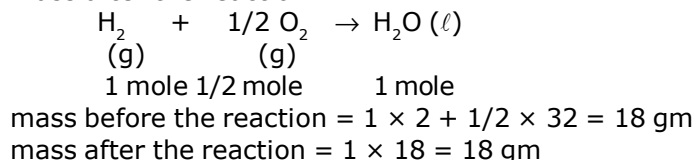


LAWS OF CHEMICAL COMBINATION**(a) Law of conservation of mass [Lavoisier]**

In a chemical change total mass remains conserved i.e. mass before the reaction is always equal to mass after the reaction.

**(b) Law of constant composition [Proust]**

All chemical compounds are found to have constant composition irrespective of their method of preparation or sources.

⇒ In H₂O, Hydrogen & oxygen combine in 2 : 1 molar ratio, this ratio remains constant whether it is Tap water, river water or seawater or produced by any chemical reaction.

(c) Law of multiple proportions [Dalton]

When one element combines with the other element to form two or more different compounds, the mass of one element, which combines with a constant mass of the other bear a simple ratio to one another.

⇒ Carbon is found to form two oxides which contain 42.9% & 27.3% of carbon respectively show that these figures show the law of multiple proportion.

	First oxide	Second oxide	
Carbon	42.9 %	27.3 %	
Oxygen	57.1 %	72.7 %	Given

In the first oxide, 57.1 parts by mass of oxygen combine with 42.9 parts of carbon.

1 part of oxygen will combine with $\frac{42.9}{57.1}$ part of carbon = 0.751

Similarly in 2nd oxide

1 part of oxygen will combine with $\frac{27.3}{72.7}$ part of carbon = 0.376

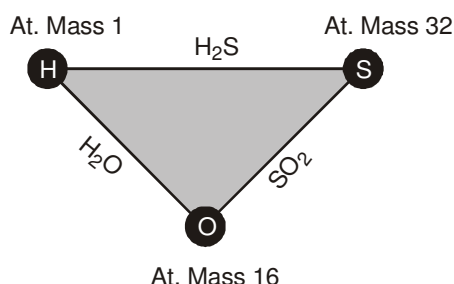
The ratio of carbon that combine with the same mass of oxygen = 0.751 : 0.376 = 2 : 1

This is a simple whole number ratio this means above data shows the law of multiple proportion.

(d) Law of reciprocal proportions [Richter]

When two elements combine separately with definite mass of a third element, then the ratio of their masses in which they do so is either the same or some whole number multiple of the ratio in which they combine with each other.

This law can be understood easily with the help of the following examples.



⇒ Let us consider three elements – hydrogen, sulphur and oxygen. Hydrogen combines with oxygen to form H_2O whereas sulphur combines with it to form SO_2 . Hydrogen and sulphur can also combine together to form H_2S . The formation of these compounds is shown in fig.

In H_2O , the ratio of masses of H and O is 2 : 16.

In SO_2 , the ratio of masses of S and O is 32 : 32. Therefore, the ratio of masses of H and S which combines with a fixed mass of oxygen (say 32 parts) will be

$$4 : 32 \text{ i.e. } 1 : 8 \quad \dots(1)$$

When H and S combine together, they form H_2S in which the ratio of masses of H and S is

$$2 : 32 \text{ i.e., } 1 : 16 \quad \dots(ii)$$

The two ratios (i) and (ii) are related to each other as

$$\frac{1}{8} : \frac{1}{16} \text{ or } 2 : 1$$

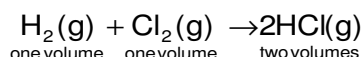
i.e., they are whole number multiples of each other.

Thus, the ratio masses of H and S which combines with a fixed mass of oxygen is a whole number multiple of the ratio in which H and S combine together.

(e) Gay Lussac law of combining volumes :

When two or more gases react with one another, their volumes bear simple whole number ratio with one another and to the volume of products (if they are also gases) provided all volumes are measured under identical conditions of temperature and pressure.

⇒ When gaseous hydrogen and gaseous chlorine react together to form gaseous hydrogen chloride according to the following equation.



It has been observed experimentally that in this reaction, one volume of hydrogen always reacts with one volume of chlorine to form two volumes of gaseous hydrogen chloride. all reactants and products are in gaseous state and their volumes bear a ratio of 1 : 1 : 2. This ratio is a simple whole number ratio.

"These are no longer useful in chemical calculations now but gives an idea of earlier methods of analysing and relating compounds by mass."

MOLE CONCEPT

Definition of mole : One mole is a collection of that many entities as there are number of atoms exactly in 12 gm of C – 12 isotope.

or 1 mole = collection of 6.02×10^{23} species

$$6.02 \times 10^{23} = N_A = \text{Avogadro's No.}$$

1 mole of atoms is also termed as 1 gm-atom, 1 mole of ions is termed as 1 gm-ion and 1 mole of molecule termed as 1 gm-molecule.

METHODS OF CALCULATIONS OF MOLE

(a) If no. of some species is given, then no. of moles = $\frac{\text{Given no.}}{N_A}$

(b) If weight of a given species is given, then no of moles = $\frac{\text{Given wt}}{\text{Atomic wt.}}$ (for atoms),

or = $\frac{\text{Given wt.}}{\text{Molecular wt.}}$ (for molecules)

(c) If volume of a gas is given along with its temperature (T) and pressure (P)

$$\text{use } n = \frac{PV}{RT}$$

where $R = 0.0821 \text{ lit-atm/mol-K}$ (when P is in atmosphere and V is in litre.)

1 mole of any gas at STP (0°C & 1 bar) occupies 22.7 litre.

1 mole of any gas at STP (0°C & 1 atm) occupies 22.4 litre.

Atom : Atom is smallest particle which can not be divided into its constituents.

