Buffer solutions (A2)

A buffer solution is a solution in which the pH remains almost unchanged when small amounts of acids or alkalis are added.

There are two types of buffer solutions:

1. Acidic buffer ($pH < 7$)
   - mixture of a weak acid and the Na or K salt of the acid.
2. Alkaline buffer ($pH > 7$)
   - mixture of a weak base and the salt of the weak base.

Acidic buffer

An example is an aqueous mixture of ethanoic acid and sodium ethanoate.

Ethanoic acid is a weak acid. It stays mostly in undissociated form (CH_3COOH) and only give rise to a low concentration of ethanoate ions in solution:

$$\underset{\text{ethanoic acid}}{CH_3COOH_{(aq)}} \rightleftharpoons H^+_{(aq)} + \underset{\text{ethanoate ion.}}{CH_3COO^-_{(aq)}}$$

Sodium ethanoate is fully ionised in aqueous solution:

$$\underset{\text{sodium ethanoate}}{CH_3COONa_{(s)}} + aq \longrightarrow Na^+_{(aq)} + \underset{\text{ethanoate ion}}{CH_3COO^-_{(aq)}}$$

The buffer solution contains relatively high concentrations of both CH_3COOH and CH_3COO^-.

There are reserve supplies of the acid (CH_3COOH) and its conjugate base (CH_3COO^-).

The pH of a buffer solution depends on the ratio of the concentration of the acid and the concentration of its conjugate base.

If this does not change very much, the pH changes very little.

In the buffer solution, ethanoic acid molecules are in equilibrium with hydrogen ions and ethanoate ions:

	$CH_3COOH_{(aq)}$ $\rightleftharpoons$	$CH_3COO^-_{(aq)}$ +	$H^+_{(aq)}$
relative concentration	HIGH	HIGH	LOW

Action of acidic buffer solution

(i) Addition of small amount of acid.

- addition of H^+ ions shifts the position of equilibrium to the left because H^+ ions combine with CH_3COO^- ions to form more CH_3COOH until equilibrium is re-established.
- the large reserve supply of CH_3COO^- ensures that the concentration of CH_3COO^- ions in solution does not change significantly.
- the large reserve supply of CH_3COOH ensures that the concentration of CH_3COOH molecules in solution does not change significantly.
- so the pH remains almost unchanged.

(ii) Addition of small amount of Alkali

- the added OH^- ions combine with H^+ ions to form water.
- this reduces the H^+ ion concentration.
- the position of equilibrium shifts to the right.
- CH_3COOH molecules ionise to form more H^+ and CH_3COO^- ions until equilibrium is re-established.
- the large reserve supply of CH_3COOH ensures that the concentration of CH_3COOH molecules in solution does not change significantly.
- the large reserve supply of CH_3COO^- ensure that the concentration of CH_3COO^- ions in solution does not change significantly.
- so the pH remains almost unchanged.

Note :

No buffer solution can cope with the excessive addition of acids or alkalis.

If very large amounts of acid or alkali are added, the pH will change significantly.

Alkaline buffer

An example is a mixture of aqueous ammonia with ammonium chloride.

Aqueous ammonia is a weak base. There is only a low concentration of ammonium ions in ammonia solution:

$$\underset{\text{ammonia}}{NH_{3(aq)}} + H_2O_{(l)} \rightleftharpoons \underset{\text{ammonium ion}}{NH_4^+{}_{(aq)}} + OH^-_{(aq)}$$

Ammonium chloride is fully ionised in aqueous solution:

$$\underset{\text{ammonium chloride}}{NH_4Cl_{(aq)}} \longrightarrow \underset{\text{ammonium ion.}}{NH_4^+{}_{(aq)}} + Cl^-_{(aq)}$$

The buffer solution contains relatively high concentrations of both NH_3 and NH_4^+.

There are reserve supplies of the base (NH_3) and its conjugate acid (NH_4^+).

In the buffer solution, ammonia molecules are in equilibrium with hydroxide ions and ammonium ions:

	$NH_{3(aq)}$ + $H_2O_{(l)}$ $\rightleftharpoons$	$NH_4^+{}_{(aq)}$	$+ OH^-_{(aq)}$
relative concentration	HIGH	HIGH	LOW

Action of alkaline buffer solution

(i) Addition of small amount of acid.

