

## 5.1: Day 36- Buffer Solutions

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### Day 36: Buffer Solutions

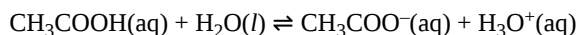
#### D36.1 Buffer Solutions

A mixture of a weak acid and its conjugate base, such as acetic acid and sodium acetate ( $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$ ), or a mixture of a weak base and its conjugate acid, such as ammonia and ammonium chloride ( $\text{NH}_3 + \text{NH}_4\text{Cl}$ ), is a buffer solution. A **buffer solution** resists changes in pH when small amounts of a strong acid or a strong base are added (Figure 1).

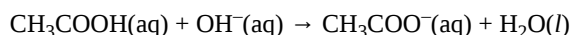


**Figure 1.** (a) The unbuffered solution on the left and the buffered solution on the right have the same pH (pH 8), showing the yellow color of the indicator methyl orange. (b) After the addition of 1 mL of a 0.01-M HCl solution, the buffered solution pH has not changed detectably. The unbuffered solution has become acidic, as indicated by the red color of the methyl orange, which turns red at a pH of about 4. (credit: modification of work by Mark Ott)

A solution of equal concentrations of  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COONa}$  is slightly acidic because the  $K_{a,\text{acetic acid}} > K_{b,\text{acetate anion}}$ . When a strong base, such as NaOH, is added to this solution, the  $\text{OH}^-$  anions react with the few  $\text{H}_3\text{O}^+$  cations, decreasing concentrations of  $\text{H}_3\text{O}^+$ . This shifts the following equilibrium to the right:

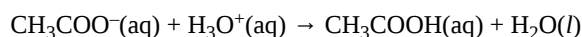


restoring  $\text{H}_3\text{O}^+$  concentration to almost the value it had before the NaOH was added. The net effect of most of the added NaOH is to convert some of the weak acid,  $\text{CH}_3\text{COOH}$ , to a weak base,  $\text{CH}_3\text{COO}^-$ :



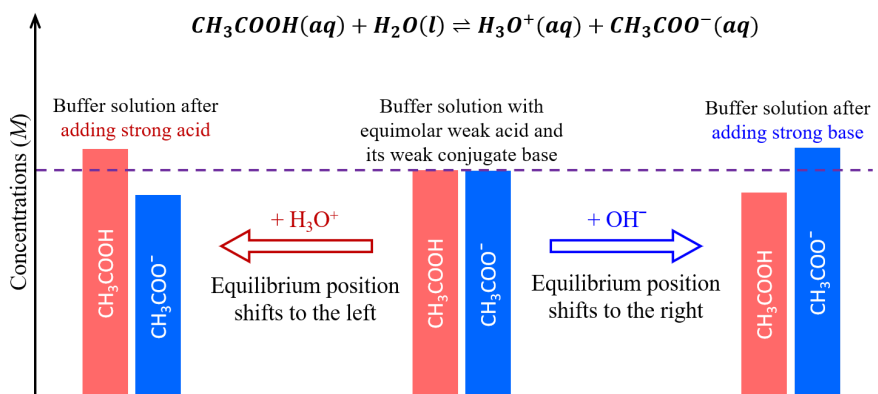
Hence, there is only a minimal decrease in  $\text{H}_3\text{O}^+$  concentration.

When a strong acid, such as HCl, is added, the net effect of most of the added  $\text{H}_3\text{O}^+$  is to convert acetate anions to acetic acid molecules:



And again, there is only a minimal increase in  $\text{H}_3\text{O}^+$  concentration.

As illustrated in Figure 2, a buffer solution can moderate changes to pH because it consists of a weak acid that can react with added strong base as well as a weak base that can react with added strong acid.



**Figure 2.** When a strong acid (producing  $\text{H}_3\text{O}^+$ ) is added to a buffer solution, the weak base is converted to its weak conjugate acid. When a strong base (producing  $\text{OH}^-$ ) is added to a buffer solution, the weak acid is converted to its weak conjugate base.

The weak base and weak acid in a buffer solution are typically a conjugate acid-base pair, which maintains one dynamic equilibrium that responds to additions of other acids and bases. If they are not a conjugate acid-base pair, then there would be two dynamic equilibria at play, which significantly complicates the buffering actions.

