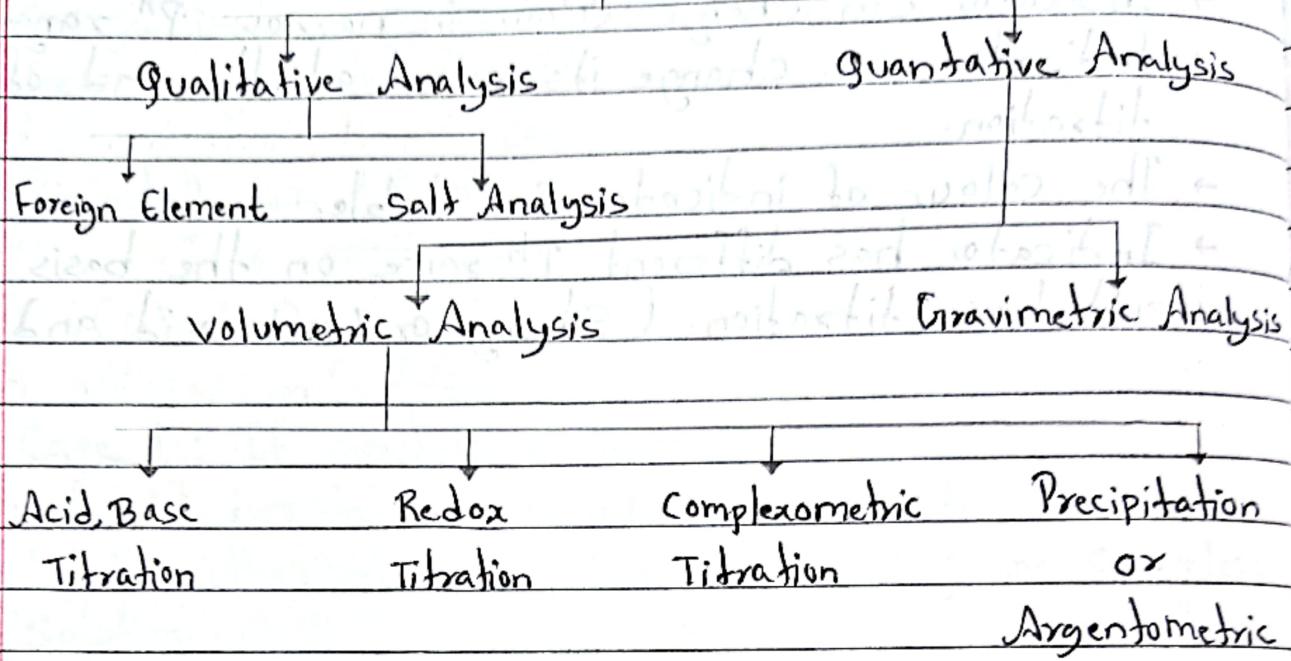


## Chemical Analysis



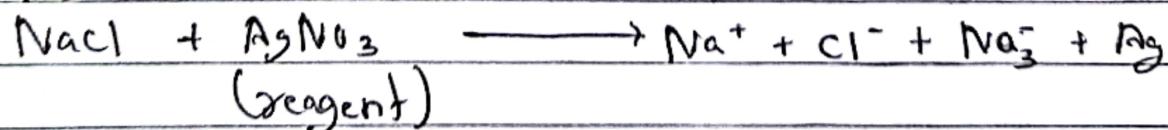
## # Gravimetric Analysis

It is an quantitative analysis in which the desired constituent of chemical can be obtained by forming its ppt. and measuring its weight.

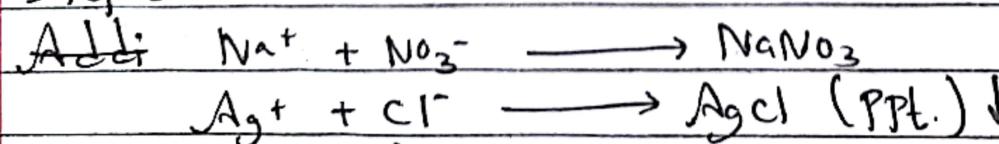
For example:

If we need to obtain the amount of  $\text{Cl}^-$  in the taken weight of  $\text{NaCl}$ , the  $\text{Cl}^-$  needs to be precipitated.

