Theory of Acid-Base Indicators 4

Certain chemicals have the special property of appearing one colour when in a solution of one pH and a different colour when in a solution of a different pH. Such chemicals are known as acid-base indicators, or simply as indicators because, when a few drops of indicator are added to a solution, the colour of the solution serves as an indication of its pH.

Accordingly, an acid/base indicator is a chemical compound used to indicate the pH values of substances by giving a recognizable color change. Hence, it can be used to detect the equivalent point (or end-point) during an acid-base titration process.

Definitions

It is a weak organic acid or a weak organic base whose un-dissociated form differs in color from its conjugated acid or its conjugated base form,and there is an equilibrium between the two forms:

$$\underset{\substack{\text{acid form}\\\text{colour 1}}}{HInd\,(aq) + H_2O} \Longleftrightarrow \underset{\substack{\text{base form}\\\text{colour 2}}}{In^{-}\,(aq) + H_3O^{+}\,(aq)} \text{ ---------(1)}$$

acid **conjugate base**

The equilibrium for a base-type indicator, In, is

$$\underset{\substack{\text{base form}\\\text{colour 1}}}{In\,(aq) + H_2O} \Longleftrightarrow \underset{\substack{\text{acid form}\\\text{colour 2}}}{InH^{+}\,(aq) + OH^{-}\,(aq)} \text{ ----------(2)}$$

When the indicator is added to the solution of interest, depending on the pH of the solution, the indicator stays in either its acid form(HIn) or its conjugate form (In^-).The two forms of any indicator depend on whether a particular hydrogen atom is present in the indicator's molecule.

- The lower pH form is designated HIn(aq)
- The higher pH form is designated In^-(aq)

Types of acid-base indicators

Several types of indicators are available for different types of titrimetric analyses. For acid-base titrations, organic dyes, which are either weak acids or bases, serve excellently as indicators.

There are two types of acid/base indicators:

1- Universal indicator - this is a mixture of several indicators. It can indicate pH values of over a range of 3 -11 by successive changes of color - this takes place at every change of one unit of pH. A universal indicator is typically composed of water, propan-1-ol, phenolphthalein sodium salt, sodium hydroxide, methyl red, bromothymol blue monosodium salt, and thymol blue monosodium salt. The colours that indicate the pH of a solution, after adding a universal indicator are:

pH range	Description	Colour
<3	Strong acid	Red
3-6	Acid	Orange/Yellow
7	Neutral	Green
8-11	Alkaline	Blue
> 11	Strong alkaline	Violet/Purple

2- Ordinary single indicator – this requires a change of about two units of pH to show a full color change. The table below gives the common indicators for acid - base titration and their pK_a (also referred to as pK_a) values are given in a table form.

Name	Acid Color	pH Range of Color Change	Base Color
Methyl violet	Yellow	0.0 - 1.6	Blue
Thymol blue	Red	1.2 - 2.8	Yellow
Methyl orange	Red	3.2 - 4.4	Yellow
Bromocresol green	Yellow	3.8 - 5.4	Blue
Methyl red	Red	4.8 - 6.0	Yellow
Litmus	Red	5.0 - 8.0	Blue
Bromothymol blue	Yellow	6.0 - 7.6	Blue
Thymol blue	Yellow	8.0 - 9.6	Blue
Phenolphthalein	Colorless	8.2 - 10.0	Pink
Thymolphthalein	Colorless	9.4 - 10.6	Blue

A good indicator must have the following properties:

- The color change must be easily detected.
- The color change must be rapid.
- The indicator molecule must not react with the substance being titrated.
- To minimize errors, the indicator should have a pK_{in} that is within one pH unit of the expected pH at the equivalence point of the titration.

Theory of 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 alkalise. Similarly if the indicator is a weak base, its ionisation is large in acids and low in alkalise 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:

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

Applying law of mass action,

$$K_a = [H^+][Ph^-]/[Hph]$$

The un-dissociated 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(common ion). Thus, the solution would remain colourless.

$$\begin{array}{lcccl} \text{HPh} & \longleftrightarrow & H^+ & + & Ph^- \\ \text{Colourless} & & & & \text{Pink} \\ \text{HCl} & \longrightarrow & H^+ & + & Cl^- \end{array}$$

Due to common ion H^+ dissociation of HPh decrease.

