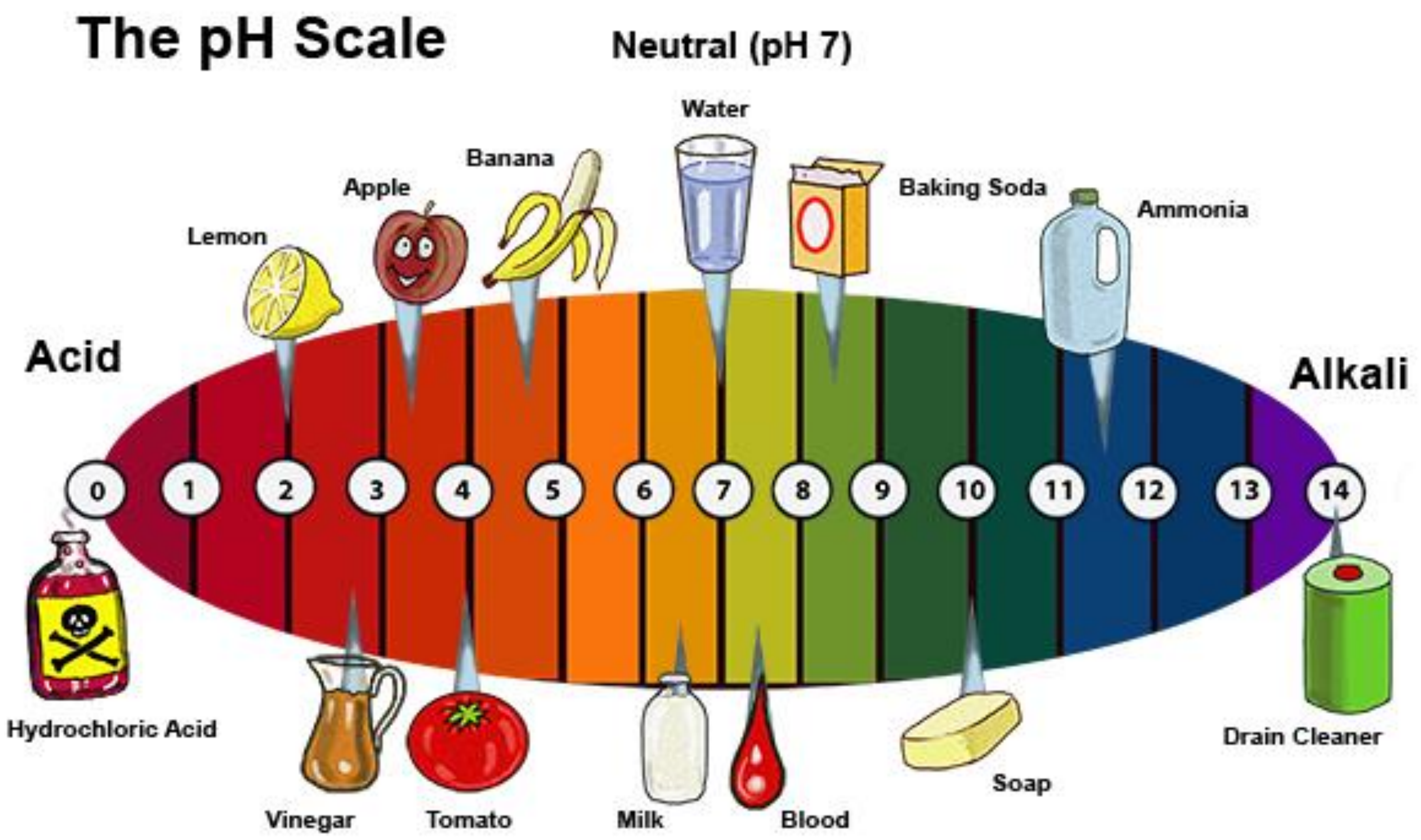
Acids And Bases



Titration

- Titration is the slow **addition of one solution of a known concentration** (called a titrant) to a **known volume of another solution of unknown concentration** until the reaction reaches neutralization.

- This is often indicated by a color change.

- In titration the known concentration is used to determine the concentration of an unknown solution.

- The **solution with known concentration is called standard solution.**

Acid-base titration

- **Acid base titration** involves adding an acid solution from a burette into a conical flask containing an alkaline solution in a controlled manner.
- Out of these two solutions **the concentration of one solution is known** and the concentration of another solution is to be determined.
- The point at which the acid solution completely neutralizes the alkali solution is called **end point**.
- **A substance known as indicator** usually used to determine the end point of acid-base titration.
- **The indicator indicates the end point** by changing the colour of the solution.

Acid-base indicators

- When the amount of the base added equals the amount of the acid in the flask, the equivalence point or the end-point is reached.
- The end-point of a titration is shown by colour change of an indicator previously added to the acid solution in the receiver flask.
- An acid-base indicator is an organic dye that signals the end-point by a visual change in colour.
- Phenolphthalein and methyl orange are two common examples of acid-base indicators.

pH range of indicators

- **Most indicators do not change color at a particular pH.**
- They **do so over a range of pH** from two to three units.
- This is called **the pH range which is different for various indicators.**

