MOLE CONCEPT

1. CLASSIFICATION OF UNIVERSE

(1) Matter
(2) Energy

(1) MATTER

The thing which occupy space and having mass which is feel by our five senses is called as matter.

ꝏ **2 Types**

(I) Physical classification
(II) Chemical classification

(I) Physical Classification

It is based on physical state under ordinary conditions of temperature and pressure, matter is classified into the following three types :

(a) Solid
(b) Liquid
(c) Gas

(a) Solid

A substance is said to be solid if it possesses a definite volume and a definite shape

Ex. sugar, iron, gold, wood etc.

(b) Liquid

A substance is said to be liquid if it possesses a definite volume but not definite shape. They take up the shape of the vessel in which they are put.

Ex. water, milk, oil, mercury, alcohol etc.

(c) Gas

A substance is said to be gas if it neither possesses a definite volume nor a definite shape. This is because they fill up the whole vessel in which they are put.

Ex. hydrogen(H_2), oxygen(O_2), carbon dioxide(CO_2), etc.'

(II) Chemical Classification

ꝏ **2 Types**

(A) Pure Substance
(B) Mixture

(A) Pure Substance

A material containing only one type of substance. Pure Substance can not be seperated into simpler substance by physical method.

Ex. Element = Na, Mg, Ca .... etc.
Compound = HCl, H_2O, CO_2, HNO_3 .... etc.

ꝏ **2 Types**

(a) Element
(b) Compound

(a) **Element :** The pure substance containing only one kind of atoms .

3 Types (depend on physical and chemical property)

(a') Metal
(b') Non-metal
(c') Metalloids

(b) Compound

It is defined as pure substance containing more than one kind of atoms which are combined together in a fixed ratio by weight and which can be decomposed into simpler substance by the suitable chemical method. The properties of a compound are diffrent from those of its components.

Ex. H_2O, HCl, HNO_3 .... etc.

2 : 16

1 : 8 **by wt.**

- **2 Types**
  - (a') Organic Compound
  - (b') Inorganic Compound

(B) Mixture

A material which contain more than one type of substances and which is mixed any ratio by wt.is called as mixture.

- The property of the mixture is the property of its components
- The mixture is seperated by simple physical method.
- **2 Types**

(a') Homogeneous mixture

(b') Hetrogeneous mixture

(a') Homogeneous Mixture

The mixture, in which all the components are present in **uniform** is called as homogeneous mixture.

Ex. Water + Salt, Water + Sugar, Water + alcohol,

(b') Hetrogeneous Mixture

The mixture in which all the components are present in **nonuniform** is called as Hetrogeneous mixture.

Ex. Water + Sand, Water + Oil,

INTRODUCTION

There are a large number of objects around us which we can see and feel.

Anything that Occupies Space and has Mass is called Matter.

It was **John Dalton** who firstly developed a theory on the structure of matter, later on which is known as **Dalton's atomic theory.**

1. DALTON'S ATOMIC THEORY

1. Matter is made up of very small undivisible particle called atoms.
2. All the atoms of a given element is identical in all respect i.e. mass, shape, size, etc.
3. Atoms cannot be created nor destroyed by any chemical process.
4. Atoms of different elements are different in nature.

2. THE LAW OF CHEMICAL COMBINATION

- **Atoine Lavoisier, John Dalton** and other scientists formulate certain law concerning the composition of matter and chemical reactions. These laws are known as the law of chemical combination.

3. THE LAW OF CONSERVATION OF MASS

It is given by **Lavoisier.**

In a chemical change total mass remains conserved.

i.e. mass before reaction is always equal to mass after reaction.

Ex.

	$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow$		H_2O(●)
Before reaction initialy	1 mole	$\frac{1}{2}$ mole	
After the reaction	0	0	1 mole

mass before reaction = mass of 1 mole $H_2(g) + \frac{1}{2}$ mole $O_2(g)$

$= 2 + 16 = 18$ g

mass after reaction = mass of 1 mole water = 18 g

4. LAW OF CONSTANT OR DEFINITE PROPORTION

It is given by **Proust.**

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

Ex. In water (H_2O), Hydrogen and Oxygen combine in 2 : 1 molar ratio, the ratio remains constant whether it is tap water, river water or sea water or produced by any chemical reaction.

