# VOLMETRIC ANALYSIS

## 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 the ~~furtion~~ 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 ~~cha~~ classes are

* Qualitative
  → Identify chemical substance
  e.g:- Instrumental method

* ~~Qual~~ Quantitative
  → Estimation of amount of known substance
  e.g:- Either gravimetric, volumetric or instrumental method.

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## 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 stable compound of composition by carrying out suitable precipitation reaction

Example:-

Determination of $Ca^{++}$ in natural water can be done by using excess of $(COOH)_2$ [oxalic acid]. It is added to aq. solution of sample [natural water, $C_2O_4^{--}$], $NH_3$ Solution is added to neutralize acid & all the Ca sample is precipitated as calcium oxalate

$$NH_3 + (COOH)_2 \longrightarrow 2NH_4^+ + C_2O_4^{--}$$

$$Ca^{++}(aq) + C_2O_4^{--}(aq) \rightarrow CaC_2O_4(s)$$

$$CaC_2O_4(s) \xrightarrow{\Delta} CaO + CO(g) + CO_2(g)$$

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Volumetric Analysis Types:-

a) Neutralization or acid

→ The strength of acid may be determined by neutralizing in the presence of an indicator with an alkalie's 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. Iodimetric - Iodometric titration
d. Precipitations titration
e. Complex formation or complexmetric 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 wate
- Composition should not changed during storage and in air during weighing
- Must possess high equivalent weight to minimize weighing errors
- Should be non-toxic

Seconday Standard Solution

→ The substance like $NaOH$, $HCl$, $Na_2SO_4$, $HNO_3$, $KMnO_4$, etc are ~~varied~~ used to prepare seconday solution. These solutes 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~~ standardized solutions are called seconday standard solutions. The substances which is used for preparation of seconday solution is called seconday substance

# Equivalent mass.

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

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

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

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

For example

1. Eq. wt of mg in $MgCl_2 = \frac{24}{2 \times 35.5} \times 35.5$
$= 12$

2. Eq wt of NO in $Na_2O = \frac{2 \times 23}{16} \times 8 = 23$

3. Eq. mass of Ca in $CaH_2 = \frac{40}{2 \times 1.008} \times 1.008$

$= 20$

Relationship between Atomic mass, equivalent ~~dengt~~ weight & valency.

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

1. Equation of weight. mass of element

Al → 13

molecular mass $= 2n + 1$

$= 2 \times 13 + 1$

$= 27$

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

$= \frac{27}{3}$

$= 9.$

Mg.

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

Oxygen

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

Na

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

Carbon

At. number = 6
At. mass = ~~k~~ 2n = 2 × 6 = 12

$$Eq.\ wt = \frac{\text{Atomic mass}}{\text{valency}} = \frac{12}{4} = 3$$

Fe O

$$\text{Eq wt of Fe} = \frac{\text{molecular mass}}{\text{valency}} = \frac{56}{3} = 18.06$$

Equivalent mass of acid.

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

i.e. Bascity of acid is the total number of replace-able $H^+$ from one mole of acid.

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

| Acids | Basicity | Eq mass = $\frac{\text{molecula}}{\text{Basity}}$ | Name of acid |
|---|---|---|---|
| $HNO_3$ | $H^+ + NO_3^-$ | $\frac{63}{1} = 63$ | monobasic |
| $H_3PO_4$ | ~~$H_3$~~ $3H^+ + PO_4^{--}$ | $\frac{98}{3} = 32.6$ | Tribasic |

Equivalent mass of base

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

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

| Base | Acidity | Eq. mass = $\frac{\text{Molecula mass}}{\text{acidity of base}}$ | Name of base |
|---|---|---|---|
| $NaOH$ | $Na^+ + OH^+$ | $\frac{40}{1} = 40$ | monoacidic base |
| $NH_4OH$ | $NH_4^+ + OH^-$ | $\frac{35}{1} = 35$ | monoacidic base |
| $Ca(OH)_2$ | $Ca^{+2} + 2OH^-$ | $\frac{74}{2} = 37$ | diacidic base |
| $Fe(OH)_3$ | $Fe^{+3} + 3OH^-$ | $\frac{107}{3} = 35.7$ | Triacidic base |

