THEORY OF INDICATORS:

An **indicator** is a substance which is used to determine the end point in a titration. In acid-base **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
Phenolphthalein	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: 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) 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:

 $\mathrm{HPh} \leftrightarrow \mathrm{H}^{+} + \mathrm{Ph}^{-}$

Colourless Pink

Applying law of mass action,

 $\mathbf{K} = [\mathbf{H}^+][\mathbf{P}\mathbf{h}^-]/[\mathbf{H}\mathbf{p}\mathbf{H}]$

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 remain colourless. 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 pink colour to the solution

Quinonoid theory:

According to this theory:

(a) The **acid-base indicators** exist in two tautomeric forms having different structures. Two forms are in equilibrium. One form is termed benzenoid form and the other quinonoid form.

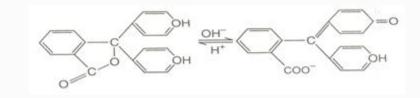


(b) The two forms have different colors. The color change in due to the interconversation of one tautomeric form into other.

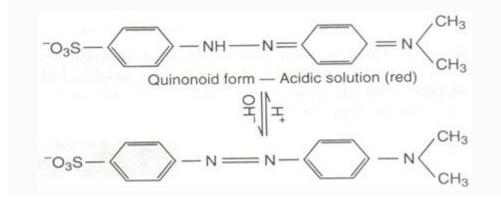
(c) One form mainly exists in acidic medium and the other in alkaline medium.

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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