Ex. 1.80 g of a certain metal burnt in oxygen gave 3.0 g of its oxide. 1.50 g of the same metal heated in steam gave 2.50 g of its oxide. Show that these results illustrate the law of constant proportion.

Sol. In the first sample of the oxide,

wt. of metal = 1.80 g,

wt. of oxygen = (3.0 – 1.80) g = 1.2 g

$$\therefore \quad \frac{\text{wt. of metal}}{\text{wt. of oxygen}} = \frac{1.80\,\text{g}}{1.2\,\text{g}} = 1.5$$

In the second sample of the oxide,

wt. of metal = 1.50 g,

wt. of oxygen = (2.50 – 1.50) g = 1 g

$$\therefore \quad \frac{\text{wt. of metal}}{\text{wt. of oxygen}} = \frac{1.50\,\text{g}}{1\,\text{g}} = 1.5$$

Thus, in both samples of the oxide the proportions of the weights of the metal and oxygen are fixed. Hence, the results follows the law of constant proportion.

5. THE LAW OF MULTIPLE PROPORTION

It is given by **Dalton.**

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

Note : Simple ratio here means the ratio between small natural numbers, such as 1 : 1, 1 : 2, 1 : 3, Later on this simple ratio becomes the valency and then oxidation state of the element.

Ex : Carbon and Oxygen when combine, can form two oxides viz CO (carbonmonoxide), CO_2 (Carbondioxides)

In CO, 12 g carbon combined with 16 g of oxygen.

In CO_2, 12 g carbon combined with 32 g of oxygen.

Thus, we can see the mass of oxygen which combine with a constant mass of carbon (12 g) bear simple ratio of 16 : 32 or 1 : 2.

Ex. Carbon is found to form two oxides, which contain 42.9% and 27.3% of carbon respectively. Show that these figures illustrate the law of multiple proportions.

Sol. **Step-1**

To calculate the percentage composition of carbon and oxygen in each of the two oxides.

	First oxide	Second oxide	
Carbon	42.9 %	27.3 %	(Given)
Oxygen (by difference)	57.1%	72.7 %	

Step-2

To calculate the masses of carbon which combine with a fixed mass i.e., one part by mass of oxygen in each of the two oxides.

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

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

In the second oxide. 72.7 parts by mass of oxygen combine with carbon = 27.3 parts.

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

Step-3.

To compare the masses of carbon which combine with the same mass of oxygen in both the oxides.

The ratio of the masses of carbon that combine with the same mass of oxygen (1 part) is .

0.751 : 0.376 or 2 : 1

Since this is simple whole number ratio, so the above data illustrate the law of multiple proportions.

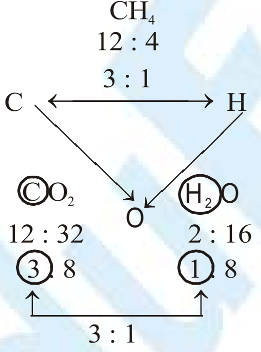
6. LAW OF RECIPROCAL PROPORTION (OR LAW OF EQUIVALENT WT.)

- It is given by **Richter**.

Statement

The ratio of the weights of two elements A and B which combine seperately with a fixed weight of the third element C is either the **same or simple ratio** of the weights in which A and B combine directly with each other.

Ex.



- **Special Note :** This law is also called as law of equivalent wt. due to each element combined in their equivalent wt. ratio.

$$E = \frac{M_w / \text{At.wt.}}{\text{V.F.}}$$

- **For Ions**

V.F. = Total no. of positive charge

or V.F. = Total no. of negative charge

EXAMPLE BASED ON LAW OF RECIPROCAL PROPORTION

Ex. Ammonia contains 82.35% of nitrogen and 17.65% of hydrogen. Water contains 88.90% of oxygen and 11.10% of hydrogen. Nitrogen trioxide contains 63.15% of oxygen and 36.85% of nitrogen. Show that these data illustrate the law of reciprocal proportions.