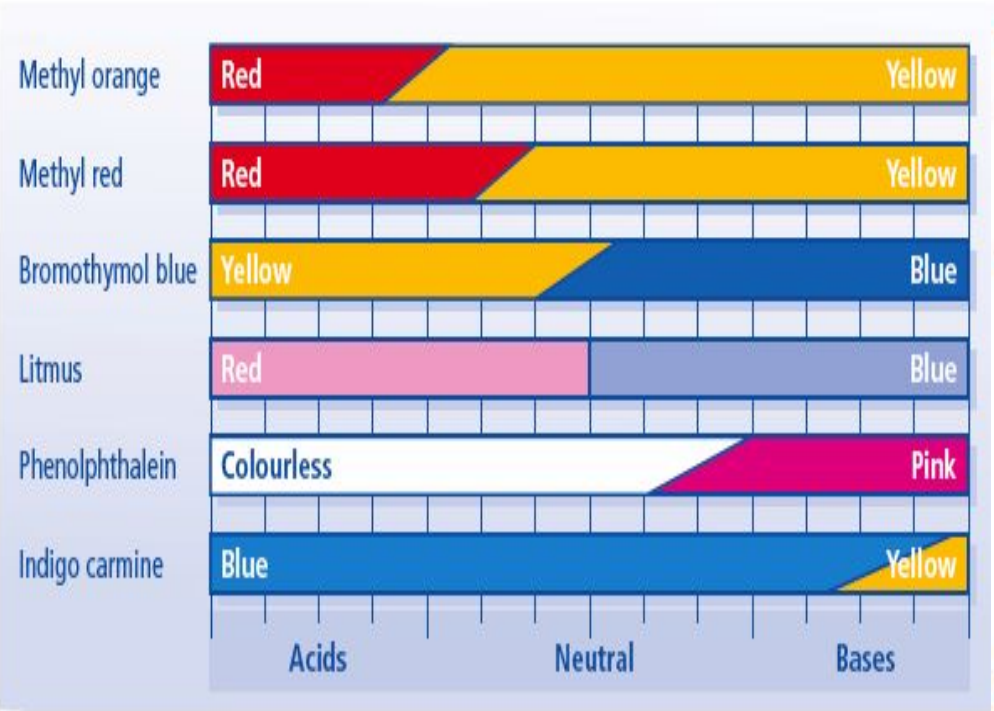


TABLE 27.5. pH RANGES OF SOME ACID-BASE INDICATORS

Indicator	Colour change (acid-base)	pH range
Methyl orange	red-orange	3.1–4.4
Methyl red	red-yellow	4.4–6.0
Litmus	red-blue	5.0–8.0
Bromothymol blue	yellow-blue	6.0–7.6
Phenolphthalein	colourless-pink	8.3–10.0

Acid-base indicators

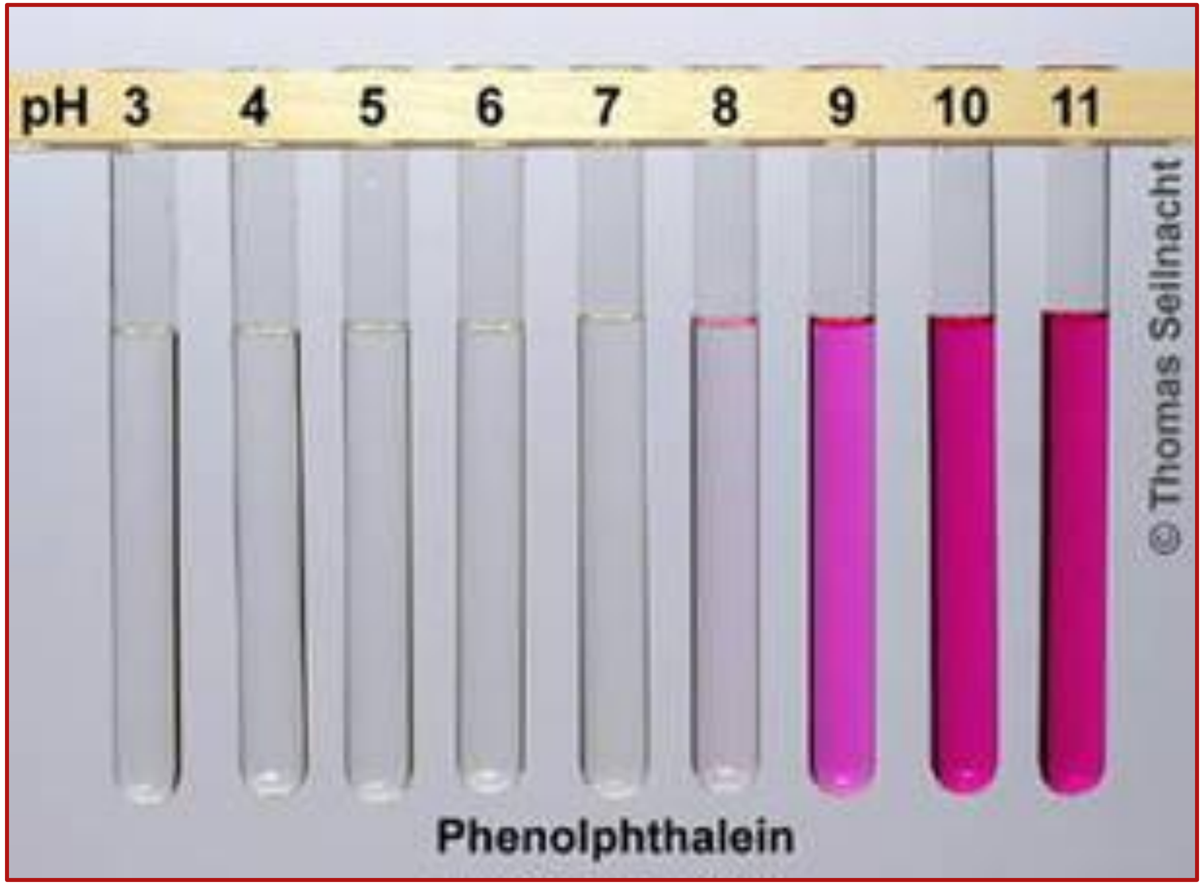
- Phenolphthalein is pink in base solution and colourless in acid solution.

