Acids and Bases

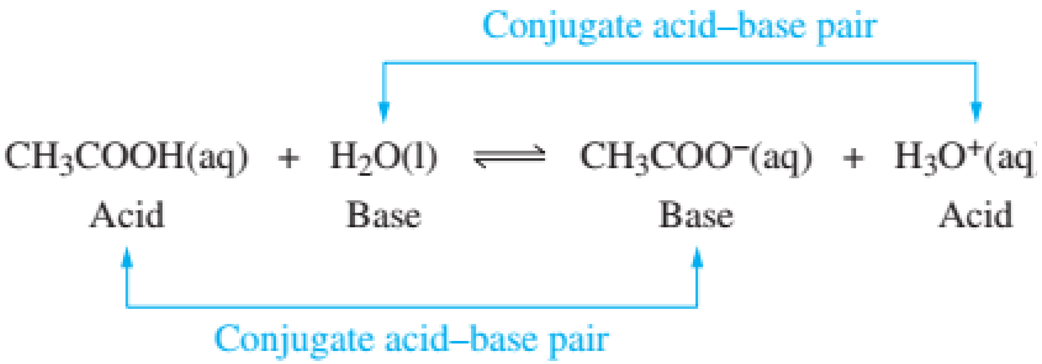
Acids, Bases, and Conjugate Acid–Base Pairs

One of the most useful theories of acids and bases, particularly for describing the reactions of acids and bases in aqueous solutions, is the Brønsted–Lowry theory. In 1923, J. N. Brønsted and T. M. Lowry in Great Britain independently proposed that an acid is a proton donor and a base is a proton acceptor. Let’s use the Brønsted–Lowry theory to describe the ionization of CH_3COOH in aqueous solution.

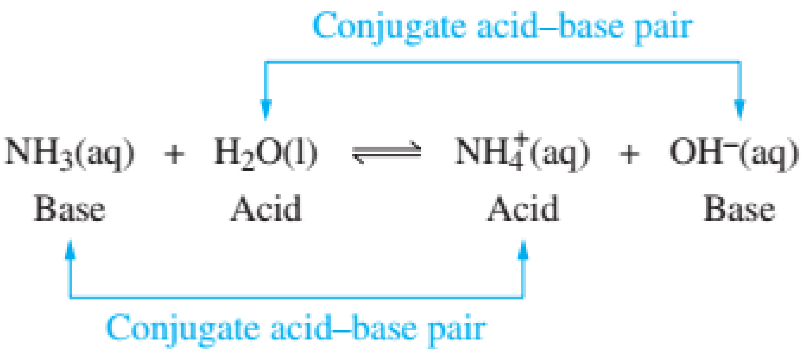
$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq) \qquad \textbf{(16.1)}$$

In reaction, CH_3COOH acts as an acid. It gives up a proton, H^+ , which is taken up by H_2O. Thus, H_2O acts as a base. In the reverse reaction, the hydronium ion, H_3O^+ acts as an acid and CH_3COO^- acts as a base.

When CH_3COOH loses a proton, it is converted into CH_3COO^- . Notice that the formulas of these two species differ by a single proton, H^+ . Species that differ by a single proton (H^+) constitute a conjugate acid–base pair. Within this pair, the species with the added H^+ is the acid, and the species without the H^+ is the base. Thus, for reaction (16.1), we can identify two conjugate acid–base pairs.



$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq$$



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

An acid contains at least one ionizable H atom, and a base contains an atom with a lone pair of electrons onto which a proton can bind.

It will be helpful to summarize some key aspects of the Brønsted–Lowry theory.

1. **An acid contains at least one ionizable H atom, and a base contains an atom with a lone pair of electrons onto which a proton can bind.** For this reason, an acid may be represented in the Brønsted–Lowry theory by the general formula HA, H_2A, H_3A, etc., depending on the number of ionizable H atoms, and a base is represented by :B. There are substances that contain both an ionizable H atom and an atom with a lone pair of electrons. Such substances may behave as either an acid or a base, depending on the situation, and are said to be amphiprotic.

2. **For a conjugate acid–base pair, the molecular formulas for the acid and base differ by a single proton (H^+).** Therefore, to identify the species in a solution that constitute a conjugate acid–base pair, we need only identify those species that have molecular formulas that differ by one H^+ ion. Once such a pair has been identified, the species with the added H is the acid, and the species without the H^+ is the base. For example, H_2O and OH^- are a conjugate acid–base pair because their formulas differ by one H . In this pair, H_2O is the acid and OH is the base. Similarly, because the formulas of NH^+_4 and NH_3 differ by one H^+ , these two species constitute a conjugate acid–base pair, with NH^+_4 as the acid and NH_3 as the base.

3. **When added to water, acids protonate water molecules to form hydronium (H_3O^+) ions and bases deprotonate water molecules to form hydroxide (OH^-) ions.** The ability of the Brønsted–Lowry theory to account for the presence these ions in solution arises from its recognition of the role played by the solvent and makes it a more general and useful theory than the Arrhenius theory.

EXAMPLE 16-1 Identifying Brønsted–Lowry Acids and Bases and Their Conjugates

For each of the following reactions, which occur in aqueous solution, identify the acids and bases in both the forward and reverse reactions.

(a) $HClO_2 + H_2O \rightleftharpoons ClO_2^- + H_3O^+$
(b) $OCl^- + H_2O \rightleftharpoons HOCl + OH^-$
(c) $NH_3 + H_2PO_4^- \rightleftharpoons NH_4^+ + HPO_4^{2-}$
(d) $HCl + H_2PO_4^- \rightleftharpoons Cl^- + H_3PO_4$

Analyze

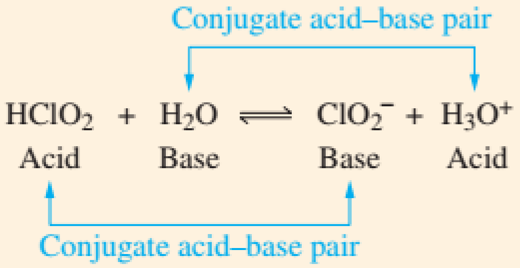
In the Brønsted–Lowry theory, an acid is a proton (H^+) donor and a base is proton acceptor. The deprotonated form of an acid is the corresponding conjugate base. The protonated form of a base is the corresponding conjugate acid. A quick way to identify the members of a conjugate acid–base pair is to identify two species that have molecular formulas that differ by a single H^+ ion.

Solve

(a) In the reaction $HClO_2 + H_2O \rightleftharpoons ClO_2^- + H_3O^+$, we see that, in the forward reaction, a H^+ ion is transferred from $HClO_2$ to H_2O. Thus, $HClO_2$ acts as an acid and H_2O acts as a base. In the reverse reaction, a H^+ ion is transferred from H_3O^+ to ClO_2^-, so H_3O^+ acts as an acid and ClO_2^- acts as a base.

$$\underset{\text{Acid}}{HClO_2} + \underset{\text{Base}}{H_2O} \rightleftharpoons \underset{\text{Base}}{ClO_2^-} + \underset{\text{Acid}}{H_3O^+}$$

When the acid $HClO_2$ gives up a H^+ ion, it becomes the ClO_2^- ion. Their formulas differ by a single H^+, and, therefore, $HClO_2$ and ClO_2^- are a conjugate acid–base pair. When the base H_2O takes a proton, it becomes H_3O^+. Thus, H_3O^+ and H_2O constitute a conjugate acid–base pair. These associations are summarized below.



We use the same approach in parts (b)–(d) to identify acids and bases. However, in labeling the acids and bases below, we use the numbers 1 and 2 to identify the acid and base in the two conjugate acid–base pairs. That is, Acid(1) and Base(1) constitute one conjugate acid–base pair and Acid(2) and Base(2) the other.

(b) $$\underset{\text{Base(1)}}{OCl^-} + \underset{\text{Acid(2)}}{H_2O} \rightleftharpoons \underset{\text{Acid(1)}}{HOCl} + \underset{\text{Base(2)}}{OH^-}$$

(c) $$\underset{\text{Base(1)}}{NH_3} + \underset{\text{Acid(2)}}{H_2PO_4^-} \rightleftharpoons \underset{\text{Acid(1)}}{NH_4^+} + \underset{\text{Base(2)}}{HPO_4^{2-}}$$

(d) $$\underset{\text{Acid(1)}}{HCl} + \underset{\text{Base(2)}}{H_2PO_4^-} \rightleftharpoons \underset{\text{Base(1)}}{Cl^-} + \underset{\text{Acid(2)}}{H_3PO_4}$$

PRACTICE EXAMPLE A: For each of the following reactions, identify the acids and bases in both the forward and reverse directions.

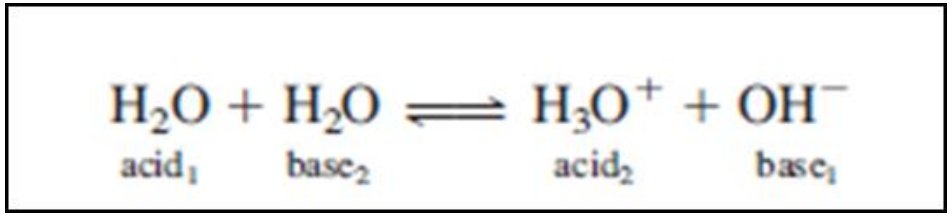
(a) $HF + H_2O \rightleftharpoons F^- + H_3O^+$

(b) $HSO_4^- + NH_3 \rightleftharpoons SO_4^{2-} + NH_4^+$

(c) $CH_3COO^- + HCl \rightleftharpoons CH_3COOH + Cl^-$

Self-Ionization of Water and the pH Scale

H_2O molecule can act as either an acid or a base it is amphiprotic. It should come as no surprise that amongst themselves water molecules can produce H_3O^+ and OH^- ions via the following self-ionization reaction or autoionization reaction:



$$\underset{\text{acid}_1}{H_2O} + \underset{\text{base}_2}{H_2O} \rightleftharpoons \underset{\text{acid}_2}{H_3O^+} + \underset{\text{base}_1}{OH^-}$$

The Ion Product of Water

In the study of acid-base reactions, the hydrogen ion concentration is key; its value indicates the acidity or basicity of the solution. Because only a very small fraction of water molecules are ionized, the concentration of water remains virtually unchanged. Therefore, the equilibrium constant for the autoionization of water, according to Equation (15.1), is

$$\boxed{\underset{\text{acid}_1}{H_2O} + \underset{\text{base}_2}{H_2O} \rightleftharpoons \underset{\text{acid}_2}{H_3O^+} + \underset{\text{base}_1}{OH^-}}$$

$$K_c = [H_3O^+][OH^-]$$

Because we use $H^+(aq)$ and $H_3O^+(aq)$ interchangeably to represent the hydrated proton, the equilibrium constant can also be expressed as

$$K_c = [H^+][OH^-]$$

To indicate that the equilibrium constant refers to the autoionization of water, we replace K_c by K_w

$$K_w = [H_3O^+][OH^-] = [H^+][OH^-] \tag{15.2}$$

where K_w is called the ***ion-product constant,*** which is *the product of the molar concentrations of* H^+ *and* OH^- *ions at a particular temperature.*

In pure water at 25°C, the concentrations of H^+ and OH^- ions are equal and found to be $[H^+] = 1.0 \times 10^{-7}\ M$ and $[OH^-] = 1.0 \times 10^{-7}\ M$. Thus, from Equation (15.2), at 25°C

$$K_w = (1.0 \times 10^{-7})(1.0 \times 10^{-7}) = 1.0 \times 10^{-14}$$

Whether we have pure water or an aqueous solution of dissolved species, the following relation *always* holds at 25°C:

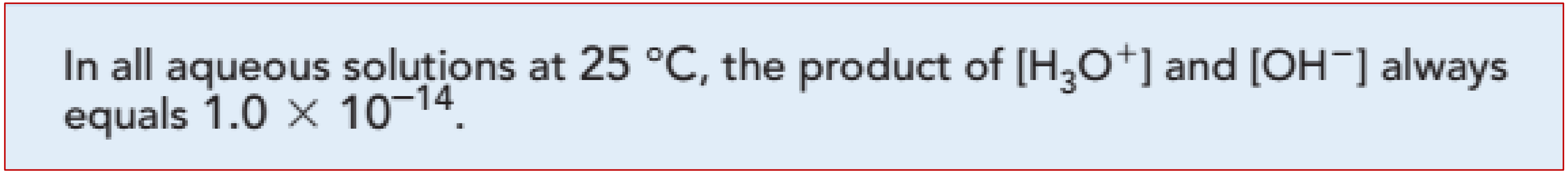
$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14} \tag{15.3}$$

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14} \tag{15.3}$$

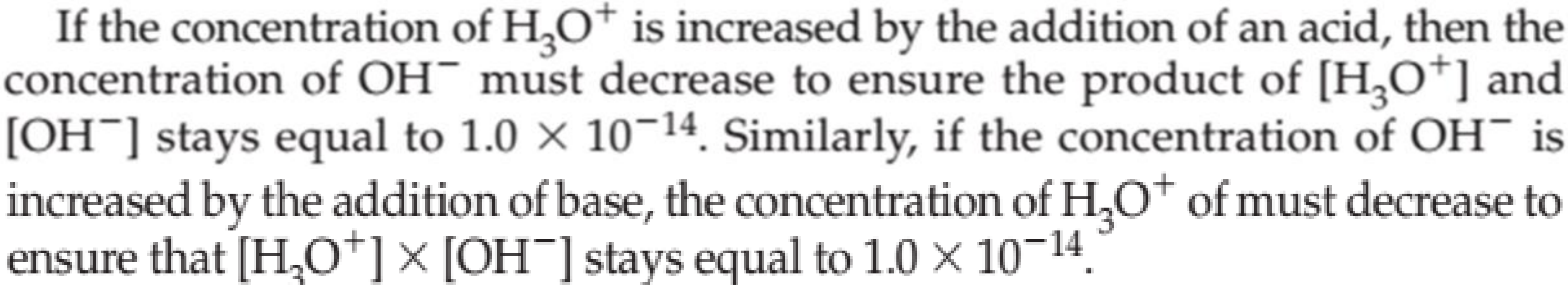
Whenever $[H^+] = [OH^-]$, the aqueous solution is said to be neutral. In an acidic solution there is an excess of H^+ ions and $[H^+] > [OH^-]$. In a basic solution there is an excess of hydroxide ions, so $[H^+] < [OH^-]$. In practice we can change the concentration of either H^+ or OH^- ions in solution, but we cannot vary both of them independently. If we adjust the solution so that $[H^+] = 1.0 \times 10^{-6}\ M$, the OH^- concentration *must* change to

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-6}} = 1.0 \times 10^{-8}\,M$$

Since reaction reaches equilibrium not only in pure water but in all aqueous solutions, we arrive at the following conclusion.



In all aqueous solutions at 25 °C, the product of $[H_3O^+]$ and $[OH^-]$ always equals 1.0×10^{-14}.



If the concentration of H_3O^+ is increased by the addition of an acid, then the concentration of OH^- must decrease to ensure the product of $[H_3O^+]$ and $[OH^-]$ stays equal to 1.0×10^{-14}. Similarly, if the concentration of OH^- is increased by the addition of base, the concentration of H_3O^+ of must decrease to ensure that $[H_3O^+] \times [OH^-]$ stays equal to 1.0×10^{-14}.

EXAMPLE 15.2

The concentration of OH^- ions in a certain household ammonia cleaning solution is 0.0025 *M*. Calculate the concentration of H^+ ions.

EXAMPLE 15.2

The concentration of OH^- ions in a certain household ammonia cleaning solution is 0.0025 *M*. Calculate the concentration of H^+ ions.

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{0.0025} = \boxed{4.0 \times 10^{-12}\,M}$$

The self-ionization of water is an important reaction, from a conceptual point of view, because it reveals an important relationship between [H_3O] and [OH^-] that applies to all aqueous solutions. From a practical standpoint, the reaction is not of much concern to us except when dealing with extremely dilute solutions.

