THEORY OF INDICATORS : QUINONOID THEORY

1. Quinonoid theory:

According to this theory:

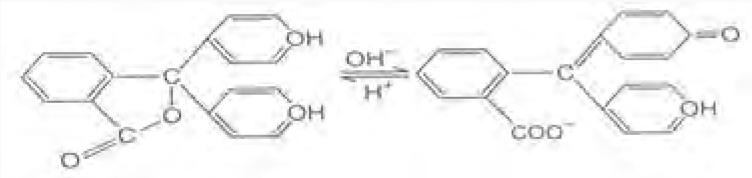
(a) The **acid-base indicators** exist in two tautomeric forms having different structures. Two forms are in equilibrium. One form is termed benzenoid form and the other quinonoid form.

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

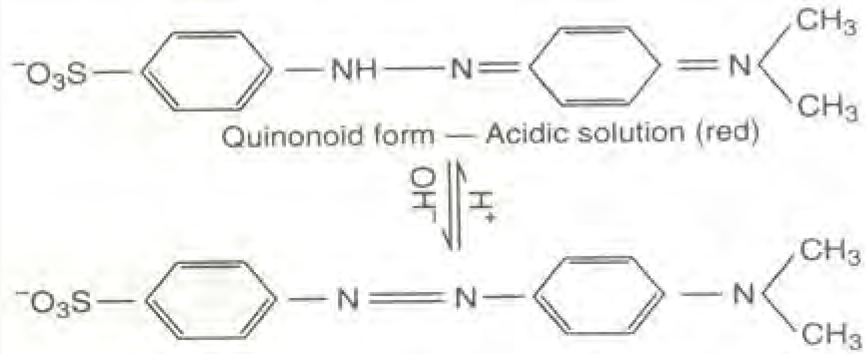
(c) One form mainly exists in acidic medium and the other in alkaline medium.

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.



Selection of suitable indicator or choice of indicator

The neutralisation reactions are of the following four types:

(i) A strong acid versus a strong base. (Fig. 10.1)

(ii) A weak acid versus a strong base. (Fig. 10.2)

(iii) A strong acid versus a weak base. (Fig. 10.3)

(iv) A weak acid versus a weak base. (Fig. 10.4)

In order to choose a suitable **indicator**, it is necessary to understand the pH changes in the above four types of **titrations**. The change in pH in the vicinity of theequivalence point is most important for this purpose. The curve obtained by plotting pH as ordinate against the volume of alkali added as abscissa is known as neutralisation or **titration curve**. The **titration curves** of the above four types of neutralisation reactions are shown in Fig. 10.1, 10.2, 10.3 and 10.4.

