LECTURE 4
Indicator Range

At a low pH, a weak acid indicator is almost entirely in the HIn form, the colour of which predominates. As the pH increases - the intensity of the colour of HIn decreases and the equilibrium is pushed to the right Therefore the intensity of the colour of In- increases. An indicator is most effective if the colour change is distinct and over a low pH range. For most indicators the range is within ±1 of the pKIn value

Indicator	Colour		pK_{In}	pH range
	Acid	Base		
Thymol Blue - 1st change	red	yellow	1.5	1.2 - 2.8
Methyl Orange	red	yellow	3.7	3.2 - 4.4
Bromocresol Green	yellow	blue	4.7	3.8 - 5.4
Methyl Red	yellow	red	5.1	4.8 - 6.0
Bromothymol Blue	yellow	blue	7.0	6.0 - 7.6
Phenol Red	yellow	red	7.9	6.8 - 8.4
Thymol Blue - 2nd change	yellow	blue	8.9	8.0 - 9.6
Phenolphthalein	colourless	pink	9.4	8.2 - 10.0

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A Universal Indicator is a mixture of indicators which give a gradual change in colour over a wide pH range - the pH of a solution can be approximately identified when a few drops of universal indicator are mixed with the solution. Indicators are used in titration solutions to signal the completion of the acid-base reaction

Theory of Indicators

An indicator is a substance which show characteristic change in its colour when comes in contact with acid or base and thus it is used to determine dicators the degree of acidity or basicity of any solution. For example litmus solution or litmus paper.

Role of indicators in chemistry is very important. They are used are also used to find out the end point in a titration.

In acid-base titrations, organic substances (weak acids or weak bases) are generally used as indicators.

Indicators change their colour within a certain pH range.

There are two theories which explain the change of colour indicators with change in pH.

Ostwald's Theory

According to Ostwald's theory

- The colour change of any indicator is due to its ionisation. The unionised form of indicator has different colour than its ionised form.

- An inidicator is either a weak acid or base, so its ionisation is highly affected in acids and bases. If an **indicator** is a weak acid, its ionisation would be very much low in acids due to common H^+ ions while it is fairly ionised in alkalies. In the same way, if the **indicator** is a weak base, its ionisation is large in acids and low in alkalies due to common OH^- ions.

Let's take examples of two important indicators **phenolphthalein** which is a weak acid and **methyl orange** which is a weak base.

1. Phenolphthalein

It is represented as HPh. This indicator being a weak acid ionises in solution to a small extent as follows:

HPh===============H+ + Ph-
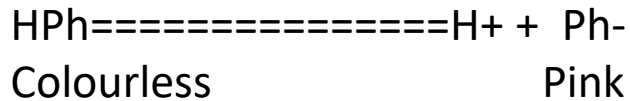
Colourless   Pink

Applying law of mass action, we get

K = [H+][Ph-]/[HPh]

The undissociated molecules of phenolphthalein are colourless while the Ph- ions are pink in colour. In presence of an acid , ionisation of HPh is practically negligible as the equilibrium shifts to left hand side due to high concentration of H+ ions. Thus, the solution would remain colourless. 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.

Let us derive Handerson equation for an indicator

$HIn + H_2O \rightleftharpoons H_3O^+ + In^-$

'Acid form'   'Base form'

|_____|

Conjugate acid-base pair

$KIn = [In][H_3O^+]/[HIn];$ KIn = Ionization constant for indicator

$[H_3O^+] = KIn * [HIn]/In^-$

$pH = -log_{10}[H_3O^+] = -log_{10}[KIn] - log_{10}[HIn]/[In^-]$

$pH = pKIn + log_{10}[In^-]/[HIn]$ (Handerson equation for indicator)

At equivalence point

$[In^-] = [HIn]$ and $pH = pKIn$

2. Methyl orange

It is a very weak base and can be represented as MeOH. It is ionized in solution to give Me+ and OH- ions.