- When added to the acid solution in the receiver flask, it shows no colour. As the added base is in slight excess, it becomes pink. Thus phenolphthalein signals the end-point by a colour change from colourless to pink.

- Similarly methyl orange indicates the end-point by a colour change from red (in acid) to yellow (in base).

Methyl Orange

Phenolphthalein



Choice of a suitable indicator

- Depends on the nature of the acid and the base involved in the titration. We may have the titration of :

(a) a strong acid with a strong base

(b) a weak acid with a strong base

(c) a strong acid with a weak base

(d) a weak acid with weak base

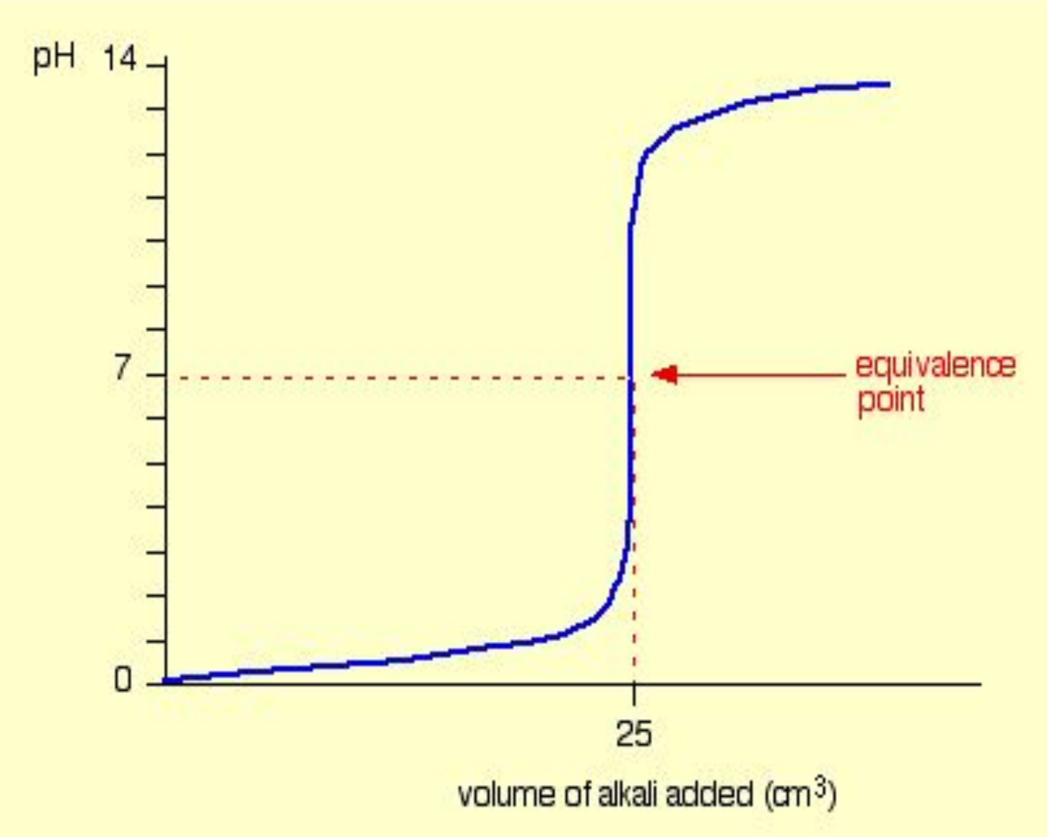
- Which indicator is suitable for a given titration, can be found by examining the titration curve of that titration.

Titrating a Strong acid with a Strong base

- We'll take hydrochloric acid and sodium hydroxide as typical of a strong acid and a strong base.

- You can see that the pH only falls a very small amount until quite near the equivalence point.

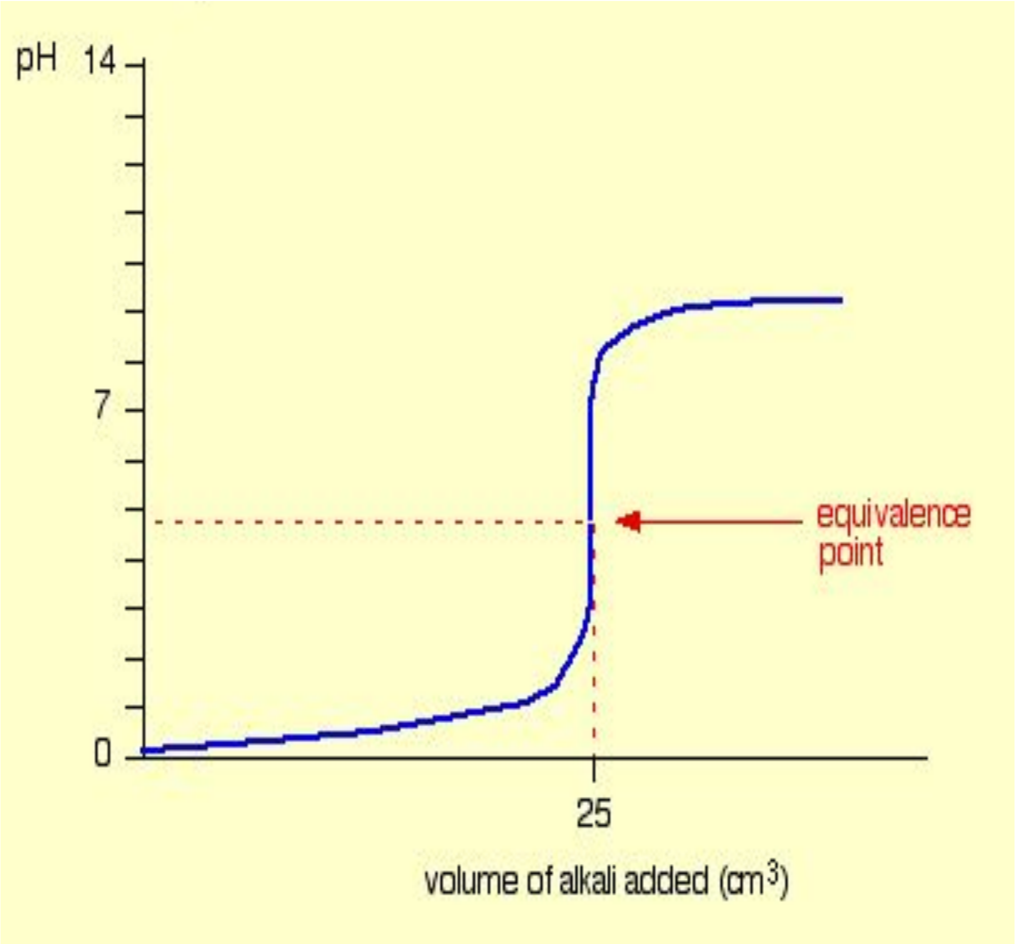
- Then there is a really steep plunge. If you calculate the values, the pH falls all the way from 11.3 when you have added 24.9 cm^3 to 2.7 when you have added 25.1 cm^3