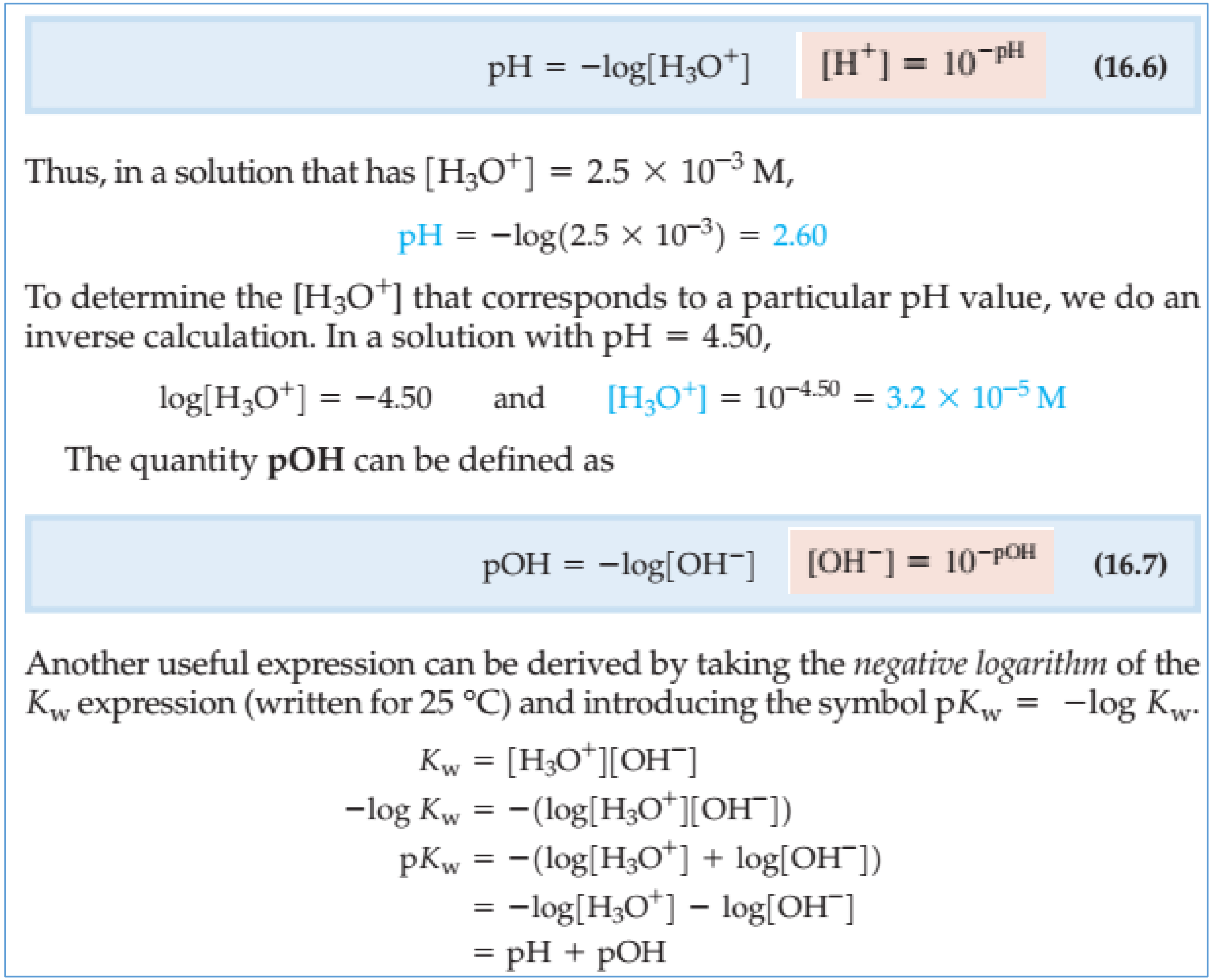
In fact, the self-ionization of water is partially suppressed by the addition of acid or base to water.

This statement is easily justified by applying Le Châtelier’s principle to reaction (16.3). When an acid is added to water, H_2O molecules are protonated and [H_3O^+] increases. The increase in [H_3O^+] causes net change to the left in reaction (16.3), and, thus, the self-ionization of water is partially suppressed. Similarly, the addition of a base to water increases [OH-], causes net change to the left, and partially suppresses the self-ionization of water.

$$2\,H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \qquad \textbf{(16.3)}$$

pH and pOH

Because the concentrations of H and OH ions in aqueous solutions are frequently very small numbers and therefore inconvenient to work with, Soren Sorensen† in 1909 proposed a more practical measure called pH. The pH of a solution is defined as the negative logarithm of the hydrogen ion concentration (in mol/L).



$$\mathrm{pH} = -\log[\mathrm{H_3O^+}] \qquad [\mathrm{H^+}] = 10^{-\mathrm{pH}} \qquad \textbf{(16.6)}$$

Thus, in a solution that has $[\mathrm{H_3O^+}] = 2.5 \times 10^{-3}$ M,

$$\mathrm{pH} = -\log(2.5 \times 10^{-3}) = 2.60$$

To determine the $[\mathrm{H_3O^+}]$ that corresponds to a particular pH value, we do an inverse calculation. In a solution with pH = 4.50,

$$\log[\mathrm{H_3O^+}] = -4.50 \qquad \text{and} \qquad [\mathrm{H_3O^+}] = 10^{-4.50} = 3.2 \times 10^{-5}\ \mathrm{M}$$

The quantity **pOH** can be defined as

$$\mathrm{pOH} = -\log[\mathrm{OH^-}] \qquad [\mathrm{OH^-}] = 10^{-\mathrm{pOH}} \qquad \textbf{(16.7)}$$

Another useful expression can be derived by taking the *negative logarithm* of the K_w expression (written for 25 °C) and introducing the symbol $\mathrm{p}K_w = -\log K_w$.

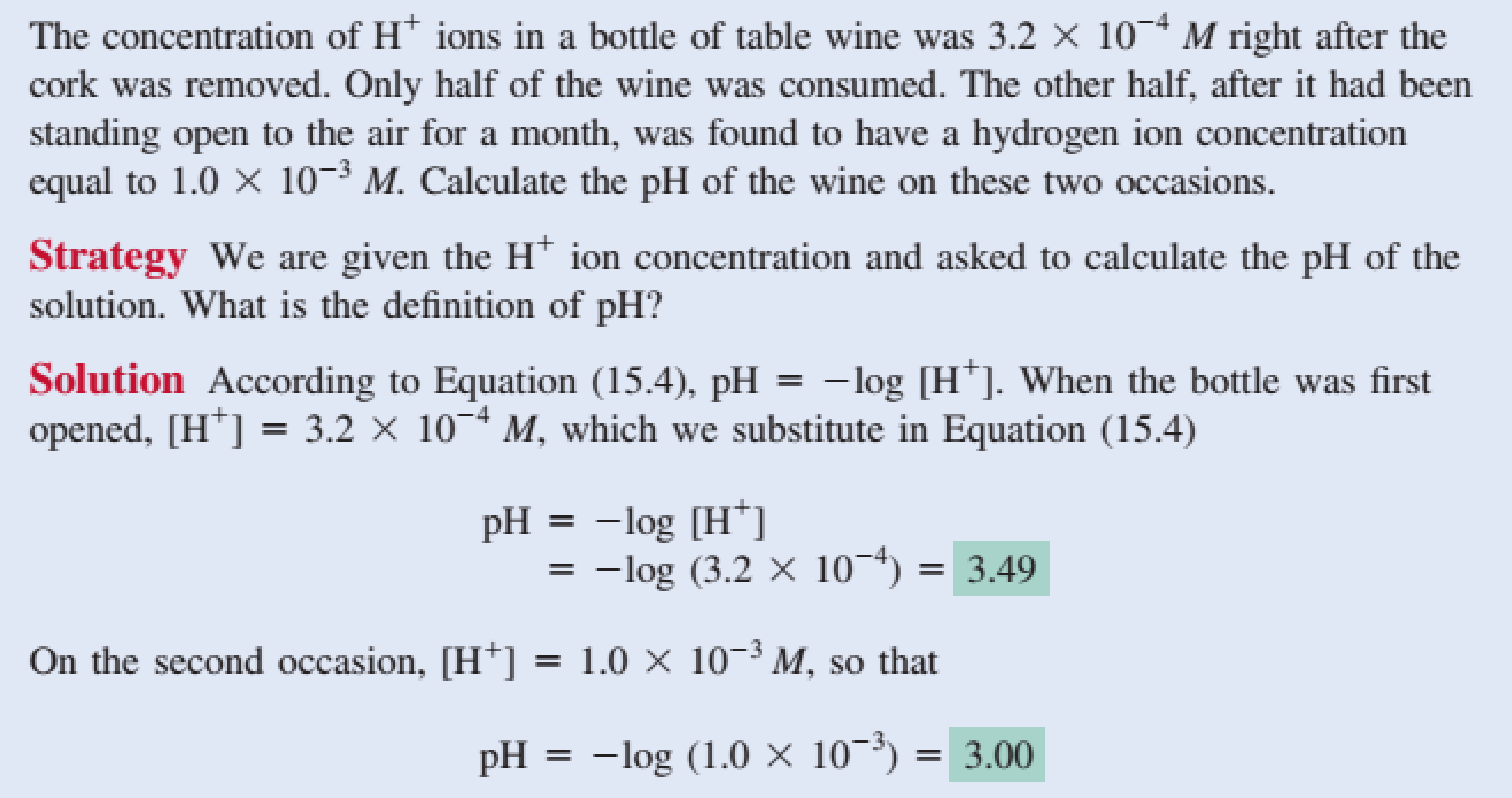
$$\begin{aligned} K_w &= [\mathrm{H_3O^+}][\mathrm{OH^-}] \\ -\log K_w &= -(\log[\mathrm{H_3O^+}][\mathrm{OH^-}]) \\ \mathrm{p}K_w &= -(\log[\mathrm{H_3O^+}] + \log[\mathrm{OH^-}]) \\ &= -\log[\mathrm{H_3O^+}] - \log[\mathrm{OH^-}] \\ &= \mathrm{pH} + \mathrm{pOH} \end{aligned}$$

Thus, in general, the sum of the pH and pOH values must equal pK_w. At 25 °C, $K_w = 1.0 \times 10^{-14}$ and pK_w = 14.00. Therefore,

$$\text{pH} + \text{pOH} = 14.00 \ \text{(at 25 °C)} \qquad \textbf{(16.8)}$$

EXAMPLE 15.3

The concentration of H^+ ions in a bottle of table wine was 3.2×10^{-4} *M* right after the cork was removed. Only half of the wine was consumed. The other half, after it had been standing open to the air for a month, was found to have a hydrogen ion concentration equal to 1.0×10^{-3} *M*. Calculate the pH of the wine on these two occasions.



The concentration of H^+ ions in a bottle of table wine was 3.2×10^{-4} *M* right after the cork was removed. Only half of the wine was consumed. The other half, after it had been standing open to the air for a month, was found to have a hydrogen ion concentration equal to 1.0×10^{-3} *M*. Calculate the pH of the wine on these two occasions.

Strategy We are given the H^+ ion concentration and asked to calculate the pH of the solution. What is the definition of pH?

Solution According to Equation (15.4), $\text{pH} = -\log [H^+]$. When the bottle was first opened, $[H^+] = 3.2 \times 10^{-4}$ *M*, which we substitute in Equation (15.4)

$$\begin{aligned} \text{pH} &= -\log [H^+] \\ &= -\log (3.2 \times 10^{-4}) = 3.49 \end{aligned}$$

On the second occasion, $[H^+] = 1.0 \times 10^{-3}$ *M*, so that

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

EXAMPLE 15.5

In a NaOH solution $[OH^-]$ is 2.9×10^{-4} *M*. Calculate the pH of the solution.

In a NaOH solution $[\mathrm{OH^-}]$ is $2.9 \times 10^{-4}\ M$. Calculate the pH of the solution.

Strategy Solving this problem takes two steps. First, we need to calculate pOH using Equation (15.7). Next, we use Equation (15.9) to calculate the pH of the solution.

Solution We use Equation (15.7):

$$\begin{aligned} \mathrm{pOH} &= -\log\,[\mathrm{OH^-}] \\ &= -\log\,(2.9 \times 10^{-4}) \\ &= 3.54 \end{aligned}$$

Now we use Equation (15.9):

$$\begin{aligned} \mathrm{pH} + \mathrm{pOH} &= 14.00 \\ \mathrm{pH} &= 14.00 - \mathrm{pOH} \\ &= 14.00 - 3.54 = 10.46 \end{aligned}$$

Acidic, Basic, and Neutral Solutions

In pure water, the concentrations of H_3O^+ and OH^- are equal. However, when an acid or a base is added to water, the H_3O^+ and OH^- ions are no longer present in equal amounts. By comparing the values of $[H_3O^+]$ and $[OH^-]$, we can classify a solution as acidic, basic, or neutral (Table 16.1).

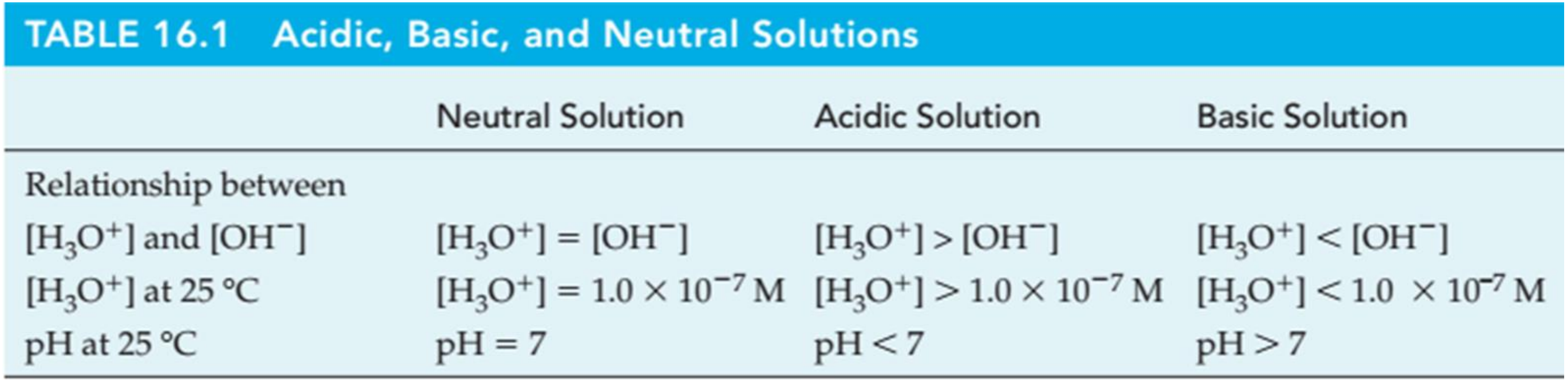
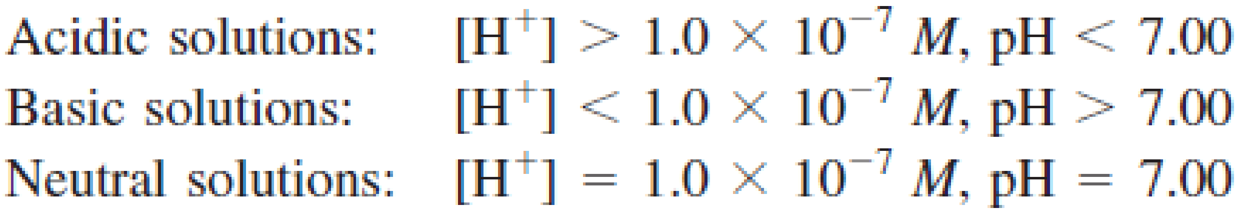


TABLE 16.1 Acidic, Basic, and Neutral Solutions

	Neutral Solution	Acidic Solution	Basic Solution
Relationship between $[H_3O^+]$ and $[OH^-]$	$[H_3O^+] = [OH^-]$	$[H_3O^+] > [OH^-]$	$[H_3O^+] < [OH^-]$
$[H_3O^+]$ at 25 °C	$[H_3O^+] = 1.0 \times 10^{-7}$ M	$[H_3O^+] > 1.0 \times 10^{-7}$ M	$[H_3O^+] < 1.0 \times 10^{-7}$ M
pH at 25 °C	$pH = 7$	$pH < 7$	$pH > 7$

