Pearson

17.2: Buffers: Solutions That Resist pH Change

Key Concept Video **Buffers**

Most solutions significantly change pH when an acid or base is added to them. As we have just learned, however, a **buffer** resists pH change by neutralizing added acid or added base. A buffer contains either:

1. significant amounts of both a weak acid and its conjugate base or
2. significant amounts of both a weak base and its conjugate acid.

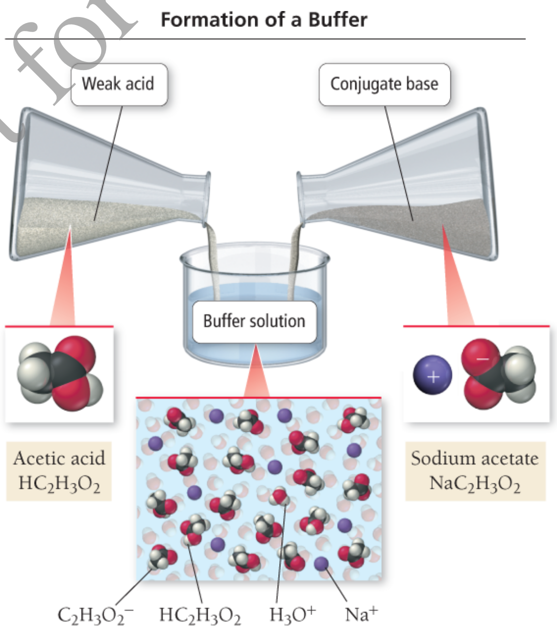
For example, the buffer in blood is composed of carbonic acid (H_2CO_3) and its conjugate base, the bicarbonate ion (HCO_3^-). When additional base is added to a buffer, the weak acid reacts with the base, neutralizing it. When additional acid is added to a buffer, the conjugate base reacts with the acid, neutralizing it. In this way, a buffer can maintain a nearly constant pH.

A weak acid by itself, even though it partially ionizes to form some of its conjugate base, does not contain sufficient base to be a buffer. Similarly, a weak base by itself, even though it partially ionizes water to form some of its conjugate acid, does not contain sufficient acid to be a buffer.

A buffer must contain significant amounts of both a weak acid and its conjugate base (or vice versa). Consider the simple buffer made by dissolving acetic acid $(HC_2H_3O_2)$ and sodium acetate $(NaC_2H_3O_2)$ in water (Figure 17.1).

Figure 17.1 **A Buffer Solution**

A buffer typically consists of a weak acid (which can neutralize added base) and its conjugate base (which can neutralize added acid).



$C_2H_3O_2^-$ is the conjugate base of $HC_2H_3O_2$

Suppose that we add a strong base, such as NaOH, to this solution. The acetic acid neutralizes the base:

$$NaOH(aq) + HC_2H_3O_2(aq) \rightarrow H_2O(l) + NaC_2H_3O_2(aq)$$

As long as the amount of added NaOH is less than the amount of $HC_2H_3O_2$ in solution, the buffer neutralizes the added NaOH and the resulting pH change is small. Suppose, on the other hand, that we add a strong acid, such as HCl, to the solution. In this case, the conjugate base, $NaC_2H_3O_2$, neutralizes the added HCl:

$$HCl(aq) + NaC_2H_3O_2(aq) \rightarrow HC_2H_3O_2(aq) + NaCl(aq)$$

As long as the amount of added HCl is less than the amount of $NaC_2H_3O_2$ in solution, the buffer neutralizes the added HCl and the resulting pH change is small.

Summarizing Buffer Characteristics:

- Buffers resist pH change.
- A buffer contains significant amounts of either: (1) a weak acid and its conjugate base, or (2) a weak base and its conjugate acid.
- The weak acid neutralizes added base.
- The weak base neutralizes added acid.

Conceptual Connection 17.1 Buffers

Interactive

Calculating the pH of a Buffer Solution

In Chapter 16, we learned how to calculate the pH of a solution containing either a weak acid or its conjugate base, but not both. How do we calculate the pH of a buffer—a solution containing both? Consider a solution that initially contains $HC_2H_3O_2$ and $NaC_2H_3O_2$, each at a concentration of 0.100 M. The acetic acid ionizes according to the reaction:

$$\begin{array}{lccccccc} & HC_2H_3O_2(aq) & + & H_2O(l) & \longrightarrow & H_3O^+(aq) & + & C_2H_3O_2^-(aq) \\ \text{Initial concentration:} & 0.100\text{ M} & & & & & & 0.100\text{ M} \end{array}$$

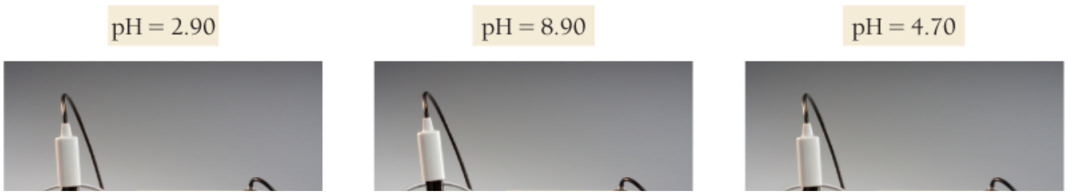
However, the ionization of $HC_2H_3O_2$ in this solution is suppressed compared to its ionization in a solution that does not initially contain any $C_2H_3O_2^-$. Why?