Atomic weight : It is the weight of an atom relative to one twelvth of weight of 1 atom of C-12

RELATIONSHIP BETWEEN GRAM AND AMU

$$1 \text{ amu} = \frac{1}{12} \text{ wt of one C - 12 atom.}$$

for C 1 mole C = 12 gm = 6.023×10^{23} atoms

wt of 6.023×10^{23} atoms = 12 gm

$$\text{wt of 1 atom of C} = \frac{12}{N_A} \text{ gm} \quad (N_A \rightarrow \text{Avogadro's number} = 6.23 \times 10^{23})$$

$$1 \text{ amu} = \frac{1}{12} \text{ wt of one C - 12 atom}$$

$$= \frac{1}{12} \times \frac{12}{N_A} \text{ gm}$$

$$1 \text{ amu} = \frac{1}{N_A} \text{ gm}$$

ELEMENTAL ANALYSIS

For n mole of a compound ($\text{C}_3\text{H}_7\text{O}_2$)

Moles of C = 3n

Moles of H = 7n

Moles of O = 2n

Ex.1 Find the wt of water present in 1.61 g of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$

Sol. Moles of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} = \frac{\text{wt. in gram}}{\text{molecular wt}} = \frac{1.61}{322} = 0.005 \text{ moles}$

$$\begin{aligned} \text{Moles of water} &= 10 \times \text{moles of } \text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} \\ &= 10 \times 0.05 = 0.05 \end{aligned}$$

$$\text{wt of water} = 0.5 \times 18 = 0.9 \text{ gm} \quad \textbf{Ans.}$$

Ex.2 Calculate the following for 49 gm of H_2SO_4

(a) moles (b) Molecules (c) Total H atoms (d) Total O atoms (e) Total electrons

Sol. Molecular wt of $\text{H}_2\text{SO}_4 = 98$

$$(a) \text{ moles} = \frac{\text{wt in gm}}{\text{molecular wt}} = \frac{49}{98} = \frac{1}{2} \text{ mole}$$

(b) Since 1 mole = 6.023×10^{23} molecules.

$$\frac{1}{2} \text{ mole} = 6.023 \times 10^{23} \times \frac{1}{2} \text{ molecules} \\ = 3.011 \times 10^{23} \text{ molecules}$$

(c) 1 molecule of H_2SO_4 Contains 2 H atom

$$3.011 \times 10^{23} \text{ of } \text{H}_2\text{SO}_4 \text{ contain } 2 \times 3.011 \times 10^{23} \text{ atoms} \\ = 6.023 \times 10^{23} \text{ atoms}$$

(d) 1 molecules of H_2SO_4 contains 4 O atoms

$$3.011 \times 10^{23} \text{ molecular of } \text{H}_2\text{SO}_4 \text{ contains } = 4 \times 3.011 \times 10^{23} = 12.044 \times 10^{23}$$

(e) 1 molecule of H_2SO_4 contains

$$2\text{H atoms} + 1\text{ S atom} + 4\text{ O atom}$$

this means 1 molecule of H_2SO_4 Contains $(2 + 16 + 4 \times 8) e^-$

So 3.011×10^{23} molecules have $3.011 \times 10^{23} \times 50$ electrons

$$1.5055 \times 10^{25} e^-$$

Ex.3 Calculate the total ions & charge present in 4.2 gm of N^{3-}

Sol. $\text{mole} = \frac{\text{wt in gm}}{\text{Ionic wt}} = \frac{4.2}{14} = 0.3$

$$\text{total no of ions} = 0.3 \times N_A \text{ ions}$$

$$\text{total charge} = 0.3 N_A \times 3 \times 1.6 \times 10^{-19} \\ = 0.3 \times 6.023 \times 10^{23} \times 3 \times 1.6 \times 10^{-19} \\ = 8.67 \times 10^4 \text{ C Ans.}$$

Ex.4 Find the total number of iron atom present in 224 amu iron.

Sol. Since 56 amu = 1 atom

$$\text{therefore } 224 \text{ amu} = \frac{1}{56} \times 224 = 4 \text{ atom Ans.}$$

AVERAGE ATOMIC WEIGHT

$$= \sum \% \text{ of isotope } \times \text{ molar mass of isotope.}$$

The % obtained by above expression (used in above expression) is by number (i.e. its a mole%)

MOLECULAR WEIGHT

It is the sum of the atomic weight of all the constituent atom.

$$(a) \text{ Average molecular weight} = \frac{\sum n_i M_i}{\sum n_i}$$

where n_i = no. of moles of any compound and m_i = molecular mass of any compound.

Make yourselves clear in the difference between mole% and mass % in question related to above.

Shortcut for % determination if average atomic weight is given for X having isotopes X^A & X^B .

$$\% \text{ of } X^A = \frac{\text{Average atomic weight} - \text{wt of } X^B}{\text{difference in weight of } X^A \text{ \& } X^B} \times 100$$

Try working out of such a shortcut for X^A , X^B , X^C

EMPIRICAL FORMULA, MOLECULAR FORMULA

Empirical formula : Formula depicting constituent atom in their simplest ratio.

Molecular formula : Formula depicting actual number of atoms in one molecule of the compound.

Relation between the two : Molecular formula = Empirical formula \times n

$$n = \frac{\text{Molecular mass}}{\text{Empirical Formula mass}}$$

Check out the importance of each step involved in calculations of empirical formula.

Ex.5 A molecule of a compound have 13 carbon atoms, 12 hydrogen atom, 3 oxygen atoms and 3.02×10^{-23} gm of other element. Find the molecular wt. of compound.

Sol. wt. of the 1 molecule of a compound = $13 \times \frac{12}{N_A} + 12 \times \frac{1}{N_A} + 3 \times \frac{16}{N_A} + 3.02 \times 10^{-23}$

$$= \frac{156 + 12 + 48 + 3.02 \times 10^{-23} N_A}{N_A} = 234.18 / N_A = 234 \text{ amu. Ans.}$$

Ex.6 A compound containing Ca, C, N and S was subjected to quantitative analysis and formula mass determination. A 0.25 g of this compound was mixed with Na_2CO_3 to convert all Ca into 0.16 g CaCO_3 . A 0.115 gm sample of compound was carried through a series of reactions until all its S was changed into SO_4^{2-} and precipitated as 0.344 g of BaSO_4 . A 0.712 g sample was processed to liberate all of its N as NH_3 and 0.155 g NH_3 was obtained. The formula mass was found to be 156. Determine the empirical and molecular formula of the compound.

