Unit-2 Volumetric Analysis 8 teaching hours

The process of determination of concentration of a solution by finding its volume that will exactly react with a definite volume of another solution of known concentration is termed as volumetric analysis.

Equivalent mass of different substances

a).Equivalent mass of element

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

For example, Eq.Wt of Mg= $\frac{24}{2}$ =12

b). Equivalent mass of acid

$$\text{Eq. Wt.}=\frac{Molecular\ mass}{Basicity}$$

Where, Basicity= number of displaceable hydrogen atom present in an acid

For example, Eq. Wt. of H_2SO_4= $\frac{98}{2}$ =49

c). Equivalent mass of base

$$\text{Eq. Wt.}=\frac{Molecular\ mass}{Acidity}$$

Where, Acidity= number of OH^- present in an alkali

For oxide base, Acidity= $\frac{2\times No.of oxygen\ atoms}{No.of\ metal\ atoms}$

For example, Eq. Wt. of NaOH= $\frac{40}{1}$ =40

Acidity of Na_2O= $\frac{2\times 1}{2}$ =1

Eq. Wt. of Na_2O= $\frac{62}{1}$ =62

b). Equivalent mass of salt

Eq. Wt.= $\frac{Molecular mass}{total\ charge\ on\ cation\ or\ anion}$

For example, Eq. wt. of $CaCl_2$= $\frac{111}{2}$ =55.5

d). Equivalent mass of radical

Eq. Wt.= $\frac{Molecular\ mass\ of\ radical}{Total\ charge\ on\ the\ radical}$

For example, Eq. Wt. of SO_4^{-2} = $\frac{96}{2}$ = 48

Expression of concentration

The amount of substance present in a definite quantity of solution is termed as concentration of the solution. The solution of known concentration is called standard solution and the solution of unknown concentration is called unknown solution. Concentration can be expressed in following terms

1).Normality: It is defined as the number of gram equivalent of substance dissolved in one liter of solution. It is denoted by N.

Mathematically, Normality (N) = $\frac{No.of\ gram\ equivalent\ of\ solute}{Volume\ of\ solution\ in\ litre}$

Or Normality (N) = $\frac{No.of\ gram\ equivalent\ of\ solute}{Volume\ of\ solution\ in\ ml} \times 1000$

Since No. of gram equivalent= $\frac{mass\ in\ gram}{Equivalent\ mass\ in\ gram}$

Therefore, Normality (N)= $\frac{Mass\ in\ gram(W)}{Eq.mass(E) \times Volume\ in\ ml\ (V)} \times 1000$

$$N = \frac{W \times 1000}{E \times V}$$

For example, find the normality of solution when 20 gram NaOH is dissolved in 250 ml solution.

Here, Mass. of NaOH (W) = 20 gm

Eq. mass of NaOH (E) =40

Volume of solution (V)=250 ml

$$\text{Normality} = \frac{W \times 1000}{E \times V} = \frac{20 \times 1000}{40 \times 250} = 2\text{ N}$$

Types of normal solutions

a). *Normal or 1N solution:* The solution that contains 1 gram equivalent mass of a substance dissolved in a liter solution is known as normal solution .It is denoted by 1N or N.

for example, If 53 gm(1 gm equivalent) anhydrous Na_2CO_3 is dissolved in 1 liter of solution then it is known as 1 N solution

b).Semi normal ($\frac{N}{2}$) solution: The solution that contains half of the gram equivalent of a substance in one liter solution is called semi normal or $\frac{N}{2}$ solution. It is denoted by $\frac{N}{2}$

for example, If 26.5 gm of anhydrous Na_2CO_3 is dissolved in one liter solution then the solution is called semi normal solution of Na_2CO_3

c).*Deci normal ($\frac{N}{10}$) solution:* The solution which contains one tenth of gram equivalent of a substance in one liter solution is known as deci normal solution. It is denoted by $\frac{N}{10}$

For example, If one liter solution contains 5.3 gm of anhydrous Na_2CO_3 , then the solution is deci normal solution.

d).*Centi normal ($\frac{N}{100}$) solution*: The solution which contains one hundredth of gm equivalent of a substance in one liter solution is called Centi normal solution. It is denoted by $\frac{N}{100}$.

For example, if one liter solution contains 0.53 gm of anhydrous Na2CO3, then the solution is called Centi normal solution.

2. Molarity: It is defined as the number of moles (gram molecular mass) of substance dissolved in one liter of solution. It is denoted by M.

