

17.3: Buffer Effectiveness: Buffer Range and Buffer Capacity

An effective buffer neutralizes small to moderate amounts of added acid or base. Recall from the opening section of this chapter, however, that a buffer can be destroyed by the addition of too much acid or too much base.

Which factors influence the effectiveness of a buffer? In this section, we examine two such factors: *the relative amounts of the acid and conjugate base* and *the absolute concentrations of the acid and conjugate base*. We then define the *capacity of a buffer* (how much added acid or base it can effectively neutralize) and the *range of a buffer* (the pH range over which a particular acid and its conjugate base can be effective).

Relative Amounts of Acid and Base

A buffer is most effective (most resistant to pH changes) when the concentrations of acid and conjugate base are equal. We can explore this idea by considering the behavior of a generic buffer composed of HA and A⁻ for which pK_a = 5.00. Let's calculate the percent change in pH upon addition of 0.010 mol of NaOH for two different 1.0-L solutions of this buffer system. Both solutions have 0.20 mol of *total* acid and conjugate base. However, solution I has equal amounts of acid and conjugate base (0.10 mol of each), while solution II has much more acid than conjugate base (0.18 mol HA and 0.020 mol A⁻). We can calculate the initial pH values of each solution using the Henderson–Hasselbalch equation. Solution I has an initial pH of 5.00, and solution II has an initial pH of 4.05.

Solution I: 0.10 mol HA and 0.10 mol A⁻; initial pH = 5.00

	$\text{OH}^-(\text{aq}) + \text{HA}(\text{aq}) \longrightarrow \text{H}_2\text{O}(\text{l}) + \text{A}^-(\text{aq})$		
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

$$\begin{aligned}
 \text{pH} &= \text{pK}_a + \log \frac{[\text{base}]}{[\text{acid}]} \\
 &= 5.00 + \log \frac{0.110}{0.090} \\
 &= 5.09 \\
 \% \text{ change} &= \frac{5.09 - 5.00}{5.00} \times 100\% \\
 &= 1.8\%
 \end{aligned}$$

Solution II: 0.18 mol HA and 0.020 mol A⁻; initial pH = 4.05

	$\text{OH}^-(\text{aq}) + \text{HA}(\text{aq}) \longrightarrow \text{H}_2\text{O}(\text{l}) + \text{A}^-(\text{aq})$	
Before addition	≈ 0.00 mol	0.18
Addition	0.010 mol	—
After addition	≈ 0.00 mol	0.17

$$\begin{aligned}
 \text{pH} &= \text{pK}_a + \log \frac{[\text{base}]}{[\text{acid}]} \\
 &= 5.00 + \log \frac{0.020}{0.18} \\
 &= 4.05 \\
 \% \text{ change} &= \frac{4.05 - 4.05}{4.05} \times 100\% \\
 &= 0\%
 \end{aligned}$$

We can see from the calculations that the buffer with equal amounts of acid and conjugate base is more resistant to pH change and is therefore the more effective buffer. A buffer becomes less effective as the difference in the relative amounts of acid and conjugate base increases. As a guideline, we say that an effective buffer must have a [base]/[acid] ratio in the range of 0.10 to 10. *In order for a buffer to be reasonably effective, the relative concentrations of acid and conjugate base should not differ by more than a factor of 10.*

Absolute Concentrations of the Acid and Conjugate

Base

A buffer is most effective (most resistant to pH changes) when the concentrations of acid and conjugate base are high. Let's explore this idea by again considering a generic buffer composed of HA and A⁻ and a pK_a of 5.00 and calculating the percent change in pH upon addition of 0.010 mol of NaOH to two 1.0-L solutions of this buffer system. In this case, both the acid and the base in solution I are ten times more concentrated than the acid and base in solution II. Both solutions have equal relative amounts of acid and conjugate base and therefore have the same initial pH of 5.00.

Solution I: 0.50 mol HA and 0.50 mol A⁻; initial pH = 5.00

	$\text{OH}^-(\text{aq}) + \text{HA}(\text{aq}) \longrightarrow \text{H}_2\text{O}(\text{l}) + \text{A}^-(\text{aq})$			
Before addition	≈ 0.00 mol	0.50 mol		0.50 mol
Addition	0.010 mol	—		—
After addition	≈ 0.00 mol	0.49 mol		0.51 mol

Solution II: 0.050 mol HA and 0.050 mol A⁻; initial pH = 5.00

	$\text{OH}^-(\text{aq}) + \text{HA}(\text{aq}) \longrightarrow \text{H}_2\text{O}(\text{l}) + \text{A}^-(\text{aq})$	
Before addition	≈ 0.00 mol	0.050 mol
Addition	0.010 mol	—
After addition	≈ 0.00 mol	0.040 mol

