Chemical stoichiometry:

Stoichiometry (pronounced "stoy-key om-e-tree") is the calculation of the quantities of reactants and products involved in a chemical reaction. That means quantitative calculations of chemical composition and reaction are referred to as stoichiometry.

Basically, this topic involves two types of calculations.

(a) Simple calculations (gravimetric analysis) and

(b) More complex calculations involving concentration and volume of solutions (volumetric analysis).

There is no borderline, which can distinguish the set of laws applicable to gravimetric and volumetric analysis. All the laws used in one are equally applicable to the other i.e., mole as well as equivalent concept. But in actual practice, the problems on gravimetric involves simpler reactions, thus mole concept is convenient to apply while volumetric reactions being complex and unknown (unknown simple means that it is not known to you, as it's not possible for you to remember all possible reactions), equivalent concept is easier to apply as it does not require the knowledge of balanced equation.

(1) **Gravimetric analysis :** In gravimetric analysis we relate the weights of two substances or a weight of a substance with a volume of a gas or volumes of two or more gases.

Problems Involving Mass-Mass Relationship

Proceed for solving such problems according to the following instructions,

(i) Write down the balanced equation to represent the chemical change.

(ii) Write the number of moles below the formula of the reactants and products. Also write the relative weights of the reactants and products (calculated from the respective molecular formula), below the respective formula.

(iii) Apply the unitary method to calculate the unknown factor (s).

Problems Involving Mass-Volume Relationship

For solving problems involving mass-volume relationship, proceed according to the following instructions,

(i) Write down the relevant balanced chemical equations (s).

(ii) Write the weights of various solid reactants and products.

(iii) Gases are usually expressed in terms of volumes. In case the volume of the gas is measured at room temperature and pressure (or under conditions other than N.T.P.), convert it into N.T.P. by applying gas equation.

(iv) Volume of a gas at any temperature and pressure can be converted into its weight and vice-versa with the help of the relation, by

$$PV = gM \times RT$$

where g is weight of gas, M is mole. wt. of gas, R is gas constant.
Calculate the unknown factor by unitary method.

Problems Based on Volume-Volume Relationship:

Such problems can be solved according to chemical equation as,

(i) Write down the relevant balanced chemical equation.

(ii) Write down the volume of reactants and products below the formula to each reactant and product with the help of the fact that $1 gm$ molecule of every gaseous substance occupies 22.4 litres at N.T.P.

(iii) In case volume of the gas is measured under particular (or room) temperature, convert it to volume at NTP by using ideal gas equation.

Take the help of Avogadro's hypothesis "*Equal volume of different gases under the similar conditions of temperature and pressure contain the same number of molecules*".

(2) **Volumetric analysis:** It is a method which involves quantitative determination of the amount of any substance present in a solution through volume measurements. For the analysis a standard solution is required. (A solution which contains a known weight of the solute present in known volume of the solution is known as standard solution.)

To determine the strength of unknown solution with the help of known (standard) solution is known as titration. Different types of titrations are possible which are summerised as follows,
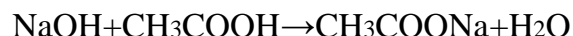
(i) *Redox titrations* : To determine the strength of oxidizing agents or reducing agents by titration with the help of standard solution of reducing agents or oxidising agents.

(ii) *Acid-base titrations* : To determine the strength of acid or base with the help of standard solution of base or acid.

Example:

$$NaOH+HCl \rightarrow NaCl+H_2O$$
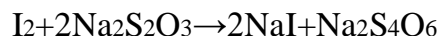
and

$$NaOH+CH_3COOH \rightarrow CH_3COONa+H_2O$$

etc.
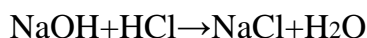
(iii) *Iodiometric titrations* : This is a simple titration involving free iodine. This involves the titration of iodine solution with known sodium thiosulphate solution whose normality is

$$N$$

. Let the volume of sodium thiosulphate is

$$V ml$$

.

$$I_2+2Na_2S_2O_3 \rightarrow 2NaI+Na_2S_4O_6$$

$$n=2$$

$$n=1$$

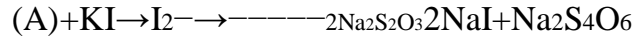Equivalents of

$$I_2 = \text{Equivalent of } Na_2S_2O_3$$

$\therefore$ Equivalents of $I_2 = N \times V \times 10^{-3}$

Moles of $I_2 = \dfrac{N \times V \times 10^{-3}}{2}$

Mass of free I_2 in the solution $= \left[\dfrac{N \times V \times 10^{-3}}{2} \times 254 \right] g$

.