### Step 1:



## Step 2:



∴ The weight of  $\text{AgCl}$  is measured to obtain the quantity of  $\text{Cl}^-$  in the  $\text{NaCl}$  solution taken.

## # Steps followed during Gravimetric Analysis

- Solution of chemical species in which our desired constituent is present is prepared. i.e. weight of such species should be known.
- Addition of suitable reagent that can precipitate the desired constituent is done.
- Filtering, washing, drying, of the obtained ppt.
- Weight of the solution obtained ppt. is measured.
- Finally, stoichiometric calculation is done to obtain the weight of the desired constituents.

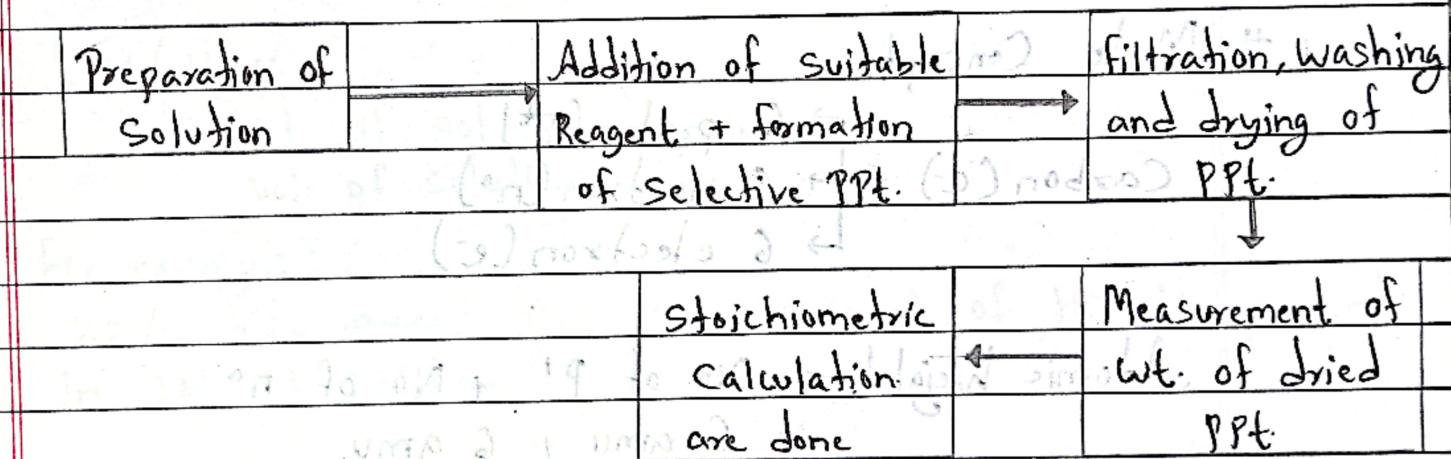


Fig: Flowchart of steps followed during gravimetric Analysis.

## # Conditions that must be considered during gravimetric Analysis.

- Complete precipitation of desired constituent.
- Ppt. formed should be pure.
- Ppt. formed should be easily filtered.

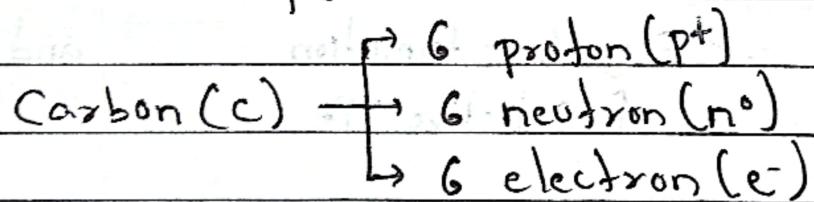
## # Advantage of gravimetric Analysis

- It is easy and accurate method of measurement.
- Inexpensive apparatus can be used.
- Measurement of weight element to six digit accuracy.

## # Disadvantages

- It is time consuming.
- Only single constituent can be measured. (multi-constituent can be precipitated but cannot be measured at a time.)
- Most of the scientific measurement doesn't use this method.
- It is only limited to mass measurement.

