

VOLMETRIC ANALYSIS

1) Volumetric Analysis

→ Volumetric analysis is a method of finding in which strength of an unknown solution is determined with the help of a standard solution.

If the volume of two solutions and strength of the standard solution can be calculated with the help of equation $n_1V_1 = n_2V_2$. This is the fundamental principle of volumetric analysis.

Analytical Chemistry

→ A branch of chemistry that involves the detection and estimation of chemical substance from the mixture and solution is called Analytical chemistry.
Its classes are

* Qualitative

→ Identify chemical substance
e.g.: Instrumental method

* Quantitative

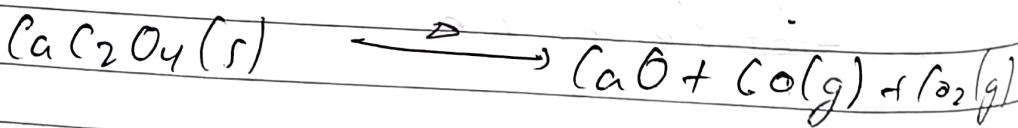
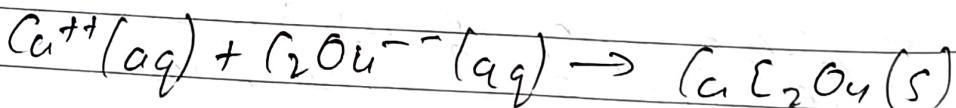
→ Estimation of amount of known substance
e.g.: Either gravimetric, volumetric or instrumental method.

Gravimetric Analysis.

→ It is quantitative analysis involved in separation of element or radical from a weighed amount of given substance into another suitable pure and soluble compound of composition by carrying out suitable precipitation reaction.

Example :-

Determination of Ca^{++} in natural water can be done by using excess of $(\text{COOH})_2$ (oxalic acid). If it is added to aq. solution of sample [natural water, $\text{C}_2\text{O}_4^{--}$], NH_3 solution is added to neutralize acid & all the Ca Sample is precipitated as calcium oxalate.



Volumetric Analysis Types:-

a) Neutralization or acid

- The strength of acid may be determined by neutralizing it in the presence of an indicator with an alkali of known strength. This type of chemical analysis is called Acidimetry.
- Similarly, the strength of an alkali may be determined by neutralizing it in the presence of indicators with an acid of known strength. This type of analysis is called Alkalimetry.

b) Redox Titrations

- The titration in which strength of oxidizing agent is determined with the help of standard solution of reducing agent or vice-versa is called Redox titration. The titration that involves the both oxidation & reduction reaction is called Redox Titrations.

c. Iodometric - Iodometric titration

d. Precipitation titration

e. Complex formation or complexometric titrations

Standard Solution:-

- A solution of known strength is called standard solution. It can also be defined as a solution which contains known weight of solute present in a known volume of it.
- A solution of unknown strength is called unknown solution.

Primary Standard Solution

- The standard solution may be obtained by dissolving a definite weight of substance in water and making definite volume of the solution called primary standard solution.
- The solution which is used for preparation of primary standard solution is called primary solution substance.

Characteristics

- Should be easily available in the state of purity.
- Should be readily soluble in water.
- Composition should not change during storage and in air during weighing.
- Must possess high equivalent weight to minimize weighing errors.
- Should be non-toxic.

Secondary Standard Solution

→ The substance like NaOH , HCl , Na_2SO_4 , HNO_3 , KMnO_4 , etc are ~~varied~~ used to prepare secondary solution. These solns cannot be weighed out correctly. Therefore, approximate weight of volume of water and then strength of these solution is determined with the help of primary standard solution. Such substances which is used for preparation of standardised solutions are called secondary standard solutions. The substance which is used for preparation of secondary solution is called secondary substance.

Equivalent mass.

Equivalent mass of a substance can be defined as number that indicates how many parts by mass of it combine or displace from 1.008 part of mass hydrogen, 8 part of mass oxygen & 35.5 part by mass of chlorine.

Equivalent mass of element

$$= \frac{\text{mass of element}}{\text{mass of hydrogen}} \times 1.008$$

or,

$$= \frac{\text{mass of element}}{\text{mass of oxygen}} \times 8$$

$$= \frac{\text{mass of the element}}{\text{mass of chlorine}} \times 8$$

$$= \frac{\text{mass of the element}}{\text{mass of chlorine}} \times 35.5$$

For example

$$\begin{aligned} 1. \text{ Eq. wt of mg in MgCl}_2 &= \frac{24}{2 \times 35.5} \times 35.5 \\ &= 12 \end{aligned}$$

$$2. \text{ Eq wt of N in Na}_2\text{O} = \frac{2 \times 23}{23 + 16} \times 8 = 23$$

$$3. \text{ Eq. mass of Ca in } \text{CaH}_2 = \frac{40}{2} \times 1.008 \\ = 20$$

Relationship between Atomic mass, equivalent weight & valency.