Titration curves for strong acid v weak base

HCl + NH3 →

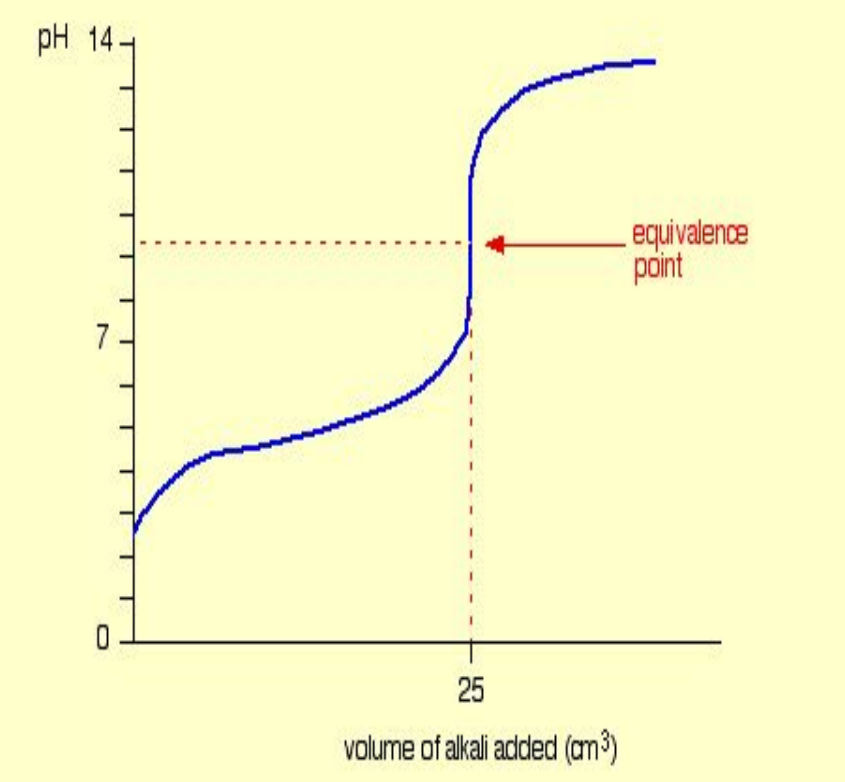
- This time we are going to use hydrochloric acid as the strong acid and ammonia solution as the weak base
- At the beginning of this titration, you have an excess of hydrochloric acid. The shape of the curve will be the same as when you had an excess of acid at the start of a titration running sodium hydroxide solution into the acid.
- It is only after the equivalence point that things become different



Titration curves for weak acid v strong base

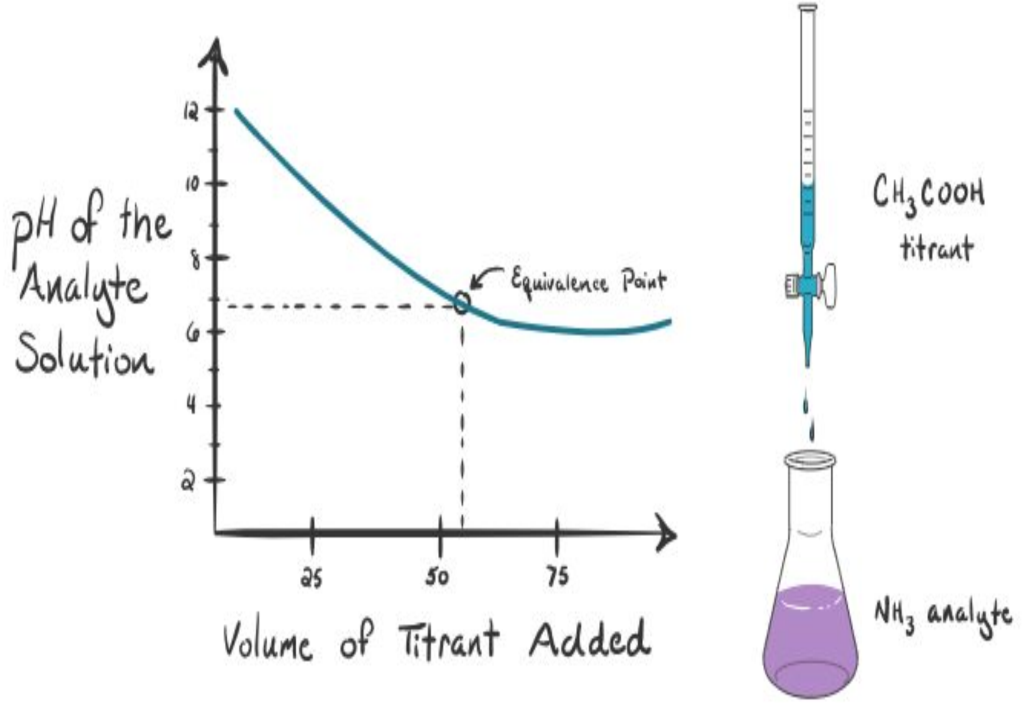
- We'll take ethanoic acid and sodium hydroxide as typical of a weak acid and a strong base

