Chemistry
The Central Science
Eighth Revised Edition

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If we assume that x is small relative to 0.10 or 0.20 M, this expression simplifies to give

$$\frac{(0.10)(x)}{0.20} = 6.8 \times 10^{-4}$$

$$x = \frac{0.20}{0.10}(6.8 \times 10^{-4}) = 1.4 \times 10^{-3}\,M = [F^-]$$

This F^- concentration is substantially smaller than it would be in a 0.20 M solution of HF with no added HCl. The common ion, H^+, has repressed the dissociation of HF. The concentration of $H^+(aq)$ is
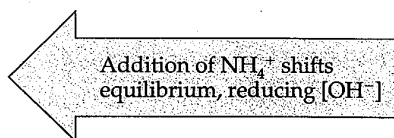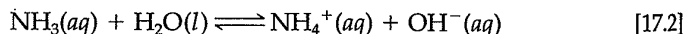
$$[H^+] = (0.10 + x)\,M \approx 0.10\,M$$

Thus, pH = 1.00. Notice that for all practical purposes, $[H^+]$ is due entirely to the HCl; the HF makes a negligible contribution by comparison.

PRACTICE EXERCISE
Calculate the formate-ion concentration and pH of a solution that is 0.050 M in formic acid, $HCHO_2$ ($K_a = 1.8 \times 10^{-4}$), and 0.10 M in HNO_3. *Answer:* $[CHO_2^-] = 9.0 \times 10^{-5}$; pH = 1.00

Sample Exercises 17.1 and 17.2 both involve weak acids. The ionization of a weak base is also decreased by the addition of a common ion. For example, the addition of NH_4^+ (as from the strong electrolyte NH_4Cl) causes the base-dissociation equilibrium of NH_3 to shift to the left, decreasing the equilibrium concentration of OH^- and lowering the pH:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \qquad [17.2]$$

Addition of NH_4^+ shifts equilibrium, reducing $[OH^-]$

17.2 Buffered Solutions

▼ **Figure 17.1** Prepackaged buffer solutions and ingredients for forming buffer solutions of predetermined pH.

Solutions like those discussed in Section 17.1, which contain a weak conjugate acid–base pair, resist drastic changes in pH. Solutions that resist a change in pH upon addition of small amounts of acid or base are called **buffered solutions** (or merely **buffers**). Human blood is an important example of a complex aqueous medium with a pH buffered at about 7.4 (see the "Chemistry and Life" box near the end of this section). Much of the chemical behavior of seawater is determined by its pH, buffered at about 8.1 to 8.3 near the surface. Buffered solutions find many important applications in the laboratory and in medicine (Figure 17.1 ◄).

Composition and Action of Buffered Solutions

Buffers resist changes in pH because they contain both an acidic species to neutralize OH^- ions and a basic one to neutralize H^+ ions. It is necessary that the acidic and basic species of the buffer do not consume each other through a neutralization reaction. These requirements are fulfilled by a weak acid–base conjugate pair such as $HC_2H_3O_2$–$C_2H_3O_2^-$ or NH_4^+–NH_3. Thus, buffers are often prepared by mixing a weak acid or a weak base with a salt of that acid or base.

For example, the $HC_2H_3O_2$–$C_2H_3O_2^-$ buffer can be prepared by adding $NaC_2H_3O_2$ to a solution of $HC_2H_3O_2$; the NH_4^+–NH_3 buffer can be prepared by adding NH_4Cl to a solution of NH_3. By choosing appropriate components and adjusting their relative concentrations, we can buffer a solution at virtually any pH.

To understand better how a buffer works, let's consider a buffer composed of a weak acid (HX) and one of its salts (MX, where M^+ could be Na^+, K^+, or other cations). The acid-dissociation equilibrium in this buffered solution involves both the acid and its conjugate base:

$$HX(aq) \rightleftharpoons H^+(aq) + X^-(aq) \qquad [17.3]$$
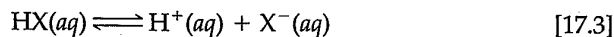
The corresponding acid-dissociation-constant expression is

$$K_a = \frac{[H^+][X^-]}{[HX]} \qquad [17.4]$$

Solving this expression for $[H^+]$, we have

$$[H^+] = K_a \frac{[HX]}{[X^-]} \qquad [17.5]$$
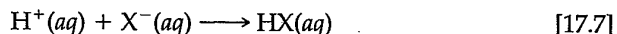
We see from this expression that $[H^+]$, and thus the pH, is determined by two factors: the value of K_a for the weak-acid component of the buffer, and the ratio of the concentrations of the conjugate acid–base pair, $[HX]/[X^-]$.

If OH^- ions are added to the buffered solution, they react with the acid component of the buffer:

$$OH^-(aq) + HX(aq) \longrightarrow H_2O(l) + X^-(aq) \qquad [17.6]$$
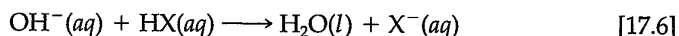
This reaction causes $[HX]$ to decrease and $[X^-]$ to increase. However, as long as the amounts of HX and X^- in the buffer are large compared to the amount of OH^- added, the ratio $[HX]/[X^-]$ doesn't change much, and thus the change in pH is small (Figure 17.2 ▼).