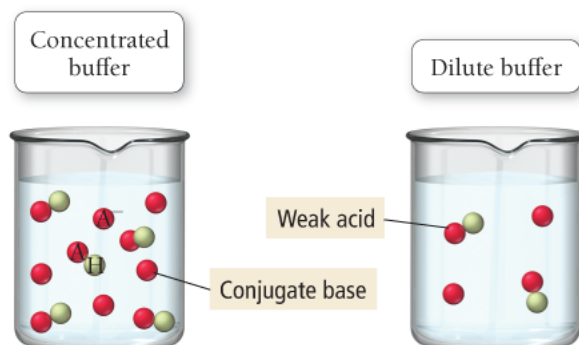
$$\begin{aligned}
 \text{pH} &= \text{pK}_a + \log \frac{[\text{base}]}{[\text{acid}]} \\
 &= 5.00 + \log \frac{0.51}{0.49} \\
 &= 5.02 \\
 \% \text{ change} &= \frac{5.02 - 5.00}{5.00} \times 100\% \\
 &= 0.4\%
 \end{aligned}$$

$$\begin{aligned}
 \text{pH} &= \text{pK}_a + \log \frac{[\text{base}]}{[\text{acid}]} \\
 &= 5.00 + \log \frac{0.040}{0.050} \\
 &= 4.90 \\
 \% \text{ change} &= \frac{5.00 - 4.90}{5.00} \times 100\% \\
 &= 2.0\%
 \end{aligned}$$

As this calculation shows, the buffer with greater amounts of acid and conjugate base is more resistant to pH changes and therefore is the more effective buffer. The more dilute the buffer components, the less effective the buffer.

Buffer Range

In light of the guideline that the relative concentrations of acid and conjugate base should not differ by more than a factor of ten in order for a buffer to be reasonably effective, we can calculate the pH range over which a particular acid and its conjugate base make an effective buffer. Since the pH of a buffer is given by the Henderson–Hasselbalch equation, we can calculate the outermost points of the effective range as follows:



A concentrated buffer contains more of the weak acid and its conjugate base than a weak buffer does. It can therefore neutralize more added acid or added base.

Lowest pH for effective buffer occurs when the base is one-tenth as concentrated as the acid.

Highest pH for effective buffer occurs when the base is ten times as concentrated as the acid.

$$\begin{aligned}\text{pH} &= \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]} \\ &= \text{p}K_a + \log 0.10 \\ &= \text{p}K_a - 1\end{aligned}$$

$$\begin{aligned}\text{pH} &= \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]} \\ &= \text{p}K_a + \log 10 \\ &= \text{p}K_a + 1\end{aligned}$$

The effective range for a buffering system is one pH unit on either side of $\text{p}K_a$. For example, we can use a weak acid with a $\text{p}K_a$ of 5.0 (and its conjugate base) to prepare a buffer in the range of 4.0–6.0. We can adjust the relative amounts of acid and conjugate base to achieve any pH within this range. As we noted earlier, however, the buffer is most effective at pH 5.0 because the buffer components are exactly equal at that pH. **Example 17.5** demonstrates how to pick an acid/conjugate base system for a buffer and how to calculate the relative amounts of acid and conjugate base required for a desired pH.

Example 17.5 Preparing a Buffer

Which acid would you choose to combine with its sodium salt to make a solution buffered at pH 4.25? For the best choice, calculate the ratio of the conjugate base to the acid required to attain the desired pH.

chlorous acid (HClO_2)	$\text{p}K_a = 1.95$	formic acid (HCHO_2)	$\text{p}K_a = 3.74$
nitrous acid (HNO_2)	$\text{p}K_a = 3.34$	hypochlorous acid (HClO)	$\text{p}K_a = 7.54$

SOLUTION The best choice is formic acid because its $\text{p}K_a$ lies closest to the desired pH. You can calculate the required ratio of conjugate base (CHO_2^-) to acid (HCHO_2) by using the Henderson–Hasselbalch equation as follows:

$$\begin{aligned}\text{pH} &= \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]} \\ 4.25 &= 3.74 + \log \frac{[\text{base}]}{[\text{acid}]} \\ \log \frac{[\text{base}]}{[\text{acid}]} &= 4.25 - 3.74 \\ &= 0.51 \\ \frac{[\text{base}]}{[\text{acid}]} &= 10^{0.51} \\ &= 3.24\end{aligned}$$

FOR PRACTICE 17.5 Which acid in **Example 17.5** would you choose to create a buffer with pH = 7.35? If you have 500.0 mL of a 0.10 M solution of the acid, what mass of the corresponding sodium salt of the conjugate base do you need to make the buffer?

Buffer Capacity

Buffer capacity is the amount of acid or base that we can add to a buffer without causing a large change in pH. Given what we just learned about the absolute concentrations of acid and conjugate base in an effective buffer, we can conclude that the *buffer capacity increases with increasing absolute concentrations of the buffer components*. The more concentrated the weak acid and conjugate base that compose the buffer, the higher the buffer capacity. In addition, *overall buffer capacity increases as the relative concentrations of the buffer components become more similar to each other*. As the ratio of the buffer components gets closer to 1, the overall capacity of the buffer

more similar to each other. As the ratio of the buffer components gets closer to 1, the overall capacity of the buffer
(the ability to neutralize added acid *and* added base) becomes greater. In some cases, however, a buffer that must neutralize primarily added acid (or primarily added base) can be overweighted in one of the buffer components.

Conceptual Connection 17.5 Buffer Capacity

Interactive

Not for Distribution