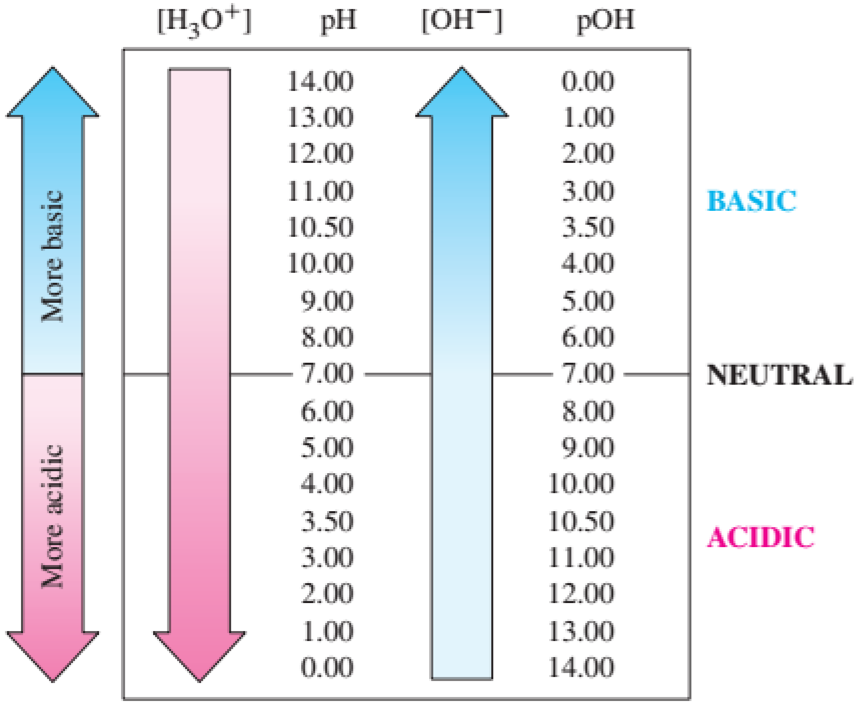


Acidic solutions: $[H^+] > 1.0 \times 10^{-7}\ M$, $pH < 7.00$

Basic solutions: $[H^+] < 1.0 \times 10^{-7}\ M$, $pH > 7.00$

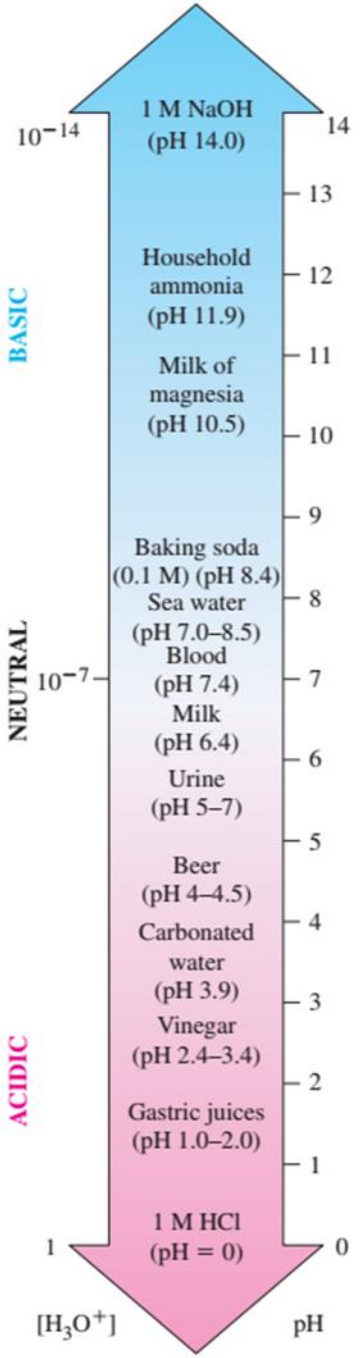
Neutral solutions: $[H^+] = 1.0 \times 10^{-7}\ M$, $pH = 7.00$

The classification can also be made, at , by focusing on either [H_3O^+] or the pH. The relationships between [H_3O], [OH], pH, and pOH, for acidic, basic, and neutral solutions, are illustrated in Figure 16-4. The pH values of a number of materials—some acidic and others basic—are depicted in Figure 16-5.



▲ FIGURE 16-4
Relating [H_3O^+], pH, [OH^-], and pOH
In aqueous solutions at 25 °C, the sum of the pH and pOH values is always equal to 14.

▲ FIGURE 16-5
The pH scale and pH values of some common materials
The scale shown here ranges from pH 0 to pH 14. Slightly negative pH values, perhaps to about −1 (corresponding to [H_3O^+] ≈ 10 M), are possible. Also possible are pH values up to about 15 (corresponding to [OH^-] ≈ 10 M). For practical purposes, however, the pH scale is useful only in the range $2 < pH < 12$, because the activities of H_3O^+ and OH^- in concentrated solutions may differ significantly from their molarities.



Ionization of Acids and Bases in Water

Figure 16-6 illustrates two ways of showing that ionization has occurred in a solution of acid. One is by the color of an acid–base indicator; the other, the response of a pH meter.

The pink color of the solution in Figure 16-7 tells us the pH of the HCl solution is less than 1.2. The pH meter registers a value of 1.20, indicating that $[H_3O\ ]=10^{-1.20}$ M=0.063 M in the HCl solution. The yellow color of the solution in Figure 16-7 indicates that the pH of 0.1 M CH_3COOH (acetic acid) is 2.8 or greater. The pH meter registers 2.80, and thus $[H_3O\ ]=10^{-2.80}$ M=0.0016 M.

Tom Pantages

▲ FIGURE 16-6
Strong and weak acids compared
The color of thymol blue indicator, which is present in both solutions, depends on the pH of the solution.

$\text{pH} < 1.2 < \text{pH} < 2.8 < \text{pH}$

Red Orange Yellow

Notice that the ionization of HCl generates a higher [H_3O^+] than does the ionization of CH_3COOH, even though the initial molarity of CH_3COOH (0.1 M) is greater than that of HCl (0.06 to 0.07 M). From this, we conclude that the ionization of HCl occurs to a greater extent than does the ionization of CH_3COOH, an indication that HCl is a much stronger acid than CH_3COOH. This conclusion is reflected in the placements of HCl and CH_3COOH in Table 16.2 which ranks a number of acids and bases in order of increasing acid or base strengths. This ordering is established by experiment.

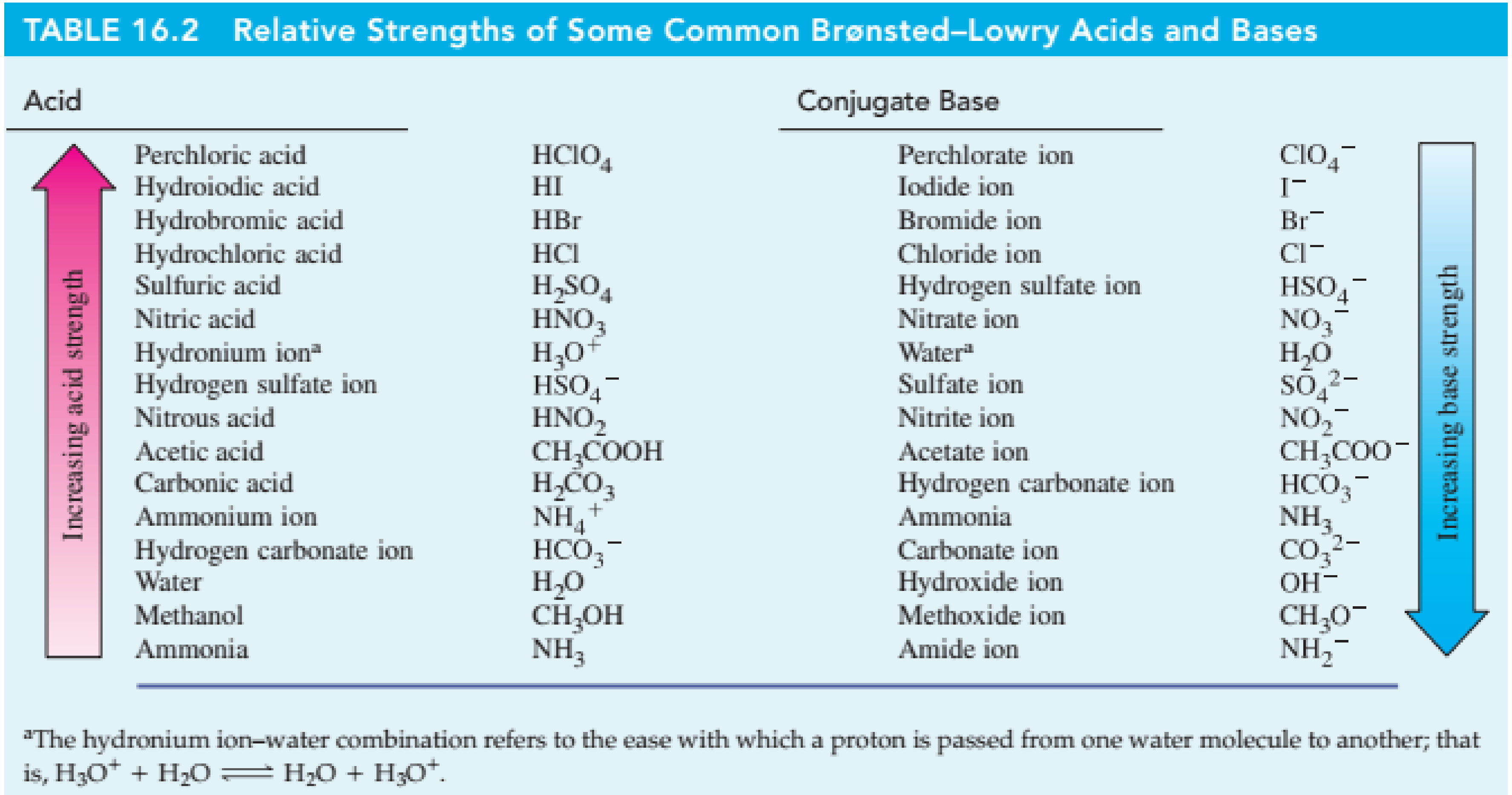
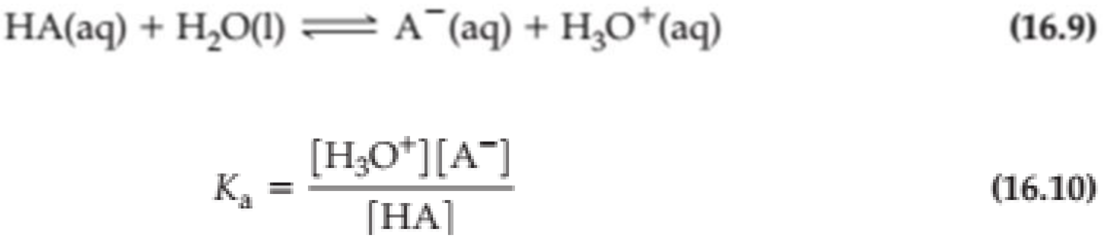


TABLE 16.2 Relative Strengths of Some Common Brønsted–Lowry Acids and Bases

Acid		Conjugate Base	
Perchloric acid	$HClO_4$	Perchlorate ion	ClO_4^-
Hydroiodic acid	HI	Iodide ion	I^-
Hydrobromic acid	HBr	Bromide ion	Br^-
Hydrochloric acid	HCl	Chloride ion	Cl^-
Sulfuric acid	H_2SO_4	Hydrogen sulfate ion	HSO_4^-
Nitric acid	HNO_3	Nitrate ion	NO_3^-
Hydronium ion[a]	H_3O^+	Water[a]	H_2O
Hydrogen sulfate ion	HSO_4^-	Sulfate ion	SO_4^{2-}
Nitrous acid	HNO_2	Nitrite ion	NO_2^-
Acetic acid	CH_3COOH	Acetate ion	CH_3COO^-
Carbonic acid	H_2CO_3	Hydrogen carbonate ion	HCO_3^-
Ammonium ion	NH_4^+	Ammonia	NH_3
Hydrogen carbonate ion	HCO_3^-	Carbonate ion	CO_3^{2-}
Water	H_2O	Hydroxide ion	OH^-
Methanol	CH_3OH	Methoxide ion	CH_3O^-
Ammonia	NH_3	Amide ion	NH_2^-

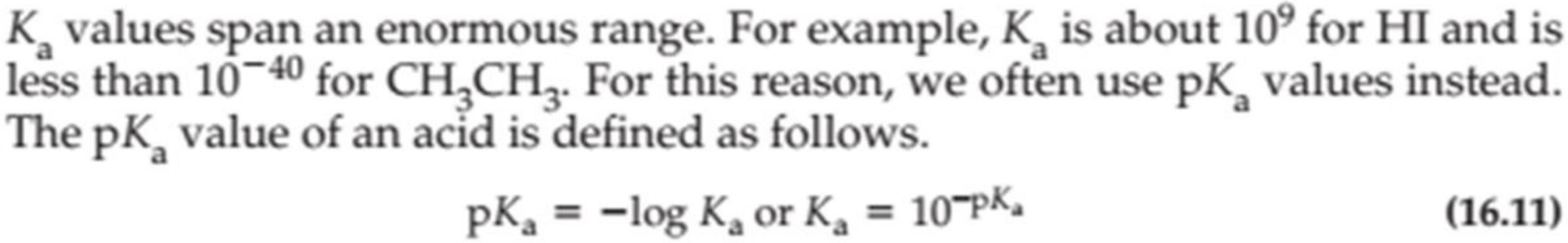
[a] The hydronium ion–water combination refers to the ease with which a proton is passed from one water molecule to another; that is, $H_3O^+ + H_2O \rightleftharpoons H_2O + H_3O^+$.

The strength of an acid or a base is quantified by the value of the equilibrium constant for the reaction describing its ionization in water. As discussed earlier, a monoprotic Brønsted–Lowry acid may be represented by the general formula HA. Therefore, the ionization of an acid may be represented generally by the following equation.



$$HA(aq) + H_2O(l) \rightleftharpoons A^-(aq) + H_3O^+(aq) \qquad \textbf{(16.9)}$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \qquad \textbf{(16.10)}$$



K_a values span an enormous range. For example, K_a is about 10^9 for HI and is less than 10^{-40} for CH_3CH_3. For this reason, we often use pK_a values instead. The pK_a value of an acid is defined as follows.

$$pK_a = -\log K_a \text{ or } K_a = 10^{-pK_a} \qquad \textbf{(16.11)}$$

Thus, for example, pK_a is equal to −9 for HI and 40 for CH_3CH_3.

In a similar manner, we may write equations representing the ionization of a base B, the **base ionization constant**, K_b, and pK_b.

$$B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq) \tag{16.12}$$

$$K_b = \frac{[BH^+][OH^-]}{[B]} \tag{16.13}$$

$$pK_b = -\log K_b \text{ or } K_b = 10^{-pK_b} \tag{16.14}$$

The value of K_a or K_b gives an indication of the strength of an acid or a base. The following points are worth remembering

1. **A strong acid or base has a large ionization constant:** Ka or Kb is much greater than 1. Therefore, we expect that the corresponding ionization reaction goes almost to completion. In most situations, we can safely assume that a strong acid or strong base is completely ionized in solution. Fortunately, there are relatively few common strong acids and strong bases

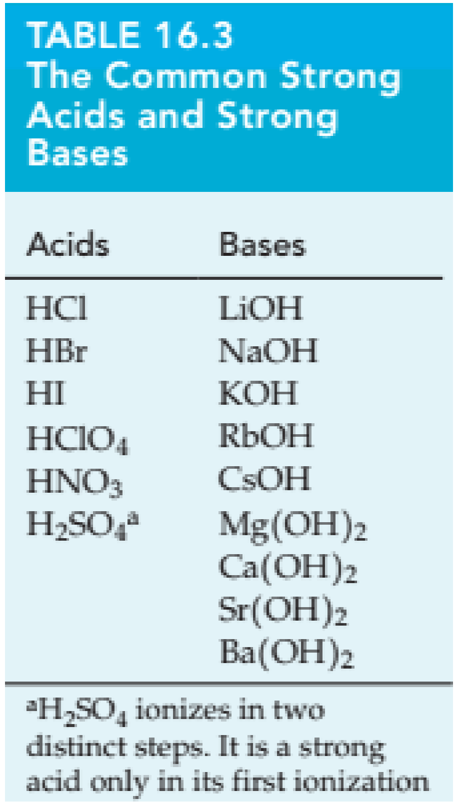


TABLE 16.3
The Common Strong Acids and Strong Bases

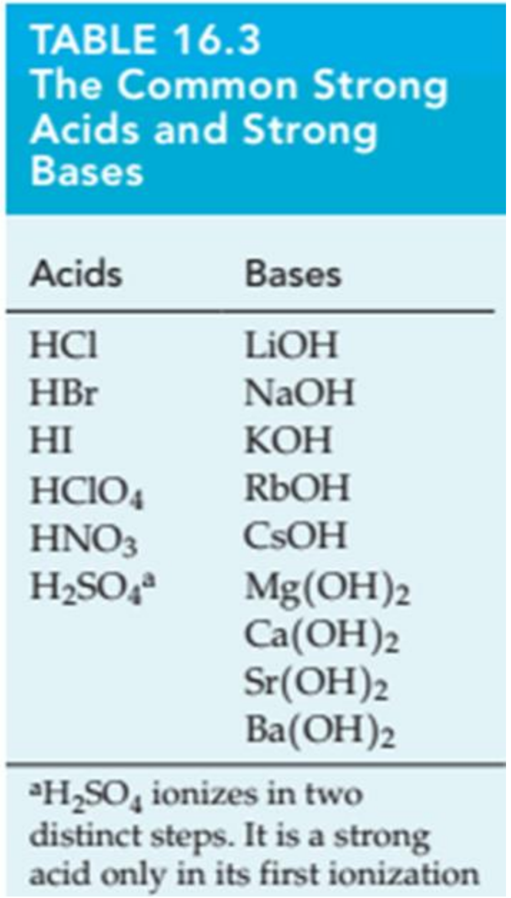
Acids	Bases
HCl	LiOH
HBr	NaOH
HI	KOH
$HClO_4$	RbOH
HNO_3	CsOH
H_2SO_4[a]	$Mg(OH)_2$
	$Ca(OH)_2$
	$Sr(OH)_2$
	$Ba(OH)_2$

[a] H_2SO_4 ionizes in two distinct steps. It is a strong acid only in its first ionization

Notice that the listing in Table 16.3 does not include Ka or Kb values; these values are not needed. The main point is that the ionization constants are large enough to ensure that the acids and bases in Table 16.3 are almost completely ionized in aqueous solution.