If H^+ ions are added, they react with the base component of the buffer:

$$H^+(aq) + X^-(aq) \longrightarrow HX(aq) \qquad [17.7]$$

This reaction can also be represented using H_3O^+:

$$H_3O^+(aq) + X^-(aq) \longrightarrow HX(aq) + H_2O(l)$$

Buffer after addition of OH^-

Buffer with equal concentrations of weak acid and its conjugate base

Buffer after addition of H^+

OH^-

H^+

$OH^- + HX \longrightarrow H_2O + X^-$

$H^+ + X^- \longrightarrow HX$
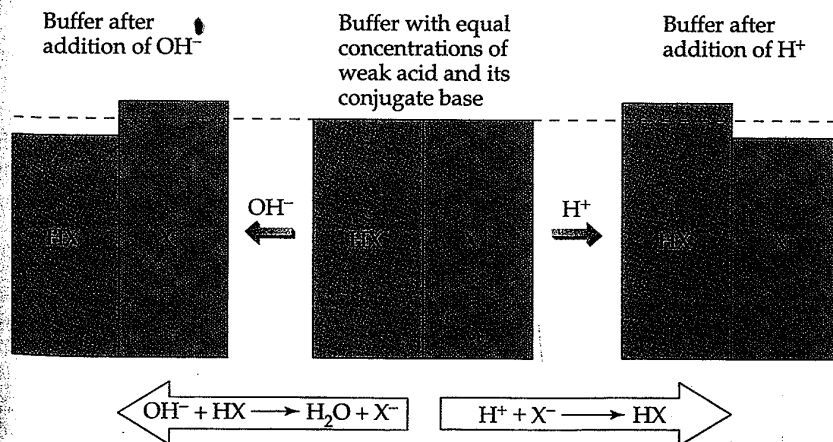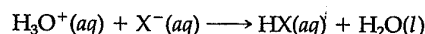
◀ **Figure 17.2** A buffer consists of a mixture of a weak conjugate acid–base pair, here represented as HX and X^-. When a small portion of OH^- is added to the buffer (left), it reacts with HX, decreasing [HX] and increasing [X^-] in the buffer. When a small portion of H^+ is added to the buffer (right), it reacts with X^-, decreasing [X^-] and increasing [HX] in the buffer.

Using either equation, we see that the reaction causes $[X^-]$ to decrease and $[HX]$ to increase. As long as the change in the ratio $[HX]/[X^-]$ is small, the change in pH will be small (Figure 17.2).

Buffers most effectively resist a change in pH in *either* direction when the concentrations of HX and X^- are about the same. From Equation 17.5 we see that when $[HX]$ equals $[X^-]$, $[H^+]$ equals K_a. For this reason, we usually try to select a buffer whose acid form has a pK_a close to the desired pH.

Buffer Capacity and pH

Two important characteristics of a buffer are its capacity and its pH. **Buffer capacity** is the amount of acid or base the buffer can neutralize before the pH begins to change to an appreciable degree. This capacity depends on the amount of acid and base from which the buffer is made. The pH of the buffer depends on the K_a for the acid and on the relative concentrations of the acid and base that comprise the buffer. For example, we can see from Equation 17.5 that $[H^+]$ for a 1-L solution that is 1 M in $HC_2H_3O_2$ and 1 M in $NaC_2H_3O_2$ will be the same as for a 1-L solution that is 0.1 M in $HC_2H_3O_2$ and 0.1 M in $NaC_2H_3O_2$. However, the first solution has a greater buffering capacity because it contains more $HC_2H_3O_2$ and $C_2H_3O_2^-$. The greater the amounts of the conjugate acid–base pair, the more resistant the ratio of their concentrations, and hence the pH, is to change.

Because conjugate acid–base pairs share a common ion, we can use the same procedures to calculate the pH of a buffer that we used in treating the common-ion effect (see Sample Exercise 17.1). However, an alternate approach is sometimes taken that is based on an equation derived from Equation 17.5. Taking the negative log of both sides of Equation 17.5, we have

$$-\log [H^+] = -\log \left(K_a \frac{[HX]}{[X^-]} \right) = -\log K_a - \log \frac{[HX]}{[X^-]}$$

Because $-\log [H^+] = pH$ and $-\log K_a = pK_a$, we have

$$pH = pK_a - \log \frac{[HX]}{[X^-]} = pK_a + \log \frac{[X^-]}{[HX]} \qquad [17.8]$$

In general,

$$pH = pK_a + \log \frac{[base]}{[acid]} \qquad [17.9]$$

Calculating pH
Using the
Henderson–Hasselbalch
Equation activity

where $[acid]$ and $[base]$ refer to the equilibrium concentrations of the conjugate acid–base pair. Note that when $[base] = [acid]$, $pH = pK_a$.

Equation 17.9 is known as the **Henderson–Hasselbalch equation**. Biologists, biochemists, and others who work frequently with buffers often use this equation to calculate the pH of buffers. In doing equilibrium calculations, we have seen that we can normally neglect the amounts of the acid and base of the buffer that ionize. Therefore, we can usually use the starting concentrations of the acid and base components of the buffer directly in Equation 17.9.

SAMPLE EXERCISE 17.3

What is the pH of a buffer that is 0.12 M in lactic acid, $HC_3H_5O_3$, and 0.10 M in sodium lactate? For lactic acid, $K_a = 1.4 \times 10^{-4}$.

Solution   We will first determine the pH using the method described in Section 17.1. The major species in solution are $HC_3H_5O_3$, Na^+, $C_3H_5O_3^-$, and H_2O. The Na^+ ion is

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