## # Mole Concept



$$\text{Atomic weight} = \text{No. of p}^+ + \text{No. of n}^\circ$$

$$= 6 \text{ amu} + 6 \text{ amu}$$

$$= 12 \text{ amu}$$

$$= 12 \times 1.67 \times 10^{-24} \text{ g}$$

$$= 12 \times 1.67 \times 10^{-24} \times 6.023 \times 10^{23}$$

$$= 12 \text{ g}$$

$$\text{Number of Mole} = \frac{\text{Given Weight}}{\text{Molecular Weight}}$$

## # Concentration Terms

1.  $(W/W)\%$ . =  $\frac{\text{wt. of Solute in gm}}{\text{wt. of solution in gm}} \times 100\%$ .
- For example: 20% w/w NaOH means in 100 gm solution 20 gm NaOH is present.

2.  $(W/V)\%$ . =  $\frac{\text{wt. of Solute}}{\text{Volume of solution in ml}} \times 100\%$ .

For example:

20% w/v NaOH means in 100 ml solution 20 gm of NaOH is present.

3.  $(V/V)\%$ . =  $\frac{\text{Vol. of solute}}{\text{Vol. of solution in ml}} \times 100\%$ .

For example:

20% v/v HCl means 20 ml of HCl is present in 100 ml solution.

## 4. Parts per million (PPM)

$$= \frac{\text{Mass of Solute}}{\text{Mass of Solution}} \times 10^6 \%$$

For example:

If a solution is 2 ppm than it means out of  $10^6$  part of solution 2 part of solution is occupied by solute.

## 5. Parts per billion (PPB)

$$= \frac{\text{Mass of Solute}}{\text{Mass of Solution}} \times 10^9 \%$$

For example:

If solution is 2 ppb than out of  $10^9$  parts ( $10^9$  g) of solution the solute occupies 2 part (2 gm)

Note:

PPM and PPB concentration term are used for solution with very very low concentration.

## 6. Mole fraction 'X' (zeta)

$X = \frac{\text{Mole of particular component}}{\text{Total mole of solution}}$

$$= \frac{n_1}{n_1 + n_2 + n_3 + \dots}$$

$$n_1 + n_2 + n_3 + \dots$$

For Example:

If 2 mole HCl is dissolved in 4 mole  $H_2SO_4$  then mole of HCl ( $n_1$ ) = 2

mole of  $H_2SO_4$  ( $n_2$ ) = 4

Total mole ( $n$ ) =  $n_1 + n_2 = 6$

Now,

$$X_{n_1} = \frac{n_1}{n} \quad \text{e.g. } \frac{2}{6} = \frac{1}{3}$$

$$X_{n_2} = \frac{n_2}{n} \quad \text{e.g. } \frac{4}{6} = \frac{2}{3}$$

## 7. Molarity (M)

It is defined as the number of mole of solution present in certain volume of solution.

For example:

If concentration of  $H_2SO_4$  solution is 1 molarity then it means 1 mole solution is present in 1 litre solution.

Molarity (M) = No. of mole of solute ~~to convert to~~  
Volume of solution in litre.

$$= \frac{\text{Given mass}}{\text{molecular mass}} \times \frac{1}{\text{Volume of solution in litre}}$$

i.e.  $M = \frac{\text{Given Mass}}{\text{Molecular mass}} \times \frac{1}{\text{Vol. of solution in litre}}$

$$= \frac{\text{g/l}}{\text{molecular mass}}$$

When solution is given in mL

$M = \frac{\text{Given mass}}{\text{molecular mass}} \times \frac{1000}{\text{Volume of solution in ml}}$

$$= \frac{\text{g/ml}}{\text{molecular mass}} \times 1000$$

## # Types of Molarity Concentration

1. 1 M

2.  $\frac{1}{10}$  M decimolar solution

3.  $\frac{1}{2}$  M Semi-molar Solution

4.  $\frac{1}{100}$  M centimolar

## 8. Normality

(N) =  $\frac{\text{No. of gm equivalent of solute}}{\text{Volume of solution in litre}}$

$$= \frac{\text{Given weight}}{\text{Equivalent weight}}$$

Volume of Soln, in ltr.

$$= \frac{\text{Given weight}}{\text{Volume of soln, in ltr}} \times \frac{1}{\text{Equivalent weight}}$$

$$= \frac{g/l}{\text{Equivalent wt}}$$

Equivalent wt

# No. of gram equivalent weight

→ Equivalent weight of any molecule is given by:

$$= \frac{\text{Molecular wt. / molar mass}}{\text{Total electron involved / n-factors}}$$

→ No. of gram equivalent : No. of electron involved

For example:

98 gm of  $\text{H}_2\text{SO}_4$

= 1 mole of  $\text{H}_2\text{SO}_4$

Now,

i. Equivalent wt. =  $\frac{1 \text{ mole weight}}{\text{Total electron involved in 1 mole } \text{H}_2\text{SO}_4}$

$$= \frac{98}{2}$$

2

$$= 49$$

ii. No. of gram equivalent = Total electron involved in

1 mole  $\times$  no. of mole

$$= 2 \times 1$$

= 2 gm equivalent is present  
in 98 gm of  $\text{H}_2\text{SO}_4$

## # Formula of gram equivalent

- No. of gm equivalent = No. of mole  $\times$  n-factor
- No. of gm equivalent = Normality (N)  $\times$  Vol. of solution in 'L'
- No. of gm equivalent =  $\frac{(w/v)\% \times 10 \times n\text{-factor}}{\text{molecular weight}}$
- No. of gm equivalent =  $\frac{\text{Given weight}}{\text{Equivalent weight}}$

Note: No. of gm equivalent of all other reactants is always equal in complete reaction.

## # Relation Between Molarity and Normality

$$\text{Normality (N)} = \frac{\text{No. of gm equivalent}}{\text{Vol. of solution in 'L'}}$$

$$\text{or, } N = \frac{\text{Given wt. of solute}}{\text{Equivalent wt.} \times \text{Vol. of solution in 'L'}}$$

$$\text{or, } N = \frac{\text{Given wt.} \times \text{Volume of solution in 'L'}}{\text{Equivalent wt.}}$$

$$\text{or, } N = \frac{\text{Given wt.} \times \text{Molecular wt.} \times \text{Volume of soln. in 'L'}}{\text{n-factor}}$$

$$\text{or, } N = \frac{\text{Given wt.} \times \text{n-factor}}{\text{molecular wt.} \times \text{Vol. of soln. in 'L'}}$$

or,  $N = \text{No. of mole} \times n\text{-factor}$

Volume in 'L'

or,  $N = \text{Molarity} \times n\text{-factor}$

or,  $N = M \times n\text{-factor}$

Cases:

- If  $n=1$ ,  $N=M$
- If  $n > 1$ ,  $N > M$

### V.V<sup>2</sup> # Normality Equation

No. of gram equivalent of one reactant = No. of gm equivalent of another reactant.

- If Vol. of 1<sup>st</sup> reactant =  $V_1$  and If  $V_2$  for another reactant.
- If conc. of 1<sup>st</sup> reactant =  $N_1$  and If  $N_2$  for another reactant. Then,

$$N_1 \times V_1 = N_2 \times V_2$$

This is called normality equation which is valid for all types of reactants.

But,

We can't write molarity equation like that:

Molarity (M) = No. of mole

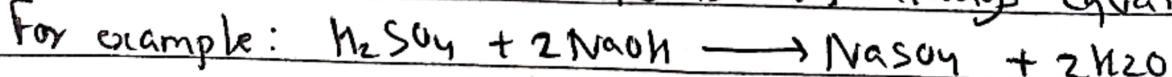
Volume of solution in 'L'

$$\therefore \text{No. of mole} = M \times \text{Vol. of soln. in 'L'}$$

No. of moles of reacting substance can be equal or not.

$$\therefore M_1 V_1 = M_2 V_2 \text{ is not true.}$$

- For all reaction no. of mole is not always equal.

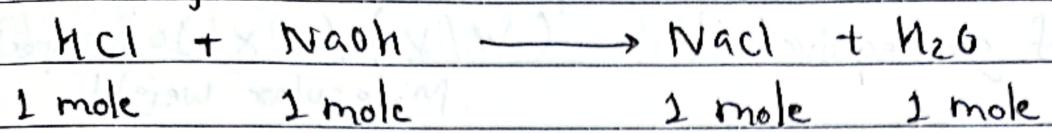


1 mole	2mole	1 mole	2mole
--------	-------	--------	-------

∴ No. of mole of  $H_2SO_4$  is not equal to mole of NaOH.

↳ But can be equal sometimes:

For example:



∴ Molarity equation is not valid for all cases.

↳ If we have to use Molarity concentration then we can change normality equation in equation having molarity term:

$$N_1 \times V_1 = N_2 \times V_2$$

$$\text{or, } M_1 \times (\text{n-factor})_1 \times V_1 = M_2 \times (\text{n-factor})_2 \times V_2$$

∴ This equation can be used if concentration is given in molarity while solving numericals.