To answer this question, consider an aqueous solution of only $HC_2H_3O_2$ at equilibrium. What happens to the position of the equilibrium if we add $C_2H_3O_2^-$ to the solution? According to Le Châtelier's principle, the reaction shifts to the left, so that less of the $HC_2H_3O_2$ is ionized. In other words, the presence of the $C_2H_3O_2^-$ ion causes the acid to ionize even less than it normally would (Figure 17.2), resulting in a less acidic solution (higher pH). This effect is known as the **common ion effect**, so named because the solution contains two substances $\left(HC_2H_3O_2 \text{ and } NaC_2H_3O_2\right)$ that share a common ion $\left(C_2H_3O_2^-\right)$. To determine the pH of a buffer solution containing common ions, we work an equilibrium problem in which the initial concentrations include both the acid and its conjugate base, as demonstrated in Example 17.1.

> Le Châtelier's principle is discussed in Section 15.9.

Figure 17.2 The Common Ion Effect

The pH of a 0.100 M acetic acid solution is 2.90. The pH of a 0.100 M sodium acetate solution is 8.90. The pH of a solution that is 0.100 M in acetic acid and 0.100 M in sodium acetate is 4.70. (The solution contains an indicator that causes the color differences.)



0.100 M
$HC_2H_3O_2$

0.100 M
$NaC_2H_3O_2$

0.100 M $HC_2H_3O_2$
0.100 M $NaC_2H_3O_2$

Example 17.1 Calculating the pH of a Buffer Solution

Calculate the pH of a buffer solution that is 0.100 M in $HC_2H_3O_2$ and 0.100 M in $NaC_2H_3O_2$.

SOLUTION

1. Write the balanced equation for the ionization of the acid and use it as a guide to prepare an ICE table showing the given concentrations of the acid and its conjugate base as the initial concentrations. Leave room in the table for the changes in concentrations and for the equilibrium concentrations.

$$HC_2H_3O_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_2H_3O_2^-(aq)$$

	$[HC_2H_3O_2]$	$[H_3O^+]$	$[C_2H_3O_2^-]$
Initial	0.100	~0.00	0.100
Change			
Equil			

2. Represent the change in the concentration of H_3O^+ with the variable x. Express the changes in the concentrations of the other reactants and products in terms of x.

$$HC_2H_3O_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_2H_3O_2^-(aq)$$

	$[HC_2H_3O_2]$	$[H_3O^+]$	$[C_2H_3O_2^-]$
Initial	0.100	≈ 0.00	0.100
Change	$-x$	$+x$	$+x$
Equil			

3. Sum each column to determine the equilibrium concentrations in terms of the initial concentrations and the variable x.

$$HC_2H_3O_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_2H_3O_2^-(aq)$$

	$[HC_2H_3O_2]$	$[H_3O^+]$	$[C_2H_3O_2^-]$
Initial	0.100	≈ 0.00	0.100
Change	$-x$	$+x$	$+x$

Equil	$0.100 - x$	x	$0.100 + x$

4. Substitute the expressions for the equilibrium concentrations (from Step 3) into the expression for the acid ionization constant.

In most cases, you can make the approximation that *x is small*. (See Sections 15.8 and 16.7 to review the *x is small* approximation.)

Substitute the value of the acid ionization constant (from Table 16.5) into the K_a expression and solve for x.

Confirm that *x is small* by calculating the ratio of x and the number it was subtracted from in the approximation. For the approximation to be valid, the ratio must be less than 0.05 (or 5%).

$$K_a = \frac{[H_3O^+][C_2H_3O^-]}{[HC_2H_3O_2]}$$
$$= \frac{x(0.100 + x)}{0.100 - x} (x \text{ is small})$$
$$1.8 \times 10^{-5} = \frac{x\,0.100}{0.100}$$
$$x = 1.8 \times 10^{-5}$$
$$\frac{1.8 \times 10^{-5}}{0.100} \times 100\,\% = 0.018\,\%$$

Therefore, the approximation is valid.

