Buffer solutions and preparation of acidic and basic buffers.

Buffer solution:A solution which resist a change in its pH by addition of small amount of an acid or a base is called buffer solution.

Preparation of acidic buffer:It is prepared by mixing equimolar solutions of weak acid and its salt with a strong base e.g. **sodium acetate and acetic acid**.

Preparation of basic buffer: It is prepared by mixing equimolar solutions of weak base and its salt with strong acid e.g. **NH₄OH ammonium hydroxide and NH₄Cl, ammonium chloride.**

Mechanism of acidic buffer:

An acidic buffer is prepared by mixing equimolar amounts of weak acid and a slat of weak acid and strong base. Eg. consider an acidic buffer obtained by mixing acetic acid and sodium acetate

CH₃COOH   CH₃COO⁻ + H⁺

CH₃COONaH ⟶   CH₃COO⁻ + Na⁺
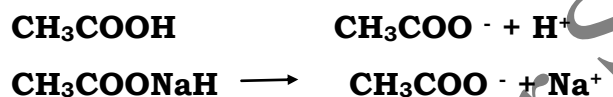
Acetic acid, being a weak acid, ionizes to a less extent while sodium acetate , being a strong electrolyte, ionizes completely. When a small amount of HCl is added to it, the added H⁺ ions combines with acetate ions to form acetic acid molecules. Thus the pH of the buffer remains unchanged.

HCl → H⁺ + Cl⁻
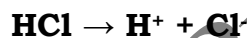
CH₃COO⁻ + H⁺ → CH₃COOH

Thus phenomenon is called reverse basicity due to acetate ions. On addition of small amount of strong base like NaOH, the following reactions occur

 NaOH → Na⁺ + OH⁻

 H⁺ + OH⁻ → H₂O

CH₃COOH   CH₃COO⁻ + H⁺

CH₃COOH + OH⁻   CH₃COO⁻ + H₂O

The combination of H^+ of CH_3COOH with OH^- disturbs the equilibrium position of acetic acid. Therefore to maintain its Ka constant it dissociates to a greater extent. Thus the OH^- ions combine with acetic acid thereby maintaining the pH of the buffer. This phenomenon is called reverse acidity due to acetic acid.
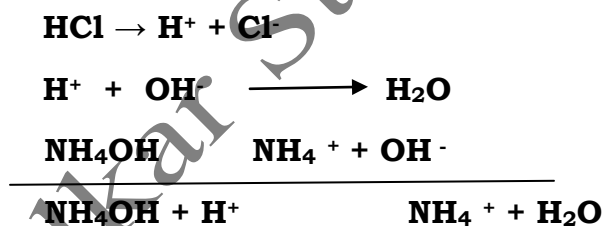
Mechanism of basic buffer:

Basic buffer is prepared by mixing equimolar amount of weak base and a salt of a weak base and strong acid. Eg. consider the basic buffer obtained by mixing ammonium hydroxide and ammonium chloride

NH₄OH   NH₄ ⁺ + OH ⁻

NH₄Cl   →   NH₄ ⁺ + Cl ⁻

NH₄OH, being a weak base, ionizes to a less extent while NH₄Cl being a strong electrolyte ionizes almost completely.

When a small amount of strong acid like HCl is added, the H^+ ions combines with OH^- to form un-dissociated water molecules. However, to maintain Ka constant, NH₄OH dissociates more thus removing H^+ ions.

$$HCl \rightarrow H^+ + Cl^-$$
$$H^+ + OH^- \longrightarrow H_2O$$
$$NH_4OH \qquad NH_4^+ + OH^-$$
$$\overline{}$$
$$NH_4OH + H^+ \qquad NH_4^+ + H_2O$$

On addition of a small amount of a strong base, the following reaction occurs.

$$NaOH \rightarrow Na^+ + OH^-$$
$$NH_4^+ + OH^- \rightarrow NH_4OH$$

Thus the OH^- ions are removed by NH_4^+ ions thereby maintaining the pH constant. This is called reserved acidity due to NH_4^+ ions.

