10.10: Buffer Solutions

> **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 10.10.1). A solution of acetic acid (CH_3COOH and sodium acetate CH_3COONa) 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 ($NH_3(aq)$) and ammonium chloride ($NH_4Cl(aq)$).

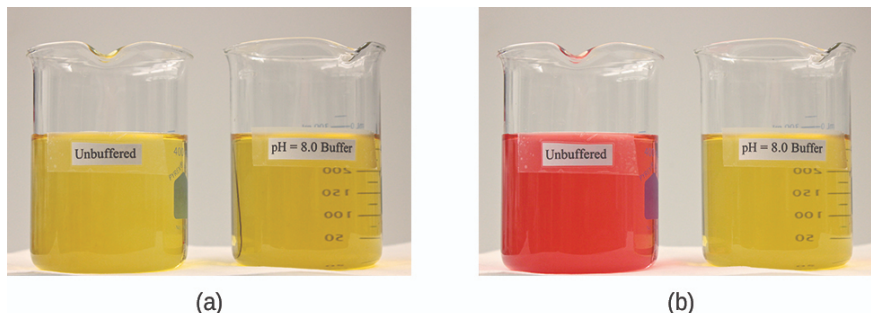(a)   (b)

Figure 10.10.1: (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)

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:

$$CH_3CO_2H(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + CH_3CO_2^-(aq)$$
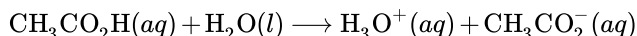
The pH changes very little. If we add an acid such as hydrochloric acid, most of the hydronium ions from the hydrochloric acid combine with acetate ions, forming acetic acid molecules:

$$H_3O^+(aq) + CH_3CO_2^-(aq) \longrightarrow CH_3CO_2H(aq) + H_2O(l)$$
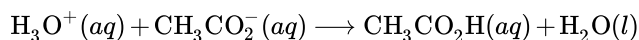
Thus, there is very little increase in the concentration of the hydronium ion, and the pH remains practically unchanged (Figure 10.10.2).

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

H$_3$O$^+$ added, equilibrium position shifts to the left

$$CH_3COOH(aq) \longleftarrow CH_3COO^-(aq) + H_3O^+$$

OH$^-$ added, equilibrium position shifts to the right

$$OH^- + CH_3COOH(aq) \longrightarrow H_2O(l) + CH_3COO^-(aq)$$

Buffer solution after addition of strong acid

CH$_3$COOH | CH$_3$COO$^-$

Buffer solution equimolar in acid and base

Buffer solution after addition of strong base

Add H$_3$O$^+$

Add OH$^-$

CH$_3$COOH | CH$_3$COO$^-$
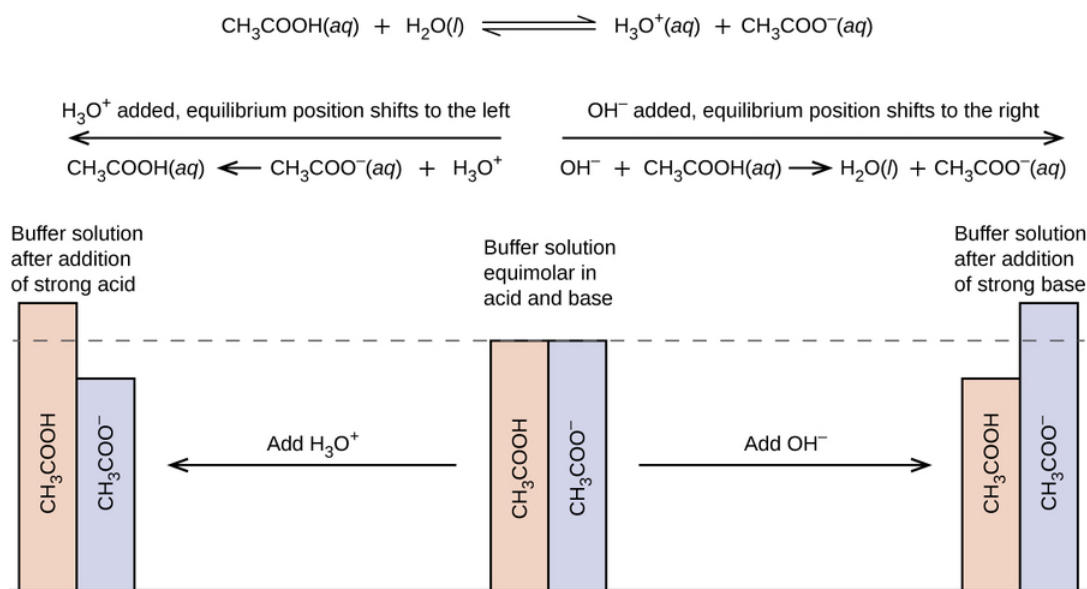
CH$_3$COOH | CH$_3$COO$^-$