5. Determine the H_3O^+ concentration from the calculated value of x and substitute into the pH equation to find pH.

$$[H_3O^+] = x = 1.8 \times 10^{-5} M$$
$$\text{pH} = -\log[H_3O^+]$$
$$= -\log(1.8 \times 10^{-5})$$
$$= 4.74$$

FOR PRACTICE 17.1 Calculate the pH of a buffer solution that is 0.200 M in $HC_2H_3O_2$ and 0.100 M in $NaC_2H_3O_2$

FOR MORE PRACTICE 17.1 Calculate the pH of the buffer that results from mixing 60.0 mL of 0.250 M $HCHO_2$ and 15.0 mL of 0.500 M $NaCHO_2$.

The Henderson–Hasselbalch Equation

We can derive an equation that relates the pH of a buffer solution to the initial concentration of the buffer components and simplify the calculation of the pH of a buffer solution. Consider a buffer containing the generic weak acid HA and its conjugate base A^-. The acid ionizes as follows:

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

We derive an expression for the concentration of H_3O^+ from the acid ionization equilibrium expression by solving the expression for $[H_3O^+]$:

[17.1]

$$K \quad = \quad \frac{[H_3O^+][A^-]}{}$$

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

If we make the same *x is small* approximation that we make for weak acid or weak base equilibrium problems, *we can consider the equilibrium concentrations of HA and A^- to be essentially identical to the initial concentrations of HA and A^-* (see Step 4 of Example 17.1). Therefore, to determine $\left[H_3O^+\right]$ for any buffer solution, we multiply K_a by the ratio of the concentrations of the acid and the conjugate base. To find the $\left[H_3O^+\right]$ of the buffer in Example 17.1 (a solution that is 0.100 M in $HC_2H_3O_2$ and 0.100 M in $NaC_2H_3O_2$), we substitute the concentrations of $HC_2H_3O_2$ and $C_2H_3O_2^-$ into Equation 17.1:

$$\begin{aligned}\left[H_3O^+\right] &= K_a\frac{\left[HC_2H_3O_2\right]}{\left[C_2H_3O_2^-\right]}\\ &= K_a\frac{0.100}{0.100}\\ &= K_a\end{aligned}$$

In this buffer solution, as in any solution in which the acid and conjugate base concentrations are equal, $\left[H_3O^+\right]$ is equal to K_a.

> Recall that the variable x in a weak acid equilibrium problem represents the change in the initial acid concentration. The *x is small* approximation is valid because so little of the weak acid ionizes compared to its initial concentration.

We can derive an equation for the pH of a buffer by taking the negative logarithm of both sides of Equation 17.1:

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

$$-\log\left[H_3O^+\right] = -\log\left(K_a\frac{[HA]}{\left[A^-\right]}\right)$$

[17.2]

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

> Recall that $\log AB = \log A + \log B$, so $-\log AB = -\log A - \log B$.

We rearrange Equation 17.2 to get:

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

> Recall that $\log(A/B) = -\log(B/A)$, so $-\log(A/B) = \log(B/A)$.

Since $pH = -\log\left[H_3O^+\right]$ and since $pK_a = -\log K_a$, we obtain the result:

$$pH = pK_a + \log\frac{\left[A^-\right]}{[HA]}$$

Since A^- is a weak base and HA is a weak acid, we can generalize the equation:

[17.3]

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

> Note that, as expected, the pH of a buffer increases with an increase in the amount of base relative to the amount of acid.

where the base is the conjugate base of the acid or the acid is the conjugate acid of the base. This equation, known as the **Henderson–Hasselbalch equation**, allows us to quickly calculate the pH of a buffer solution from the initial concentrations of the buffer components *as long as the x is small approximation is valid*. In Example 17.2, we demonstrate two ways to find the pH of a buffer: in the left column we solve a common ion effect equilibrium problem using a method similar to the one we used in Example 17.1; in the right column we use the Henderson–Hasselbalch equation.

Example 17.2 Calculating the pH of a Buffer Solution as an Equilibrium Problem and with the Henderson–Hasselbalch Equation

Calculate the pH of a buffer solution that is 0.050 M in benzoic acid $\left(HC_7H_5O_2\right)$ and 0.150 M in sodium benzoate $\left(NaC_7H_5O_2\right)$. For benzoic acid, $K_a = 6.5 \times 10^{-5}$.

SOLUTION

<table>
<tr><th>Equilibrium Approach</th><th>Henderson–Hasselbalch Approach</th></tr>
<tr><td>
Write the balanced equation for the ionization of the acid and use it as a guide to prepare an ICE table.

$$HC_7H_5O_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_7H_5O_2^-(aq)$$

<table>
<tr><th></th><th>$[HC_7H_5O_2]$</th><th>$[H_3O^+]$</th><th>$[C_7H_5O_2^-]$</th></tr>
<tr><td>Initial</td><td>0.050</td><td>≈0.00</td><td>0.150</td></tr>
<tr><td>Change</td><td>−x</td><td>+x</td><td>+x</td></tr>
<tr><td>Equil</td><td>0.050 − x</td><td>x</td><td>0.150 − x</td></tr>
</table>
</td><td>
To find the pH of this solution, determine which component is the acid and which is the base and substitute their concentrations into the Henderson–Hasselbalch equation to calculate pH.