Properties of buffer solutions.

A buffer solution has following properties

i) Its pH remains constant even when small amounts of acids or bases are added.

ii) Its pH remains unaffected even on dilution.

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**iii)** Its pH remains unchanged even when the solution is kept for long

time.

Applications of buffer solutions.

i) Buffers are used for biological studies and control of manufacturing

processes based on biological reactions such as brewing industry,

manufacture of fungal anti-biotics etc.

ii) Buffer solutions of NH_4OH + NH_4Cl is used in qualitative analysis to
precipitate radicals of group IIIA in the pH range 8-10.

iii) Sodium benzoate acts as a buffer in the preservation of jams and

jellies.

iv) Buffer solutions in human blood maintain the pH within the range of 7.35 to

7.45.Any change of pH in blood from 7.3 to 7 may prove fatal to the person.

v) Penicillin preparations are stabilised by addition of sodium acetate which

acts as a buffer.

vi) Citric acid when added to milk of magnesia forms magnesium citrate

which stabilizes it by acting as a buffer.

Henderson's equation for acidic buffer

Consider an acidic buffer obtained by mixing weak acid **HA** and salt of weak acid
and strong base **BA**.

The acid **HA** being weak dissociates slightly while the salt **BA** dissociates
completely

$$HA \Longleftrightarrow H^+ + A^- \quad \text{------I}$$

$$BA \longrightarrow B^+ + A^-$$
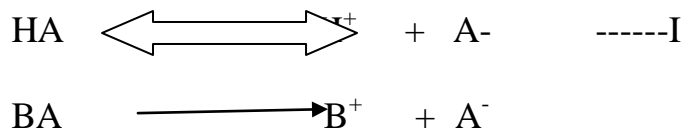
By applying law of mass action to equation I, we get

$$K_a = \frac{[H^+][A^-]}{} \quad \text{---------------II}$$

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[HA]

On rearranging equation **II**, we get

$$[H^+] = \frac{K_a \cdot [HA]}{[A^-]} \quad\quad \text{--------------- III}$$

$[A^-]$ = [salt] because the maximum number of A^- ions are obtained from the salt BA

[HA] = concentration of acid

Taking log on both sides of equation III, we get

$$\log_{10}[H^+] = \log_{10}K_a + \log_{10}\frac{[acid]}{[salt]}$$

Introducing negative sign on both sides, we get

$$-\log_{10}[H^+] = -\log_{10}K_a - \log_{10}\frac{[acid]}{[salt]}$$

But pH = $-\log_{10}[H^+]$ and $pK_a = -\log_{10}K_a$
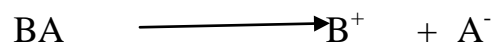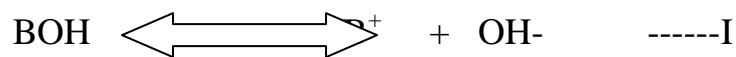
$$\text{Thus } pH = pK_a - \log_{10}\frac{[acid]}{[salt]}$$

$$\mathbf{pH = pK_a + \log_{10}\frac{[salt]}{[acid]}} \quad\quad \text{-----------IV}$$

Equation IV is called Henderson's equation for acidic buffer.

Henderson's equation for basic buffer.

Consider a basic buffer obtained by mixing weak base **BOH** and a salt of weak base and strong acid **BA**.
The base **BOH** being weak, dissociates slightly while the salt **BA** dissociates completely

$$\text{BOH} \iff B^+ + OH^- \quad\quad \text{------I}$$

$$\text{BA} \longrightarrow B^+ + A^-$$

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By applying law of mass action to equation I, we get

$$K_b = \frac{[B^+][OH^-]}{[BOH]} \qquad \text{----------------II}$$

On rearranging equation II, we get

$$[OH^-] = \frac{K_b \cdot [OH^-]}{[B^+]} \qquad \text{--------------- III}$$

$[B^+]$ = [salt] because the maximum number of B^+ ions are obtained from

the salt BA

[BOH] = concentration of base.