MeOH   Me+ + OH-

Yellow   Red

Applying law of mass action,

 K = [Me+][OH-]/[MeOH]

In presence of an acid, OH- ions are removed in the form of water molecules and the above equilibrium shifts to right hand side. Thus, sufficient Me+ ions are produced which impart red colour to the solution. On addition of alkali, the concentra¬tion of OH- ions increases in the solution and the equilibrium shifts to left hand side, i.e., the ionisation of MeOH is practi¬cally negligible. Thus, the solution acquires the colour of unionised methyl orange molecules, i.e., yellow

This theory also explains the reason why phenolphthalein is not a suitable indicator for titrating a weak base against strong acid. The OH- ions furnished by a weak base are not sufficient to shift the equilibrium towards right hand side considerably, i.e., pH is not reached to 8.3. Thus, the solution does not attain pink colour. Similarly, it can be explained why methyl orange is not a suitable indicator for the titration of weak acid with strong base

Quinonoid theory

According to quinonoid theory, an acid-base indicators exist in two tautomeric forms having different structures which are in equilibrium. One form is termed benzenoid form and the other quinonoid form.
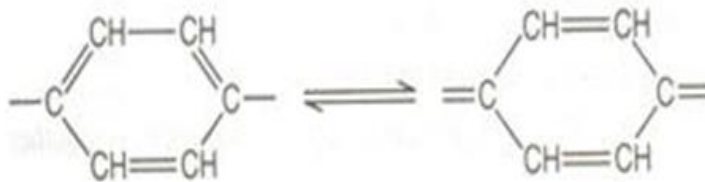

The two forms have different colors. The color change is due to the inter conversation of one tautomeric form into other. One form mainly exists in acidic medium and the other in alkaline medium.

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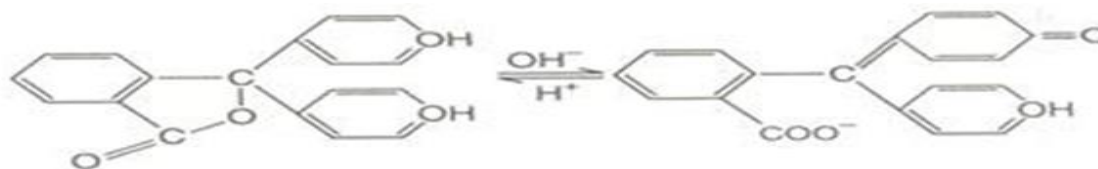
Methyl orange has quinonoid form in acidic solution and benzenoid form in alkaline solution. The color of benzenoid form is yellow while that of quinoniod form is red.

Quinonoid form — Acidic solution (red)
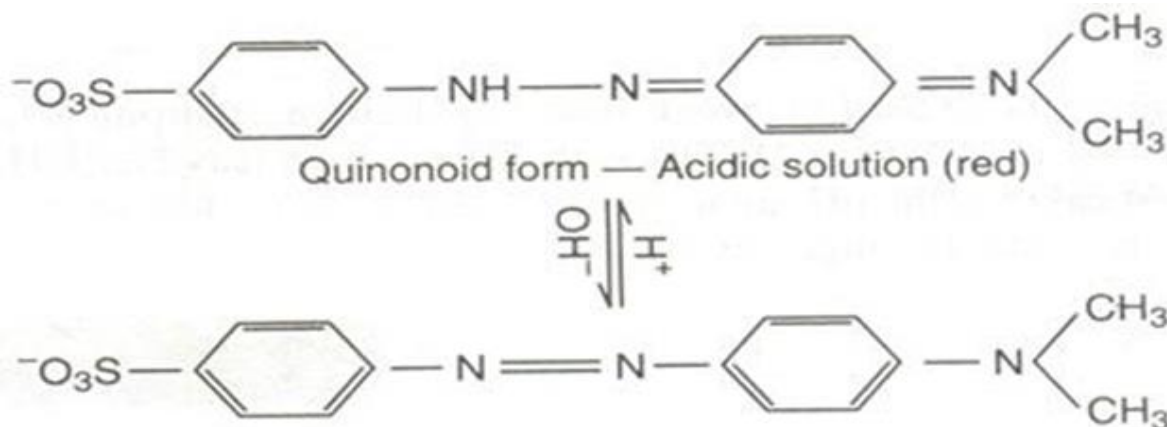
Choosing indicators for titrations

Remember that the equivalence point of a titration is where you have mixed the two substances in exactly equation proportions. You obviously need to choose an indicator which changes colour as close as possible to that equivalence point. That varies from titration to titration.

