

BUFFERS

HOW BUFFER SOLUTIONS WORK

In acidic buffers, the weak acid forms an equilibrium mixture, e.g. $\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$. Adding CH_3COO^- pushes the position of equilibrium left, leaving large amounts of both CH_3COOH and CH_3COO^- . The buffer will not work if either of these begins to run out.

If acid is added, the concentration of H^+ ions increases and the position of equilibrium moves left, reducing the concentration of H^+ very close to its original level.

If base is added, the concentration of H^+ ions decreases and the equilibrium moves right, increasing the concentration of H^+ ions very close to its original level.

In basic buffers, the weak base forms an equilibrium mixture, e.g. $\text{NH}_3 + \text{H}^+ \rightleftharpoons \text{NH}_4^+$. Adding NH_4^+ pushes the position of equilibrium left, leaving large amounts of both NH_3 and NH_4^+ . The buffer will not work if either of these begins to run out.

If acid is added, the concentration of H^+ ions increases and the position of equilibrium moves right, reducing the concentration of H^+ very close to its original level.

If base is added, the concentration of H^+ ions decreases and the equilibrium moves left, increasing the concentration of H^+ ions very close to its original level.

CALCULATING THE PH OF ACIDIC BUFFER SOLUTIONS

The concentration of H^+ ions in a buffer solution is calculated like this: $[\text{H}^+] = K_a \times \frac{[\text{acid}]}{[\text{conjugate base}]}$

This assumes that $[\text{acid}]_{\text{equilibrium}} = [\text{acid}]_{\text{initial}}$, which is fair as most of the acid must be undissociated for the buffer to work.

Example 1

What is the pH of a buffer made from adding 0.0085 mol of sodium benzoate to 100 cm^3 of a 0.050 mol dm^{-3} solution of benzoic acid? K_a for benzoic acid = $6.4 \times 10^{-5} \text{ mol dm}^{-3}$

$$[\text{conjugate base}] = \frac{0.0085 \text{ mol}}{0.100 \text{ dm}^3} = 0.085 \text{ mol dm}^{-3}$$

$$[\text{H}^+] = 6.4 \times 10^{-5} \times \frac{0.050}{0.085} \text{ mol dm}^{-3} \text{ and so } \text{pH} = -\log(3.8 \times 10^{-5}) = 4.42$$

EXAM TIP

The pH of a buffer should be close to the $\text{p}K_a$ of whichever acid it is made from. Calculate the $\text{p}K_a$ to check your answer.

Example 2

What is the pH of a buffer made from adding 50 cm^3 of a 0.50 mol dm^{-3} solution of sodium hydroxide to 200 cm^3 of a 0.250 mol dm^{-3} solution of ethanoic acid? K_a for ethanoic acid = $1.8 \times 10^{-5} \text{ mol dm}^{-3}$

$$\text{Moles of NaOH added} = \frac{50}{1000} \times 0.50 = 0.025 \text{ moles of acid added} = \frac{200}{1000} \times 0.25 = 0.050 \text{ Total volume} = 0.050 + 0.200 = 0.250 \text{ dm}^3$$

The NaOH reacts with the acid in a 1:1 ratio to make the conjugate base: $\text{NaOH} + \text{CH}_3\text{COOH} \rightarrow \text{CH}_3\text{COO}^- \text{Na}^+ + \text{H}_2\text{O}$

This means the number of moles of conjugate base = the number of moles of NaOH, and the number of moles of acid is reduced by this same number.

$$[\text{acid}] = \frac{(0.050 - 0.025) \text{ mol}}{0.250 \text{ dm}^3} = 0.100 \text{ mol dm}^{-3} [\text{conjugate base}] = \frac{0.025 \text{ mol}}{0.250 \text{ dm}^3} = 0.100 \text{ mol dm}^{-3}$$

$$[\text{H}^+] = 1.8 \times 10^{-5} \times \frac{0.100}{0.100} = 1.8 \times 10^{-5} \text{ mol dm}^{-3} \text{ and so } \text{pH} = -\log(1.8 \times 10^{-5}) = 4.74$$

EXAM TIP

When $[\text{acid}] = [\text{conjugate base}]$ the pH of the buffer will be identical to the $\text{p}K_a$ of the acid.

Example 3

What ratio of $[\text{HCOOH}]$ to $[\text{HCOO}^-]$ is needed to make a methanoic acid buffer with a pH of 3.50? K_a for methanoic acid = $1.8 \times 10^{-4} \text{ mol dm}^{-3}$

$$[\text{H}^+] = 10^{-3.50} = 3.2 \times 10^{-4} \text{ mol dm}^{-3}$$

$$\text{Rearranging } [\text{H}^+] = K_a \times \frac{[\text{acid}]}{[\text{conjugate base}]} \text{ gives } \frac{[\text{acid}]}{[\text{conjugate base}]} = \frac{[\text{H}^+]}{K_a} = \frac{3.2 \times 10^{-4}}{1.8 \times 10^{-4}} = 1.8$$

You need a ratio of $[\text{HCOOH}]$ to $[\text{HCOO}^-]$ of 1.8 : 1

EXAM TIP

When you have more acid than conjugate base, the pH of the buffer is less than the $\text{p}K_a$ of the acid. With more conjugate base than acid, the pH will be greater than the $\text{p}K_a$ of the acid.

DEFINITION

A buffer minimises changes in pH if a small amount of acid or base is added to it, or if it is diluted by addition of a small amount of water.

MAKING A BUFFER SOLUTION

Acidic buffers are made by combining a weak acid (e.g. ethanoic acid, CH_3COOH) and a soluble salt of that acid, usually a sodium salt (e.g. sodium ethanoate, CH_3COONa) in the same solution.

The soluble salt of the acid is a source of the acid's conjugate base (for ethanoic acid it is the ethanoate ion, CH_3COO^-).

Basic buffers consist of a weak base (e.g. ammonia, NH_3) and a soluble salt of that base (e.g. NH_4Cl) in the same solution.

The soluble salt of the base is a source of the base's conjugate acid (in the example with ammonia it is the ammonium ion, NH_4^+).

APPLICATION OF A BUFFER: CONTROLLING BLOOD PH

Our blood must remain very close to pH 7.40 for our bodies to remain healthy. A change in blood pH by as little as 0.5 units can be fatal.

The main way in which blood pH is controlled is through the carbonic acid-hydrogencarbonate buffer.

When carbon dioxide dissolves in blood plasma it forms a weak acid called carbonic acid: $\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3$

Carbonic acid forms an equilibrium mixture with the conjugate base, the hydrogencarbonate ion: $\text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$

If H^+ ions enter the bloodstream, the pH is prevented from falling below 7.35 (leading to a condition called acidosis) because the excess H^+ ions react with HCO_3^- , forming H_2CO_3 .

If a basic substance enters the bloodstream and removes H^+ ions, the pH is prevented from rising above 7.45 (leading to a condition called alkalosis) because H_2CO_3 dissociates into H^+ and HCO_3^- , replacing the lost H^+ ions.

Blood pH rises ($[\text{H}^+]$ falls)
Equilibrium moves right
 $[\text{H}^+]$ increases, pH restored



Blood pH falls ($[\text{H}^+]$ rises)
Equilibrium moves left
 H^+ removed, pH restored

Many things can cause acids or bases to enter the blood stream, e.g. a chemical that is ingested, injected or administered as a drip