Memorizing the list in Table 16.3 can be extremely helpful. For example, if the situation we are dealing with involves a strong acid or base, we can safely assume the strong acid or base will react to completion. On the other hand, if the situation we are considering involves an acid and a base that are not listed in Table 16.3, we can safely assume that the acid and base are weak and react to a limited extent only.

The strong acids listed in Table 16.3 are molecular compounds whereas the strong bases are soluble ionic compounds called hydroxides. Molecular compounds ionize in water: Neutral HA molecules produce H_3O^+ and A^- ions by reacting with water (equation 16.9). On the other hand, soluble ionic hydroxides dissociate in water: Positive and negative ions (for example, Na and OH), which are already present in the solid structure, enter the solution as free ions.



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	$Sr(OH)_2$
	$Ba(OH)_2$

[a] H_2SO_4 ionizes in two distinct steps. It is a strong acid only in its first ionization

$$HA(aq) + H_2O(l) \rightleftharpoons A^-(aq) + H_3O^+(aq) \tag{16.9}$$

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

2. A weak acid or base has a small ionization constant: Ka or Kb is much less than 1. For a weak acid or base, the corresponding ionization reaction occurs to a limited extent, with a significant fraction of the acid or base not ionized. To determine the equilibrium composition of a solution of a weak acid or weak base, we need to solve an equilibrium problem, typically by using an ICE table and the value of the appropriate ionization constant, Ka or K b. Ionization constants of some weak acids and weak bases are provided in Table 16.4.

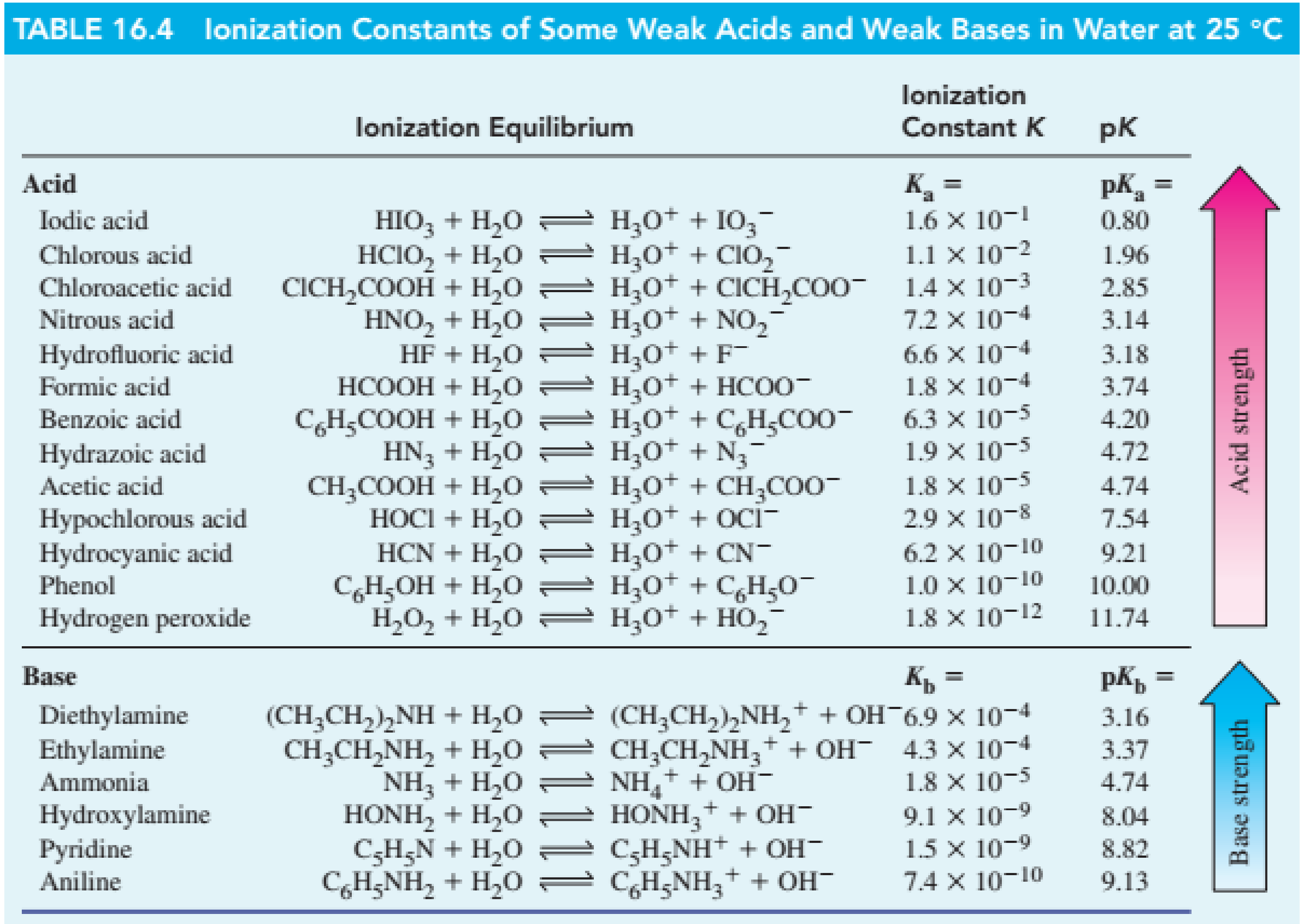
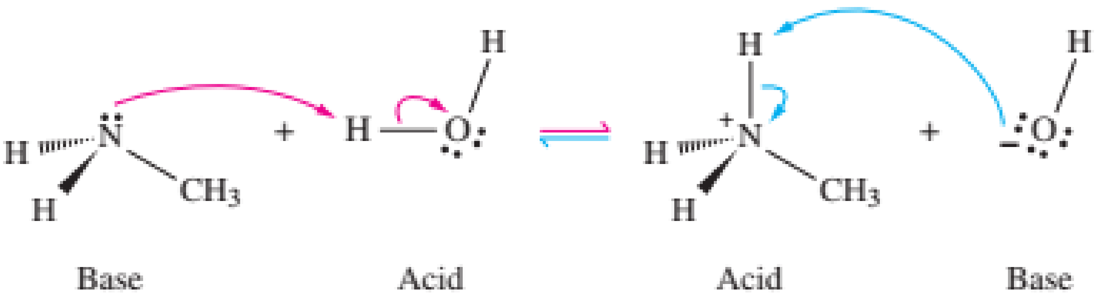


TABLE 16.4 Ionization Constants of Some Weak Acids and Weak Bases in Water at 25 °C

	Ionization Equilibrium	Ionization Constant K	pK
Acid		K_a =	pK_a =
Iodic acid	$HIO_3 + H_2O \rightleftharpoons H_3O^+ + IO_3^-$	1.6×10^{-1}	0.80
Chlorous acid	$HClO_2 + H_2O \rightleftharpoons H_3O^+ + ClO_2^-$	1.1×10^{-2}	1.96
Chloroacetic acid	$ClCH_2COOH + H_2O \rightleftharpoons H_3O^+ + ClCH_2COO^-$	1.4×10^{-3}	2.85
Nitrous acid	$HNO_2 + H_2O \rightleftharpoons H_3O^+ + NO_2^-$	7.2×10^{-4}	3.14
Hydrofluoric acid	$HF + H_2O \rightleftharpoons H_3O^+ + F^-$	6.6×10^{-4}	3.18
Formic acid	$HCOOH + H_2O \rightleftharpoons H_3O^+ + HCOO^-$	1.8×10^{-4}	3.74
Benzoic acid	$C_6H_5COOH + H_2O \rightleftharpoons H_3O^+ + C_6H_5COO^-$	6.3×10^{-5}	4.20
Hydrazoic acid	$HN_3 + H_2O \rightleftharpoons H_3O^+ + N_3^-$	1.9×10^{-5}	4.72
Acetic acid	$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$	1.8×10^{-5}	4.74
Hypochlorous acid	$HOCl + H_2O \rightleftharpoons H_3O^+ + OCl^-$	2.9×10^{-8}	7.54
Hydrocyanic acid	$HCN + H_2O \rightleftharpoons H_3O^+ + CN^-$	6.2×10^{-10}	9.21
Phenol	$C_6H_5OH + H_2O \rightleftharpoons H_3O^+ + C_6H_5O^-$	1.0×10^{-10}	10.00
Hydrogen peroxide	$H_2O_2 + H_2O \rightleftharpoons H_3O^+ + HO_2^-$	1.8×10^{-12}	11.74
Base		K_b =	pK_b =
Diethylamine	$(CH_3CH_2)_2NH + H_2O \rightleftharpoons (CH_3CH_2)_2NH_2^+ + OH^-$	6.9×10^{-4}	3.16
Ethylamine	$CH_3CH_2NH_2 + H_2O \rightleftharpoons CH_3CH_2NH_3^+ + OH^-$	4.3×10^{-4}	3.37
Ammonia	$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$	1.8×10^{-5}	4.74
Hydroxylamine	$HONH_2 + H_2O \rightleftharpoons HONH_3^+ + OH^-$	9.1×10^{-9}	8.04
Pyridine	$C_5H_5N + H_2O \rightleftharpoons C_5H_5NH^+ + OH^-$	1.5×10^{-9}	8.82
Aniline	$C_6H_5NH_2 + H_2O \rightleftharpoons C_6H_5NH_3^+ + OH^-$	7.4×10^{-10}	9.13

Notice that several of the weak acids listed in Table 16.4 contain the group as part of the molecule. This grouping of atoms is called a carboxyl group and is a common feature of many organic acids, including such biologically important acids as lactic acid and all the amino acids, including glycine. Organic acids are also called carboxylic acids. The H atom of the carboxyl group is removed as a proton when a carboxylic acid reacts with a base.

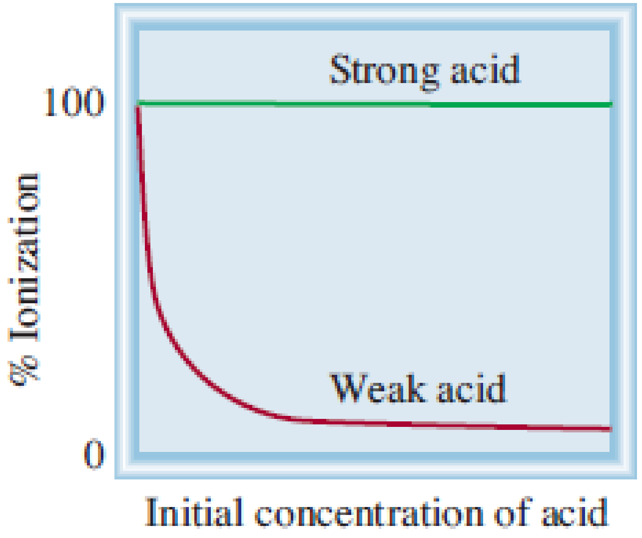
The weak bases listed in Table 16.4 all contain an N atom. Not all weak bases contain an N atom, yet so many of them do that it worth noting the following points. For these weak bases, it is the N atom that is protonated when the base reacts with a Brønsted–Lowry acid. The protonation of the N atom is illustrated below for the ionization of CH_3NH_2 in water.



Percent Ionization

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

$$\text{percent ionization} = \frac{\text{ionized acid concentration at equilibrium}}{\text{initial concentration of acid}} \times 100\% \qquad (15.11)$$

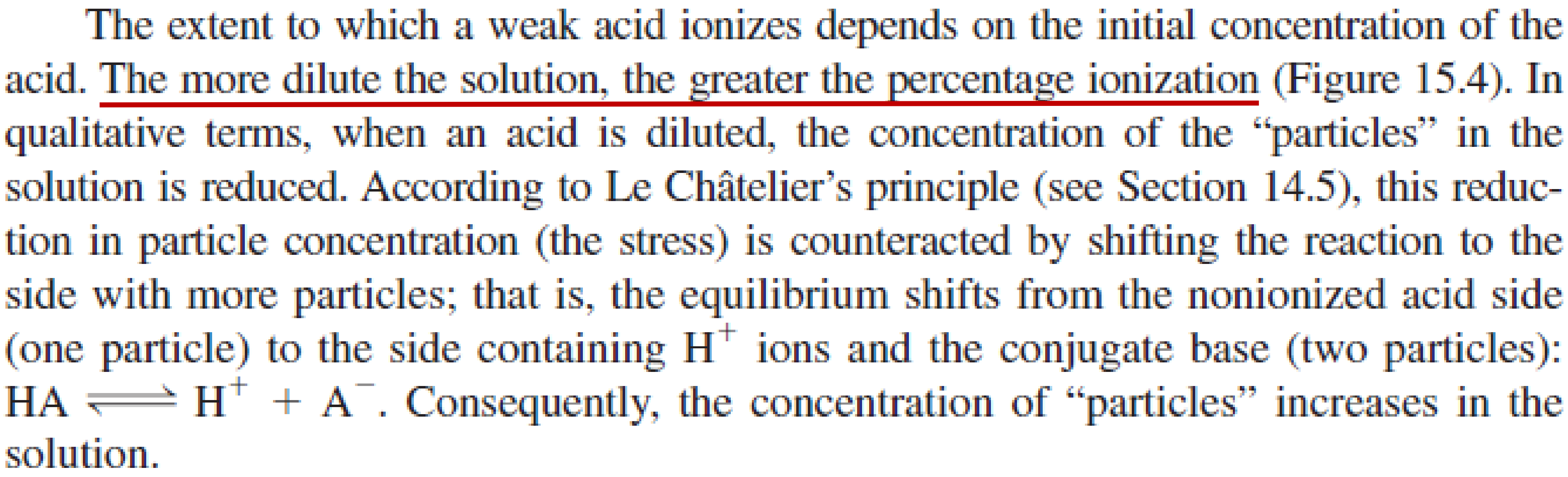


The stronger the acid, the greater the percent ionization. For a monoprotic acid HA, the concentration of the acid that undergoes ionization is equal to the concentration of the H^+ ions or the concentration of the A^- ions at equilibrium. Therefore, we can write the percent ionization as

$$\text{percent ionization} = \frac{[H^+]}{[HA]_0} \times 100\%$$

where $[H^+]$ is the concentration at equilibrium and $[HA]_0$ is the initial concentration.

For a weak acid or a weak base, the degree of ionization increases with increasing dilution.



The extent to which a weak acid ionizes depends on the initial concentration of the acid. The more dilute the solution, the greater the percentage ionization (Figure 15.4). In qualitative terms, when an acid is diluted, the concentration of the "particles" in the solution is reduced. According to Le Châtelier's principle (see Section 14.5), this reduction in particle concentration (the stress) is counteracted by shifting the reaction to the side with more particles; that is, the equilibrium shifts from the nonionized acid side (one particle) to the side containing H^+ ions and the conjugate base (two particles): $HA \rightleftharpoons H^+ + A^-$. Consequently, the concentration of "particles" increases in the solution.

EXAMPLE 16-3 Calculating Percent Ionization in an Aqueous Solution of an Acid

Calculate the equilibrium concentration and the percent ionization of HA in 1.00 M HA(aq) at 25 °C, assuming K_a is equal to 1.00×10^{-5}.

(b) In this case, $K_a \ll 1$. The following equilibrium summary is appropriate.