Sol. Moles of $\text{CaCO}_3 = \frac{0.16}{100} = \text{Moles of Ca}$

$$\text{Wt of Ca} = \frac{0.16}{100} \times 40$$

$$\text{Mass \% of Ca} = \frac{0.16}{100} \times 40 \times \frac{100}{0.25} = 25.6$$

Similarly Mass % of S = $\frac{0.344}{233} \times \frac{32 \times 100}{0.115} = 41$

Similarly Mass % of N = $\frac{0.155}{17} \times \frac{14}{0.712} \times 100 = 17.9$

$$\Rightarrow \text{Mass \% of C} = 15.48$$

Now :

Elements	Ca	S	N	C
Mass %	25.6	41	17.9	15.48
Mol ratio	0.64	1.28	1.28	1.29
Simple ratio	1	2	2	2

Empirical formula = $\text{CaC}_2\text{N}_2\text{S}_2$,

Molecular formula wt = 156

$$n \times 156 = 156 \Rightarrow n = 1$$

Hence, molecular formula = $\text{CaC}_2\text{N}_2\text{S}_2$

● **Density :**

(a) Absolute density

(b) Relative density

$$\text{Absolute density} = \frac{\text{Mass}}{\text{volume}}$$

$$\text{Relative density} = \frac{\text{density of substance}}{\text{density of standard substance}}$$

$$\text{Specific gravity} = \frac{\text{density of substance}}{\text{density of H}_2\text{O at 4}^\circ\text{C}}$$

Vapour density : It is defined only for gas.

It is a density of gas with respect to H_2 gas at same temp & press

$$\text{V.D} = \frac{d_{\text{gas}}}{d_{\text{H}_2}} = \frac{P M_{\text{gas}} / RT}{P M_{\text{H}_2} / RT} = \frac{M_{\text{gas}}}{M_{\text{H}_2}} = \frac{M}{2}$$

$$\text{V.D} = \frac{M}{2}$$

$$\text{V.D} = \frac{\text{Molecular wt of gas}}{\text{Molecular wt of H}_2 \text{ gas}}$$

- density of Cl_2 gas with respect to O_2 gas

$$= \frac{\text{Molecular wt of Cl}_2 \text{ gas}}{\text{Molecular wt of O}_2 \text{ gas}}$$

- **STOICHIOMETRY :** Stoichiometry is the calculations of the quantities of reactants and products involved in a chemical reaction. Following methods can be used for solving problems.

- (a) Mole Method (For Balance reaction)
- (b) POAC method } Balancing not required but common sense ----- use it with slight care.
- (c) Equivalent concept

● **CONCEPT OF LIMITING REAGENT.**

Limiting Reagent :

It is very important concept in chemical calculation. It refers to reactant which is present in minimum stoichiometry quantity for a chemical reaction. It is reactant consumed fully in a chemical reaction. So all calculations related to various products or in sequence of reactions are made on the basis of limiting reagent.

- It comes into picture when reaction involves two or more reactants. For solving any such reactions, first step is to calculate L.R.

Calculation of Limiting Reagent.

- (a) By calculating the required amount by the equation and comparing it with given amount.
[Useful when only two reactant are there]
- (b) By calculating amount of any one product obtained taking each reactant one by one irrespective of other reactants. The one giving least product is limiting reagent.
- (c) Divide given moles of each reactant by their stoichiometric coefficient, the one with least ratio is limiting reagent. [Useful when number of reactants are more than two.]

● **PERCENTAGE YIELD :**

The percentage yield of product = $\frac{\text{actual yield}}{\text{the theoretical maximum yield}} \times 100$

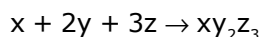
- The actual amount of any limiting reagent consumed in such incomplete reactions is given by [% yield \times given moles of limiting reagent] [For reversible reactions]
- For irreversible reaction with % yield less than 100, the reactants is converted to product (desired and waste.)

Ex.7 A compound which contains one atom of X and two atoms of y for each three atoms of z is made of mixing 5 gm of x, 1.15×10^{23} atoms of Y and 0.03 mole of Z atoms. Given that only 4.40 gm of compound results. Calculate the atomic weight of Y if atomic weight of X and Z are 60 and 80 respectively.

Sol. Moles of x = $\frac{5}{60} = \frac{1}{12} = 0.083$

moles of y = $\frac{1.15 \times 10^{23}}{6.023 \times 10^{23}} = 0.19$

moles of z = 0.03



for limiting reagent, $0.083/1 = 0.083$

$$\frac{0.19}{2} = 0.095, \frac{0.03}{3} = 0.01$$

Hence z is limiting reagent

wt of $xy_2z_3 = 4.4 \text{ gm} = \text{moles} \times \text{molecular wt.}$

moles of $xy_2z_3 = \frac{1}{3} \times 0.03 = 0.01$

$300 + 2m = 440 \Rightarrow 2m = 440 - 300 \Rightarrow m = 70$ **Ans.**

Ex.8 A polystyrene having formula $\text{Br}_3\text{C}_6\text{H}_3(\text{C}_3\text{H}_8)_n$ found to contain 10.46% of bromine by weight. Find the value of n. (At. wt. Br = 80)

Sol. Let the wt of compound is 100 gm & molecular wt is M

Then moles of compound = $\frac{100}{M}$

Moles of Br = $\frac{100}{M} \times 3$

wt of Br = $\frac{100}{M} \times 3 \times 80 = 10.46$

$M = 2294.45 = 240 + 75 + 44n$

Hence n = 45 **Ans.**

Ex.9 A sample of clay was partially dried and then analysed to 50% silica and 7% water. The original clay contained 12% water. Find the percentage of silica in the original sample.