Sol. In NH_3, 17.65g of H combine with N = 82.35g

$\therefore$ 1 g of H combine with $N = \frac{82.35}{17.65}$ g = 4.67 g

In H_2O, 11.10 g of H combine with O = 88.90 g

$\therefore$ 1 g of H combine with $O = \frac{88.90}{11.10}$ g = 8.01 g

$\therefore$ Ratio of the weights of N and O which combine with fixed weight (=1g) of H

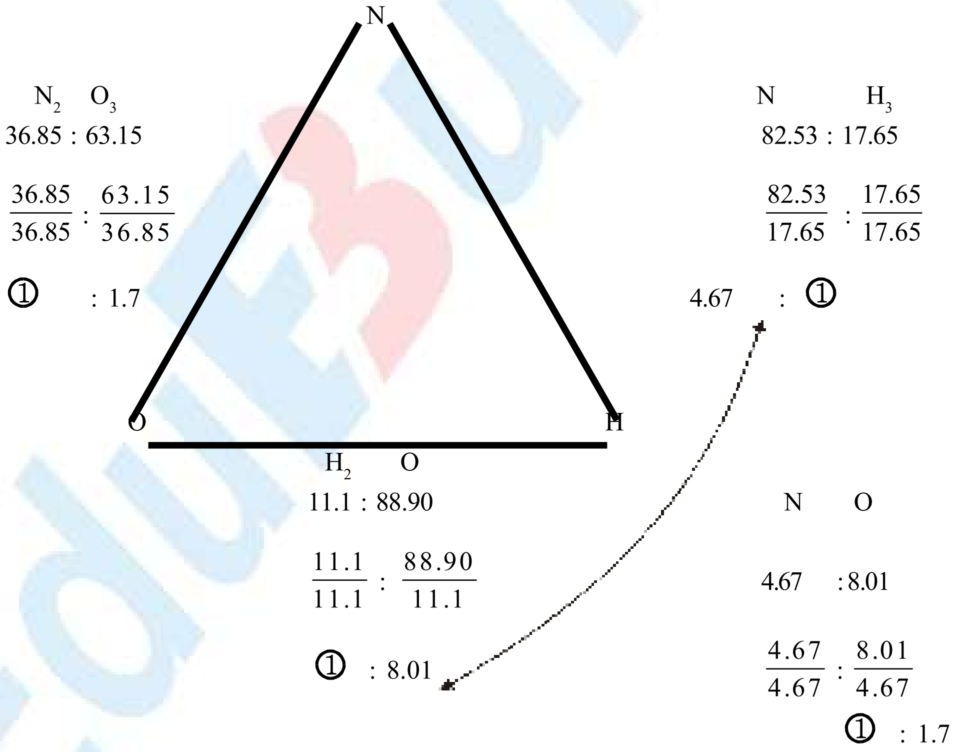
= 4.67 : 8.01 = 1 : 1.7

In N_2O_3, ratio of weights of N and O which combine with each other = 36.85 : 63.15

= 1 : 1.7

Thus the two ratios are the same. Hence it illustrates the law of reciprocal proportions.

Other Method



Thus the two ratios are the same. Hence it illustrates the law of reciprocal proportions.

7. RELATIVE ATOMIC MASS

One of the most important concept come out from Dalton's atomic theory was that of relative atomic mass or relative atomic weight. This is done by expressing mass of one atom with respect to a fixed standard. Dalton used hydrogen as the standard (H = 1). Later on oxygen (O = 16) replaced hydrogen as the reference. Therefore relative atomic mass is given as

$$\text{Relative atomic mass (R.A.M.)} = \frac{\text{Mass of one atom of an element}}{\text{mass of one hydrogen atoms}} = \frac{\text{Mass of one atom of an element}}{\frac{1}{16} \times \text{mass of one Oxygen atom}}$$

- The present standard unit which was adopted internationally in 1961, is based on the mass of one carbon-12 atom.

