pH units.

Some common indicators are listed in ▲ **FIGURE 16.7**. The chart tells us, for instance, that methyl red changes color over the pH interval from about 4.5 to 6.0. Below pH 4.5 it is in the acid form, which is red. In the interval between 4.5 and 6.0, it is gradually converted to its basic form, which is yellow. Once the pH rises above 6 the conversion is complete, and the solution is yellow. This color change, along with that of the indicators bromthymol blue and phenolphthalein, is shown in ◀ **FIGURE 16.8**. Paper tape impregnated with several indicators is widely used for determining approximate pH values.

16.5 STRONG ACIDS AND BASES

The chemistry of an aqueous solution often depends critically on pH. It is therefore important to examine how pH relates to acid and base concentrations. The simplest cases are those involving strong acids and strong bases. Strong acids and bases are *strong electrolytes*, existing in aqueous solution entirely as ions. There are relatively few common strong acids and bases (see Table 4.2).

Strong Acids

The seven most common strong acids include six monoprotic acids (HCl, HBr, HI, HNO_3, $HClO_3$, and $HClO_4$), and one diprotic acid (H_2SO_4). Nitric acid (HNO_3) exemplifies the behavior of the monoprotic strong acids. For all practical purposes, an aqueous solution of HNO_3 consists entirely of H_3O^+ and NO_3^- ions:

$$HNO_3(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + NO_3^-(aq) \quad \text{(complete ionization)} \qquad [16.21]$$

We have not used equilibrium arrows for this equation because the reaction lies entirely to the right. ∞ (Section 4.1) As noted in Section 16.3, we use $H_3O^+(aq)$ and $H^+(aq)$ interchangeably to represent the hydrated proton in water. Thus, we can simplify this acid ionization equation to

$$HNO_3(aq) \longrightarrow H^+(aq) + NO_3^-(aq)$$

In an aqueous solution of a strong acid, the acid is normally the only significant source of H^+ ions.* As a result, calculating the pH of a solution of a strong monoprotic acid is straightforward because $[H^+]$ equals the original concentration of acid. In a 0.20 *M* solution of $HNO_3(aq)$, for example, $[H^+] = [NO_3^-] = 0.20\ M$. The situation with the diprotic acid H_2SO_4 is more complex, as we will see in Section 16.6.

SAMPLE EXERCISE 16.8 Calculating the pH of a Strong Acid

What is the pH of a 0.040 *M* solution of $HClO_4$?

SOLUTION

Analyze and Plan Because $HClO_4$ is a strong acid, it is completely ionized, giving $[H^+] = [ClO_4^-] = 0.040\ M$.

Solve

$$\text{pH} = -\log(0.040) = 1.40.$$

Check Because $[H^+]$ lies between 1×10^{-2} and 1×10^{-1}, the pH will be between 2.0 and 1.0. Our calculated pH falls within the estimated range. Furthermore, because the concentration has two significant figures, the pH has two decimal places.

PRACTICE EXERCISE

An aqueous solution of HNO_3 has a pH of 2.34. What is the concentration of the acid?

Answer: 0.0046 *M*

Strong Bases

The most common soluble strong bases are the ionic hydroxides of the alkali metals, such as NaOH, KOH, and the ionic hydroxides heavier alkaline earth metals, such as $Sr(OH)_2$. These compounds completely dissociate into ions in aqueous solution. Thus, a solution labeled 0.30 *M* NaOH consists of 0.30 *M* $Na^+(aq)$ and 0.30 *M* $OH^-(aq)$; there is essentially no undissociated NaOH.

GIVE IT SOME THOUGHT

Which solution has the higher pH, a 0.001 *M* solution of NaOH or a 0.001 *M* solution of $Ba(OH)_2$?

SAMPLE EXERCISE 16.9 Calculating the pH of a Strong Base

What is the pH of (**a**) a 0.028 *M* solution of NaOH, (**b**) a 0.0011 *M* solution of $Ca(OH)_2$?

SOLUTION

Analyze We are asked to calculate the pH of two solutions of strong bases.

Plan We can calculate each pH by either of two equivalent methods. First, we could use Equation 16.16 to calculate $[H^+]$ and then use Equation 16.17 to calculate the pH. Alternatively, we could use $[OH^-]$ to calculate pOH and then use Equation 16.20 to calculate the pH.

Solve

(**a**) NaOH dissociates in water to give one OH^- ion per formula unit. Therefore, the OH^- concentration for the solution in (a) equals the stated concentration of NaOH, namely 0.028 *M*.

Method 1:

$$[H^+] = \frac{1.0 \times 10^{-14}}{0.028} = 3.57 \times 10^{-13}\ M \qquad \text{pH} = -\log(3.57 \times 10^{-13}) = 12.45$$

Method 2:

$$\text{pOH} = -\log(0.028) = 1.55 \qquad \text{pH} = 14.00 - \text{pOH} = 12.45$$

---

*If the concentration of the acid is 10^{-6} *M* or less, we also need to consider H^+ ions that result from H_2O autoionization. Normally, the concentration of H^+ from H_2O is so small that it can be neglected.

(b) $Ca(OH)_2$ is a strong base that dissociates in water to give two OH^- ions per formula unit. Thus, the concentration of $OH^-(aq)$ for the solution in part (b) is $2 \times (0.0011\ M) = 0.0022\ M$.

Method 1:

$$[H^+] = \frac{1.0 \times 10^{-14}}{0.0022} = 4.55 \times 10^{-12}\ M \qquad pH = -\log(4.55 \times 10^{-12}) = 11.34$$

Method 2:

$$pOH = -\log(0.0022) = 2.66 \qquad pH = 14.00 - pOH = 11.34$$

PRACTICE EXERCISE

What is the concentration of a solution of **(a)** KOH for which the pH is 11.89, **(b)** $Ca(OH)_2$ for which the pH is 11.68?

Answers: **(a)** $7.8 \times 10^{-3}\ M$, **(b)** $2.4 \times 10^{-3}\ M$

Although all of the alkali metal hydroxides are strong electrolytes, LiOH, RbOH, and CsOH are not commonly encountered in the laboratory. The hydroxides of the heavier alkaline earth metals—$Ca(OH)_2$, $Sr(OH)_2$, and $Ba(OH)_2$—are also strong electrolytes. They have limited solubility, however, so they are used only when high solubility is not critical.

Strongly basic solutions are also created by certain substances that react with water to form $OH^-(aq)$. The most common of these contain the oxide ion. Ionic metal oxides, especially Na_2O and CaO, are often used in industry when a strong base is needed. The O^{2-} reacts with water to form OH^-, leaving virtually no O^{2-} in the solution:

$$O^{2-}(aq) + H_2O(l) \longrightarrow 2\ OH^-(aq) \qquad [16.22]$$

Thus, a solution formed by dissolving 0.010 mol of $Na_2O(s)$ in enough water to form 1.0 L of solution has $[OH^-] = 0.020\ M$ and a pH of 12.30.

GIVE IT SOME THOUGHT

The CH_3^- ion is the conjugate base of CH_4, and CH_4 shows no evidence of being an acid in water. What happens when CH_3^- is added to water?

16.6 WEAK ACIDS

Most acidic substances are weak acids and therefore only partially ionized in aqueous solution (▶ **FIGURE 16.9**). We can use the equilibrium constant for the ionization reaction to express the extent to which a weak acid ionizes. If we represent a general weak acid as HA, we can write the equation for its ionization in either of the following ways, depending on whether the hydrated proton is represented as $H_3O^+(aq)$ or $H^+(aq)$:

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq) \qquad [16.23]$$

or

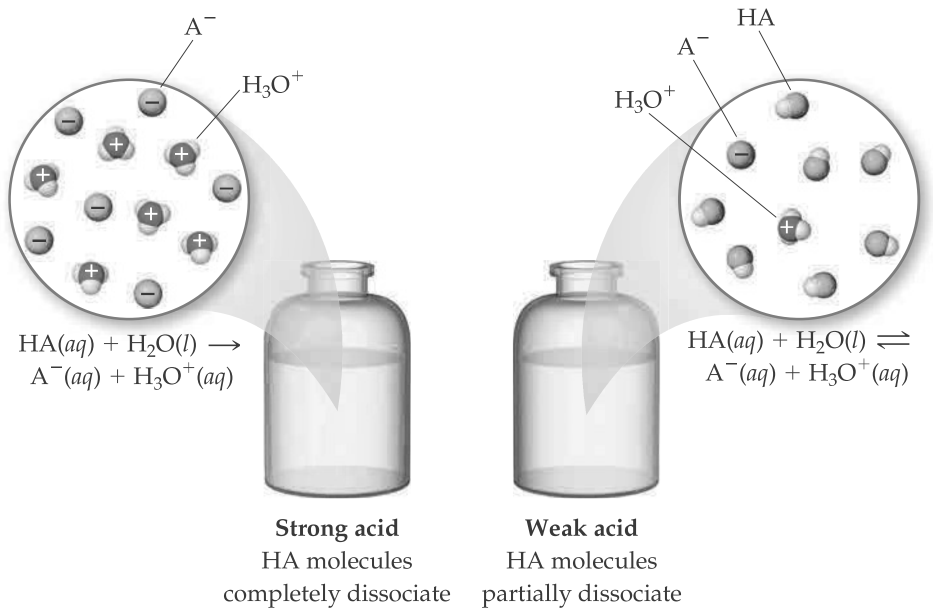
$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq) \qquad [16.24]$$

Because H_2O is the solvent, it is omitted from the equilibrium-constant expression. (Section 15.4) Thus, we can write the equilibrium-constant expression as either

$$K_c = \frac{[H_3O^+][A^-]}{[HA]} \quad \text{or} \quad K_c = \frac{[H^+][A^-]}{[HA]}$$

As we did for the ion-product constant for the autoionization of water, we change the subscript on this equilibrium constant to indicate the type of equation to which it corresponds:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \quad \text{or} \quad K_a = \frac{[H^+][A^-]}{[HA]} \qquad [16.25]$$

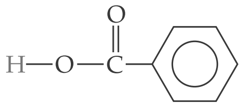
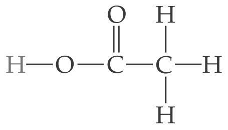
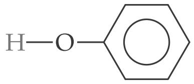


▲ **FIGURE 16.9** **Species present in a solution of a strong acid and a weak acid.**

The subscript *a* denotes that K_a is an equilibrium constant for the ionization of an acid, so K_a is called the **acid-dissociation constant**.

▼ **TABLE 16.2** shows the structural formulas, conjugate bases, and K_a values for a number of weak acids. Appendix D provides a more complete list. Many weak acids are organic compounds composed entirely of carbon, hydrogen, and oxygen. These compounds usually contain some hydrogen atoms bonded to carbon atoms and some bonded to oxygen atoms. In almost all cases, the hydrogen atoms bonded to carbon do not ionize in water; instead, the acidic behavior of these compounds is due to the hydrogen atoms attached to oxygen atoms.

TABLE 16.2 • Some Weak Acids in Water at 25 °C

Acid	Structural Formula*	Conjugate Base	K_a
Chlorous ($HClO_2$)	H—O—Cl—O	ClO_2^-	1.0×10^{-2}
Hydrofluoric (HF)	H—F	F^-	6.8×10^{-4}
Nitrous (HNO_2)	H—O—N=O	NO_2^-	4.5×10^{-4}
Benzoic (C_6H_5COOH)		$C_6H_5COO^-$	6.3×10^{-5}
Acetic (CH_3COOH)	 $H-O-\overset{\overset{\displaystyle O}{\Vert}}{C}-\underset{\underset{\displaystyle H}{\vert}}{\overset{\overset{\displaystyle H}{\vert}}{C}}-H$	CH_3COO^-	1.8×10^{-5}
Hypochlorous (HOCl)	H—O—Cl	OCl^-	3.0×10^{-5}
Hydrocyanic (HCN)	H—C≡N	CN^-	4.9×10^{-10}
Phenol (HOC_6H_5)		$C_6H_5O^-$	1.3×10^{-10}

*The proton that ionizes is shown in red.

The magnitude of K_a indicates the tendency of the acid to ionize in water: *The larger the value of K_a, the stronger the acid*. Chlorous acid ($HClO_2$), for example, is the strongest acid in Table 16.2, and phenol (HOC_6H_5) is the weakest. For most weak acids K_a values range from 10^{-2} to 10^{-10}.

GIVE IT SOME THOUGHT

Based on the entries in Table 16.2, which element is most commonly bonded to the acidic hydrogen?

Calculating K_a from pH

In order to calculate either the K_a value for a weak acid or the pH of its solutions, we will use many of the skills for solving equilibrium problems developed in Section 15.5. In many cases the small magnitude of K_a allows us to use approximations to simplify the problem. In doing these calculations, it is important to realize that proton-transfer reactions are generally very rapid. As a result, the measured or calculated pH for a weak acid always represents an equilibrium condition.

SAMPLE EXERCISE 16.10 Calculating K_a from Measured pH

A student prepared a 0.10 *M* solution of formic acid (HCOOH) and found its pH at 25 °C to be 2.38. Calculate K_a for formic acid at this temperature.

SOLUTION

Analyze We are given the molar concentration of an aqueous solution of weak acid and the pH of the solution, and we are asked to determine the value of K_a for the acid.

Plan Although we are dealing specifically with the ionization of a weak acid, this problem is very similar to the equilibrium problems we encountered in Chapter 15. We can solve this problem using the method first outlined in Sample Exercise 15.9, starting with the chemical reaction and a tabulation of initial and equilibrium concentrations.

Solve The first step in solving any equilibrium problem is to write the equation for the equilibrium reaction. The ionization of formic acid can be written as

$$HCOOH(aq) \rightleftharpoons H^+(aq) + HCOO^-(aq)$$

The equilibrium-constant expression is

$$K_a = \frac{[H^+][HCOO^-]}{[HCOOH]}$$

From the measured pH, we can calculate $[H^+]$:

$$pH = -\log[H^+] = 2.38$$

$$\log[H^+] = -2.38$$

$$[H^+] = 10^{-2.38} = 4.2 \times 10^{-3}\ M$$

To determine the concentrations of the species involved in the equilibrium, we imagine that the solution is initially 0.10 *M* in HCOOH molecules. We then consider the ionization of the acid into H^+ and $HCOO^-$. For each HCOOH molecule that ionizes, one H^+ ion and one $HCOO^-$ ion are produced in solution. Because the pH measurement indicates that $[H^+] = 4.2 \times 10^{-3}\ M$ at equilibrium, we can construct the following table:

	$HCOOH(aq)$ $\rightleftharpoons$	$H^+(aq)$ +	$HCOO^-(aq)$
Initial	$0.10\ M$	0	0
Change	$-4.2 \times 10^{-3}\ M$	$+4.2 \times 10^{-3}\ M$	$+4.2 \times 10^{-3}\ M$
Equilibrium	$(0.10 - 4.2 \times 10^{-3})\ M$	$4.2 \times 10^{-3}\ M$	$4.2 \times 10^{-3}\ M$

Notice that we have neglected the very small concentration of $H^+(aq)$ due to H_2O autoionization. Notice also that the amount of HCOOH that ionizes is very small compared with the initial concentration of the acid. To the number of significant figures we are using, the subtraction yields 0.10 *M*:

$$(0.10 - 4.2 \times 10^{-3})\ M \simeq 0.10\ M$$

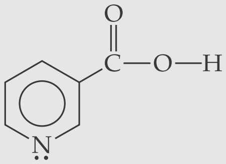
We can now insert the equilibrium concentrations into the expression for K_a:

$$K_a = \frac{(4.2 \times 10^{-3})(4.2 \times 10^{-3})}{0.10} = 1.8 \times 10^{-4}$$

Check The magnitude of our answer is reasonable because K_a for a weak acid is usually between 10^{-2} and 10^{-10}.

PRACTICE EXERCISE

Niacin, one of the B vitamins, has the molecular structure



A 0.020 *M* solution of niacin has a pH of 3.26. What is the acid-dissociation constant for niacin?

Answer: 1.5×10^{-5}

Percent Ionization

We have seen that the magnitude of K_a indicates the strength of a weak acid. Another measure of acid strength is **percent ionization**, defined as

$$\text{Percent ionization} = \frac{\text{concentration ionized}}{\text{original concentration}} \times 100\% \qquad [16.26]$$

The stronger the acid, the greater the percent ionization.

For any acid, the concentration of acid that ionizes equals the concentration of $H^+(aq)$ that forms, assuming that H_2O autoionization is negligible. Thus, the percent ionization for an acid HA is also given by

$$\text{Percent ionization} = \frac{[H^+]_{\text{equilibrium}}}{[HA]_{\text{initial}}} \times 100\% \qquad [16.27]$$

For example, a 0.035 *M* solution of HNO_2 contains $3.7 \times 10^{-3}\ M\ H^+(aq)$ and its percent ionization is

$$\text{Percent ionization} = \frac{[H^+]_{\text{equilibrium}}}{[HNO_2]_{\text{initial}}} \times 100\% = \frac{3.7 \times 10^{-3}\ M}{0.035\ M} \times 100\% = 11\%$$

SAMPLE EXERCISE 16.11 **Calculating Percent Ionization**

As calculated in Sample Exercise 16.10, a 0.10 *M* solution of formic acid (HCOOH) contains $4.2 \times 10^{-3}\ M\ H^+(aq)$. Calculate the percentage of the acid that is ionized.

SOLUTION

Analyze We are given the molar concentration of an aqueous solution of weak acid and the equilibrium concentration of $H^+(aq)$ and asked to determine the percent ionization of the acid.

Plan The percent ionization is given by Equation 16.27.

Solve

$$\text{Percent ionization} = \frac{[H^+]_{\text{equilibrium}}}{[HCOOH]_{\text{initial}}} \times 100\% = \frac{4.2 \times 10^{-3}\ M}{0.10\ M} \times 100\% = 4.2\%$$

PRACTICE EXERCISE

A 0.020 *M* solution of niacin has a pH of 3.26. Calculate the percent ionization of the niacin.

Answer: 2.7%

Using K_a to Calculate pH

Knowing the value of K_a and the initial concentration of a weak acid, we can calculate the concentration of $H^+(aq)$ in a solution of the acid. Let's calculate the pH at 25 °C of a 0.30 *M* solution of acetic acid (CH_3COOH), the weak acid responsible for the characteristic odor and acidity of vinegar.

1. Our first step is to write the ionization equilibrium:

$$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq) \qquad [16.28]$$

Notice that the hydrogen that ionizes is the one attached to an oxygen atom.

