

## 6.3: Buffers

### Learning Objectives

- Describe the composition and function of acid–base buffers
- Calculate the pH of a buffer before and after the addition of added acid or base

A mixture of a weak acid and its conjugate base (or a mixture of a weak base and its conjugate acid) is called a buffer solution, or a buffer. Buffer solutions resist a change in pH when small amounts of a strong acid or a strong base are added (Figure 6.3.1). A solution of acetic acid ( $\text{CH}_3\text{COOH}$ ) and sodium acetate ( $\text{CH}_3\text{COONa}$ ) is an example of a buffer that consists of a weak acid and its salt. An example of a buffer that consists of a weak base and its salt is a solution of ammonia ( $\text{NH}_3(\text{aq})$ ) and ammonium chloride ( $\text{NH}_4\text{Cl}(\text{aq})$ ).

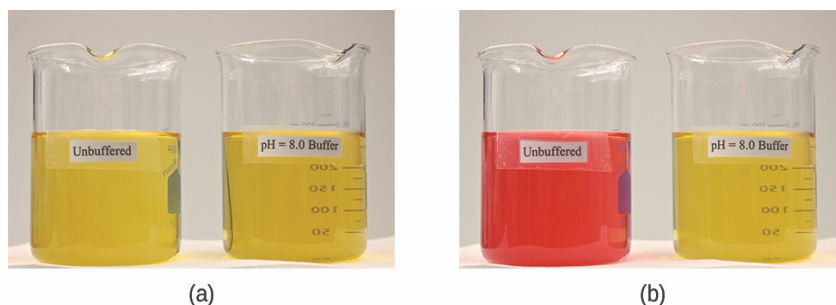


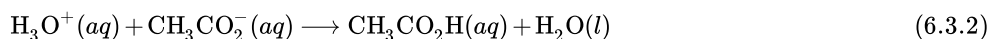
Figure 6.3.1: (a) The unbuffered solution on the left and the buffered solution on the right have the same pH (pH 8); they are basic, showing the yellow color of the indicator methyl orange at this pH. (b) After the addition of 1 mL of a 0.01-M HCl solution, the buffered solution has not detectably changed its pH but the unbuffered solution has become acidic, as indicated by the change in color of the methyl orange, which turns red at a pH of about 4. (credit: modification of work by Mark Ott)

### 6.3.1: How Buffers Work

A mixture of acetic acid and sodium acetate is acidic because the  $K_a$  of acetic acid is greater than the  $K_b$  of its conjugate base acetate. It is a buffer because it contains both the weak acid and its salt. Hence, it acts to keep the hydronium ion concentration (and the pH) almost constant by the addition of either a small amount of a strong acid or a strong base. If we add a base such as sodium hydroxide, the hydroxide ions react with the few hydronium ions present. Then more of the acetic acid reacts with water, restoring the hydronium ion concentration almost to its original value:



The pH changes very little. If we add an acid such as hydrochloric acid, most of the hydronium ions from the hydrochloric acid combine with acetate ions, forming acetic acid molecules:



Thus, there is very little increase in the concentration of the hydronium ion, and the pH remains practically unchanged (Figure 6.3.2).

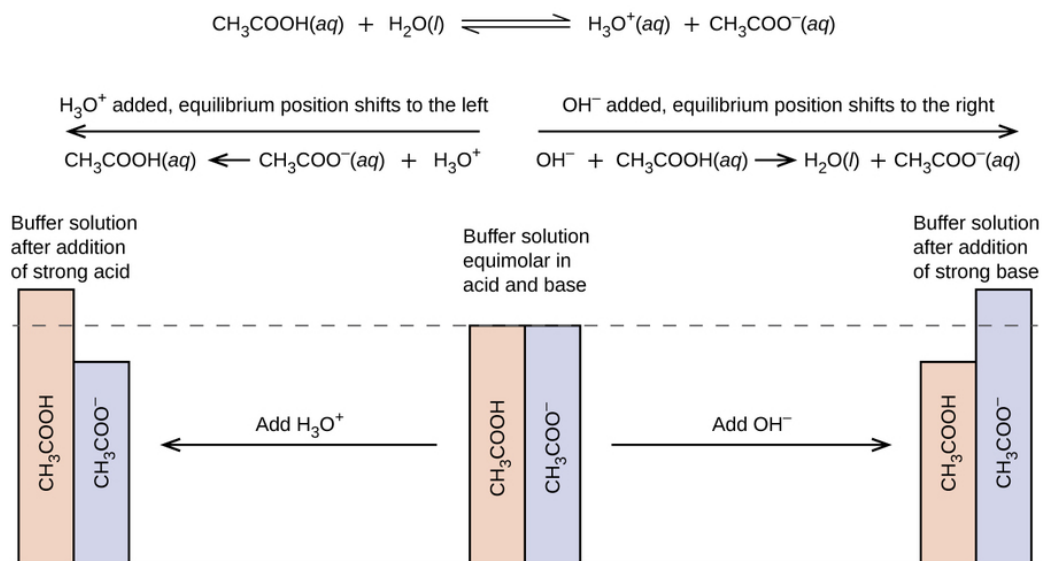
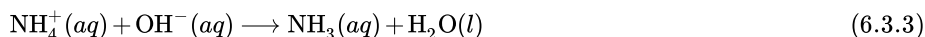
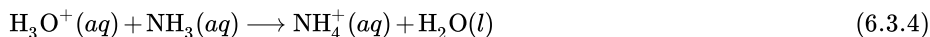