Equivalent mass = $\frac{\text{molecular mass}}{\text{Valency}}$

1. Equivalent weight. mass of element
 $A \rightarrow 13$

$$\text{molecular mass} = 2n + 1 \\ = 2 \times 13 + 1 \\ = 27$$

$$\text{Eq. wt (weight)} = \frac{\text{molecular mass}}{V}$$

$$\frac{27}{3} \\ = 9.$$

Mg.
 $\text{Eq. wt} = \frac{24}{2} = 12$

Oxygen
 $\text{Eq. wt} = \frac{16}{2} = 8$

Na
 $\text{Eq. wt} = \frac{23}{1} = 23$

Carbon

At. number = 6

At. mass = $2n = 2 \times 6 = 12$

$$\text{Eq. wt} = \frac{\text{Atomic mass}}{\text{Valency}}$$

$$= \frac{12}{4} = 3$$

Fe O

$$\text{Eq wt of Fe} = \frac{\text{molecular mass}}{\text{Valency}}$$

$$= \frac{56}{3}$$

$$= 18.06$$

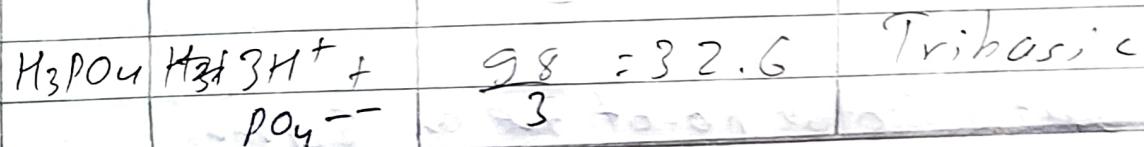
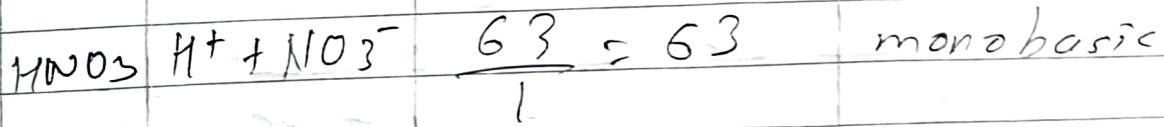
Equivalent mass of acid.

$$= \frac{\text{molecular mass of acid}}{\text{Basicity of acid}}$$

Basicity of acid is the total number of replaceable H^+ from one mole of acid.

Acids	Basicity	$\text{Eq mass} = \frac{\text{molecular mass}}{\text{Basicity}}$	Name of acid
HCl	$HCl \rightarrow H^+ + Cl^-$	$1 + 35.5 / 1 = 36.5$	monobasic acid
H_2SO_4	$2H^+ + SO_4^{2-}$	$98 / 2 = 49$	dibasic acid

Acids	Basicity	<u>Eq.mass = molecular mass / basicity</u>	Nature of acid
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Equivalent mass of base

Equivalent mass of an base
 $= \frac{\text{molecular mass of base}}{\text{acidity of base}}$

Acidity of base is the total number of replaceable OH^- from 1 mole of base.

Base	Acidity	<u>Eq. mass = Molecular mass / acidity of base</u>	Nature of base
NaOH	$\text{Na}^+ + \text{OH}^-$	$\frac{40}{1} = 40$	monoaacidic base
NH_4OH	$\text{NH}_4^+ + \text{OH}^-$	$\frac{35}{1} = 35$	monoaacidic base
Ca(OH)_2	$\text{Ca}^{2+} + 2\text{OH}^-$	$\frac{74}{2} = 37$	diacidic base
Fe(OH)_3	$\text{Fe}^{3+} + 3\text{OH}^-$	$\frac{107}{3} = 35.7$	Triacidic base

Equivalent mass of salt

Equivalent mass of salt

= molecular mass of salt

Total no of +ve or -ve charge per molecule

Salt	Total no. of +ve or -ve charge produced by one molecule of salt	$\frac{\text{Eq mass} = \text{molecular mass}}{\text{Total no of +ve/-ve chrg per molecule}}$
NaCl	$\text{Na}^+ + \text{Cl}^-$	$\frac{58.5}{1} = 58.5$
Na_2CO_3	$\text{Na}_2\text{CO}_3 \rightarrow 2\text{Na}^+ + \text{CO}_3^{2-}$	$\frac{106}{2} = 53$
$\text{Ca}_3(\text{PO}_4)_2$	$3\text{Ca}^{2+} + 2\text{PO}_4^{3-}$	$\frac{310}{6} = 51.67$

Equivalent mass of ion

The ratio of mass of an ion to the charge present on it is called equivalent mass of ion.