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## Equivalent mass of salt

$$\text{Equivalent mass of salt} = \frac{\text{molecule mass of salt}}{\text{Total no of +ve or -ve charge per molecule}}$$

| Salt | Total no. of +ve or -ve charge produce by one molecule of Salt | Eq mass = molecule mass / Total no of +ve/-ve charge per molecul- |
|---|---|---|
| NaCl | $Na^{+} + Cl^{-}$ | $\frac{58.5}{1} = 58.5$ |
| $Na_2CO_3$ | $Na_2CO_3 \rightarrow 2Na^{+} + CO_3^{--}$ | $\frac{106}{2} = 53$ |
| $Ca_3(PO_4)_2$ | $3Ca^{+2} + 2PO_4^{---}$ | $\frac{310}{6} = 51.67$ |

## Equivalent mass of ion

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

$$\text{Eq mass of ion} = \frac{\text{ionic mass of ion}}{\text{Charge on it}}$$

| Ions or Radicals | Charge of ions | Eq mass = formula mass / Charge on it. |
| --- | --- | --- |
| $Na^+$ | 1 | $\frac{23}{1} = 23$ |
| $NO_3^-$ | 1 | $\frac{14+3\times16}{1} = \frac{62}{1}$ |
| $CO_3^{--}$ | 2 | $\frac{12+3\times16}{2} = 30$ |
| $SO_4^{--}$ | 2 | $\frac{32+4\times16}{2} = 48$ |

Equivalent mass of oxidising & Reducing agent

Equivalent mass of O.A a Reducing agent

$$= \frac{\text{molecula mass}}{\text{Total change in ON per molecule}}$$

For example

(1) Eq wt of KmnO4 is different media

a. In acidic medium

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + H_2O + 5[O]$$

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

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

b. In neutral medium

$2KMnO_4 + H_2O \longrightarrow MnO_2 + 2KOH + [O]$

Change in ON of $KMnO_4$ in neutral medium
$= \frac{158}{7-4} = \frac{158}{3} = 52.67$.

c. In basic medium

$\underset{+7}{2KMnO_4} + 2KOH \longrightarrow \underset{+6}{2K_2MnO_4} + H_2O + [O]$

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

Eq. mass of $K_2Cr_2O_7$ in acidic medium

$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 3[O]$

Change in ON $= 6 - 3 = 3$

Eq. wt of $K_2Cr_2O_7$ = $\frac{\text{molecular mass}}{\text{Change in ON or RN per molecule}}$

$$= \frac{294}{3 \times 2}$$

$$= 49.$$

Method of expressing concentration of solution

a) 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 eg:-
$5\%\left(\frac{w}{V}\right)$ means 5 gm solute is dissolved in 100 ml of solution

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

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

For eg
$5\%(w/w)$ means 5 gm of solute is dissolved in 100 gm of solution

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

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

5% of (v/v) means 5ml of solute (ethyl) alcohol dissolve in 100ml of solution

2. Parts per million (ppm)

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

3. Parts per billion (ppb)

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

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4. Gram per litre (g/L)

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

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

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

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

Decimolar solution (0.1 or 1/10 m)
→ The solution in which 0.1 mole of solute is dissolved in 1 l solution

Semi-molar solution (0.2m or 1/5)
→ The solution in which 0.2 mole of solute is dissolved in 1 l solution

Centi-molar solution (1/100 or 0.01m)
→ The solution in which 0.01 mole or 1/100 molar solution dissolve in 1 lite of solution

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7. Normal Solution (1N)
→ The solution in which 1 gram equivalent solute is dissolved in volume of solution in 1 liter.

Decinormal Solution (1/10 or 0.1N)
→ The solution in which 0.1 or 1/10 gm equivalent solute is dissolved in volume of solution in 1 liter.

Seminormal (1/5 or 0.2N)
→ The solution in which 0.2 or 1/5 gram equivalent solute is dissolved in volume of solu

Centi-normal (1/100 or 0.01N)
→ The solution in which 0.01 or 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.

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

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## Relationship between Normality and MOLARITY

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

$$\text{normality} \times \text{equivalent weight} = g/L$$

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

$$\text{molarity} \times \text{molecular mass} = g/L$$

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

$$\text{Normality} \times \cancel{\text{Equivalent weight}} = \text{molarity} \times \text{equivalent weight} \times \text{n-factor}$$

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

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 or −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.

~~Her~~

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

or,

49 gm $H_2SO_4$ in 1000ml completely react ⟶ 40gm of NaOH of 1000ml

Normality equation

$$N_1V_1 = N_2V_2$$

where,

$N_1$ → normality of solution A

$V_1$ → volume of Solution A

$N_2$ → normality of Solution B

$V_2$ → Volume of Solution B