Figure 6.3.2: This diagram shows the buffer action of these reactions.

A mixture of ammonia and ammonium chloride is basic because the  $K_b$  for ammonia is greater than the  $K_a$  for the ammonium ion. It is a buffer because it also contains the salt of the weak base. If we add a base (hydroxide ions), ammonium ions in the buffer react with the hydroxide ions to form ammonia and water and reduce the hydroxide ion concentration almost to its original value:



If we add an acid (hydronium ions), ammonia molecules in the buffer mixture react with the hydronium ions to form ammonium ions and reduce the hydronium ion concentration almost to its original value:



The three parts of the following example illustrate the change in pH that accompanies the addition of base to a buffered solution of a weak acid and to an unbuffered solution of a strong acid.

### ✓ Example 6.3.1: pH Changes in Buffered and Unbuffered Solutions

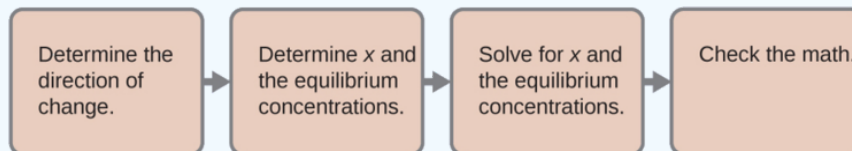
Acetate buffers are used in biochemical studies of enzymes and other chemical components of cells to prevent pH changes that might change the biochemical activity of these compounds.

- Calculate the pH of an acetate buffer that is a mixture with 0.10 M acetic acid and 0.10 M sodium acetate.
- Calculate the pH after 1.0 mL of 0.10 M NaOH is added to 100 mL of this buffer, giving a solution with a volume of 101 mL.

#### Solution

- Calculate the pH of an acetate buffer that is a mixture with 0.10 M acetic acid and 0.10 M sodium acetate.

To determine the pH of the buffer solution we use a typical equilibrium calculation (as illustrated in earlier Examples):



- Determine the direction of change.* The equilibrium in a mixture of  $\text{H}_3\text{O}^+$ ,  $\text{CH}_3\text{CO}_2^-$ , and  $\text{CH}_3\text{CO}_2\text{H}$  is:



The equilibrium constant for  $\text{CH}_3\text{CO}_2\text{H}$  is not given, so we look it up in Table E1:  $K_a = 1.8 \times 10^{-5}$ . With  $[\text{CH}_3\text{CO}_2\text{H}] = [\text{CH}_3\text{CO}_2^-] = 0.10 \text{ M}$  and  $[\text{H}_3\text{O}^+] = \sim 0 \text{ M}$ , the reaction shifts to the right to form  $\text{H}_3\text{O}^+$ .

- Determine x and equilibrium concentrations.* A table of changes and concentrations follows:

	$[\text{CH}_3\text{CO}_2\text{H}] + [\text{H}_2\text{O}] \rightleftharpoons \text{H}_3\text{O}^+ + [\text{CH}_3\text{CO}_2^-]$		
Initial concentration (M)	0.10	~0	0.10
Change (M)	-x	x	x
Equilibrium constant (M)	0.10 - x	x	0.10 + x

3. Solve for  $x$  and the equilibrium concentrations. We find:

$$x = 1.8 \times 10^{-5} \text{ M} \quad (6.3.6)$$

and

$$[\text{H}_3\text{O}^+] = 0 + x = 1.8 \times 10^{-5} \text{ M} \quad (6.3.7)$$

Thus:

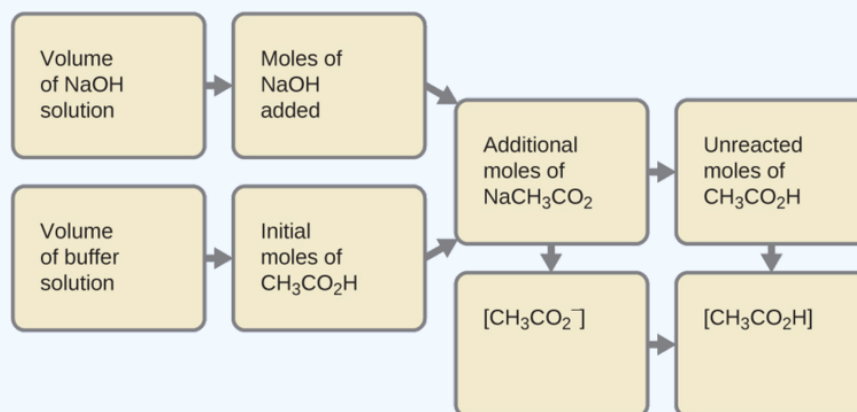
$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(1.8 \times 10^{-5}) \quad (6.3.8)$$

$$= 4.74 \quad (6.3.9)$$

4. Check the work. If we calculate all calculated equilibrium concentrations, we find that the equilibrium value of the reaction coefficient,  $Q = K_a$ .

(b) Calculate the pH after 1.0 mL of 0.10 M NaOH is added to 100 mL of this buffer, giving a solution with a volume of 101 mL.

First, we calculate the concentrations of an intermediate mixture resulting from the complete reaction between the acid in the buffer and the added base. Then we determine the concentrations of the mixture at the new equilibrium:



1. Determine the moles of NaOH. One milliliter (0.0010 L) of 0.10 M NaOH contains:

$$0.0010 \text{ L} \times \left( \frac{0.10 \text{ mol NaOH}}{1 \text{ L}} \right) = 1.0 \times 10^{-4} \text{ mol NaOH} \quad (6.3.10)$$

2. Determine the moles of  $\text{CH}_3\text{CO}_2\text{H}$ . Before reaction, 0.100 L of the buffer solution contains:

$$0.100 \text{ L} \times \left( \frac{0.100 \text{ mol CH}_3\text{CO}_2\text{H}}{1 \text{ L}} \right) = 1.00 \times 10^{-2} \text{ mol CH}_3\text{CO}_2\text{H} \quad (6.3.11)$$

3. Solve for the amount of  $\text{NaCH}_3\text{CO}_2$  produced. The  $1.0 \times 10^{-4}$  mol of NaOH neutralizes  $1.0 \times 10^{-4}$  mol of  $\text{CH}_3\text{CO}_2\text{H}$ , leaving:

$$(1.0 \times 10^{-2}) - (0.01 \times 10^{-2}) = 0.99 \times 10^{-2} \text{ mol CH}_3\text{CO}_2\text{H} \quad (6.3.12)$$

and producing  $1.0 \times 10^{-4}$  mol of  $\text{NaCH}_3\text{CO}_2$ . This makes a total of:

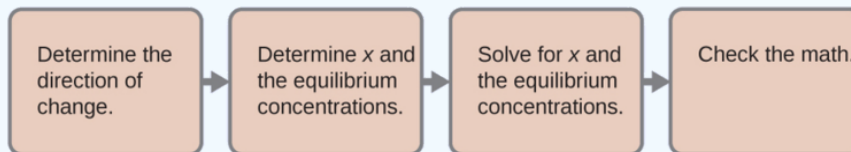
$$[\text{NaCH}_3\text{CO}_2] = (1.0 \times 10^{-4}) + (0.01 \times 10^{-2}) = 1.01 \times 10^{-2} \text{ mol NaCH}_3\text{CO}_2$$

4. Find the molarity of the products. After reaction,  $\text{CH}_3\text{CO}_2\text{H}$  and  $\text{NaCH}_3\text{CO}_2$  are contained in 101 mL of the intermediate solution, so:

$$[\text{CH}_3\text{CO}_2\text{H}] = \frac{9.9 \times 10^{-3} \text{ mol}}{0.101 \text{ L}} = 0.098 \text{ M} \quad (6.3.13)$$

$$[\text{NaCH}_3\text{CO}_2] = \frac{1.01 \times 10^{-2} \text{ mol}}{0.101 \text{ L}} = 0.100 \text{ M} \quad (6.3.14)$$

Now we calculate the pH after the intermediate solution, which is 0.098 M in  $\text{CH}_3\text{CO}_2\text{H}$  and 0.100 M in  $\text{NaCH}_3\text{CO}_2$ , comes to equilibrium. The calculation is very similar to that in part (a) of this example:



This series of calculations gives a  $\text{pH} = 4.75$ . Thus the addition of the base barely changes the pH of the solution.