- The start of the graph shows a relatively rapid rise in pH but this slows down as a buffer solution containing ethanoic acid and sodium ethanoate is produced. Beyond the equivalence point (when the sodium hydroxide is in excess) the curve is just the same as that end of the HCl - NaOH graph



Titration curves for weak acid v weak base

- The common example of this would be ethanoic acid and ammonia
- If we start plotting the pH of the analyte against the volume of acetic acid that we are adding from the burette, we will get a titration curve as shown below
- there isn't any steep bit in this plot. There is just what we call a 'point of inflexion' at the equivalence point.
- Lack of any steep change in pH throughout the titration renders titration of a weak base versus a weak acid difficult



The Choice of indicators based on the type of titration is tabulated below

Types of titration	Indicators
Strong acid-strong base	Phenolphthalein is usually preferred because of its more easily seen colour change.
Weak acid-strong base	Phenolphthalein is used and changes sharply at the equivalence point and would be a good choice.
Strong acid-weak base	Methyl orange will change sharply at the equivalence point.
Weak acid-weak base	Neither phenolphthalein, nor methyl orange is suitable. No indicator is suitable because it requires a vertical portion of the curve over two pH units.

Theories of acid-base indicators

Two theories have been put forward to explain the indicator action in acid-base titrations :

(1) The Ostwald's theory

(2) The Quinonoid theory

The Ostwald's theory

According to this theory :

(1) an acid-base indicator is a weak organic acid (HIn) or a weak organic base (InOH), where the letter "In" stands for a complex orange group. Methyl orange and phenolphthalein are both weak acids.

(2) the un-ionised indicator, HIn, has a colour different from the In– ions produced by the ionization of the indicator in aqueous solution.

(3) the degree of ionisation of the indicator determines the visible colour of the indicator solution.

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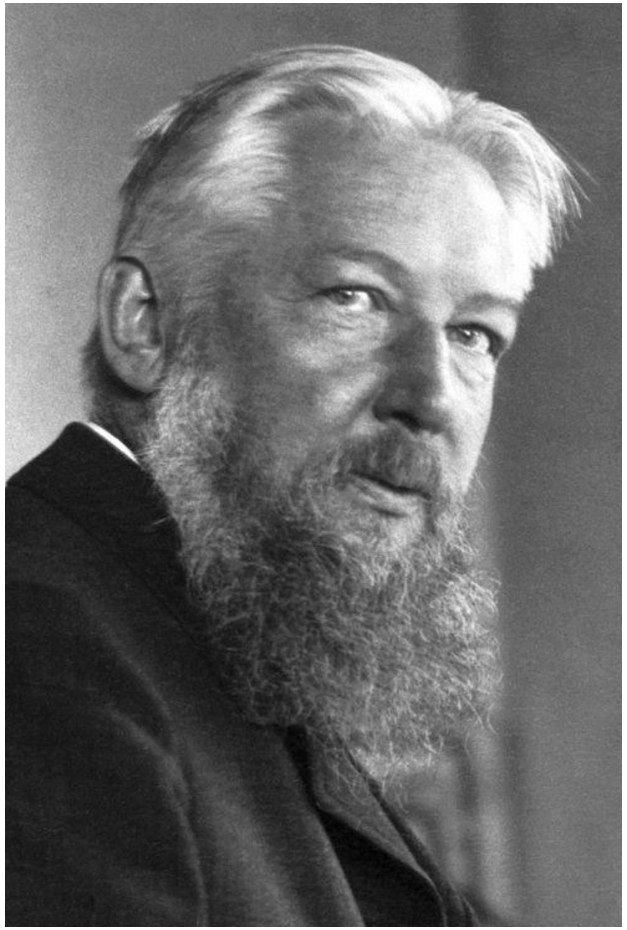
Wilhelm Ostwald 1853-1932



The **Nobel Prize in Chemistry 1909** was awarded to Wilhelm Ostwald "**in recognition of his work on catalysis and for his investigations into the fundamental principles** governing chemical equilibria and rates of reaction."