8. ATOMIC MASS UNIT (or amu)

The atomic mass unit (amu) is equal to one twelvth $\left(\frac{1}{12}\right)$ the mass of one atom of carbon-12 isotope.

$$\therefore \quad 1\text{ amu} = \frac{1}{12} \times \text{mass of one C-12 atom} = 1.66 \times 10^{-24}\text{ g or } 1.66 \times 10^{-27}\text{ kg}$$

- **One amu is also called One Dalton (Da).**

Now the relative atomic mass is given as

$$\text{Relative atomic mass} = \frac{\text{mass of one atom of the element}}{\frac{1}{12} \times \text{mass of one C} - 12\text{ atom}}$$

$$\text{R.A.M.} = \frac{\text{Atomic mass}}{1\text{ amu}}$$

Atomic mass = R.A.M. × 1 amu

$$\text{Relative molecular mass} = \frac{\text{mass of one molecule of the substance}}{\frac{1}{12} \times \text{mass of one C} - 12\text{ atom}}$$

$\therefore$ Molecular mass = Relative molecular mass × 1 amu

Note : Relative atomic mass is nothing but the number of nucleons present in the atom.

Ex. Find the relative atomic mass of 'O' atom and its atomic mass.

Sol. The number of nucleons present in 'O' atom is 16.

$\therefore$ relative atomic mass of 'O' atom = 16.

Atomic mass = R.A.M × 1 amu = 16 × 1 amu = 16 amu

9. MOLE

A mole is the amount of a substance that contains as many entities (atoms, molecules or other particles) as there are atoms exactly in 0.012 kg (or 12 g) of the carbon - 12 isotope.

From mass spectrometer we found that there are 6.023×10^{23} atoms are present in 12 g of C-12 isotope.

The number of entities in 1 mol is so important that it is given a separate name and symbol known as Avogadro constant denoted by N_A.

i.e. on the whole we can say that 1 mole is the collection of 6.02×10^{23} entities. Here entities may represent atoms, ions, molecules or even pens, chair, paper etc.

1 mole of atom is also termed as 1 g – atom
1 mole of ions is also termed as 1 g – ion
1 mole of molecule is also termed as 1 g – molecule

Methods of Calculations of Mole

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

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

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

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

use $n = \dfrac{PV}{RT}$

where R = 0.0821 lit-atm/mol-K (when P is in atmosphere and V is in litre)

1 mole of any gas at STP occupies 22.4 litre.

Ex. Chlorophyll the green colouring material of plants contains 3.68 % of magnesium by mass. Calculate the number of magnesium atom in 5.00 g of the complex.

Sol. Mass of magnesium in 5.0 g of complex $= \dfrac{3.68}{100} \times 5.00 = 0.184$ g

Atomic mass of magnesium = 24

24 g of magnesium contain $= 6.023 \times 10^{23}$ atoms

$\therefore$ 0.184 g of magnesium would contain $= \dfrac{6.023 \times 10^{23}}{24} \times 0.184 = 4.617 \times 10^{21}$ atom

Therefore, 5.00 g of the given complex would contain 4.617×10^{21} atoms of magnesium.

10. GRAM ATOMIC MASS

The atomic mass of an element expressed in gram is called gram atomic mass of the element.

or

It is also defined as mass of 6.02×10^{23} atoms.

or

It is also defined as the mass of one mole atoms.

For Example for Oxygen Atom

Atomic mass of 'O' atom = mass of one 'O' atom = 16 amu

gram atomic mass = mass of 6.02×10^{23} 'O' atoms

$= 16 \text{ amu} \times 6.02 \times 10^{23}$

$= 16 \times 1.66 \times 10^{-24} \text{ g} \times 6.02 \times 10^{23} = 16 \text{ g}$

(✈ $1.66 \times 10^{-24} \times 6.02 \times 10^{23} \simeq 1$)

☞ Now see the table given below and understand the definition given before.