(c) For comparison, calculate the pH after 1.0 mL of 0.10 M NaOH is added to 100 mL of a solution of an unbuffered solution with a pH of 4.74 (a  $1.8 \times 10^{-5}$ -M solution of HCl). The volume of the final solution is 101 mL.

#### Solution

This  $1.8 \times 10^{-5}$ -M solution of HCl has the same hydronium ion concentration as the 0.10-M solution of acetic acid-sodium acetate buffer described in part (a) of this example. The solution contains:

$$0.100 \text{ L} \times \left( \frac{1.8 \times 10^{-5} \text{ mol HCl}}{1 \text{ L}} \right) = 1.8 \times 10^{-6} \text{ mol HCl}$$

As shown in part (b), 1 mL of 0.10 M NaOH contains  $1.0 \times 10^{-4}$  mol of NaOH. When the NaOH and HCl solutions are mixed, the HCl is the limiting reagent in the reaction. All of the HCl reacts, and the amount of NaOH that remains is:

$$(1.0 \times 10^{-4}) - (1.8 \times 10^{-6}) = 9.8 \times 10^{-5} \text{ M}$$

The concentration of NaOH is:

$$\frac{9.8 \times 10^{-5} \text{ M NaOH}}{0.101 \text{ L}} = 9.7 \times 10^{-4} \text{ M}$$

The pOH of this solution is:

$$\text{pOH} = -\log[\text{OH}^-] = -\log(9.7 \times 10^{-4}) = 3.01$$

The pH is:

$$\text{pH} = 14.00 - \text{pOH} = 10.99$$

The pH changes from 4.74 to 10.99 in this unbuffered solution. This compares to the change of 4.74 to 4.75 that occurred when the same amount of NaOH was added to the buffered solution described in part (b).

#### ? Exercise 6.3.1

Show that adding 1.0 mL of 0.10 M HCl changes the pH of 100 mL of a  $1.8 \times 10^{-5}$  M HCl solution from 4.74 to 3.00.

#### Answer

Initial pH of  $1.8 \times 10^{-5}$  M HCl;  $\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log[1.8 \times 10^{-5}] = 4.74$

Moles of  $\text{H}_3\text{O}^+$  added by addition of 1.0 mL of 0.10 M HCl:  $0.10 \text{ moles/L} \times 0.0010 \text{ L} = 1.0 \times 10^{-4}$  moles; final pH after addition of 1.0 mL of 0.10 M HCl:

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log \left( \frac{\text{total moles } \text{H}_3\text{O}^+}{\text{total volume}} \right) = -\log \left( \frac{1.0 \times 10^{-4} \text{ mol} + 1.8 \times 10^{-6} \text{ mol}}{101 \text{ mL} \left( \frac{1 \text{ L}}{1000 \text{ mL}} \right)} \right) = 3.00 \quad (6.3.15)$$

### 6.3.2: Buffer Capacity

Buffer solutions do not have an unlimited capacity to keep the pH relatively constant (Figure 6.3.3). If we add so much base to a buffer that the weak acid is exhausted, no more buffering action toward the base is possible. On the other hand, if we add an excess of acid, the weak base would be exhausted, and no more buffering action toward any additional acid would be possible. In fact, we do not even need

to exhaust all of the acid or base in a buffer to overwhelm it; its buffering action will diminish rapidly as a given component nears depletion.

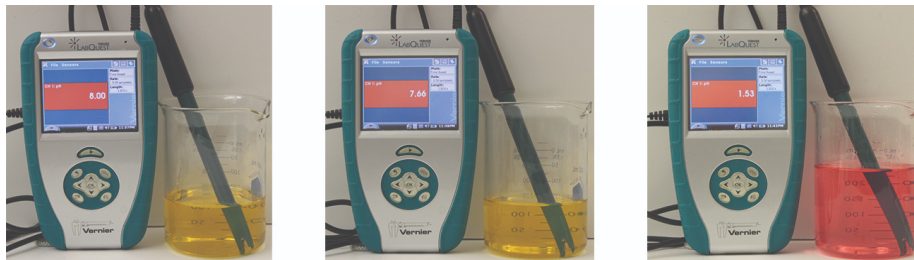


Figure 6.3.3: The indicator color (methyl orange) shows that a small amount of acid added to a buffered solution of pH 8 (beaker on the left) has little effect on the buffered system (middle beaker). However, a large amount of acid exhausts the buffering capacity of the solution and the pH changes dramatically (beaker on the right). (credit: modification of work by Mark Ott)