## ***Strong acid v strong base***

The next diagram shows the pH curve for adding a strong acid to a strong base. Superimposed on it are the pH ranges for methyl orange and phenolphthalein.

pH 14

phenolphthalein

7   ← equivalence point

methyl orange

0

volume of acid added (cm^3)
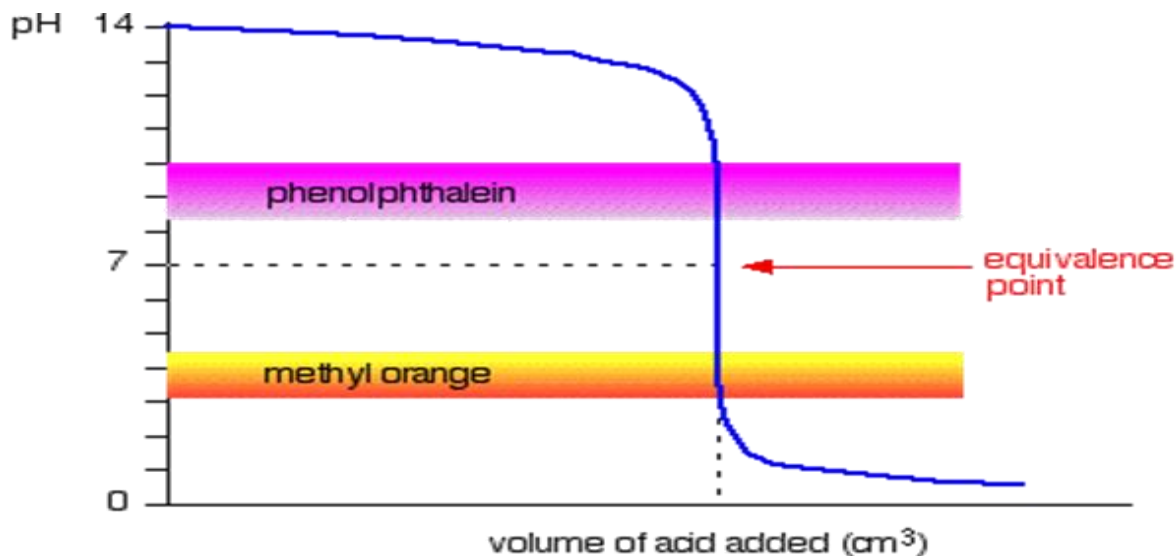
You can see that neither indicator changes colour at the equivalence point. However, the graph is so steep at that point that there will be virtually no difference in the volume of acid added whichever indicator you choose. However, it would make sense to titrate to the best possible colour with each indicator.

If you use phenolphthalein, you would titrate until it just becomes colourless (at pH 8.3) because that is as close as you can get to the equivalence point.

On the other hand, using methyl orange, you would titrate until there is the very first trace of orange in the solution. If the solution becomes red, you are getting further from the equivalence point.