# Molarity (M) vs Molality (m) which is best concentration term?

We know,

$$\text{Molarity (M)} = \frac{\text{Given weight}}{\text{Molecular wt.} \times \text{Volume in L}}$$

Here,

Volume can be ↑ or ↓ (affected) by temperature and pressure.

∴ Concentration is also change though having equal number of mole.

Also,

$$\text{Molality (m)} = \frac{\text{No. of mole of Solute}}{\text{Weight of Solvent in kg}}$$

Here,

No. of mole of Solute and Weight of Solvent is not affected by temperature and pressure.

∴ Concentration in Molality term is best than molarity (M).

# Gram Per Litre :  $\text{g/L} = \text{Molarity} \times \text{Molecular Weight}$

$\text{g/l} = \text{Normality} \times \text{Equivalent Weight}$

No. of gm equivalent =  $(W/V) \times 10 \times \frac{\text{specific gravity}}{\text{Molecular weight}}$

# Different Types of Substance (Chemical) used during Titration.

1. Primary Standard Substance

↳ Those solution in which composition of chemical species remains same for long term is called primary solution. Such types of solution is prepared by dissolving suitable chemical species called primary substance. Such primary solution are called standard solution.

↳ They are called standard solution because in such solution composition of primary substance remains same for long term thus used to determine the concentration volume of secondary solution.

Example of Primary Standard substance:

$\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$  [Mohr's salt], Anhydrous  $\text{Na}_2\text{CO}_3$ ,  $\text{As}_2\text{O}_3$  (Arsenous oxide),  $(\text{COOK})_2 \cdot 2\text{H}_2\text{O}$  (oxalic acid),  $\text{KClO}_3$  (Potassium Chlorate),  $\text{KIO}_3$  (Potassium Iodate) etc.

# Criteria of Primary Substance

- i. It should be easily available in the pure state.
- ii. It should not be hygroscopic (मोर्टि पानी absorb करते) deliquescent ( $\text{NaOH}, \text{MgCl}_2, \text{FeCl}_3$ ) [जूँ जूँ moisture absorb करते solution होते], Efflorescent (loses water) [ $\text{CaSO}_4 \cdot 5\text{H}_2\text{O}, \text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$ ]

- iii. It shouldn't react with  $\text{CO}_2$  and air.
- iv. Its composition mustn't change even after storing it for longer time.
- v. It should form stable solution.

## 2. Secondary Substance

Those Solution whose composition is determined by the help of primary standard substance is Secondary Solution.

Secondary Solution are prepared after standardizing with the help of primary solution. Secondary substances are unstable thus their composition changes in room temperature.  $\therefore$  Their solution composition needs to be finalized by the help of primary standard solution.

The solution of secondary substance after standardization is secondary standard solution which is used in several Titration.

### Examples of Secondary Substance:

Salts  $\longrightarrow$   $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$

Base  $\longrightarrow$   $\text{NaOH}$ ,  $\text{KOH}$

Acid  $\longrightarrow$   $\text{HCl}$ ,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$

## # Normality Factor

The error in the weighing of the chemical substance for the preparation of the solution of desired concentration in normality is called normality factor.

Mathematically,

$$\text{Normality factor (F)} = \frac{\text{Weight taken}}{\text{Weight to be taken}}$$

Case 1 : If wt. taken > wt. to be taken which gives  $f > 1$  which means, the prepared solution will be more concentrated than required in normality.

Case 2 : If wt. taken < wt. to be taken which gives  $f < 1$  which means, the prepared solution will be more less concentrated than required in normality.

Case 3 : If wt. taken = wt. to be taken which gives  $F = 1$  which means, the prepared solution will be in concentration required by us in normality.

For Example :

If we need to make 1 normal solution of NaOH, 20 gm NaOH needs to be taken but if we take 18 gm then,

$$\text{Normality factor (F)} = \frac{\text{wt. taken}}{\text{wt. to be taken}}$$

$$= \frac{18}{20}$$

$$= 0.9$$

$$\therefore \text{The prepared solution is: } 1 \text{ N} (\text{desired conc.}) \times f = (0.9)$$
$$= 1 \times 0.9 \quad \begin{matrix} \leftarrow \\ \text{error in} \end{matrix}$$
$$= 0.9 \text{ N} \quad \begin{matrix} \leftarrow \\ \text{measurement} \end{matrix}$$

## # Titration

The method of obtaining the concentration of unknown solution by the help of standard (known) solution in the presence of suitable indicator is called titration.