Taking log on both sides of equation III, we get

$$\log_{10}[OH^-] = \log_{10}K_b + \log_{10}\frac{[base]}{[salt]}$$

Introducing negative sign on both sides, we get

$$-\log_{10}[OH-] = -\log_{10}K_b - \log_{10}\frac{[base]}{[salt]}$$

But $pOH = -\log_{10}[OH^-]$ and $pK_b = -\log_{10}K_b$

Thus $pOH = pK_b - \log_{10}\dfrac{[base]}{[salt]}$

$$\mathbf{pOH = pK_b + \log_{10}\frac{[salt]}{[base]}} \qquad \text{-----------IV}$$

But $pH = 14 - pOH$

$$= pK_w - pK_b - \log_{10}\mathbf{\frac{[salt]}{[base]}} \qquad \text{----------------V}$$

Equation V is called Henderson's equation for basic buffer.

Buffer capacity: The magnitude of the buffer action is determined by its capacity. It is defined as the amount of strong acid or strong base required to produce a change in the pH of the buffer by one unit.

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where db is the small amount of acid or base added to produce a change in pH equal to dpH. An indication of the buffer capacity of any acid base system can thus be obtained directly from pH neutralization curve. It is a plot of pH against volume of NaOH added.

Volume of base added $\rightarrow$
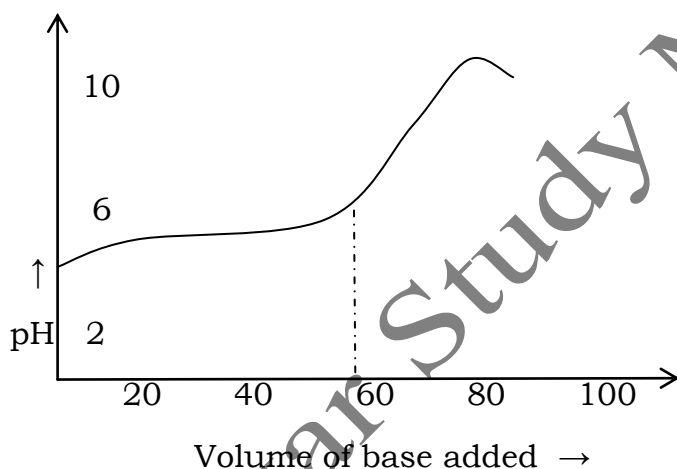
Consider the neutralization of 0.1M CH_3COOH with 0.1M NaOH. Initially , the pH is low. With successive addition of 1 ml NaOH, the pH increases. At the same time, the amount of salt formed also increases. At the equivalence point, the pH suddenly rises. At that point, [salt]=[acid] and hence according to Henderson's equation

pH = pKa for acid buffer

pOH = pKb for basic buffer

At this point, the slope d(pH)/db is the smallest and hence the buffer capacity is maximum. However, if the ratio of acid to salt is increased or decreased ten fold, ie. 10 :1 or 12 : 1 then according to Henderson's equation of acid buffer,

pH = pKa + log$_{10}$([salt]/[acid]), the pH ranges to pKa+1 or pKa -1 respectively. If the pH lies within the range pKa$\pm$1 the buffer capacity is appreciable, but outside this range it falls off to such an extent as to be of no practical use.

It follows therefore that a given acid or base buffer has useful buffer section over the range, pH = pKa $\pm$ 1 for acid buffer and pOH = pKb $\pm$ 1 for basic buffer

To prepare an acidic or basic buffer of desired pH, the acid or base selected should have pKa or pKb values near to the required pH. The pH of a buffer solution is determined by the ratio of concentrations of the salt and acid and not by their amounts. However the buffer capacity at a given pH does depend upon the actual concentration.

Reserved acidity: The property of a buffer to remove the added OH$^-$ ions from its solution with the help of an acid so as to maintain its pH value constant is called reserved acidity.

Reserved basicity: The property of a buffer to remove the added H$^+$ ions from its solution with the help of an base so as to maintain its pH value constant is called reserved basicity.

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