Sol. In the partially dried clay the total percentage of silica + water = 57%. The rest of 43% must be some impurity. Therefore the ratio of wts. of silica to impurity = $\frac{50}{43}$. This would be true in the original sample of silica.

The total percentage of silica + impurity in the original sample is 88. If x is the percentage of silica,

$\frac{x}{88-x} = \frac{50}{43}; \quad x = 47.3\%$ **Ans.**

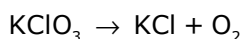
Ex.10 A mixture of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ was heated until all the water was driven-off. if 5.0 g of mixture gave 3 g of anhydrous salts, what was the percentage by mass of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in the original mixture ?

Sol. Let the mixture contain x g $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

$$\Rightarrow \frac{x}{249.5} \times 159.5 + \frac{5-x}{246} \times 120 = 3 \Rightarrow x = 3.56$$

$$\Rightarrow \text{Mass percentage of } \text{CuSO}_4 \cdot 5\text{H}_2\text{O} = \frac{3.56}{5} \times 100 = 71.25 \% \text{ Ans.}$$

P O A C Rule : P O A C is the simple mass conservation.



Apply the POAC on K.

moles of K in KClO_3 = moles of K in KCl

1 × moles of KClO_3 = 1 × moles of KCl

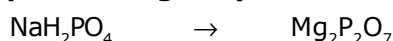
moles of KClO_3 = moles of KCl

Apply POAC on O

moles O in KClO_3 = moles of O in O_2

3 × moles of KClO_3 = 2 × moles of O_2

Ex.11 In the gravimetric determination of phosphorous, an aqueous solution of dihydrogen phosphate ion (H_2PO_4^-) is treated with a mix of ammonium & magnesium ions to precipitate magnesium ammonium phosphate $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$. This is heated and decomposed to magnesium Pyrophosphate, $\text{Mg}_2\text{P}_2\text{O}_7$, which is weighted. A solution of H_2PO_4^- yielded 1.054 gm of $\text{Mg}_2\text{P}_2\text{O}_7$, what weight of NaH_2PO_4 was present originally.



apply POAC on P

Let wt of NaH_2PO_4 = w gm

moles of P in NaH_2PO_4 = moles of P in $\text{Mg}_2\text{P}_2\text{O}_7$

$$\frac{w}{120} \times 1 = \frac{1.054}{232} \times 2$$

$$w = 1.054 \times \frac{120}{232} \times 2 = 1.09 \text{ gm Ans.}$$

Ex.12 367.5 gm KClO_3 ($M = 122.5$) when heated, How many litre of oxygen gas is produced at S.T.P.

Sol. $\text{KClO}_3 \rightarrow \text{KCl} + \text{O}_2$

Applying POAC on O

moles of O in KClO_3 = moles of O in O_2

3 × moles of KClO_3 = 2 × moles of O_2

$$3 \times \frac{367.5}{122.5} = 2 \times n$$

$$n = \frac{3}{2} \times \frac{367.5}{122.5}$$

Volume of O_2 gas at S.T.P = moles × 22.4

$$= \frac{3}{2} \times \frac{367.5}{122.5} \times 22.4 = 9 \times 11.2 = 100.8 \text{ lit Ans.}$$

SOME EXPERIMENTAL METHODS

FOR DETERMINATION OF ATOMIC MASS

Dulong's and Petit's Law :

Atomic weight \times specific heat (cal/gm°C) ≈ 6.4

Gives approximate atomic weight and is applicable for metals only. Take care of units of specific heat.

FOR MOLECULAR MASS DETERMINATION**(a) Victor Maeyer's process :** (for volatile substance)

Procedure : Some known weight of a volatile substance (w) is taken, converted to vapour and collected over water. The volume of air displaced over water is given (V) and the following expressions are used.

$$M = \frac{w}{PV}RT \quad \text{or} \quad M = \frac{w}{(P - P')V}RT$$

If aq. tension is not given

If aq. tension is P'

Aqueous tension : Pressure exerted due to water vapours at any given temperature.

This comes in picture when any gas is collected over water. Can you guess why ?

(b) Silver salt method : (for organic acids)

Basicity of an acid : No. of replaceable H^+ atoms in an acid (H bonded to more electronegative atom is acidic)

Procedure : Some known amount of silver salt (w_1 gm) is heated to obtain w_2 gm of white shining residue of silver. Then if the basicity of acid is n , molecular weight of acid would be



Ag_nA is the salt

$$\left(\frac{w_2}{108} \times \frac{1}{n}\right) \times M_{\text{salt}} = w_1 \text{ and molecular weight of acid} = M_{\text{salt}} - n(108)$$

This is one good practice application of POAC.

(c) Chloroplatinate salt method : (for organic bases)

Lewis acid : electron pair acceptor

Lewis base : electron pair donor

Procedure : Some amount of organic base is reacted with H_2PtCl_6 and forms salt known as chloroplatinate. If base is denoted by B then salt formed.

(i) with monoacidic base = $B_2H_2PtCl_6$

(ii) with diacidic base = $B_2(H_2PtCl_6)_2$

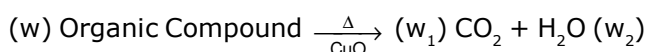
(iii) with triacidic base = $B_2(H_2PtCl_6)_3$

The known amount (w_1 gm) of salt is heated and pt residue is measured. (w_2 gm). If acidity of base is

$$'n' \text{ then } \left(\frac{w_2}{195} \times \frac{1}{n}\right) \times M_{\text{salt}} = w_1 \text{ and } M_{\text{base}} = \frac{M_{\text{salt}} - n(410)}{2}$$

● For % determination of elements in organic compounds :

- All these methods are applications of POAC
- Do not remember the formulas, derive them using the concept, its easy.

