BUFFER SOLUTION

A buffer solution is one that remains stable in terms of pH, even when a small quantity of strong acid or base (less than 1%) is introduced, or when the solution is diluted. The ability of a solution to maintain its pH stability is referred to as buffer capacity, and the process by which a buffer solution achieves this is known as buffer action.

Types of Buffer Solutions

(A) Simple buffer solution
(B) Mixed buffer solution

(A) Simple Buffer Solution

A salt of weak acid and weak base in water e.g., CH_3COONH_4, $HCOONH_4$, AgCN, NH_4CN.

Buffer Action of Simple Buffer Solution

Consider a simple buffer solution of CH_3COONH_4, since it is a salt will dissociate completely.

$$CH_3COONH_4 \longrightarrow CH_3COO^- + NH_4^+$$

If a strong acid such as HCl is added then

$$HCl \longrightarrow H^+ + Cl^-$$

The H^+ ions from the added acid (HCl) combine with CH_3COO^- ions to form CH_3COOH, which is a weak acid so will not further ionized.

Thus, there is no rise in H^+ ion concentration and the pH remain constant.

$$CH_3COO^- + H^+ \leftrightarrow CH_3COOH \text{ (Weak acid)}$$

If a strong base is added as NaOH

$$NaOH \longrightarrow Na^+ + OH^-$$

$$NH_4^+ + OH^- \leftrightarrow NH_4(OH) \text{ (Weak base)}$$

Thus, change in OH^- ion concentration is resisted by $NH^+{}_4$ ions by forming NH_4OH which is a weak base. So it will not further ionized and pH remains constant.

(B) Mixed Buffer Solutions

(a) Acidic Buffer

An acidic buffer solution comprises a combination of a weak acid solution and its corresponding salt with a strong base. A well-known example is the blend of an acetic acid solution and its salt with a strong base, such as CH_3COONa.

Other example :

$$HCN + KCN, (H_2CO_3 + NaHCO_3) \longrightarrow \text{blood}$$

$$CH_3COOH \leftrightarrow CH_3COO^- + H^+ \text{ (Weakly ionised)}$$

$$CH_3COONa \longrightarrow CH_3COO^- + Na^+ \text{ (Highly ionised)}$$

Upon adding a few drops of an acid like HCl to the solution, the H^+ ions from the added acid (HCl) combine with the CH_3COO^- ions to produce CH_3COOH. As a result, the concentration of H+ ions do not increase, and the pH of the solution remains constant. Conversely, when a few drops of a base like

NaOH are introduced, the OH^- ions from the added base react with acetic acid to yield non-ionized water and acetate ions.

$$CH_3COOH + OH^- \leftrightarrow H_2O + CH_3COO^-.$$

Thus there is no increase in OH^- ion concentration and hence the pH of the solution remains constant.
pH of an Acidic Buffer Solution (Henderson Equation)
Consider a buffer mixture (acidic buffer)

$$HA + NaA\ (CH_3COOH + CH_3COONa)$$

where $A = CH_3COO, A^- = CH_3COO^-$

$$HA \leftrightarrow H^+ + A^-$$

$$NaA \longrightarrow Na^+ + A^-$$

Applying law of mass action to dissociation equilibrium of HA

$$K_a = \frac{[H^+][A^-]}{[HA]}; \text{ so } [H^+] = \frac{K_a[HA]}{[A^-]}$$

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

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

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

$[A^-]$ = Initial concentration of salt as it is mainly coming from salt.
[HA] = Initial concentration of the acid.

$$pH = pK_a + \log \frac{[Salt]}{[Acid]}$$

(It is known as Henderson-Hasselbalch equation.)

(b) Basic Buffer

A fundamental buffer solution comprises a blend of a weak base and its salt with a strong acid. One of the most widely recognized examples is the combination of NH_4OH and NH_4Cl.

$$NH_4OH \leftrightarrow NH_4^+ + OH^- \quad \text{(Weakly ionised)}$$

$$NH_4Cl \longrightarrow NH_4^+ + Cl^- \quad \text{(Highly ionised)}$$

When a few drops of a base (NaOH) are added, the OH^- ions from NaOH combine with NH_4^+ ions to form feebly ionised NH_4OH thus there is no rise in the concentration of OH^-ions and hence the pH value remains constant.

$$NH_4^+ + OH^- \longrightarrow NH_4OH$$

If a few drops of an acid (HCl) are added the H^+ from acid combine with NH_4OH to form H_2O and NH_4^+ ions.

$$NH_4OH + H^+ \longrightarrow NH_4^+ + H_2O$$

Thus the addition of acid does not increase the H^+ ion concentration and hence pH remains unchanged.