Strong acid v weak base
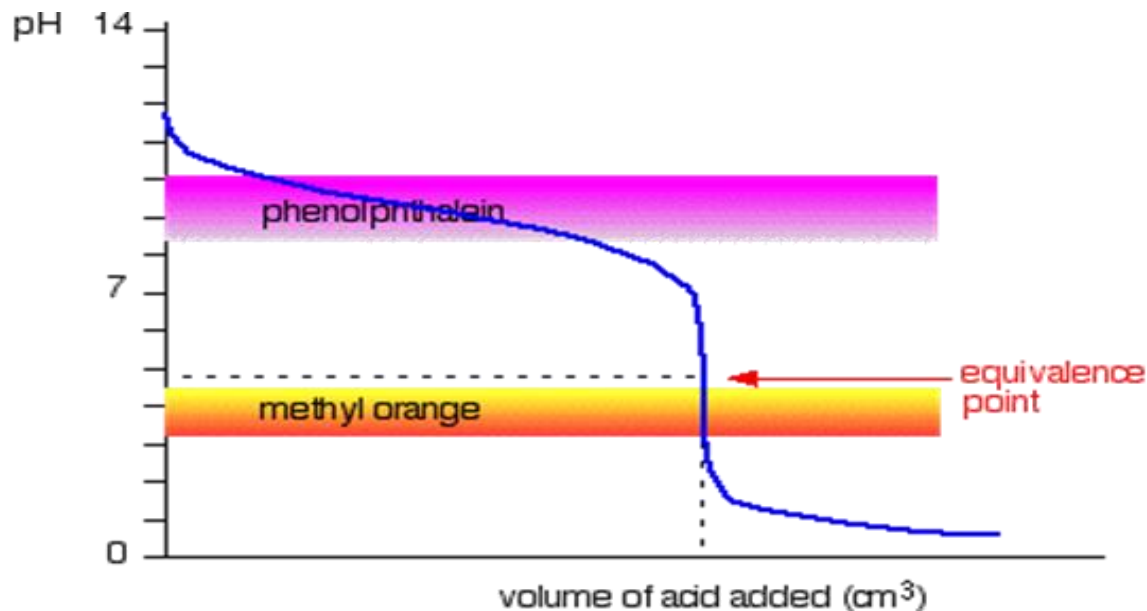
This time it is obvious that phenolphthalein would be completely useless. However, methyl orange starts to change from yellow towards orange very close to the equivalence point.
You have to choose an indicator which changes colour on the steep bit of the curve
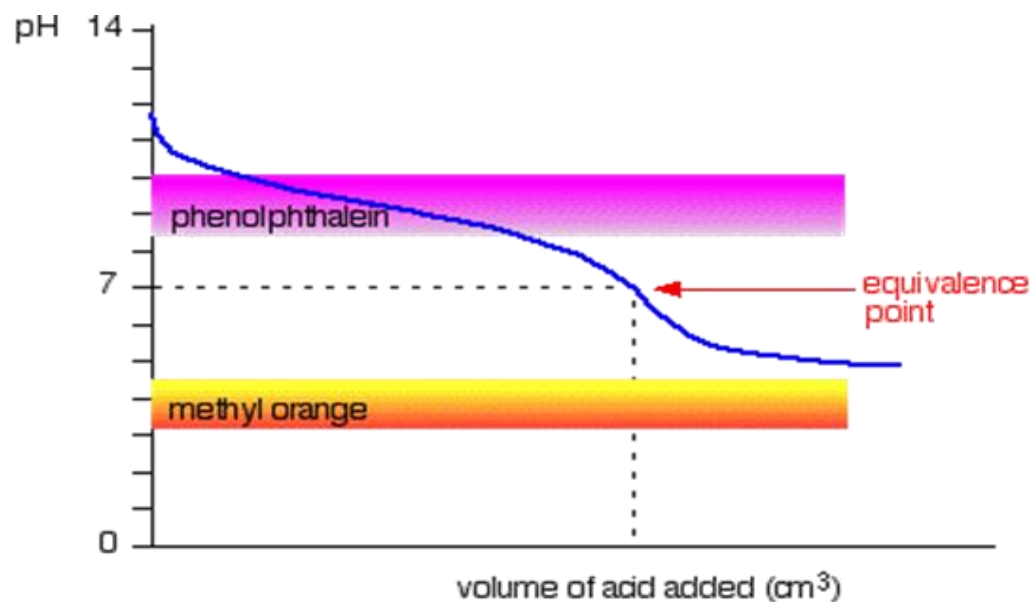
Weak acid v strong base
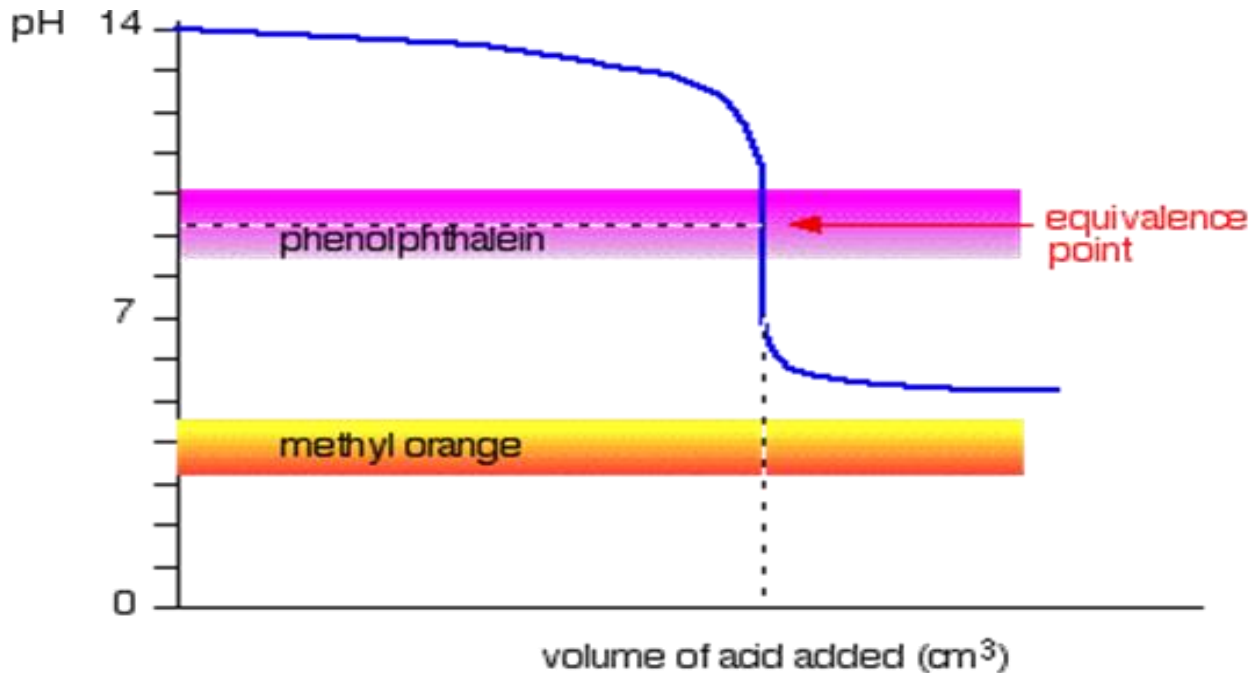
This time, the methyl orange is hopeless! However, the phenolphthalein changes colour exactly where you want it to.

