**2) Redox titration**

The titration in which one reactant is oxidized and the other is reduced is known as redox titration.

$$2KMnO_4 + 10FeSO_4 + 8\,H_2SO_4 \longrightarrow K_2SO_4 + 5Fe_2(SO_4)_3 + 2\,MnSO_4 + 8\,H_2O$$

In this oxidation reduction reaction, $KMnO_4$ is oxidizing agent and $FeSO_4$ is reducing agent.

**3) Precipitation titration**

The precipitation titration involves the formation of an insoluble precipitate when the reactants are mixed together.

$$AgNO_3 + NaCl \longrightarrow AgCl\downarrow + NaNO_3$$

**4) Complexometric titration**

The titration in which the stable, soluble and stoichiometric complex is formed by the reaction between a metal ion and the complexing agent.

e.g. The reaction between $Zn^{2+}$ ion and sodium salt of ethylenediamine tetra acetic acid (EDTA) forms complex with $Zn^{2+}$ ion.

$$\underset{\text{Sodium Salt of EDTA}}{Zn^{2+} + Na_2H_2\,EDTA} \longrightarrow \underset{\text{Zn – Complex}}{[Zn - EDTA]^{2-}} + 2\,Na^+ + 2H^+$$

**5) Diazotization titration**

The titration in which simple aromatic amino compound determined quantitatively by finding the volume of standard sodium nitrate solution required to convert it into diazonium salt.

$$NaNO_2 + HCl \longrightarrow NaCl + HNO_2$$

$$Ar\,NH_2.\,HCl + HONO \longrightarrow ArN_2^+ + 2\,H_2O$$

**2.10 Acid – base or neutralization titration**

The reaction between acids and bases are termed as neutralization reaction.

e.g. $HCl + NaOH \longrightarrow NaCl + H_2O$

The determination of strength of acid solution by using base of a known strength is called acidimetry, whereas the strength of base solution determine by titration with acid of known strength is termed as alkalimetry.

The indicator used in acid – base titration to show end point of titration. The indicators have one color in acid solution while different color in alkaline solution. At equivalence point, the pH of the solution could be equal to, greater than or less than 7, depending on relative strength of the acid and alkali.

**Types of acid-base titration**

The acid – base titration classify as bellow.

i) Titration of strong acid with strong base. e.g. Titration of HCl with NaOH.
ii) Titration of strong acid with weak base. e.g. Titration of HCl with $NH_4OH$.
iii) Titration of weak acid with strong base. e.g. Titration of $CH_3COOH$ with NaOH.
iv) Titration of weak acid with weak base. e.g. Titration of $CH_3COOH$ with $NH_4OH$.

**pH variation during acid base titration.**

In acid base titration, if both the acid and alkali are strong electrolyte, the resulting solution would be neutral and pH = 7 at equivalence point. On the other hand, if acid or base or both acid and base are weak, the salt formed hydrolyzed to a certain extent and the resulting solution would be slightly acidic or alkaline at the equivalence point and pH will not be seven.

In the acid-base titration, there is reaction between acid and base. The acid-base titration can be divided into two categories

i) Acidimetry ii) Alkalimetry

In acidimetry, a known volume of an alkaline substance or base taken in a conical flask titrated with standard solution of acid taken in a burette. If both acid and alkali are strong electrolyte the solution is neutral and pH = 7 at equivalent point. If the acid or base or both acid and base are weak electrolytes, the salt formed hydrolyzed and solution would be slightly acidic or alkaline at the equivalent point and pH will not be seven.

In alkalimetry, a known volume of acidic substance taken in a conical flask titrated with standard solution of an alkali or base taken in a burette. Similarly in acidimetry, alkalimetry have pH equal to, less than or greater than 7, depends on strong or weak electrolytic nature of acid or base.

When base taken in a burette, all the $H^+$ ions in acid taken in a conical flask consumed by base at the equivalence point. After that concentration of $HO^-$ increases due to excess addition of base and the pH suddenly rises. The pH range near the equivalence point is different for a different type of acid-base titration depends on electrolytic nature of acid or base (Fig 2.1) as given in Table 2.1.

**Table 2.1: Types of acid- base titrations**

| Types of titration | pH range |
|---|---|
| Strong acid with strong base | 3.3 to 10.5 |
| Strong acid with weak base | 3.5 to 7.5 |
| Weak acid with strong base | 6.5 to 7.5 |
| Weak acid with weak base | 6.5 to 7.5 |

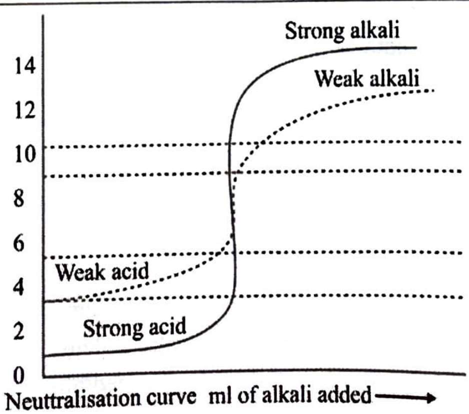



**Fig. 2.1: Variation of pH during Acid-base titration**

## 2.11 Acid-base or neutralization indicators

In acid-base titration indicator is used to show the end point of titration. The indicators used in acid-base titration have one color in acidic solution while different colour in alkaline solution. At end point, indicator shows sharp change in colour. The colour change of an acid-base indicator is not sudden but takes place within a small range of pH. The pH range of solution in which indicator shows change in colour, this range is known as pH range of an indicator.