## # Terms Used in Titration

- a. Unknown Solution : Whose concentration needs to be determined.
- b. Known Solution : It is a standard solution, whose concentration is already known and by the help of which concentration of other unknown solution is determined.
- c. Standardization : Sometime we need solution of secondary substance for titration for that the concentration of secondary solution needs to be known for that we use primary standard solution. Thus, the work of knowing the conc. of secondary solution by the help of primary standard solution is known as standardization.
- d. Titrant : kept in burette . i.e. Whose conc. is known
- e. Titrant : kept in conical flask . i.e. Whose conc. needs to be known.
- f. Equivalence point and End point  
The point during the titration process at which the number of gram equivalent weight of unknown solution is equal to the no. of gm equivalent of standard solution is called equivalence point or theoretical end point.  
End point is the exact point at which the reaction is completed during the titration that is indicated by the change of colour of indicators.

#	End Point Vs Equivalence Point	
	End Point	Equivalence Point
i.	End point is the point in the titration in which the no. of gm equivalent of analyte is greater than the no. of gm equivalent of titrant.	Equivalence point is the stoichiometric point in the titration in which the no. of gm equivalent of analyte is equal to the no. of gm equivalent of titrant.
ii.	The point during the titration process which is indicated by colour change of the indicator is called end point.	The point during the titration process where the chemical reaction in the titration mixture ends is called equivalence point.
iii.	This point is obtained just after the equivalence point.	This point is obtained just before the end point.
iv.	Weak acid can show only one end point during titration.	Weak acid can show multiple equivalence point during titration.

## # Titration Error

During the titration, end point comes just after the equivalence point. The difference between end point and equivalence point is the titration error. The main aim of titration is to minimize the titration error.

## # Neutral Point

Neutral point is the point during the titration between acid and alkali, at which the pH of the resulting solution is exactly 7.

## # Principle of Volumetric Analysis

### 1. Law of Chemical Equivalence

It states that, "No. of gm equivalent of reactants should be equal for completion of reaction. (Neutralization)

Example:

$$0.5N \text{ of } 200 \text{ ml NaOH} = 1N \text{ of } 100 \text{ ml HCl}$$

### 2. Law of Dilution

It states that, "On increasing the dilution (volume) by certain proportion the conc. of solution is decreased by same proportion to maintain same no. of gm equivalent."

Example:

$$2N \text{ of } 200 \text{ ml HCl} = 1N \text{ of } 400 \text{ ml HCl} = 0.1N \text{ of } 4000 \text{ ml HCl}$$

### 3. Law of Addition

It states that, "If certain solution of same types of chemical species (Acid + Acid) or (Base + Base) of certain gm equivalent is mixed then the no. of gm equivalent of mixture is obtained by addition of gram equivalent of solution of mixing chemical species".

For Example:

If one solution having  $V_1, N_1$  gm equivalent is mixed with solution of same types of species having gm equivalent  $V_2, N_2$  then the gm equivalent of mixture is given by addition

$$V_m \times N_m = N_1 V_1 + N_2 V_2$$

$$\text{or, } (V_1 + V_2) \times N_m = N_1 V_1 + N_2 V_2$$

$$\therefore N_m = \frac{N_1 V_1 + N_2 V_2}{(V_1 + V_2)}$$

### 4. Law of Subtraction

It states that, "If solution of same types of chemical species (Acid + Acid Base) or (Base + Acid) of certain

gm equivalent is mixed then the no. of gm equivalent of mixture is obtained by subtraction of gram equivalent of solution of mixing chemical species.

Example:

If one solution having  $N_1 V_1$  gm equivalent is mixed with solution of different types of species having gm equivalent,  $N_2 V_2$  then the gm equivalence of mixture is given by;

$$N_m \times V_m = N_1 V_1 + N_2 V_2$$

$$\text{or, } (V_1 + V_2) N_m = N_1 V_1 + N_2 V_2$$

$$\therefore N_m = N_1 V_1 - N_2 V_2$$

↳ Conditions:

If  $N_1 V_1 = \text{Acid}$  and  $N_2 V_2 = \text{Base}$

If  $N_{\text{mix}}$  value is +ve  $\rightarrow$  Mixed solution is acidic

If  $N_{\text{mix}}$  value is -ve  $\rightarrow$  Mixed solution is base

If  $N_{\text{mix}}$  value is 0  $\rightarrow$  Mixed solution is neutral

## # Types of Titration

### 1. Acid-Base Titration

The titration of standard acid solution with unknown base solution or vice versa is called acid-base titration.