2. The second step is to write the equilibrium-constant expression and the value for the equilibrium constant. Taking $K_a = 1.8 \times 10^{-5}$ from Table 16.2, we write

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = 1.8 \times 10^{-5} \qquad [16.29]$$

3. The third step is to express the concentrations involved in the equilibrium reaction. This can be done with a little accounting, as described in Sample Exercise 16.10. Because we want to find the equilibrium value for $[H^+]$, let's call this quantity x. The concentration of acetic acid before any of it ionizes is 0.30 *M*. The chemical equation tells us that for each molecule of CH_3COOH that ionizes, one $H^+(aq)$ and one $CH_3COO^-(aq)$ are formed. Consequently, if x moles per liter of $H^+(aq)$ form at equilibrium, x moles per liter of $CH_3COO^-(aq)$ must also form and x moles per liter of CH_3COOH must be ionized:

	$CH_3COOH(aq)$ $\rightleftharpoons$	$H^+(aq)$ +	$CH_3COO^-(aq)$
Initial	0.30 *M*	0	0
Change	$-x$ *M*	$+x$ *M*	$+x$ *M*
Equilibrium	$(0.30 - x)$ *M*	x *M*	x *M*

4. The fourth step is to substitute the equilibrium concentrations into the equilibrium-constant expression and solve for x:

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = \frac{(x)(x)}{0.30 - x} = 1.8 \times 10^{-5} \qquad [16.30]$$

This expression leads to a quadratic equation in x, which we can solve by using either an equation-solving calculator or the quadratic formula. We can simplify the problem, however, by noting that the value of K_a is quite small. As a result, we anticipate that the equilibrium lies far to the left and that x is much smaller than the initial concentration of acetic acid. Thus, we *assume* that x is negligible relative to 0.30, so that $0.30 - x$ is essentially equal to 0.30. We can (and should!) check the validity of this assumption when we finish the problem. By using this assumption, Equation 16.30 becomes

$$K_a = \frac{x^2}{0.30} = 1.8 \times 10^{-5}$$

Solving for x, we have

$$x^2 = (0.30)(1.8 \times 10^{-5}) = 5.4 \times 10^{-6}$$
$$x = \sqrt{5.4 \times 10^{-6}} = 2.3 \times 10^{-3}$$
$$[H^+] = x = 2.3 \times 10^{-3}\,M$$
$$\text{pH} = -\log(2.3 \times 10^{-3}) = 2.64$$

Now we check the validity of our simplifying assumption that $0.30 - x \simeq 0.30$. The value of x we determined is so small that, for this number of significant figures, the assumption is entirely valid. We are thus satisfied that the assumption was a reasonable one to make. Because x represents the moles per liter of acetic acid that ionize, we see that, in this particular case, less than 1% of the acetic acid molecules ionize:

$$\text{Percent ionization of } CH_3COOH = \frac{0.0023\ M}{0.30\ M} \times 100\% = 0.77\%$$

As a general rule, if x is more than about 5% of the initial concentration value, it is better to use the quadratic formula. You should always check the validity of any simplifying assumptions after you have finished solving a problem.

GIVE IT SOME THOUGHT

Why can we generally assume that the equilibrium concentration of a weak acid equals its initial concentration?

Finally, we can compare the pH value of this weak acid with the pH of a solution of a strong acid of the same concentration. The pH of the 0.30 *M* acetic acid is 2.64, but the pH of a 0.30 *M* solution of a strong acid such as HCl is $-\log(0.30) = 0.52$. As expected, the pH of a solution of a weak acid is higher than that of a solution of a strong acid of the same molarity. (Remember, the higher the pH value, the *less* acidic the solution.)

SAMPLE EXERCISE 16.12 Using K_a to Calculate pH

Calculate the pH of a 0.20 *M* solution of HCN. (Refer to Table 16.2 or Appendix D for the value of K_a.)

SOLUTION

Analyze We are given the molarity of a weak acid and are asked for the pH. From Table 16.2, K_a for HCN is 4.9×10^{-10}.

Plan We proceed as in the example just worked in the text, writing the chemical equation and constructing a table of initial and equilibrium concentrations in which the equilibrium concentration of H^+ is our unknown.

Solve Writing both the chemical equation for the ionization reaction that forms $H^+(aq)$ and the equilibirium-constant (K_a) expression for the reaction:

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

$$K_a = \frac{[H^+][CN^-]}{[HCN]} = 4.9 \times 10^{-10}$$

Next, we tabulate the concentrations of the species involved in the equilibrium reaction, letting $x = [H^+]$ at equilibrium:

	$HCN(aq)$ $\rightleftharpoons$	$H^+(aq)$ +	$CN^-(aq)$
Initial	$0.20\ M$	0	0
Change	$-x\ M$	$+x\ M$	$+x\ M$
Equilibrium	$(0.20 - x)\ M$	$x\ M$	$x\ M$

Substituting the equilibrium concentrations into the equilibrium-constant expression yields

$$K_a = \frac{(x)(x)}{0.20 - x} = 4.9 \times 10^{-10}$$

We next make the simplifying approximation that x, the amount of acid that dissociates, is small compared with the initial concentration of acid, $0.20 - x \simeq 0.20$. Thus,

$$\frac{x^2}{0.20} = 4.9 \times 10^{-10}$$

Solving for x, we have

$$x^2 = (0.20)(4.9 \times 10^{-10}) = 0.98 \times 10^{-10}$$

$$x = \sqrt{0.98 \times 10^{-10}} = 9.9 \times 10^{-6}\ M = [H^+]$$

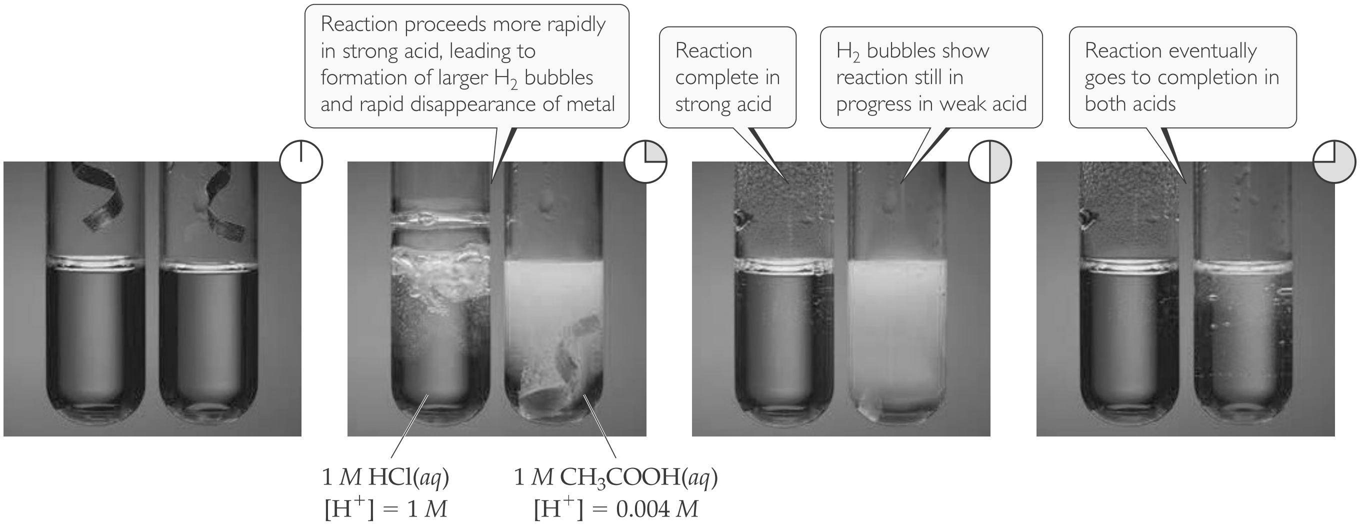
A concentration of $9.9 \times 10^{-6}\ M$ is much smaller than 5% of 0.20, the initial HCN concentration. Our simplifying approximation is therefore appropriate. We now calculate the pH of the solution:

$$\text{pH} = -\log[H^+] = -\log(9.9 \times 10^{-6}) = 5.00$$

PRACTICE EXERCISE

The K_a for niacin (Practice Exercise 16.10) is 1.5×10^{-5}. What is the pH of a 0.010 *M* solution of niacin?

Answer: 3.41



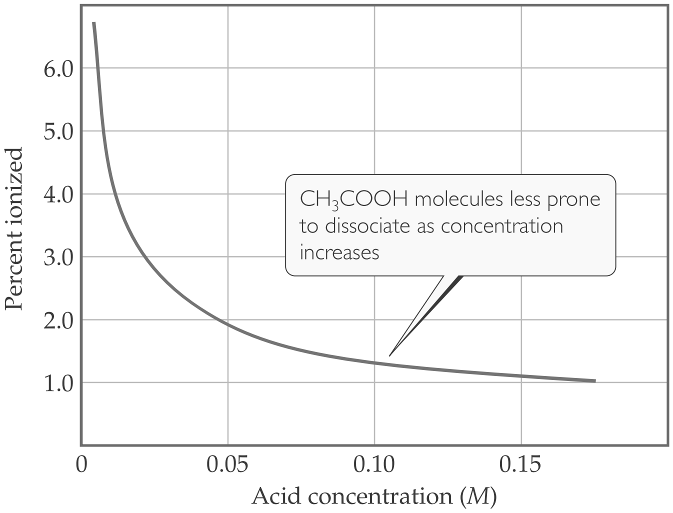
▲ **FIGURE 16.10 Rates of the same reaction run in a weak acid and a strong acid.** The bubbles are H_2 gas, which along with metal cations, is produced when a metal is oxidized by an acid (Section 4.4).

The properties of an acid solution that relate directly to the concentration of $H^+(aq)$, such as electrical conductivity and rate of reaction with an active metal, are less evident for a solution of a weak acid than for a solution of a strong acid of the same concentration. ▲ **FIGURE 16.10** presents an experiment that demonstrates this difference with $1\ M$ CH_3COOH and $1\ M$ HCl. The $1\ M$ CH_3COOH contains only $0.004\ M$ $H^+(aq)$, whereas the $1\ M$ HCl solution contains $1\ M$ $H^+(aq)$. As a result, the reaction rate with the metal is much faster in the HCl solution.

As the concentration of a weak acid increases, the equilibrium concentration of $H^+(aq)$ increases, as expected. However, as shown in ▼ **FIGURE 16.11**, *the percent ionization decreases as the concentration increases*. Thus, the concentration of $H^+(aq)$ is not directly proportional to the concentration of the weak acid. For example, doubling the concentration of a weak acid does not double the concentration of $H^+(aq)$.

GO FIGURE

Is the trend observed in this graph consistent with Le Châtelier's principle? Explain.



▲ **FIGURE 16.11 Effect of concentration on percent ionization in an acetic acid solution.**

SAMPLE EXERCISE 16.13 Using K_a to Calculate Percent Ionization

Calculate the percentage of HF molecules ionized in **(a)** a 0.10 *M* HF solution, **(b)** a 0.010 *M* HF solution.

SOLUTION

Analyze We are asked to calculate the percent ionization of two HF solutions of different concentration. From Appendix D, we find $K_a = 6.8 \times 10^{-4}$.

Plan We approach this problem as we have previous equilibrium problems. We begin by writing the chemical equation for the equilibrium and tabulating the known and unknown concentrations of all species. We then substitute the equilibrium concentrations into the equilibrium-constant expression and solve for the unknown concentration, that of H^+.

Solve

(a) The equilibrium reaction and equilibrium concentrations are as follows:

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

	$HF(aq)$	$H^+(aq)$	$F^-(aq)$
Initial	0.10 M	0	0
Change	$-x\,M$	$+x\,M$	$+x\,M$
Equilibrium	$(0.10 - x)\,M$	x M	x M

The equilibrium-constant expression is

$$K_a = \frac{[H^+][F^-]}{[HF]} = \frac{(x)(x)}{0.10 - x} = 6.8 \times 10^{-4}$$

When we try solving this equation using the approximation $0.10 - x \simeq 0.10$ (that is, by neglecting the concentration of acid that ionizes), we obtain

$$x = 8.2 \times 10^{-3}\,M$$

Because this value is greater than 5% of 0.10 *M*, however, we should work the problem without the approximation. Rearranging our equation and writing it in standard quadratic form, we have

$$\begin{aligned} x^2 &= (0.10 - x)(6.8 \times 10^{-4}) \\ &= 6.8 \times 10^{-5} - (6.8 \times 10^{-4})x \end{aligned}$$

$$x^2 + (6.8 \times 10^{-4})x - 6.8 \times 10^{-5} = 0$$

Substituting these values in the standard quadratic formula gives

$$\begin{aligned} x &= \frac{-6.8 \times 10^{-4} \pm \sqrt{(6.8 \times 10^{-4})^2 - 4(-6.8 \times 10^{-5})}}{2} \\ &= \frac{-6.8 \times 10^{-4} \pm 1.6 \times 10^{-2}}{2} \end{aligned}$$

Of the two solutions, only the one that gives a positive value for *x* is chemically reasonable. Thus,

$$x = [H^+] = [F^-] = 7.9 \times 10^{-3}\,M$$

From our result, we can calculate the percent of molecules ionized:

$$\begin{aligned} \text{Percent ionization of HF} &= \frac{\text{concentration ionized}}{\text{original concentration}} \times 100\% \\ &= \frac{7.9 \times 10^{-3}\,M}{0.10\,M} \times 100\% = 7.9\% \end{aligned}$$

(b) Proceeding similarly for the 0.010 *M* solution, we have

$$\frac{x^2}{0.010 - x} = 6.8 \times 10^{-4}$$

Solving the resultant quadratic expression, we obtain

$$x = \left[H^+\right] = \left[F^-\right] = 2.3 \times 10^{-3}\,M$$

The percentage of molecules ionized is

$$\frac{0.0023\,M}{0.010\,M} \times 100\% = 23\%$$

Comment Notice that if we do not use the quadratic formula, we calculate 8.2% ionization for (a) and 26% ionization for (b). Notice also that in diluting the solution by a factor of 10, the percentage of molecules ionized increases by a factor of 3. This result is in accord with what we see in Figure 16.11. It is also what we expect from Le Châtelier's principle. (Section 15.7) There are more "particles" or reaction components on the right side of the equation than on the left. Dilution causes the reaction to shift in the direction of the larger number of particles (toward the product side) because this counters the effect of the decreasing concentration of particles.

PRACTICE EXERCISE

In Practice Exercise 16.11, we found that the percent ionization of niacin ($K_a = 1.5 \times 10^{-5}$) in a 0.020 *M* solution is 2.7%. Calculate the percentage of niacin molecules ionized in a solution that is **(a)** 0.010 *M*, **(b)** $1.0 \times 10^{-3}\,M$.

Answers: **(a)** 3.9%, **(b)** 12%

Polyprotic Acids

Many acids have more than one ionizable H atom. These acids are known as **polyprotic acids**. For example, with sulfurous acid (H_2SO_3) we have the successive ionizations

$$H_2SO_3(aq) \rightleftharpoons H^+(aq) + HSO_3^-(aq) \qquad K_{a1} = 1.7 \times 10^{-2} \qquad [16.31]$$

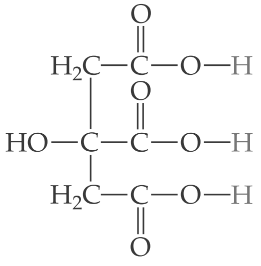
$$HSO_3^-(aq) \rightleftharpoons H^+(aq) + SO_3^{2-}(aq) \qquad K_{a2} = 6.4 \times 10^{-8} \qquad [16.32]$$

Note that the acid-dissociation constants are labeled K_{a1} and K_{a2}. The numbers on the constants refer to the particular proton of the acid that is ionizing. Thus, K_{a2} always refers to the equilibrium involving removal of the second proton of a polyprotic acid.

Note that K_{a2} for sulfurous acid is much smaller than K_{a1}. Because of electrostatic attractions, we would expect a positively charged proton to be lost more readily from the neutral H_2SO_3 molecule than from the negatively charged HSO_3^- ion. This observation is general: *It is always easier to remove the first proton from a polyprotic acid than to remove the second*. Similarly, for an acid with three ionizable protons, it is easier to remove the second proton than the third. Thus, the K_a values become successively smaller as successive protons are removed.

GO FIGURE

Citric acid has four hydrogens bonded to oxygen. How does the hydrogen that is not an acidic proton differ from the other three?



▲ **FIGURE 16.12 The structure of the polyprotic acid, citric acid.**

GIVE IT SOME THOUGHT

What is meant by the symbol K_{a3} for H_3PO_4?

The acid-dissociation constants for common polyprotic acids are listed in ▼ **TABLE 16.3**, and Appendix D provides a more complete list. The structure of citric acid illustrates the presence of multiple ionizable protons ◀ **FIGURE 16.12**.

Notice in Table 16.3 that in most cases the K_a values for successive losses of protons differ by a factor of at least 10^3. Notice also that the value of K_{a1} for sulfuric acid is listed simply as "large." Sulfuric acid is a strong acid with respect to the removal of the first proton. Thus, the reaction for the first ionization step lies completely to the right:

$$H_2SO_4(aq) \longrightarrow H^+(aq) + HSO_4^-(aq) \quad \text{(complete ionization)}$$

However, HSO_4^- is a weak acid for which $K_{a2} = 1.2 \times 10^{-2}$.

For many polyprotic acids K_{a1} is much larger than subsequent dissociation constants, in which case the $H^+(aq)$ in the solution comes almost entirely from the first ionization reaction. As long as successive K_a values differ by a factor of 10^3 or more, it is possible to obtain a satisfactory estimate of the pH of polyprotic acid solutions by treating the acids as if they were monoprotic, considering only K_{a1}.

TABLE 16.3 • Acid-Dissociation Constants of Some Common Polyprotic Acids

Name	Formula	K_{a1}	K_{a2}	K_{a3}
Ascorbic	$H_2C_6H_6O_6$	8.0×10^{-5}	1.6×10^{-12}	
Carbonic	H_2CO_3	4.3×10^{-7}	5.6×10^{-11}	
Citric	$H_3C_6H_5O_7$	7.4×10^{-4}	1.7×10^{-5}	4.0×10^{-7}
Oxalic	$H_2C_2O_4$	5.9×10^{-2}	6.4×10^{-5}	
Phosphoric	H_3PO_4	7.5×10^{-3}	6.2×10^{-8}	4.2×10^{-13}
Sulfurous	H_2SO_3	1.7×10^{-2}	6.4×10^{-8}	
Sulfuric	H_2SO_4	Large	1.2×10^{-2}	
Tartaric	$H_2C_4H_4O_6$	1.0×10^{-3}	4.6×10^{-5}	

SAMPLE EXERCISE 16.14 Calculating the pH of a Polyprotic Acid Solution

The solubility of CO_2 in water at 25 °C and 0.1 atm is 0.0037 *M*. The common practice is to assume that all the dissolved CO_2 is in the form of carbonic acid (H_2CO_3), which is produced in the reaction

$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$

What is the pH of a 0.0037 *M* solution of H_2CO_3?

SOLUTION

Analyze We are asked to determine the pH of a 0.0037 *M* solution of a polyprotic acid.

Plan H_2CO_3 is a diprotic acid; the two acid-dissociation constants, K_{a1} and K_{a2} (Table 16.3), differ by more than a factor of 10^3. Consequently, the pH can be determined by considering only K_{a1}, thereby treating the acid as if it were a monoprotic acid.