Figure 10.10.2: 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:

$$NH_4^+(aq) + OH^-(aq) \longrightarrow NH_3(aq) + H_2O(l)$$
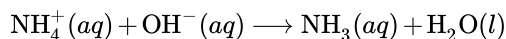
If we add an acid (hydronium ions), ammonia molecules in the buffer mixture react with the hydronium ions to form ammonium ions and reduce the hydronium ion concentration almost to its original value:

$$H_3O^+(aq) + NH_3(aq) \longrightarrow NH_4^+(aq) + H_2O(l)$$
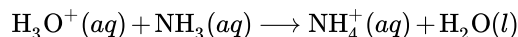
The three parts of the following example illustrate the change in pH that accompanies the addition of base to a buffered solution of a weak acid and to an unbuffered solution of a strong acid.

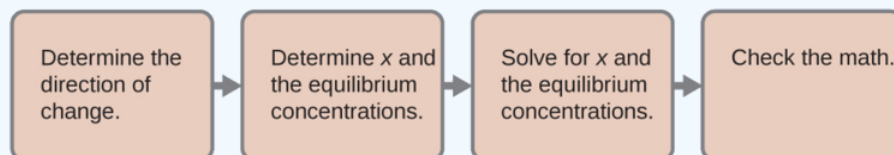> ✔ Example 10.10.1: pH Changes in Buffered and Unbuffered Solutions
>
> Acetate buffers are used in biochemical studies of enzymes and other chemical components of cells to prevent pH changes that might change the biochemical activity of these compounds.
>
> a. Calculate the pH of an acetate buffer that is a mixture with 0.10 M acetic acid and 0.10 M sodium acetate.
> 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.
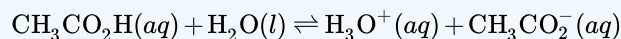>
> **Solution**
> a. Calculate the pH of an acetate buffer that is a mixture with 0.10 M acetic acid and 0.10 M sodium acetate.
>
> To determine the pH of the buffer solution we use a typical equilibrium calculation (as illustrated in earlier Examples):
>
> Determine the direction of change. → Determine x and the equilibrium concentrations. → Solve for x and the equilibrium concentrations. → Check the math.
>
> 1. *Determine the direction of change.* The equilibrium in a mixture of H$_3$O$^+$, $CH_3CO_2^-$, and CH$_3$CO$_2$H is:
>
> $$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq)$$
>
> The equilibrium constant for CH$_3$CO$_2$H is not given, so we look it up in Table E1: $K_a = 1.8 \times 10^{-5}$. With [CH$_3$CO$_2$H] = [$CH_3CO_2^-$] = 0.10 M and [H$_3$O$^+$] = ~0 M, the reaction shifts to the right to form H$_3$O$^+$.

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

	$[CH_3CO_2H] + [H_2O] \rightleftharpoons H_3O^+ + [CH_3CO_2^-]$		
Initial concentration (*M*)	0.10	~0	0.10
Change (*M*)	−x	x	x
Equilibrium constant (*M*)	0.10 − x	x	0.10 + x

- *Solve for x and the equilibrium concentrations.* We find:

$$x = 1.8 \times 10^{-5} \ M$$

- and

$$[\mathrm{H_2O^+}] = 0 + x = 1.8 \times 10^{-5} \ M$$

Thus:

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

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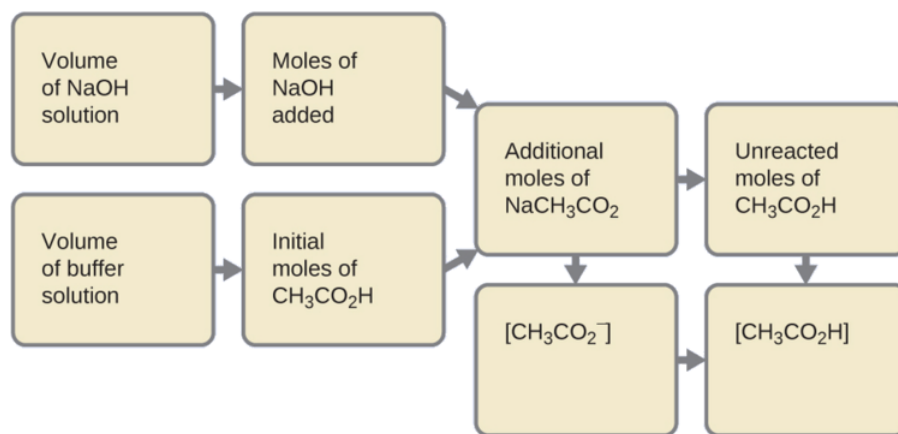
1. *Determine the moles of NaOH.* One milliliter (0.0010 L) of 0.10 *M* NaOH contains:

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

2. *Determine the moles of CH$_2$CO$_2$H.* Before reaction, 0.100 L of the buffer solution contains:

$$0.100 \ \mathrm{L} \times \left(\frac{0.100 \ \mathrm{mol \ CH_3CO_2H}}{1 \ \mathrm{L}} \right) = 1.00 \times 10^{-2} \ \mathrm{mol \ CH_3CO_2H}$$

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

$$(1.0 \times 10^{-2}) - (0.01 \times 10^{-2}) = 0.99 \times 10^{-2} \ \mathrm{mol \ CH_3CO_2H}$$

and producing 1.0×10^{-4} mol of $NaCH_3CO_2$. This makes a total of:

$$\mathrm{(1.0 \times 10^{-2}) + (0.01 \times 10^{-2}) = 1.01 \times 10^{-2}\:mol\:NaCH_3CO_2}$$

4. *Find the molarity of the products.* After reaction, CH_3CO_2H and $NaCH_3CO_2$ are contained in 101 mL of the intermediate solution, so:

$$[CH_3CO_2H] = \frac{9.9 \times 10^{-3} \text{ mol}}{0.101 \text{ L}} = 0.098 \; M$$

$$[NaCH_3CO_2] = \frac{1.01 \times 10^{-2} \text{ mol}}{0.101 \text{ L}} = 0.100 \; M$$

Now we calculate the pH after the intermediate solution, which is 0.098 M in CH_3CO_2H and 0.100 M in $NaCH_3CO_2$, comes to equilibrium. The calculation is very similar to that in part (a) of this example:
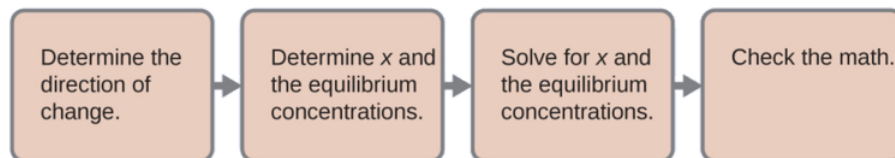
This series of calculations gives a pH = 4.75. Thus the addition of the base barely changes the pH of the solution.

(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 1.8×10^{-5}-M solution of HCl). The volume of the final solution is 101 mL.

Solution

This 1.8×10^{-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 1.0×10^{-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:

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

The concentration of NaOH is:

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

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 10.10.1**
>
> Show that adding 1.0 mL of 0.10 M HCl changes the pH of 100 mL of a 1.8×10^{-5} M HCl solution from 4.74 to 3.00.
>
> **Answer**
>
> Initial pH of 1.8×10^{-5} M HCl; pH = $-\log[H_3O^+]$ = $-\log[1.8 \times 10^{-5}]$ = 4.74
>
> Moles of H_3O^+ added by addition of 1.0 mL of 0.10 M HCl: 0.10 moles/L $\times$ 0.0010 L = 1.0×10^{-4} moles; final pH after addition of 1.0 mL of 0.10 M HCl:

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}] = -\log\left(\frac{\text{total moles } \mathrm{H_3O^+}}{\text{total volume}}\right) = -\log\left(\frac{1.0 \times 10^{-4}\text{ mol} + 1.8 \times 10^{-6}\text{ mol}}{101\text{ mL}\left(\dfrac{1\text{ L}}{1000\text{ mL}}\right)}\right) = 3.00$$

Buffer Capacity

Buffer solutions do not have an unlimited capacity to keep the pH relatively constant (Figure 10.10.3). 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.
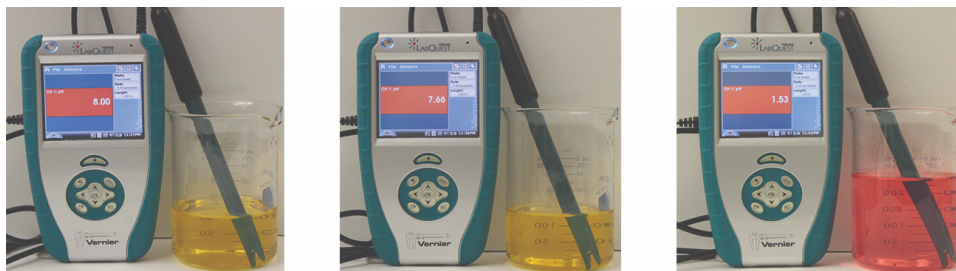

Figure 10.10.3: The indicator color (methyl orange) shows that a small amount of acid added to a buffered solution of pH 8 (beaker on the left) has little affect on the buffered system (middle beaker). However, a large amount of acid exhausts the buffering capacity of the solution and the pH changes 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.

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 10.10.4 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.
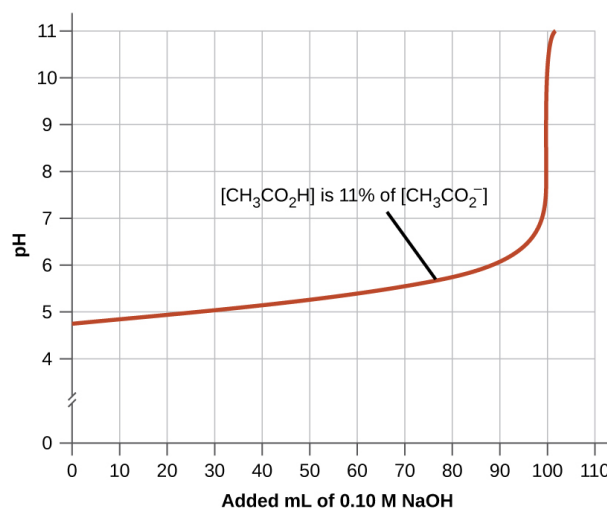
Figure 10.10.4: The graph, an illustration of buffering action, shows change of pH as an increasing amount of a 0.10-M NaOH solution is added to 100 mL of a buffer solution in which, initially, $[CH_3CO_2H] = 0.10\ M$ and $[CH_3CO_2^-] = 0.10\ M$.

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, H_2CO_3, and the bicarbonate ion, HCO_3^-. When an excess of hydrogen ion enters the blood stream, it is removed primarily by the reaction:

$$H_3O^+(aq) + HCO_3^-(aq) \longrightarrow H_2CO_3(aq) + H_2O(l)$$
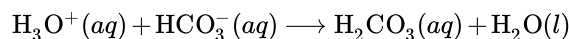
When an excess of the hydroxide ion is present, it is removed by the reaction:

$$OH^-(aq) + H_2CO_3(aq) \longrightarrow HCO_3^-(aq) + H_2O(l)$$
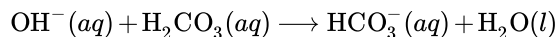
The pH of human blood thus remains very near 7.35, that is, slightly basic. Variations are usually less than 0.1 of a pH unit. A change of 0.4 of a pH unit is likely to be fatal.