Mathematically, $$\text{Molarity (M)} = \frac{No.of\ gm\,molecular\ mass(moles)}{Volume\,of\ solution\,in\,litre}$$

Or $$\text{Molarity (N)} = \frac{moles\,of\ subs\tan ce}{Volume\,of\ solution\,in\,ml} \times 1000$$

Since No. of moles= $\frac{mass\ in\ gram}{molecular\ mass\ in\ gram}$

Therefore, Molarity (M)= $\frac{Mass\ in\ gram(W)}{Molecular\ \ mass(M)\times Volume\ in\ ml\ (V)}\times 1000$

$$M=\frac{W\times 1000}{M\times V}$$

For example, find the Molarity of solution when 20 gram anhydrous Na_2CO_3 is dissolved in 250 ml solution.

Here, Mass. of Na_2CO_3 (W) = 20 gm

Molecular mass of Na_2CO_3 (W) =106 gm

Volume of solution (V)=250 ml

$$\text{Molarity} = \frac{W\times 1000}{M\times V} = \frac{20\times 1000}{106\times 250} = 0.754\ \text{N}$$

Types of molar solutions

a).*Molar or 1Msolution:* The solution that contains 1 mole of a substance dissolved in a liter solution is known as molar or *1M* solution .It is denoted by 1M.

for example, If 106 gm(1 mole) anhydrous Na_2CO_3 is dissolved in 1 liter of solution then it is known as 1M solution*.*

b)Semi molar($\frac{M}{2}$*) solution*: The solution that contains half of mole(gm molecular mass) of a substance in one liter solution is called semi molar or $\frac{M}{2}$ solution. It is denoted by $\frac{M}{2}$

for example, If 53 gm of anhydrous Na_2CO_3 is dissolved in one liter solution then the solution is called semi molar solution of Na_2CO_3

c).*Deci normal (*$\frac{M}{10}$*) solution:* The solution which contains one tenth of mole (gram molecular mass) of a substance in one liter solution is known as deci Molar solution. It is denoted by $\frac{M}{10}$

For example, If one liter solution contains 10.6 gm of anhydrous Na_2CO_3, then the solution is deci molar solution.

3. Molality: It is defined as the number of moles of substance dissolved in 1 kg of solvent. It is denoted by m.

Mathematically, molality = $\frac{No.of\ moles\ of\ substance}{wt.of\ solvent\ in\ kg}$

$$\text{molality}=\frac{No.of\ moles\ of\ substance}{wt.of\ solvent\ in\ gram}\times 1000$$

4. Gram per liter: The amount of substance in gram present in a liter of its solution is known as gram per liter solution. It is written in short form as g/l or gl^{-}.

Mathematically, gram per liter (g/l)= $\frac{Wt.of\ substance\ in\ gram}{Vol.of\ solution\ in\ liter}$

$$\text{gram per liter (g/l)}=\frac{Wt.of\ substance\ in\ gram}{Vol.of\ solution\ in\ ml}\times 1000$$

For example, 6 gram of NaOH is dissolved in 500 ml solution. Find out concentration of solution in gram per liter.

$$\text{gram per liter (g/l)}=\frac{6}{500}\times 1000=12\ gl^{-}$$

5. Percentage of solution: It is defined as the number of parts of the substance present in 100 parts of solution. Percentage can be expressed in different ways

i).Percentage as W/W: It is defined as the amount of substance in gram present in 100 gm of solution.

$$\%\ w/w=\frac{Wt.of\ substance\ in\ gram}{Wt.of\ solution\ in\ gm}\times 100$$

ii).Percentage as w/v: It is defined as the amount of substance in gram present in 100 ml of solution.

$$\%\ w/v=\frac{Wt.of\ substance\ in\ gram}{Vol.of\ solution\ in\ ml}\times 100$$

iii).Percentage v/v: It is defined as the amount of substance in ml present in 100 ml of solution.

$$\%\ w/v=\frac{Vol.of\ substance\ in\ ml}{Vol.of\ solution\ in\ ml}\times 100$$

6.Part per million (ppm) : it is defined as the weight of solute present in one million (10^6) parts by weight of the solution. For very dilute solution, concentration of solute is expressed as part per million (ppm)