Eq mass of ion = ionic mass of ion
Charge on it

Ions or Radicals

Charge of ions

i.e.

Eq mas = formula mass

Charge on it.

Na^+

1

$$\frac{23}{1} = 23$$

NO_3^-

3

$$\frac{14 + 3 \times 16 - 6}{3} = \underline{\underline{6}}$$

CO_3^{2-}

2

$$\frac{12 + 3 \times 16 - 6}{2} = 30$$

SO_4^{2-}

2

$$\frac{32 + 4 \times 16 - 6}{2} = 48$$

Equivalent mass of oxidising & Reducing agent

Equivalent mass of O.A or Reducing agent

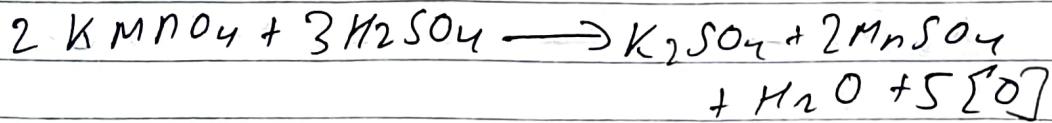
= molecular mass

Total charge on O.N per molecule

For example

Q) Eq wt of KMnO_4 is different media

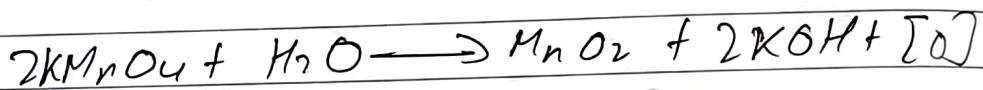
a. In acidic medium



Change in O.N of KMnO_4 is
 $= 7 - 2$
 $= 5$

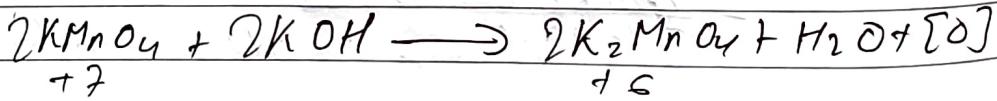
Eq. wt of KMnO_4 in acidic medium
 $= \frac{158}{5} = 31.6$.

b. In neutral medium



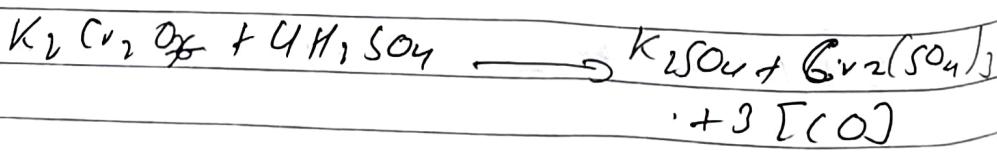
Change in O.N of KMnO_4 in neutral medium
 $= \frac{158}{7-4} = \frac{158}{3} = 52.62$.

c. In basic medium



$$\text{Eq. wt} = \frac{158}{7-6} = \frac{158}{1} = 158$$

Eq. wt of $\text{K}_2\text{Cr}_2\text{O}_7$ in acidic medium



Change in ON = 6 - 3 = 3

Eg. at of $K_2Cr_2O_7$ = molecular mass
Change in ON of $K_2Cr_2O_7$ per
molecule

$$\begin{aligned} &= \frac{294}{3 \times 2} \\ &= 49. \end{aligned}$$

Method of expressing concentration
of solution

1) Percentage.

