15. THEORY OF INDICATORS

An acid base indicator is a substance which possesses one colour in acid solutions and a different one in alkaline solution. Two theories have been put forward to explain this colour change. We will discuss these with reference to the two important acid-base indicators namely phenolphthalein and methyl orange.

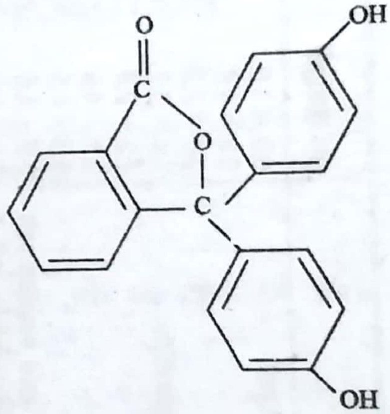
1. Ostwald's Theory based on Ionisation
2. The Quinonoid theory.

1. OSTWALD'S THEORY BASED ON IONISATION

According to the ionic theory, the colour of a solution is due to the presence of coloured ions water. Ostwald maintained that an indicator is either a weak organic acid or weak organic base whose undissociated molecule has a colour different from the ions furnished by it. These differently coloured ions come into solution under the influence of strong acid or a strong base.

E.g. 1. **Phenolphthalein** (HPh) which ia weak acid. Its undissociated molecule is colourless. Or dissociation it gives H^+ ions which are also colourless and the rest of the molecule i.e. ph^- ions which posses a deep pink colour.

$$\underset{\text{(colourless)}}{HPh} \rightleftharpoons \underset{\text{(colourless)}}{H^+} + \underset{\text{(pink colour)}}{ph^-}$$



In the presence of an acid, due to an increase in the concentration of Hydrogen ions, **the dissociation of Hph is practically nil**, so that, the solution would remain colourless. On the addition of a strong Alkali like NaOH, the O H ions from it combine with the H^+ ions from phenolphthalein to form the feebly ionised water so that the equilibrium is disturbed and ion of the phenolphthalein ionises to restore this equilibrium.

The pH^- ions so produced combine with Na^+ ions to form the strongly ionised sodium salt Naph and thus remain in solution in the ionic stage and impart a pink colour.

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

$$NaOH \rightleftharpoons OH^- + Na^+$$

$$\updownarrow \qquad \updownarrow$$

$$\underset{\text{(Feebly ionised)}}{H_2O} + \underset{\text{(Strongly ionised)}}{NaPh} \quad \text{(Pink colour)}$$

2. Methyl orange:

It is a weak base represented for convenience as MeOH whose undissociated molecule is yellow. On ionisation it gives the colourless OH^- ions and red coloured Me^+ ions.

In acid solution the methyl orange gives red colour.

$$\underset{\text{(Yellow)}}{MeOH} \rightleftharpoons Me^{+} + OH^{-}$$

$$HCl \rightleftharpoons Cl^{-} + H^{+}$$

$$\downarrow\uparrow \qquad \downarrow\uparrow$$

$$\underset{\text{(Strongly ionised)}}{MeCl} + \underset{\text{(Feebly ionised)}}{H_2O} \text{ (Red colour)}$$

2. Quinonoid Theory

According to the early theories of Bernthsen, Friedlander and Witt, the term chromophore was applied to the system responsible for imparting colour to a compound.

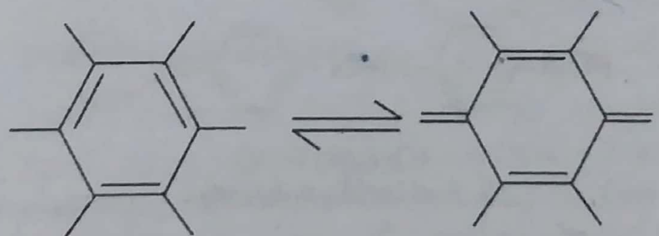
Chromophore - Greek word - color carrier.

e.g. $C = C, C \equiv C, C = 0, C \equiv N, N = 0, N = N$ etc.

As most of the acid-base indicators are organic aromatic derivatives, the quinonoid theory attempts to explain the colour changes on the basis of "**Intramolecular change**" rather than ionisation. It is believed that an indicator consists of an equilibrium mixture of atleast two tautomeric forms, one of which can exist in an acid solution and the other in alkaline solution.