(a) Liebig's method : (Carbon and hydrogen)

$$\% \text{ of C} = \frac{w_1}{44} \times \frac{12}{w} \times 100$$

$$\% \text{ of H} = \frac{w_2}{18} \times \frac{2}{w} \times 100$$

where w_1 = wt. of CO_2 produced, w_2 = wt. of H_2O produced,
 w = wt. of organic compound taken

(b) Duma's method : (for nitrogen)

(w) Organic Compound $\xrightarrow[\text{CuO}]{\Delta} \text{N}_2 \rightarrow (\text{P, V, T given})$

use $PV = nRT$ to calculate moles of N_2 , n .

$$\therefore \% \text{ of N} = \frac{n \times 28}{w} \times 100$$

w = wt of organic compound taken

(c) Kjeldahl's method : (for nitrogen)

(w) $\text{O.C.} + \text{H}_2\text{SO}_4 \rightarrow (\text{NH}_4)_2\text{SO}_4 \xrightarrow{\text{NaOH}} \text{NH}_3 + \text{H}_2\text{SO}_4 \rightarrow (\text{molarity M and volume } (V_1) \text{ consumed given})$

$$\Rightarrow \% \text{ of N} = \frac{MV_1 \times 2 \times 14}{w} \times 100$$

where M = molarity of H_2SO_4 .

- Some N containing compounds do not give the above set of reaction as in Kjeldahl's method.

(d) Sulphur :

(w) $\text{O.C.} + \text{HNO}_3 \rightarrow \text{H}_2\text{SO}_4 + \text{BaCl}_2 \rightarrow (w_1) \text{BaSO}_4$

$$\Rightarrow \% \text{ of S} = \frac{w_1}{233} \times 1 \times \frac{32}{w} \times 100$$

where w_1 = wt. of BaSO_4 , w = wt. of organic compound

(e) Phosphorus :

$\text{O.C.} + \text{HNO}_3 \rightarrow \text{H}_3\text{PO}_4 + [\text{NH}_3 + \text{magnesia mixture ammonium molybdate}] \rightarrow \text{MgNH}_4\text{PO}_4 \xrightarrow{\Delta} \text{Mg}_2\text{P}_2\text{O}_7$

$$\% \text{ of P} = \frac{w_1}{222} \times \frac{2 \times 31}{w} \times 100$$

(f) Carius method : (Halogens)

$\text{O.C.} + \text{HNO}_3 + \text{AgNO}_3 \rightarrow \text{AgX}$

If X is Cl then colour = white

If X is Br then colour = dull yellow

If X is I then colour = bright yellow

- Flourine can't be estimated by this

$$\% \text{ of X} = \frac{w_1}{(\text{M.weight of AgX})} \times \frac{1 \times (\text{At.wt of X})}{w} \times 100$$

Ex.13 0.607 g of a silver salt of a tribasic organic acid was quantitatively reduced to 0.370 g of pure silver. Calculate the molecular weight of the acid ($\text{Ag} = 108$)

Sol. Suppose the tribasic acid is H_3A .



acid salt

0.607 g 0.37 g

Since Ag atoms are conserved, applying POAC for Ag atoms,
 moles of Ag atoms in Ag_3A = moles of Ag atoms in the product
 $3 \times \text{moles of Ag}_3\text{A} = \text{moles of Ag in the product}$

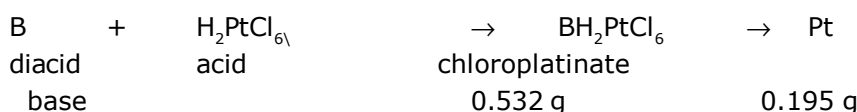
$$3 \times \frac{0.607}{\text{mol. wt. of Ag}_3\text{A}} = \frac{0.37}{108} \quad (\text{Ag} = 108)$$

mol. wt. of $\text{Ag}_3\text{A} = 531$.

\therefore mol. weight of tribasic acid (H_3A)
 = mol wt. of the salt (Ag_3A) – $3 \times \text{at. wt. of Ag}$
 $+ 3 \times \text{at. wt. of H}$
 = $531 - 324 + 3 = 210$ **Ans.**

Ex.14 0.532 g of the chloroplatinate of a diacid base on ignition left 0.195 g of residue of Pt. Calculate molecular weight of the base (Pt = 195)

Sol. Suppose the diacid base is B.



Since Pt atoms are conserved, applying POAC for Pt atoms,
 moles of Pt atoms in BH_2PtCl_6 = moles of Pt atoms in the product
 $1 \times \text{moles of BH}_2\text{PtCl}_6 = \text{moles of Pt in the product}$

$$\frac{0.532}{\text{mol. wt. of BH}_2\text{PtCl}_6} = \frac{0.195}{195}$$

\therefore mol. wt. of $\text{BH}_2\text{PtCl}_6 = 532$

From the formula BH_2PtCl_6 , we get

mol. wt. of B = mol. wt. of BH_2PtCl_6 – mol. wt. of H_2PtCl_6
 = $532 - 410 = 122$. **Ans.**

EUDIOMETRY

[For reactions involving gaseous reactants and products]

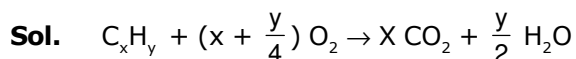
- The stoichiometric coefficient of a balanced chemical reactions also gives that ratio of volumes in which gaseous reactants are reacting and products are formed at same temperature and pressure. The volume of gases produced is often given by mentioning certain solvent which absorb contain gases.

Solvent **gas(es) absorb**

KOH	$\text{CO}_2, \text{SO}_2, \text{Cl}_2$
Ammon Cu_2Cl_2	CO
Turpentine oil	O_3
Alkaline pyrogallol	O_2
water	NH_3, HCl
$\text{CuSO}_4/\text{CaCl}_2$	H_2O

Assumption : On cooling the volume of water is negligible

Ex.15 7.5 mL of a hydrocarbon gas was exploded with excess of oxygen. On cooling, it was found to have undergone a contraction of 15 mL. If the vapour density of the hydrocarbon is 14, determine its molecular formula. (C = 12, H = 1)



7.5 ml 15
on cooling the volume contraction = 15 ml
i.e. The volume of H_2O (g) = 15 ml
V.D. of hydrocarbon = 14
Molecular wt. of C_xH_y = 28
 $12x + y = 28 \dots (1)$
From reaction

$$7.5 \frac{y}{2} = 15 \Rightarrow y = 4$$

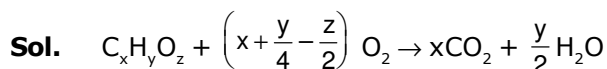
$$12x + 4 = 28$$

$$12x = 24$$

$$x = 2$$

Hence Hydrocalbon is C_2H_4 .