(C) Salt Buffer

This is a salt solution that functions as a buffer due to its composition. Specifically, it is a salt derived from a weak acid and a weak base.

Take, for instance, the example of CH_3COONH_4, which undergoes an equilibrium reaction represented as:

$$CH_3COONH_4 \rightleftharpoons NH_4^+ + CH_3COO^-$$

In the presence of an acid, the acid reacts with CH_3COO^-, leading to the formation of CH_3COOH. Conversely, when a base is introduced, it reacts with NH_4^+, resulting in the production of NH_4OH. The inherent properties of this salt allow it to resist drastic changes in pH, making it an effective buffer solution.

Buffer Capacity

Buffer capacity indicates a buffer's ability to withstand pH changes. The greater the buffer capacity, the less the pH will change, making the buffer more effective.

$$\text{Buffer capacity} = \frac{\textbf{No.of mole of acid or bases added per litre}}{\textbf{change in pH}}$$

Buffer capacity reflects a buffer's resistance to pH changes. The greater the buffer capacity, the smaller the pH shift, resulting in a more efficient buffer.

Acid Base Titration

Indicator

An indicator is a substance that undergoes a color change at the endpoint or neutral point of an acid-base titration. These substances used to signify the neutral point in an acid-base titration are referred to as indicators.

At End Point: $N_1V_1 = N_2V_2$

Indicators are of two types

(i) Acidic

(ii) Basic

(i) Phenolphthalein (HPh):

HPh is acid indicator. It ionizes in water to give colourless H^+ ions and pink coloured anions.

$$\underset{}{HPh} \leftrightarrow \underset{\text{Colourless}}{H^+} + \underset{\text{Pink}}{Ph^-}$$

If $[Hph] > [Ph^-] \longrightarrow \text{Colourless}$

$$[Hph] < [Ph^-] \longrightarrow \text{Pink}$$

In an acidic environment, the dissociation of HPh is nearly nonexistent, resulting in no color change. This is because the presence of the common ion H^+ in the acid strongly hinders the ionization of HPh, causing the solution to remain colorless.

$$HPh \leftrightarrow H^+ + Ph^-$$

$$HCl \longrightarrow H^+ + Cl^-$$

In alkaline medium, the OH^- ions combine with H^+ ions of the indicator to form water.

$$HPh\ H^+ + Ph^-$$

$$NaOH \longrightarrow Na^+ + OH^-$$

Thus Ph^- ions give pink colour in alkaline medium.

(ii) Methyl Orange (MeOH):

It is a weak base and dissociates as:

$$\underset{\text{Yellow}}{\mathrm{MeOH}} \leftrightarrow \underset{\text{Red}}{\mathrm{Me^{+}}} + \underset{\text{Colourless}}{\mathrm{OH^{-}}}$$

If $[\mathrm{MeOH}] > [\mathrm{Me^{+}}] \longrightarrow \text{Yellow}$

$[\mathrm{MeOH}] < [\mathrm{Me^{+}}] \longrightarrow \text{Red}$

MeOH is not dissociated in alkaline medium due to the presence of common ions OH^{-} and the solution remains yellow.

$$\mathrm{MeOH} \leftrightarrow \mathrm{Me^{+}} + \mathrm{OH^{-}}$$

$$\mathrm{NaOH} \longrightarrow \mathrm{Na^{+}} + \mathrm{OH^{-}}$$

In acidic medium OH^{-} combine with H^{+} thus increase the ionisation of MeOH. Hence yellow colour of solution change to red colour.

$$\mathrm{MeOH} \leftrightarrow \mathrm{Me^{+}} + \mathrm{OH^{-}}$$

$$\mathrm{HCl} \longrightarrow \mathrm{H^{+}} + \mathrm{Cl^{-}}$$

Modern Quinonoid Theory

According to this theory,

(i) An acid-base indicator comprises a dynamic equilibrium mixture of two distinct tautomeric forms, typically one being benzenoid, and the other quinonoid.