The Henderson-Hasselbalch Approximation

The ionization-constant expression for a solution of a weak acid can be written as:

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

Rearranging to solve for $[H_3O^+]$, we get:

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

Taking the negative logarithm of both sides of this equation, we arrive at:

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

which can be written as

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

where pK_a is the negative of the common logarithm of the ionization constant of the weak acid ($pK_a = -\log K_a$). This equation relates the pH, the ionization constant of a weak acid, and the concentrations of the weak acid and its salt in a buffered solution.

Scientists often use this expression, called the Henderson-Hasselbalch approximation, to calculate the pH of buffer solutions. It is important to note that the "x is small" assumption must be valid to use this equation.
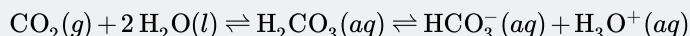
> **⚑ Lawrence Joseph Henderson and Karl Albert Hasselbalch**
>
> Lawrence Joseph Henderson (1878–1942) was an American physician, biochemist and physiologist, to name only a few of his many pursuits. He obtained a medical degree from Harvard and then spent 2 years studying in Strasbourg, then a part of Germany, before returning to take a lecturer position at Harvard. He eventually became a professor at Harvard and worked there his entire life. He discovered that the acid-base balance in human blood is regulated by a buffer system formed by the dissolved carbon dioxide in blood. He wrote an equation in 1908 to describe the carbonic acid-carbonate buffer system in blood. Henderson was broadly knowledgeable; in addition to his important research on the physiology of blood, he also wrote on the adaptations of organisms and their fit with their environments, on sociology and on university education. He also founded the Fatigue Laboratory, at the Harvard Business School, which examined human physiology with specific focus on work in industry, exercise, and nutrition.
>
> In 1916, Karl Albert Hasselbalch (1874–1962), a Danish physician and chemist, shared authorship in a paper with Christian Bohr in 1904 that described the Bohr effect, which showed that the ability of hemoglobin in the blood to bind with oxygen was inversely related to the acidity of the blood and the concentration of carbon dioxide. The pH scale was introduced in 1909 by another Dane, Sørensen, and in 1912, Hasselbalch published measurements of the pH of blood. In 1916, Hasselbalch expressed Henderson's equation in logarithmic terms, consistent with the logarithmic scale of pH, and thus the Henderson-Hasselbalch equation was born.

> **⚑ Medicine: The Buffer System in Blood**
>
> The normal pH of human blood is about 7.4. The carbonate buffer system in the blood uses the following equilibrium reaction:
>
> $$CO_2(g) + 2\,H_2O(l) \rightleftharpoons H_2CO_3(aq) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$$
>
> The concentration of carbonic acid, H_2CO_3 is approximately 0.0012 M, and the concentration of the hydrogen carbonate ion, HCO_3^-, is around 0.024 M. Using the Henderson-Hasselbalch equation and the pK_a of carbonic acid at body temperature, we can calculate the pH of blood:
>
> $$pH = pK_a + \log \frac{[\text{base}]}{[\text{acid}]} = 6.1 + \log \frac{0.024}{0.0012} = 7.4$$
>
> The fact that the H_2CO_3 concentration is significantly lower than that of the HCO_3^- ion may seem unusual, but this imbalance is due to the fact that most of the by-products of our metabolism that enter our bloodstream are acidic. Therefore, there must be a larger proportion of base than acid, so that the capacity of the buffer will not be exceeded.
>
> Lactic acid is produced in our muscles when we exercise. As the lactic acid enters the bloodstream, it is neutralized by the HCO_3^- ion, producing H_2CO_3. An enzyme then accelerates the breakdown of the excess carbonic acid to carbon dioxide and water, which can be eliminated by breathing. In fact, in addition to the regulating effects of the carbonate buffering system on the pH of blood, the body uses breathing to regulate blood pH. If the pH of the blood decreases too far, an increase in breathing removes CO_2 from the blood through the lungs driving the equilibrium reaction such that $[H_3O^+]$ is lowered. If the blood is too alkaline, a lower breath rate increases CO_2 concentration in the blood, driving the equilibrium reaction the other way, increasing $[H^+]$ and restoring an appropriate pH.

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).

Key Equations

- $pK_a = -\log K_a$
- $pK_b = -\log K_b$
- $pH = pK_a + \log \dfrac{[A^-]}{[HA]}$

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