Ex.16 10 mL of a gaseous organic compound containing C, H and O only was mixed with 100 mL of oxygen and exploded under conditions which allowed the water formed to condense. The volume of the gas after explosion was 90 mL. On treatment with potash solution, a further contraction of 20 mL in volume was observed. Given that the vapour density of the compound is 23, deduce the molecular formula. All volume measurements were carried out under the same conditions.



10 ml
after explosion volume of gas = 90 ml
 $90 = \text{volume of CO}_2 \text{ gas} + \text{volume of unreacted O}_2$
on treatment with KOH solution volume reduces by 20 ml. This means the volume of $\text{CO}_2 = 20 \text{ ml}$
the volume of unreacted $\text{O}_2 = 70 \text{ ml}$
volume of reacted $\text{O}_2 = 30 \text{ ml}$
V.D of compound = 23
molecular wt $12x + y + 16z = 46 \quad \dots(1)$
from equation we can write

$$10\left(x + \frac{y}{4} - \frac{z}{2}\right) = 30$$

$$x + \frac{y}{4} - \frac{z}{2} = 3$$

$$4x + y - 2z = 12 \quad \dots(11)$$

$$\& \quad 10x = 20 \quad \Rightarrow \quad x = 2$$

from eq. (1) & (2)

$z = 1$ & $y = 6$ Hence C_2H_6O **Ans.**

Ex.17 A sample of coal gas contained H_2 , CH_4 and CO. 20 mL of this mixture was exploded with 80 mL of oxygen. On cooling, the volume of gases was 68 mL. There was a contraction of 10 mL. When treated with KOH. Find the composition of the original mixture.

Sol. $\text{H}_2 + \text{CH}_4 + \text{CO}$
 at $\text{H}_2 = x \text{ ml}$
 $\text{CH}_4 = y \text{ ml}$
 $\text{CO} = (20 - x - y) \text{ ml}$
 $\text{H}_2 + \text{CH}_4 + \text{CO} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$
 $x \quad y \quad 20 - x - y$
 on cooling the volume of gases = 68 ml
 $68 = \text{volume of CO}_2 + \text{unreacted O}_2$
 volume contraction due to KOH = 10 ml
 this means volume of $\text{CO}_2 = 10 \text{ ml}$
 volume of unreacted $\text{O}_2 = 58 \text{ ml}$
 volume of reacted $\text{O}_2 = 80 - 58 = 22 \text{ ml}$
 Applying POAC on C
 $y + 20 - x - y = \text{volume of CO}_2$
 $20 - x = 10 \Rightarrow x = 10$
 Applying POAC on H
 $2x + 4y = 2x \text{ moles of H}_2\text{O}$
 moles of $\text{H}_2\text{O} = x + 2y$
 Applying POAC on O
 $1 \times \text{moles of CO} + 2 \times \text{moles of O}_2$
 $= 2 \times \text{moles of CO}_2 + 1 \times \text{moles of H}_2\text{O}$
 $1 \times 20 - x - y + 2 \times 22 = 2 \times 10 + x + 2y$
 $20 - x - y + 44 = 20 + x + 2y$
 $2x + 3y = 44$
 $3y = 44 - 20 = 24$
 $y = 8 \text{ ml}$
 $x = 10 \text{ ml}$
 volume of CO = $20 - x - y \Rightarrow = 2 \text{ ml}$ **Ans.**

CONCENTRATION OF SOLUTION

Concentration of solution can be expressed in any of the following ways.

- (a) **% by wt** \Rightarrow amount of solute dissolved in 100 gm of solution
4.9% H_2SO_4 by wt.
 \Rightarrow 100 gm of solution contains 4.9 gm of H_2SO_4
- (b) **% by volume** \Rightarrow volume of solute dissolved in 100 ml of solution
x% H_2SO_4 by volume
 \Rightarrow 100 ml of solution contains x ml H_2SO_4
- (c) **% wt by volume** \Rightarrow wt. of solute present in 100 ml of solution
- (d) **% volume by wt.** \Rightarrow volume of solute present in 100 gm of solution.

CONCENTRATION TERMS

- **Molarity (M)** : No. of moles of solute present in 1000 ml of solution.

$$\text{molarity (M)} = \frac{\text{moles of solute}}{\text{volume of solution (lit)}}$$

$$M = \frac{\text{m. moles of solute}}{\text{volume of solution (ml)}}$$

MOLALITY (m)

No. of moles of solute present in 1000 gm of solvent

$$m = \frac{\text{moles of solute}}{\text{wt. of solvent in kg}}$$

$$m = \frac{\text{m. moles of solute}}{\text{wt. of solvent in gm}}$$

NORMALITY (N)

No of gm equivalents of solute present in 1000 ml of solution

$$N = \frac{\text{gm equivalents of solute}}{\text{volume of solution (lit)}} = \frac{\text{m. equivalent of solute}}{\text{volume of solution in (ml)}}$$

FORMALITY (f)

The formality is the no. of gm -formula weights of the ionic solute present in 1000 ml of solution.

$$f = \frac{\text{wt in gm}}{\text{formula wt} \times \text{volume of solution (lit)}}$$

MOLE FRACTION

The mole fraction of a particular component in a solution is defined as the number of moles of that component per mole of solution.

