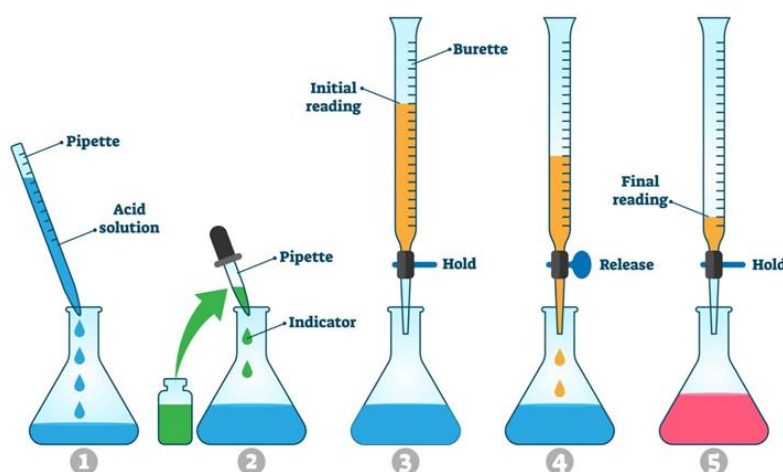


Volumetric analysis (titration analysis)

- ❖ Are the most useful and accurate analytical techniques, especially for millimole amounts of analyte.
- ❖ They are rapid and can be automated, and they can be applied to smaller amounts of analyte when combined with a sensitive instrumental technique for detecting the completion of the titration reaction, for example, pH measurement.
- ❖ In a titration the test substance (analyte) in a flask react with a reagent added from a Burette as a solution of known concentration.
- ❖ This is referred to as a standard solution and is called the titrant. The volume of titrant required to just completely react with the analyte is measured.
- ❖ Since we know the concentration as well as the reaction between the analyte and the reagent, we can calculate the amount of analyte.



The requirements of a titration:

- (1) reaction must be stoichiometric, must be a well defined and known reaction between the analyte and the titrant.
- (2) The reaction should be rapid. Most ionic reactions.
- (3) There should be no side reaction, and the reaction should be specific.
- (4) There should be a marked change in some property of the solution when the reaction is complete. This may be a change in color of the solution or in some electrical or other physical property of the solution (by used indicator or pH meter).

- (5) The point at which an equivalent or stoichiometric amount of titrant is added is called the equivalence point, which is The point at which the reaction is observed to be complete is called the end point, that is, when a change in some property of the solution.
- (6) The reaction should be quantitative. That's mean, the equilibrium of the reaction should be far to the right so that a sufficiently sharp change will occur at the end point to obtain the desired accuracy.

The equivalence point is the theoretical end of the titration where

The number of moles of titrant = number of moles of analyte.

$$M_1 V_1 = M_2 V_2 \quad M = \frac{n}{v}$$

The end point is observed at the end of the titration.

Standard solution: A solution is prepared by dissolving an accurately weighed quantity of a highly pure material called a primary standard and diluting to an accurately known volume in a volumetric flask.

A primary standard should fulfill these requirements

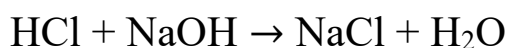
- (1) It should be 100.00% pure, although 0.01 % to 0.02% impurity is tolerable if it is accurately known.
- (2) It should be stable to drying temperature, and it should be stable indefinitely at room temperature. The primary standard is always dried before weighing.
- (3) It should be readily available and fairly inexpensive.
- (4) If it is to be used in titration, it should possess the properties required for a titration listed above. In particular, the equilibrium of the reaction should be far to the right so that a very sharp end point will be obtained.

A solution standardized by titrating a primary standard is itself with the secondary standard. It will be less accurate than a primary standard solution due to the errors of titrations.

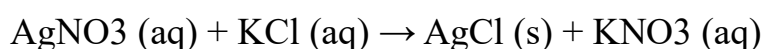
A high formula weight means a larger weight must be taken for a given number of moles. This reduces the error in weighing.