	$HA(aq)$	+	$H_2O(l)$	$\rightleftharpoons$	$A^-(aq)$	+	$H_3O^+(aq)$
initial concns:	1.00 M						
changes:	$-x$ M				$+x$ M		$+x$ M
equil concns:	$(1.00 - x)$ M				x M		x M

Because K_a is small, we expect a very small amount of the HA to react. In others, we expect x to be much less than 1. By assuming $x \ll 1$, we obtain

$$K_a = \frac{[A^-][H_3O^+]}{[HA]} \approx \frac{(x)(x)}{1.00} = \frac{x^2}{1.00} \quad \text{and } x = \sqrt{1.00 \times K_a} = 3.16 \times 10^{-3}$$

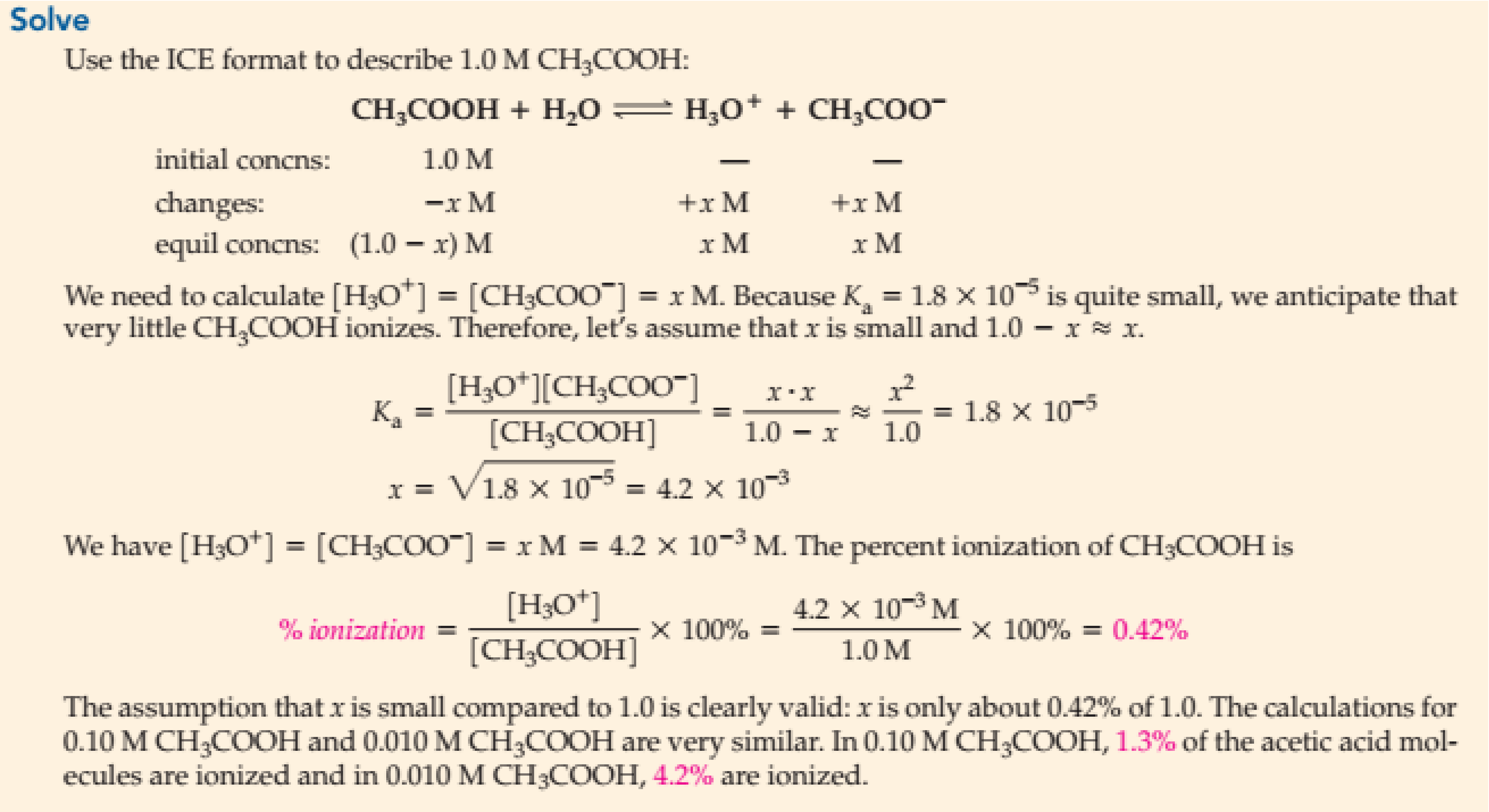
Therefore: $[HA] = (1.00 - 0.00316)\ \text{M} = 1.00\ \text{M}$

$$\text{percent ionization} = \frac{3.16 \times 10^{-3}\ \text{M}}{1.00\ \text{M}} \times 100\% = 0.316\%$$

PRACTICE EXAMPLE A: For HNO_3, K_a has a value of about 20 at 25 °C. What is the degree of ionization of HNO_3 in 0.010 M $HNO_3(aq)$ at 25 °C?

EXAMPLE 16-4 Determining Percent Ionization as a Function of Initial Concentration

What is the percent ionization of acetic acid, CH_3COOH, in 1.0 M, 0.10 M, and 0.010 M CH_3COOH?



Solve

Use the ICE format to describe 1.0 M CH_3COOH:

$$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$$

initial concns:	1.0 M	—	—
changes:	$-x$ M	$+x$ M	$+x$ M
equil concns:	$(1.0 - x)$ M	x M	x M

We need to calculate $[H_3O^+] = [CH_3COO^-] = x$ M. Because $K_a = 1.8 \times 10^{-5}$ is quite small, we anticipate that very little CH_3COOH ionizes. Therefore, let's assume that x is small and $1.0 - x \approx x$.

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = \frac{x \cdot x}{1.0 - x} \approx \frac{x^2}{1.0} = 1.8 \times 10^{-5}$$

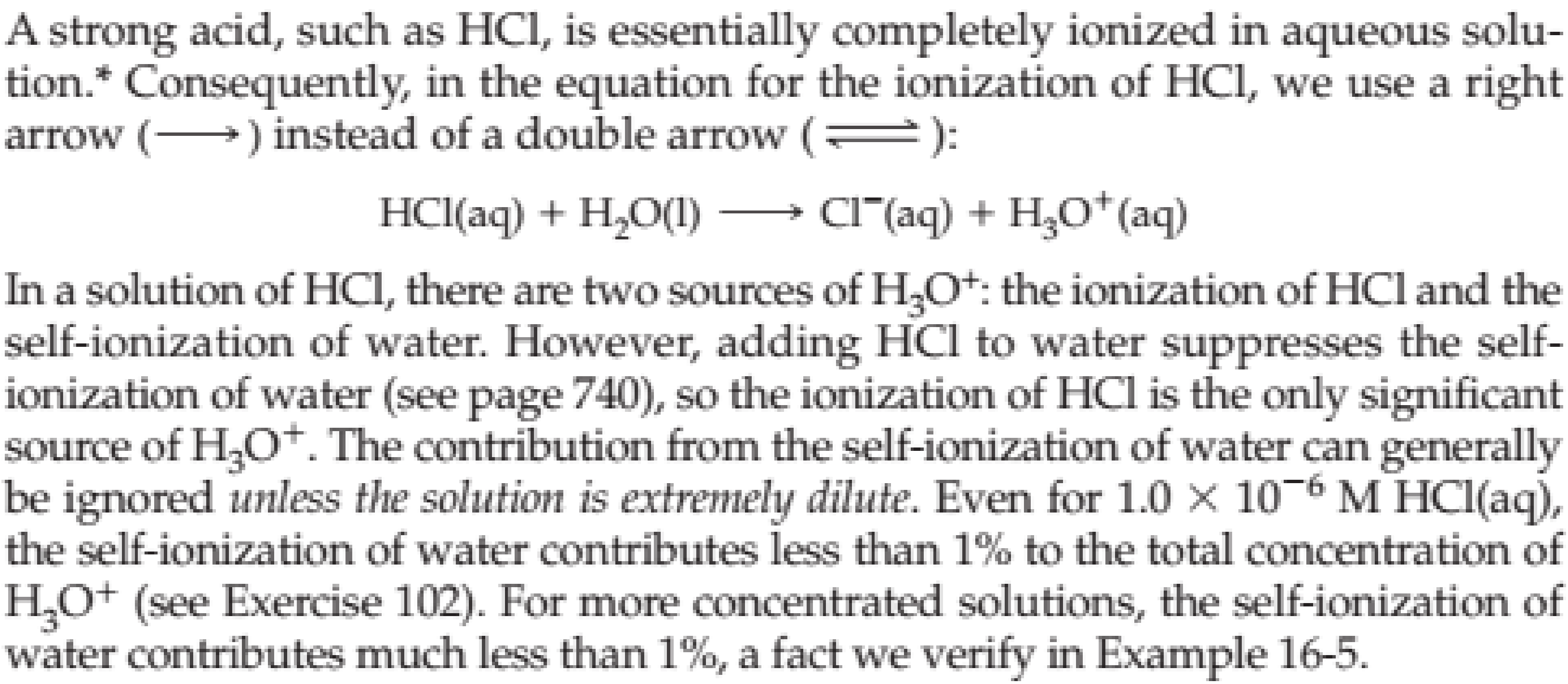
$$x = \sqrt{1.8 \times 10^{-5}} = 4.2 \times 10^{-3}$$

We have $[H_3O^+] = [CH_3COO^-] = x \text{ M} = 4.2 \times 10^{-3}$ M. The percent ionization of CH_3COOH is

$$\textit{\% ionization} = \frac{[H_3O^+]}{[CH_3COOH]} \times 100\% = \frac{4.2 \times 10^{-3}\text{ M}}{1.0\text{ M}} \times 100\% = 0.42\%$$

The assumption that x is small compared to 1.0 is clearly valid: x is only about 0.42% of 1.0. The calculations for 0.10 M CH_3COOH and 0.010 M CH_3COOH are very similar. In 0.10 M CH_3COOH, 1.3% of the acetic acid molecules are ionized and in 0.010 M CH_3COOH, 4.2% are ionized.

Strong Acids and Strong Bases



A strong acid, such as HCl, is essentially completely ionized in aqueous solution.* Consequently, in the equation for the ionization of HCl, we use a right arrow ($\longrightarrow$) instead of a double arrow ($\rightleftharpoons$):

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

In a solution of HCl, there are two sources of H_3O^+: the ionization of HCl and the self-ionization of water. However, adding HCl to water suppresses the self-ionization of water (see page 740), so the ionization of HCl is the only significant source of H_3O^+. The contribution from the self-ionization of water can generally be ignored *unless the solution is extremely dilute*. Even for 1.0×10^{-6} M HCl(aq), the self-ionization of water contributes less than 1% to the total concentration of H_3O^+ (see Exercise 102). For more concentrated solutions, the self-ionization of water contributes much less than 1%, a fact we verify in Example 16-5.

EXAMPLE 16-5 Calculating Ion Concentrations in an Aqueous Solution of a Strong Acid

Calculate $[H_3O^+]$, $[Cl^-]$, and $[OH^-]$ in 0.015 M HCl(aq).

Solve

The ionization of HCl is represented by the following equation, the right arrow ($\longrightarrow$) emphasizing that the reaction goes essentially to completion.

$$\mathrm{HCl(aq) + H_2O(l) \longrightarrow Cl^-(aq) + H_3O^+(aq)}$$

Therefore,

$$[\mathrm{H_3O^+}] = 0.015\ \mathrm{M}$$

Because one $\mathrm{Cl^-}$ ion is produced for every $\mathrm{H_3O^+}$ ion,

$$[\mathrm{Cl^-}] = [\mathrm{H_3O^+}] = 0.015\ \mathrm{M}$$

To calculate $[\mathrm{OH^-}]$, we must use the following facts.

1. All the $\mathrm{OH^-}$ is derived from the self-ionization of water, by reaction (16.3).
2. $[\mathrm{OH^-}]$ and $[\mathrm{H_3O^+}]$ must have values consistent with K_w for water.

$$K_w = [\mathrm{H_3O^+}][\mathrm{OH^-}] = 1.0 \times 10^{-14}$$

So we have

$$[\mathrm{OH^-}] = \frac{1.0 \times 10^{-14}}{1.5 \times 10^{-2}} = 6.7 \times 10^{-13}\ \mathrm{M}$$

EXAMPLE 16-6 Calculating the pH of an Aqueous Solution of a Strong Base

Calcium hydroxide (slaked lime), $Ca(OH)_2$, is the cheapest strong base available. It is generally used for industrial operations in which a high concentration of OH^- is not required. $Ca(OH)_2(s)$ is soluble in water only to the extent of 0.16 g $Ca(OH)_2$/100.0 mL solution at 25 °C. What is the pH of saturated $Ca(OH)_2(aq)$ at 25 °C?

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Analyze

Because the volume of solution is not specified, let's assume it is 100.0 mL = 0.1000 L. The resulting solution will be basic, so we should focus on the hydroxide ion. To solve this problem, we first calculate the molarity of the solution, and then determine the concentration of hydroxide ion in this solution. Finally, we calculate pOH and then pH.

Solve

Express the solubility of $Ca(OH)_2$ on a molar basis.

$$\text{molarity} = \frac{0.16\ \text{g Ca(OH)}_2 \times \dfrac{1\ \text{mol Ca(OH)}_2}{74.1\ \text{g Ca(OH)}_2}}{0.1000\ \text{L}} = 0.022\ \text{M Ca(OH)}_2$$

Relate the molarity of OH^- to the molarity of $Ca(OH)_2$.

$$[\text{OH}^-] = \frac{0.022\ \text{mol Ca(OH)}_2}{1\ \text{L}} \times \frac{2\ \text{mol OH}^-}{1\ \text{mol Ca(OH)}_2} = 0.044\ \text{M}$$

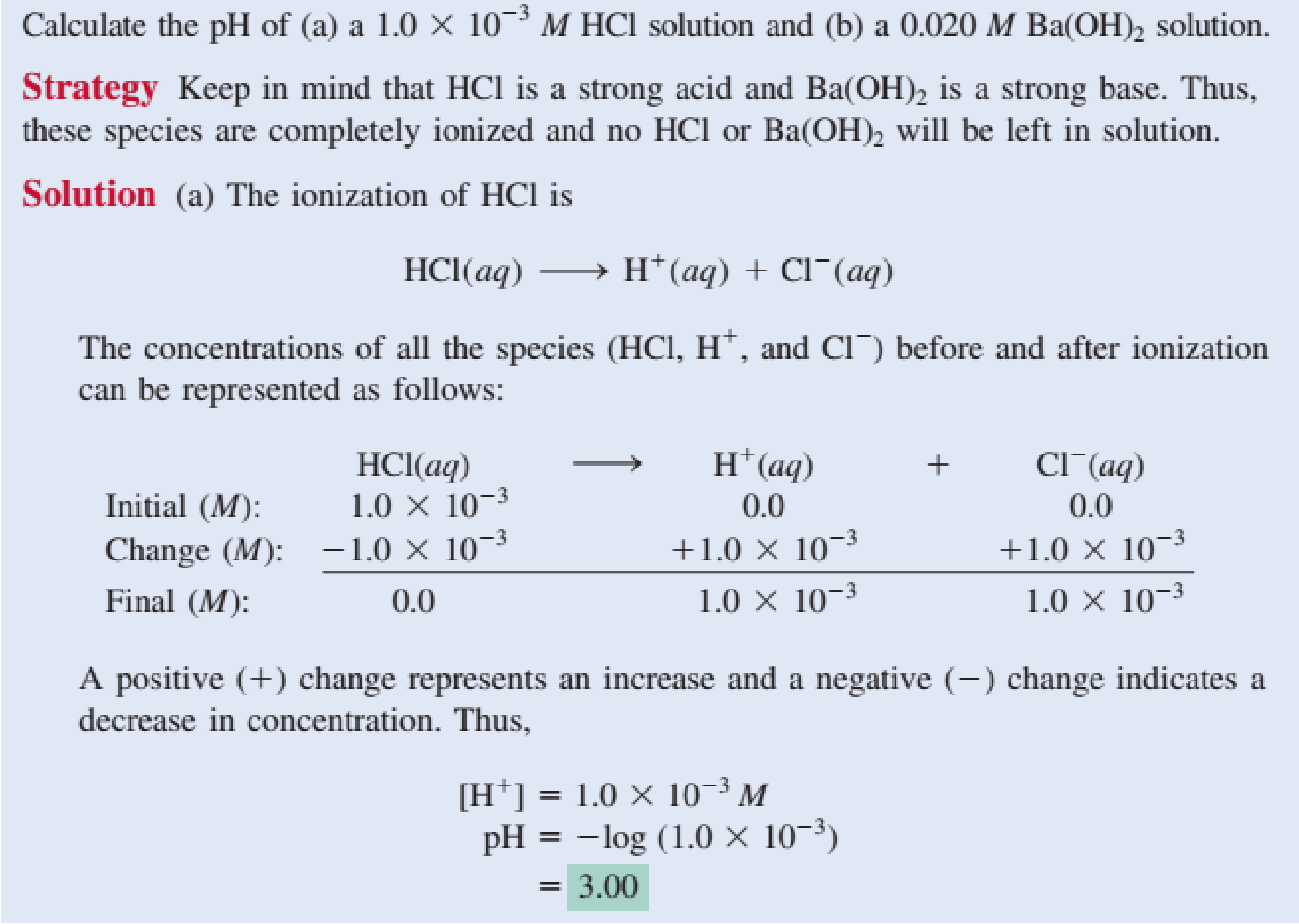
Calculate the pOH and, from it, the pH.

$$\text{pOH} = -\log[\text{OH}^-] = -\log 0.044 = 1.36$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 1.36 = 12.64$$

EXAMPLE 15.6

Calculate the pH of (a) a 1.0×10^{-3} M HCl solution and (b) a 0.020 M $Ba(OH)_2$ solution.