The added H^+ ions will react with the NH_3 to form NH_4^+

$$NH_{3(aq)} + H^+_{(aq)} \longrightarrow NH_4^+{}_{(aq)}$$

(ii) Addition of small amount of alkali

The added OH^- ions will react with the NH_4^+ to form water and NH_3

$$NH_4^+{}_{(aq)} + OH^-_{(aq)} \longrightarrow NH_{3(aq)} + H_2O_{(l)}$$

Exercise

A mixture of 0.500 mol dm^{-3} aqueous ammonia and 0.500 mol dm^{-3} ammonium chloride acts as a buffer solution.

a. Explain how this buffer solution minimises changes in pH on addition of:

i) dilute hydrochloric acid.

ii) dilute sodium hydroxide.

b. Explain why dilute aqueous ammonia alone will not act as a buffer solution.

Workings.

a. The equilibrium exists in the buffer system is:

$$NH_{3(aq)} + H_2O_{(l)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-_{(aq)}$$

i) When small amount of hydrochloric acid is added, the additional H^+ ions combine with the OH^- ions in the equilibrium mixture to form H_2O.
The position of equilibrium shifts to the right.
Because there are relatively high concentrations of ammonia (base) and ammonium ions (conjugate acid) present compared with the concentration of added H^+ ions, the pH remains almost unchanged.

ii) When small amount of sodium hydroxide is added, the additional OH^- ions shift the position of equilibrium to the left.
More ammonia and water is formed.
Because there are relatively high concentrations of ammonia and ammonium ions present compared with the concentration of added OH^- ions, the pH remains almost unchanged.

b. Ammonia is a weak base. The equilibrium lies well over to the left.
There are not enough NH_4^+ ions in the equilibrium mixture to remove added OH^- ions.

Uses of buffer solutions

Buffers are vital in biological systems.

In humans, the pH of the blood is kept between 7.35 and 7.45.

There are a number of different buffers in the blood:

- hydrogencarbonate ions, HCO_3^-.*
- haemoglobin and plasma proteins.
- dihydrogenphosphate ($H_2PO_4^-$) and hydrogenphosphate (HPO_4^-) ions.

The cells in our body produce carbon dioxide as a product of aerobic respiration (the oxidation of glucose to provide energy).

Carbon dioxide combines with water in the blood to form a solution containing hydrogen ions.

$$CO_2(aq) + H_2O(aq) \rightleftharpoons H^+(aq) + \underbrace{HCO_3^-(aq)}_{\text{hydrogencarbonate ion.}}$$

This reaction is catalysed by enzyme carbonic anhydrase.

When the blood passed through the small blood vassels around our lungs, hydrogencarbonate ions are rapidly converted to carbon dioxide and water.

The carbon dioxide escapes into the lungs.

The production of H^+ ions, if left unchecked, would lower the pH of the blood and cause 'acidosis'. This may disrupt some body functions and eventually lead to coma.

The equilibrium between carbon dioxide and hydrogencarbonate is the most important buffering system in the blood.

If <u>[H^+] increases</u>:

- the position of equilibrium shifts to the left.
- H^+ ions combine with HCO_3^- ions to form carbon dioxide and water until equilibrium is restored.
- this reduces [H^+] in the blood and helps keep the pH constant.

If <u>[H^+] decreases</u>:

- the position of equilibrium shifts to the right.
- some carbon dioxide and water combine to form H^+ and HCO_3^- ions until equilibrium is restored.
- this increases [H^+] in the blood and helps keep the pH constant.

Other uses of buffer solutions

- industrial processes eg. electroplating, the manufacture of dye and in the treatment of leather.
- culturing and selection of bacteria.
- make sure that pH meters record the correct pH.

Exercise

a. One of the buffers in blood plasma is a mixture of dihydrogenphosphate ($H_2PO_4^-$) ions and hydrogenphosphate (HPO_4^{2-}) ions.

(i). Identify the conjugate acid and base in this buffer.

(ii). Write a balanced equation for the equilibrium between these two ions.

b. Some proteins in the blood can act as buffers. The equation below shows a simplified equilibrium equation for this reaction. (Pr = protein)

$$HPr \rightleftharpoons H^+ + Pr^-$$

Explain how this system can act as a buffer to prevent the blood getting too acidic.

Workings

a. (i) conjugate acid = $H_2PO_4^-$

base = HPO_4^{2-}

(ii) $H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+$

b. The addition of hydrogen ions shifts the position of equilibrium to the left.

Pr^- (the deprotonated form of the protein) combines with the extra hydrogen ions to form HPr (the protonated form of the protein) until equilibrium is re-established.

As long as the added H^+ ions are not excessively high, the reserve supply of Pr^- able to convert them to HPr.

The protein buffer system can help to maintain the pH of the blood almost constant.