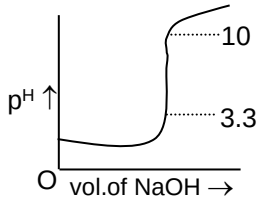
Indicators:

Indicators are the substances which indicate completion of reaction.

- Based on the nature of reaction indicators are of many types.
  1) Acid base indicators→ used in neutralisation reaction.
     Eg: methyl orange, phenolphthalein
- 2) Redox indicators→used in redox reactions.
  Eg : $KMnO_4$ [self indicator]
- 3) Tracer indicators → used in detecting reaction mechanisms
  Eg: O^{18}, D^2
- 4) Absorption indicators → starch absorbs iodine. It is used in titration reactions. In the titration of hypo indicator used is $CuSO_4$.

Acid – Base indicators:

- The substances which are used to detect the end point or equivalent point in acid base titrations are called acid – base indicators.
- The point at which neutralisation is complete and change in p^H is very sharp is called end point or equivalent point for example, in the titration of 0.1 M HCl, 0.1 M NaOH p^H gradually increases from 1 to 3.3 with the addition of NaOH to HCl. At this stage if one or two drops of NaOH are added the solution suddenly becomes basic and the p^H value increases from 3.3 to 10.



Theories of acid – base indicators:

1) Quinonoid theory
2) Ostwald's theory

- The above theories will explain the functioning of indicators.

Ostwald's theory :

- Indicators are either weak organic acids or weak organic bases.
- An acid indicator exhibits color change in basic solution and basic indicator exhibits color change in acidic solution. That is acid indicator show light color in acid solution and deep color in basic solution and basic indicator shows light color in basic solution and deep color in acidic solution.

  Molecule of indicator has one color and its ions will have another color. Thus, the color change of indicator depends on the extent of ionization.

Eg: Phenolphthalein : [Ph H]

It is acid indicator . It ionizes as follows

$PhH \rightleftharpoons ph^- + H^+$

(colorless) (pink)

If phenolphthalein is added to acid solution, it remains colorless because the above equilibrium shifts to left side.

$Ph^- + H^+ \rightarrow Ph\ H$

- If phenolphthalein is added to basic solution, it exhibits pink color because the equilibrium shifts to right side and ionization increases.

$PhH \rightarrow Ph^- + H^+$

(pink)

Methyl orange (MeOH):

It is basic indicator and it ionizes as follows

$MeOH \rightleftharpoons Me^+ + OH^-$

(yellow) (red)

- If methyl orange is added to acidic solution. It exhibits red color as it ionizes more and equilibrium shifts to right side.

$H^+ + OH^- \rightarrow H_2O$

$MeOH \rightarrow Me^+ + OH^-$

(red)

- If methyl orange is added to basic solution. It remains yellow color because the ionization is suppressed and equilibrium shifts towards left side.

$Me^+ + OH^- \rightarrow MeOH$

(yellow)

p^H of indicators :

Eg: $In\ H \rightleftharpoons In^- + H^+$

$K_{In} = \frac{[In^-][H^+]}{[InH]} \Rightarrow [H^+] = K_{In}\frac{[InH]}{In^-}$

Apply - log on both sides

$$-log[H^+] = -log\ K_{In} - log\left[\frac{InH}{In^-}\right]$$

$$p^H = p^{K_{In}} + log\left[\frac{In}{InH}\right]$$

- Similarly for basic indicators also p^H expression can be derived as shown above.

Eg : HI_n if 50% ionised

$[In^-] = [H\ In]$

then $p^H = p^{K_{In}}$

colour→ mixture of both molecules and ions.

If HIn is > 90% ionised

[HIn] < 10%

then $p^H = p^{K_{In}} + 1$

colour → ions

If Hin is < 10 % ionised

$[In^-] < 10\%$

[HIn] > 90%

then $p^H = p^{K_{In}} - 1$

colour → molecular

p^H range of indicators : The range of p^H values where an indicator can exhibit a sharp change in colour is called p^H range of indicators.

$p^H = p^{Kn} \pm 1$

Eg: phenolphthalein

It's p^{Kn} is equal to 9.7

There fore it exhibits colour change in between p^H values 8.3 and 10 below 8.3 it is colouless and above 10 it is pink colour.

Methyl orange : It's $p^{K_{In}}$= 3.7 and its p^H range is from 3.1 to 4.4.

It is yellow coloured above 4.4 and red coloured below 3.1.

Indicator	**p^H range**	**Colour in Acid solution**	**Colour in basic solution**
PhH	8.3 – 10	Colourless	Pink
MeOH	3.1 – 4.4	Red	Yellow
Methyl red	4.2 – 6.3	Red	Yellow
Phenol red	6.8 – 8.4	Yellow	Red
Thymol blue	8 – 9.6	Yellow	Red

- **Change in p^H at the end point :**

  The sharp change in p^H at the end point will depend on

  1) Nature of the acid and base involved
  2) Concentration of acid and base

- **Strong acid Vs strong base :**

  a) 1 M HCl Vs 1 M NaOH $\rightarrow$ 3.3 – 10.7

  b) 0.1 M HCl Vs 1 M NaOH $\rightarrow$ 5.5 – 8.5

Weak acid Vs strong bases :

0.1M CH_3COOH Vs 0.1 M NaOH$\rightarrow$ 7.7 – 9.7

Weak base Vs strong acid

0.1 M NH_4OH Vs 0.1 M HCl $\rightarrow$ 6.3 – 4

Weak acid Vs weak base : There is no sharp change in p^H at the end point because both acid and are too weak to neutralise each other.

Solution of indicators : The choice of indicator depends on

1) nature of the acid and base involved
2) concentrations of acid and base
3) change in p^H at the end point.
4) p^H range of indicator

Strong acid Vs strong base : Any indicator is suitable because p^H range of any indicator matches with the change in p^H at the end point.

- **Weak acid Vs strong base :** The suitable indicator is phenolphthalein because it's p^H range perfectly matches with the change in p^H at the end point.
- **Weak base Vs strong acid :** The suitable indicator is methyl orange because it's p^H range matches with the change in p^H at the end point.
- **Universal indicator :** It is the mixture of several known indicators, mixed in required proportion.

  Example : 0.1 gm of phenolphthalein
  0.2 gm of methyl red
  0.3 gm of methyl yellow
  0.4 gm of bromo thymol blue
  0.5 gm of thymol blue
  are dissolved in 500 ml of absolute alcohol and excess of NaOH is added. The resulting universal indicator has yellow colour.
- Universal indicator has a very big range of p^H. That is if gives different colours at different p^H values.
  Eg : $p^H = 2 \rightarrow$ red
  $p^H = 4 \rightarrow$ orange
  $p^H = 6 \rightarrow$ yellow
  $p^H = 8 \rightarrow$ green
  $p^H = 10 \rightarrow$ blue
  Therefore the universal indicator is useful to know the p^H of unknown solution.