$HC_7H_5O_2$ is the acid and $NaC_7H_5O_2$ is the base. Therefore, you calculate the pH as follows:

$$\begin{aligned} pH &= pK_a + \log\frac{[\text{base}]}{[\text{acid}]} \\ &= -\log\left(6.5 \times 10^{-5}\right) + \log\frac{0.150}{0.050} \\ &= 4.18{}^{-}7 + 0.47{}^{-}7 = 4.66 \end{aligned}$$
</td></tr>
<tr><td>
Substitute the expressions for the equilibrium concentrations into the expression for the acid ionization constant. Make the *x is small* approximation and solve for *x*.

$$\begin{aligned} K_a &= \frac{\left[H_3O^+\right]\left[C_7H_5O_2^-\right]}{\left[HC_7H_5O_2\right]} \\ &= \frac{x(0.150 + x)}{0.050 - x} (x \textit{ is small}) \end{aligned}$$

$$6.5 \times 10^{-5} = \frac{x(0.150)}{0.050}$$

$$x = 2.2 \times 10^{-5}$$

Since $\left[H_3O^+\right] = x$, you calculate pH as follows:

$$\begin{aligned} pH &= -\log\left[H_3O^+\right] \\ &= -\log\left(2.2 \times 10^{-5}\right) \\ &= 4.66 \end{aligned}$$
</td><td></td></tr>
<tr><td>
Confirm that the *x is small* approximation is valid by calculating the ratio of *x* to the smallest number it was subtracted from in the approximation. For the approximation to be valid the ratio must be less than 0.05 (or 5%). (See Sections 15.8 and 16.7 to review the *x is small* approximation.)
</td><td>
Confirm that the *x is small* approximation is valid by calculating the $\left[H_3O^+\right]$ from the pH. Since $\left[H_3O^+\right]$ is formed by
</td></tr>
</table>

$$\frac{2.2 \times 10^{-5}}{0.050} \times 100\,\% = 0.044\,\%$$

The approximation is valid.

pH. Since $\left[H_3O^+\right]$ is formed by ionization of the acid, the calculated $\left[H_3O^+\right]$ has to be less than 0.05 (or 5%) of the initial concentration of the acid in order for the *x is small* approximation to be valid.

$$\mathrm{pH} = 4.66 = -\log\left[H_3O^+\right]$$

$$\left[H_3O^+\right] = 10^{-4.66} = 2.2 \times 10^{-5}\mathrm{M}$$

$$\frac{2.2 \times 10^{-5}}{0.050} \times 100\,\% = 0.044\,\%$$

The approximation is valid.

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FOR PRACTICE 17.2 Calculate the pH of a buffer solution that is 0.250 M in HCN and 0.170 M in KCN. For HCN, $K_a = 4.9 \times 10^{-10}\left(\mathrm{p}K_a = 9.31\right)$. Use both the equilibrium approach and the Henderson–Hasselbalch approach.

Interactive Worked Example 17.2 **Calculating the pH of a Buffer Solution as an Equilibrium Problem and with the Henderson–Hasselbalch Equation**

How do you decide whether to use the equilibrium approach or the Henderson–Hasselbalch equation when calculating the pH of buffer solutions? The answer depends on the specific problem. In cases where you can make the *x is small* approximation, the Henderson–Hasselbalch equation is adequate. However, as you can see from Example 17.2, checking the *x is small* approximation is not as convenient with the Henderson–Hasselbalch equation (because the approximation is implicit). Thus, the equilibrium approach, though lengthier, gives you a better sense of the important quantities in the problem and the nature of the approximation.

When first working buffer problems, use the equilibrium approach until you get a good sense for when the *x is small* approximation is valid. Then, you can switch to the more streamlined approach in cases where the approximation applies (and only in those cases). In general, remember that the *x is small* approximation applies to problems in which both of the following are true: (a) the initial concentrations of acids (and/or bases) are not too dilute; and (b) the equilibrium constant is fairly small. Although the exact values depend on the details of the problem, for many buffer problems this means that the initial concentrations of acids and conjugate bases should be at least $10^2 - 10^3$ times greater than the equilibrium constant (depending on the required accuracy).