Weak acid v weak base

The curve is for a case where the acid and base are both equally weak - for example, ethanoic acid and ammonia solution. In other cases, the equivalence point will be at some other pH.

You can see that neither indicator is any use. Phenolphthalein will have finished changing well before the equivalence point, and methyl orange falls off the graph altogether.

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You can see that neither indicator is any use. Phenolphthalein will have finished changing well before the equivalence point, and methyl orange falls off the graph altogether.
It may be possible to find an indicator which starts to change or finishes changing at the equivalence point, but because the pH of the equivalence point will be different from case to case, you can't generalise.

Sodium carbonate solution and dilute hydrochloric acid
This is an interesting special case. If you use phenolphthalein or methyl orange, both will give a valid titration result - but the value with phenolphthalein will be exactly half the methyl orange one.
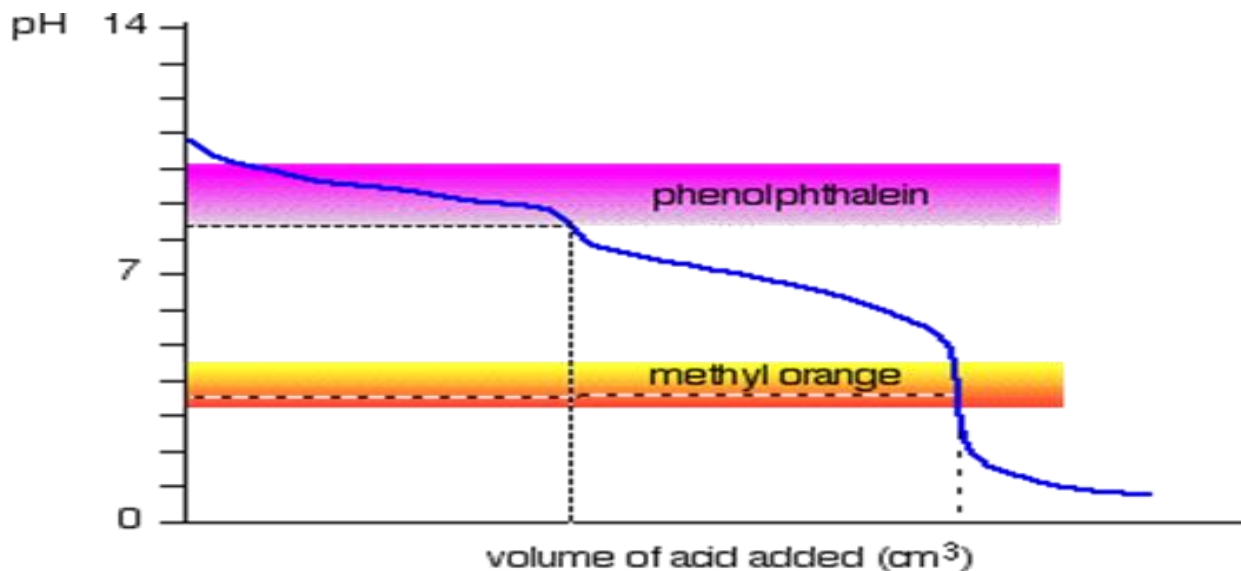
It so happens that the phenolphthalein has finished its colour change at exactly the pH of the equivalence point of the first half of the reaction in which sodium hydrogencarbonate is produced.

$$Na_2CO_{3(aq)} + HCl_{(aq)} \longrightarrow NaCl_{(aq)} + NaHCO_{3(aq)}$$

The methyl orange changes colour at exactly the pH of the equivalence point of the second stage of the reaction.

$$NaHCO_{3(aq)} + HCl_{(aq)} \longrightarrow NaCl_{(aq)} + CO_{2(g)} + H_2O_{(l)}$$