(a) Mass by volume percentage $\left(\frac{w}{V}\right)\%$

$$= \frac{\text{mass of Solute (gm)}}{\text{Volume of Solution in (ml)}} \times 100$$

For e.g. :-
 $S\cdot\% \left(\frac{w}{V}\right)$ means 5 gm solute is dissolved
in 100 ml of solution

(b) Mass by mass percentage $\left(\frac{w}{w}\right)\%$

$$= \frac{\text{mass of solute (gm)}}{\text{mass of solution (gm)}} \times 100$$

For e.g.
 $S\cdot\% \left(\frac{w}{w}\right)$ means 5 gm of solute is dissolved
in 100 gm of solution

(c) Volume by Volume Percentage ($\frac{V}{V} \%$)

$$= \frac{\text{Volume of solute (ml)}}{\text{Volume of solution (ml)}} \times 100\%$$

$S\%$ of ($\frac{V}{V} \%$) means $S\text{ ml}$ of solute
Cethyl alcohol dissolve in 100 ml of
solution

2. Parts per million (ppm)

$$\text{ppm} = \frac{\text{mass of Solute in gm}}{\text{Volume of Solution in ml}} \times 10^6$$

3. Parts per billion (ppb)

$$\text{ppb} = \frac{\text{mass of solute in gm}}{\text{Volume of solution in ml}} \times 10^9$$

4. Gram per Litre (g/L)

$\text{g/L} = \frac{\text{mass of solute in gm}}{\text{Volume of solution in L}}$

5. Molarity

The no. of moles, of solute dissolved in solution of 1 litre (1000ml) is called molarity.

molarity = $\frac{\text{no. of moles of solute}}{\text{Volume of solution in L}}$

1M \rightarrow 1 molar solution. The solution in which one mole of solute is dissolved in 1 l solution

Decimolar solution (0.1 or $\frac{1}{10}$ M)

\rightarrow The solution in which 0.1 mole of solute is dissolved in 1 l solution

Semi-molar solution (0.2 M or $\frac{1}{5}$ M)

\rightarrow The solution in which 0.2 mole of solute is dissolved in 1 l solution

Centi-molar solution ($\frac{1}{100}$ or 0.01 M)

\rightarrow The solution in which 0.01 mole or $\frac{1}{100}$ molar solution dissolve in 1 litre of solution

7. Normal Solution (1N)

→ The solution in which 1 gram equivalent solute is dissolved in volume of solution in 1 liter.

Decinormal Solution ($\frac{1}{10}$ or 0.1N)

→ The solution in which 0.1 or $\frac{1}{10}$ gm equivalent solute is dissolved in volume of solution in 1 liter.

Seminormal ($\frac{1}{5}$ or 0.2N)

→ The solution in which 0.2 or $\frac{1}{5}$ gram equivalent solute is dissolved in volume of solution.

F (Centi-normal ($\frac{1}{100}$ or 0.01N))

→ The solution in which 0.01 or $\frac{1}{100}$ gram equivalent solute is dissolved in volume of solution in 1 liter solution.

FORMALITY (F)

→ The number of formula mass of solute dissolve in 1 liter solution is called formality.

Formality and normality are generally equivalent but formality is used for ionic solute like NaCl , KCl , etc.

$$F = \frac{\text{No. of formula mass of solute}}{\text{Volume of solution in liters.}}$$

Relationship between Normality and MOLARITY

$$\text{Normality} = \frac{\text{g/L}}{E}$$

$$\text{normality} \times \text{equivalent weight} = \frac{\text{g}}{E}$$

$$\text{molarity} = \frac{\text{g/L}}{m}$$

$$\text{molarity} \times \text{molecular mass} = \frac{\text{g LL}}{m}$$

$$\text{Normality} \times \text{Equivalent weight} = \text{Molarity} \times \text{molecular mass}$$

$$\frac{\text{Normality} \times \text{Equivalent weight}}{n} = \frac{\text{molarity} \times \text{equivalent weight}}{n}$$

\times
 $n = \text{factor}$

$$\text{normality} = \text{molarity} \times n - \text{factor}$$

- i. for acid $n \rightarrow$ Basicity of acid
- ii. for base $n \rightarrow$ acidity of base
- iii. For salt $n \rightarrow$ Total no. of +ve & -ve charge.

Principle of Volumetric analysis

According to this law of equivalence one substance combine with another substance in the proportional of their equivalent weight

Number of gram equivalent of 1 substance
= no. of gram equivalent of another substance.

Ex:

36.5 gm in 2HCl in 250 ml completely react \rightarrow 40 gm of NaOH of 250 ml [Completely neutral nature]

or,

49 gm H_2SO_4 in 1000 ml completely react \rightarrow 40 gm of NaOH of 1000 ml

Normality equation

$$N_1 V_1 = N_2 V_2$$

where,

$N_1 \rightarrow$ normality of solution A

$V_1 \rightarrow$ volume of Solution A

$N_2 \rightarrow$ normality of Solution B

$V_2 \rightarrow$ Volume of Solution B