Conceptual Connection 17.2 **pH of Buffer Solutions**

Interactive

Calculating pH Changes in a Buffer Solution

Key Concept Video **Finding pH and pH Changes in Buffer Solutions**

When we add acid or base to a buffer, the buffer resists a pH change. Nonetheless, the pH does change by a small amount. Calculating the pH change in a buffer solution requires breaking up the problem into two parts:

1. **The stoichiometry calculation** in which we calculate how the addition changes the relative amounts of acid and conjugate base.

and conjugate base.

2. **The equilibrium calculation** in which we calculate the pH based on the new amounts of acid and conjugate base.

We demonstrate this calculation with a 1.0-L buffer solution that is 0.100 M in the generic acid HA and 0.100 M in its conjugate base A^-. Since the concentrations of the weak acid and the conjugate base are equal, the pH of the buffer is equal to pK_a. Let's calculate the pH of the solution after we add 0.025 mol of strong acid (H^+) (assuming that the change in volume from adding the acid is negligible).

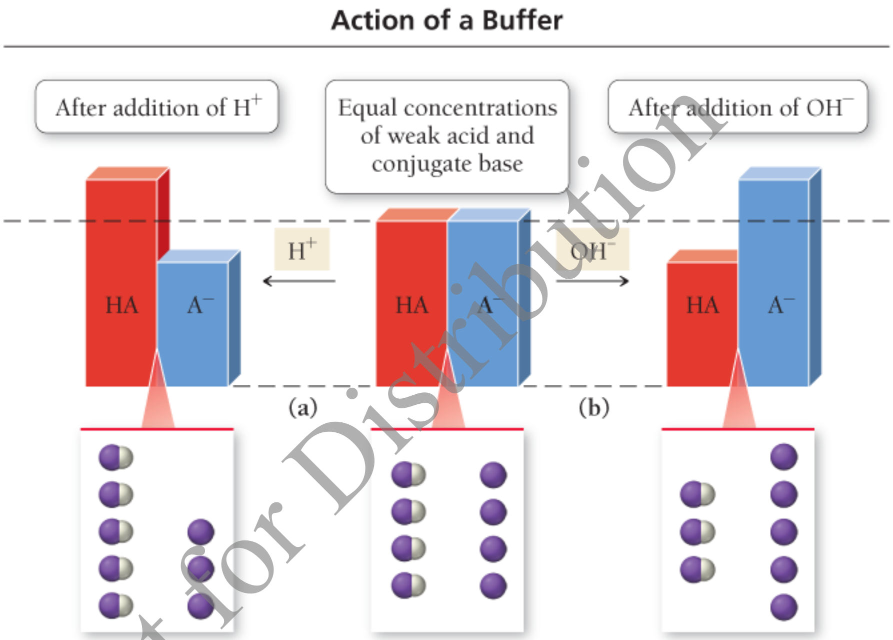
The Stoichiometry Calculation

As the added acid is neutralized, it converts a stoichiometric amount of the base into its conjugate acid through the neutralization reaction (Figure 17.3a):

$$H^+_{\text{added acid}}(aq) + A^-(aq) \rightarrow HA(aq)_{\text{weak base in buffer}}$$

Figure 17.3 Buffering Action

(**a**) When an acid is added to a buffer, a stoichiometric amount of the weak base is converted to the conjugate acid. (**b**) When a base is added to a buffer, a stoichiometric amount of the weak acid is converted to the conjugate base.



Neutralizing 0.025 mol of the strong acid (H^+) requires 0.025 mol of the weak base (A^-) Consequently, the amount of A^- *decreases* by 0.025 mol, and the amount of HA *increases* by 0.025 mol (because of the 1:1:1 stoichiometry of the neutralization reaction). We track these changes in tabular form as follows:

	$H^+(aq)$ +	$A^-(aq)$ ⟶	$HA(aq)$
Before addition	≈0.00 mol	0.100 mol	0.100 mol
Addition	+0.025 mol	—	—
After addition	≈0.00 mol	0.075 mol	0.125 mol

> It is best to work with amounts in moles instead of concentrations when tracking these changes.

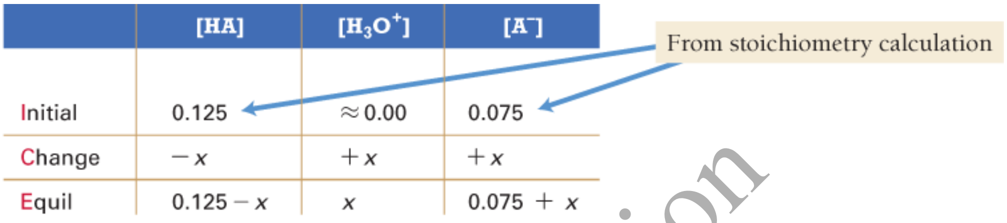
Notice that this table is not an ICE table. This table simply tracks the stoichiometric changes that occur during the neutralization of the added acid. We write ≈ 0.00 mol for the amount of H^+ because the amount is so small compared to the amounts of A^- and HA. (Remember that weak acids ionize only to a small extent and that the presence of the common ion further suppresses the ionization.) The amount of H^+ of course, is not *exactly* zero, as we can see by completing the equilibrium part of the calculation.