### Activity 1: pH of a Buffer Solution

## D36.2 Henderson-Hasselbalch Equation

The ionization constant expression for a weak acid HA is:

$$K_a = \frac{[\text{H}_3\text{O}^+]_e [\text{A}^-]_e}{[\text{HA}]_e}$$

Rearranging gives:

$$[\text{H}_3\text{O}^+]_e = K_a \times \frac{[\text{HA}]_e}{[\text{A}^-]_e}$$

Taking the negative logarithm of both sides, we have:

$$-\log[\text{H}_3\text{O}^+]_e = -\log K_a - \log \frac{[\text{HA}]_e}{[\text{A}^-]_e}$$

$$\text{pH} = \text{p}K_a - \log \frac{[\text{HA}]_e}{[\text{A}^-]_e}$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]_e}{[\text{HA}]_e}$$

It is much more convenient to deal with the initial concentrations of the weak acid and weak base when preparing a buffer solution. (The initial concentration is the amount of weak acid and weak base added to the solution mixture divide by the volume.) Therefore:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]_0 + x}{[\text{HA}]_0 - x}$$

“x” is the increase in concentration of  $\text{H}_3\text{O}^+$  as the solution reaches equilibrium (see activity 1 above) and  $[\text{HA}]_0$  and  $[\text{A}^-]_0$  are the concentration of HA and  $\text{A}^-$  before any reaction occurs. When the approximation that x is at least 100 times smaller than the concentrations of HA and  $\text{A}^-$  is valid, we have the **Henderson-Hasselbalch equation**:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]_0}{[\text{HA}]_0}$$

Note that when  $[\text{A}^-]_0 = [\text{HA}]_0$ ,  $\text{pH} = \text{p}K_a + \log(1) = \text{p}K_a$ .

The Henderson-Hasselbalch equation can be used to calculate the buffer solution pH, given the  $K_a$  and the initial concentrations, or it can be used to determine the ratio of initial concentrations of weak acid and base required to achieve a desired pH.

*The Henderson-Hasselbalch equation applies only to buffer solutions in which the ratio*

$$\frac{[\text{A}^-]_0}{[\text{HA}]_0}$$

*is between 0.1 and 10.* If enough strong acid or strong base is added to the buffer solution to exceed this range, the pH begins to change significantly (in other words, the solution is no longer a buffer solution).

## D36.3 Selection of a Suitable Buffer

A buffer solution moderates changes in pH because it contains both a weak acid that can react with added strong base and a weak base that can react with added strong acid. This leads to several criteria for selecting a suitable buffer solution for a given purpose.

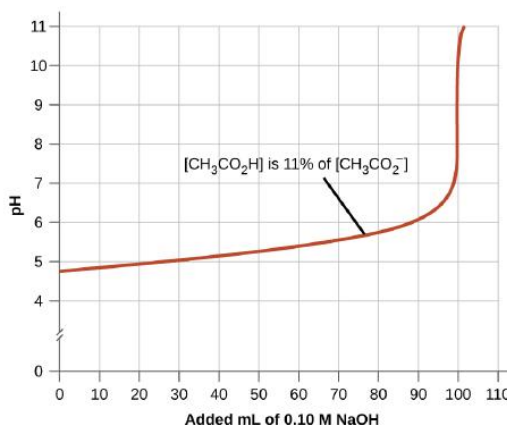
1. The  $pK_a$  of the weak acid in the buffer should be close to the desired pH of the buffer solution. According to the Henderson-Hasselbalch equation, if the concentrations of weak acid and weak base are equal, the pH of the buffer solution equals the  $pK_a$  of the weak acid involved.
2. A buffer solution should have approximately equal concentrations of the weak acid and weak base. A

$$\frac{[A^-]_0}{[HA]_0}$$

ratio of  $>10$  or  $<0.1$  makes for a poor buffer solution. Figure 3 shows how the pH of an acetic acid-acetate ion buffer increases as strong base is added. The initial pH is  $pK_a = 4.74$ . When pH reaches 5.74, a change of 1 pH unit, the ratio

$$\frac{[\text{acetic acid}]}{[\text{acetate anion}]} = 0.11 = 11\%$$

After that the pH increases more rapidly and the solution no longer provides significant buffering.



**Figure 3.** The graph, an illustration of buffering action, shows change of pH as an increasing amount of a 0.10-M NaOH solution is added to 100 mL of a buffer solution in which, initially,  $[CH_3COOH] = [CH_3COO^-] = 0.10\text{ M}$ .

1. The larger the amounts (mol) of weak acid and weak base are the greater is the amount (mol) of strong base or strong acid that can be added before there is a significant change in pH.

When designing a buffer system, look for weak conjugate acid-base pairs that have  $pK_a$  of the weak acid near the desired pH. Then adjust the ratio of the weak base to weak acid concentrations to achieve the exact pH desired. Make certain that the concentrations of weak base and weak acid are large enough to react with the quantities of acid or base that might be added to the buffer solution.

### Activity 2: Preparing a Buffer Solution with a Desired pH

#### D36.4 Buffer Capacity

We can see how a buffer solution works by comparing quantitatively the pH of a buffered solution with the pH of an unbuffered solution upon addition of a strong acid or base.