Element	R.A.M. (Relative Atomic Mass)	Atomic mass (mass of one atom)	Gram Atomic mass/weight
N	14	14 amu	14 gm
He	4	4 amu	4 gm
C	12	12 amu	12 gm

Average atomic weight = Σ % of isotopes X molar mass of isotopes.

11. GRAM MOLECULAR MASS

The molecular mass of a substance expressed in gram is called the gram-molecular mass of the substance.

or

It is also defined as mass of 6.02×10^{23} molecules

or

It is also defined as the mass of one mole molecules.

For Example for 'O_2' Molecule

Molecular mass of '$\mathbf{O_2}$' molecule = mass of one '$\mathbf{O_2}$' molecule
= 2 × mass of one 'O' atom
= 2 × 16 amu
= 32 amu

gram molecular mass = mass of 6.02×10^{23} '$\mathbf{O_2}$' molecules
$= 32 \text{ amu} \times 6.02 \times 10^{23}$
$= 32 \times 1.66 \times 10^{-24}\text{g} \times 6.02 \times 10^{23}$
= 32 gm

Average molecule wt. $= \dfrac{\Sigma n_i M_i}{\Sigma n_i}$ where n_i = no. of moles of compound, m_i = molecular mass of compound

Ex. The molecular mass of H_2SO_4 is 98 amu. Calculate the number of moles of each element in 294 g of H_2SO_4.

Sol. Gram molecular mass of H_2SO_4 = 98 gm

$$\text{moles of } H_2SO_4 = \frac{294}{98} = 3 \text{ moles}$$

H_2SO_4	H	S	O
One molecule	2 atom	one atom	4 atom
$1 \times N_A$	$2 \times N_A$ atoms	$1 \times N_A$ atoms	$4 \times N_A$ atoms
∴ one mole	2 mole	one mole	4 mole
∴ **3 mole**	**6 mole**	**3 mole**	**12 mole**

12. GAY-LUSSAC'S LAW OF COMBINING VOLUME

According to him elements combine in a simple ratio of atoms, gases combine in a simple ratio of their volumes provided all measurements should be done in the same temperature and pressure

$$\underset{1\ \text{vol}}{H_2\,(g)} + \underset{1\ \text{vol}}{Cl_2\,(g)} \longrightarrow \underset{2\ \text{vol}}{2HCl}$$

13. AVOGADRO'S HYPOTHESIS

Equal volume of all gases have equal number of molecules (not atoms) at same temperature and pressures conditions.

S.T.P. (Standard Temperature and Pressure)

At S.T.P. condition :

temperature = 0°C or 273 K
pressure = 1 atm = 760 mm of Hg

and volume of one mole of gas at STP is found to be experimentaly equal to 22.4 litres which is known as molar volume.

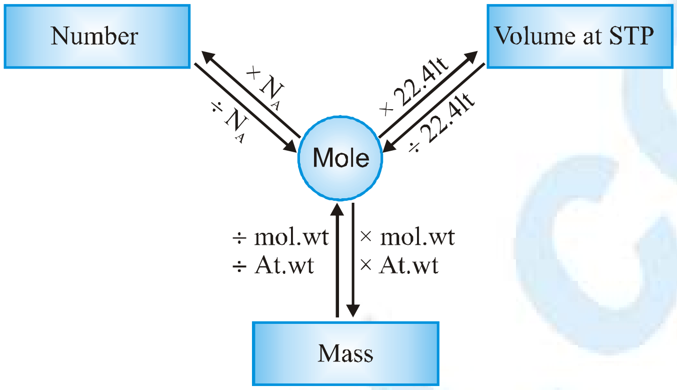
Note : Measuring the volume is equivalent to counting the number of molecules of the gas.

Ex. Calculate the volume in litres of 20 g hydrogen gas at STP.