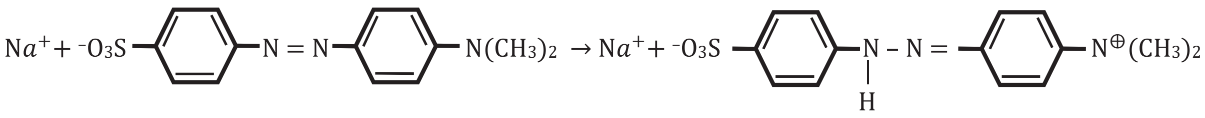
(ii) These two forms exhibit dissimilar colors.

(iii) One of these forms predominates in an acidic solution, while the other is prevalent in an alkaline solution.

(iv) Shifts in pH lead to the transformation of the benzenoid form into the quinonoid form, and vice versa, thereby resulting in a change in color.

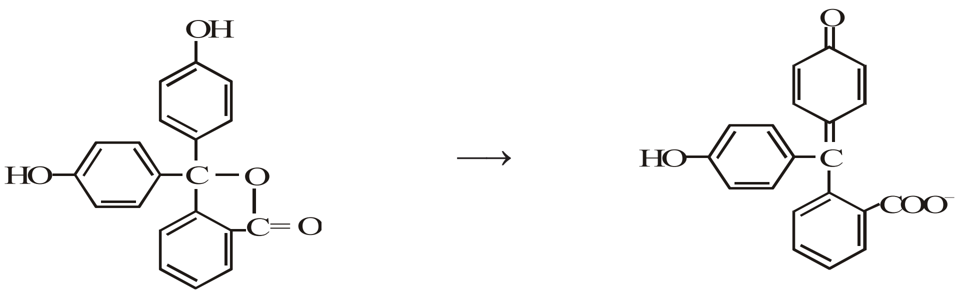
Ex.

(a) For methyl orange



Yellow benzenoid form (in bases) Red quinonoid form (in acids)

(b) For Phenolphthalein



Colourless benzenoid form (in Acid) Red quinonoid form (in Alkali)

Theories Of Indicators

According to this theory

(i) Indicators are organic, aromatic compounds with characteristics of weak acids or weak bases.

(ii) The alteration in color is a consequence of the ionization of the acid-base indicator. The un-ionized form displays a distinct color from the ionized form.

(iii) Each indicator exhibits color modifications in contrasting environments as a result of the conversion of the non-ionized portion into the ionized form.
For example phenolphthalein shows pink colour in basic medium and methyl orange shows red colour in acidic medium.

Note: Redox reactions do not employ indicators since they proceed rapidly. Additionally, indicators are not employed in colored solutions.

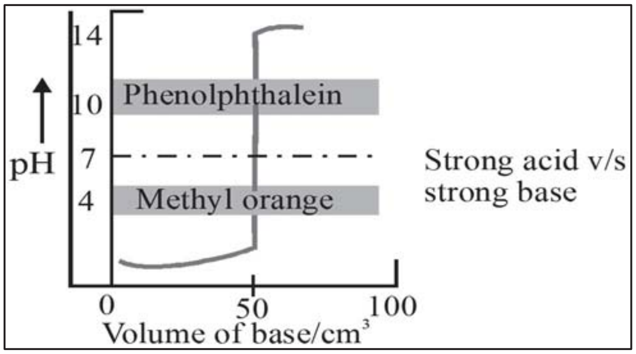
Titration Of Strong Acid Against Strong Alkali

The graph (A) shows how pH changes during the titration of 50 cm3 of 0.1 M HCl with 0.1 M NaOH.

$$\text{NaOH (aq)} + \text{HCl (aq)} \longrightarrow \text{NaCl (aq)} + H_2O\ (\ell)$$

Initially, the pH of a 0.1 M HCl solution is 1. As alkali is introduced, the pH undergoes gradual changes at first. However, at the equivalence point, the pH shifts rapidly from approximately 3.5 to 10. By performing simple calculations, it can be determined that the pH of the solution is 3.7 after the addition of 49.8 cm^3 of 0.1 M NaOH solution. Following the addition of 50.1 cm^3 of NaOH solution, the pH abruptly rises to 10. Consequently, any indicator with a pH range spanning from 3.5 to 10 can effectively indicate the equivalence point. This means that indicators such as phenolphthalein, methyl orange, or bromothymol blue can all be utilized.