- 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

$$\begin{array}{lcccl} \text{HPh} & \longleftrightarrow & H^+ & + & Ph^- \\ \text{Colourless} & & & & \text{Pink} \\ \text{NaOH} & \longrightarrow & OH^- & + & Na^+ \end{array}$$

The undissociated molecules of methyl orange (MeOH) are yellow while (Me^+) ions are pink in colour.

On addition of acid, OH^- ions are removed by H^+ ions in the form of water molecules(Neutralization reaction) and the equilibrium shifts to right hand side. Thus, the concentration of MeOH ions decreases in solution and they impart pink colour to the solution.

$$\begin{array}{lcccl} \text{MeOH} & \longleftrightarrow & Me^+ & + & OH \\ \text{Yellow} & & \text{Pink} & & \\ \text{HCl} & \longrightarrow & Cl- & + & H^+ \end{array}$$

But, when add strong base (e.g. NaOH), the ionisation of MeOH is practically negligible as the equilibrium shifts to left hand side due to high concentration of OH^- ions(common ion). Thus, the solution would turn to yellow.

$$\begin{array}{lcccl} \text{MeOH} & \longleftrightarrow & Me^+ & + & OH^- \\ \text{Yellow} & & \text{Pink} & & \\ \text{NaOH} & \longrightarrow & Na^+ & + & OH^- \end{array}$$

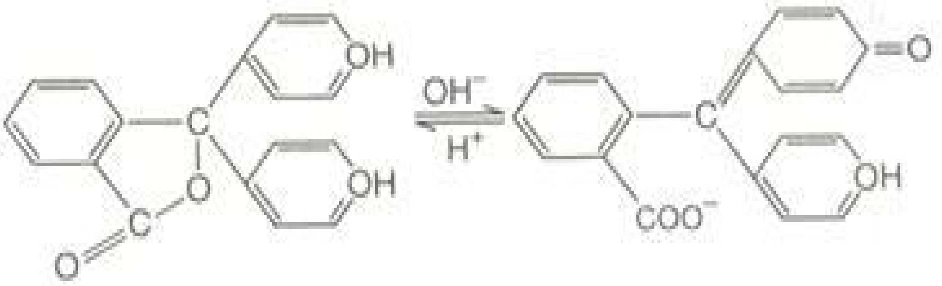
2-<u>Quinonoid theory:</u> According to this theory:

**(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.

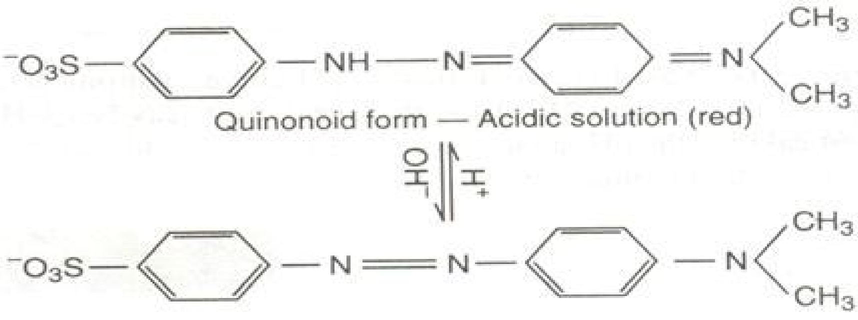
(c) One form mainly exists in acidic medium and the other in alkaline medium. Thus, during titration the medium changes from acidic to alkaline or vice-versa. The change in pH converts one tautomeric form into other and thus, the colour change occurs.