Sol. No. of moles of hydrogen gas $= \dfrac{\text{Mass}}{\text{Molecular mass}} = \dfrac{20\text{ gm}}{2\text{ gm}} = 10$ mol

volume of hydrogen gas at STP = 10 × 22.4 lt.

14. Y-MAP



15. PERCENTAGE COMPOSITION AND MOLECULAR FORMULA

Here we are going to find out the percentage of each element in the compound by knowing the molecular formula of compound.

We known that according to law of definite proportions any sample of a pure compound always possess constant ratio with their combining elements.

Ex.

Every molecule of ammonia always has formula NH_3 irrespective of method of preparation or sources. i.e. 1 mole of ammonia always contains 1 mol of N and 3 mole of H. In other wards 17 g of NH_3 always contains 14 g of N and 3 g of H. Now find out % of each element in the compound.

Mass % of N in $NH_3 = \dfrac{\text{Mass of N in 1 mol } NH_3}{\text{Mass of 1 mol of } NH_3} \times 100 = \dfrac{14\text{ g}}{17} \times 100 = 82.35\ \%$

Mass % of H in $NH_3 = \dfrac{\text{Mass of H is 1 mol } NH_3}{\text{Mass of 1 mol of } NH_3} \times 100 = \dfrac{3}{17} \times 100 = 17.65\%$

16. EMPIRICAL AND MOLECULAR FORMULA

We have just seen that knowing the molecular formula of the compound we can calculate percentage composition of the elements. Conversely if we know the percentage composition of the elements initially, we can calculate the relative number of atoms of each element in the molecules of the compound. This gives as the empirical formula of the compound. Further if the molecular mass is known then the molecular formula can be easily determined.

Thus, the empirical formula of a compound is a chemical formula showing the relative number of atoms in the simplest ratio, the molecular formula gives the actual number of atoms of each element in a molecule.

i.e. **Empirical Formula :** Formula depicting constituent atom in their simplest ratio.

Molecular Formula : Formula depicting actual number of atom in onemolecule of the compound.

The molecular formula is generally an integral multiple of the empirical formula.

i.e. molecular formula = empirical formula × n

where $n = \dfrac{\text{molecular formula mass}}{\text{empirical formula mass}}$

Ex. Acetylene and benzene both have the empirical formula CH. The molecular masses of acetylene and benzene are 26 and 78 respectively. Deduce their molecular formulae.

Sol. ✈ Empirical Formula is CH

Step-1 The empirical formula of the compound is CH

∴ Empirical formula mass = (1 × 12) + 1 = 13.

Molecular mass = 26

Step-2 To calculate the value of 'n'

$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}} = \frac{26}{13} = 2$$

Step-3 To calculate the molecular formula of the compound.

Molecular formula = n × (Empirical formula of the compound)

$$= 2 \times CH = C_2H_2$$

Thus the molecular formula is C_2H_2

Similarly for benzene

To calculate the value of 'n'

$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}} = \frac{78}{13} = 6$$

thus the molecular formula is 6 × CH = C_6H_6

Ex. An organic substance containing carbon, hydrogen and oxygen gave the following percentage composition.

C = 40.687 % ; H = 5.085 % and O = 54.228 %

The molecular weight of the compound is 118. Calculate the molecular formula of the compound.

Sol. **Step-1**

To calculate the empirical formula of the compound.

Element	Symbol	Percentage of element	At. mass of element	Relative no. of atoms = $\frac{\text{Percentage}}{\text{At.mass}}$	Simplest atomic ratio	Simplest whole no. atomic ratio
Carbon	C	40.687	12	$\frac{40.687}{12} = 3.390$	$\frac{3.390}{3.389} = 1$	2
Hydrogen	H	5.085	1	$\frac{5.085}{1} = 5.035$	$\frac{5.085}{3.389} = 1.5$	3
Oxygen	O	54.228	16	$\frac{54.228}{16} = 3.389$	$\frac{3.389}{3.389} = 1$	2

∴ Empirical formula is $C_2H_3O_2$

Step - 2

To calculate the empirical formula mass.

