

3. Buffer Solution

What Is a Buffer Solution?

- The buffer solution is a solution able to maintain its hydrogen ion concentration (pH) with only minor changes in the dilution or addition of a small amount of either acid or base.
- Buffer solutions are used in fermentation, food preservatives, drug delivery, electroplating, printing and the activity of enzymes, and the blood oxygen-carrying capacity needs specific hydrogen ion concentration (pH).
- Solutions of a weak acid and its conjugate base or weak base and its conjugate acid are able to maintain pH and are buffer solutions.

3.1 Types of Buffer Solutions

- The two primary types into which buffer solutions are broadly classified are acidic and alkaline buffers.

3.1.2 Acidic Buffers

- As the name suggests, these solutions are used to maintain acidic environments. Acid buffer has acidic pH and is prepared by mixing a weak acid and its salt with a strong base. An aqueous solution of an equal concentration of acetic acid and sodium acetate has a pH of 4.74.
- The pH of these solutions is below seven.
- These solutions consist of a weak acid and a salt of a weak acid.
- An example of an acidic buffer solution is a mixture of sodium acetate and acetic acid (pH = 4.75).

3.1.3 Alkaline Buffers

These buffer solutions are used to maintain basic conditions. A basic buffer has a basic pH and is prepared by mixing a weak base and its salt with

strong acid. The aqueous solution of an equal concentration of ammonium hydroxide and ammonium chloride has a pH of 9.25.

- The pH of these solutions is above seven.
- They contain a weak base and a salt of the weak base.
- An example of an alkaline buffer solution is a mixture of ammonium hydroxide and ammonium chloride (pH = 9.25).

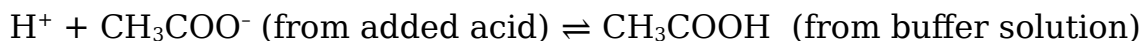
3.2 Mechanism of a Buffering Action

In solution, the salt is completely ionised, and the weak acid is partly ionised.

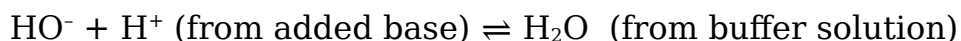
- $\text{CH}_3\text{COONa} \rightleftharpoons \text{Na}^+ + \text{CH}_3\text{COO}^-$
- $\text{CH}_3\text{COOH} \rightleftharpoons \text{H}^+ + \text{CH}_3\text{COO}^-$

3.2.1 On Addition of Acid and Base

1. On addition of acid, the released protons of acid will be removed by the acetate ions to form an acetic acid molecule.



2. On addition of the base, the hydroxide released by the base will be removed by the hydrogen ions to form water.



3.3 Preparation of a Buffer Solution

If the dissociation constant of the acid (pK_a) and of the base (pK_b) is known, a buffer solution can be prepared by controlling the salt-acid or the salt-base ratio.

As discussed earlier, these solutions are prepared by mixing the weak bases with their corresponding conjugate acids or by mixing weak acids with their corresponding conjugate bases.

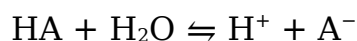
An example of this method of preparing buffer solutions can be given by the preparation of a phosphate buffer by mixing HPO_4^{2-} and H_2PO_4^- . The pH

maintained by this solution is 7.4.

3.4 Handerson-Hasselbalch Equation

3.4.1 Preparation of Acid Buffer

Consider an acid buffer solution containing a weak acid (HA) and its salt (KA) with a strong base (KOH). Weak acid HA ionises, and the equilibrium can be written as



Acid dissociation constant = $K_a = [\text{H}^+][\text{A}^-]/\text{HA}$

Taking the negative log of RHS and LHS,

$$-\log K_a = -\log [\text{H}^+] - \log \left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$$

$$\text{p}K_a = \text{pH} - \log \left(\frac{[\text{salt}]}{[\text{acid}]}\right)$$

$$\text{pH of acid buffer} = \text{p}K_a + ([\text{salt}]/[\text{acid}])$$

The equation is the Henderson-Hasselbalch equation, popularly known as the Henderson equation.

3.4.2 Preparation of a Base Buffer

Consider a base buffer solution containing a weak base (B) and its salt (BA) with strong acid.

pOH, can be derived as above.