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

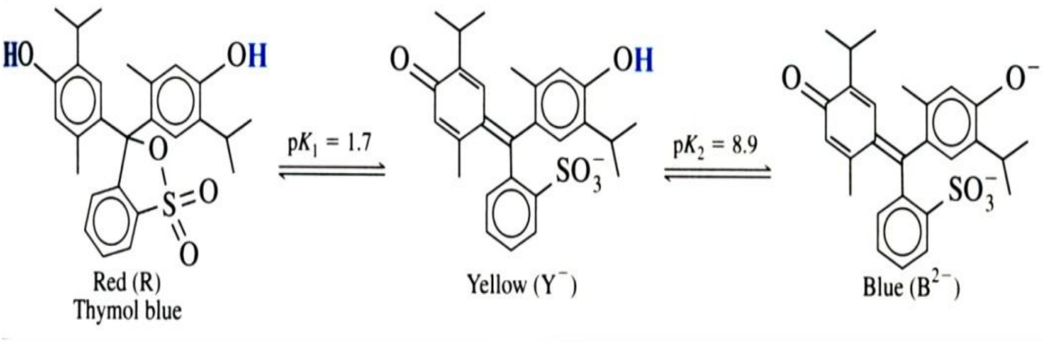


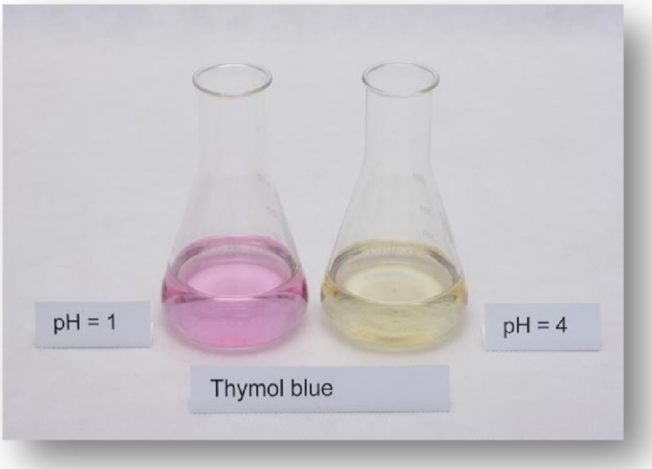
Colorless pink

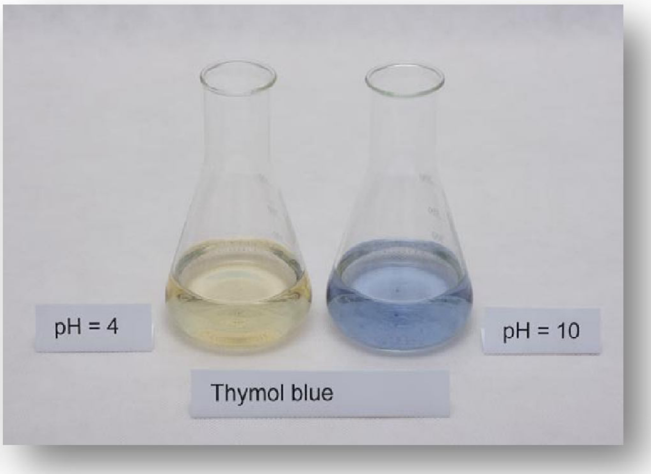
Methyl orange has quinonoid form in acidic solution and benzenoid form in alkaline solution. The color of benzenoid form is yellow while that of quinoniod form is red



Also for thymol blue indicator







Thymol blue changes from red to yellow in the pH range of 1.2 to 2.8, then from yellow to blue in the pH range of 8.0 to 9.6. What is happening here is that thymol blue acts as a diprotic acid, having three forms each with a different colour. In solutions below pH 1.2, it exists primarily in its red H_2In form. As the pH increases, the H_2In is converted to yellow HIn^-, which dominates the solution between pH 2.8 and 8.0. As the pH increases beyond 8.0, blue In^{2-} begins to appear, until the blue dominates the solution at any pH above 9.6. Because it has two protons that can dissociate, thymol blue also has two pK_a values: one at a pH of 2.0 and the other at a pH of 8.8.