Calculate the pH of (a) a 1.0×10^{-3} *M* HCl solution and (b) a 0.020 *M* $Ba(OH)_2$ solution.

Strategy Keep in mind that HCl is a strong acid and $Ba(OH)_2$ is a strong base. Thus, these species are completely ionized and no HCl or $Ba(OH)_2$ will be left in solution.

Solution (a) The ionization of HCl is

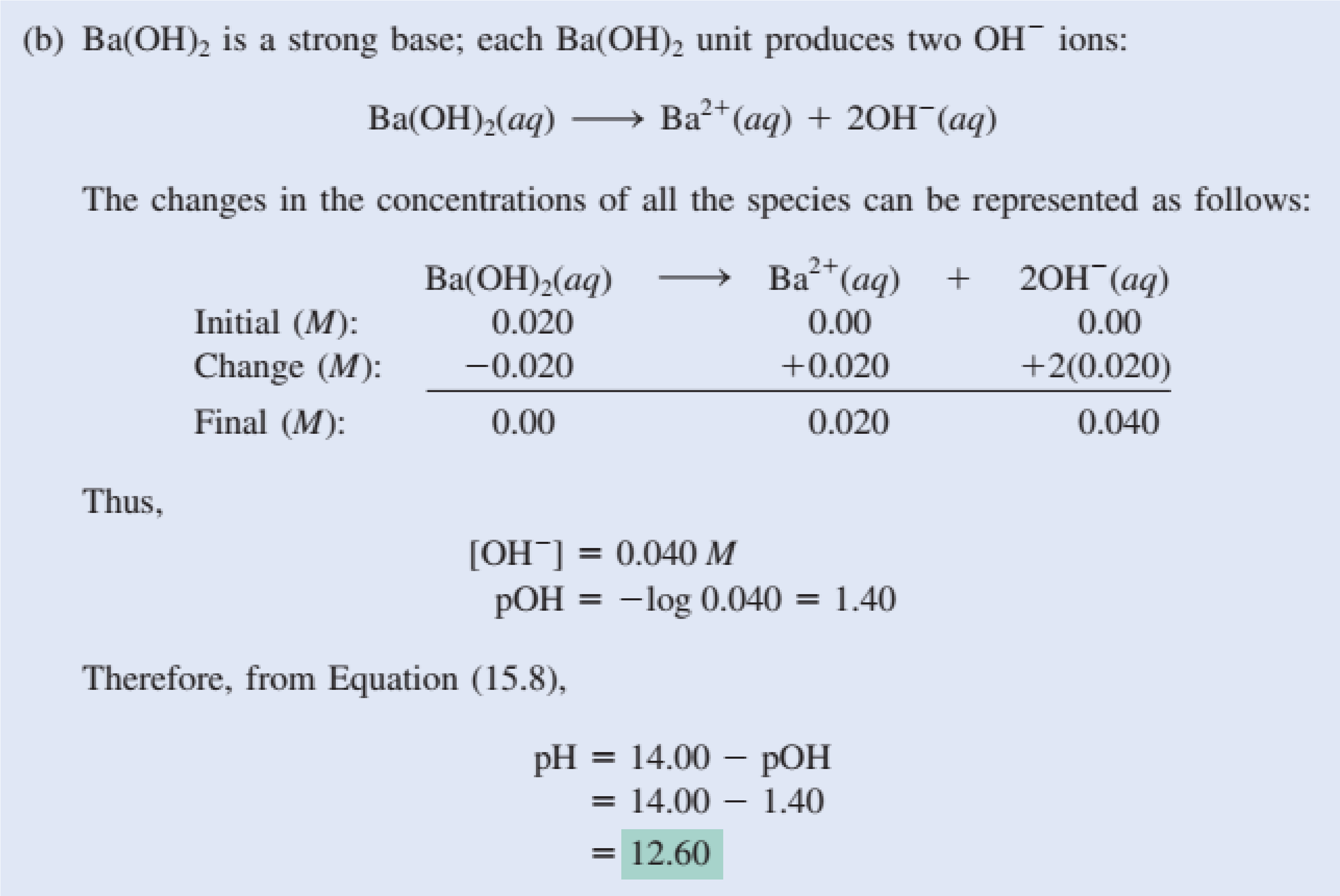
$$HCl(aq) \longrightarrow H^+(aq) + Cl^-(aq)$$

The concentrations of all the species (HCl, H^+, and Cl^-) before and after ionization can be represented as follows:

	$HCl(aq)$	$\longrightarrow$	$H^+(aq)$	$+$	$Cl^-(aq)$
Initial (*M*):	1.0×10^{-3}		0.0		0.0
Change (*M*):	-1.0×10^{-3}		$+1.0 \times 10^{-3}$		$+1.0 \times 10^{-3}$
Final (*M*):	0.0		1.0×10^{-3}		1.0×10^{-3}

A positive (+) change represents an increase and a negative (−) change indicates a decrease in concentration. Thus,

$$[H^+] = 1.0 \times 10^{-3}\ M$$
$$pH = -\log(1.0 \times 10^{-3})$$
$$= 3.00$$



(b) $Ba(OH)_2$ is a strong base; each $Ba(OH)_2$ unit produces two OH^- ions:

$$Ba(OH)_2(aq) \longrightarrow Ba^{2+}(aq) + 2OH^-(aq)$$

The changes in the concentrations of all the species can be represented as follows:

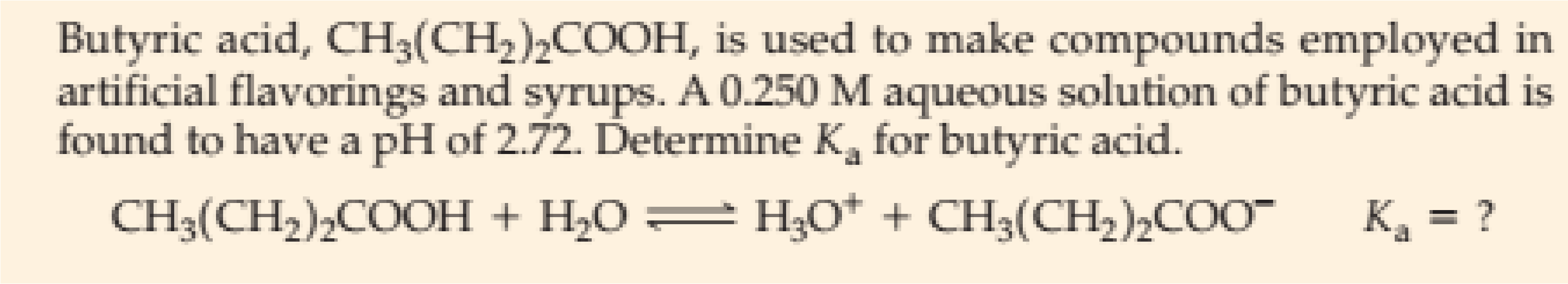
	$Ba(OH)_2(aq)$	$\longrightarrow$	$Ba^{2+}(aq)$	$+$	$2OH^-(aq)$
Initial (*M*):	0.020		0.00		0.00
Change (*M*):	−0.020		+0.020		+2(0.020)
Final (*M*):	0.00		0.020		0.040

Thus,

$$[OH^-] = 0.040\ M$$
$$pOH = -\log 0.040 = 1.40$$

Therefore, from Equation (15.8),

$$\begin{aligned} pH &= 14.00 - pOH \\ &= 14.00 - 1.40 \\ &= 12.60 \end{aligned}$$



Butyric acid, $CH_3(CH_2)_2COOH$, is used to make compounds employed in artificial flavorings and syrups. A 0.250 M aqueous solution of butyric acid is found to have a pH of 2.72. Determine K_a for butyric acid.

$$CH_3(CH_2)_2COOH + H_2O \rightleftharpoons H_3O^+ + CH_3(CH_2)_2COO^- \qquad K_a = ?$$

Solve

$$CH_3(CH_2)_2COOH + H_2O \rightleftharpoons H_3O^+ + CH_3(CH_2)_2COO^-$$

	$CH_3(CH_2)_2COOH$	H_3O^+	$CH_3(CH_2)_2COO^-$
initial concns:	0.250 M	—	—
changes:	$-x$ M	$+x$ M	$+x$ M
equil concns:	$(0.250 - x)$ M	x M	x M

But x M is a known quantity. It is the $[H_3O^+]$ in solution, which we can determine from the pH.

$$\log[H_3O^+] = -pH = -2.72$$
$$[H_3O^+] = 10^{-2.72}\text{ M} = 1.9 \times 10^{-3}\text{ M} = x\text{ M}$$

Now we can solve the following expression for K_a, by substituting in the value $x = 1.9 \times 10^{-3}$.

$$K_a = \frac{[H_3O^+][CH_3(CH_2)_2COO^-]}{[CH_3(CH_2)_2COOH]} = \frac{x \cdot x}{0.250 - x}$$
$$= \frac{(1.9 \times 10^{-3})(1.9 \times 10^{-3})}{0.250 - (1.9 \times 10^{-3})} = 1.5 \times 10^{-5}$$

The key to solving these equilibrium problems is to be able to imagine what is going on. Here are some questions to ask yourself.

- Which are the principal species in solution?
- What are the chemical reactions that produce them?
- Can some reactions (for example, the self-ionization of water) be ignored?
- Can you make any assumptions that allow you to simplify the equilibrium calculations?
- What is a reasonable answer to the problem? For instance, should the final solution be acidic or basic

EXAMPLE 16-9 Calculating the pH of a Solution of a Weak Base

What is the pH of a solution that is 0.00250 M $CH_3NH_2(aq)$? For methylamine, $K_b = 4.2 \times 10^{-4}$.

Solve

	CH_3NH_2	$+$	H_2O	$\rightleftharpoons$	$CH_3NH_3^+$	$+$	OH^-
initial concns:	0.00250 M				—		—
changes:	$-x$ M				$+x$ M		$+x$ M
equil concns:	$(0.00250 - x)$ M				x M		x M

$$K_b = \frac{[CH_3NH_3^+][OH^-]}{[CH_3NH_2]} = \frac{x \cdot x}{0.00250 - x} = 4.2 \times 10^{-4}$$

Now let's assume that x is very much less than 0.00250 and that $0.00250 - x \approx 0.00250$.

$$\frac{x^2}{0.00250} = 4.2 \times 10^{-4} \qquad x^2 = 1.1 \times 10^{-6} \qquad [OH^-] = x\,\text{M} = 1.0 \times 10^{-3}\,\text{M}$$

The value of x is nearly half as large as 0.00250—too large to ignore. This means using the *quadratic* formula.

$$\frac{x^2}{0.00250 - x} = 4.2 \times 10^{-4}$$

$$x^2 + (4.2 \times 10^{-4}x) - (1.1 \times 10^{-6}) = 0$$

$$x = \frac{(-4.2 \times 10^{-4}) \pm \sqrt{(4.2 \times 10^{-4})^2 + 4 \times 1.1 \times 10^{-6}}}{2}$$

The expression above provides two values of x, one positive and one negative. The negative value can be ignored because it yields a nonphysical result—a negative value for $[OH^-]$.

$$[OH^-] = x\,\text{M} = \frac{(-4.2 \times 10^{-4}) + (2.1 \times 10^{-3})}{2}\,\text{M} = 8.4 \times 10^{-4}\,\text{M}$$

$$\text{pOH} = -\log[OH^-] = -\log(8.4 \times 10^{-4}) = 3.08$$

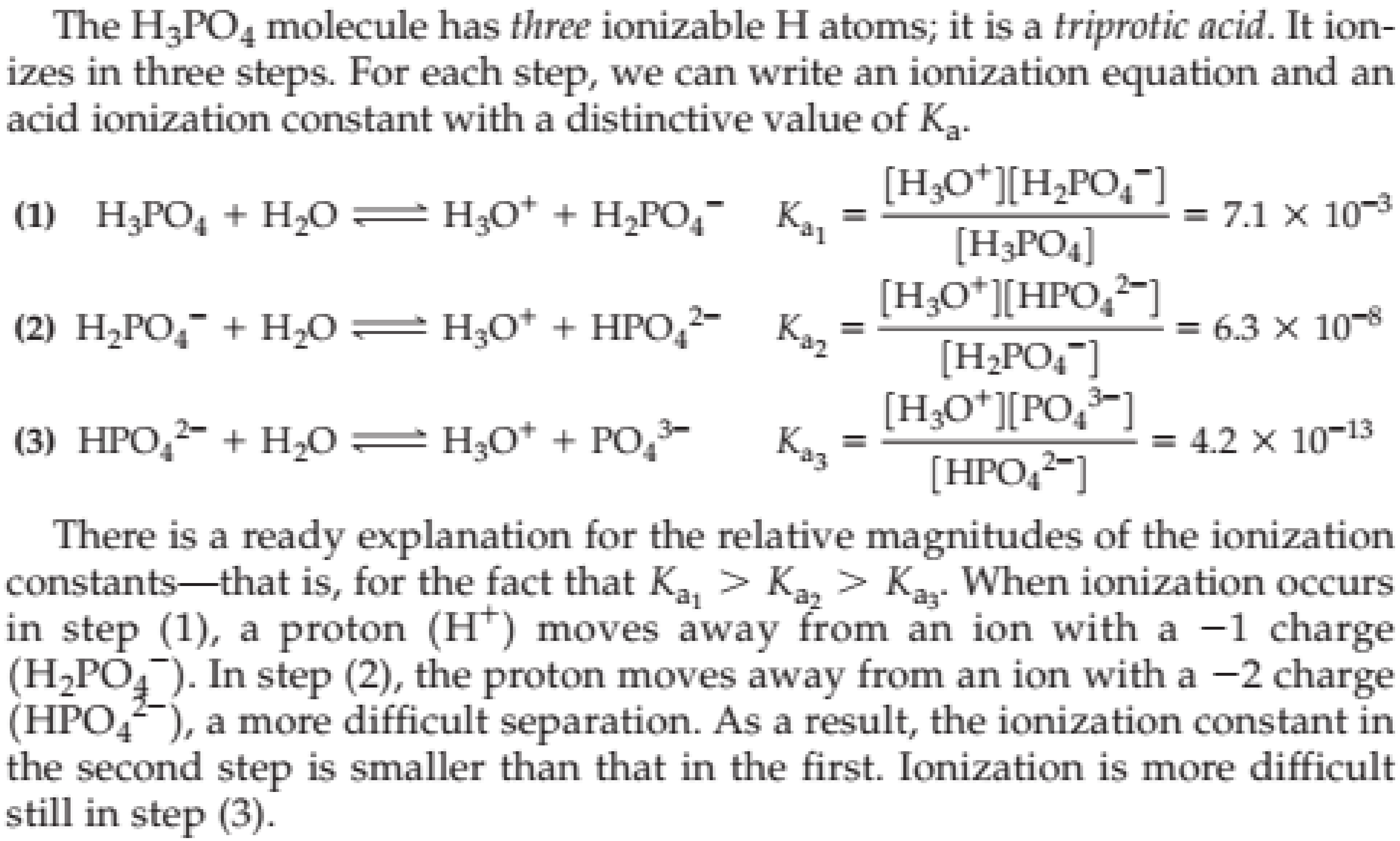
$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 3.08 = 10.92$$

PRACTICE EXAMPLE A: What is the pH of 0.015 M $CH_2FCOOH(aq)$?

$$CH_2FCOOH + H_2O \rightleftharpoons H_3O^+ + CH_2FCOO^- \qquad K_a = 2.6 \times 10^{-3}$$

Polyprotic Acids

All the acids listed in Table 16.4 are weak monoprotic acids, meaning that their molecules have only one ionizable H atom, even though several of these acids contain more than one H atom. But some acids have more than one ionizable H atom per molecule. These are polyprotic acids. Table 16.5 lists ionization constants for several polyprotic acids.



The H_3PO_4 molecule has *three* ionizable H atoms; it is a *triprotic acid*. It ionizes in three steps. For each step, we can write an ionization equation and an acid ionization constant with a distinctive value of K_a.

$$\textbf{(1)}\quad H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^- \qquad K_{a_1} = \frac{[H_3O^+][H_2PO_4^-]}{[H_3PO_4]} = 7.1 \times 10^{-3}$$

$$\textbf{(2)}\quad H_2PO_4^- + H_2O \rightleftharpoons H_3O^+ + HPO_4^{2-} \qquad K_{a_2} = \frac{[H_3O^+][HPO_4^{2-}]}{[H_2PO_4^-]} = 6.3 \times 10^{-8}$$

$$\textbf{(3)}\quad HPO_4^{2-} + H_2O \rightleftharpoons H_3O^+ + PO_4^{3-} \qquad K_{a_3} = \frac{[H_3O^+][PO_4^{3-}]}{[HPO_4^{2-}]} = 4.2 \times 10^{-13}$$

There is a ready explanation for the relative magnitudes of the ionization constants—that is, for the fact that $K_{a_1} > K_{a_2} > K_{a_3}$. When ionization occurs in step (1), a proton (H^+) moves away from an ion with a −1 charge ($H_2PO_4^-$). In step (2), the proton moves away from an ion with a −2 charge (HPO_4^{2-}), a more difficult separation. As a result, the ionization constant in the second step is smaller than that in the first. Ionization is more difficult still in step (3).