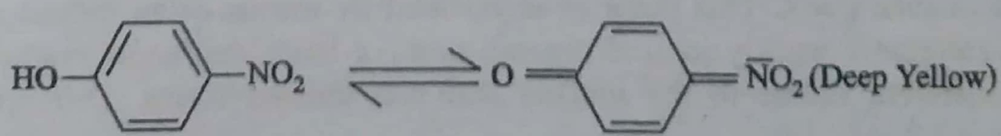
The two forms possess different colours and as the PH of the solution combining such a indicator alters, the solution shows a change of colour due to the passing of one form in the other. i.e. Benzenoid to Quinonoid or vice versa

The quinonoid form is usually deeper in colour than the benzenoid form



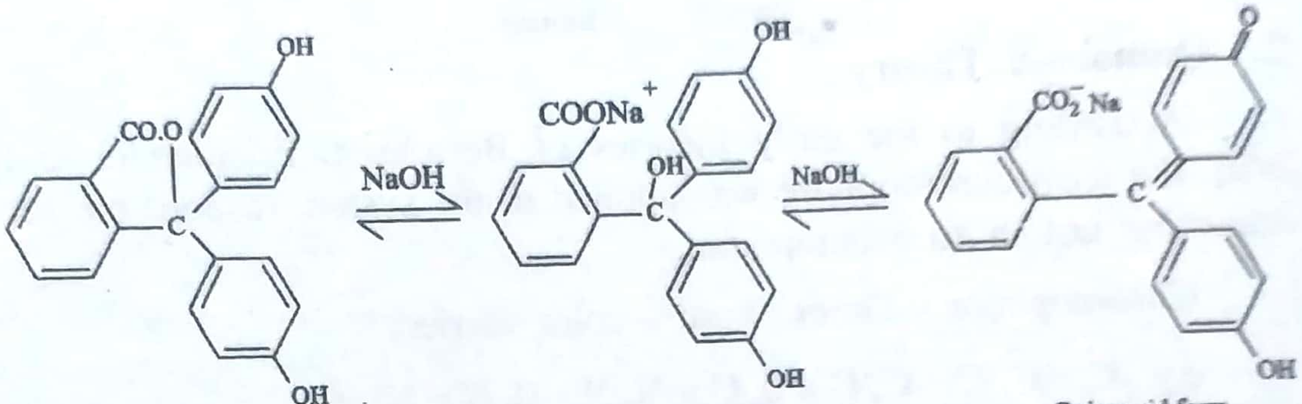
Benzenoid (colourless) Quinonoid (coloured)

E.g.: **P-nirtrophenol** in Alkaline solution Yellow colour and while in acid solution is colourless due to benzenoid form.



Phenolphthalein

The indicator phenolphthalein is colourless in the acid form (Benzenoid structure) but possesses as a Red or Pink colour in the tautomeric form which exists in an alkaline solution (Quinonoid structure).



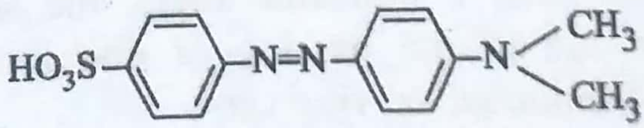
Benzenoid form
(colourless in acid solution)
(pH: less than 7)

Benzenoid form
(colourlessO
(pH: 7-8)

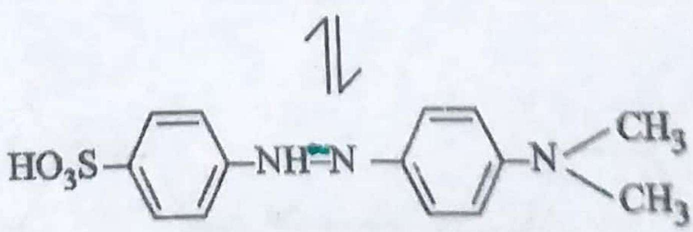
Quinonoid form
(Red in alkaline solution)
(pH: 8-10)

Methyl Orange

We have two tautomeric forms of methyl orange, the red form existing in the acidic solution but passing to the yellow form as the pH value alters to the alkaline side.



(Benzenoid form)
Yellow (Basic solution)



(Quinoid form)
Red (acidic solution)