Choice of indicator for acid-base titration system

The equilibrium between the two forms for the acid-type indicator HInd is :

$$\underset{\text{colour 1}}{\underset{\text{acid form}}{HInd\,(aq) + H_2O}} \Longleftrightarrow \underset{\text{colour 2}}{\underset{\text{base form}}{In^-\,(aq) + H_3O^+\,(aq)}} \text{ --------(1)}$$

and the equilibrium for a base-type indicator, In, is

$$\underset{\text{colour 1}}{\underset{\text{base form}}{In\,(aq) + H_2O}} \Longleftrightarrow \underset{\text{colour 2}}{\underset{\text{acid form}}{InH^+\,(aq) + OH^-\,(aq)}} \text{ --------- (2)}$$

K_a for acid-type indicator(eq.1) takes the form;

$$K_a = \frac{[H_3O^+][In^-]}{[HIn]}$$

Rearrangement;

$$\Longrightarrow \quad [H_3O^+] = K_a \frac{[HIn]}{[In^-]}$$

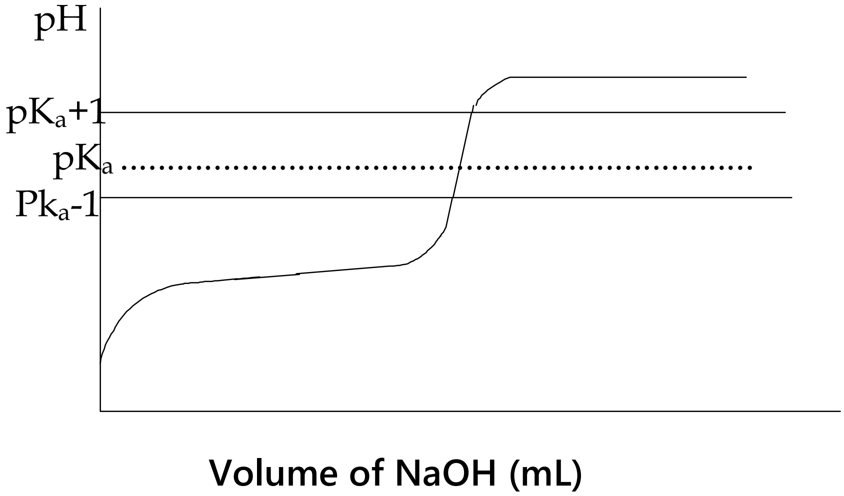
$$pH = pK_a + \log \frac{[In]}{[HIn]}$$

- **For the reaction mixture to impart colour 1 with confidence; the ratio[HIn] / [In] has to be ≤ 1/10**
- **For the reaction mixture to impart colour 2 with confidence, the ratio [In]/[HIn] ≥ 10**

In other words, for the reaction mixture to impart colour 1 with confidence, pH value of the solution should be pKa- 1 or lower, and for the reaction mixture to impart colour 2 with confidence, pH value of the solution should be pKa+1 or higher. Hence pH range of an indicator = pKa ±1.

$$pH = pKa \pm 1$$

As shown in the pH titration curve for a weak acid with a strong alkali, pH range of the indicator cuts the steepest part of the pH variation curve. Thus the rapid change in pH value at the equivalent point matches with a sharp change in colour of the indicator at the end point. This is the criterion of choosing a suitable indicator for acid-base titration.



As acid-base indicators are very sensitive to small changes in pH, careful choice of

indicator will ensure that the end point will closely match the equivalence point of the reaction.

EXAMPLE 1:

Consider the indicator phenol red, which has a yellow HIn form, a red In^- form, and a K_a of 5.0x10-8. Now imagine that a few drops of this indicator are added to a solution of pH 2.3. What colour would the solution be?