Classification of volumetric or titration methods:

- (1) **Neutralization (acid-base) titrations:** Many compounds, both inorganic and organic, are either acids or bases can be titrated with a standard solution of a strong base or a strong acid. The end point of these titrations are easy to detect, either by means of indicator or by following the change in pH with a pH meter.



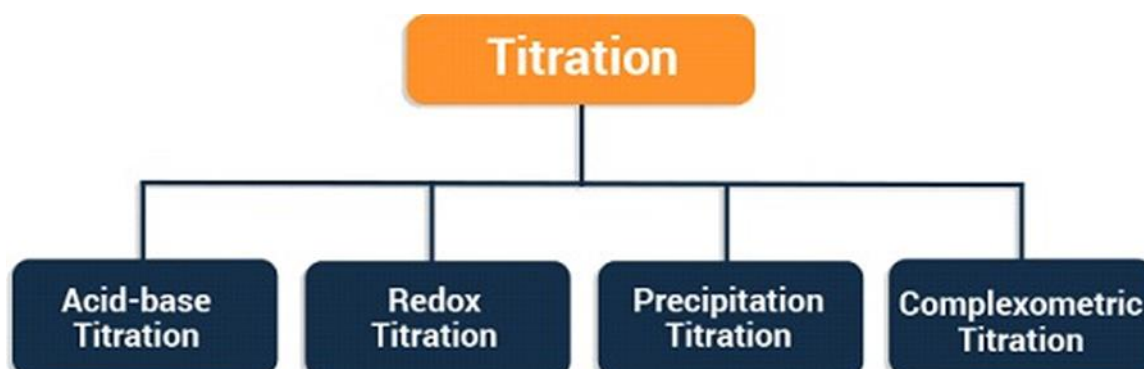
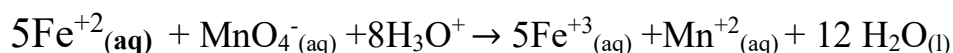
- (2) **Precipitation titrations:** In the case of precipitation, the titrant forms an insoluble product with the analyte. An example is the titration of chloride ion with silver nitrate solution to form silver chloride precipitate.



- (3) **Complexometric titrations:** In Complexometric titrations, the titrant is a reagent that forms a water-soluble complex with the analyte, a metal ion. The titrant is often a chelating.



- (4) **Reduction-Oxidation titrations:** These (redox) titrations involve the titration of an oxidizing agent with a reducing agent, or vice versa. An oxidizing agent gains electrons and a reducing agent loses electrons in a reaction between them.



1- Acid-Base Titrations

An Acid-Base titration involves a neutralization reaction in which an acid is reacted with an equivalent amount of base at equivalence point or endpoint. The titration is always a strong acid or strong base.

A) Titration of strong acid versus strong base:

Four types of calculations must be done in order to construct the hypothetical curve for titrating a solution of a strong acid with a strong base. Each of these types corresponds to a distinct stage in the titration:

- (1) initial pre-titration.
- (2) pre- equivalence.
- (3) equivalence point.
- (4) post-equivalence.

- ❖ In the pre-equivalence stage, we compute the concentration of the acid or base from its starting concentration and the amount of base or acid added.
- ❖ At the equivalence point, the hydronium and hydroxide ions are present in equal concentrations, and the hydronium ion concentration can be calculated directly from the ion-product constant for water, K_w .
- ❖ In the post-equivalence stage, the analytical concentration of the excess base or acid is computed, and the hydroxide ion or hydronium ion concentration is assumed to be equal to excess base or acid.

Example:- Calculate the pH at (0, 5, 45, 50 and 55 mL) of 0.1 M NaOH react with 50.0mL of 0.10M HCl during the titration process.