We can make three key statements about the ionization of phosphoric acid, as illustrated in Example 16-10.

1. K_{a_1} is so much larger than K_{a_2} and K_{a_3} that essentially all the H_3O^+ is produced in the first ionization step.
2. So little of the $H_2PO_4^-$ formed in the first ionization step ionizes any further that we can assume $[H_2PO_4^-] = [H_3O^+]$ in the solution.
3. $[HPO_4^{2-}] \approx K_{a_2}$, regardless of the molarity of the acid.*

Although statement (1) seems essential if statements (2) and (3) are to be valid, it is not as crucial as might first appear. Even for polyprotic acids whose K_a values do not differ greatly between successive ionizations, H_3O^+ is often still determined almost exclusively by the K_{a_1} expression, and statements (2) and (3) remain valid. As long as the polyprotic acid is weak in its first ionization step, the concentration of the anion produced in this step will be so much less than the molarity of the acid that additional $[H_3O^+]$ produced in the second ionization remains negligible.

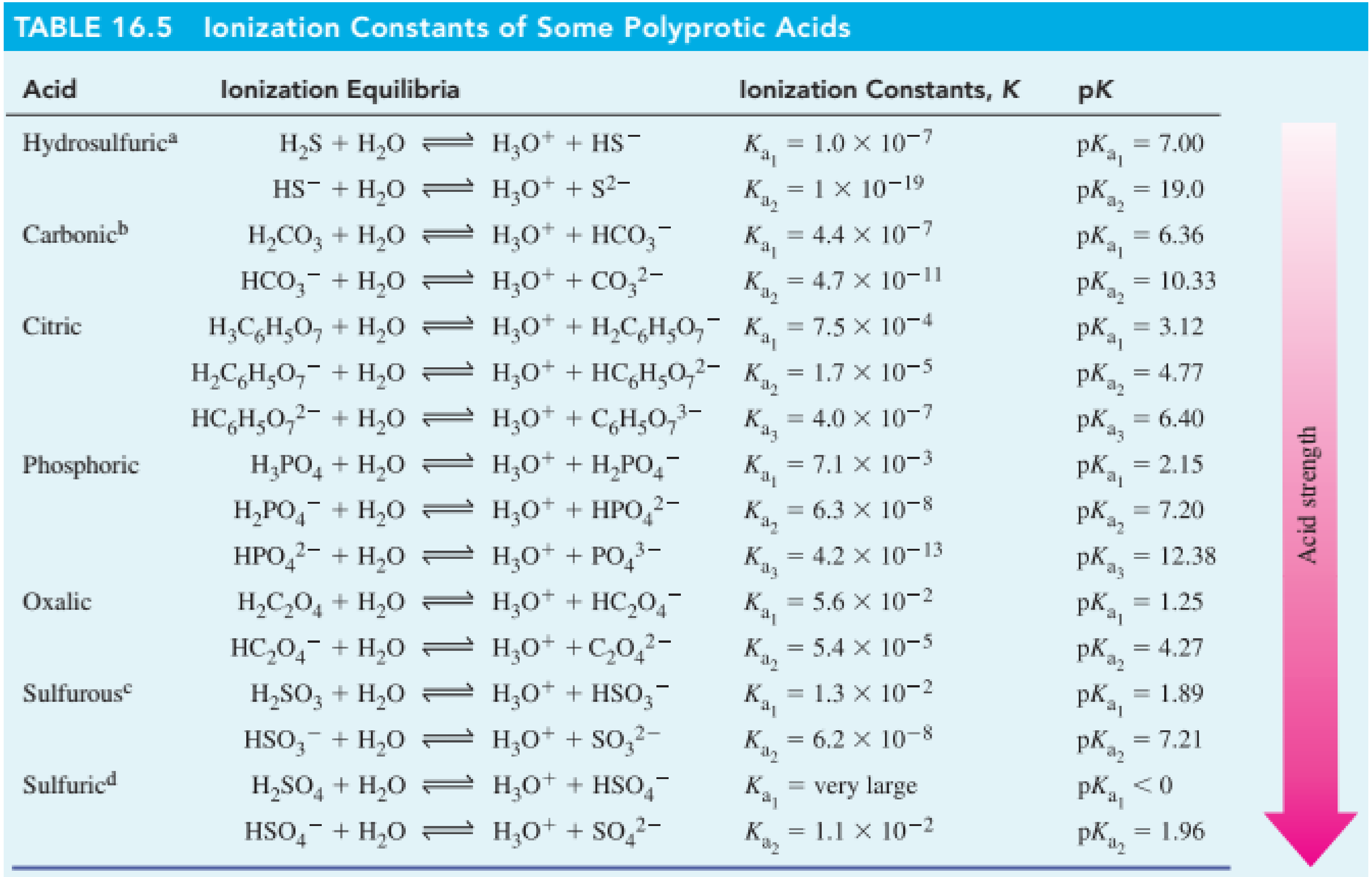


TABLE 16.5 Ionization Constants of Some Polyprotic Acids

Acid	Ionization Equilibria	Ionization Constants, *K*	pK
Hydrosulfuric[a]	$H_2S + H_2O \rightleftharpoons H_3O^+ + HS^-$	$K_{a_1} = 1.0 \times 10^{-7}$	$pK_{a_1} = 7.00$
	$HS^- + H_2O \rightleftharpoons H_3O^+ + S^{2-}$	$K_{a_2} = 1 \times 10^{-19}$	$pK_{a_2} = 19.0$
Carbonic[b]	$H_2CO_3 + H_2O \rightleftharpoons H_3O^+ + HCO_3^-$	$K_{a_1} = 4.4 \times 10^{-7}$	$pK_{a_1} = 6.36$
	$HCO_3^- + H_2O \rightleftharpoons H_3O^+ + CO_3^{2-}$	$K_{a_2} = 4.7 \times 10^{-11}$	$pK_{a_2} = 10.33$
Citric	$H_3C_6H_5O_7 + H_2O \rightleftharpoons H_3O^+ + H_2C_6H_5O_7^-$	$K_{a_1} = 7.5 \times 10^{-4}$	$pK_{a_1} = 3.12$
	$H_2C_6H_5O_7^- + H_2O \rightleftharpoons H_3O^+ + HC_6H_5O_7^{2-}$	$K_{a_2} = 1.7 \times 10^{-5}$	$pK_{a_2} = 4.77$
	$HC_6H_5O_7^{2-} + H_2O \rightleftharpoons H_3O^+ + C_6H_5O_7^{3-}$	$K_{a_3} = 4.0 \times 10^{-7}$	$pK_{a_3} = 6.40$
Phosphoric	$H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^-$	$K_{a_1} = 7.1 \times 10^{-3}$	$pK_{a_1} = 2.15$
	$H_2PO_4^- + H_2O \rightleftharpoons H_3O^+ + HPO_4^{2-}$	$K_{a_2} = 6.3 \times 10^{-8}$	$pK_{a_2} = 7.20$
	$HPO_4^{2-} + H_2O \rightleftharpoons H_3O^+ + PO_4^{3-}$	$K_{a_3} = 4.2 \times 10^{-13}$	$pK_{a_3} = 12.38$
Oxalic	$H_2C_2O_4 + H_2O \rightleftharpoons H_3O^+ + HC_2O_4^-$	$K_{a_1} = 5.6 \times 10^{-2}$	$pK_{a_1} = 1.25$
	$HC_2O_4^- + H_2O \rightleftharpoons H_3O^+ + C_2O_4^{2-}$	$K_{a_2} = 5.4 \times 10^{-5}$	$pK_{a_2} = 4.27$
Sulfurous[c]	$H_2SO_3 + H_2O \rightleftharpoons H_3O^+ + HSO_3^-$	$K_{a_1} = 1.3 \times 10^{-2}$	$pK_{a_1} = 1.89$
	$HSO_3^- + H_2O \rightleftharpoons H_3O^+ + SO_3^{2-}$	$K_{a_2} = 6.2 \times 10^{-8}$	$pK_{a_2} = 7.21$
Sulfuric[d]	$H_2SO_4 + H_2O \rightleftharpoons H_3O^+ + HSO_4^-$	K_{a_1} = very large	$pK_{a_1} < 0$
	$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-}$	$K_{a_2} = 1.1 \times 10^{-2}$	$pK_{a_2} = 1.96$

EXAMPLE 16-10 Calculating Ion Concentrations in a Polyprotic Acid Solution

For a 3.0 M H_3PO_4 solution, calculate **(a)** $[H_3O^+]$; **(b)** $[H_2PO_4^-]$; **(c)** $[HPO_4^{2-}]$; and **(d)** $[PO_4^{3-}]$.

(a) For the reasons discussed above, let's assume that all the H_3O^+ forms in the *first* ionization step. This is equivalent to thinking of H_3PO_4 as though it were a monoprotic acid, ionizing only in the first step.

$$\mathbf{H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^-}$$

	H_3PO_4	H_3O^+	$H_2PO_4^-$
initial concns:	3.0 M	—	—
changes:	$-x$ M	$+x$ M	$+x$ M
after first ionization:	$(3.0 - x)$ M	x M	x M

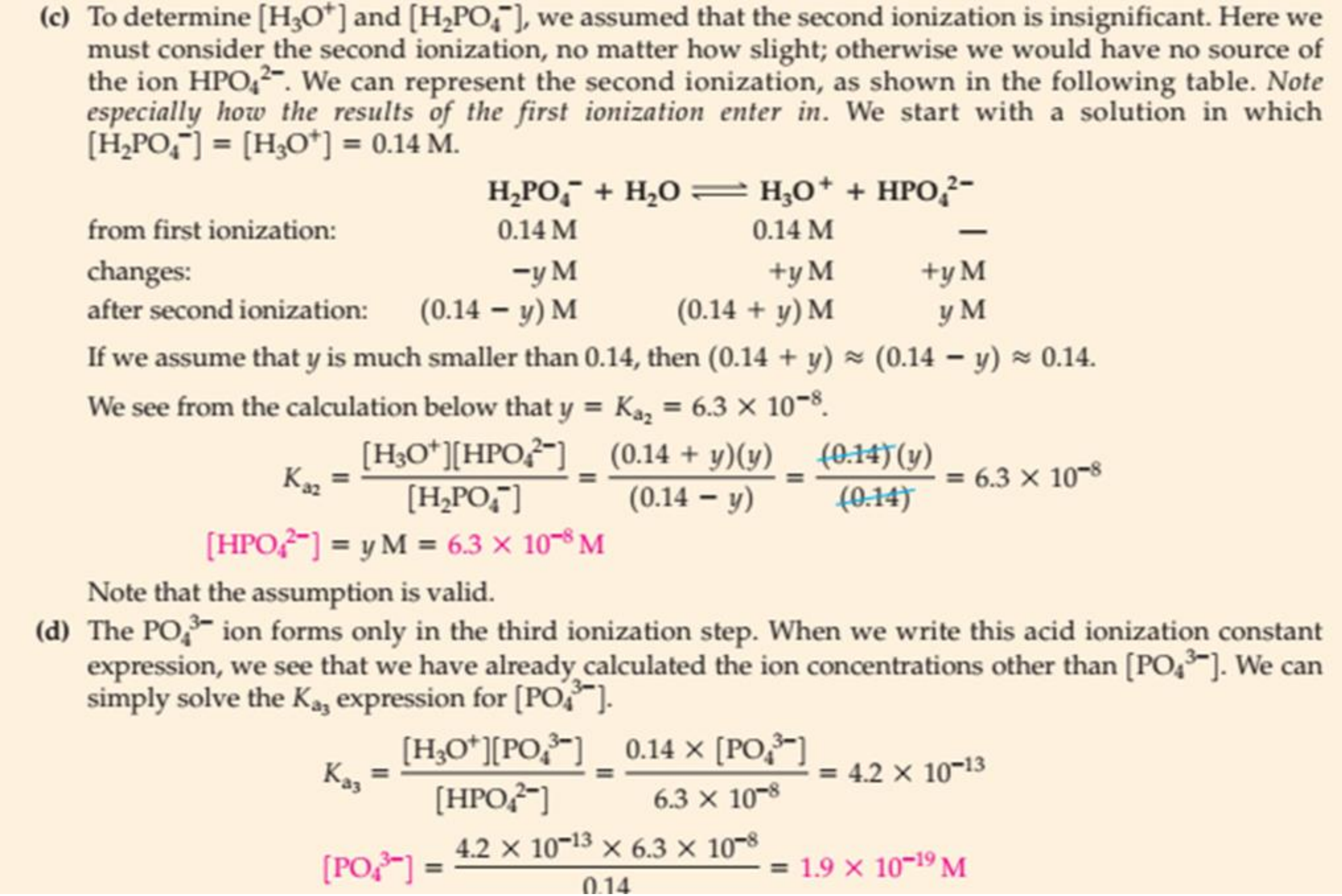
Following the usual assumption that x is much smaller than 3.0 and that $3.0 - x \approx 3.0$, we obtain

$$K_{a_1} = \frac{[H_3O^+][H_2PO_4^-]}{[H_3PO_4]} = \frac{x \cdot x}{(3.0 - x)} = \frac{x^2}{3.0} = 7.1 \times 10^{-3}$$

$$x^2 = 0.021 \qquad x = 0.14 \qquad [H_3O^+] = x\text{ M} = 0.14\text{ M}$$

In the assumption $3.0 - x \approx 3.0$, $x = 0.14$, which is 4.7% of 3.0. This is about the maximum error that can be tolerated for an acceptable assumption.

(b) From part (a), $x = [H_2PO_4^-] = [H_3O^+] = 0.14$ M.



(c) To determine $[H_3O^+]$ and $[H_2PO_4^-]$, we assumed that the second ionization is insignificant. Here we must consider the second ionization, no matter how slight; otherwise we would have no source of the ion HPO_4^{2-}. We can represent the second ionization, as shown in the following table. *Note especially how the results of the first ionization enter in.* We start with a solution in which $[H_2PO_4^-] = [H_3O^+] = 0.14$ M.

	$H_2PO_4^- + H_2O \rightleftharpoons$	$H_3O^+ +$	HPO_4^{2-}
from first ionization:	0.14 M	0.14 M	—
changes:	$-y$ M	$+y$ M	$+y$ M
after second ionization:	$(0.14 - y)$ M	$(0.14 + y)$ M	y M

If we assume that y is much smaller than 0.14, then $(0.14 + y) \approx (0.14 - y) \approx 0.14$.

We see from the calculation below that $y = K_{a_2} = 6.3 \times 10^{-8}$.

$$K_{a_2} = \frac{[H_3O^+][HPO_4^{2-}]}{[H_2PO_4^-]} = \frac{(0.14 + y)(y)}{(0.14 - y)} = \frac{\cancel{(0.14)}(y)}{\cancel{(0.14)}} = 6.3 \times 10^{-8}$$

$$[HPO_4^{2-}] = y\text{ M} = 6.3 \times 10^{-8}\text{ M}$$

Note that the assumption is valid.

(d) The PO_4^{3-} ion forms only in the third ionization step. When we write this acid ionization constant expression, we see that we have already calculated the ion concentrations other than $[PO_4^{3-}]$. We can simply solve the K_{a_3} expression for $[PO_4^{3-}]$.

$$K_{a_3} = \frac{[H_3O^+][PO_4^{3-}]}{[HPO_4^{2-}]} = \frac{0.14 \times [PO_4^{3-}]}{6.3 \times 10^{-8}} = 4.2 \times 10^{-13}$$

$$[PO_4^{3-}] = \frac{4.2 \times 10^{-13} \times 6.3 \times 10^{-8}}{0.14} = 1.9 \times 10^{-19}\text{ M}$$

PRACTICE EXAMPLE A: Malonic acid, $HOOCCH_2COOH$, is a diprotic acid used in the manufacture of barbiturates.

$$HOOCCH_2COOH + H_2O \rightleftharpoons H_3O^+ + HOOCCH_2COO^- \qquad K_{a_1} = 1.4 \times 10^{-3}$$

$$HOOCCH_2COO^- + H_2O \rightleftharpoons H_3O^+ + {}^-OOCCH_2COO^- \qquad K_{a_2} = 2.0 \times 10^{-6}$$

Calculate $[H_3O^+]$, $[HOOCCH_2COO^-]$, and $[{}^-OOCCH_2COO^-]$ in a 1.00 M solution of malonic acid.