(A)



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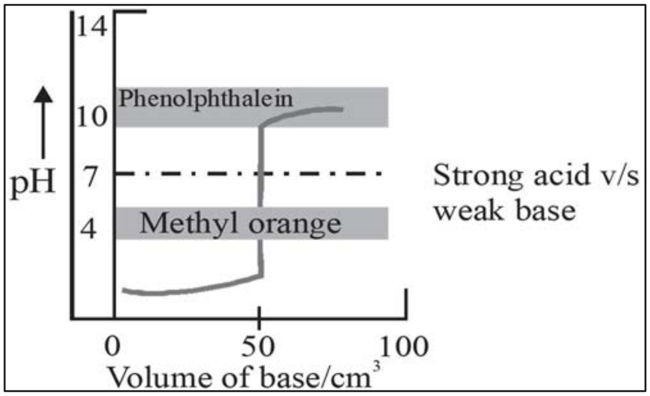
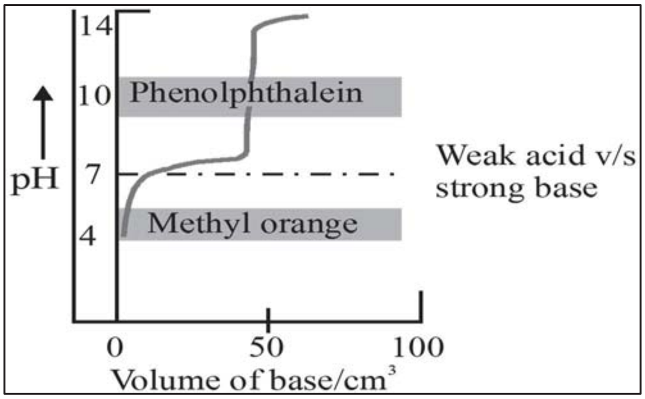
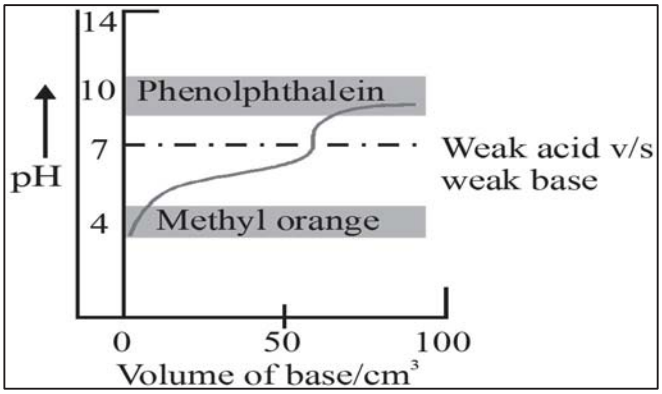


(C)



(D)



Titration Of Strong Acid Against Weak Alkali

The graph (B) shows how pH changes during titration of 50 cm^3 of 0.1 M HCl with 0.1 M NH_3.

$$HCl\ (aq) + NH_4OH\ (aq) \longrightarrow NH_4Cl\ (aq) + H_2O\ (\ell)$$

In this scenario, the pH experiences a swift transition from 3.5 to 7.0 upon reaching the equivalence point. Appropriate indicators for this type of titration include methyl orange, methyl red, and bromo cresol green. Phenolphthalein, on the other hand, is not well-suited as its pH range falls outside the steep section of the curve.

Titration Of Weak Acid Against Strong Base

The graph (C) shows how pH changes during titration of 50 cm^3 of 0.1 M CH_3COOH with 0.1 M NaOH.

$$CH_3COOH\ (aq) + NaOH\ (aq) \longrightarrow CH_3COONa\ (aq) + H_2O\ (\lambda)$$

The vertical segment of this titration curve spans the pH range from 7 to 10.6. Phenolphthalein serves as an appropriate indicator for this titration. In contrast, methyl orange is unsuitable for this titration because its pH range aligns with the flat section of the curve.

Titration Of Weak Acid Against Weak Base

The graph (D) represents the titration curve obtained for titration of 50 cm^3 of 0.1 M CH_3COOH with 0.1 M NH_3.

$$CH_3COOH\ (aq) + NH_4OH\ (aq) \longrightarrow CH_3COONH_4\ (aq) + H_2O\ (\lambda)$$

In this specific titration, there is no distinct or abrupt rise in pH at the equivalence point. Consequently, no indicator is appropriate for this kind of titration.