The Equilibrium Calculation

We have just seen that adding a small amount of acid to a buffer is equivalent to changing the initial concentrations of the acid and conjugate base present in the buffer (in this case, since the volume is 1.0 L, [HA] increased from 0.100 M to 0.125 M and $\left[A^-\right]$ decreased from 0.100 M to 0.075 M). Knowing these new initial concentrations, we can calculate the new pH in the same way that we calculate the pH of any buffer: either by working a full equilibrium problem or by using the Henderson–Hasselbalch equation (see Examples 17.1 and 17.2). In this case, we work the full equilibrium problem.

We begin by writing the balanced equation for the ionization of the acid and using it as a guide to prepare an ICE table. The initial concentrations for the ICE table are those that we calculated in the stoichiometry part of the calculation:

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



	[HA]	[H₃O⁺]	[A⁻]
Initial	0.125	≈0.00	0.075
Change	−x	+x	+x
Equil	0.125 − x	x	0.075 + x

From stoichiometry calculation

We then substitute the expressions for the equilibrium concentrations into the expression for the acid ionization constant. As long as K_a is sufficiently small relative to the initial concentrations, we can make the *x is small* approximation and solve for *x*, which is equal to $\left[H_3O^+\right]$

$$\begin{aligned} K_a &= \frac{\left[H_3O^+\right]\left[A^-\right]}{[HA]} \\ &= \frac{x(0.075+x)}{0.125-x} (x \text{ is small}) \\ K_a &= \frac{x(0.075)}{0.125} \\ x &= \left[H_3O^+\right] = K_a\frac{0.125}{0.075} \end{aligned}$$

Once we calculate $\left[H_3O^+\right]$ we can calculate the pH with the equation $pH = -\log\left[H_3O^+\right]$.

Notice that, since the expression for *x* contains a *ratio* of concentrations $[HA]/\left[A^-\right]$ we can substitute the *amounts of acid and base in moles* in place of concentration because, in a single buffer solution, the volume is the same for both the acid and the base. Therefore, the volumes cancel:

$$[HA]/\left[A^-\right] = \frac{\frac{n_{HA}}{V}}{\frac{n_{A^-}}{V}} = n_{HA}/n_{A^-}$$

The effect of adding a small amount of strong base to the buffer is exactly the opposite of adding acid. The added base converts a stoichiometric amount of the acid into its conjugate base through the neutralization reaction (Figure 17.3b):

$$\underset{\text{added base}}{OH^-(aq)} \quad + \quad HA(aq) \rightarrow H_2O(l) + \underset{\text{weak acid in buffer}}{A^-(aq)}$$

If we add 0.025 mol of OH^- the amount of A^- goes *up* by 0.025 mol and the amount of HA goes *down* by 0.025 mol as shown in the following table:

	$OH^-(aq)$	$+ HA(aq)$	$\longrightarrow H_2O(l)$	$+ A^-(aq)$
Before addition	≈0.00 mol	0.100 mol		0.100 mol
Addition	+0.025 mol	—		—
After addition	≈0.00 mol	0.075 mol		0.125 mol

When you calculate the pH of a buffer after adding small amounts of acid or base, remember the following:

- Adding a small amount of strong acid to a buffer converts a stoichiometric amount of the base to the conjugate acid and decreases the pH of the buffer. (Adding acid decreases pH just as we would expect.)
- Adding a small amount of strong base to a buffer converts a stoichiometric amount of the acid to the conjugate base and increases the pH of the buffer. (Adding base increases the pH just as we would expect.)

> The easiest way to remember these changes is relatively simple: adding acid creates more acid; adding base creates more base.

Example 17.3 and the For Practice Problems that follow it involve calculating pH changes in a buffer solution after small amounts of strong acid or strong base are added. As we have seen, these problems generally have two parts:

- Part I. Stoichiometry—use the stoichiometry of the neutralization equation to calculate the changes in the amounts (in moles) of the buffer components upon addition of the acid or base.
- Part II. Equilibrium—use the new amounts of buffer components to work an equilibrium problem to find pH. (For most buffers, this can also be done with the Henderson–Hasselbalch equation.)