Part per million (ppm)= $\frac{wt.of solute}{wt.of solution}\times 10^6$

Relation between normality and molarity

We know,

$$\text{Normality (N)}=\frac{Mass\, in\, gram}{Eq.mass\times Volume\, in\, liter}$$

$$\text{Normality(N)}=\frac{1}{Eq.mass}\times\frac{mass\, in\, gram}{Vol.in\, liter}$$

$$\text{Normality(N)}=\frac{1}{Eq.mass}\times\frac{Gm}{liter}$$

Gm/liter=Normality × Eq. mass. i

Similarly Gm/liter=Morality × molecular mass. ii

From equation eq. i and eq.ii

Normality × Eq. mass= Morality × molecular mass

$$\text{Normality=molarity} \times \frac{molecular\ mass}{Eq.mass}$$

Since $\frac{molecular\ mass}{Eq.mass}$ =basicity or acidity

Normality= molarity × basicity for acid

Normality= molarity × basicity for base

1. **Calculate the normality of 4% caustic soda.**

   100 ml of solution contains 4 gm NaOH

   1000 ml of solution contains 40 gm of NaOH

   Therefore, gram per liter (gm/l) = 40

   Equivalent Wt. of NaOH = 40

Normality=$\frac{gm/l}{eq.wt.}$ = 40/40=1N

2. **Calculate the normality of 95.87% pure sulphuric acid of specific gravity 1.84 gm/cc.**

Specific gravity=1.84 gm/cc

Percentage purity = 95.87%

Weight of H2SO4 present=1.84 gm/cc × 95.87%

Concentration of H2SO4 in gm/l=$\frac{1.84 \times 95.87 \times 1000}{100}$ =1764 g/l

Equivalent wt. of H2SO4=49

Normality=$\frac{g/l}{Eq.Wt.}$ =1764/49=36N

Normality factor (f)

Normality factor is defined as the ratio of actual weight of the solute taken to the weight of solute to be taken.

Normality factor (f)=$\frac{weight\ of\ solute\ taken}{weight\ of\ solute\ tobe\ taken}$

The actual normality of solution is the product of provided normality and normality factor

Actual normality= given normality × normality factor (f)

Preparation of primary standard solution

1.preparation of deci normal solution of anhydrous sodium carbonate.

For the preparation of N/10 solution of anhydrous sodium carbonate in 250 ml volumetric flask, required amount of Na_2CO_3 is calculated as

Eq. wt. of Na_2CO_3 (E) = $\frac{106}{2}$ =53

Vol. of solution to be prepared (V) = 250 ml

Normality of solution (N)=0.1N

Required wt. of Na_2CO_3 = $\frac{NEV}{1000}$ = $\frac{0.1 \times 53 \times 250}{1000}$ =1.325 gm

1.325 gm anhydrous sodium carbonate is taken in 250 ml volumetric flask and then dissolved by adding little amount of water at first. Finally, v. f. is filled with water up to mark on the neck

Titration

The process of determining the strength of unknown solution by reacting it with the standard solution via volume measurement usually in presence of suitable indicator is known as titration. There are different types titrations, among them two are

a).Acid-base titration: The technique of determination of strength of either acid or base by finding its volume that will exactly react with a definite volume of base or acid solution of known strength in presence of suitable indicator (methyl orange, phenolphthalein) is known as acid-base.For example, titration of HCl Vs Na_2CO_3 solution, Titration of oxalic acid Vs NaOH solution.

b).Redox titration: The technique of determination of strength of an solution by titrating it against another primary standard solution in which one chemical species gets reduced and other gets oxidized is known. In redox titration, one chemical species itself acts as indicator. For example, Titration of $KMnO_4$ solution Vs Oxalic acid. Here $KMnO_4$ acts as self indicator. At the end point pink color of $KMnO_4$ gets persist.

$$2KMnO_4 + 3H_2SO_4 + 5C_2H_2O_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$$

Different terms involved in titration

i).Primary standard substance: The chemical substance that can be weighed in exact amount in order to prepare the primary standard solution is known as primary standard substance. Primary standard substance should possess following properties.

* It should be available in pure and dry form.

* It should not be hygroscopic and deliquescent.

* It should have high equivalent wit so that error can be minimized during weighing.

* Composition should not be changed

* Concentration in the solution should not be altered for long period of storage.

ii).Primary standard solution: The solution that can be prepared by dissolving known weight of pure, dry and stable primary substance in the known volume of solution is known as primarystandard solution. For e.g. N/5 of oxalic acid, N/10 of Na_2CO_3 solution.

iii).Secondary standard solution: The solution which has been standardized with the help of primary standard solution is known as secondary standard solution. For e.g. N/10 HCl, N/5 H_2SO_4.

i).Titrant: The solution. is taken in burette is called titrant or the solution whose concentration is known is called titrant.

ii).Titrand: The solution whose strength is determined with help of titrant is known as titrand or titrate. Generally it is taken in conical flask.

iii).End point: The point which indicates the completion of reaction between titrant and titrand by changing the color of indicator is known as end point. It is practical point observed during titration.

iv).Equivalent point: The theoretical end point at which equal number of gram equivalent of one chemical substance is completely neutralized with same number of gram equivalent of another chemical substance.

v).Titration error: The difference between end point and equivalent point is called titration error. It can be minimized by choosing the suitable indicator.