Solve Proceeding as in Sample Exercises 16.12 and 16.13, we can write the equilibrium reaction and equilibrium concentrations as

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

	$H_2CO_3(aq)$	$H^+(aq)$	$HCO_3^-(aq)$
Initial	0.0037 *M*	0	0
Change	$-x\ M$	$+x\ M$	$+x\ M$
Equilibrium	$(0.0037 - x)\ M$	$x\ M$	$x\ M$

The equilibrium-constant expression is

$$K_{a1} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = \frac{(x)(x)}{0.0037 - x} = 4.3 \times 10^{-7}$$

Solving this equation using an equation-solving calculator, we get

$$x = 4.0 \times 10^{-5}\ M$$

Alternatively, because K_{a1} is small, we can make the simplifying approximation that x is small, so that

$$0.0037 - x \simeq 0.0037$$

Thus,

$$\frac{(x)(x)}{0.0037} = 4.3 \times 10^{-7}$$

Solving for x, we have

$$x^2 = (0.0037)(4.3 \times 10^{-7}) = 1.6 \times 10^{-9}$$

$$x = [H^+] = [HCO_3^-] = \sqrt{1.6 \times 10^{-9}} = 4.0 \times 10^{-5}\ M$$

Because we get the same value (to 2 significant figures) our simplifying assumption was justified. The pH is therefore

$$pH = -\log[H^+] = -\log(4.0 \times 10^{-5}) = 4.40$$

Comment If we were asked for $[CO_3^{2-}]$, we would need to use K_{a2}. Let's illustrate that calculation. Using our calculated values of $[HCO_3^-]$ and $[H^+]$ and setting $[CO_3^{2-}] = y$, we have

$$HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq)$$

	$HCO_3^-(aq)$	$H^+(aq)$	$CO_3^{2-}(aq)$
Initial	$4.0 \times 10^{-5}\ M$	$4.0 \times 10^{-5}\ M$	0
Change	$-y\ M$	$+y\ M$	$+y\ M$
Equilibrium	$(4.0 \times 10^{-5} - y)\ M$	$(4.0 \times 10^{-5} + y)\ M$	y M

Assuming that y is small relative to 4.0×10^{-5}, we have

$$K_{a2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = \frac{(4.0 \times 10^{-5})(y)}{4.0 \times 10^{-5}} = 5.6 \times 10^{-11}$$

$$y = 5.6 \times 10^{-11}\ M = [CO_3^{2-}]$$

This value is indeed very small compared with 4.0×10^{-5}, showing that our assumption was justified. It also shows that the ionization of HCO_3^- is negligible relative to that of H_2CO_3, as far as production of H^+ is concerned. However, it is the *only* source of CO_3^{2-}, which has a very low concentration in the solution. Our calculations thus tell us that in a solution of carbon dioxide in water, most of the CO_2 is in the form of CO_2 or H_2CO_3, only a small fraction ionizes to form H^+ and HCO_3^-, and an even smaller fraction ionizes to give CO_3^{2-}. Notice also that $[CO_3^{2-}]$ is numerically equal to K_{a2}.

PRACTICE EXERCISE

(**a**) Calculate the pH of a 0.020 *M* solution of oxalic acid ($H_2C_2O_4$). (See Table 16.3 for K_{a1} and K_{a2}.) (**b**) Calculate the concentration of oxalate ion, $[C_2O_4^{2-}]$, in this solution.

Answers: (**a**) pH = 1.80, (**b**) $[C_2O_4^{2-}] = 6.4 \times 10^{-5}\ M$

16.7 WEAK BASES

Many substances behave as weak bases in water. Weak bases react with water, abstracting protons from H_2O, thereby forming the conjugate acid of the base and OH^- ions:

$$B(aq) + H_2O(l) \rightleftharpoons HB^+(aq) + OH^-(aq) \qquad [16.33]$$

The equilibrium-constant expression for this reaction can be written as

$$K_b = \frac{[BH^+][OH^-]}{[B]} \qquad [16.34]$$

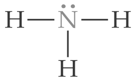
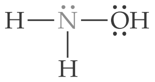
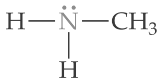
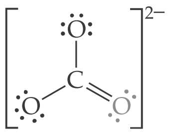
Water is the solvent, so it is omitted from the equilibrium-constant expression. The most commonly encountered weak base is ammonia:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \quad K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} \qquad [16.35]$$

As with K_w and K_a, the subscript b in K_b denotes that the equilibrium constant refers to a particular type of reaction, namely the ionization of a weak base in water. The constant K_b, the **base-dissociation constant**, *always refers to the equilibrium in which a base reacts with H_2O to form the corresponding conjugate acid and OH^-.*

▼ **TABLE 16.4** lists the Lewis structures, conjugate acids, and K_b values for a number of weak bases in water. Appendix D includes a more extensive list. These bases contain one or more lone pairs of electrons because a lone pair is necessary to form the bond with H^+. Notice that in the neutral molecules in Table 16.4, the lone pairs are on nitrogen atoms. The other bases listed are anions derived from weak acids.

TABLE 16.4 • Some Weak Bases in Water at 25 °C

Base	Structural Formula*	Conjugate Acid	K_b
Ammonia (NH_3)	 $\mathrm{H-\underset{\mid\atop H}{\ddot{N}}-H}$	NH_4^+	1.8×10^{-5}
Pyridine (C_5H_5N)		$C_5H_5NH^+$	1.7×10^{-9}
Hydroxylamine ($HONH_2$)	 $\mathrm{H-\underset{\mid\atop H}{\ddot{N}}-\ddot{\underset{..}{O}}H}$	$HONH_3^+$	1.1×10^{-8}
Methylamine (CH_3NH_2)	 $\mathrm{H-\underset{\mid\atop H}{\ddot{N}}-CH_3}$	$CH_3NH_3^+$	4.4×10^{-4}
Hydrosulfide ion (HS^-)	$\left[\mathrm{H-\ddot{\underset{..}{S}}:}\right]^-$	H_2S	1.8×10^{-7}
Carbonate ion (CO_3^{2-})		HCO_3^-	1.8×10^{-4}
Hypochlorite ion (ClO^-)	$\left[:\ddot{\underset{..}{\mathrm{Cl}}}-\ddot{\underset{..}{\mathrm{O}}}:\right]^-$	HClO	3.3×10^{-7}

*The atom that accepts the proton is shown in blue.

SAMPLE EXERCISE 16.15 Using K_b to Calculate OH^-

Calculate the concentration of OH^- in a 0.15 *M* solution of NH_3.

SOLUTION

Analyze We are given the concentration of a weak base and asked to determine the concentration of OH^-.

Plan We will use essentially the same procedure here as used in solving problems involving the ionization of weak acids, that is, write the chemical equation and tabulate initial and equilibrium concentrations.

Solve The ionization reaction and equilibrium-constant expression are

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

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

The equilibrium concentrations are (We ignore the concentration of H_2O because it is not involved in the equilibrium-constant expression.)

	$NH_3(aq)$ +	$H_2O(l)$ $\rightleftharpoons$	$NH_4^+(aq)$ +	OH^-
Initial	0.15 *M*	—	0	0
Change	$-x\ M$	—	$+x\ M$	$+x\ M$
Equilibrium	$(0.15 - x)\ M$	—	$x\ M$	$x\ M$

Inserting these quantities into the equilibrium-constant expression gives

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{(x)(x)}{0.15 - x} = 1.8 \times 10^{-5}$$

Because K_b is small, the amount of NH_3 that reacts with water is much smaller than the NH_3 concentration, and so we can neglect *x* relative to 0.15 *M*. Then we have

$$\frac{x^2}{0.15} = 1.8 \times 10^{-5}$$

$$x^2 = (0.15)(1.8 \times 10^{-5}) = 2.7 \times 10^{-6}$$

$$x = [NH_4^+] = [OH^-] = \sqrt{2.7 \times 10^{-6}} = 1.6 \times 10^{-3}\ M$$

Check The value obtained for *x* is only about 1% of the NH_3 concentration, 0.15 *M*. Therefore, neglecting *x* relative to 0.15 was justified.

Comment You may be asked to find the pH of a solution of a weak base. Once you have found $[OH^-]$, you can proceed as in Sample Exercise 16.9, where we calculated the pH of a strong base. In the present sample exercise, we have seen that the 0.15 *M* solution of NH_3 contains $[OH^-] = 1.6 \times 10^{-3}\ M$. Thus, $pOH = -\log(1.6 \times 10^{-3}) = 2.80$, and $pH = 14.00 - 2.80 = 11.20$. The pH of the solution is above 7 because we are dealing with a solution of a base.

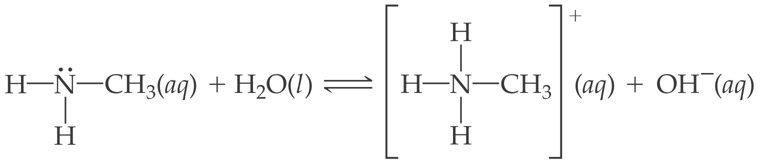
PRACTICE EXERCISE

Which of the following compounds should produce the highest pH as a 0.05 *M* solution: pyridine, methylamine, or nitrous acid?

Answer: methylamine (because it has the larger K_b value of the two amine bases in the list)

Types of Weak Bases

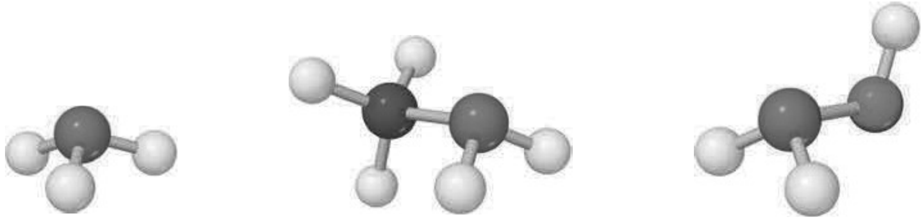
Weak bases fall into two general categories. The first category is neutral substances that have an atom with a nonbonding pair of electrons that can accept a proton. Most of these bases, including all uncharged bases in Table 16.4, contain a nitrogen atom. These substances include ammonia and a related class of compounds called **amines** (▶ **FIGURE 16.13**). In organic amines, at least one N—H bond in NH_3 is replaced with an N—C bond. Like NH_3, amines can abstract a proton from a water molecule by forming an N—H bond, as shown here for methylamine:



$$H{-}\ddot{N}H{-}CH_3(aq) + H_2O(l) \rightleftharpoons [H{-}NH_2{-}CH_3]^+(aq) + OH^-(aq) \qquad [16.36]$$

GO FIGURE

When hydroxylamine acts as a base, which atom accepts the proton?



Ammonia NH_3

Methylamine CH_3NH_2

Hydroxylamine NH_2OH

▲ **FIGURE 16.13 Structures of ammonia and two simple amines.**

Anions of weak acids make up the second general category of weak bases. In an aqueous solution of sodium hypochlorite (NaClO), for example, NaClO dissociates to Na^+ and ClO^- ions. The Na^+ ion is always a spectator ion in acid–base reactions. ∞ (Section 4.3) The ClO^- ion, however, is the conjugate base of a weak acid, hypochlorous acid. Consequently, the ClO^- ion acts as a weak base in water:

$$ClO^-(aq) + H_2O(l) \rightleftharpoons HClO(aq) + OH^-(aq) \qquad K_b = 3.3 \times 10^{-7} \qquad [16.37]$$

In Figure 16.5 we saw that bleach is quite basic (pH values of 12–13). Common chlorine bleach is typically a 5% NaOCl solution.

SAMPLE EXERCISE 16.16 Using pH to Determine the Concentration of a Salt

A solution made by adding solid sodium hypochlorite (NaClO) to enough water to make 2.00 L of solution has a pH of 10.50. Using the information in Equation 16.37, calculate the number of moles of NaClO added to the water.

SOLUTION

Analyze NaClO is an ionic compound consisting of Na^+ and ClO^- ions. As such, it is a strong electrolyte that completely dissociates in solution into Na^+, a spectator ion, and ClO^- ion, a weak base with $K_b = 3.3 \times 10^{-7}$ (Equation 16.37). Given this information we must calculate the number of moles of NaClO needed to raise the basicity of 2.00-L of water to 10.50.

Plan From the pH, we can determine the equilibrium concentration of OH^-. We can then construct a table of initial and equilibrium concentrations in which the initial concentration of ClO^- is our unknown. We can calculate $[ClO^-]$ using the expression for K_b.

Solve We can calculate $[OH^-]$ by using either Equation 16.16 or Equation 16.20; we will use the latter method here:

$$pOH = 14.00 - pH = 14.00 - 10.50 = 3.50$$
$$[OH^-] = 10^{-3.50} = 3.2 \times 10^{-4}\ M$$

This concentration is high enough that we can assume that Equation 16.37 is the only source of OH^-; that is, we can neglect any OH^- produced by the autoionization of H_2O. We now assume a value of x for the initial concentration of ClO^- and solve the equilibrium problem in the usual way.

	$ClO^-(aq)$	+ $H_2O(l)$ $\rightleftharpoons$	$HClO(aq)$	+ $OH^-(aq)$
Initial	x M	—	0	0
Change	$-3.2 \times 10^{-4}\ M$	—	$+3.2 \times 10^{-4}\ M$	$+3.2 \times 10^{-4}\ M$
Equilibrium	$(x - 3.2 \times 10^{-4})\ M$	—	$3.2 \times 10^{-4}\ M$	$3.2 \times 10^{-4}\ M$

We now use the expression for the base-dissociation constant to solve for x:

$$K_b = \frac{[HClO][OH^-]}{[ClO^-]} = \frac{(3.2 \times 10^{-4})^2}{x - 3.2 \times 10^{-4}} = 3.3 \times 10^{-7}$$

$$x = \frac{(3.2 \times 10^{-4})^2}{3.3 \times 10^{-7}} + (3.2 \times 10^{-4}) = 0.31\ M$$

We say that the solution is 0.31 *M* in NaClO even though some of the ClO^- ions have reacted with water. Because the solution is 0.31 *M* in NaClO and the total volume of solution is 2.00 L, 0.62 mol of NaClO is the amount of the salt that was added to the water.

PRACTICE EXERCISE

What is the molarity of an aqueous NH_3 solution that has a pH of 11.17?

Answer: 0.12 *M*

16.8 RELATIONSHIP BETWEEN K_a AND K_b

We have seen in a qualitative way that the stronger acids have the weaker conjugate bases. To see if we can find a corresponding *quantitative* relationship, let's consider the NH_4^+ and NH_3 conjugate acid–base pair. Each species reacts with water. For the acid, NH_4^+ the reaction is:

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$$

or written in its simpler form:

$$NH_4^+(aq) \rightleftharpoons NH_3(aq) + H^+(aq) \qquad [16.38]$$

and for the base NH_3:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \qquad [16.39]$$

and each equilibrium is expressed by a dissociation constant:

$$K_a = \frac{[NH_3][H^+]}{[NH_4^+]} \qquad K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

When we add Equations 16.38 and 16.39, the NH_4^+ and NH_3 species cancel and we are left with the autoionization of water:

$$\begin{array}{r}
NH_4^+(aq) \rightleftharpoons NH_3(aq) + H^+(aq) \\
NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \\
\hline
H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)
\end{array}$$

Recall that when two equations are added to give a third, the equilibrium constant associated with the third equation equals the product of the equilibrium constants of the first two equations. ∞ (Section 15.3)

Applying this rule to our present example, when we multiply K_a and K_b, we obtain

$$\begin{aligned} K_a \times K_b &= \left(\frac{[NH_3][H^+]}{[NH_4^+]}\right)\left(\frac{[NH_4^+][OH^-]}{[NH_3]}\right) \\ &= [H^+][OH^-] = K_w \end{aligned}$$

Thus, the product of K_a and K_b is the ion-product constant for water, K_w (Equation 16.16). We expect this result because adding Equations 16.38 and 16.39 gave us the autoionization equilibrium for water, for which the equilibrium constant is K_w.

This relationship is so important that it should receive special attention: *The product of the acid-dissociation constant for an acid and the base-dissociation constant for its conjugate base equals the ion-product constant for water:*

$$K_a \times K_b = K_w \qquad [16.40]$$

As the strength of an acid increases (K_a gets larger), the strength of its conjugate base must decrease (K_b gets smaller) so that the product $K_a \times K_b$ remains 1.0×10^{-14} at 25 °C. ▶ **TABLE 16.5** demonstrates this relationship. Remember, this important relationship applies *only* to conjugate acid–base pairs.

By using Equation 16.40, we can calculate K_b for any weak base if we know K_a for its conjugate acid. Similarly, we can calculate K_a for a weak acid if we know K_b for its conjugate base. As a practical consequence, ionization constants are often listed for only one member of a conjugate acid–base pair. For example, Appendix D does not contain K_b

TABLE 16.5 • Some Conjugate Acid–Base Pairs

Acid	K_a	Base	K_b
HNO_3	(Strong acid)	NO_3^-	(Negligible basicity)
HF	6.8×10^{-4}	F^-	1.5×10^{-11}
$HC_2H_3O_2$	1.8×10^{-5}	$C_2H_3O_2^-$	5.6×10^{-10}
H_2CO_3	4.3×10^{-7}	HCO_3^-	2.3×10^{-8}
NH_4^+	5.6×10^{-10}	NH_3	1.8×10^{-5}
HCO_3^-	5.6×10^{-11}	CO_3^{2-}	1.8×10^{-4}
OH^-	(Negligible acidity)	O^{2-}	(Strong base)

values for the anions of weak acids because they can be readily calculated from the tabulated K_a values for their conjugate acids.

If you look up the values for acid- or base-dissociation constants in a chemistry handbook, you may find them expressed as pK_a or pK_b (that is, $-\log K_a$ or $-\log K_b$) (Section 16.4). Equation 16.40 can be written in terms of pK_a and pK_b by taking the negative logarithm of both sides:

$$pK_a + pK_b = pK_w = 14.00 \quad \text{at } 25\ °C \qquad [16.41]$$

GIVE IT SOME THOUGHT

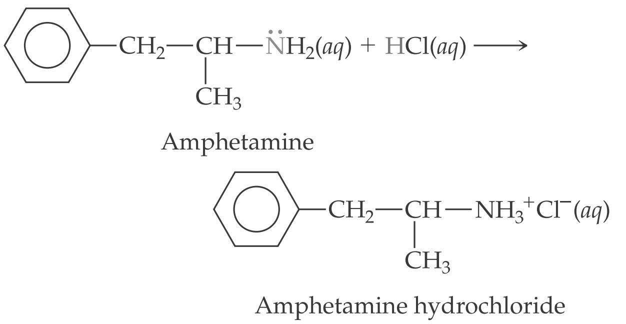
What is the pK_a value for HF? What is the pK_b value for F^-?

CHEMISTRY PUT TO WORK

Amines and Amine Hydrochlorides

Many low-molecular-weight amines have a fishy odor. Amines and NH_3 are produced by the anaerobic (absence of O_2) decomposition of dead animal or plant matter. Two such amines with very disagreeable odors are $H_2N(CH_2)_4NH_2$, *putrescine*, and $H_2N(CH_2)_5NH_2$, *cadaverine*.

Many drugs, including quinine, codeine, caffeine, and amphetamine, are amines. Like other amines, these substances are weak bases; the amine nitrogen is readily protonated upon treatment with an acid. The resulting products are called *acid salts*. If we use A as the abbreviation for an amine, the acid salt formed by reaction with hydrochloric acid can be written AH^+Cl^-. It can also be written as A·HCl and referred to as a hydrochloride. Amphetamine hydrochloride, for example, is the acid salt formed by treating amphetamine with HCl:


Amphetamine

Amphetamine hydrochloride

Acid salts are much less volatile, more stable, and generally more water soluble than the corresponding amines. For this reason, many drugs that are amines are sold and administered as acid salts. Some examples of over-the-counter medications that contain amine hydrochlorides as active ingredients are shown in ▼ **FIGURE 16.14**.