THEORY OF INDICATORS:

1. Ostwald's theory:

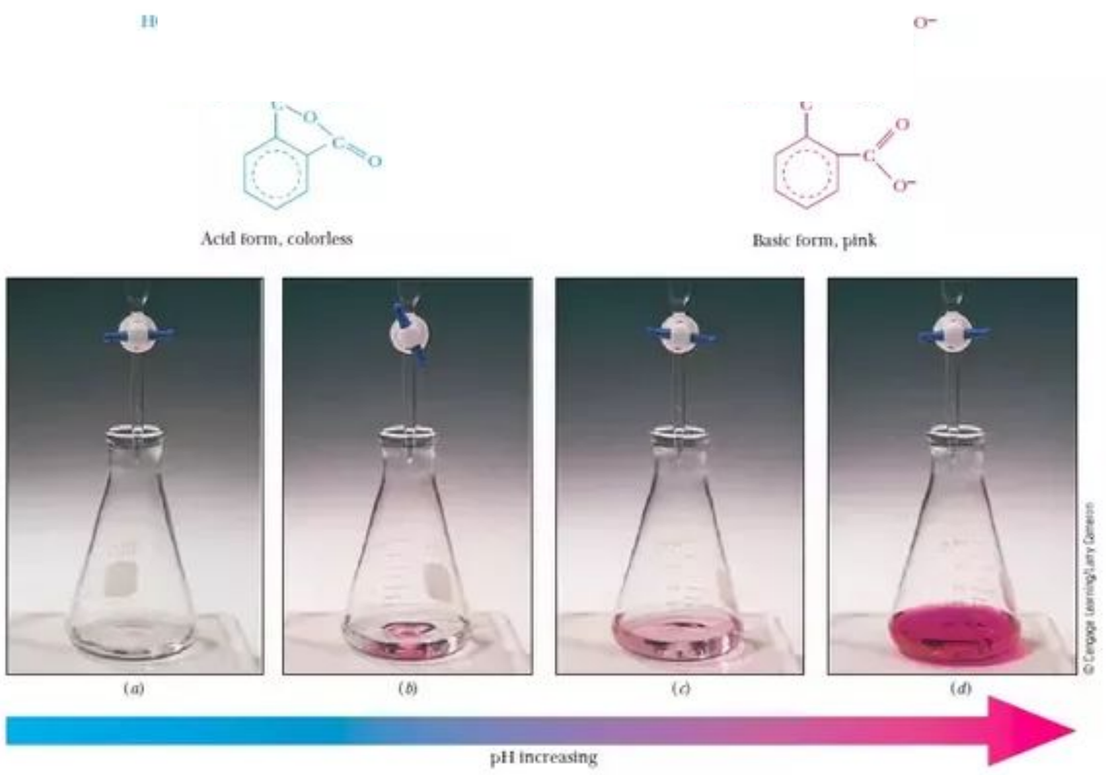
Phenolphthalein: It can be represented as HPh. It ionises in solution to a small extent as:

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

Colourless Pink

The undissociated molecules of phenolphthalei colourless while Ph^{-} ions are pink in colour. In presenc acid the ionisation of HPh is practically negligible equilibrium shifts to left hand side due to high concer of H^{+} ions. Thus, the solution would remain colourle addition of alkali, hydrogen ions are removed by OH^{-} the form of water molecules and the equilibrium sl right hand side. Thus, the concentration of Ph^{-} ions in in solution and they impart pink colour to the solution.

$$\underset{\text{(colorless)}}{HPh} \rightleftharpoons \underset{\text{(colorless)}}{H^{+}} + \underset{\text{(pink color)}}{Ph^{-}}$$



Phenolphthalein. Drawings show the acid and base forms of phenolphthalein, an indicator commonly used for the titration of an acid with strong base. *(a)* The acidic solution is initially clear. *(b)* When base is added, the solution turns pink momentarily but disappears with swirling. *(c)* The first permanent pink indicates the endpoint. *(d)* The solution is vividly colored beyond the equivalence point, where base is in excess.

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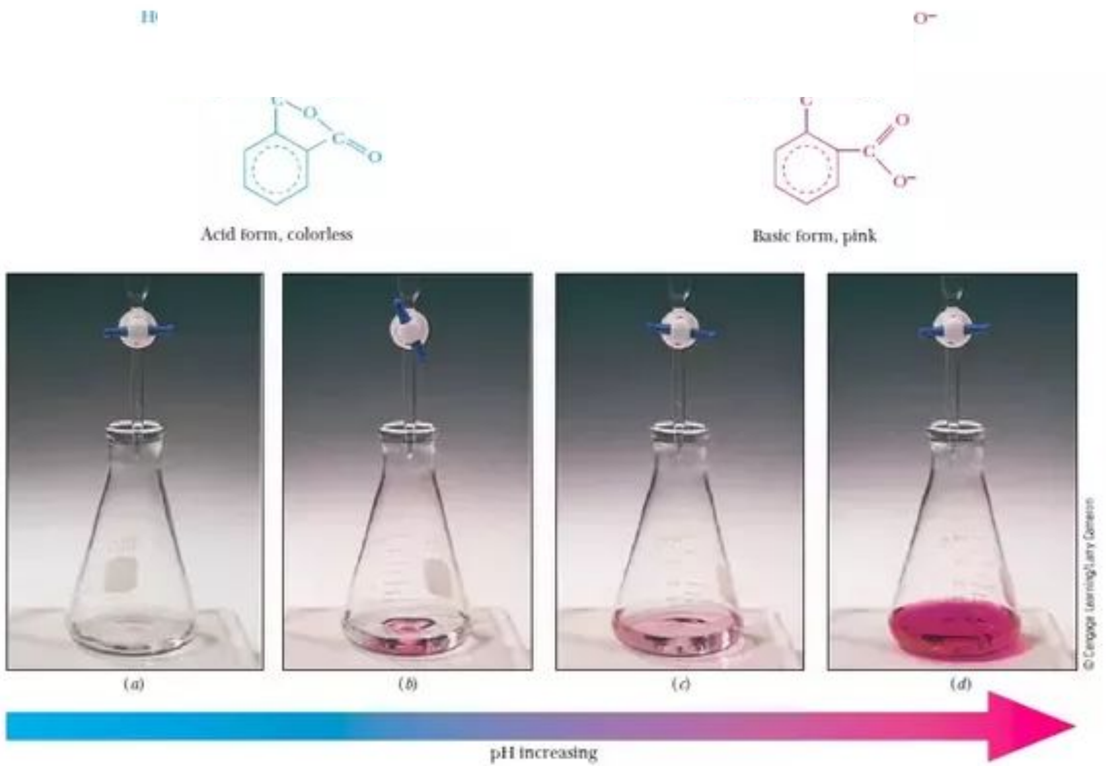