↳ If concentration of unknown acid needs to be known then such titration is acidimetry.

↳ If concentration of unknown base needs to be known then such titration is alkalimetry.

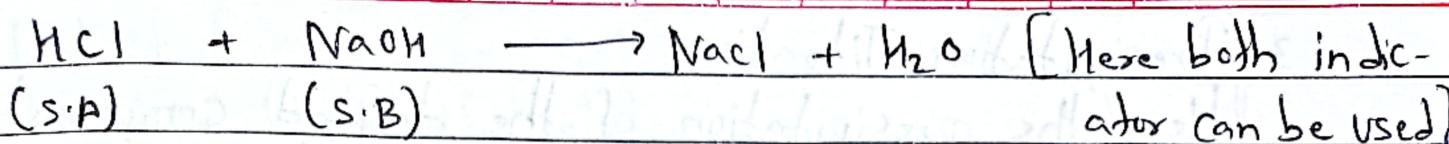
↳ Indicators of suitable pH range is used for end point determination.

Example: Methyl orange

$$pH = 3.2 - 4.5$$

Phenolphthalein

$$pH = 8 - 10$$

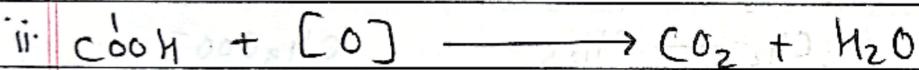
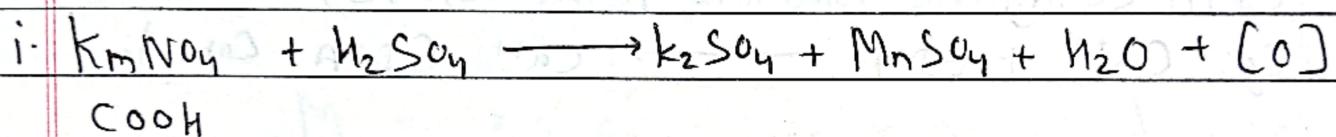


## 2. Redox Titration

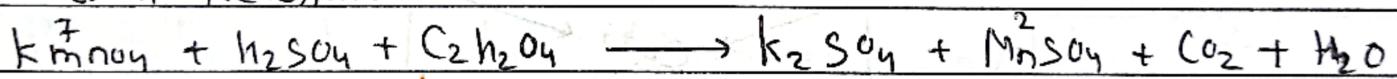
It is the titration of oxidizing agents like  $\text{KMnO}_4$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{KIO}_3$ ,  $\text{KBrO}_3$  with reducing agents like oxalic acid  $(\text{COOH})_2$ , sodium thiosulphate  $(\text{Na}_2\text{S}_2\text{O}_3)$  etc.

### a. Permanganometric Titration:

Example: Titration of acidified  $\text{KMnO}_4$  with oxalic acid.



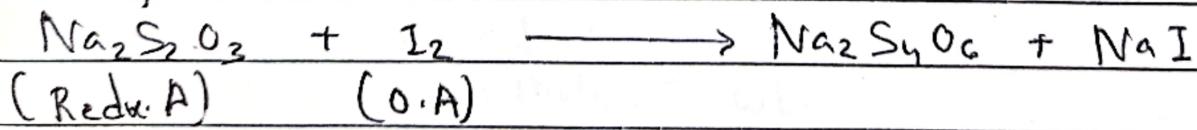
Overall Reaction:



### b. Iodometric Titration

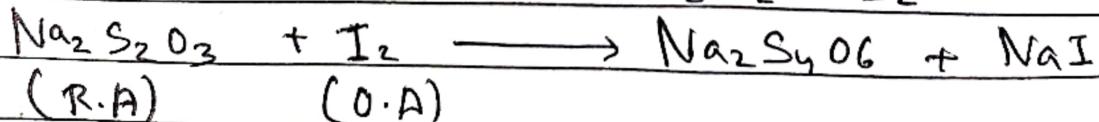
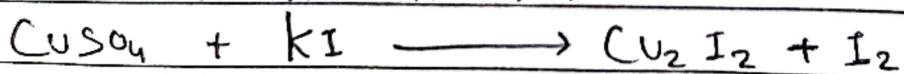
Standard oxidizing agent  $\text{I}_2$  given from outside is directly titrated with reducing agent.