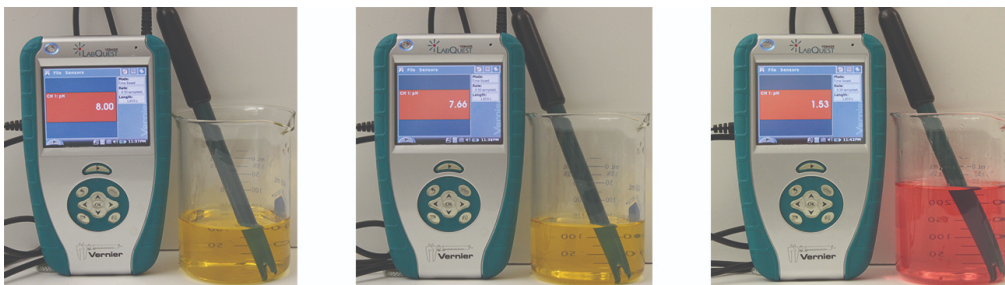
### Activity 3: Calculating pH Change for a Buffer Solution

### Activity 4: pH Change in an Unbuffered Solution

We can see from the above activities that the change in pH is much more significant in the unbuffered solution compared to the buffered solution.

However, buffer solutions do not have an unlimited capacity to keep the pH relatively constant (Figure 4). For example, if we add sufficient strong base to a buffer that all the weak acid has reacted, no more buffering action toward the base is possible. Similarly, if we add an excess of strong acid, the weak base would all be reacted, and no more buffering action toward any additional acid would be possible. In fact, we do not even need to react away all the weak acid or base in a buffer to make significant change in pH: buffering action diminishes rapidly as a given component nears depletion. This was seen in Figure 3 in the above section,

where reducing the concentration of weak acid to 11% of the concentration of weak base caused a change of 1 pH unit. The curve in Figure 3 goes up rapidly after that, indicating that the buffer has been “broken” and no longer resists changes in pH.



**Figure 4. Adding acid to a buffer solution.** The color of the indicator (methyl orange) shows that a small amount of acid added to a buffered solution of pH 8 (beaker on the left) has little effect on the pH of the buffer (middle beaker). However, a large amount of acid exhausts the buffering capacity of the solution and the pH changes dramatically (beaker on the right). (credit: modification of work by Mark Ott)

The **buffer capacity** is the amount (mol) of acid or base that can be added to a given volume of a buffer solution before the pH changes by  $\pm 1$  from the  $pK_a$  of the weak acid. (Recall that if equal concentrations of weak acid and conjugate base are in a buffer solution,  $pH = pK_a$ .)

Buffer capacity depends on the amount (mol) of weak acid and its conjugate base that are in a buffer mixture. For example, a 1 L solution of 1.0 M  $CH_3COOH$  and 1.0 M  $CH_3COONa$  has a greater buffer capacity than a 1 L solution of 0.10 M  $CH_3COOH$  and 0.10 M  $CH_3COONa$ , even though both solutions have the same pH. The first solution has more buffer capacity because it contains more moles of acetic acid and acetate ion.

It takes 0.82 mol HCl to change the buffer pH from 4.74 to 3.74 in the first solution:

$$\begin{aligned} 3.74 &= 4.74 + \log \frac{[CH_3COO^-]_0}{[CH_3COOH]_0} \\ 10^{3.74-4.74} &= \frac{[CH_3COO^-]_0}{[CH_3COOH]_0} \\ 0.10 &= \frac{(1.0 \text{ mol} - x)/(1 \text{ L})}{(1.0 \text{ mol} + x)/(1 \text{ L})} \\ 0.10(1.0 \text{ mol} + x) &= 1.0 \text{ mol} - x \\ 1.1x &= 0.90 \\ x &= 0.82 \text{ mol} \end{aligned}$$

On the other hand, for the solution where the concentrations of weak acid and conjugate base are 0.10 M, it takes only one-tenth as much HCl, 0.082 mol HCl, to change the buffer pH from 4.74 to 3.74:

$$\frac{[CH_3COO^-]_0}{[CH_3COOH]_0} = 10^{-1} = 0.1 = \frac{0.1 \text{ mol} - x}{0.1 \text{ mol} + x} \quad x = 0.082 \text{ mol}$$

If a buffer solution does not have equal concentrations of weak acid and weak base, the buffer capacity when strong acid is added is different from the buffer capacity when strong base is added.

### Podia Question

A solution is prepared by adding 50.0 mL 0.50-M acetic acid and 50.0 mL 0.30-M NaOH to a beaker and stirring. Is this solution a buffer solution? If so, calculate the pH of the buffer. If not, explain why the solution does not resist change in pH when 1.0 mL 0.5-M HCl is added.

Two days before the next whole-class session, this Podia question will become live on [Podia](#), where you can submit your answer.

**Comments.** If you found any inconsistencies, errors, or other things you would like to report about this module, please use [this link](#) to report them. A similar link will be included in each day’s material. We appreciate your comments.

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