- $$\text{pOH of a basic buffer} = \text{p}K_b + \log ([\text{salt}]/[\text{acid}])$$

- **pH of a basic buffer = $pK_a - \log ([\text{salt}]/[\text{acid}])$**

3.4.3 Significance of the Handerson Equation

Handerson equation can be used to

1. Calculate the pH of the buffer prepared from a mixture of salt and weak acid/base.
2. Calculate the pK_a value.
3. Prepare buffer solution of needed pH.

3.4.4 Limitations of Henderson-Hasselbalch Equation

The Henderson-Hasselbalch equation cannot be used for strong acids and strong bases.

Buffering Capacity

The number of millimoles of acid or base to be added to a litre of buffer solution to change the pH by one unit is the buffer capacity of the buffer.

$$B = \text{millimoles } /(\Delta\text{pH})$$

Problems on Buffer Solution

Problem 1: What is the ratio of base to acid when $\text{pH} = pK_a$ in buffer solution? How about when $\text{pH} = PK_a + 1$?

Sol:

$\text{pH} = pK_a$ when the ratio of base to acid is 1 because $\log 1 = 0$

When $\log (\text{base/acid}) = 1$, then the ratio of base to acid is 10:1

Problem 2: What is the pH of a buffered solution of 0.5 M ammonia and 0.5 M ammonium chloride when enough hydrochloric acid corresponds to make 0.15 M HCl?

Sol:

The pK_b of ammonia is 4.75.

$$pK_a = 14 - pK_b = 9.25$$

0.15 M H^+ reacts with 0.15 M ammonia to form 0.15 M more ammonium.

So, the ammonium ion is 0.65 M and 0.35 M remaining ammonia (base).

Using the Henderson-Hasselbalch equation,

$$pK_a - \log ([\text{salt}]/[\text{acid}]) = 9.25 - \log (.65/.35) = 9.25 - .269 = 8.98$$

Problem 3: How many moles of sodium acetate and acetic acid must you use to prepare 1.00 L of a 0.100 mol/L buffer with pH 5.00?

Sol:

$$pH = pK_a + \log([A^-]/[HA])$$

$$5.00 = 4.74 + \log([A^-]/[HA])$$

$$\log([A^-]/[HA]) = 0.26$$

$$[A^-]/[HA] = 10^{0.26} = 1.82$$

$$[A^-] = 1.82[HA]$$

$$\text{Also, } [A^-] + [HA] = 0.100 \text{ mol/L}$$

$$1.82[HA] + [HA] = 0.100 \text{ mol/L}$$

$$2.82[HA] = 0.100 \text{ mol/L}$$

$$[HA] = 0.0355 \text{ mol/L}$$

$$[A^-] = (0.100 - 0.0355) \text{ mol/L} = 0.0645 \text{ mol/L}$$

0.0355 mol of acetic acid and 0.0645 mol of sodium acetate is required to prepare 1 L of the buffer solution.

3.5 pH Maintenance

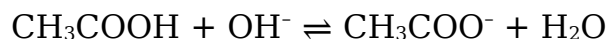
In order to understand how buffer solutions maintain a constant pH, let us consider the example of a buffer solution containing sodium acetate and acetic acid.

In this example, it can be noted that the sodium acetate almost completely undergoes ionisation, whereas the acetic acid is only weakly ionised. These equilibrium reactions can be written as

- $\text{CH}_3\text{COOH} \rightleftharpoons \text{H}^+ + \text{CH}_3\text{COO}^-$
- $\text{CH}_3\text{COONa} \rightleftharpoons \text{Na}^+ + \text{CH}_3\text{COO}^-$

When strong acids are added, the H^+ ions combine with the CH_3COO^- ions to give a weakly ionised acetic acid, resulting in a negligible change in the pH of the environment.

When strongly alkaline substances are introduced to this buffer solution, the hydroxide ions react with the acids which are free in the solution to yield water molecules, as shown in the reaction given below.



Therefore, the hydroxide ions react with the acid to form water, and the pH remains the same.

3.5.1 Uses of Buffer Solutions

- There exist a few alternate names that are used to refer to buffer solutions, such as pH buffers or hydrogen ion buffers.
- An example of the use of buffers in pH regulation is the use of bicarbonate and carbonic acid buffer system in order to regulate the pH of animal blood.
- Buffer solutions are also used to maintain an optimum pH for enzyme activity in many organisms.
- The absence of these buffers may lead to the slowing of the enzyme action, loss in enzyme properties, or even denaturing of the enzymes. This denaturation process can even permanently deactivate the catalytic action of the enzymes.