Solution:

To figure this out, we need the above equation:

$$pH = pK_a + \log([In^-]/[HIn])$$

$$pH = -\log(K_a) + \log([In^-]/[HIn])$$

$$2.3 = 7.3 + \log([In^-]/[HIn])$$

$$-5.0 = \log([In^-]/[HIn])$$

$$1.0\times10^{-5} = [In^-]/[HIn]$$

Thus, the ratio of In^- to HIn is 1 to 100 000. Since In^- is red and HIn is yellow, there are 100000 yellow molecules in solution for every red molecule. For coloured species, this is an enormous ratio, and the red molecules will be undetectable. Thus, the solution will appear yellow

EXAMPLE 2:

What is the best pKa for the indicator if a strong acid is being titrated with a strong base? If a strong base is being titrated with a strong acid?

Solution:

For a strong acid-strong base titration, the equivalence point occurs at pH 7. When an acid is being titrated with a base, the first observable colour change will occur when the In- to HIn ratio is approximately 1 to 10.

$$pH = pK_a + \log([In^-]/[HIn])$$
$$7 = pK_a + \log(1/10)$$
$$7 = pK_a - 1$$
$$pKa = 8$$

When a base is being titrated with an acid, the first observable colour change will occur when the In to HIn ratio is approximately 10 to 1.

$$pH = pK_a + \log([In^-]/[HIn])$$
$$7 = pK_a + \log(10)$$
$$7 = pK_a + 1$$
$$pK_a = 6$$

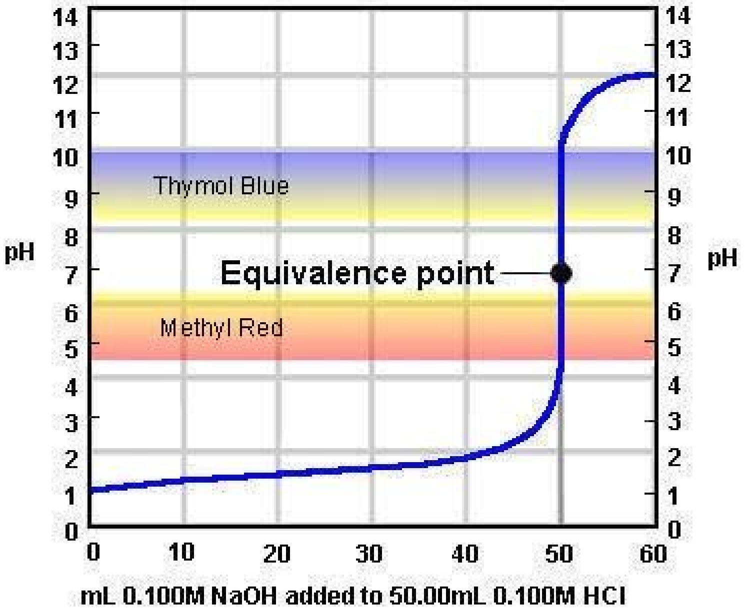
So, we see that we actually want different indicators for the two titrations. In practice, the first colour change does not necessarily have to happen right at the equivalence point. Since we only care about being able to use the colour change to detect when the equivalence point has been reached, the crucial requirement for choosing a good indicator is that it begins to change colour after the volume of titrant required to reach the equivalence point has been added.

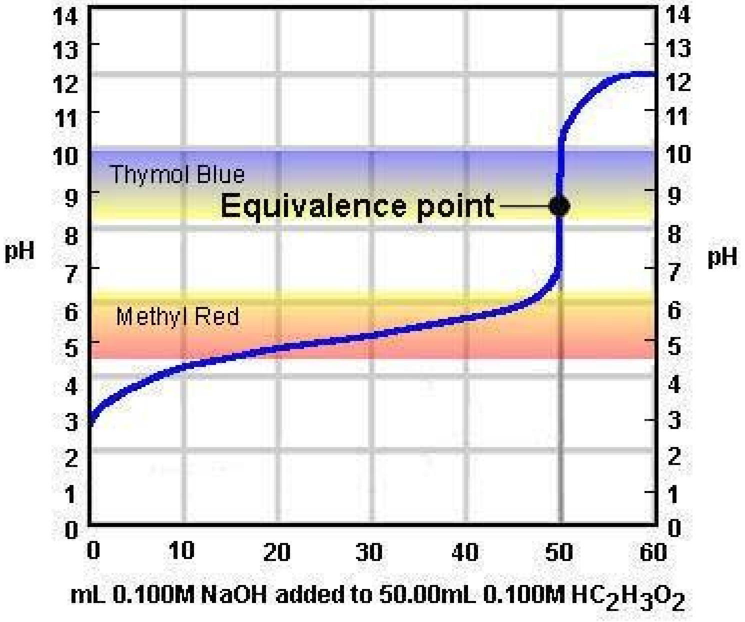
For example, a strong acid-strong base has a very sharp equivalence point, meaning that a very large change in pH occurs due to the addition of a very small amount of titrant, often a single drop. Therefore, any pH in this range will be reached after the addition of the same number of drops. This means that any indicator that starts to change colour in this range will signal equally well that the equivalence point has been reached. It also means that the pH range over which the indicator changes colour will likely be passed in a single drop of titrant, resulting in a very sharp endpoint.