Conceptual Connection 17.3 **Buffering Action**

Example 17.3 Calculating the pH Change in a Buffer Solution after the Addition of a Small Amount of Strong Acid or Base

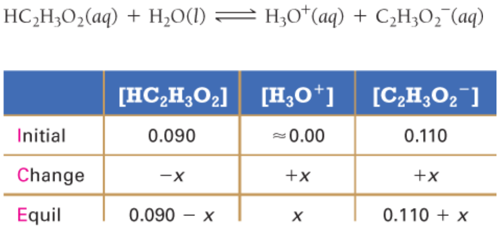
A 1.0-L buffer solution contains 0.100 mol $HC_2H_3O_2$ and 0.100 mol $NaC_2H_3O_2$. The value of K_a for $HC_2H_3O_2$ is 1.8×10^{-5}. Because the initial amounts of acid and conjugate base are equal, the pH of the buffer is equal to $pK_a = -\log\left(1.8 \times 10^{-5}\right) = 4.74$. Calculate the new pH after adding 0.010 mol of solid NaOH to the buffer. For comparison, calculate the pH after adding 0.010 mol of solid NaOH to 1.0 L of pure water. (Ignore any small changes in volume that might occur upon addition of the base.)

SOLUTION

Part I: Stoichiometry. The addition of the base converts a stoichiometric amount of acid to the conjugate base (adding base creates more base). Write an equation showing the neutralization reaction and then set up a table to track the changes.

	$OH^-(aq)$	$+ HC_2H_3O_2(aq)$	$\longrightarrow H_2O(l)$	$+ C_2H_3O_2^-(aq)$
Before addition	≈0.00 mol	0.100 mol		0.100 mol
Addition	0.010 mol	—		—
After addition	≈0.00 mol	0.090 mol		0.110 mol

Part II: Equilibrium. Write the balanced equation for the ionization of the acid and use it as a guide to prepare an ICE table. Use the amounts of acid and conjugate base from part I as the initial amounts of acid and conjugate base in the ICE table.



$$HC_2H_3O_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_2H_3O_2^-(aq)$$

	$[HC_2H_3O_2]$	$[H_3O^+]$	$[C_2H_3O_2^-]$
Initial	0.090	≈0.00	0.110
Change	$-x$	$+x$	$+x$
Equil	$0.090 - x$	x	$0.110 + x$

Substitute the expressions for the equilibrium concentrations of acid and conjugate base into the expression for the acid ionization constant. Make the *x is small* approximation and solve for *x*. Calculate the pH from the value of *x*, which is equal to $\left[H_3O^+\right]$

$$K_a = \frac{\left[H_3O^+\right]\left[C_2H_3O_2^-\right]}{\left[HC_2H_3O_2\right]}$$

$$= \frac{x(0.110 + x)}{0.090 - x}(x \text{ is small})$$

$$1.8 \times 10^{-5} = \frac{x(0.110)}{0.090}$$

$$x = \left[H_3O^+\right] = 1.4^{-}7 \times 10^{-5}\text{M}$$

$$\text{pH} = -\log\left[H_3O^+\right]$$

$$= -\log\left(1.4^{-}7 \times 10^{-5}\right)$$

$$= 4.83$$

Confirm the validity of the *x is small* approximation by calculating the ratio of *x* to the smallest number it was subtracted from in the approximation. The ratio must be less than 0.05 (or 5%).

$$\frac{1.4^{-}7 \times 10^{-5}}{0.090} \times 100\,\% = 0.016\,\%$$

The approximation is valid.

Part II: Equilibrium Alternative (using the Henderson–Hasselbalch equation). As long as the *x is small* approximation is valid, you can substitute

$$\text{pH} = \text{p}K_a + \log\frac{[\text{base}]}{[\text{acid}]}$$

$$= -\log\left(1.8 \times 10^{-5}\right) + \log\frac{0.110}{0.090}$$

$$= 4.74 + 0.087$$

$$= 4.83$$

the quantities of acid and conjugate base after the addition (from part I) into the Henderson–Hasselbalch equation and calculate the new pH.	
The pH of 1.0 L of water after adding 0.010 mol of NaOH is calculated from the $\left[\mathrm{OH^-}\right]$ For a strong base, $\left[\mathrm{OH^-}\right]$ is simply the number of moles of $\mathrm{OH^-}$ divided by the number of liters of solution.	$\left[\mathrm{OH^-}\right] = \frac{0.010\ \mathrm{mol}}{1.0\ \mathrm{L}} = 0.010\ \mathrm{M}$ $\mathrm{pOH} = -\log\left[\mathrm{OH^-}\right] = -\log(0.010)$ $= 2.00$ $\mathrm{pOH}+\mathrm{pH} = 14.00$ $\mathrm{pH} = 14.00 - \mathrm{pOH}$ $= 14.00 - 2.00$ $= 12.00$
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CHECK Notice that the buffer solution changed from pH = 4.74 to pH = 4.83 upon addition of the base (a small fraction of a single pH unit). In contrast, the pure water changed from pH = 7.00 to pH = 12.00 five whole pH units 10^5 Notice also that even the buffer solution got slightly more basic upon addition of a base, as you would expect. To check your answer, always make sure the pH goes in the direction you expect: adding base should make the solution more basic (higher pH); adding acid should make the solution more acidic (lower pH).