RELATED EXERCISES: 16.75, 16.76, 16.104, 16.113, and 16.122

◀ **FIGURE 16.14 Some over-the-counter medications in which an amine hydrochloride is a major active ingredient.**

SAMPLE EXERCISE 16.17 **Calculating K_a or K_b for a Conjugate Acid–Base Pair**

Calculate (**a**) K_b for the fluoride ion, (**b**) K_a for the ammonium ion.

SOLUTION

Analyze We are asked to determine dissociation constants for F^-, the conjugate base of HF, and NH_4^+, the conjugate acid of NH_3.

Plan We can use the tabulated K values for HF and NH_3 and the relationship between K_a and K_b to calculate the ionization constants for their conjugates, F^- and NH_4^+.

Solve

(**a**) For the weak acid HF, Table 16.2 and Appendix D give $K_a = 6.8 \times 10^{-4}$. We can use Equation 16.40 to calculate K_b for the conjugate base, F^-:

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{6.8 \times 10^{-4}} = 1.5 \times 10^{-11}$$

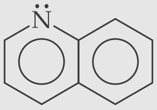
(**b**) For NH_3, Table 16.4 and in Appendix D give $K_b = 1.8 \times 10^{-5}$, and this value in Equation 16.40 gives us K_a for the conjugate acid, NH_4^+:

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

Check The respective K values for $F^-$and NH_4^+ are listed in Table 16.5, where we see that the values calculated here agree with those in Table 16.5.

PRACTICE EXERCISE

(**a**) Which of these anions has the largest base-dissociation constant: NO_2^-, PO_4^{3-}, or N_3^-?
(**b**) The base quinoline has the structure



Its conjugate acid is listed in handbooks as having a pK_a of 4.90. What is the base-dissociation constant for quinoline?

Answers: (**a**) PO_4^{3-} ($K_b = 2.4 \times 10^{-2}$), (**b**) $K_b = 7.9 \times 10^{-10}$

16.9 ACID–BASE PROPERTIES OF SALT SOLUTIONS

Even before you began this chapter, you were undoubtedly aware of many substances that are acidic, such as HNO_3, HCl, and H_2SO_4, and others that are basic, such as NaOH and NH_3. However, our discussion up to this point in the chapter has indicated that ions can also exhibit acidic or basic properties. For example, we calculated K_a for NH_4^+ and K_b for F^- in Sample Exercise 16.17. Such behavior implies that salt solutions can be acidic or basic. Before proceeding with further discussions of acids and bases, let's examine the way dissolved salts can affect pH.

Because nearly all salts are strong electrolytes, we can assume that any salt dissolved in water is completely dissociated. Consequently, the acid–base properties of salt solutions are due to the behavior of the cations and anions. Many ions react with water to generate $H^+(aq)$ or $OH^-(aq)$ ions. This type of reaction is often called **hydrolysis**. The pH of an aqueous salt solution can be predicted qualitatively by considering the salt's cations and anions.

An Anion's Ability to React with Water

In general, an anion X^- in solution can be considered the conjugate base of an acid. For example, Cl^- is the conjugate base of HCl, and CH_3COO^- is the conjugate base of CH_3COOH. Whether or not an anion reacts with water to produce hydroxide ions depends on the strength of the anion's conjugate acid. To identify the acid and assess its strength, we add a proton to the anion's formula. If the acid HX determined in this way is one of the seven strong acids listed on page 664, the anion has a negligible tendency to abstract protons from water and does not affect the pH of the solution. The presence of

Cl^- in an aqueous solution, for example, does not result in the production of any OH^- and does not affect the pH. Thus, Cl^- is always a spectator ion in acid–base chemistry.

If HX is *not* one of the seven strong acids, it is a weak acid. In this case, the conjugate base X^- is a weak base and it reacts to a small extent with water to produce the weak acid and hydroxide ions:

$$X^-(aq) + H_2O(l) \rightleftharpoons HX(aq) + OH^-(aq) \qquad [16.42]$$

The OH^- ion generated in this way increases the pH of the solution, making it basic. Acetate ion, for example, being the conjugate base of a weak acid, reacts with water to produce acetic acid and hydroxide ions, thereby increasing the pH of the solution:

$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq) \qquad [16.43]$$

GIVE IT SOME THOUGHT

What effect will NO_3^- ions have on the pH of a solution? What effect will CO_3^{2-} ions have?

The situation is more complicated for salts containing anions that have ionizable protons, such as HSO_3^-. These salts are amphiprotic (Section 16.2), and how they behave in water is determined by the relative magnitudes of K_a and K_b for the ion, as shown in Sample Exercise 16.19. If $K_a > K_b$, the ion causes the solution to be acidic. If $K_b > K_a$, the solution is made basic by the ion.

A Cation's Ability to React with Water

Polyatomic cations containing one or more protons can be considered the conjugate acids of weak bases. The NH_4^+ ion, for example, is the conjugate acid of the weak base NH_3. Thus, NH_4^+ is a weak acid and will donate a proton to water, producing hydronium ions and thereby lowering the pH:

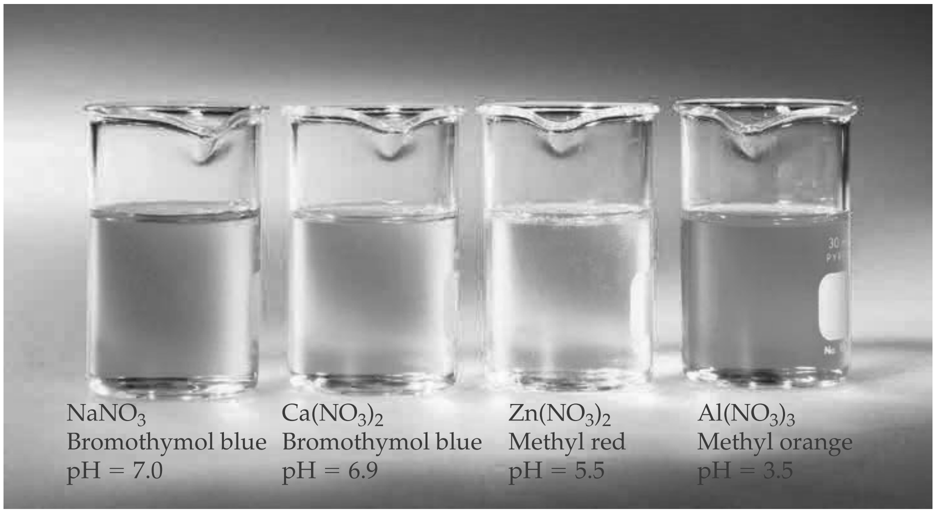
$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq) \qquad [16.44]$$

Many metal ions react with water to decrease the pH of an aqueous solution. This effect is most pronounced for small, highly charged cations like Fe^{3+} and Al^{3+}, as illustrated by the K_a values for metal cations in ◀ **TABLE 16.6**. A comparison of Fe^{2+} and Fe^{3+} values in the table illustrates how acidity increases as ionic charge increases.

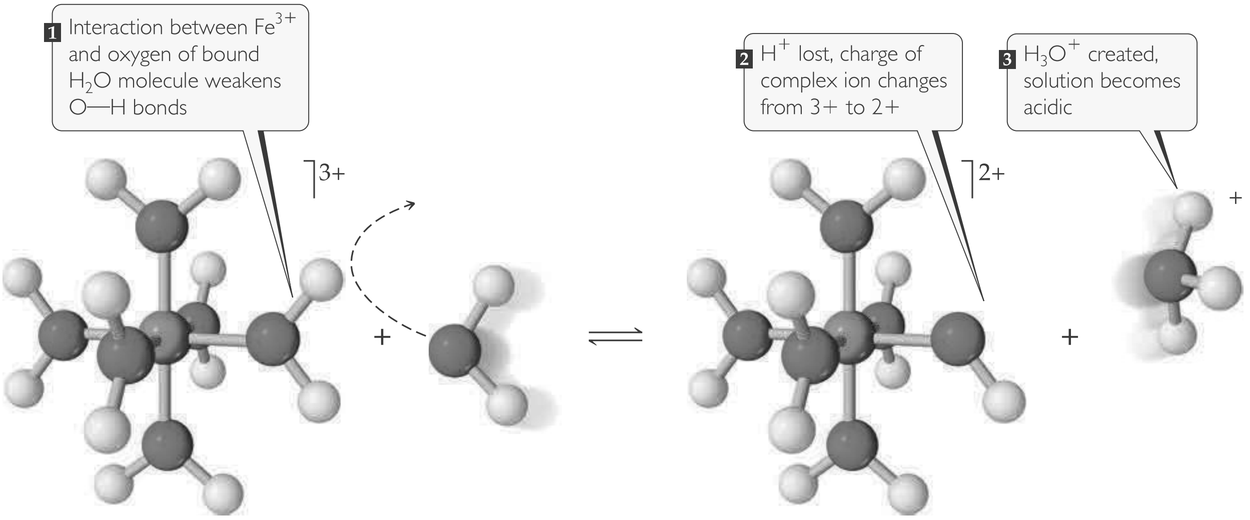
TABLE 16.6 • Acid-Dissociation Constants for Metal Cations in Aqueous Solution at 25 °C

Cation	K_a
Fe^{2+}	3.2×10^{-10}
Zn^{2+}	2.5×10^{-10}
Ni^{2+}	2.5×10^{-11}
Fe^{3+}	6.3×10^{-3}
Cr^{3+}	1.6×10^{-4}
Al^{3+}	1.4×10^{-5}

Notice that K_a values for the 3+ ions in Table 16.6 are comparable to the values for familiar weak acids, such as acetic acid ($K_a = 1.8 \times 10^{-5}$). The ions of alkali and alkaline earth metals, being relatively large and not highly charged, do not react with water and therefore do not affect pH. Note that these are the same cations found in the strong bases (Section 16.5). The different tendencies of four cations to lower the pH of a solution are illustrated in ▼ **FIGURE 16.15**.



▶ **FIGURE 16.15 Effect of cations on solution pH.** The pH values of 1.0 *M* solutions of four nitrate salts are estimated using acid–base indicators.



$$[Fe(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+}(aq) + H_3O^+(aq)$$

▲ **FIGURE 16.16 A hydrated Fe^{3+} ion acts as an acid by donating an H^+ to a free H_2O molecule, forming H_3O^+.**

The mechanism by which metal ions produce acidic solutions is shown in ▲ **FIGURE 16.16**. Because metal ions are positively charged, they attract the unshared electron pairs of water molecules and become hydrated. ∞ (Section 13.1) The larger the charge on the metal ion, the stronger the interaction between the ion and the oxygen of its hydrating water molecules. As the strength of this interaction increases, the O—H bonds in the hydrating water molecules become weaker. This facilitates transfer of protons from the hydration water molecules to solvent water molecules.

Combined Effect of Cation and Anion in Solution

To determine whether a salt forms an acidic, a basic, or a neutral solution when dissolved in water, we must consider the action of both cation and anion. There are four possible combinations.

1. If the salt contains an anion that does not react with water and a cation that does not react with water, we expect the pH to be neutral. Such is the case when the anion is a conjugate base of a strong acid and the cation is either from group 1A or one of the heavier members of group 2A (Ca^{2+}, Sr^{2+}, and Ba^{2+}). *Examples*: **NaCl, $Ba(NO_3)_2$, $RbClO_4$**.
2. If the salt contains an anion that reacts with water to produce hydroxide ions and a cation that does not react with water, we expect the pH to be basic. Such is the case when the anion is the conjugate base of a weak acid and the cation is either from group 1A or one of the heavier members of group 2A (Ca^{2+}, Sr^{2+}, and Ba^{2+}). *Examples*: **NaClO, RbF, $BaSO_3$**.
3. If the salt contains a cation that reacts with water to produce hydronium ions and an anion that does not react with water, we expect the pH to be acidic. Such is the case when the cation is a conjugate acid of a weak base or a small cation with a charge of 2+ or greater. *Examples*: **NH_4NO_3, $AlCl_3$, $Fe(NO_3)_3$**.
4. If the salt contains an anion and a cation *both* capable of reacting with water, both hydroxide ions and hydronium ions are produced. Whether the solution is basic, neutral, or acidic depends on the relative abilities of the ions to react with water. *Examples*: **NH_4ClO, $Al(CH_3COO)_3$, CrF_3**.

SAMPLE EXERCISE 16.18 Determining Whether Salt Solutions Are Acidic, Basic, or Neutral

Determine whether aqueous solutions of each of these salts are acidic, basic, or neutral: **(a)** $Ba(CH_3COO)_2$, **(b)** NH_4Cl, **(c)** CH_3NH_3Br, **(d)** KNO_3, **(e)** $Al(ClO_4)_3$.

SOLUTION

Analyze We are given the chemical formulas of five ionic compounds (salts) and asked whether their aqueous solutions will be acidic, basic, or neutral.

Plan We can determine whether a solution of a salt is acidic, basic, or neutral by identifying the ions in solution and by assessing how each ion will affect the pH.

Solve

(a) This solution contains barium ions and acetate ions. The cation is an ion of a heavy alkaline earth metal and will therefore not affect the pH. The anion, CH_3COO^-, is the conjugate base of the weak acid CH_3COOH and will hydrolyze to produce OH^- ions, thereby making the solution basic (combination 2).

(b) In this solution, NH_4^+ is the conjugate acid of a weak base (NH_3) and is therefore acidic. Cl^- is the conjugate base of a strong acid (HCl) and therefore has no influence on the pH of the solution. Because the solution contains an ion that is acidic (NH_4^+) and one that has no influence on pH (Cl^-), the solution of NH_4Cl will be acidic (combination 3).

(c) Here $CH_3NH_3^+$ is the conjugate acid of a weak base (CH_3NH_2, an amine) and is therefore acidic, and Br^- is the conjugate base of a strong acid (HBr) and therefore pH neutral. Because the solution contains one ion that is acidic and one that has no influence on pH, the solution of CH_3NH_3Br will be acidic (combination 3).

(d) This solution contains the K^+ ion, which is a cation of group 1A, and the NO_3^- ion, which is the conjugate base of the strong acid HNO_3. Neither of the ions will react with water to any appreciable extent, making the solution neutral (combination 1).

(e) This solution contains Al^{3+} and ClO_4^- ions. Cations, such as Al^{3+}, that have a charge of 3+ or higher are acidic. The ClO_4^- ion is the conjugate base of a strong acid ($HClO_4$) and therefore does not affect pH. Thus, the solution of $Al(ClO_4)_3$ will be acidic (combination 3).

PRACTICE EXERCISE

Indicate which salt in each of the following pairs forms the more acidic (or less basic) 0.010 *M* solution: **(a)** $NaNO_3$ or $Fe(NO_3)_3$, **(b)** KBr or KBrO, **(c)** CH_3NH_3Cl or $BaCl_2$, **(d)** NH_4NO_2 or NH_4NO_3.

Answers: **(a)** $Fe(NO_3)_3$, **(b)** KBr, **(c)** CH_3NH_3Cl, **(d)** NH_4NO_3

SAMPLE EXERCISE 16.19 Predicting Whether the Solution of an Amphiprotic Anion Is Acidic or Basic

Predict whether the salt Na_2HPO_4 forms an acidic solution or a basic solution when dissolved in water.

SOLUTION

Analyze We are asked to predict whether a solution of Na_2HPO_4 is acidic or basic. This substance is an ionic compound composed of Na^+ and HPO_4^{2-} ions.

Plan We need to evaluate each ion, predicting whether it is acidic or basic. Because Na^+ is a cation of group 1A, it has no influence on pH. Thus, our analysis of whether the solution is acidic or basic must focus on the behavior of the HPO_4^{2-} ion. We need to consider the fact that HPO_4^{2-} can act as either an acid or a base:

$$\text{As acid} \qquad HPO_4^{2-}(aq) \rightleftharpoons H^+(aq) + PO_4^{3-}(aq) \qquad [16.45]$$

$$\text{As base} \qquad HPO_4^{2-}(aq) + H_2O \rightleftharpoons H_2PO_4^-(aq) + OH^-(aq) \qquad [16.46]$$

Of these two reactions, the one with the larger equilibrium constant determines whether the solution is acidic or basic.

Solve The value of K_a for Equation 16.45 is 4.2×10^{-13} (Table 16.3). For Equation 16.46, we must calculate K_b for the base HPO_4^{2-} from the value of K_a for its conjugate acid, $H_2PO_4^-$, and the relationship $K_a \times K_b = K_w$ (Equation 16.40). Using the value $K_a(H_2PO_4^-) = 6.2 \times 10^{-8}$ from Table 16.3, we have

$$K_b(HPO_4^{2-}) \times K_a(H_2PO_4^-) = K_w = 1.0 \times 10^{-14}.$$

$$K_b(HPO_4^{2-}) = \frac{1.0 \times 10^{-14}}{6.2 \times 10^{-8}} = 1.6 \times 10^{-7}$$

This K_b value is more than 10^5 times larger than K_a for HPO_4^{2-}; thus, the reaction in Equation 16.46 predominates over that in Equation 16.45, and the solution is basic.

PRACTICE EXERCISE

Predict whether the dipotassium salt of citric acid ($K_2HC_6H_5O_7$) forms an acidic or basic solution in water (see Table 16.3 for data).

Answer: acidic

16.10 ACID–BASE BEHAVIOR AND CHEMICAL STRUCTURE

When a substance is dissolved in water, it may behave as an acid, behave as a base, or exhibit no acid–base properties. How does the chemical structure of a substance determine which of these behaviors is exhibited by the substance? For example, why do some substances that contain OH groups behave as bases, releasing OH^- ions into solution, whereas others behave as acids, ionizing to release H^+ ions? In this section we discuss briefly the effects of chemical structure on acid–base behavior.

Factors That Affect Acid Strength

A molecule containing H will act as a proton donor (an acid) only if the H—X bond is polarized in this way:

$$\overset{+\!\!\!\longrightarrow}{\mathrm{H{-}X}}$$

In ionic hydrides, such as NaH, the reverse is true: the H atom possesses a negative charge and behaves as a proton acceptor (a base). Nonpolar H—X bonds, such as the H—C bond in CH_4, produce neither acidic nor basic aqueous solutions.

A second factor that helps determine whether a molecule containing an H—X bond will donate a proton is the strength of the bond. Very strong bonds are less easily broken than weaker ones. This factor is important, for example, in the hydrogen halides. The H—F bond is the most polar H—X bond. You therefore might expect HF to be a very strong acid if bond polarity were all that mattered. However, the H—X bond strength increases as you move up the group: 299 kJ/mol in HI, 366 kJ/mol in HBr, 431 kJ/mol in HCl, and 567 kJ/mol in HF. Because HF has the highest bond strength among the hydrogen halides, it is a weak acid, whereas all the other hydrogen halides are strong acids in water.