While in the titration involving a weak acid or base, however, has a less steep equivalent point with a less dramatic pH change. Thus, there is a smaller range of pH's that will be passed at the same time as the pH as the

equivalence point, meaning that the chosen indicator must begin to change colour closer to the equivalence point than in a strong acid-strong base titration, and that the endpoint will be wider.

Here are the titrations of both a strong acid and a weak acid with a strong base, using methyl red and thymol blue as possible indicators.





In the strong acid titration, both indicators begin to change colour at the equivalence point (50 mL of base) so both work equally well. In the weak acid titration, thymol blue changes colour at the equivalence point, but methyl red begins to change colour after only 15mL of base are added, which is far from the equivalence point, illustrating the importance of choosing an appropriate indicator.

In general, the faster the pH changes in the range where the indicator changes colour, the sharper the endpoint of the titration will be and the more different indicators will be suitable for the titration.

One limitation of using indicators to find the equivalence point of a titration is that the approximate pH of the equivalence point must be known in order to choose an indicator that will accurately locate the equivalence point. This means that if the approximate pH of the equivalence point is not known, it will be difficult to locate the equivalence point. However, even if we do not know the pH of the equivalence point, we can get around this problem by using trial and error to choose the best indicator. To do this, we can repeat the titration several times with several different indicators, taking note of how sharp or wide the endpoints are-that is, how quickly the colour changes. Since the endpoint is sharpest when it is closest to the equivalence point, we can simply look for the indicator that gave the sharpest endpoint and assume that that one will be most accurate for finding the equivalence point.

Example 3:

In the titration of 30.0 mL of 0.10 M HF with 0.20 M KOH, the pH of the solution mixtures at 10.0, 15.0, and 20.0 mL additions of the strong alkali are 3.76, 8.14, and 12.30, respectively. If phenol red (whose pKvalue is 7.5 and its acid colour is yellow and its base colour is red) were to be used as an indicator for the titration reaction, what colour would the indicator be at the 10, 15, and 20 mL additions of KOH?

Solution:

At 10 mL, the pH is 3.76. This is very acidic; the colour will be yellow.

At 15 mL, the pH is 8.14. This is just within the of the pK, so it will be orange.

Likely a reddish-orange colour.

At 20 mL, the pH is 12.30. This is very basic; and hence the colour will be red.

Since it changes colour at the equivalence point (it doesn't have to hit exactly),
this would be a reasonable choice indicator

Titration Errors Associated with Acid/Base Indicators

Titrations will always be susceptible to both systematic and random errors. The best we can do is to recognize that they are present and make every effort to minimize their effects on the analysis. The systematic error occurs because the pH at which the indicator changes color differs from the pH at the equivalence point.
This is called the titration error or indicator error.
The effects of the titration error can be minimized by selecting the proper indicator – one that changes color at the appropriate pH range. The magnitude of the titration error can be estimated through the analysis of a blank sample.
The random error is due to the limited ability of the eye to reproducibly distinguish the intermediate color of the indicator. The indicator is usually added to the analyte solution at low concentration; otherwise, a titration error is introduced because the indicator is titrated as well as the analyte.