Analytical Chemistry

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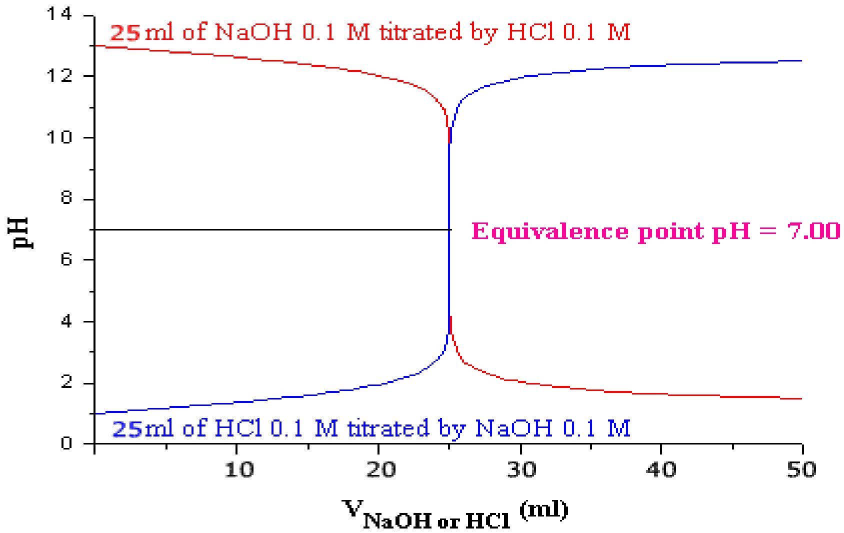
Strong acid strong base titrations

Titration curves are the graphs obtained by plotting the pH of the reaction mixture against the volume of base (or acid) added during the titration of either an acid by a base or vice versa.

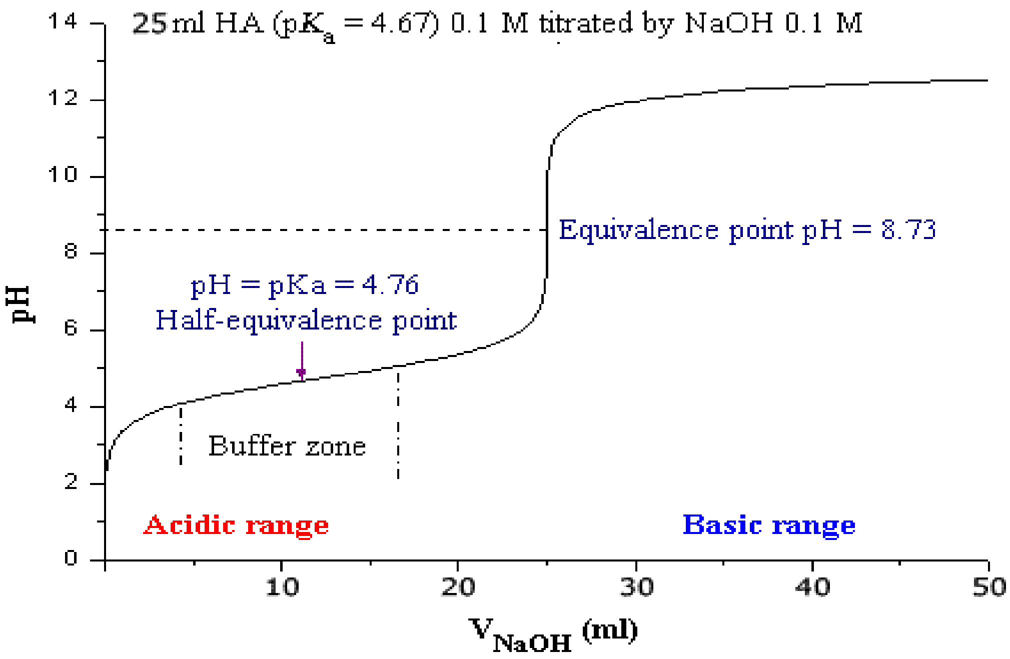
A typical strong acid - strong base titration curve looks like this:



The blue curve represents the titration of 25 cm^3 hydrochloric acid (0.1M) by additions of 0.1M Sodium hydroxide solution. The pH starts off at 1 and increases only very slowly at first. Near the equivalence point there is a rapid and dramatic increase in pH. This means that most indicators are suitable for carrying out ths type of titration.