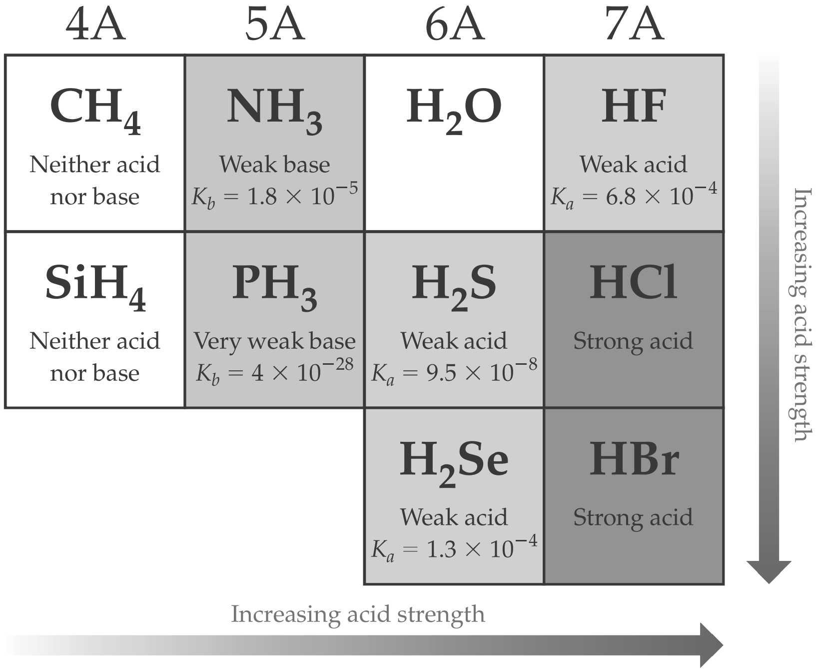
A third factor that affects the ease with which a hydrogen atom ionizes from HX is the stability of the conjugate base, X^-. In general, the greater the stability of the conjugate base, the stronger the acid.

The strength of an acid is often a combination of all three factors.

Binary Acids

For a series of binary acids HX in which X represents members of the same *group* in the periodic table, the strength of the H—X bond is generally the most important factor determining acid strength. The strength of an H—X bond tends to decrease as the element X increases in size. As a result, the bond strength decreases and acidity increases down a group. Thus, HCl is a stronger acid than HF, and H_2S is a stronger acid than H_2O.

Bond polarity is the major factor determining acidity for binary acids HX when X represents members of the same *period*. Thus, acidity increases as the electronegativity of the element X increases, as it generally does moving from left to right across a period. For example, the difference in acidity of the period 2 elements is $CH_4 < NH_3 \ll H_2O < HF$. Because the C—H bond is essentially nonpolar, CH_4 shows no tendency to form H^+ and CH_3^- ions. Although the N—H bond is polar, NH_3 has a nonbonding pair of electrons on the nitrogen atom that dominates its chemistry, so NH_3 acts as a base rather than an acid.



4A	5A	6A	7A
CH_4 Neither acid nor base	NH_3 Weak base $K_b = 1.8 \times 10^{-5}$	H_2O	HF Weak acid $K_a = 6.8 \times 10^{-4}$
SiH_4 Neither acid nor base	PH_3 Very weak base $K_b = 4 \times 10^{-28}$	H_2S Weak acid $K_a = 9.5 \times 10^{-8}$	HCl Strong acid
		H_2Se Weak acid $K_a = 1.3 \times 10^{-4}$	HBr Strong acid

▶ **FIGURE 16.17 Trends in acid strength for the binary hydrides of periods 2–4.**

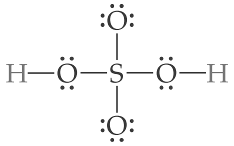
The periodic trends in the acid strengths of binary compounds of hydrogen and the nonmetals of periods 2 and 3 are summarized in ▲ **FIGURE 16.17**.

GIVE IT SOME THOUGHT

What is the major factor determining the increase in acidity of binary acids going down a group? What is the major factor going across a period?

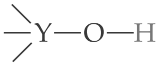
Oxyacids

Many common acids, such as sulfuric acid, contain one or more O—H bonds:



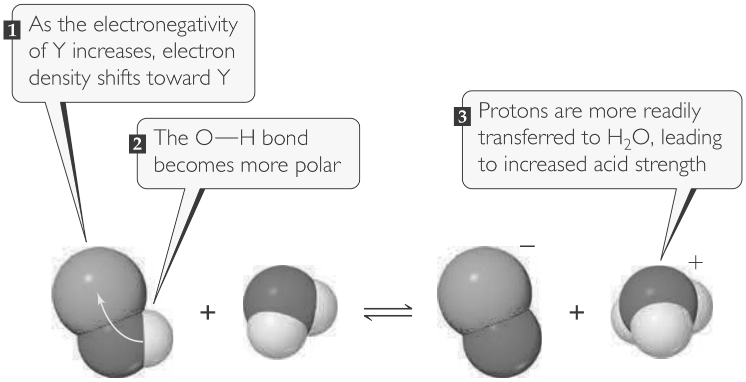
Acids in which OH groups and possibly additional oxygen atoms are bound to a central atom are called **oxyacids**. At first it may seem confusing that the OH group, which we know behaves as a base, is also present in some acids. Let's take a closer look at what factors determine whether a given OH group behaves as a base or as an acid.

Consider an OH group bound to some atom Y, which might in turn have other groups attached to it:



At one extreme, Y might be a metal, such as Na or Mg. Because of the low electronegativity of metals, the pair of electrons shared between Y and O is completely transferred to oxygen, and an ionic compound containing OH^- is formed. Such compounds are therefore sources of OH^- ions and behave as bases, as in NaOH and $Mg(OH)_2$.

When Y is a nonmetal, the bond to O is covalent and the substance does not readily lose OH^-. Instead, these compounds are either acidic or neutral. *Generally, as the electronegativity of Y increases, so does the acidity of the substance*. This happens for two reasons: First, as electron density is drawn toward Y, the O—H bond becomes weaker and more polar, thereby favoring loss of H^+. Second, because the conjugate base of any acid YOH is usually an anion, its stability generally increases as the electronegativity of



1 As the electronegativity of Y increases, electron density shifts toward Y

2 The O—H bond becomes more polar

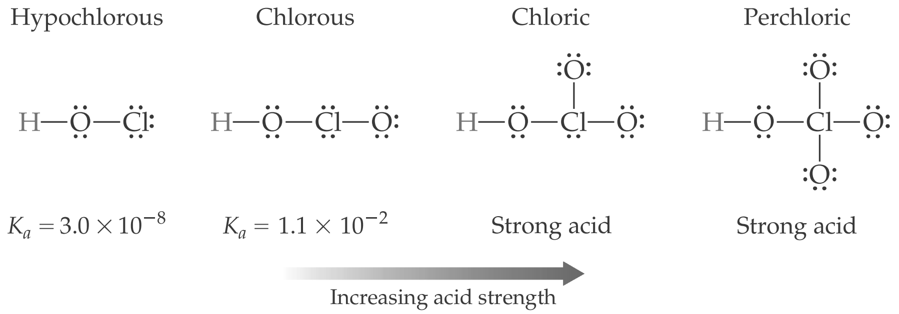
3 Protons are more readily transferred to H_2O, leading to increased acid strength

Substance	Y—OH	Electronegativity of Y	Dissociation constant
Hypochlorous acid	Cl—OH	3.0	$K_a = 3.0 \times 10^{-8}$
Hypobromous acid	Br—OH	2.8	$K_a = 2.5 \times 10^{-9}$
Hypoiodous acid	I—OH	2.5	$K_a = 2.3 \times 10^{-11}$
Water	H—OH	2.1	$K_w = 1.0 \times 10^{-14}$

◀ **FIGURE 16.18** **Acidity of the hypohalous oxyacids (YOH) as a function of electronegativity of Y.**

Y increases. This trend is illustrated by the K_a values of the hypohalous acids (YOH acids where Y is a halide ion), which decrease as the electronegativity of the halogen atom decreases (▲ **FIGURE 16.18**).

Many oxyacids contain additional oxygen atoms bonded to the central atom Y. These atoms pull electron density from the O—H bond, further increasing its polarity. Increasing the number of oxygen atoms also helps stabilize the conjugate base by increasing its ability to "spread out" its negative charge. Thus, *the strength of an acid increases as additional electronegative atoms bond to the central atom Y*. For example, the strength of the chlorine oxyacids (Y = Cl) steadily increases as O atoms are added:



Because the oxidation number of Y increases as the number of attached O atoms increases, this correlation can be stated in an equivalent way: In a series of oxyacids, the acidity increases as the oxidation number of the central atom increases.

GIVE IT SOME THOUGHT

Which acid has the larger acid-dissociation constant, HIO_2 or $HBrO_3$?

SAMPLE EXERCISE 16.20 Predicting Relative Acidities from Composition and Structure

Arrange the compounds in each series in order of increasing acid strength: (**a**) AsH_3, HBr, KH, H_2Se; (**b**) H_2SO_4, H_2SeO_3, H_2SeO_4.

SOLUTION

Analyze We are asked to arrange two sets of compounds in order from weakest acid to strongest acid. In (**a**), the substances are binary compounds containing H, and in (**b**) the substances are oxyacids.

Plan For the binary compounds, we will consider the electronegativities of As, Br, K, and Se relative to the electronegativity of H. The higher the electronegativity of these atoms, the higher the partial positive charge on H and so the more acidic the compound.

For the oxyacids, we will consider both the electronegativities of the central atom and the number of oxygen atoms bonded to the central atom.

Solve

(**a**) Because K is on the left side of the periodic table, it has a very low electronegativity (0.8, from Figure 8.7). As a result, the hydrogen in KH carries a negative charge. Thus, KH should be the least acidic (most basic) compound in the series.

Arsenic and hydrogen have similar electronegativities, 2.0 and 2.1, respectively. This means that the As—H bond is nonpolar, and so AsH_3 has little tendency to donate a proton in aqueous solution.

The electronegativity of Se is 2.4, and that of Br is 2.8. Consequently, the H—Br bond is more polar than the H—Se bond, giving HBr the greater tendency to donate a proton. (This expectation is confirmed by Figure 16.17, where we see that H_2Se is a weak acid and HBr a strong acid.) Thus, the order of increasing acidity is $KH < AsH_3 < H_2Se < HBr$.

(**b**) The acids H_2SO_4 and H_2SeO_4 have the same number of O atoms and the same number of OH groups. In such cases, the acid strength increases with increasing electronegativity of the central atom. Because S is slightly more electronegative than Se (2.5 vs 2.4), we predict that H_2SO_4 is more acidic than H_2SeO_4.

For acids with the same central atom, the acidity increases as the number of oxygen atoms bonded to the central atom increases. Thus, H_2SeO_4 should be a stronger acid than H_2SeO_3. We predict the order of increasing acidity to be $H_2SeO_3 < H_2SeO_4 < H_2SO_4$.

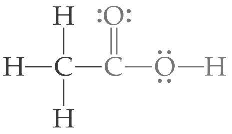
PRACTICE EXERCISE

In each pair, choose the compound that give the more acidic (or less basic) solution: (**a**) HBr, HF; (**b**) PH_3, H_2S; (**c**) HNO_2, HNO_3; (**d**) H_2SO_3, H_2SeO_3.

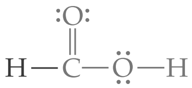
Answers: (**a**) HBr, (**b**) H_2S, (**c**) HNO_3, (**d**) H_2SO_3

Carboxylic Acids

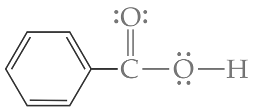
Another large group of acids is illustrated by acetic acid, a weak acid ($K_a = 1.8 \times 10^{-5}$):



The portion of the structure shown in red is called the *carboxyl group*, which is often written COOH. Thus, the chemical formula of acetic acid is written as CH_3COOH, where only the hydrogen atom in the carboxyl group can be ionized. Acids that contain a carboxyl group are called **carboxylic acids**, and they form the largest category of organic acids. Formic acid and benzoic acid are further examples of this large and important category of acids:

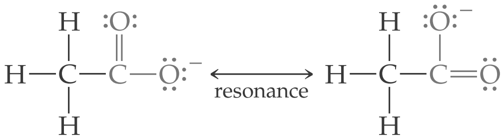


Formic acid



Benzoic acid

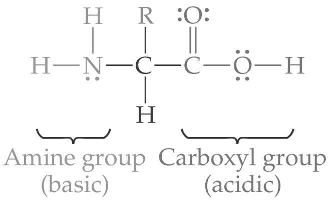
Two factors contribute to the acidic behavior of carboxylic acids. First, the additional oxygen atom attached to the carbon of the carboxyl group draws electron density from the O—H bond, increasing its polarity and helping to stabilize the conjugate base. Second, the conjugate base of a carboxylic acid (a *carboxylate anion*) can exhibit resonance ∞ (Section 8.6), which contributes to the stability of the anion by spreading the negative charge over several atoms:



CHEMISTRY AND LIFE

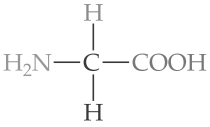
THE AMPHIPROTIC BEHAVIOR OF AMINO ACIDS

The general structure of *amino acids*, the building blocks of proteins, is



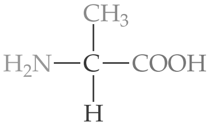
$$\underbrace{\mathrm{H{-}\underset{\cdot\cdot}{\overset{H}{N}}}}_{\text{Amine group (basic)}}\mathrm{{-}\overset{R}{\underset{H}{C}}{-}}\underbrace{\mathrm{\overset{:O:}{\overset{\|}{C}}{-}\ddot{O}{-}H}}_{\text{Carboxyl group (acidic)}}$$

where different amino acids have different R groups attached to the central carbon atom. For example, in *glycine*, the simplest amino acid, R is a hydrogen atom, and in *alanine* R is a CH_3 group:



$$\mathrm{H_2N{-}\overset{H}{\underset{H}{C}}{-}COOH}$$

Glycine



$$\mathrm{H_2N{-}\overset{CH_3}{\underset{H}{C}}{-}COOH}$$

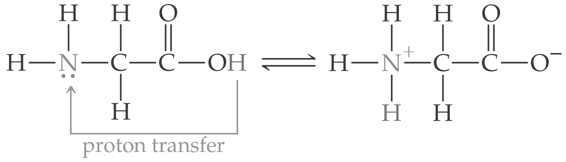
Alanine

Amino acids contain a carboxyl group and can therefore serve as acids. They also contain an NH_2 group, characteristic of amines (Section 16.7), and thus they can also act as bases. Amino acids, therefore, are amphiprotic. For glycine, we might expect the acid and base reactions with water to be

$$\textit{Acid:}\ \mathrm{H_2N{-}CH_2{-}COOH}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_2N{-}CH_2{-}COO^-}(aq) + \mathrm{H_3O^+}(aq) \qquad [16.47]$$

$$\textit{Base:}\ \mathrm{H_2N{-}CH_2{-}COOH}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{{}^+H_3N{-}CH_2{-}COOH}(aq) + \mathrm{OH^-}(aq) \qquad [16.48]$$

The pH of a solution of glycine in water is about 6.0, indicating that it is a slightly stronger acid than base. The acid–base chemistry of amino acids is more complicated than shown in Equations 16.47 and 16.48, however. Because the COOH group can act as an acid and the NH_2 group can act as a base, amino acids undergo a "self-contained" Brønsted–Lowry acid–base reaction in which the proton of the carboxyl group is transferred to the basic nitrogen atom:



$$\mathrm{H{-}\underset{\cdot\cdot}{\overset{H}{N}}{-}\overset{H}{\underset{H}{C}}{-}\overset{O}{\overset{\|}{C}}{-}OH} \rightleftharpoons \mathrm{H{-}\overset{H}{\underset{H}{\overset{+}{N}}}{-}\overset{H}{\underset{H}{C}}{-}\overset{O}{\overset{\|}{C}}{-}O^-}$$

Neutral molecule Zwitterion

Although the form of the amino acid on the right in this equation is electrically neutral overall, it has a positively charged end and a negatively charged end. A molecule of this type is called a *zwitterion* (German for "hybrid ion").

Do amino acids exhibit any properties indicating that they behave as zwitterions? If so, their behavior should be similar to that of ionic substances. ∞ (Section 8.2) Crystalline amino acids have relatively high melting points, usually above 200 °C, which is characteristic of ionic solids. Amino acids are far more soluble in water than in nonpolar solvents. In addition, the dipole moments of amino acids are large, consistent with a large separation of charge in the molecule. Thus, the ability of amino acids to act simultaneously as acids and bases has important effects on their properties.

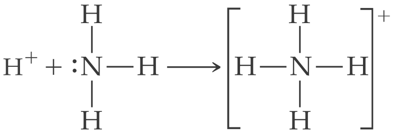
RELATED EXERCISE: 16.113

GIVE IT SOME THOUGHT

What group of atoms is present in all carboxylic acids?

16.11 LEWIS ACIDS AND BASES

For a substance to be a proton acceptor (a Brønsted–Lowry base), it must have an unshared pair of electrons for binding the proton, as, for example, in NH_3. Using Lewis structures, we can write the reaction between H^+ and NH_3 as

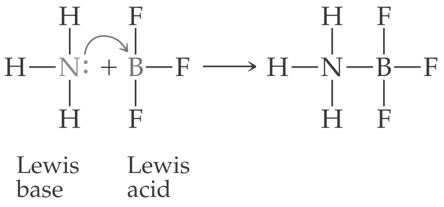


$$\mathrm{H^+ + :\overset{H}{\underset{H}{N}}{-}H \longrightarrow \left[H{-}\overset{H}{\underset{H}{N}}{-}H\right]^+}$$

G. N. Lewis was the first to notice this aspect of acid–base reactions. He proposed a definition of acid and base that emphasizes the shared electron pair: A **Lewis acid** is an electron-pair acceptor, and a **Lewis base** is an electron-pair donor.

Every base that we have discussed thus far—whether OH^-, H_2O, an amine, or an anion—is an electron-pair donor. Everything that is a base in the Brønsted–Lowry sense (a proton acceptor) is also a base in the Lewis sense (an electron-pair donor). In the Lewis theory, however, a base can donate its electron pair to something other than H^+.

The Lewis definition therefore greatly increases the number of species that can be considered acids; in other words, H^+ is a Lewis acid but not the only one. For example, the reaction between NH_3 and BF_3 occurs because BF_3 has a vacant orbital in its valence shell. (Section 8.7) It therefore acts as an electron-pair acceptor (a Lewis acid) toward NH_3, which donates the electron pair:



GIVE IT SOME THOUGHT

What feature must any molecule or ion have in order to act as a Lewis base?

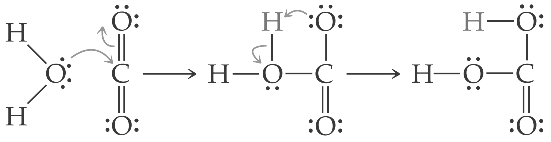
Our emphasis throughout this chapter has been on water as the solvent and on the proton as the source of acidic properties. In such cases we find the Brønsted–Lowry definition of acids and bases to be the most useful. In fact, when we speak of a substance as being acidic or basic, we are usually thinking of aqueous solutions and using these terms in the Arrhenius or Brønsted–Lowry sense. The advantage of the Lewis definitions of acid and base is that they allow us to treat a wider variety of reactions, including those that do not involve proton transfer, as acid–base reactions. To avoid confusion, a substance such as BF_3 is rarely called an acid unless it is clear from the context that we are using the term in the sense of the Lewis definition. Instead, substances that function as electron-pair acceptors are referred to explicitly as "Lewis acids."