(1) At 0 titration: before addition of 0.1M NaOH

$$\text{pH} = -\log[\text{H}^+] = -\log 0.1 = 1.0$$

HCl is completely dissociated to form H^+ and Cl^-

(2) At 5 mL titration: before equivalence point

$$\text{mmol NaOH added} = M \times V = 0.1 \times 5 = 0.5$$

$$\text{mmol HCl} = M \times V = 0.1 \times 50 = 5.0$$

$$\begin{aligned}\text{mmol HCl remaining} &= \text{mmol HCl total} - \text{mmol NaOH added} \\ &= 5.0 - 0.5 = 4.5\end{aligned}$$

$$M_{\text{HCl}} = \frac{\text{mmol}}{V_{\text{T}}} = \frac{4.5}{50 + 5} = 0.0818\text{M}$$

$$\text{pH} = -\log 0.0818 = 1.09$$

At any point before equivalent Calculate the reagent (titrant) amount added and subtract from the remaining amount (analyte)

(3) At 45 mL titration: before equivalence point

$$\text{mmol. NaOH added} = M \times V = 0.1 \times 45 = 4.5$$

$$\text{mmol. HCl remaining (unreacted)} = 5.0 - 4.5 = 0.5$$

$$M_{\text{HCl}} = \frac{\text{mmol}}{V_{\text{T}}} = \frac{0.5}{50 + 45} = 0.00526\text{M}$$

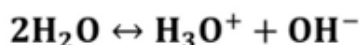
$$\text{pH} = -\log 0.00526 = 2.28$$

(4) At 50 mL titration: Equivalence Point

At the equivalence point, the amount of reagent (titrant) is equal the amount (analyte)

$$\text{mmol. NaOH added} = M \times V = 0.1 \times 50 = 5.0$$

$$\text{mmol. NaOH added (5.0)} = \text{mmol HCl (5.0)}$$



$$K_w = 1 \times 10^{-14} = [\text{H}^+][\text{OH}^-] = X^2$$

$$X = \sqrt{1 \times 10^{-14}} = [\text{H}^+] = [\text{OH}^-] = 1 \times 10^{-7}\text{M}$$

$$\text{pH} = -\log 1 \times 10^{-7} = 7 \text{ (neutrization step)}$$

(5) At 55 mL titration: after equivalence point

$$\text{mmol. NaOH added} = M \times V = 0.1 \times 55 = 5.5$$

$$\text{mmol NaOH remaining (excess)} = 5.5 - 5 = 0.5$$

After equivalence point, the amount of reagent (titrant) is more than the amount of (analyte), calculate the excess amount of the reagent.

$$M_{\text{NaOH}} = \frac{\text{mmol}}{V_T} = \frac{0.5}{50 + 55} = 0.00476\text{M}$$