Vi).Indicators: The chemical substance that indicates the completion of the chemical reaction by changing their own color at the end point is known as indicator. Different indicators have different P^H range of their sharp change in color. Some example of indicators are methyl orange, phenolphthalein, litmus paper, Eriochrome black T , litmus paper etc. According to the use, indicators are of following types

Types of indicators

a). Internal indicator: The indicators which are added in the reaction mixture in the conical flask is known as internal indicators. for e.g. phenolphthalein, methyl orange etc.

b).External indicator: The indicators which are not added to the reaction mixture but are placed outside the titrating flask are known as external indicators. For example,$K_3[Fe(CN)_6]$ acts as external indicator in the titration of $FeSO_4$ with $K_2Cr_2O_7$.

c).Self indicator: When one of the reactants in the titration can self acts as indicator, then, it is known as self indicator. For e.g. $KMnO_4$ act as self indicator in the titration of $KMnO_4$ Vs oxalic acid.

Characteristics of good indicators

1. Indicator should have narrow working PH range.

2. The color change should be sharp and stable.

3. Small drop of indicator should have capacity to indicate end point.

Principle of volumetric analysis

Volumetric analysis is governed by following principles,

1.Equal volume of one solution neutralizes equal volume of another solution if their concentration is same.For example,

1 ml of 1N HCl=1ml of 1N NaOH

10 ml of 1N $KMnO_4$ =10 ml of 1N oxalic acid

So, A ml of B N solution = (AxB) ml of 1N solution.

2. If the volume of solution increases, the strength of solution decreases by same factor and vice versa.

For example,

1oo ml 1N HCl = 200 ml 0.5 N HCl

=10 ml 10N HCl

=1000 ml 0.1N HCl

3.At the equivalent point of neutralization, the following normality equation hold true.

$S_1V_1=S_2V_2$ or N1V1=N2V2

Where, S1= strength of one solution (acid)

V1= volume of one solution (acid)

S2= strength of another solution (base)

V2= volume of another solution (base)

This is the law of chemical equivalence or normality equation.

Derivation of Normality equation

From the law of chemical equivalence, when one substance is equally balanced or neutralized another substance, then.

No. of gram equivalent of acid=No. of gram equivalent of base ....(i)

We have, Normality $= \dfrac{Wt.of\ substance\ in\ gram}{Vol.of\ sol.in\ liter \times equivalent\ wt.}$

Or Normality × Vol. of sol. In liter $= \dfrac{Wt.of\ substance\ in\ gram}{Equivalent\ wt.}$

Since No. of gram equivalent= $\dfrac{Wt.of\ substance\ in\ gram}{Equivalent\ wt.}$

Therefore, Normality × Vol. of sol. In liter= No. of gram equivalent..................(ii)

From eq.(i) and eq.(ii)

Normality of acid × vol. of acid in liter= normality of base × volume of base in liter

Or $N_A \times V_A = N_B \times V_B$ or $S_1 V_1 = S_2 V_2$

This equation is used for dilution of solution of all type of concentration and for neutralization reaction of normal solution.

Some examples

1. Find the strength of H_2SO_4 solution when 50 ml water is added to the 200 ml of 0 .1N is H2SO4..

Initial vol. V1=200 ml

Initial Normality N1=0.1N

Final vol. V2=200+50=250ml

Final normality=?

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

$$N2 = \frac{V1 \times N1}{V2}$$

$$= \frac{200 \times 0.1}{250}$$

$$=0.08N$$

2. Find the volume of N/10 of HCl solution required to completely neutralize 500ml of N/20 of NaOH solution.

3. What volume of deci normal solution of HCl is required to neutralize 25 ml NaOH containing 8 gm NaOH in one liter solution.

Strength in gm/l=8

Eq. wt. of NaOH=40

Normality of NaOH (N1)= $\frac{8}{40}$ =0.2N

Normality of HCl (N2)=0.1N

Volume of NaOH (V1)=25ml

vol. of HCl (V2)=?

From normality equation

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

$$V2 = \frac{V1 \times N1}{N2} = \frac{25 \times 0.2}{0.1} = 50 \text{ ml}$$

3. X gm of Na_2CO_3 reacts completely with 20 ml of 1M HCl. Calculate the value of x.

4. X gm of $CaCO_3$ reacts completely with 20 ml of 1 M HCl. Calculate the value of X.

5. X gm Na_2CO_3 reacts completely with 20 ml of 1M HCl. Calculate the value of X.