Lewis acids include molecules that, like BF_3, have an incomplete octet of electrons. In addition, many simple cations can function as Lewis acids. For example, Fe^{3+} interacts strongly with cyanide ions to form the ferricyanide ion:

$$\mathrm{Fe}^{3+} + 6[:\mathrm{C}{\equiv}\mathrm{N}:]^{-} \longrightarrow [\mathrm{Fe}(\mathrm{C}{\equiv}\mathrm{N}:)_6]^{3-}$$

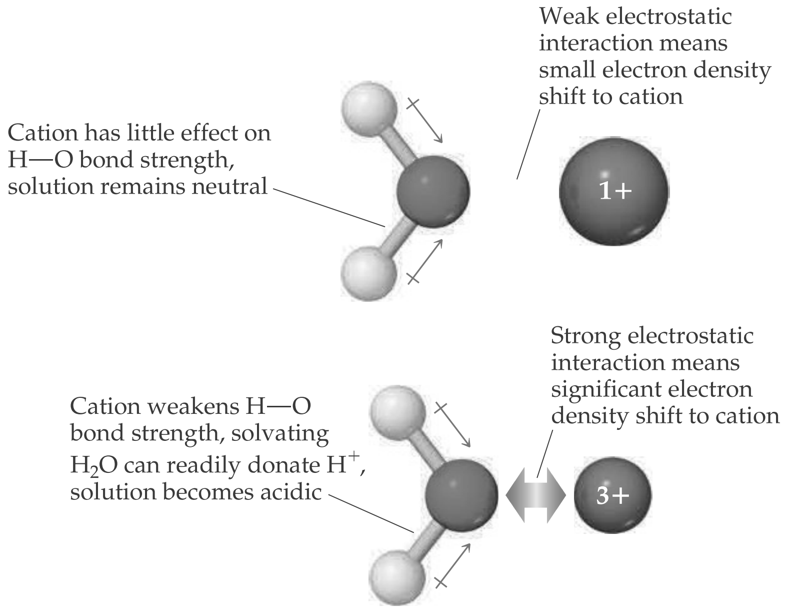
The Fe^{3+} ion has vacant orbitals that accept the electron pairs donated by the cyanide ions. (We will learn more in Chapter 23 about just which orbitals are used by the Fe^{3+} ion.) The metal ion is highly charged, too, which contributes to the interaction with CN^- ions.

Some compounds containing multiple bonds can behave as Lewis acids. For example, the reaction of carbon dioxide with water to form carbonic acid (H_2CO_3) can be pictured as an attack by a water molecule on CO_2, in which the water acts as an electron-pair donor and the CO_2 as an electron-pair acceptor:



One electron pair of one of the carbon–oxygen double bonds is moved onto the oxygen, leaving a vacant orbital on the carbon, which means the carbon can accept an electron pair donated by H_2O. The initial acid–base product rearranges by transferring a proton from the water oxygen to a carbon dioxide oxygen, forming carbonic acid.

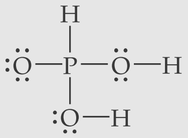
The hydrated cations we encountered in Section 16.9, such as $[Fe(H_2O)_6]^{3+}$ in Figure 16.16, form through the reaction between the cation acting as a Lewis acid and the water molecules acting as Lewis bases. When a water molecule interacts with the positively charged metal ion, electron density is drawn from the oxygen (**▶ FIGURE 16.19**). This flow of electron density causes the O—H bond to become more polarized; as a result, water molecules bound to the metal ion are more acidic than those in the bulk solvent. This effect becomes more pronounced as the charge of the cation increases, which explains why 3+ cations are much more acidic than cations with smaller charges.



◀ **FIGURE 16.19 The acidity of a hydrated cation depends on cation charge.**

SAMPLE INTEGRATIVE EXERCISE **Putting Concepts Together**

Phosphorous acid (H_3PO_3) has the Lewis structure



$$\begin{array}{c} \mathrm{H} \\ | \\ :\ddot{\underset{..}{\mathrm{O}}}-\mathrm{P}-\ddot{\underset{..}{\mathrm{O}}}-\mathrm{H} \\ | \\ :\underset{..}{\mathrm{O}}-\mathrm{H} \end{array}$$

(**a**) Explain why H_3PO_3 is diprotic and not triprotic. (**b**) A 25.0-mL sample of an H_3PO_3 solution titrated with 0.102 *M* NaOH requires 23.3 mL of NaOH to neutralize both acidic protons. What is the molarity of the H_3PO_3 solution? (**c**) The original solution from part (b) has a pH of 1.59. Calculate the percent ionization and K_{a1} for H_3PO_3, assuming that $K_{a1} \gg K_{a2}$. (**d**) How does the osmotic pressure of a 0.050 *M* solution of HCl compare qualitatively with that of a 0.050 *M* solution of H_3PO_3? Explain.

SOLUTION

We will use what we have learned about molecular structure and its impact on acidic behavior to answer part (a). We will then use stoichiometry and the relationship between pH and $[H^+]$ to answer parts (b) and (c). Finally, we will consider percent ionization in order to compare the osmotic pressure of the two solutions in part (d).

(**a**) Acids have polar H—X bonds. From Figure 8.7 we see that the electronegativity of H is 2.1 and that of P is also 2.1. Because the two elements have the same electronegativity, the H—P bond is nonpolar. ∞ (Section 8.4) Thus, this H cannot be acidic. The other two H atoms, however, are bonded to O, which has an electronegativity of 3.5. The H—O bonds are, therefore, polar with H having a partial positive charge. These two H atoms are consequently acidic.

(**b**) The chemical equation for the neutralization reaction is

$$H_3PO_3(aq) + 2\,NaOH(aq) \longrightarrow Na_2HPO_3(aq) + 2\,H_2O(l)$$

From the definition of molarity, $M = \text{mol/L}$, we see that moles $= M \times \text{L}$. ∞ (Section 4.5) Thus, the number of moles of NaOH added to the solution is

$$(0.0233\ \text{L})(0.102\ \text{mol/L}) = 2.38 \times 10^{-3}\ \text{mol NaOH}$$

The balanced equation indicates that 2 mol of NaOH is consumed for each mole of H_3PO_3. Thus, the number of moles of H_3PO_3 in the sample is

$$(2.38 \times 10^{-3}\ \text{mol NaOH})\left(\frac{1\ \text{mol}\ H_3PO_3}{2\ \text{mol NaOH}}\right) = 1.19 \times 10^{-3}\ \text{mol}\ H_3PO_3$$

The concentration of the H_3PO_3 solution, therefore, equals $(1.19 \times 10^{-3}\,\text{mol})/(0.0250\,\text{L}) = 0.0476\,M$.

(**c**) From the pH of the solution, 1.59, we can calculate $[H^+]$ at equilibrium:

$$[H^+] = \text{antilog}(-1.59) = 10^{-1.59} = 0.026\ M \text{ (two significant figures)}$$

Because $K_{a1} \gg K_{a2}$, the vast majority of the ions in solution are from the first ionization step of the acid.

$$H_3PO_3(aq) \rightleftharpoons H^+(aq) + H_2PO_3^-(aq)$$

Because one $H_2PO_3^-$ ion forms for each H^+ ion formed, the equilibrium concentrations of H^+ and $H_2PO_3^-$ are equal: $[H^+] = [H_2PO_3^-] = 0.026\ M$. The equilibrium concentration of H_3PO_3 equals the initial concentration minus the amount that ionizes to form H^+ and $H_2PO_3^-$: $[H_3PO_3] = 0.0476\ M - 0.026\ M = 0.022\ M$ (two significant figures). These results can be tabulated as follows:

	$H_3PO_3(aq)$	$\rightleftharpoons$ $H^+(aq)$	$+$ $H_2PO_3^-(aq)$
Initial	$0.0476\ M$	0	0
Change	$-0.026\ M$	$+0.026\ M$	$+0.026\ M$
Equilibrium	$0.022\ M$	$0.026\ M$	$0.026\ M$

The percent ionization is

$$\text{percent ionization} = \frac{[H^+]_{\text{equilibrium}}}{[H_3PO_3]_{\text{initial}}} \times 100\% = \frac{0.026\ M}{0.0476\ M} \times 100\% = 55\%$$

The first acid-dissociation constant is

$$K_{a1} = \frac{[H^+][H_2PO_3^-]}{[H_3PO_3]} = \frac{(0.026)(0.026)}{0.022} = 0.031$$

(**d**) Osmotic pressure is a colligative property and depends on the total concentration of particles in solution. (Section 13.5) Because HCl is a strong acid, a 0.050 *M* solution will contain 0.050 *M* $H^+(aq)$ and 0.050 *M* $Cl^-(aq)$, or a total of 0.100 mol/L of particles. Because H_3PO_3 is a weak acid, it ionizes to a lesser extent than HCl and, hence, there are fewer particles in the H_3PO_3 solution. As a result, the H_3PO_3 solution will have the lower osmotic pressure.

CHAPTER SUMMARY AND KEY TERMS

SECTION 16.1 Acids and bases were first recognized by the properties of their aqueous solutions. For example, acids turn litmus red, whereas bases turn litmus blue. Arrhenius recognized that the properties of acidic solutions are due to $H^+(aq)$ ions and those of basic solutions are due to $OH^-(aq)$ ions.

SECTION 16.2 The Brønsted–Lowry concept of acids and bases is more general than the Arrhenius concept and emphasizes the transfer of a proton (H^+) from an acid to a base. The H^+ ion, which is merely a proton with no surrounding valence electrons, is strongly bound to water. For this reason, the **hydronium ion**, $H_3O^+(aq)$, is often used to represent the predominant form of H^+ in water instead of the simpler $H^+(aq)$.

A **Brønsted–Lowry acid** is a substance that donates a proton to another substance; a **Brønsted–Lowry base** is a substance that accepts a proton from another substance. Water is an **amphiprotic** substance, one that can function as either a Brønsted–Lowry acid or base, depending on the substance with which it reacts.

The **conjugate base** of a Brønsted–Lowry acid is the species that remains when a proton is removed from the acid. The **conjugate acid** of a Brønsted–Lowry base is the species formed by adding a proton to the base. Together, an acid and its conjugate base (or a base and its conjugate acid) are called a **conjugate acid–base pair**.

The acid–base strengths of conjugate acid–base pairs are related: The stronger an acid, the weaker is its conjugate base; the weaker an acid, the stronger is its conjugate base. In every acid–base reaction, the position of the equilibrium favors the transfer of the proton from the stronger acid to the stronger base.

SECTION 16.3 Water ionizes to a slight degree, forming $H^+(aq)$ and $OH^-(aq)$. The extent of this **autoionization** is expressed by the **ion-product constant** for water: $K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$ (25 °C). This relationship describes both pure water and aqueous solutions. The K_w expression indicates that the product of $[H^+]$ and $[OH^-]$ is a constant. Thus, as $[H^+]$ increases, $[OH^-]$ decreases. Acidic solutions are those that contain more $H^+(aq)$ than $OH^-(aq)$, whereas basic solutions contain more $OH^-(aq)$ than $H^+(aq)$.

SECTION 16.4 The concentration of $H^+(aq)$ can be expressed in terms of **pH**: $\text{pH} = -\log[H^+]$. At 25 °C the pH of a neutral solution is 7.00, whereas the pH of an acidic solution is below 7.00, and the pH of a basic solution is above 7.00. The pX notation is also used to represent the negative logarithm of other small quantities, as in pOH and pK_w. The pH of a solution can be measured using a pH meter, or it can be estimated using acid–base indicators.

SECTION 16.5 Strong acids are strong electrolytes, ionizing completely in aqueous solution. The common strong acids are HCl, HBr, HI, HNO_3, $HClO_3$, $HClO_4$, and H_2SO_4. The conjugate bases of strong acids have negligible basicity.

Common strong bases are the ionic hydroxides of the alkali metals and the heavy alkaline earth metals.

SECTION 16.6 Weak acids are weak electrolytes; only some of the molecules exist in solution in ionized form. The extent of ionization is expressed by the **acid-dissociation constant**, K_a, which is the equilibrium constant for the reaction $HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$, which can also be written $HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$.

The larger the value of K_a, the stronger is the acid. For solutions of the same concentration, a stronger acid also has a larger **percent ionization**. The concentration of a weak acid and its K_a value can be used to calculate the pH of a solution.

Polyprotic acids, such as H_2SO_3, have more than one ionizable proton. These acids have acid-dissociation constants that decrease in magnitude in the order $K_{a1} > K_{a2} > K_{a3}$. Because nearly all the $H^+(aq)$ in a polyprotic acid solution comes from the first dissociation step, the pH can usually be estimated satisfactorily by considering only K_{a1}.

SECTION 16.7 Weak bases include NH_3, **amines**, and the anions of weak acids. The extent to which a weak base reacts with water to generate the corresponding conjugate acid and OH^- is measured by the **base-dissociation constant**, K_b. This is the equilibrium constant for the reaction $B(aq) + H_2O(l) \rightleftharpoons HB^+(aq) + OH^-(aq)$, where B is the base.

SECTION 16.8 The relationship between the strength of an acid and the strength of its conjugate base is expressed quantitatively by the equation $K_a \times K_b = K_w$, where K_a and K_b are dissociation constants for conjugate acid–base pairs.

SECTION 16.9 The acid–base properties of salts can be ascribed to the behavior of their respective cations and anions. The reaction of ions with water, with a resultant change in pH, is called **hydrolysis**. The cations of the alkali metals and the alkaline earth metals as well as the anions of strong acids, such as Cl^-, Br^-, I^-, and NO_3^-, do not undergo hydrolysis. They are always spectator ions in acid–base chemistry.

SECTION 16.10 The tendency of a substance to show acidic or basic characteristics in water can be correlated with its chemical structure. Acid character requires the presence of a highly polar H—X bond. Acidity is also favored when the H—X bond is weak and when the X^- ion is very stable.

For **oxyacids** with the same number of OH groups and the same number of O atoms, acid strength increases with increasing electronegativity of the central atom. For oxyacids with the same central atom, acid strength increases as the number of oxygen atoms attached to the central atom increases. **Carboxylic acids**, which are organic acids containing the COOH group, are the most important class of organic acids. The presence of delocalized pi bonding in the conjugate base is partially responsible for the acidity of these compounds.

SECTION 16.11 The Lewis concept of acids and bases emphasizes the shared electron pair rather than the proton. A **Lewis acid** is an electron-pair acceptor, and a **Lewis base** is an electron-pair donor. The Lewis concept is more general than the Brønsted–Lowry concept because it can apply to cases in which the acid is some substance other than H^+.

KEY SKILLS

- Define and identify Arrhenius acids and bases. (Section 16.1)
- Understand the nature of the hydrated proton, represented as either $H^+(aq)$ or $H_3O^+(aq)$. (Section 16.2)
- Define and identify Brønsted–Lowry acids and bases and identify conjugate acid–base pairs. (Section 16.2)
- Relate the strength of an acid to the strength of its conjugate base. (Section 16.2)
- Understand how the equilibrium position of a proton-transfer reaction relates the strengths of the acids and bases involved. (Section 16.3)
- Describe the autoionization of water and understand how $[H_3O^+]$ and $[OH^-]$ are related. (Section 16.3)
- Calculate the pH of a solution given $[H_3O^+]$ or $[OH^-]$. (Section 16.4)
- Calculate the pH of a strong acid or strong base given its concentration. (Section 16.5)
- Calculate K_a or K_b for a weak acid or weak base given its concentration and the pH of the solution. (Sections 16.6 and 16.7)
- Calculate the pH of a weak acid or weak base or its percent ionization given its concentration and K_a or K_b. (Sections 16.6 and 16.7)
- Calculate K_b for a weak base given K_a of its conjugate acid, and similarly calculate K_a from K_b. (Section 16.8)
- Predict whether an aqueous solution of a salt will be acidic, basic, or neutral. (Section 16.9)
- Predict the relative strength of a series of acids from their molecular structures. (Section 16.10)
- Define and identify Lewis acids and bases. (Section 16.11)

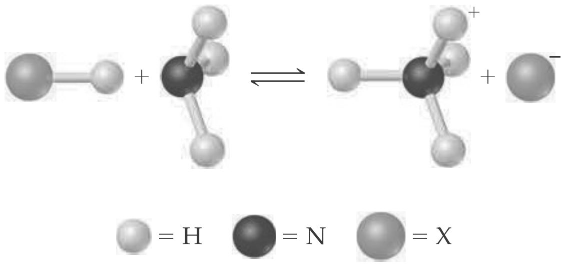
KEY EQUATIONS

• $K_w = [H_3O^+][OH^-] = [H^+][OH^-] = 1.0 \times 10^{-14}$	[16.16]	Ion product of water at 25 °C
• $pH = -\log[H^+]$	[16.17]	Definition of pH
• $pOH = -\log[OH^-]$	[16.18]	Definition of pOH
• $pH + pOH = 14.00$	[16.20]	Relationship between pH and pOH
• $K_a = \frac{[H_3O^+][A^-]}{[HA]}$ or $K_a = \frac{[H^+][A^-]}{[HA]}$	[16.25]	Acid dissociation constant for a weak acid, HA
• $\text{Percent ionization} = \frac{[H^+]_{\text{equilibrium}}}{[HA]_{\text{initial}}} \times 100\%$	[16.27]	Percent ionization of a weak acid
• $K_b = \frac{[BH^+][OH^-]}{[B]}$	[16.34]	Base-dissociation constant for a weak base, B
• $K_a \times K_b = K_w$	[16.40]	Relationship between acid- and base-dissociation constants of a conjugate acid–base pair

EXERCISES

VISUALIZING CONCEPTS

16.1 (**a**) Identify the Brønsted–Lowry acid and base in the reaction

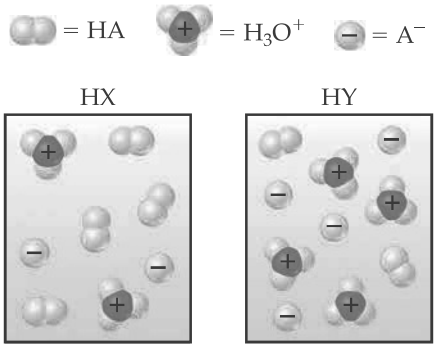


(**b**) Identify the Lewis acid and base in the reaction. [Sections 16.2 and 16.11]

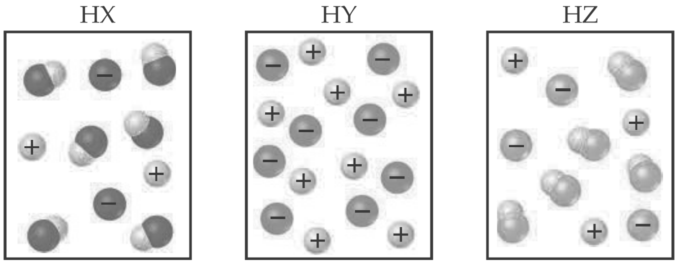
16.2 The following diagrams represent aqueous solutions of two monoprotic acids, HA (A = X or Y). The water molecules have been omitted for clarity. (**a**) Which is the stronger acid, HX or HY? (**b**) Which is the stronger base, X^- or Y^-? (**c**) If you mix equal concentrations of HX and NaY, will the equilibrium

$$HX(aq) + Y^-(aq) \rightleftharpoons HY(aq) + X^-(aq)$$

lie mostly to the right ($K_c > 1$) or to the left ($K_c < 1$)? [Section 16.2]



16.3 The following diagrams represent aqueous solutions of three acids, HX, HY, and HZ. The water molecules have been omitted for clarity, and the hydrated proton is represented as H^+ rather than H_3O^+. (**a**) Which of the acids is a strong acid? Explain. (**b**) Which acid would have the smallest acid-dissociation constant, K_a? (**c**) Which solution would have the highest pH? [Sections 16.5 and 16.6]



16.4 In which of the following cases is the approximation that the equilibrium concentration of $H^+(aq)$ is small relative to the initial concentration of HA likely to be most valid: (**a**) initial [HA] = 0.100 M and $K_a = 1.0 \times 10^{-6}$, (**b**) initial [HA] = 0.100 M and $K_a = 1.0 \times 10^{-4}$, (**c**) initial [HA] = 1.00 M and $K_a = 1.0 \times 10^{-6}$? [Section 16.6]

16.5 The indicator methyl orange has been added to both of these solutions. Based on the colors, classify each statement as true or false:

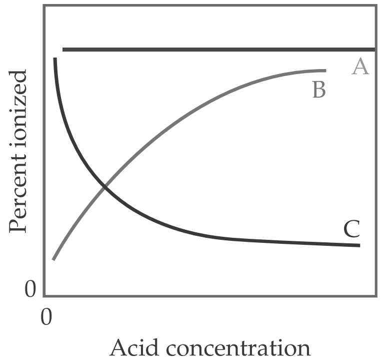
(**a**) The pH of solution A is definitely less than 7.00.

