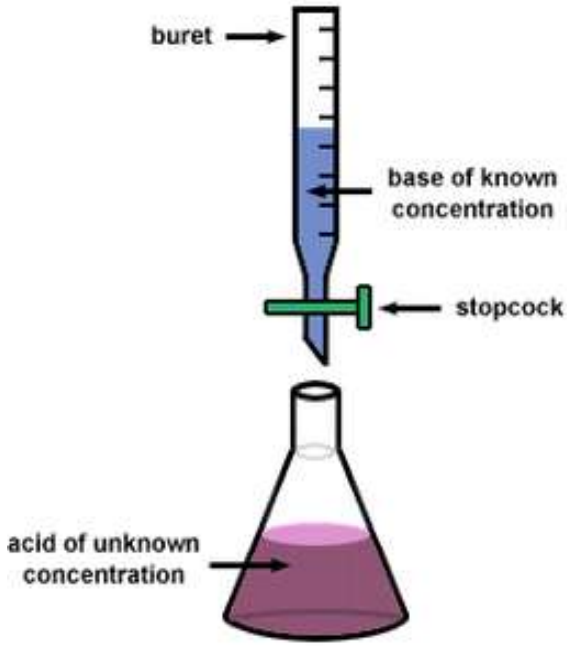
Theory of Indicator
Acid-base Indicators and Titration



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Theory of Indicator:

- An indicator is a substance which is used to determine the end point in a titration.
- In acidbase titrations, organic substances (weak acids or weak bases) are generally used as indicators.
- They change their colour within a certain pH range.

The colour change and the pH range of some common indicators are tabulated below

Indicator	pH range	Colour change
Methyl orange	**3.2-4.5**	**Pink to yellow**
Methyl red	**4.4-6.5**	**Red to yellow**
Litmus	**5.5-7.5**	**Red to blue**
Phenol red	**6.8-8.4**	**Yellow to red**
Phenolphthale	**8.3-10.5**	**Colourless to pink**

Theory of acid-base indicators: Two theories have been proposed to explain the change of colour of acid-base indicators with change in pH.

1) **Ostwald's theory**
2) **Quinonoid theory**

1) Ostwald's theory

According to this theory:

(a) The colour change is due to ionisation of the acid-base indicator. The unionised form has different colour than the ionised form.

(b) (b) The ionisation of the indicator is largely affected in acids and bases as it is either a weak acid or a weak base.

In case, the indicator is a weak acid, its ionisation is very much low in acids due to common H+ ions while it is fairly ionised in alkalies. Similarly if the indicator is a weak base, its ionisation is large in acids and low in alkalies due to common OH- ions.

Considering two important indicators phenolphthalein (a weak acid) and methyl orange (a weak base), Ostwald theory can be illustrated as follows:

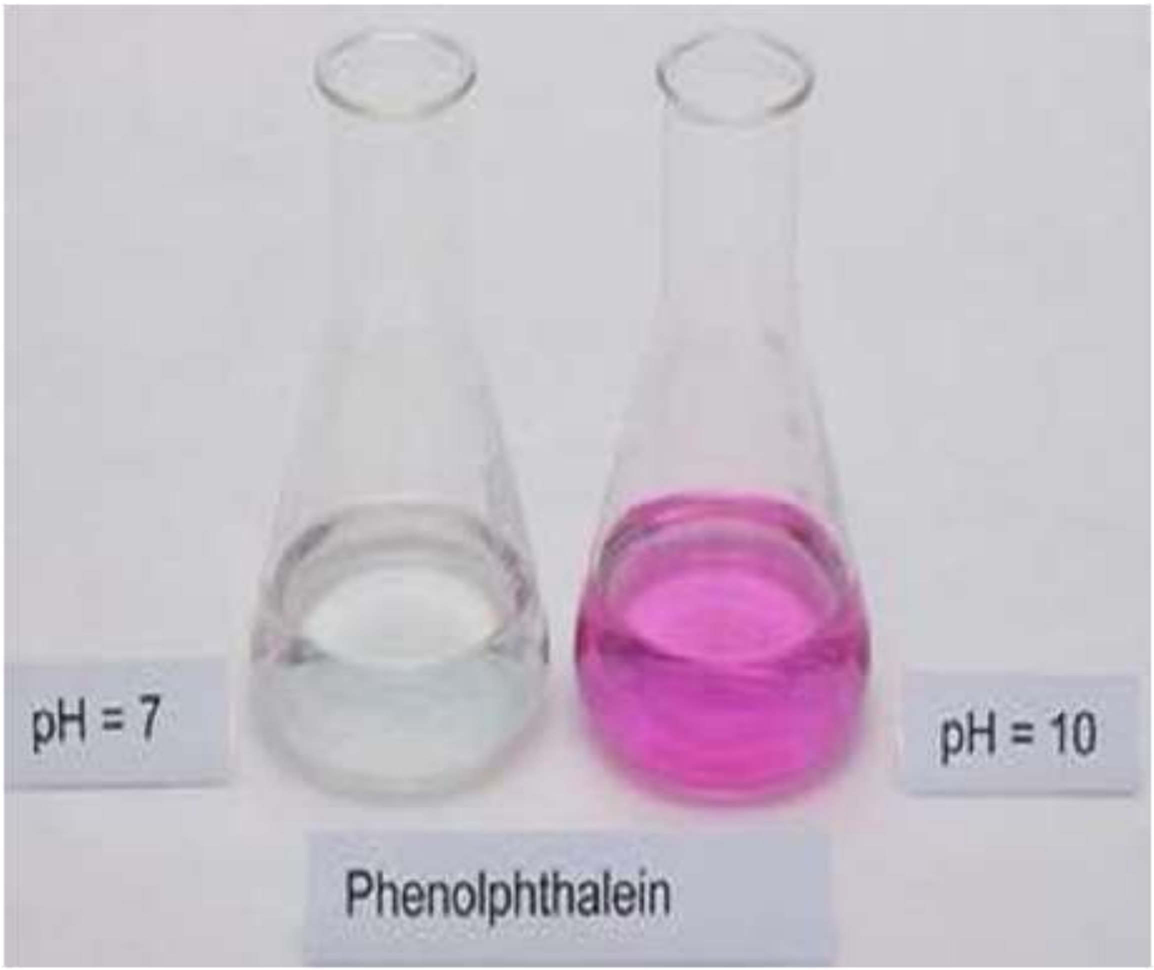
Phenolphthalein: It can be represented as HPh. It ionises in solution to a small extent as:

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

Applying law of mass action
K = [H+][Ph-]/[HpH]

- The undissociated molecules of phenolphthalein are colourless while Ph- ions are pink in colour.
- In presence of an acid the ionisation of HPh is practically negligible as the equilibrium shifts to left hand side due to high concentration of H+ ions. Thus, the solution would <u>remain colourless</u>.
- On addition of alkali, hydrogen ions are removed by OH- ions in the form of water molecules and the equilibrium shifts to right hand side.
- Thus, the concentration of Ph- ions increases in solution and they impart <u>pink colour</u> to the solution.

Colure change in solution



Let us derive Handerson equation for an indicator

$HIn + H2O \quad \leftrightarrow \quad H+_3O \; + \; In^-$

'Acid form' 'Base form‘

(Conjugate acid-base pair)

KIn = [In][H+ 3O]/[HIn]

KIn = Ionization constant for indicator

$[H^+{}_3O] = KIn * [HIn]/In^-$

$pH = -\log_{10} [H^+{}_3O] = -\log_{10}[KIn] - \log_{10}[HIn]/[In^-]$

$pH = pKIn + \log10[In^-]/[HIn]$

(Handerson equation for indicator)

At equivalence point:

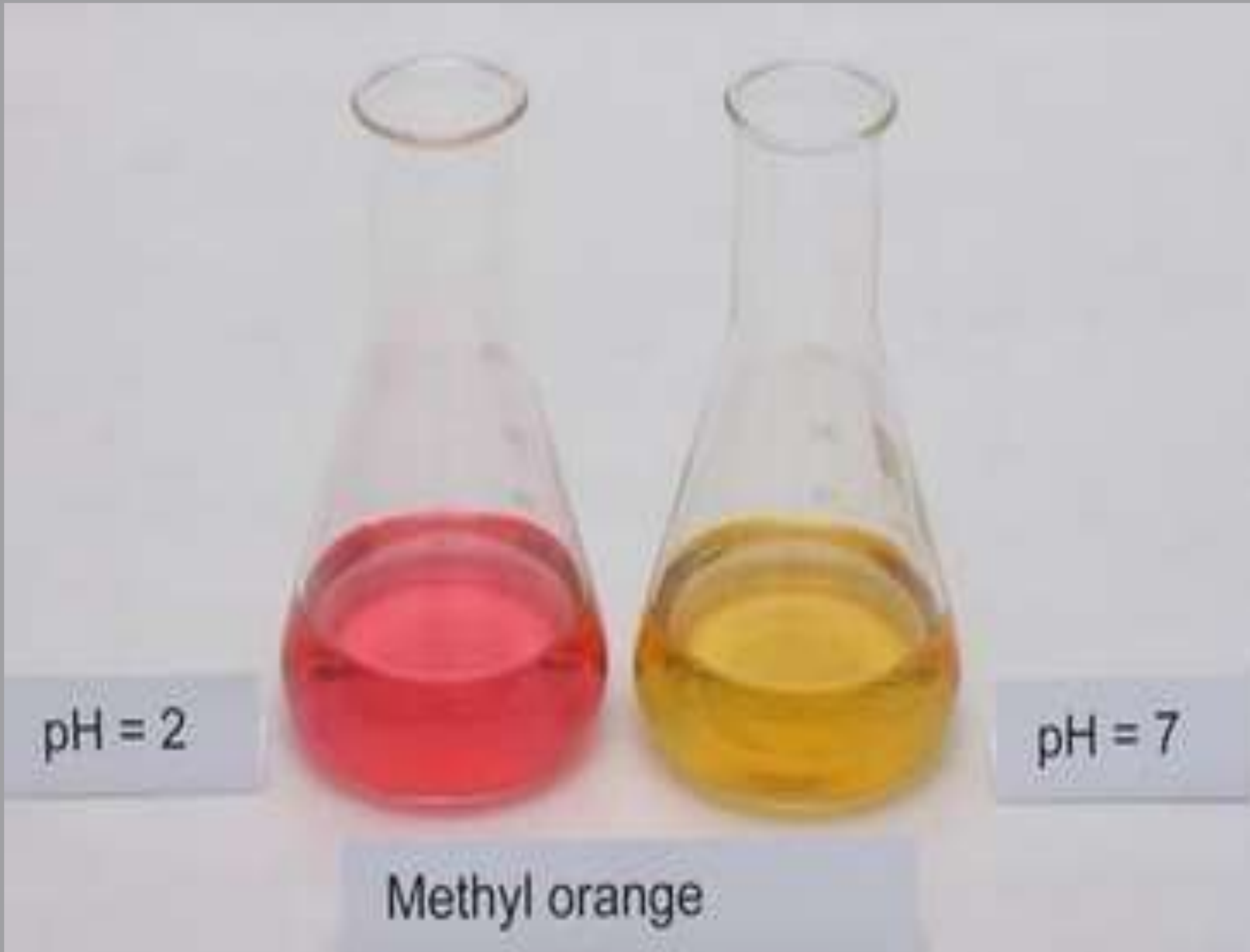
[In-] = [HIn] and pH = pKIn

Methyl orange: It is a very weak base and can be represented as MeOH. It is ionized in solution to give Me+ and OH- ions.

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

Yellow Red

- In presence of an acid, OH- ions are removed in the form of water molecules and the above equilibrium shifts to right hand side.
- Thus, sufficient Me+ ions are produced which impart red colour to the solution. On addition of alkali, the concentration of OH" ions increases in the solution and the equilibrium shifts to left hand side, i.e., the ionisation of MeOH is practically negligible. Thus, the solution acquires the colour of unionised methyl orange molecules, i.e., yellow.


pH = 2
Methyl orange
pH = 7

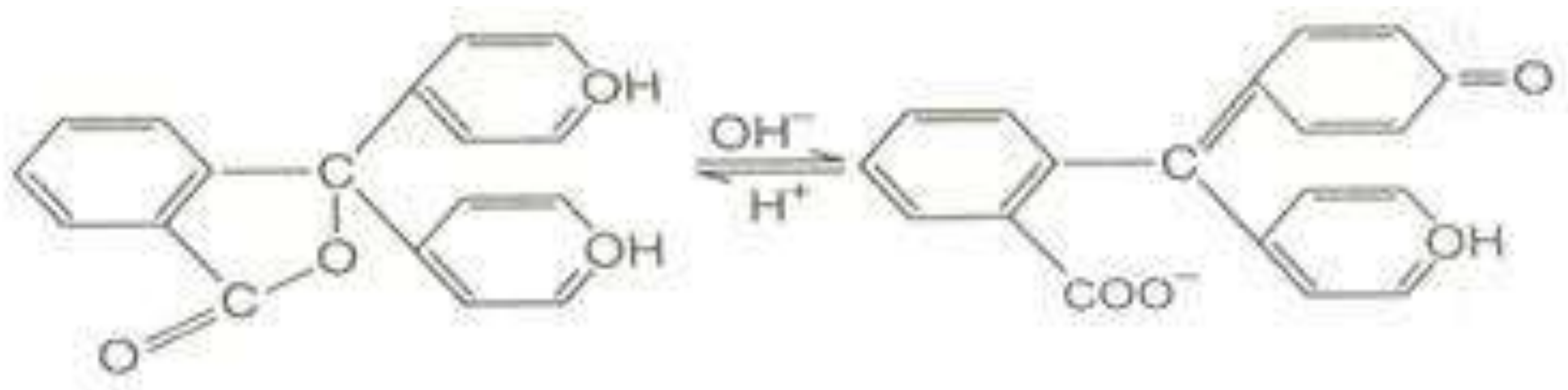
- This theory also explains the reason why phenolphthalein is not a suitable indicator for titrating a weak base against strong acid.
- The OH" ions furnished by a weak base are not sufficient to shift the equilibrium towards right hand side considerably, i.e., pH is not reached to 8.3.
- Thus, the solution does not attain pink colour. Similarly, it can be explained why methyl orange is not a suitable indicator for the titration of weak acid with strong base.