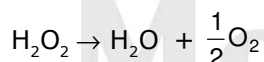
If a solution has n_A mole A & n_B mole of B.

$$\text{mole fraction of A } (X_A) = \frac{n_A}{n_A + n_B}$$

$$\text{mole fraction of B } (X_B) = \frac{n_B}{n_A + n_B}$$

$$X_A + X_B = 1$$

● **Parts per million (ppm) :** $= \frac{\text{Mass of solute}}{\text{Mass of solvent}} \times 10^6 \cong \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^6$

VOLUME STRENGTH OF H₂O₂Strength of H₂O₂ is represented as 10V, 20V, 30V etc.**20V H₂O₂** means **one litre** of this sample of H₂O₂ on decomposition gives 20 It of O₂ gas at S.T.P.Decomposition of H₂O₂ is given as

$$\begin{aligned} 1 \text{ mole } & \frac{1}{2} \times 22.4 \text{ It } O_2 \text{ at S.T.P.} \\ = 34 \text{ g} & = 11.2 \text{ It } O_2 \text{ at S.T.P.} \end{aligned}$$

- To obtain 11.2 litre O₂ at S.T.P. at least 34 gm H₂O₂ must be decomposed

- for 20 It O₂, we should decompose at least $\frac{34}{11.2} \times 20$ gm H₂O₂

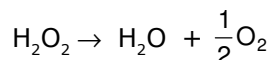
$$\therefore 1 \text{ It solution of } H_2O_2 \text{ contains } \frac{34}{11.2} \times 20 \text{ gm } H_2O_2$$

$$\therefore 1 \text{ It solution of } H_2O_2 \text{ contains } \frac{34}{11.2} \times \frac{20}{17} \text{ equivalents of } H_2O_2 \quad (E_{H_2O_2} = \frac{M}{2} = \frac{34}{2} = 17)$$

- Normality of H₂O₂ = $\frac{34}{11.2} \times \frac{20}{17} = \frac{20}{5.6}$

$$\text{Normality of H}_2\text{O}_2(\text{N}) = \frac{\text{Volume, strength of H}_2\text{O}_2}{5.6}$$

$$\therefore M_{\text{H}_2\text{O}_2} = \frac{N_{\text{H}_2\text{O}_2}}{\text{v.f.}} = \frac{N_{\text{H}_2\text{O}_2}}{2}$$

Ind Method :

From law of equivalence

gm eq. of O_2 = gm eq. of H_2O_2

$$\text{gm eq. of O}_2 = \text{moles} \times \text{n factor of O}_2 = \frac{20}{22.4} \times 4 = \frac{20}{5.6}$$

$$\text{gm. eq. of H}_2\text{O}_2 = \frac{20}{5.6}$$

and the volume of H_2O_2 is 1 lit.

this means 1 lit of H_2O_2 have $\frac{20}{5.6}$ gm eq.

i.e. Normality

$$N = \frac{20}{5.6}$$

NORMALITY OF H_2O_2

$$= \frac{\text{volume strength of H}_2\text{O}_2}{5.6}$$

$$\bullet \quad \text{Molarity of H}_2\text{O}_2(\text{M}) = \frac{\text{Volume, strength of H}_2\text{O}_2}{11.2}$$

Strength (in g/l) : Denoted by S

Strength = molarity \times mol. wt.

$$= \text{molarity} \times 34$$

strength = Normality \times Eq. weight.

$$= \text{Normality} \times 17$$

Ex.18 A bottle labeled with " $12\text{V H}_2\text{O}_2$ " contain 700 ml solution. If a student mix 300 ml water in it what is the g/litre strength & normality and volume strength of final solution.

Sol. $N = \frac{12}{5.6}$

$$\text{meq. of H}_2\text{O}_2 = \frac{12}{5.6} \times 700$$

let the normality of H_2O_2 on dilution is N

meq. before dilution = meq. after dilution

$$N \times 1000 = \frac{12}{5.6} \times 700$$

$$N = \frac{12}{5.6} \times \frac{7}{10} = 1.5$$

$$M = \frac{1.5}{2}$$

$$\text{strength gm/lit} = \frac{1.5}{2} \times 34 = 25.5$$

$$\text{volume strength} = N \times 5.6 = \frac{84}{10} = 8.4 \text{ V Ans.}$$

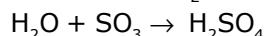
Strength of Oleum

Oleum is SO_3 dissolved in 100% H_2SO_4 . Sometimes, oleum is reported as more than 100% by weight, say $y\%$ (where $y > 100$). This means that $(y - 100)$ grams of water, when added to 100 g of given oleum sample, will combine with all the free SO_3 in the oleum to give 100% sulphuric acid.

$$\text{Hence weight \% of free SO}_3 \text{ in oleum} = \frac{80(y - 100)}{18}$$

Ex.19 Calculate the percentage of free SO_3 in an oleum (considered as a solution of SO_3 in H_2SO_4) that is labelled ' $109\% \text{H}_2\text{SO}_4$ '.

Sol. ' $109\% \text{H}_2\text{SO}_4$ ' refers to the total mass of pure H_2SO_4 , i.e., 109 g that will be formed when 100 g of oleum is diluted by 9 g of H_2O which (H_2O) combines with all the free SO_3 present in oleum to form H_2SO_4



1 mole of H_2O combines with 1 mole of SO_3

or 18 g of H_2O combines with 80 g of SO_3

or 9 g of H_2O combines with 40 g of SO_3 .

Thus, 100 g of oleum contains 40 g of SO_3 or oleum contains 40% of free SO_3 .

Ex.20 A 62% by mass of an aqueous solution of acid has specific gravity 1.8. This solution is diluted such that the specific gravity of solution became 1.2. Find the % by wt of acid in new solution.