A Somewhat Different Case: H_2SO_4

Sulfuric acid differs from most polyprotic acids in this important respect: It is a *strong* acid in its first ionization and a *weak* acid in its second. Ionization is complete in the first step, which means that in most $H_2SO_4(aq)$ solutions, $[H_2SO_4] \approx 0$ M. Thus, if a solution is 0.50 M H_2SO_4, we can treat it as though it were 0.50 M H_3O^+ and 0.50 M HSO_4^- initially. Then we can determine the extent to which ionization of HSO_4^- produces additional H_3O^+ and SO_4^{2-}, as illustrated in Example 16-11.

EXAMPLE 16-11 Calculating Ion Concentrations in Sulfuric Acid Solutions: Strong Acid Ionization Followed by Weak Acid Ionization

Calculate $[H_3O^+]$, $[HSO_4^-]$, and $[SO_4^{2-}]$ in 0.50 M H_2SO_4.

Analyze

We will modify the approach we used in Example 16-10 to incorporate the fact that for H_2SO_4 the first ionization step goes to completion.

Solve

	H_2SO_4	+	H_2O	$\longrightarrow$	H_3O^+	+	HSO_4^-
initial concn:	0.50 M				—		—
changes:	−0.50 M				+0.50 M		+0.50 M
after first ionization:	≈ 0				0.50 M		0.50 M

	HSO_4^-	+	H_2O	$\rightleftharpoons$	H_3O^+	+	SO_4^{2-}
from first ionization:	0.50 M				0.50 M		—
changes:	$-x$ M				$+x$ M		$+x$ M
after second ionization:	$(0.50 - x)$ M				$(0.50 + x)$ M		x M

We need to deal only with the ionization constant expression for K_{a_2}. If we assume that x is much smaller than 0.50, then $(0.50 + x) \approx (0.50 - x) \approx 0.50$ and

$$K_{a_2} = \frac{[H_3O^+][SO_4^{2-}]}{[HSO_4^-]} = \frac{(0.50 + x)\cdot x}{(0.50 - x)} = \frac{\cancel{0.50}\cdot x}{\cancel{0.50}} = 1.1 \times 10^{-2}$$

Our results, then, are

$[H_3O^+] = 0.50 + x = 0.51$ M; $[HSO_4^-] = 0.50 - x = 0.49$ M

$[SO_4^{2-}] = x = K_{a_2} = 0.011$ M

The Relationship Between the Ionization Constants of Acids and Their Conjugate Bases

An important relationship between the acid ionization constant and the ionization constant of its conjugate base can be derived as follows, using acetic acid as an example:

$$\mathrm{CH_3COOH}(aq) \rightleftharpoons \mathrm{H^+}(aq) + \mathrm{CH_3COO^-}(aq)$$

$$K_a = \frac{[\mathrm{H^+}][\mathrm{CH_3COO^-}]}{[\mathrm{CH_3COOH}]}$$

The conjugate base, $\mathrm{CH_3COO^-}$, supplied by a sodium acetate ($\mathrm{CH_3COONa}$) solution, reacts with water according to the equation

$$\mathrm{CH_3COO^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{CH_3COOH}(aq) + \mathrm{OH^-}(aq)$$

and we can write the base ionization constant as

$$K_b = \frac{[\mathrm{CH_3COOH}][\mathrm{OH^-}]}{[\mathrm{CH_3COO^-}]}$$

The product of these two ionization constants is given by

$$\begin{aligned} K_aK_b &= \frac{[\mathrm{H^+}][\cancel{\mathrm{CH_3COO^-}}]}{[\cancel{\mathrm{CH_3COOH}}]} \times \frac{[\cancel{\mathrm{CH_3COOH}}][\mathrm{OH^-}]}{[\cancel{\mathrm{CH_3COO^-}}]} \\ &= [\mathrm{H^+}][\mathrm{OH^-}] \\ &= K_w \end{aligned}$$

This result may seem strange at first, but if we add the two equations we see that the sum is simply the autoionization of water.

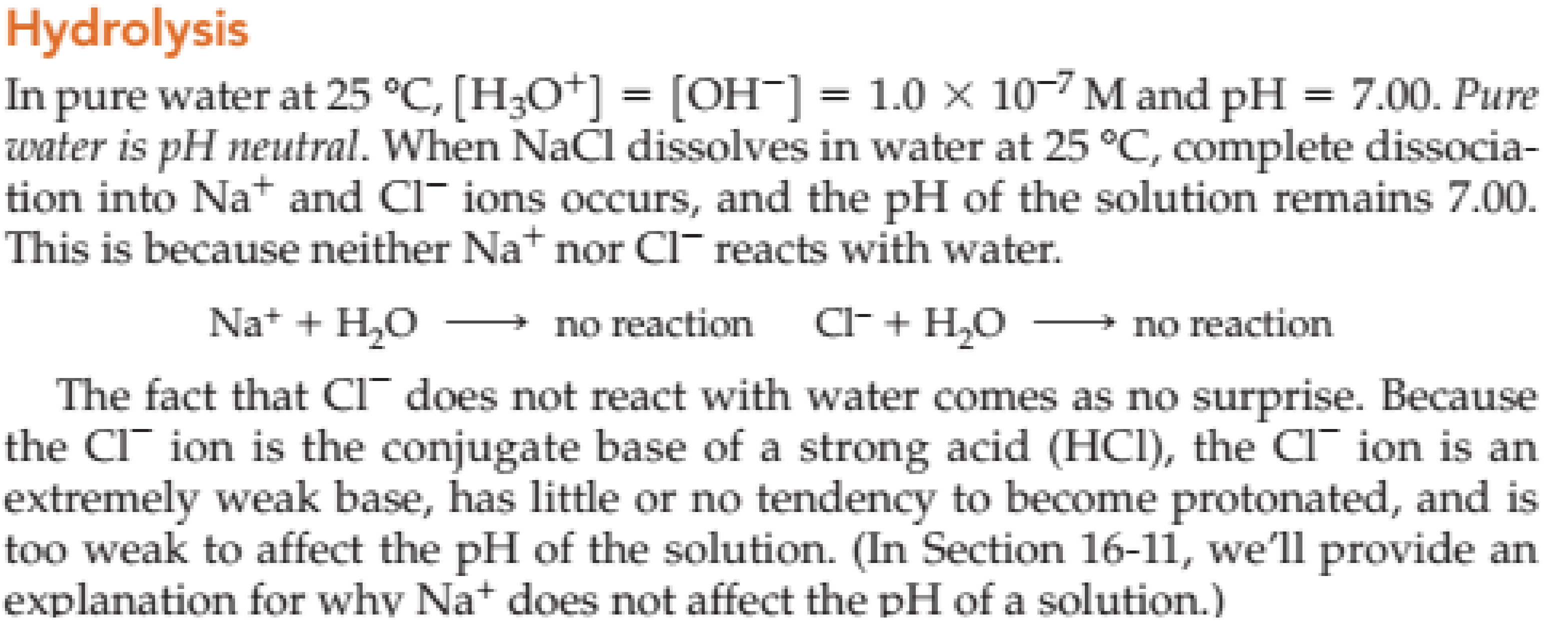
$$\begin{array}{lrcll}
(1) & CH_3COOH(aq) & \rightleftharpoons & H^+(aq) + CH_3COO^-(aq) & K_a \\
(2) & CH_3COO^-(aq) + H_2O(l) & \rightleftharpoons & CH_3COOH(aq) + OH^-(aq) & K_b \\
\cline{2-4}
(3) & H_2O(l) & \rightleftharpoons & H^+(aq) + OH^-(aq) & K_w
\end{array}$$

This example illustrates one of the rules for chemical equilibria: When two reactions are added to give a third reaction, the equilibrium constant for the third reaction is the product of the equilibrium constants for the two added reactions (see Section 14.2). Thus, for any conjugate acid-base pair it is always true that

$$K_aK_b = K_w \tag{15.12}$$

Expressing Equation (15.12) as

$$K_a = \frac{K_w}{K_b} \qquad K_b = \frac{K_w}{K_a}$$



Hydrolysis

In pure water at 25 °C, $[H_3O^+] = [OH^-] = 1.0 \times 10^{-7}$ M and pH = 7.00. *Pure water is pH neutral*. When NaCl dissolves in water at 25 °C, complete dissociation into Na^+ and Cl^- ions occurs, and the pH of the solution remains 7.00. This is because neither Na^+ nor Cl^- reacts with water.

$$Na^+ + H_2O \longrightarrow \text{no reaction} \qquad Cl^- + H_2O \longrightarrow \text{no reaction}$$

The fact that Cl^- does not react with water comes as no surprise. Because the Cl^- ion is the conjugate base of a strong acid (HCl), the Cl^- ion is an extremely weak base, has little or no tendency to become protonated, and is too weak to affect the pH of the solution. (In Section 16-11, we'll provide an explanation for why Na^+ does not affect the pH of a solution.)

As shown in Figure 16-9, when NH_4Cl is added to water, the pH falls below 7. This means that $[H_3O^+] > [OH^-]$ in the solution. A reaction producing H_3O^+ must occur.

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$$

The reaction between NH_4^+ and H_2O is fundamentally no different from other acid–base reactions. A reaction between an ion and water, however, is often called a **hydrolysis** reaction. We say that ammonium ion *hydrolyzes* (and chloride ion does not).

When sodium acetate is dissolved in water, the pH rises above 7 (see Figure 16-9). This means that $[OH^-] > [H_3O^+]$ in the solution. Here, acetate ion hydrolyzes.

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$

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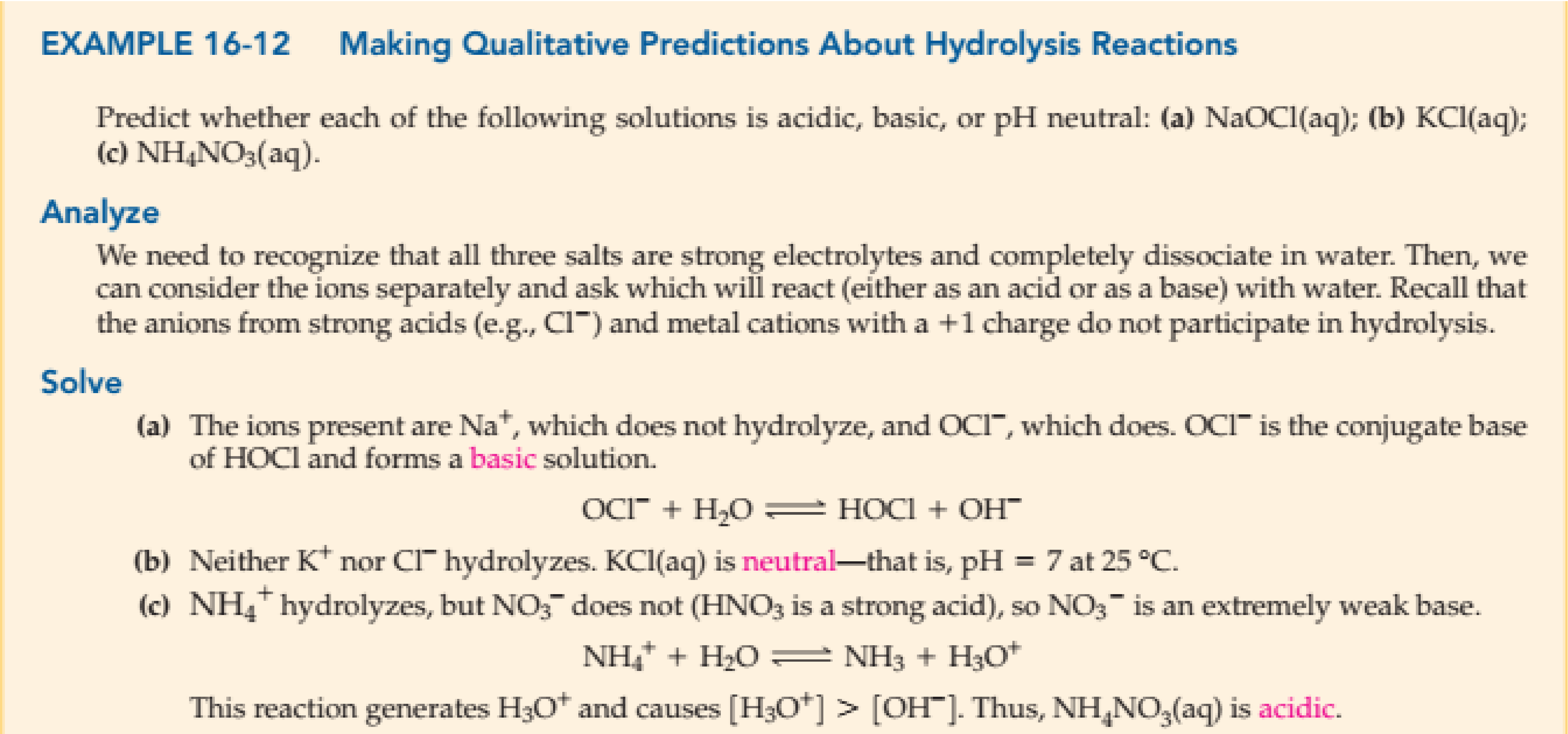
▲ FIGURE 16-9
Ions as acids and bases
Each of these 1 M solutions contains bromthymol blue indicator, which has the following colors:

pH < 7	pH = 7	pH > 7
Yellow	Green	Blue

(Left) $NH_4Cl(aq)$ is acidic. (Center) $NaCl(aq)$ is neutral. (Right) $NaCH_3COO(aq)$ is basic.

EXAMPLE 16-12 Making Qualitative Predictions About Hydrolysis Reactions

Predict whether each of the following solutions is acidic, basic, or pH neutral: **(a)** $NaOCl(aq)$; **(b)** $KCl(aq)$; **(c)** $NH_4NO_3(aq)$.



EXAMPLE 16-12 Making Qualitative Predictions About Hydrolysis Reactions

Predict whether each of the following solutions is acidic, basic, or pH neutral: **(a)** NaOCl(aq); **(b)** KCl(aq); **(c)** NH_4NO_3(aq).

Analyze

We need to recognize that all three salts are strong electrolytes and completely dissociate in water. Then, we can consider the ions separately and ask which will react (either as an acid or as a base) with water. Recall that the anions from strong acids (e.g., Cl^-) and metal cations with a +1 charge do not participate in hydrolysis.

Solve

(a) The ions present are Na^+, which does not hydrolyze, and OCl^-, which does. OCl^- is the conjugate base of HOCl and forms a basic solution.

$$OCl^- + H_2O \rightleftharpoons HOCl + OH^-$$

(b) Neither K^+ nor Cl^- hydrolyzes. KCl(aq) is neutral—that is, pH = 7 at 25 °C.

(c) NH_4^+ hydrolyzes, but NO_3^- does not (HNO_3 is a strong acid), so NO_3^- is an extremely weak base.

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$$

This reaction generates H_3O^+ and causes $[H_3O^+] > [OH^-]$. Thus, NH_4NO_3(aq) is acidic.

EXAMPLE 16-14 Calculating the pH of a Solution in Which Hydrolysis Occurs

Sodium cyanide, NaCN, is extremely poisonous, but it has very useful applications in gold and silver metallurgy and in the electroplating of metals. Aqueous solutions of cyanides are especially hazardous if they become acidified, because toxic hydrogen cyanide gas, HCN(g), is released. Are NaCN(aq) solutions normally acidic, basic, or pH neutral? What is the pH of 0.50 M NaCN(aq)? Note that solutions containing cyanide ion must be handled with extreme caution. They should be handled only in a fume hood by an operator wearing protective clothing.

Analyze

Na^+ does not hydrolyze, but as represented below, CN^- does hydrolyze, producing a basic solution. The question now becomes a hydrolysis equilibrium problem.

Solve

In the tabulation of the concentrations of the species involved in the hydrolysis reaction, let $[OH^-] = x$ M.

	CN^-	+	H_2O	$\rightleftharpoons$	HCN	+	OH^-
initial concns:	0.50 M				—		—
changes:	$-x$ M				$+x$ M		$+x$ M
equil concns:	$(0.50 - x)$ M				x M		x M

Use equation (16.20) to obtain a value of K_b.

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

Now return to the tabulated data.

$$K_b = \frac{[\text{HCN}][\text{OH}^-]}{[\text{CN}^-]} = \frac{x \cdot x}{0.50 - x} = \frac{x^2}{0.50 - x} = 1.6 \times 10^{-5}$$

Assume: $x \lll 0.50$ and $0.50 - x \approx 0.50$.

$$x^2 = 0.50 \times 1.6 \times 10^{-5} = 0.80 \times 10^{-5} = 8.0 \times 10^{-6}$$

$$x = (8.0 \times 10^{-6})^{1/2} = 2.8 \times 10^{-3}$$

$$[\text{OH}^-] = x\ \text{M} = 2.8 \times 10^{-3}\ \text{M}$$

$$\text{pOH} = -\log[\text{OH}^-] = -\log(2.8 \times 10^{-3}) = 2.55$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 2.55 = 11.45$$