2) Quinonoid theory

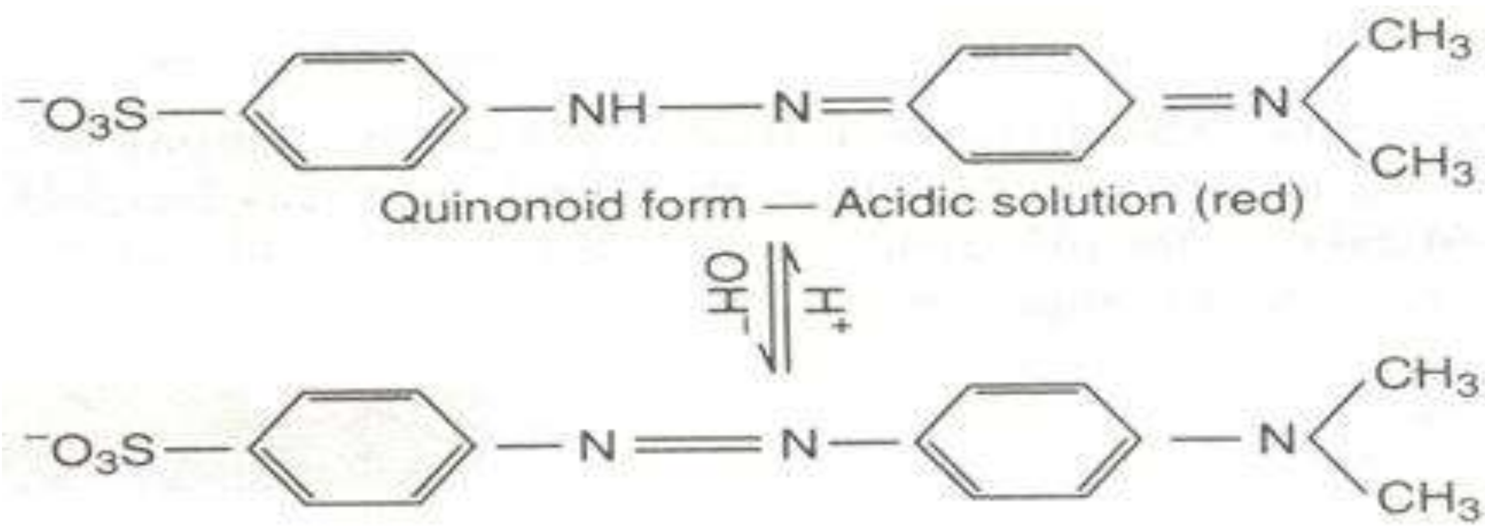
- According to quinonoid theory, an **acid-base indicators** exist in two tautomeric forms having different structures which are in equilibrium.
- One form is termed benzenoid form and the other quinonoid form.

- The two forms have different colors. The color change is due to the interconversation of one tautomeric form into other. One form mainly exists in acidic medium and the other in alkaline medium.
- Thus, during **titration** the medium changes from acidic to alkaline or vice-versa. The change in pH converts one tautomeric form into other and thus, the colour change occurs.

Phenolphthalein has benziod form in acidic medium and thus, it is colourless while it has quinonoid form in alkaline medium which has pink colour.



Methyl orange has quinonoid form in acidic solution and benzenoid form in alkaline solution. The color of benzenoid form is yellow while that of quinoniod form is red.

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