(**b**) The pH of solution B is definitely greater than 7.00.

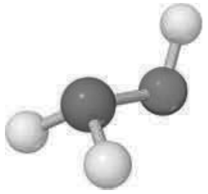
(**c**) The pH of solution B is greater than that of solution A. [Section 16.4]

Solution A Solution B

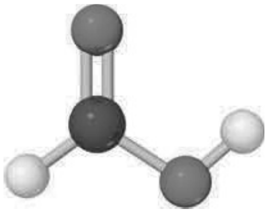
16.6 (**a**) Which of these three lines represents the effect of concentration on the percent ionization of a weak acid? (**b**) Explain in qualitative terms why the curve you chose has the shape it does. [Section 16.6]



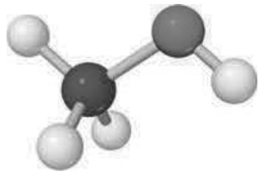
16.7 Each of the three molecules shown here contains an OH group, but one molecule acts as a base, one as an acid, and the third is neither acid nor base. (**a**) Which one acts as a base? Why does only this molecule act as a base? (**b**) Which one acts as an acid? (**c**) Why is the remaining molecule neither acidic nor basic? [Sections 16.6 and 16.7]



Molecule A

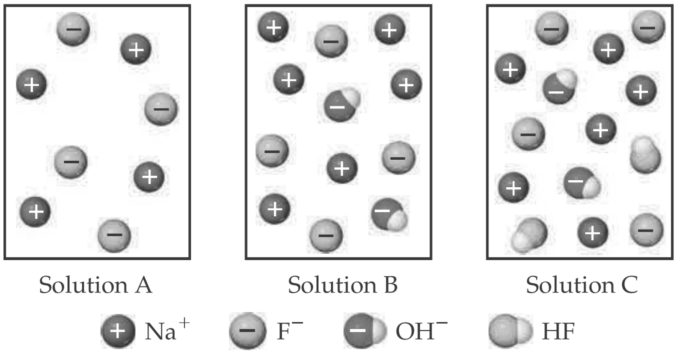


Molecule B

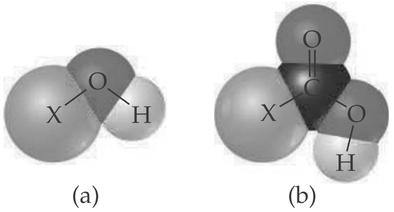


Molecule C

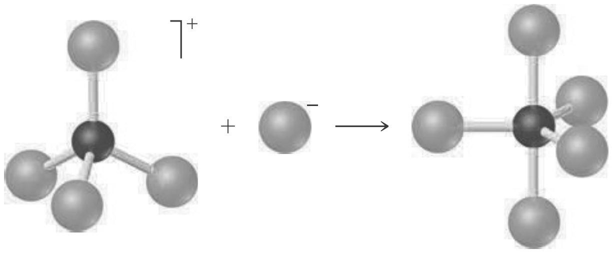
16.8 Which of the following diagrams best represents an aqueous solution of NaF? The water molecules are not shown for clarity. Will this solution be acidic, neutral, or basic? [Section 16.9]


Solution A Solution B Solution C

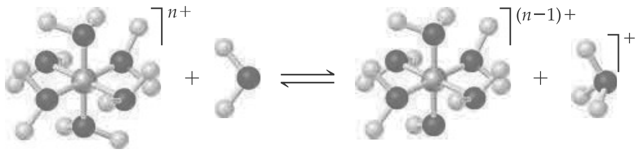
16.9 Consider the molecular models shown here, where X represents a halogen atom. (**a**) If X is the same atom in both molecules, which one will be more acidic? (**b**) Does the acidity of each molecule increase or decrease as the electronegativity of the atom X increases? [Section 16.10]



16.10 (**a**) The following diagram represents the reaction of PCl_4^+ with Cl^-. Draw the Lewis structures for the reactants and products, and identify the Lewis acid and the Lewis base in the reaction.



(**b**) The following reaction represents a hydrated cation losing a proton. How does the equilibrium constant for the reaction change as the charge of the cation increases? [Sections 16.9 and 16.11]



ARRHENIUS AND BRØNSTED–LOWRY ACIDS AND BASES (sections 16.1 and 16.2)

16.11 Although HCl and H_2SO_4 have very different properties as pure substances, their aqueous solutions possess many common properties. List some general properties of these solutions, and explain their common behavior in terms of the species present.

16.12 Although pure NaOH and NH_3 have very different properties, their aqueous solutions possess many common properties. List some general properties of these solutions, and explain their common behavior in terms of the species present.

16.13 (**a**) What is the difference between the Arrhenius and the Brønsted–Lowry definitions of an acid? (**b**) $NH_3(g)$ and $HCl(g)$ react to form the ionic solid $NH_4Cl(s)$. Which substance is the Brønsted–Lowry acid in this reaction? Which is the Brønsted–Lowry base?

16.14 (**a**) What is the difference between the Arrhenius and the Brønsted–Lowry definitions of a base? (**b**) Can a substance behave as an Arrhenius base if it does not contain an OH group? Explain.

16.15 (**a**) Give the conjugate base of the following Brønsted–Lowry acids: (**i**) HIO_3, (**ii**) NH_4^+. (**b**) Give the conjugate acid of the following Brønsted–Lowry bases: (**i**) O^{2-}, (**ii**) $H_2PO_4^-$.

16.16 (**a**) Give the conjugate base of the following Brønsted–Lowry acids: (**i**) HCOOH, (**ii**) HPO_4^{2-}. (**b**) Give the conjugate acid of the following Brønsted–Lowry bases: (**i**) SO_4^{2-}, (**ii**) CH_3NH_2.

16.17 Designate the Brønsted–Lowry acid and the Brønsted–Lowry base on the left side of each of the following equations, and also designate the conjugate acid and conjugate base of each on the right side:

(**a**) $NH_4^+(aq) + CN^-(aq) \rightleftharpoons HCN(aq) + NH_3(aq)$

(**b**) $(CH_3)_3N(aq) + H_2O(l) \rightleftharpoons (CH_3)_3NH^+(aq) + OH^-(aq)$

(**c**) $HCOOH(aq) + PO_4^{3-}(aq) \rightleftharpoons HCOO^-(aq) + HPO_4^{2-}(aq)$

16.18 Designate the Brønsted–Lowry acid and the Brønsted–Lowry base on the left side of each equation, and also designate the conjugate acid and conjugate base of each on the right side.

(**a**) $HBrO(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + BrO^-(aq)$

(**b**) $HSO_4^-(aq) + HCO_3^-(aq) \rightleftharpoons SO_4^{2-}(aq) + H_2CO_3(aq)$

(**c**) $HSO_3^-(aq) + H_3O^+(aq) \rightleftharpoons H_2SO_3(aq) + H_2O(l)$

16.19 (**a**) The hydrogen oxalate ion ($HC_2O_4^-$) is amphiprotic. Write a balanced chemical equation showing how it acts as an acid toward water and another equation showing how it acts as a base toward water. (**b**) What is the conjugate acid of $HC_2O_4^-$? What is its conjugate base?

16.20 (**a**) Write an equation for the reaction in which $H_2C_6H_7O_5^-(aq)$ acts as a base in $H_2O(l)$. (**b**) Write an equation for the reaction in which $H_2C_6H_7O_5^-(aq)$ acts as an acid in $H_2O(l)$. (**c**) What is the conjugate acid of $H_2C_6H_7O_5^-(aq)$? What is its conjugate base?

16.21 Label each of the following as being a strong base, a weak base, or a species with negligible basicity. In each case write the formula of its conjugate acid, and indicate whether the conjugate acid is a strong acid, a weak acid, or a species with negligible acidity: (**a**) CH_3COO^-, (**b**) HCO_3^-, (**c**) O^{2-}, (**d**) Cl^-, (**e**) NH_3.

16.22 Label each of the following as being a strong acid, a weak acid, or a species with negligible acidity. In each case write the formula of its conjugate base, and indicate whether the conjugate base is a strong base, a weak base, or a species with negligible basicity: (**a**) HCOOH, (**b**) H_2, (**c**) CH_4, (**d**) HF, (**e**) NH_4^+.

16.23 (**a**) Which of the following is the stronger Brønsted–Lowry acid, HBrO or HBr? (**b**) Which is the stronger Brønsted–Lowry base, F^- or Cl^-? Briefly explain your choices.

16.24 (**a**) Which of the following is the stronger Brønsted–Lowry acid, $HClO_3$ or $HClO_2$? (**b**) Which is the stronger Brønsted–Lowry base, HS^- or HSO_4^-? Briefly explain your choices.

16.25 Predict the products of the following acid–base reactions, and predict whether the equilibrium lies to the left or to the right of the equation:

(**a**) $O^{2-}(aq) + H_2O(l) \rightleftharpoons$

(**b**) $CH_3COOH(aq) + HS^-(aq) \rightleftharpoons$

(**c**) $NO_2^-(aq) + H_2O(l) \rightleftharpoons$

16.26 Predict the products of the following acid–base reactions, and predict whether the equilibrium lies to the left or to the right of the equation:

(**a**) $NH_4^+(aq) + OH^-(aq) \rightleftharpoons$

(**b**) $CH_3COO^-(aq) + H_3O^+(aq) \rightleftharpoons$

(**c**) $HCO_3^-(aq) + F^-(aq) \rightleftharpoons$

AUTOIONIZATION OF WATER (section 16.3)

16.27 If a neutral solution of water, with pH = 7.00, is heated to 50 °C, the pH drops to 6.63. Does this mean that the concentration of $[H^+]$ is greater than the concentration of $[OH^-]$? Explain.

16.28 (**a**) Write a chemical equation that illustrates the autoionization of water. (**b**) Write the expression for the ion-product constant for water, K_w. Why is $[H_2O]$ absent from this expression? (**c**) A solution is described as basic. What does this statement mean?

16.29 Calculate $[H^+]$ for each of the following solutions, and indicate whether the solution is acidic, basic, or neutral: (**a**) $[OH^-] = 0.00045\ M$; (**b**) $[OH^-] = 8.8 \times 10^{-9}\ M$; (**c**) a solution in which $[OH^-]$ is 100 times greater than $[H^+]$.

16.30 Calculate $[OH^-]$ for each of the following solutions, and indicate whether the solution is acidic, basic, or neutral: (**a**) $[H^+] = 0.0505\ M$; (**b**) $[H^+] = 2.5 \times 10^{-10}\ M$; (**c**) a solution in which $[H^+]$ is 1000 times greater than $[OH^-]$.

16.31 At the freezing point of water (0 °C), $K_w = 1.2 \times 10^{-15}$. Calculate $[H^+]$ and $[OH^-]$ for a neutral solution at this temperature.

16.32 Deuterium oxide (D_2O, where D is deuterium, the hydrogen-2 isotope) has an ion-product constant, K_w, of 8.9×10^{-16} at 20 °C. Calculate $[D^+]$ and $[OD^-]$ for pure (neutral) D_2O at this temperature.

THE pH SCALE (section 16.4)

16.33 By what factor does $[H^+]$ change for a pH change of (**a**) 2.00 units, (**b**) 0.50 units?

16.34 Consider two solutions, solution A and solution B. $[H^+]$ in solution A is 250 times greater than that in solution B. What is the difference in the pH values of the two solutions?

16.35 (**a**) If NaOH is added to water, how does $[H^+]$ change? How does pH change? (**b**) Use the pH values in Figure 16.5 to estimate the pH of a solution with $[H^+] = 0.0006\ M$. Is the solution acidic or basic? (**c**) If the pH of a solution is 5.2, first estimate and then calculate the molar concentrations of $H^+(aq)$ and $OH^-(aq)$ in the solution.

16.36 (**a**) If HNO_3 is added to water, how does $[OH^-]$ change? How does pH change? (**b**) Use the pH values in Figure 16.5 to estimate the pH of a solution with $[OH^-] = 0.014\ M$. Is the solution acidic or basic? (**c**) If pH = 6.6, first estimate and then calculate the molar concentrations of $H^+(aq)$ and $OH^-(aq)$ in the solution.

16.37 Complete the following table by calculating the missing entries and indicating whether the solution is acidic or basic.

16.38 Complete the following table by calculating the missing entries. In each case indicate whether the solution is acidic or basic.

$[H^+]$	$OH^-(aq)$	pH	pOH	Acidic or basic?
$7.5 \times 10^{-3}\ M$				
	$3.6 \times 10^{-10}\ M$			
		8.25		
			5.70	

16.39 The average pH of normal arterial blood is 7.40. At normal body temperature (37 °C), $K_w = 2.4 \times 10^{-14}$. Calculate $[H^+]$, $[OH^-]$, and pOH for blood at this temperature.

pH	pOH	$[H^+]$	$[OH^-]$	Acidic or basic?
5.25				
	2.02			
		$4.4 \times 10^{-10}\ M$		
			$8.5 \times 10^{-2}\ M$	

16.40 Carbon dioxide in the atmosphere dissolves in raindrops to produce carbonic acid (H_2CO_3), causing the pH of clean, unpolluted rain to range from about 5.2 to 5.6. What are the ranges of $[H^+]$ and $[OH^-]$ in the raindrops?

STRONG ACIDS AND BASES (section 16.5)

16.41 (**a**) What is a strong acid? (**b**) A solution is labeled 0.500 *M* HCl. What is $[H^+]$ for the solution? (**c**) Which of the following are strong acids: HF, HCl, HBr, HI?

16.42 (**a**) What is a strong base? (**b**) A solution is labeled 0.035 *M* $Sr(OH)_2$. What is $[OH^-]$ for the solution? (**c**) Is the following statement true or false? Because $Mg(OH)_2$ is not very soluble, it cannot be a strong base. Explain.

16.43 Calculate the pH of each of the following strong acid solutions: (**a**) 8.5×10^{-3} *M* HBr, (**b**) 1.52 g of HNO_3 in 575 mL of solution, (**c**) 5.00 mL of 0.250 *M* $HClO_4$ diluted to 50.0 mL, (**d**) a solution formed by mixing 10.0 mL of 0.100 *M* HBr with 20.0 mL of 0.200 *M* HCl.

16.44 Calculate the pH of each of the following strong acid solutions: (**a**) 0.0167 *M* HNO_3, (**b**) 0.225 g of $HClO_3$ in 2.00 L of solution, (**c**) 15.00 mL of 1.00 *M* HCl diluted to 0.500 L, (**d**) a mixture formed by adding 50.0 mL of 0.020 *M* HCl to 125 mL of 0.010 *M* HI.

16.45 Calculate $[OH^-]$ and pH for (**a**) 1.5×10^{-3} *M* $Sr(OH_2)$, (**b**) 2.250 g of LiOH in 250.0 mL of solution, (**c**) 1.00 mL of 0.175 *M* NaOH diluted to 2.00 L, (**d**) a solution formed by adding 5.00 mL of 0.105 *M* KOH to 15.0 mL of 9.5×10^{-2} *M* $Ca(OH)_2$.

16.46 Calculate $[OH^-]$ and pH for each of the following strong base solutions: (**a**) 0.182 *M* KOH, (**b**) 3.165 g of KOH in 500.0 mL of solution, (**c**) 10.0 mL of 0.0105 *M* $Ca(OH)_2$ diluted to 500.0 mL, (**d**) a solution formed by mixing 20.0 mL of 0.015 *M* $Ba(OH)_2$ with 40.0 mL of 8.2×10^{-3} *M* NaOH.

16.47 Calculate the concentration of an aqueous solution of NaOH that has a pH of 11.50.

16.48 Calculate the concentration of an aqueous solution of $Ca(OH)_2$ that has a pH of 10.05.

WEAK ACIDS (section 16.6)

16.49 Write the chemical equation and the K_a expression for the ionization of each of the following acids in aqueous solution. First show the reaction with $H^+(aq)$ as a product and then with the hydronium ion: (**a**) $HBrO_2$, (**b**) C_2H_5COOH.

16.50 Write the chemical equation and the K_a expression for the acid dissociation of each of the following acids in aqueous solution. First show the reaction with $H^+(aq)$ as a product and then with the hydronium ion: (**a**) C_6H_5COOH, (**b**) HCO_3^-.

16.51 Lactic acid ($CH_3CH(OH)COOH$) has one acidic hydrogen. A 0.10 *M* solution of lactic acid has a pH of 2.44. Calculate K_a.

16.52 Phenylacetic acid ($C_6H_5CH_2COOH$) is one of the substances that accumulates in the blood of people with phenylketonuria, an inherited disorder that can cause mental retardation or even death. A 0.085 *M* solution of $C_6H_5CH_2COOH$ has a pH of 2.68. Calculate the K_a value for this acid.

16.53 A 0.100 *M* solution of chloroacetic acid ($ClCH_2COOH$) is 11.0% ionized. Using this information, calculate $[ClCH_2COO^-]$, $[H^+]$, $[ClCH_2COOH]$, and K_a for chloroacetic acid.

16.54 A 0.100 *M* solution of bromoacetic acid ($BrCH_2COOH$) is 13.2% ionized. Calculate $[H^+]$, $[BrCH_2COO^-]$, $[BrCH_2COOH]$ and K_a for bromoacetic acid.