The pH range of various acid-base indicators are given bellow (Table 2.2)

**Table 2.2: pH range of various acid - base indicators**

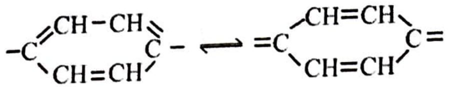
| Indicator | pH range | Colour in Acid | Colour in Alkali |
|---|---|---|---|
| Phenolphthalein | 8.2 – 10.0 | Colourless | Pink |
| Methyl red | 4.8 – 6.0 | Yellow | Red |
| Methyl Orange | 3.2 – 4.4 | Red | Yellow |
| Litmus | 4.5 – 8.3 | Red | Blue |
| Thymol blue | 1.2 – 2.8 | Red | Yellow |
| Bromocresol Green | 3.8 – 5.4 | Yellow | Blue |
| Bromothymol blue | 6.0 – 7.6 | Yellow | Blue |
| Phenol Red | 6.8 – 8.4 | Yellow | Red |
| Alizarin Yellow | 10.0 – 12.0 | Yellow | Orange Red |
| Cresol Purple | 11.2 to 2.8 | Red | Yellow |
| Congo Red | 3.0 – 5.0 | Violet | Red |

## 2.12 Modern theory (Quinonoid theory) of acid-base indicator

An indicator is a substance which is used to indicate the end point of titration, in acid-base titration, indicator used generally is weak acid or weak base. An indicator changes its color at different pH. The modern theory (Quinonoid theory) has been proposed to explain the change of color of acid-base indicator with change in pH.

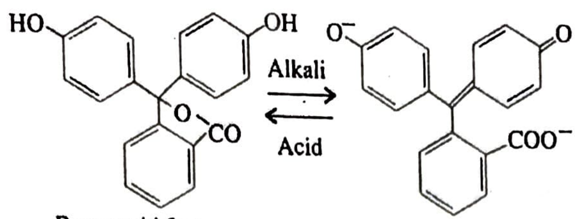
According to modern theory,

a) The acid-base indicator exists in two tautomeric forms, one benzenoid form and other quinonoid form. These both forms are in equilibrium.



b) These two forms of acid-base indicator have different colours. The acid-base indicator shows colour change due to interconvert ion of one tautomeric form into other.

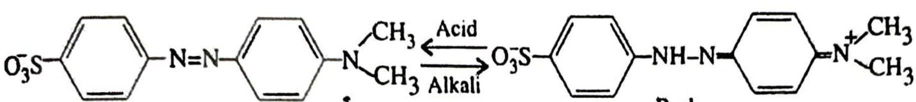
c) Out of these two tautomeric form, one form exists in acidic medium and the other in alkaline medium. During acid-base titration, the medium changes from acidic to alkaline and vice-versa. The benzenoid form of phenolphthalein in acidic medium is colourless and its quinonoid form has pink colour in alkaline medium.




Benzenoid form
(colourless )

Quinonoid form
(pink)

Methyl orange has quinonoid form in acidic solution and has red colour, while benzenoid form in alkaline solution has yellow in colour.




Yellow

Red

Phenolphthalein is weak acid. The dissociation of phenolphthalein (HIn) represented as

$$HIn \rightleftharpoons H^{+} + In^{-}$$

| | |
|---|---|
| Colourless | Pink |
| (In Acid solution) | (In Basic Solution) |

When acid taken in a conical flask, phenolphthalein remain in a non-dissociated form due to presence of more concentration of $H^{+}$ ion. So solution is colourless. At end point, colour changes from colourless to pink. When basic solution taken in a conical flask, phenolphthalein undergo dissociation and solution become pink in colour. At end point, colour changes from pink to colourless due to consumption of all $OH^{-}$ ion.

In Similar manner, methyl orange (InOH) shows different colour in dissociated and non-dissociated form.

$$InOH \rightleftharpoons In^{+} + {}^{-}OH$$

| | |
|---|---|
| Yellow | Pink |
| (In basic solution) | (In acidic solution) |

Hence when acid taken in a conical flask, colour changes from pink to yellow, and in case of alkali colour changes from yellow to pink.

## 2.13 Choice of suitable indicator for different acid base titration

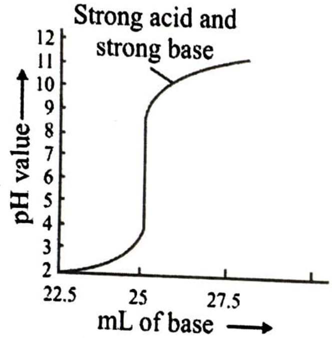
The acid-base (neutralization)/titration has following four types.

i) A strong acid versus a strong base
ii) A weak acid versus a strong base.
iii) A strong acid versus a weak base.
iv) A weak acid versus a weak base.