The buffer capacity is the amount of acid or base that can be added to a given volume of a buffer solution before the pH changes significantly, usually by one unit. Buffer capacity depends on the amounts of the weak acid and its conjugate base that are in a buffer mixture. For example, 1 L of a solution that is 1.0 M in acetic acid and 1.0 M in sodium acetate has a greater buffer capacity than 1 L of a solution that is 0.10 M in acetic acid and 0.10 M in sodium acetate even though both solutions have the same pH. The first solution has more buffer capacity because it contains more acetic acid and acetate ion.

### 6.3.3: Selection of Suitable Buffer Mixtures

There are two useful rules of thumb for selecting buffer mixtures:

1. A good buffer mixture should have about equal concentrations of both of its components. A buffer solution has generally lost its usefulness when one component of the buffer pair is less than about 10% of the other. Figure 6.3.4 shows an acetic acid-acetate ion buffer as base is added. The initial pH is 4.74. A change of 1 pH unit occurs when the acetic acid concentration is reduced to 11% of the acetate ion concentration.

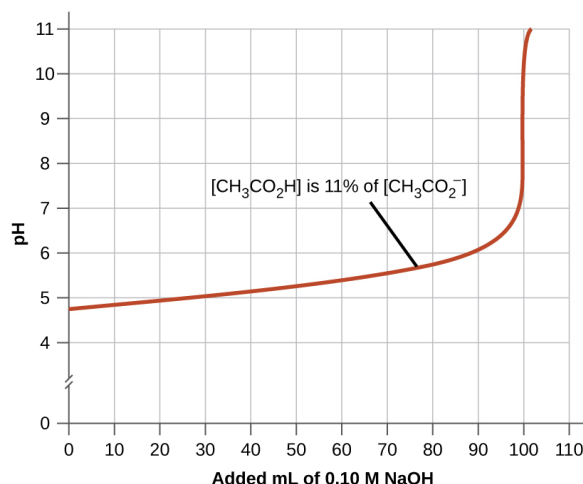
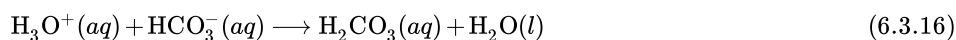


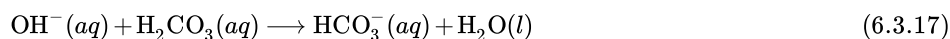
Figure 6.3.4: The graph, an illustration of buffering action, shows change of pH as an increasing amount of a 0.10-M NaOH solution is added to 100 mL of a buffer solution in which, initially,  $[\text{CH}_3\text{CO}_2\text{H}] = 0.10\text{ M}$  and  $[\text{CH}_3\text{CO}_2^-] = 0.10\text{ M}$ .

2. Weak acids and their salts are better as buffers for pHs less than 7; weak bases and their salts are better as buffers for pHs greater than 7.

Blood is an important example of a buffered solution, with the principal acid and ion responsible for the buffering action being carbonic acid,  $\text{H}_2\text{CO}_3$ , and the bicarbonate ion,  $\text{HCO}_3^-$ . When an excess of hydrogen ion enters the blood stream, it is removed primarily by the reaction:



When an excess of the hydroxide ion is present, it is removed by the reaction:



The pH of human blood thus remains very near 7.35, that is, slightly basic. Variations are usually less than 0.1 of a pH unit. A change of 0.4 of a pH unit is likely to be fatal.

#### 6.3.4: Summary

A solution containing a mixture of an acid and its conjugate base, or of a base and its conjugate acid, is called a buffer solution. Unlike in the case of an acid, base, or salt solution, the hydronium ion concentration of a buffer solution does not change greatly when a small amount of acid or base is added to the buffer solution. The base (or acid) in the buffer reacts with the added acid (or base).

#### 6.3.5: Key Equations

- $pK_a = -\log K_a$
- $pK_b = -\log K_b$

### Glossary

**buffer capacity**

amount of an acid or base that can be added to a volume of a buffer solution before its pH changes significantly (usually by one pH unit)

**buffer**

mixture of a weak acid or a weak base and the salt of its conjugate; the pH of a buffer resists change when small amounts of acid or base are added

**Henderson-Hasselbalch equation**

equation used to calculate the pH of buffer solutions

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