(iv) *Iodometric titrations* : This is an indirect method of estimation of iodine. An oxidising agent is made to react with excess of solid KI. The oxidising agent oxidizes I^- to I_2. This iodine is then made to react with $Na_2S_2O_3$ solution.

Oxidising Agent

$$(A) + KI \rightarrow I_2 \xrightarrow{-\cdots\cdots\cdots} 2NaI + Na_2S_4O_6$$
$$ {}^{2Na_2S_2O_3}$$

Let the normality of $Na_2S_2O_3$ solution is N and the volume of thiosulphate consumed to V ml.

Equivalent of A = Equivalent of I_2 = Equivalents of $Na_2S_2O_3$

Equivalents of I_2 liberated from $KI = N \times V \times 10^{-3}$

Moles of I_2 liberated from $KI = \dfrac{N \times V \times 10^{-3}}{2}$

Mass of I_2 liberated from $KI = \left[\dfrac{N \times V \times 10^{-3}}{2} \times 254 \right] g$

.

(v) *Precipitation titrations* : To determine the anions like CN^-, AsO_3^{-3}, PO_4^{-3}, X^- etc, by precipitating with $AgNO_3$ provides examples of precipitation titrations.

$$NaCl + AgNO_3 \rightarrow AgCl\downarrow + NaNO_3$$

$$KSCN + AgNO_3 \rightarrow AgSCN\downarrow + KNO_3$$
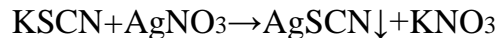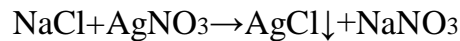
End point and equivalence point : *The point at which titration is stopped is known as end point, while the point at which the acid and base* (*or oxidising and reducing agents*) *have been added in equivalent quantities is known as equivalence point.* Since the purpose of the indicator is to stop the titration close to the point at which the reacting substances were added in equivalent quantities, it is important that the equivalent point and the end point be as close as possible.

Normal solution : *A solution containing one gram equivalent weight of the solute dissolved per litre is called a normal solution*; *e.g.* when 40 *g* of *NaOH* are present in one litre of *NaOH* solution, the solution is known as normal (*N*) solution of *NaOH*. Similarly, a solution containing a fraction of gram equivalent weight of the solute dissolved per litre is known as subnormal solution. For example, a solution of *NaOH* containing 20 *g* (1/2 of *g* eq. wt.) of *NaOH* dissolved per litre is a sub-normal solution. It is written as *N*/2 or 0.5 *N* solution.

Formula used in solving numerical problems on volumetric analysis

(1) Strength of solution = Amount of substance in g litre^{-1}

(2) Strength of solution = Amount of substance in $g\ moles$ litre^{-1}

(3) Strength of solution = Normality × Eq. wt. of the solute

$$= \text{molarity} \times \text{ Mol. wt. of solute}$$

(4) Molarity = (Moles of solute)/(Volume in litre)

(5) Number of moles = (Wt. in gm)/(Mol. wt.) = $M \times V_{(inl)}$

$$= \text{(Volume in litres at NTP)}/\ 22.4 \qquad \text{(only for gases)}$$

(6) Number of millimoles = (Wt. in gm × 1000)/(mol. wt.)

= Molarity × Volume in ml.

(7) Number of equivalents

$$= \text{(Wt. in gm)/(Eq. wt.)} = x \times \text{No. of moles} \times \text{Normality} \times \text{Volume in litre}$$

(8) Number of milliequivalents (meq.)

= (Wt. in gm × 1000)/(Eq. wt.)

= normality × Volume in ml.

(9) Normality = $x \times$ No. of millimoles

= $x \times$ Molarity

= (Strength in gm litre^{-1})/(Eq. wt.)

where

$$x = \text{(Mol. wt.)/(Eq. wt.)}$$

, x = valency or change in oxi. Number.

(10) Normality formula,

$$N_1 V_1 = N_2 V_2$$

(11) % by weight

$$= \text{(Wt. of solvent)/(Wt. of solution)} \times 100$$

(12) % by volume

$$= \text{(Wt. of solvent)/(Vol. of solution)} \times 100$$

(13) % by strength

$$= \text{(Vol. of solvent)/(Vol. of solution)} \times 100$$

(14) Specific gravity

$$=(\text{Wt. of solution})/(\text{Vol. of solution})=\text{Wt. of 1 ml. of solution}$$

(15) Formality

$$=(\text{Wt. of ionic solute})/(\text{Formula Wt. of solute}) \times V_{inl}$$

(16) Mol. Wt. = V.D ´ 2 (For gases only)