FOR PRACTICE 17.3 Calculate the pH of the solution in Example 17.3 upon addition of 0.015 mol of NaOH to the original buffer.

FOR MORE PRACTICE 17.3 Calculate the pH of the solution in Example 17.3 upon addition of 10.0 mL of 1.00 M HCl to the original buffer in Example 17.3

Interactive Worked Example 17.3 **Calculating the pH Change in a Buffer Solution after the Addition of a Small Amount of Strong Acid or Base**

Conceptual Connection 17.4 Adding Acid or Base to a Buffer

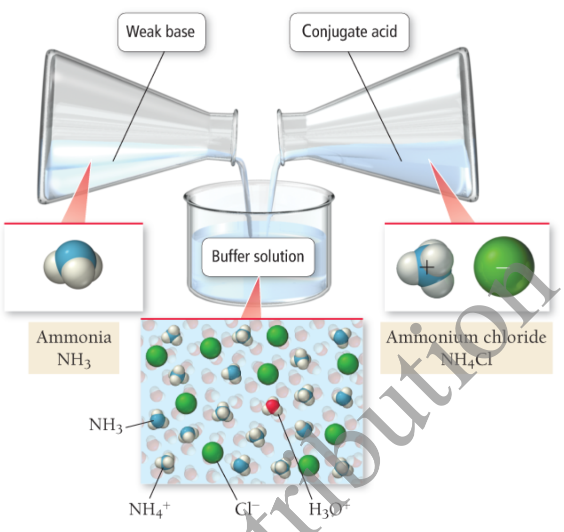
Buffers Containing a Base and Its Conjugate Acid

So far, we have seen examples of buffers composed of an acid and its conjugate base (where the conjugate base is an ion). A buffer can also be composed of a base and its conjugate acid (where the conjugate acid is an ion). For example, a solution containing significant amounts of both NH_3 and NH_4Cl acts as a buffer (Figure 17.4). The NH_3 is a weak base that neutralizes small amounts of added acid, and the NH_4^+ ion is the conjugate acid that neutralizes small amounts of added base.

Figure 17.4 Buffer Containing a Base

A buffer can also consist of a weak base and its conjugate acid.

Formation of a Buffer



We calculate the pH of a solution like this in the same way that we calculated the pH of a buffer containing a weak acid and its conjugate base. When using the Henderson–Hasselbalch equation, however, we must first calculate pK_a for the conjugate acid of the weak base. Recall from Section 16.9 that for a conjugate acid–base pair, $K_a \times K_b = K_w$ and $pK_a \times pK_b = 14$. Consequently, we can find pK_a of the conjugate acid by subtracting pK_b of the weak base from 14. Example 17.4 illustrates the procedure for calculating the pH of a buffer composed of a weak base and its conjugate acid.

Example 17.4 Using the Henderson–Hasselbalch Equation to Calculate the pH of a Buffer Solution Composed of a Weak Base and Its Conjugate Acid

Use the Henderson–Hasselbalch equation to calculate the pH of a buffer solution that is 0.50 M in NH_3 and 0.20 M in NH_4Cl. For ammonia, $pK_b = 4.75$.

SOLUTION

Since K_b for (1.8×10^{-5}) is much smaller than the initial concentrations in this problem, you can use the Henderson–Hasselbalch equation to calculate the pH of the buffer. First calculate pK_a from pK_b.

$$\begin{aligned} pK_a &+ pK_b = 14 \\ pK_a &= 14 - pK_b \\ &= 14 - 4.75 \\ &= 9.25 \end{aligned}$$

Then substitute the given quantities into the Henderson–Hasselbalch equation and calculate pH.

$$\begin{aligned} pH &= pK_a + \log\frac{[\text{base}]}{[\text{acid}]} \\ &= 9.25 + \log\frac{0.50}{0.20} \\ &= 9.25 + 0.40 \\ &= 9.65 \end{aligned}$$

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FOR PRACTICE 17.4 Calculate the pH of 1.0 L of the solution in Example 17.4 upon addition of 0.010 mol of solid NaOH to the original buffer solution.

FOR MORE PRACTICE 17.4 Calculate the pH of 1.0 L of the solution in Example 17.4 upon addition of 30.0 mL of 1.0 M HCl to the original buffer solution.

Interactive Worked Example 17.4 **Using the Henderson–Hasselbalch Equation to Calculate the pH of a Buffer Solution Composed of a Weak Base and Its Conjugate Acid**

Processing math: 100%