In the acid-base titration, the curve obtained by plotting pH against the volume of alkali added is known as neutralization or titration curve. In every acid base titration, titration curve becomes almost vertical for some distance and then bends away. This region indicates the change in pH at equivalence point. The color change of acid-base indicator takes place within a small range of pH value. This range is called the pH range of indicator. The selection of indicator depends on pH range of indicator matches with pH range of indicator matches with pH range near the equivalent point of concern acid-base titration.

**1) Strong acid versus strong base.** (e.g. HCl + NaOH)

The pH curve (titration curve) of strong acid (HCl) and strong base (NaOH) is almost vertical over the pH range 3.3-10.5. The titration curve indicates that up to neutralization, pH slightly increases up to 3.3. After addition excess of NaOH, concentration of $HO^-$ increases and pH suddenly rises to 10.5. The indicator pH range matches with selected strong acid and strong base titration pH range 3.3 – 10.5. So phenolphthalein, Methyl orange, methyl red, etc. are suitable for such titration.

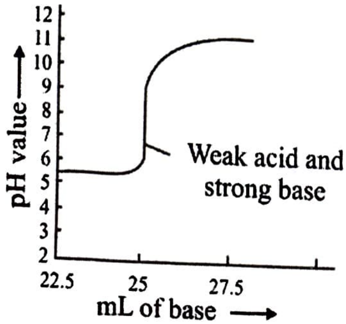



| Suitable Indicator | pH range |
|---|---|
| Methyl Orange | 3.2 – 4.5 |
| Methyl Red | 4.4 – 6.5 |
| Litmus | 5.5 – 7.5 |
| Phenolphthalein | 8.4 – 10.5 |

**Fig. 2.2: Neutralization curve for strong acid and strong base titration.**

**2) Weak acid versus Strong base** (e.g. $CH_3COOH$ and NaOH)

The titration curve of weak acid ($CH_3COOH$) and strong base (NaOH) is vertical over the approximate pH range 6.5 to 10.5. Due to weak strength of acid, solution is alkaline at end point. The phenolphthalein is suitable indicator available for the titration between weak acid and weak base.

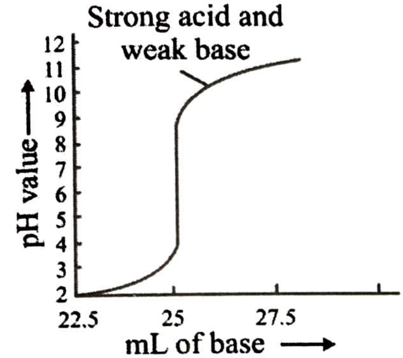



| Suitable Indicator | pH range |
|---|---|
| Phenolphthalein | 8.4 – 10.5 |
| Bromothymol blue | 6.0 – 7.6 |

**Fig. 2.3: Neutralization curve for weak acid and strong base titration.**

**3) Strong acid versus weak base** (e.g. HCl and $NH_4OH$)

The titration curve of strong acid (HCl) with a weak base ($NH_4OH$) is vertical over the pH range 3.5 to 7.0. After the neutralization, the pH varies from 3.5 to 7.0, so methyl red and methyl orange are suitable for such a titration.




| Suitable Indicator | pH range |
|---|---|
| Methyl orange | 3.2 – 4.5 |
| Methyl Red | 4.4 – 6.5 |

**Fig. 2.4: Neutralization curve for strong acid and weak base titration.**

**4) Weak acid versus weak base** e.g. ($CH_3COOH$ and $NH_4OH$)

In weak acid versus weak base titration, pH varies in very narrow pH range as the curved is not vertical. Hence, no suitable indicator available for the titration between weak acid and weak base.

**Suitable Indicator:** No suitable indicator

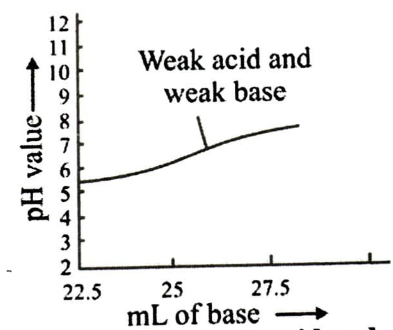



**Fig. 2.5: Neutralization curve for weak acid and weak base titration.**

**2.14 Redox titration**

The titration in which one reactant is oxidized and the other is reduced is known as redox titration. The titration reaction involves a transfer of electron from one substance to another.

The process of releasing electron is oxidation and the process of gaining electron is known as reduction. In redox titration, both oxidation and reduction process takes place simultaneously.

The reagent which oxidizes to other substance and itself reduces; this substance is called as oxidizing agent (oxidant) i.e. oxidizing agent gain electrons and reduced itself to lower valency state. The reagent which reduces to other substance and itself oxidizes this