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- The anion In– is yellow and the nonionised form HIn– is red.
- If an acid is added to the solution, the hydrogen ion concentration, [H+], in the equilibrium expression (1) increases.
- To maintain K_{in} constant, the equilibrium shifts to the left. Thereby the concentration of [In–] is reduced and the concentration of [HIn] increases so that the solution is red

How an acid-base indicator works

Let us explain the indicator action by taking example of methyl orange. Methyl orange is a weak acid and gives the following ionisation equilibrium in solution.

$$\underset{\text{red}}{HIn} \rightleftharpoons H^+ + \underset{\text{yellow}}{In^-}$$

In accordance with the law of mass action,

$$K_{in} = \frac{[H^+][In^-]}{[HIn]} \quad ...(1)$$

where K_{in} is the dissociation constant of the indicator and is called the **Indicator constant.**

Relation of Indicator colour to pH

The indicator solution contains both the yellow In^- and the red HIn molecules. The actual colour shade of the indicator depends on the ratio of concentration of In^- and HIn present in solution. From the equilibrium constant expression (1) we can write

$$[H^+] = K_{in}\frac{[In^-]}{[HIn]} \quad ...(2)$$

If $[H^+]$ is large, the concentration of In^- ions is also large and the colour is yellow. When $[H^+]$ is small, [HIn] is large and the solution is red. At the equivalence point, $[In^-]$ = [HIn] and the colour is orange (red + yellow). Obviously the **indicator colour is controlled by hydrogen ion concentration or pH of the solution.**

Taking logarithms and using definition of pH and K_{in}, the expression (2) can be converted to the Henderson-Hasselbalch equation.

$$pH = pK_{in} + \log\frac{[In^-]}{[HIn]} \quad ...(3)$$

At the equivalence point, $[In^-]$ = [HIn] and methyl orange in solution is orange. Then,

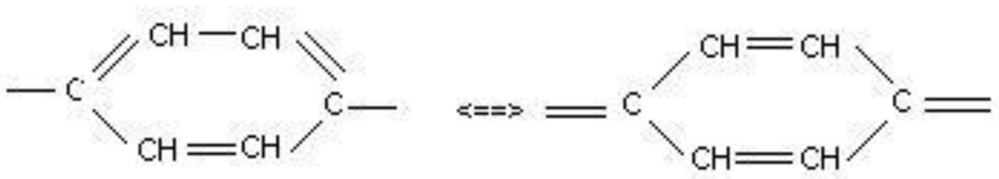
$$pH = pK_{in}$$

Quinonoid 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** (light colour) and the other **quinonoid form** (deep colour).

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

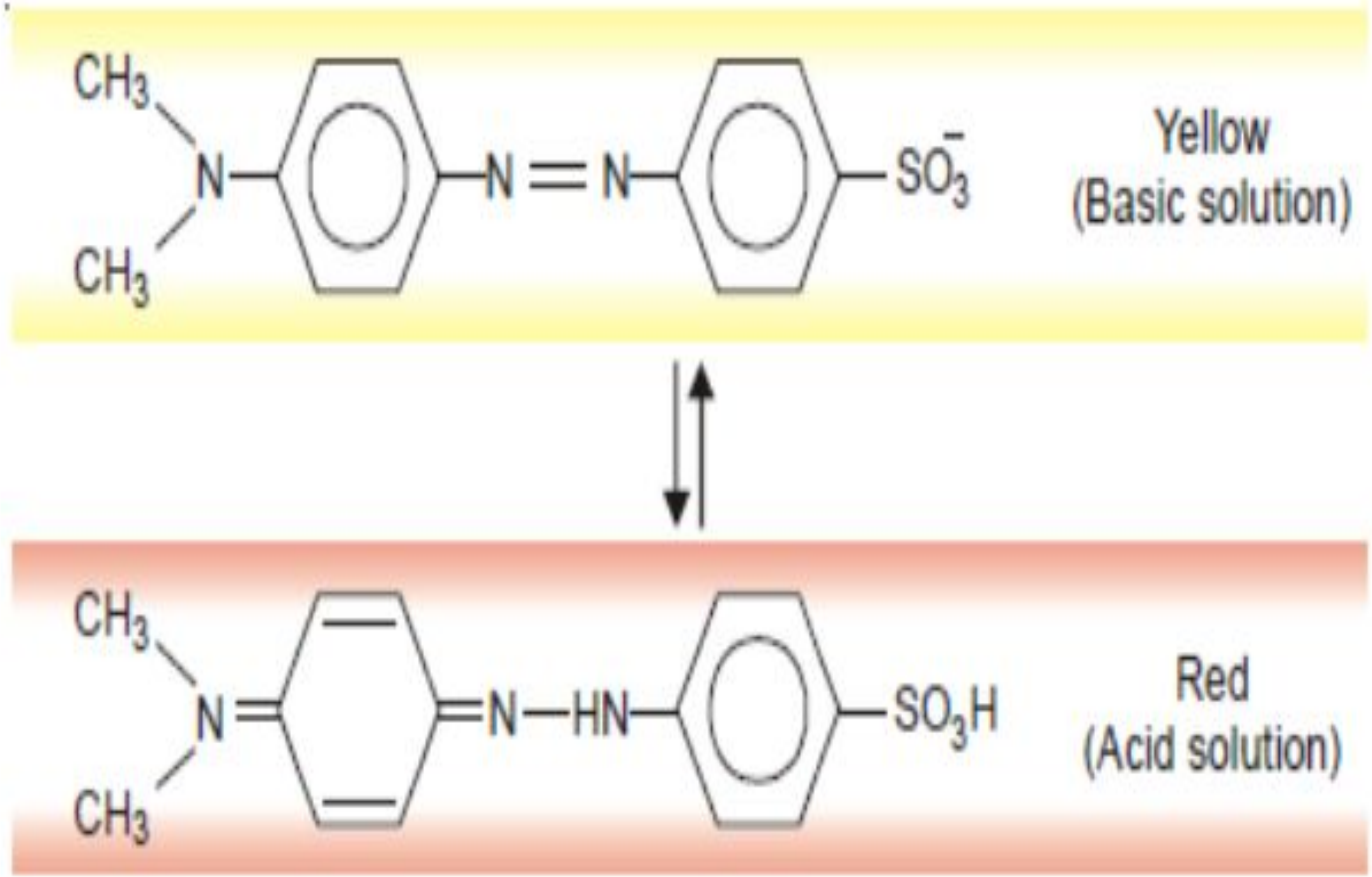
c) One form mainly exists in acidic medium and the other in alkaline medium.