16.55 A particular sample of vinegar has a pH of 2.90. If acetic acid is the only acid that vinegar contains ($K_a = 1.8 \times 10^{-5}$), calculate the concentration of acetic acid in the vinegar.

16.56 If a solution of HF ($K_a = 6.8 \times 10^{-4}$) has a pH of 3.65, calculate the concentration of hydrofluoric acid.

16.57 The acid-dissociation constant for benzoic acid (C_6H_5COOH) is 6.3×10^{-5}. Calculate the equilibrium concentrations of H_3O^+, $C_6H_5COO^-$, and C_6H_5COOH in the solution if the initial concentration of C_6H_5COOH is 0.050 *M*.

16.58 The acid-dissociation constant for chlorous acid ($HClO_2$) is 1.1×10^{-2}. Calculate the concentrations of H_3O^+, ClO_2^-, and $HClO_2$ at equilibrium if the initial concentration of $HClO_2$ is 0.0125 *M*.

16.59 Calculate the pH of each of the following solutions (K_a and K_b values are given in Appendix D): (**a**) 0.095 *M* propionic acid (C_2H_5COOH), (**b**) 0.100 *M* hydrogen chromate ion ($HCrO_4^-$), (**c**) 0.120 *M* pyridine (C_5H_5N).

16.60 Determine the pH of each of the following solutions (K_a and K_b values are given in Appendix D): (**a**) 0.095 *M* hypochlorous acid, (**b**) 0.0085 *M* hydrazine, (**c**) 0.165 *M* hydroxylamine.

16.61 Saccharin, a sugar substitute, is a weak acid with $pK_a = 2.32$ at 25 °C. It ionizes in aqueous solution as follows:

$$HNC_7H_4SO_3(aq) \rightleftharpoons H^+(aq) + NC_7H_4SO_3^-(aq)$$

What is the pH of a 0.10 *M* solution of this substance?

16.62 The active ingredient in aspirin is acetylsalicylic acid ($HC_9H_7O_4$), a monoprotic acid with $K_a = 3.3 \times 10^{-4}$ at 25 °C. What is the pH of a solution obtained by dissolving two extra-strength aspirin tablets, containing 500 mg of acetylsalicylic acid each, in 250 mL of water?

16.63 Calculate the percent ionization of hydrazoic acid (HN_3) in solutions of each of the following concentrations (K_a is given in Appendix D): (**a**) 0.400 *M*, (**b**) 0.100 *M*, (**c**) 0.0400 *M*.

16.64 Calculate the percent ionization of propionic acid (C_2H_5COOH) in solutions of each of the following concentrations (K_a is given in Appendix D): (**a**) 0.250 *M*, (**b**) 0.0800 *M*, (**c**) 0.0200 *M*.

16.65 Show that for a weak acid, the percent ionization should vary as the inverse square root of the acid concentration.

16.66 For solutions of a weak acid, a graph of pH versus the logarithm of the initial acid concentration should be a straight line. What is the magnitude of the slope of that line?

16.67 Citric acid, which is present in citrus fruits, is a triprotic acid (Table 16.3). Calculate the pH of a 0.040 *M* solution of citric acid. Explain any approximations or assumptions you make in your calculations. Is the concentration of citrate ion $(C_6H_5O_7)^{3-}$ equal to, less than, or greater than the H^+ ion concentration?

16.68 Tartaric acid is found in many fruits, including grapes, and is partially responsible for the dry texture of certain wines. Calculate the pH and the tartarate ion ($C_4H_4O_6^{2-}$) concentration for a 0.250 *M* solution of tartaric acid, for which the acid-dissociation constants are listed in Table 16.3. Explain any approximations or assumptions that you make in your calculation.

WEAK BASES (section 16.7)

16.69 Consider the base hydroxylamine, NH_2OH. (**a**) What is the conjugate acid of hydroxylamine? (**b**) When it acts as a base, which atom in hydroxylamine accepts a proton? (**c**) There are two atoms in hydroxylamine that have nonbonding electron pairs that could act as proton acceptors. Use Lewis structures and formal charges (Section 8.5) to rationalize why one of these two atoms is a much better proton acceptor than the other.

16.70 The hypochlorite ion, ClO^-, acts as a weak base. (**a**) Is ClO^- a stronger or weaker base than hydroxylamine? (**b**) When ClO^- acts as a base, which atom, Cl or O, acts as the proton acceptor? (**c**) Can you use formal charges to rationalize your answer to part (b)?

16.71 Write the chemical equation and the K_b expression for the reaction of each of the following bases with water: (**a**) dimethylamine, $(CH_3)_2NH$; (**b**) carbonate ion, CO_3^{2-}; (**c**) formate ion, CHO_2^-.

16.72 Write the chemical equation and the K_b expression for the reaction of each of the following bases with water: (**a**) propylamine, $C_3H_7NH_2$; (**b**) monohydrogen phosphate ion, HPO_4^{2-}; (**c**) benzoate ion, $C_6H_5CO_2^-$.

16.73 Calculate the molar concentration of OH^- ions in a 0.075 *M* solution of ethylamine ($C_2H_5NH_2$; $K_b = 6.4 \times 10^{-4}$). Calculate the pH of this solution.

16.74 Calculate the molar concentration of OH^- ions in a 0.724 *M* solution of hypobromite ion (BrO^-; $K_b = 4.0 \times 10^{-6}$). What is the pH of this solution?

16.75 Ephedrine, a central nervous system stimulant, is used in nasal sprays as a decongestant. This compound is a weak organic base:

$$C_{10}H_{15}ON(aq) + H_2O(l) \rightleftharpoons C_{10}H_{15}ONH^+(aq) + OH^-(aq)$$

A 0.035 *M* solution of ephedrine has a pH of 11.33. (**a**) What are the equilibrium concentrations of $C_{10}H_{15}ON$, $C_{10}H_{15}ONH^+$, and OH^-? (**b**) Calculate K_b for ephedrine.

16.76 Codeine ($C_{18}H_{21}NO_3$) is a weak organic base. A 5.0×10^{-3} *M* solution of codeine has a pH of 9.95. Calculate the value of K_b for this substance. What is the pK_b for this base?

THE K_a–K_b RELATIONSHIP; ACID–BASE PROPERTIES OF SALTS (sections 16.8 and 16.9)

16.77 Although the acid-dissociation constant for phenol (C_6H_5OH) is listed in Appendix D, the base-dissociation constant for the phenolate ion ($C_6H_5O^-$) is not. (**a**) Explain why it is not necessary to list both K_a for phenol and K_b for the phenolate ion. (**b**) Calculate K_b for the phenolate ion. (**c**) Is the phenolate ion a weaker or stronger base than ammonia?

16.78 Use the acid-dissociation constants in Table 16.3 to arrange these oxyanions from strongest base to weakest: SO_4^{2-}, CO_3^{2-}, SO_3^{2-}, and PO_4^{3-}.

16.79 (**a**) Given that K_a for acetic acid is 1.8×10^{-5} and that for hypochlorous acid is 3.0×10^{-8}, which is the stronger acid? (**b**) Which is the stronger base, the acetate ion or the hypochlorite ion? (**c**) Calculate K_b values for CH_3COO^- and ClO^-.

16.80 (**a**) Given that K_b for ammonia is 1.8×10^{-5} and that for hydroxylamine is 1.1×10^{-8}, which is the stronger base? (**b**) Which is the stronger acid, the ammonium ion or the hydroxylammonium ion? (**c**) Calculate K_a values for NH_4^+ and H_3NOH^+.

16.81 Using data from Appendix D, calculate $[OH^-]$ and pH for each of the following solutions: (**a**) 0.10 *M* NaBrO, (**b**) 0.080 *M* NaHS, (**c**) a mixture that is 0.10 *M* in $NaNO_2$ and 0.20 *M* in $Ca(NO_2)_2$.

16.82 Using data from Appendix D, calculate $[OH^-]$ and pH for each of the following solutions: (**a**) 0.105 *M* NaF, (**b**) 0.035 *M* Na_2S, (**c**) a mixture that is 0.045 *M* in CH_3COONa and 0.055 *M* in $(CH_3COO)_2Ba$.

16.83 Predict whether aqueous solutions of the following compounds are acidic, basic, or neutral: (**a**) NH_4Br, (**b**) $FeCl_3$, (**c**) Na_2CO_3, (**d**) $KClO_4$, (**e**) $NaHC_2O_4$.

16.84 Predict whether aqueous solutions of the following substances are acidic, basic, or neutral: (**a**) $AlCl_3$, (**b**) NaBr, (**c**) NaClO, (**d**) $[CH_3NH_3]NO_3$, (**e**) Na_2SO_3.

16.85 An unknown salt is either NaF, NaCl, or NaOCl. When 0.050 mol of the salt is dissolved in water to form 0.500 L of solution, the pH of the solution is 8.08. What is the identity of the salt?

16.86 An unknown salt is either KBr, NH_4Cl, KCN, or K_2CO_3. If a 0.100 *M* solution of the salt is neutral, what is the identity of the salt?

ACID–BASE CHARACTER AND CHEMICAL STRUCTURE (section 16.10)

16.87 How does the acid strength of an oxyacid depend on (**a**) the electronegativity of the central atom; (**b**) the number of nonprotonated oxygen atoms in the molecule?

16.88 (**a**) Why is NH_3 a stronger base than H_2O? (**b**) Why is NH_3 a stronger base than CH_4?

16.89 Explain the following observations: (**a**) HNO_3 is a stronger acid than HNO_2; (**b**) H_2S is a stronger acid than H_2O; (**c**) H_2SO_4 is a stronger acid than HSO_4^-; (**d**) H_2SO_4 is a stronger acid than H_2SeO_4; (**e**) CCl_3COOH is a stronger acid than CH_3COOH.

16.90 Explain the following observations: (**a**) HCl is a stronger acid than H_2S; (**b**) H_3PO_4 is a stronger acid than H_3AsO_4; (**c**) $HBrO_3$ is a stronger acid than $HBrO_2$; (**d**) $H_2C_2O_4$ is a stronger acid than $HC_2O_4^-$; (**e**) benzoic acid (C_6H_5COOH) is a stronger acid than phenol (C_6H_5OH).

16.91 Based on their compositions and structures and on conjugate acid–base relationships, select the stronger base in each of the following pairs: (**a**) BrO^- or ClO^-, (**b**) BrO^- or BrO_2^-, (**c**) HPO_4^{2-} or $H_2PO_4^-$.

16.92 Based on their compositions and structures and on conjugate acid–base relationships, select the stronger base in each of the following pairs: (**a**) NO_3^- or NO_2^-, (**b**) PO_4^{3-} or AsO_4^{3-}, (**c**) HCO_3^- or CO_3^{2-}.

16.93 Indicate whether each of the following statements is true or false. For each statement that is false, correct the statement to make it true. (**a**) In general, the acidity of binary acids increases from left to right in a given row of the periodic table. (**b**) In a series of acids that have the same central atom, acid strength increases with the number of hydrogen atoms bonded to the central atom. (**c**) Hydrotelluric acid (H_2Te) is a stronger acid than H_2S because Te is more electronegative than S.

16.94 Indicate whether each of the following statements is true or false. For each statement that is false, correct the statement to make it true. (**a**) Acid strength in a series of H—X molecules increases with increasing size of X. (**b**) For acids of the same general structure but differing electronegativities of the central atoms, acid strength decreases with increasing electronegativity of the central atom. (**c**) The strongest acid known is HF because fluorine is the most electronegative element.

LEWIS ACIDS AND BASES (section 16.11)

16.95 If a substance is an Arrhenius base, is it necessarily a Brønsted–Lowry base? Is it necessarily a Lewis base? Explain.

16.96 If a substance is a Lewis acid, is it necessarily a Brønsted–Lowry acid? Is it necessarily an Arrhenius acid? Explain.

16.97 Identify the Lewis acid and Lewis base among the reactants in each of the following reactions:

(**a**) $Fe(ClO_4)_3(s) + 6\,H_2O(l) \rightleftharpoons Fe(H_2O)_6^{3+}(aq) + 3\,ClO_4^-(aq)$

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

(**c**) $(CH_3)_3N(g) + BF_3(g) \rightleftharpoons (CH_3)_3NBF_3(s)$

(**d**) $HIO(lq) + NH_2^-(lq) \rightleftharpoons NH_3(lq) + IO^-(lq)$

(*lq* denotes liquid ammonia as solvent)

16.98 Identify the Lewis acid and Lewis base in each of the following reactions:

(**a**) $HNO_2(aq) + OH^-(aq) \rightleftharpoons NO_2^-(aq) + H_2O(l)$

(**b**) $FeBr_3(s) + Br^-(aq) \rightleftharpoons FeBr_4^-(aq)$

(**c**) $Zn^{2+}(aq) + 4\,NH_3(aq) \rightleftharpoons Zn(NH_3)_4^{2+}(aq)$

(**d**) $SO_2(g) + H_2O(l) \rightleftharpoons H_2SO_3(aq)$

16.99 Predict which member of each pair produces the more acidic aqueous solution: (**a**) K^+ or Cu^{2+}, (**b**) Fe^{2+} or Fe^{3+}, (**c**) Al^{3+} or Ga^{3+}. Explain.

16.100 Which member of each pair produces the more acidic aqueous solution: (**a**) $ZnBr_2$ or $CdCl_2$, (**b**) CuCl or $Cu(NO_3)_2$, (**c**) $Ca(NO_3)_2$ or $NiBr_2$? Explain.

ADDITIONAL EXERCISES

16.101 Triethylamine, $(C_2H_5)_3N$, has a pK_b value of 2.99. Is triethylamine a stronger base than ammonia, NH_3?

16.102 Indicate whether each of the following statements is correct or incorrect. For those that are incorrect, explain why they are wrong.

(**a**) Every Brønsted–Lowry acid is also a Lewis acid.

(**b**) Every Lewis acid is also a Brønsted–Lowry acid.

(**c**) Conjugate acids of weak bases produce more acidic solutions than conjugate acids of strong bases.

(**d**) K^+ ion is acidic in water because it causes hydrating water molecules to become more acidic.

(**e**) The percent ionization of a weak acid in water increases as the concentration of acid decreases.

16.103 Use Figure 16.3 to predict whether the equilibrium lies to the right or to the left in the following reactions:

(**a**) $NH_4^+(aq) + PO_4^{3-}(aq) \rightleftharpoons NH_3(aq) + HPO_4^{2-}(aq)$

(**b**) $CH_3COOH(aq) + F^-(aq) \rightleftharpoons CH_3COO^-(aq) + HF(aq)$

16.104 The odor of fish is due primarily to amines, especially methylamine (CH_3NH_2). Fish is often served with a wedge of lemon, which contains citric acid. The amine and the acid react forming a product with no odor, thereby making the less-than-fresh fish more appetizing. Using data from Appendix D, calculate the equilibrium constant for the reaction of citric acid with methylamine, if only the first proton of the citric acid (K_{a1}) is important in the neutralization reaction.

16.105 Hemoglobin plays a part in a series of equilibria involving protonation-deprotonation and oxygenation-deoxygenation. The overall reaction is approximately as follows:

$$HbH^+(aq) + O_2(aq) \rightleftharpoons HbO_2(aq) + H^+(aq)$$

where Hb stands for hemoglobin and HbO_2 for oxyhemoglobin. (**a**) The concentration of O_2 is higher in the lungs and lower in the tissues. What effect does high $[O_2]$ have on the position of this equilibrium? (**b**) The normal pH of blood is 7.4. Is the blood acidic, basic, or neutral? (**c**) If the blood pH is lowered by the presence of large amounts of acidic metabolism products, a condition known as acidosis results. What effect does lowering blood pH have on the ability of hemoglobin to transport O_2?

[16.106] Calculate the pH of a solution made by adding 2.50 g of lithium oxide (Li_2O) to enough water to make 1.500 L of solution.

16.107 Which of the following solutions has the higher pH? (**a**) a 0.1 *M* solution of a strong acid or a 0.1 *M* solution of a weak acid, (**b**) a 0.1 *M* solution of an acid with $K_a = 2 \times 10^{-3}$ or one with $K_a = 8 \times 10^{-6}$, (**c**) a 0.1 *M* solution of a base with $pK_b = 4.5$ or one with $pK_b = 6.5$.

16.108 What is the pH of a solution that is 2.5×10^{-9} in NaOH? Does your answer make sense? What assumption do we normally make that is not valid in this case?

16.109 Caproic acid ($C_5H_{11}COOH$) is found in small amounts in coconut and palm oils and is used in making artificial flavors. A saturated solution of the acid contains 11 g/L and has a pH of 2.94. Calculate K_a for the acid.

16.110 Butyric acid is responsible for the foul smell of rancid butter. The pK_a of butyric acid is 4.84. (**a**) Calculate the pK_b for the butyrate ion. (**b**) Calculate the pH of a 0.050 *M* solution of butyric acid. (**c**) Calculate the pH of a 0.050 *M* solution of sodium butyrate.

16.111 Arrange the following 0.10 *M* solutions in order of increasing acidity (decreasing pH): (i) NH_4NO_3, (ii) $NaNO_3$, (iii) CH_3COONH_4, (iv) NaF, (v) CH_3COONa.

[**16.112**] Many moderately large organic molecules containing basic nitrogen atoms are not very soluble in water as neutral molecules, but they are frequently much more soluble as their acid salts. Assuming that pH in the stomach is 2.5, indicate whether each of the following compounds would be present in the stomach as the neutral base or in the protonated form: nicotine, $K_b = 7 \times 10^{-7}$; caffeine, $K_b = 4 \times 10^{-14}$; strychnine, $K_b = 1 \times 10^{-6}$; quinine, $K_b = 1.1 \times 10^{-6}$.

[**16.113**] The amino acid glycine ($H_2N—CH_2—COOH$) can participate in the following equilibria in water:

$$H_2N—CH_2—COOH + H_2O \rightleftharpoons H_2N—CH_2—COO^- + H_3O^+ \quad K_a = 4.3 \times 10^{-3}$$

$$H_2N—CH_2—COOH + H_2O \rightleftharpoons {}^+H_3N—CH_2—COOH + OH^- \quad K_b = 6.0 \times 10^{-5}$$

(**a**) Use the values of K_a and K_b to estimate the equilibrium constant for the intramolecular proton transfer to form a zwitterion:

$$H_2N—CH_2—COOH \rightleftharpoons {}^+H_3N—CH_2—COO^-$$

What assumptions did you need to make? (**b**) What is the pH of a 0.050 *M* aqueous solution of glycine? (**c**) What would be the predominant form of glycine in a solution with pH 13? With pH 1?

16.114 The structural formula for acetic acid is shown in Table 16.2. Replacing hydrogen atoms on the carbon with chlorine atoms causes an increase in acidity, as follows:

Acid	Formula	K_a(25 °C)
Acetic	CH_3COOH	1.8×10^{-5}
Chloroacetic	$CH_2ClCOOH$	1.4×10^{-3}
Dichloroacetic	$CHCl_2COOH$	3.3×10^{-2}
Trichloroacetic	CCl_3COOH	2×10^{-1}

Using Lewis structures as the basis of your discussion, explain the observed trend in acidities in the series. Calculate the pH of a 0.010 *M* solution of each acid.