Example:



↳ Starch is used as indicator

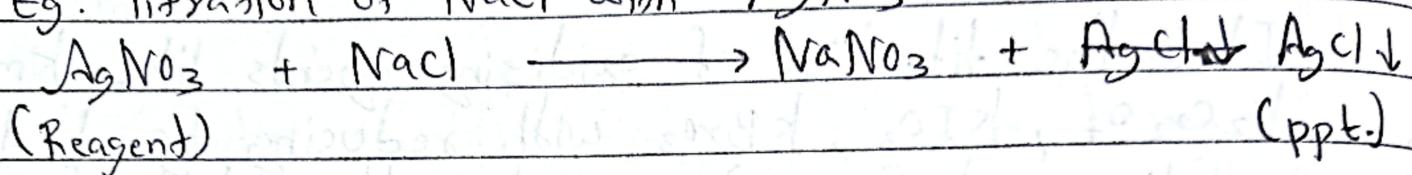
### c. Iodo-Iodometric Titration



### 3. Precipitation Titration

Here, the precipitation of the desired component takes place by the help of suitable reagent.

Eg: Titration of NaCl with  $\text{AgNO}_3$



### 4. Complexometric Titration

In such titration, complex is formed between metal ion [monovalent =  $\text{Na}^+$ ] or [divalent =  $\text{Ca}^{++}$ ] or [Trivalent =  $\text{Al}^{3+}$ ] and complexing agent like DMG (Dimethyl glyoxime), EDTA (Ethylene diamine tetraacetate).

Eg:  $\text{Ca}^{++} + \text{EDTA} \longrightarrow \text{Ca}^{++}\text{EDTA} + \text{Complex}$

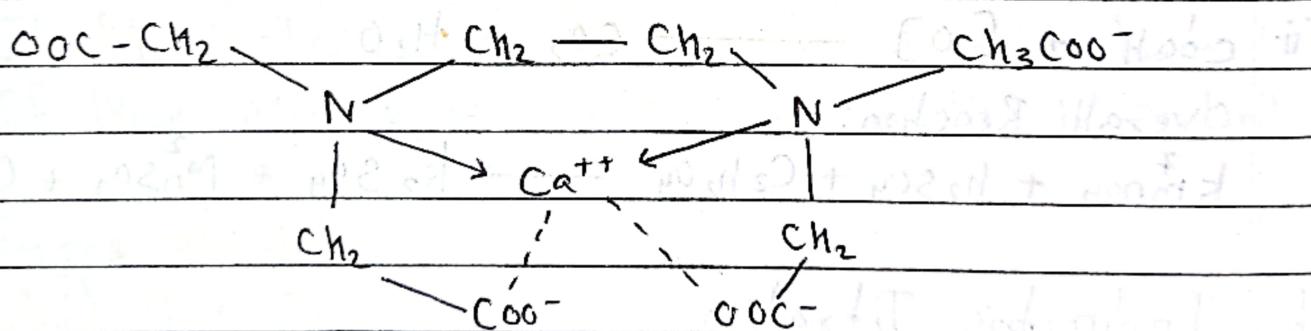


Fig:  $\text{Ca}^{++}$  EDTA Complex

## # List of formulae for Solving Numericals

1. If  $\% \text{ (w/v)}$  of solute is given in solution

$$N = \% \text{ of solute} \times 10$$

Eg. wt. of solute

$$M = \% \text{ of solute} \times 10$$

molecular wt. of solute

2. If specific gravity and  $\% \text{ (w/w)}$  of solute or percentage purity are given then:

$$N = \% \text{ of solute} \times \text{sp. gravity} \times 10$$

Eg. wt. of solute

$$M = \% \text{ of solute} \times \text{sp. gravity} \times 10$$

molecular wt. of solute

3. Percentage by Volume ( $w/v$ ) =  $\frac{\text{gram/Litre}}{20}$ 4. Percentage by weight ( $w/w$ ) =  $\frac{\text{g/L}}{\text{sp. gravity} \times 10}$ 5. No. of mole =  $\frac{\text{wt. in gram}}{\text{molecular wt.}}$ = Molarity  $\times$  volume of soln, in litre