Indicator	pH range	Colour change	pK_a Neutral colour pH
Methyl orange	3.2 – 4.5	Pink to yellow	3.7
Methyl red	4.4 – 6.5	Red to yellow	5.1
Litmus	5.5 – 7.5	Red to blue	7.0
Phenol red	6.8 – 8.4	Yellow to red	7.8
Phenolphthalein	8.3 – 10.5	Colourless to pink	9.6

Indicator Constant

The equilibrium represented by $HIn \rightleftharpoons H^+ + In^-$ is characterized by the indicator constant, denoted as K_{In}. This constant is determined by the expression $K_{In} = \frac{([H^+][In^-])}{([HIn])}$.

Similar to other constants, the value of K_{In} is contingent upon the prevailing temperature. In this equation, $[H^+]$ signifies the concentration of hydrogen ions, $[In^-]$ denotes the concentration of the indicator ion, and $[H_{In}]$ represents the concentration of the uncharged indicator molecule. The indicator constant is a crucial factor in understanding the equilibrium dynamics of the reaction, with its value adjusting in response to temperature variations.

Indicator Range

The equilibrium expression $H^+ = K_{In}\frac{[HIn]}{[In^-]}$ forms the basis for understanding the pH of a solution given by the equation, $pH = pK_{In} + \log\frac{[In^-]}{[HIn]}$.

This equation illuminates the intricate relationship between the concentration of hydrogen ions, uncharged indicator molecules ([HIn]), and indicator ions ($[In^-]$), with the indicator constant (K_{In}) playing a crucial role.

The vibrancy of a colored solution is generally contingent upon the presence of color-imparting species. In the case of a solution harboring two colored species, namely I^- and HIn, the resultant color is determined by the relative proportions of these two entities. Typically, the solution adopts the distinctive color characteristics of In^-, with its concentration being approximately 10 times higher than that of HIn, thus influencing the overall color intensity.

At a specific pH value of $pK_{In} - 1$

The ratio of $\frac{[In^-]}{[HIn]}$ in the solution equates to $\frac{1}{10}$.

This condition signifies a critical point where the percentage ionization of the indicator is calculated as: $\frac{[In^-]}{[In^- + HIn]} \times 100$, resulting in 9.1%.

Conversely,

At $pH = pK_{In} + 1$

The percentage ionization of the indicator surges to 91.1%. Within the pH range spanning from pK_{In} - 1 to $pK_{In} + 1$, a transition of color takes place, indicating a crucial range where visual changes in the equilibrium between the colored species become apparent.

Selection of Indicator

Same the equivalence point in an acid-base titration, there is a pronounced and rapid change in the pH of the solution. The extent of this sharp pH transition is influenced by the specific acid-base pair undergoing titration. In the case of titrations involving weak acids or weak bases, the resulting salt undergoes hydrolysis, leading to a final pH value either greater than 7 or less than 7. Therefore, the choice of an appropriate indicator becomes crucial, as it should exhibit a color change in close proximity to the pH of the solution at the equivalence point.

The criteria for selecting an indicator are as follows:

1.The selection should ensure that the sharp segment of the titration curve near the equivalence point spans a range of pH values at least as wide as the pH transition range of the indicator.

2.The pH transition range of the indicator should align with the steep portion of the titration curve.

Acid-base indicators, exemplified by various substances, exhibit distinct color changes depending on their acid or base forms at specific pH values:

Phenolphthalein:

Acid Form: Colorless ; Acid Form at pH: 8.3
Base Form: Pink ; Base Form at pH: 10.0

Malachite Green:

Acid Form: Yellow ; Acid Form at pH: 0.0
Base Form: Green ; Base Form at pH: 2.0

Alizarin Blues:

Acid Form: Green ; Acid Form at pH: 11.0
Base Form: Blue ; Base Form at pH: 13.0

Methyl Orange:

Acid Form: Red ; Acid Form at pH: 3.1
Base Form: Yellow ; Base Form at pH: 4.4

Litmus:

Acid Form: Red ; Acid Form at pH: 4.5
Base Form: Blue ; Base Form at pH: 8.3

It's important to note that phenolphthalein is not suitable as an indicator in titrations involving a strong acid and a weak base. The careful consideration of these factors ensures the optimal selection of an indicator for an acid-base titration, aligning with the specific characteristics of the titrated substances.