Sol. $\text{density} = \frac{\text{mass}}{\text{volume}}$

$$1.8 = \frac{100}{\text{volume of sol}^n} \Rightarrow \text{volume of solution} = \frac{100}{1.8}$$

Let x gm water is added in solution

then $d = \frac{\text{mass}}{\text{volume}}$

$$1.2 = \frac{100 + x}{\frac{100}{1.8} + x}$$

$$1.2 \times \frac{100}{1.8} \times 1.2x = 100 + x$$

$$\frac{200}{3} + 1.2x = 100 + x$$

$$0.2x = 100 - \frac{200}{3} = \frac{100}{3}$$

$$x = \frac{100}{3 \times 0.2} = \frac{1000}{6} = \frac{500}{3} = 166.67$$

mass of new solution = $100 + 166.67 = 266.67$

266.67 gm solution contains 62 gm of acid

$$\% \text{ by mass} = \frac{62}{266.67} \times 100 = 23.24 \%$$

RELATION SHIP BETWEEN MOLARITY, MOLALITY & DENSITY OF SOLUTION

Let the molarity of solution be 'M', molality be 'm' and the density of solution be d gm/ml.

Molarity implies that there are M moles of solute in 1000 ml of solution
wt of solution = density × volume

$$= 1000 d \text{ gm}$$

$$\text{wt of solute} = MM_1$$

where M_1 is the molecular wt of solute

$$\text{wt of solvent} = (1000d - MM_1) \text{ gm}$$

(1000d - MM_1) gm of solvent contains M moles of solute

$$1000 \text{ gm of solvent have} = \frac{M}{1000d - MM_1} \times 1000 \text{ mole} = \text{Molality}$$

$$\text{no. of moles of solute present in 1000 gm of solvent} = \frac{1000 \times M}{1000d - MM_1} = \text{Molality}$$

$$\text{on simplyfying } d = M \left[\frac{1}{m} + \frac{M_1}{1000} \right]$$

RELATION SHIP BETWEEN MOLALITY & MOLE FRACTION

consider a binary solution consisting of two components A (Solute) and B (Solvent).

Let x_A & x_B are the mole fraction of A & B respectively.

$$x_A = \frac{n_A}{n_A + n_B}, \quad x_B = \frac{n_B}{n_A + n_B}$$

If molality of solution be m then

$$m = \frac{n_A}{\text{mass of solvent}} \times 1000 = \frac{n_A}{n_B \times M_B} \times 1000$$

where M_B is the molecular wt of the solvent B

$$m = \frac{x_A}{x_B} \times \frac{1000}{M_B}$$

$$\text{molality} = \frac{\text{mole fraction of A}}{\text{mole fraction of B}} \times \frac{1000}{M_B}$$

$$m = \frac{\text{mole fraction of solute}}{\text{mole fraction of solvent}} \times \frac{1000}{\text{molecular wt. of solvent}}$$

Ex.21 An aqueous solution is 1.33 molal in methanol. Determine the mole fraction of methanol & H_2O

Sol.
$$\text{molality} = \frac{\text{mole fraction of solute}}{\text{mole fraction of solvent} \times \text{mol.wt of solvent}} \times 1000$$

$$1.33 = \frac{x_A}{x_B \times M_B} \times 1000$$

$$\frac{1.33 \times 18}{1000} = \frac{x_A}{x_B}$$

$$\frac{23.94}{1000} = \frac{x_A}{x_B}$$

$$\Rightarrow x_A = 0.02394 x_B$$

$$x_A + x_B = 1$$

$$\Rightarrow 1.02394 x_B = 1$$

$$x_B = \frac{1}{1.02394} = 0.98$$

$$x_A = 0.02 \text{ Ans.}$$

Second Method : Let wt of solvent = 1000 gm molality = 1.33
= moles of solute

mole fraction of solute = $\frac{\text{moles of solute}}{\text{moles of solute} + \text{moles of solvent}}$

$$= \frac{m}{m + \frac{1000}{18}} = \frac{1.33}{1.33 + 1000/18}$$

mole fraction of solute = 0.02

mole fraction of solvent = $1 - 0.02 = 0.98$

Ex.22 The density of 3 M solution of sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$) is 1.25 g/mL. Calculate

(i) amount of sodium thiosulphate

(ii) mole fraction of sodium thiosulphate

(iii) molality of Na^+ and $\text{S}_2\text{O}_3^{2-}$ ions

Sol. (i) Let us consider one litre of sodium thiosulphate solution.

$$\therefore \text{wt. of the solution} = \text{density} \times \text{volume (mL)}$$

$$= 1.25 \times 1000 = 1250 \text{ g.}$$

$$\text{wt. of } \text{Na}_2\text{S}_2\text{O}_3 \text{ present in 1 L of the solution}$$

$$= \text{molarity} \times \text{mol. wt.}$$

$$= 3 \times 158 = 474 \text{ g. Ans.}$$

$$\text{wt. \% of } \text{Na}_2\text{S}_2\text{O}_3 = \frac{474}{1250} \times 100 = 37.92\%$$

(ii) Wt. of solute ($\text{Na}_2\text{S}_2\text{O}_3$) = 474 g.

$$\text{Moles of solute} = \frac{474}{158} = 3 \text{ Ans.}$$

$$\text{Wt. of solvent (H}_2\text{O)} = 1250 - 474 = 776 \text{ g}$$

$$\text{Moles of solvent} = \frac{776}{18} = 43.11$$

$$\therefore \text{mole fraction of } \text{Na}_2\text{S}_2\text{O}_3 = \frac{3}{3 + 43.11} = 0.063$$

$$\text{(iii) Molality of } \text{Na}_2\text{S}_2\text{O}_3 = \frac{\text{moles of } \text{Na}_2\text{S}_2\text{O}_3}{\text{wt. of solvent in grams}} \times 1000 = \frac{3}{776} \times 1000 = 3.865$$

\therefore 1 mole of $\text{Na}_2\text{S}_2\text{O}_3$ contains 2 moles of Na^+ ions and 1 mole of $\text{S}_2\text{O}_3^{2-}$ ions.

\therefore molality of $\text{Na}^+ = 2 \times 3.865 = 7.73 \text{ m}$

Molality of $\text{S}_2\text{O}_3^{2-} = 3.865 \text{ m. Ans.}$