The red curve represents the titration of a 25cm3 sample of sodium hyroxide (0.1M) by successive additions of 0.1M hydrochloric acid. Again a rapid inflexion is seen near the equivalence point.

Weak acid - strong base titration



The curve shows the titration of 25 cm^3 ethanoic acid (0.1M) by additions of 0.1M sodium hydroxide solution. The pH starts off at 2.4 and increases steadily at first. Near the equivalence point there is a rapid increase in pH. Only indicators that change colour in the region pH 6 - 10 are suitable for carrying out this type of titration.

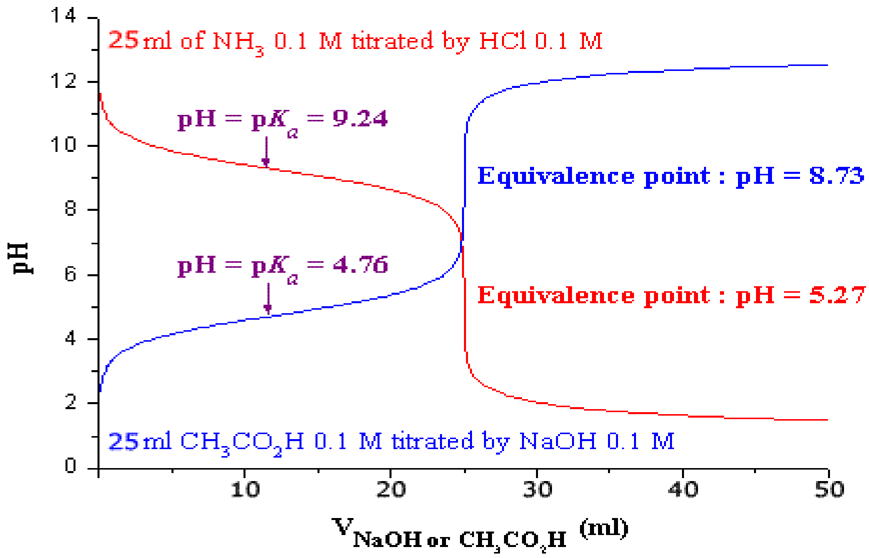
Phenolphthalein is the indicator of choice fopr this type of titration. It registers colourless in the acidic region and changes to red in base. The first hint of pink is taken as the end point.

Take care with phenlphthalein, as the red colour fades fairly rapidly if the solution is left standing.

Weak base strong acid titration

The red curve represents the titration of 25 cm3 ammonia (0.1M) by additions of 0.1M hydrochloric acid solution. The pH starts off near 12 and decreases steadily towards the equivalence point where there is a rapid decrease in pH. This means that only indicators that act in the acidic pH region are suitable for carrying out ths type of titration.

Methyl orange is the indicator of choice. It registers red in acid and yellow in base with the endpoint being orange.



INDICATORS

Indicators are the organic substances, the presence of very small amount of which indicates the termination of a chemical reaction by a change of colour. Indicators are of various types, e.g., acid-base indicators, redox indicators, adsorption indicator, etc. Acid-base indicators are the organic substances, which have one colour in acid solution while different colour in alkaline solution. The following theories have been put forward to explain the colour change of the acid base indicator.

THEORY OF INDICATORS:

An **indicator** is a substance which is used to determine the end point in a titration. In acid-base **titrations**, organic substances (weak acids or weak bases) are generally used as **indicators**. They change their colour within a certain pH range. The colour change and the pH range of some common **indicators** are tabulated below:

Indicator	pH range	Colour change
Methyl orange	3.2-4.5	Pink to yellow
Methyl red	4.4-6.5	Red to yellow
Litmus	5.5-7.5	Red to blue
Phenol red	6.8-8.4	Yellow to red
Phenolphthalein	8.3-10.5	Colourless to pink

Theory of acid-base 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 alkalies. Similarly if the **indicator** is a weak base, its ionisation is large in acids and low in alkalies due to common OH^- ions.

