

# THEORY OF INDICATORS : OSTWALD'S THEORY

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:



Colourless      Pink

Applying law of mass action,

$$K = \frac{[\text{H}^+][\text{Ph}^-]}{[\text{HPh}]}$$

The undissociated molecules of **phenolphthalein** are colourless while  $\text{Ph}^-$  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  $\text{H}^+$  ions. Thus, the solution would remain colourless. On addition of alkali, hydrogen ions are removed by  $\text{OH}^-$  ions in the form of water molecules and the equilibrium shifts to right hand side. Thus, the concentration of  $\text{Ph}^-$  ions increases in solution and they impart pink colour to the solution.

Let us derive Handerson equation for an indicator



'Acid form'                      'Base form'



Conjugate acid-base pair

$$K_{\text{In}} = \frac{[\text{In}^-][\text{H}_3\text{O}^+]}{[\text{HIn}]}; \quad K_{\text{In}} = \text{Ionization constant for indicator}$$

$$[\text{H}_3\text{O}^+] = K_{\text{In}} * \frac{[\text{HIn}]}{[\text{In}^-]}$$

$$\text{pH} = -\log_{10} [\text{H}_3\text{O}^+] = -\log_{10}[K_{\text{In}}] - \log_{10}[\text{HIn}]/[\text{In}^-]$$

$$\text{pH} = \text{p}K_{\text{In}} + \log_{10}[\text{In}^-]/[\text{HIn}] \quad (\text{Handerson equation for indicator})$$

At equivalence point

$$[\text{In}^-] = [\text{HIn}] \text{ and } \text{pH} = \text{pK}_{\text{In}}$$

**Methyl orange:** It is a very weak base and can be represented as MeOH. It is ionized in solution to give  $\text{Me}^+$  and  $\text{OH}^-$  ions.



Yellow      Red

Applying law of mass action,

$$K = \frac{[\text{Me}^+][\text{OH}^-]}{[\text{MeOH}]}$$

In presence of an acid,  $\text{OH}^-$  ions are removed in the form of water molecules and the above equilibrium shifts to right hand side. Thus, sufficient  $\text{Me}^+$  ions are produced which impart red colour to the solution. On addition of alkali, the concentration of  $\text{OH}^-$  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.

This theory also explains the reason why **phenolphthalein** is not a suitable **indicator** for **titrating** a weak base against strong acid. The  $\text{OH}^-$  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.

Source : <http://ciseche10.files.wordpress.com/2013/12/ionic-equilibrium.pdf>