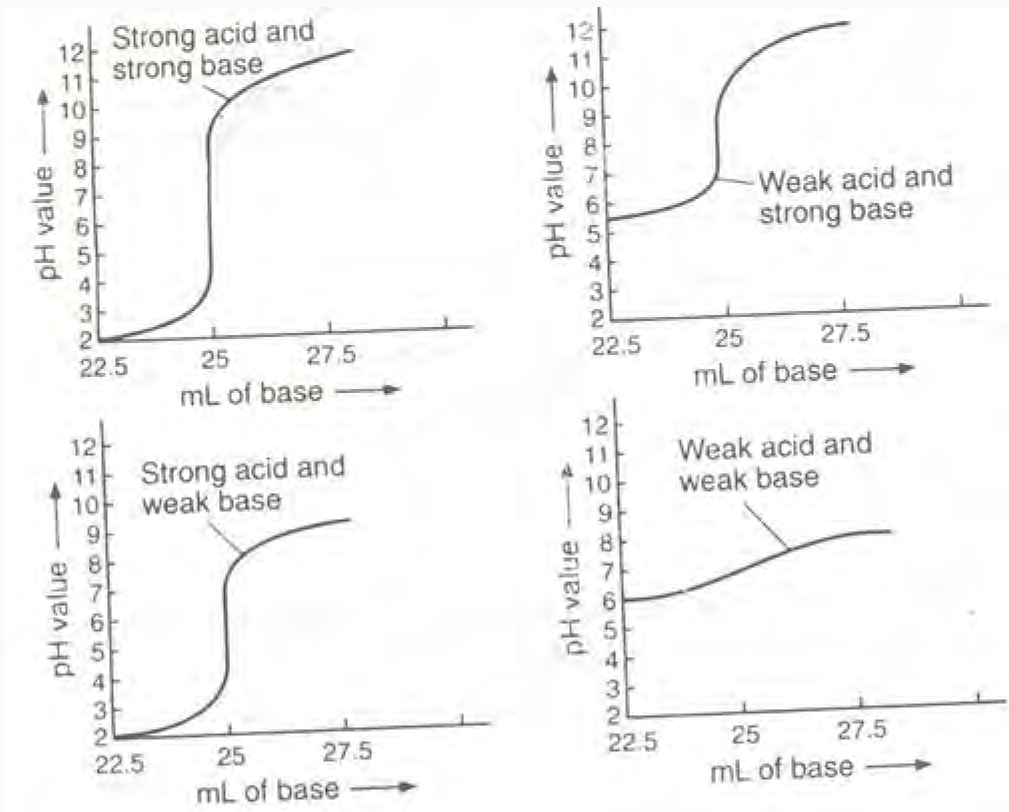
In each case 25 mL of the acid (N/10) has been **titrated** against a standard solution of a base (N/10). Each **titration curve** becomes almost vertical for somedistance (except curve 10.4) and then bends away again. This region of abrupt change in pH indicates the equivalence point. For a particular **titration**, the **indicator** should be so selected that it changes its colour within vertical distance of the curve.

(i) Strong acid vs. strong base:

pH curve of strong acid (say HCI) and strong base (say NaOH) is vertical over almost the pH range 4-10. So the indicators **phenolphthalein** (pH range 8.3 to 10.5), methyl red (pH range 4.4-6.5) and **methyl orange** (pH range 3.2-4.5) are suitable for such a **titration**.

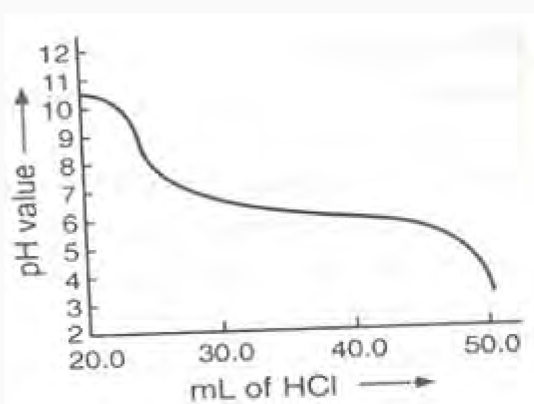
(ii) Weak acid vs. weak base:

pH curve of weak acid (say CH_3COOH of oxalic acid) and strong base (say NaOH) is vertical over the approximate pH range 7 to 11. So phenolphthalein is the suitable indicator for such a titration.



(iii) Strong acid vs. weak base:

pH curve of strong acid (say HCl or H_2SO_4 or HNO_3) with a weak base (say NH_4OH) is vertical over the pH range of 4 to 7. So the **indicators** methyl red and **methyl orange** are suitable for such a **titration**.



(iii) Weak acid vs. weak base:

pH curve of weak acid and weak base indicates that there is no vertical part and hence, no suitable **indicator** can be used for such a **titration**.

Titration of soluble carbonate with strong acid.

pH curve of sodium carbonate with HCI shows two inflection points (Fig. 10.5). First inflection point (pH 8.5) indicates conversion of carbonate into bicarbonate.

$Na_2CO_3 + HCI \rightarrow NaHCO_3 + NaCl$

As the inflection point lies in the pH range 8 to 10, phenolphthalein can be used to indicate the above conversion. The second inflection point (pH 4.3) indicates the following reaction:

$NaHCO_3 + HCI \rightarrow NaCl + CO_2 + H_2O$

As the point lies between 3 to 5, **methyl orange** can be used.

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