Considering weak acids (HIn) & bases (InOH) whose colours are different from that of the indicator-ion formed by their dissociation. The equilibria in the aqueous solution may be written as:

HIn --------------------------- H^+ + In^-
InOH ----------------------- OH^- + In^+
Unionized ionized
colour colour

If the indicator is a free amine or substituted amine the equilibrium is:

In + H_2O --------------------- OH^- + HIn^+

Indicator-acids HIn dissociate in aqueous solution as follows:

HIn ----------------------- H^+ + In^-

Applying the law of mass action to this dissociation

$$\frac{[H^+][In^-]}{[HIn]} = K\text{a} \quad \ldots\ldots\ldots\ldots(1)$$

from which

$$[H^+] = K\text{a}\,\frac{[HIn]}{[In^-]} \quad \ldots\ldots\ldots\ldots\ldots\ldots(2)$$

The actual colour of the indicator, which depends upon the ratio of the concentration of the ionized and unionized forms, is thus directly related to the hydrogen–ion concentration. Eq. (2) may be written as

$$pH = \log \frac{[In^-]}{[HIn]} + pK_a \ldots\ldots\ldots\ldots(3)$$

In this equation [HIn] represents the concentration of the undissociated indicator molecule whose colour is called 'acid colour' while [In −] denotes the concentration of the indicator-anions, the colour of which is called 'alkaline colour'. *K*a is the dissociation constant of the indicator- acid.
The indicator base may be characterized similarly to the indicator acid

$$InOH \rightleftharpoons In^+ + OH^-$$

$$\frac{[In^+][OH^-]}{[InOH]} = K_b \ldots\ldots\ldots\ldots(4)$$

taking the ionic product of water into consideration

$$\frac{[In^+]\ K_w}{[H^+][InOH]} = K_b \ldots\ldots\ldots\ldots(5)$$

$$[H^+] = \frac{K_b}{K_W}\ \frac{[In^+]}{[InOH]} \ldots\ldots\ldots\ldots(6)$$

$$pH = Pk_W - Pk_b + \log \frac{[InOH]}{[In^+]} \ldots\ldots\ldots\ldots(7)$$

where *K*w represents the ionic product of water, *K*b denotes the dissociation constant of the indicator base, the colour of which is the alkaline colour ; the acid colour is due to the In^+ ions.

2- Modern Quinoid Theory According to this theory:

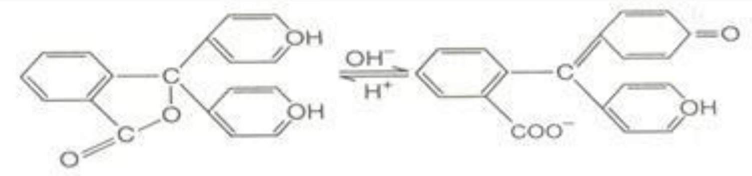
(a) The **acid-base indicators** exist in two tautomeric forms having different structures. Two forms are in equilibrium. One form is termed benzenoid form and the other quinonoid form.

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

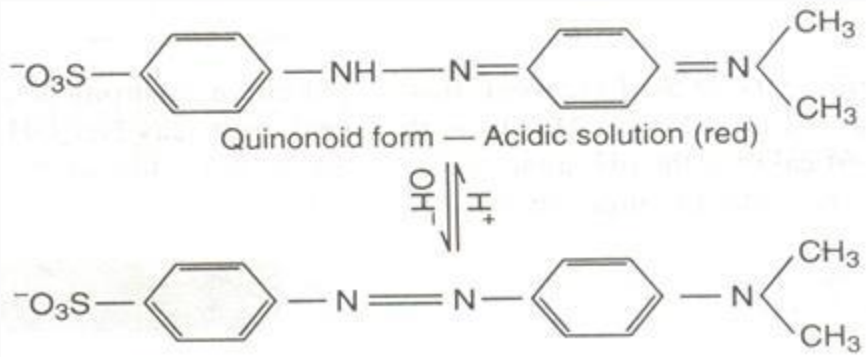
(c) One form mainly exists in acidic medium and the other in alkaline medium.

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.

(ii) A weak acid versus a strong base

(iii) A strong acid versus a weak base.

(iv) A weak acid versus a weak base.

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**.