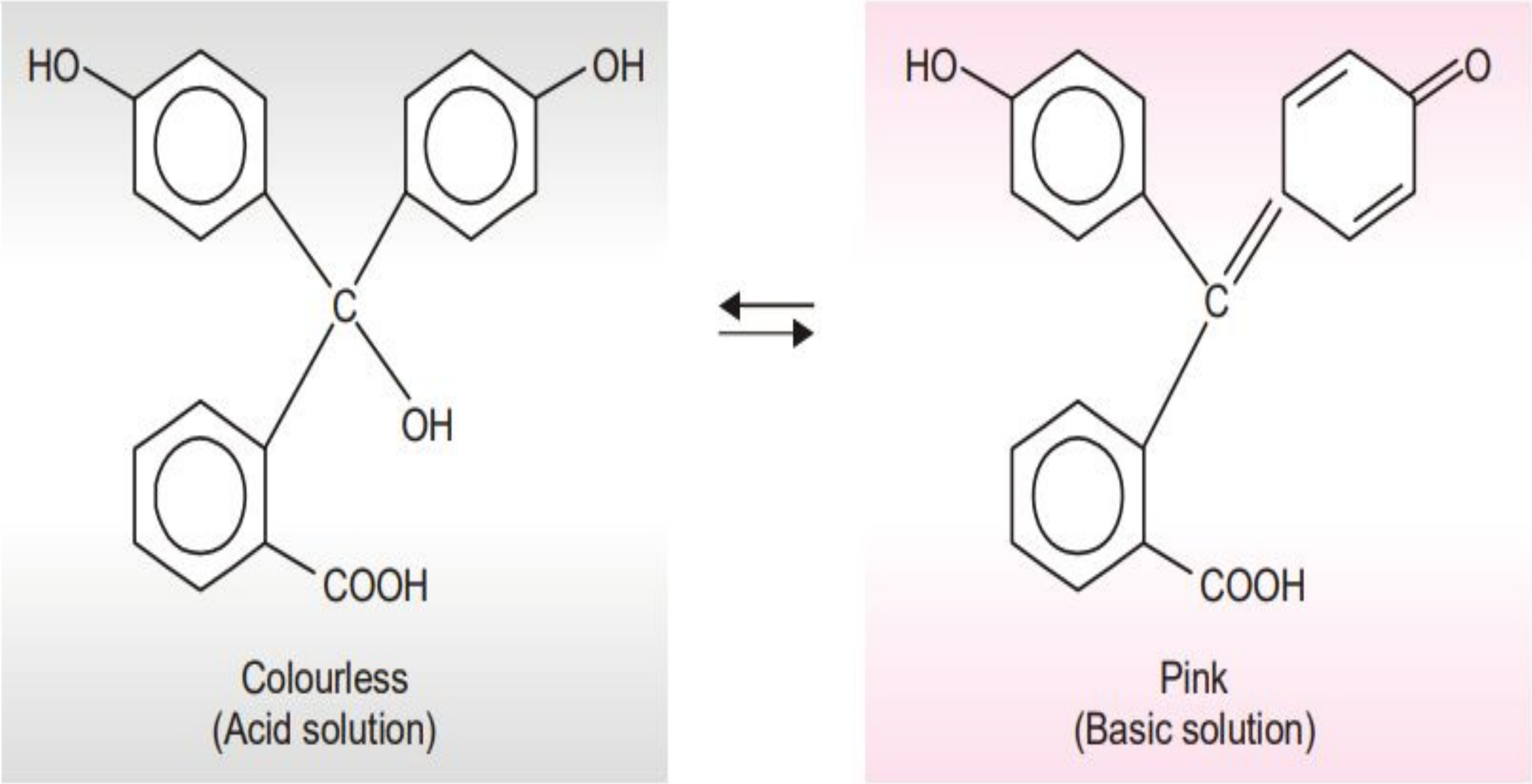
Benzenoid form

Quinonoid form

Methyl Orange



Phenolphthalein



Thank you!