$$\text{pOH} = -\log 0.00476 = 2.32$$

$$\text{pH} = 14 - 2.32 = 11.68$$

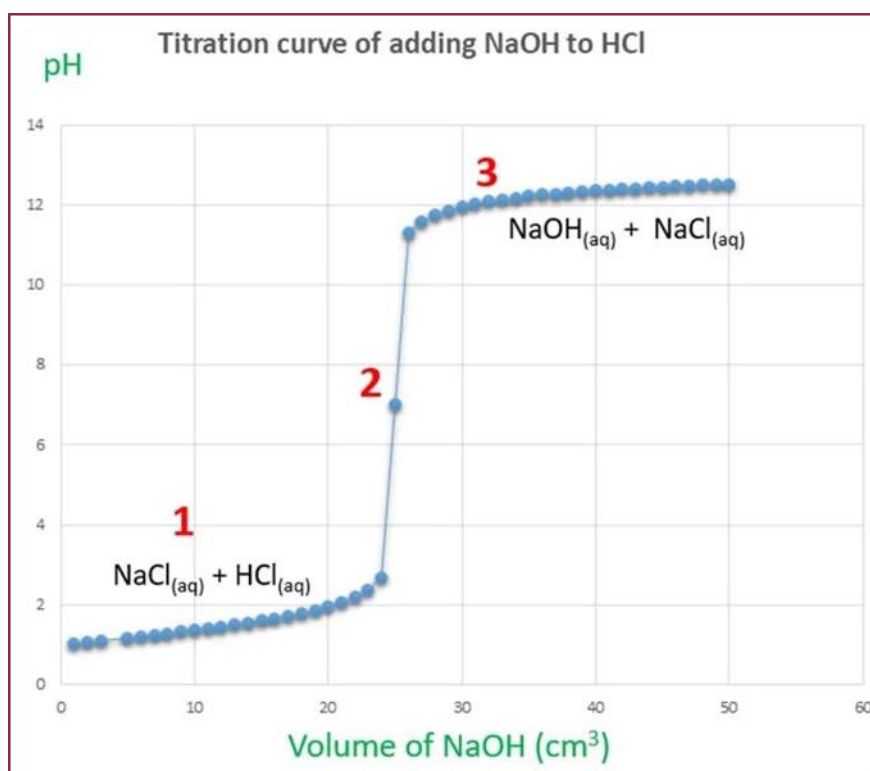
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Construction (plot) titration curve of strong acid versus strong base:-

The relationship between pH calculated for HCl remaining or unreacted (excess) or NaOH on Y axis and the volume of titrant (0.1M NaOH) added on X axis, this curve called titration curve. This curve used for estimation the equivalence point (theoretically) and selection of the indicator for detecting the endpoint reaction By the color change of indicator

There are three sections of titration curve of when strong base is added to the strong acid.

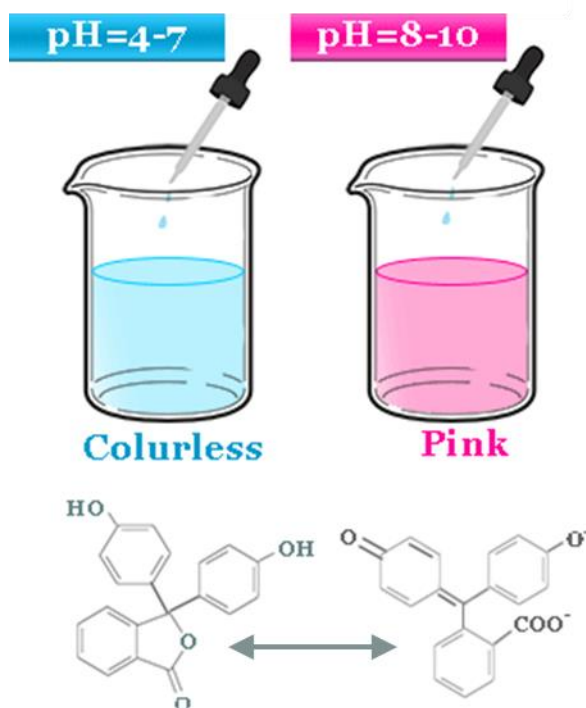
1. pH increases slowly before equivalence point.
2. Steep increment of pH due to unreacted of NaOH, no HCl exist furthermore in the aqueous solution. Solution become neutral or become basic.
3. Slow increment of pH after equivalence point



Note:

- ❖ The selection of the indicator is critical as the solution become more diluted and the sharpness endpoint decrease as the concentration increase.
- ❖ The point at which the reaction is observed to be complete at the indicator color where changed is called **endpoint**.
- ❖ **Indicators (Acid-Base):-** are substances which change its color with change pH.

- ❖ They are usually weak acids or bases, which when dissolved in water dissociate slightly to form ions.
- ❖ **Phenolphthalein** is a colorless, weak acid which dissociates in water forming pink anions.
- ❖ In acidic conditions, the equilibrium is to the left, and the concentration of the anions is too low for the **pink color** to be observed.



However, under alkaline conditions, the equilibrium is to the right, and the concentration of the anion becomes sufficient for the pink color to be observed