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:

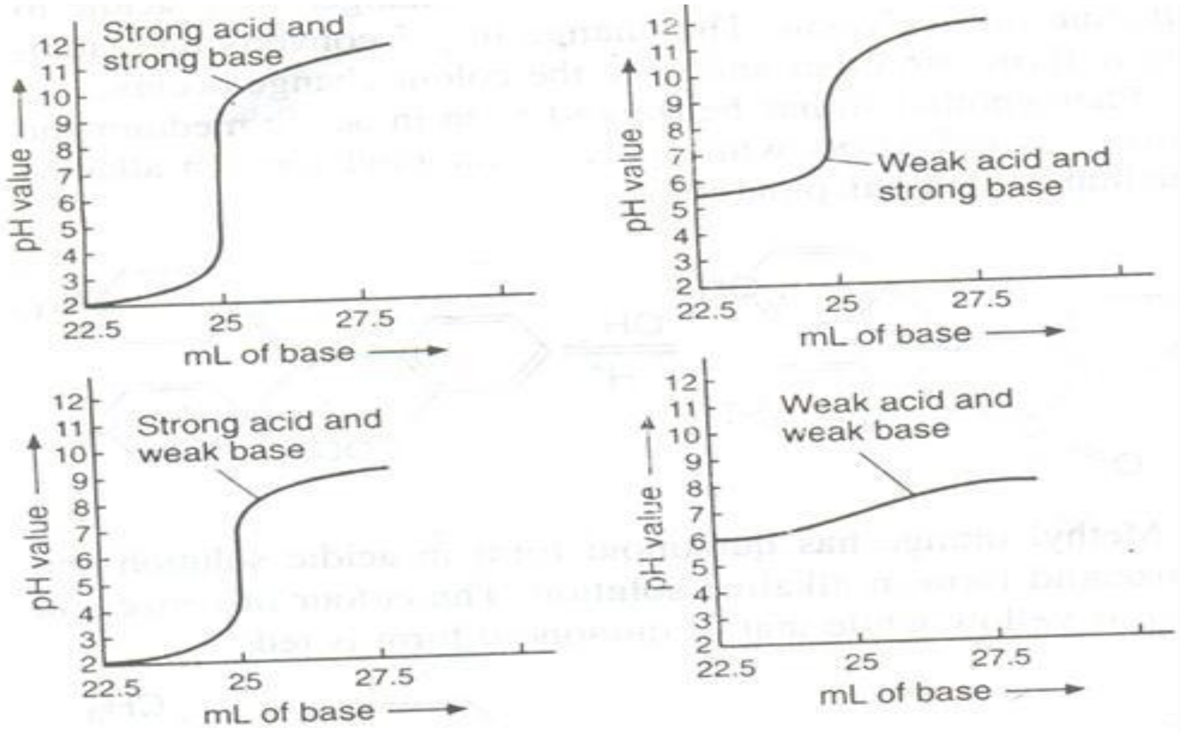
pH curve of weak acid (say CH_3COOH of oxalic acid) and strong base (say NaOH) is vertical over the approximate pH range 7 to 11. So phenolphthalein is the suitable indicator for such a titration.

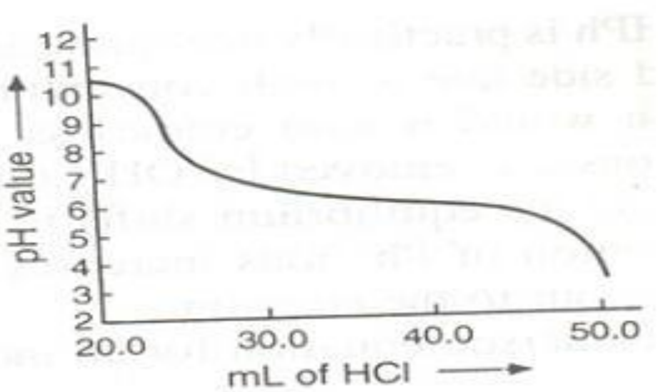
(iii) Strong acid vs. weak base:

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**.


Strong acid and strong base
pH value
mL of base
22.5
25
27.5
Weak acid and strong base
Strong acid and weak base
Weak acid and weak base


pH value
mL of HCl
20.0
30.0
40.0
50.0