The empirical formula of the compound is $C_2H_3O_2$.

∴ Empirical formula mass

= (2 × 12) + (3 × 1) + (2 × 16) = 59.

- **Step - 3**

To calculate the value of 'n'

$$n = \frac{\text{molecular mass}}{\text{Empirical formula mass}} = \frac{118}{59} = 2$$

- **Step - 4**

To calculate the molecular formula of the salt

$$\text{Molecular formula} = n \times (\text{Empirical formula})$$

$$= 2 \times C_2H_3O_2 = C_4H_6O_4$$

Thus the molecular formula is $C_4H_6O_4$.

17. DENSITY

It is of two type.

1. Absolute density **2.** Relative density

For Liquid and Solids

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

$$\text{Relative density or specific gravity} = \frac{\text{density of the substance}}{\text{density of water at } 4°\text{C}}$$

For Gases

$$\text{Absolute density (mass / volume)} = \frac{PM}{RT}$$

where P is pressure of gas, M = mol. wt. of gas, R is the gas constant, T is the temperature.

18. RELATIVE DENSITY OR VAPOUR DENSITY

Vapour density is defined as the density of the gas with respect to hydrogen gas at the same temperature and pressure.

$$\text{Vapour density} = \frac{d_{gas}}{d_{H_2}} = \frac{PM_{gas/RT}}{PM_{H_2/RT}}$$

$$\text{V.D.} = \frac{M_{gas}}{M_{H_2}} = \frac{M_{gas}}{2} \Rightarrow \boxed{M_{gas} = 2\,\text{V.D.}}$$

19. CHEMICAL EQUATION

All chemical reaction are represented by chemical equations by using formule of reactant and products. Qualitatively a chemical equation simply describes what the reactants and products are. However, a balanced chemical equation gives us a lot of quantitative information mainly the molar ratio in which reactants combine and the molar ratio in which products are formed.

Ex.

When potassium chlorate ($KClO_3$) is heated it gives potassium chloride (KCl) and oxygen (O_2).

$$KClO_3 \xrightarrow{\Delta} KCl + O_2 \text{ (unbalanced chemical equation)}$$

$$2KClO_3 \xrightarrow{\Delta} 2\,KCl + 3\,O_2 \text{ (balanced chemical equation)}$$

- Remember a balanced chemical equation is one which contains an equal number atoms of each element on both sides of equation.

20. GRAVIMETRIC ANALYSIS

Once we get a balanced chemical equation then we can interpret a chemical equation by following ways

1. Mass - mass analysis
2. Mass - volume analysis
3. Mole - mole analysis
4. Vol - Vol analysis (separately discussed as eudiometry or gas analysis)

Now you can understand the above analysis by following example

1. Mass - Mass Analysis

Consider the reaction $2\,KClO_3 \longrightarrow 2KCl + 3O_2$ According to stoichiometry of the reaction

mass-mass ratio : $2\times122.5 : 2\times74.5 : 3\times32$

or $$\frac{\text{Mass of } KClO_3}{\text{Mass of } KCl} = \frac{2\times122.5}{2\times74.5} \quad \Bigg| \quad \frac{\text{Mass of } KClO_3}{\text{Mass of } O_2} = \frac{2\times122.5}{3\times32}$$

Ex. Calculate the weight of iron which will be converted into its oxide by the action of 36 g of steam. (Given : $3Fe + 4H_2O \longrightarrow Fe_3O_4 + H_2$)

Sol. Mole ratio of reaction suggests,

$$\frac{\text{Mole of Fe}}{\text{Mole of } H_2O} = \frac{3}{4}$$

$$\therefore \text{ Mole of Fe} = \frac{3}{4} \times \text{ mol of } H_2O$$

$$= \frac{3}{4}\times\frac{36}{18} = \frac{3}{2}$$

$$\text{wt. of Fe} = \frac{3}{2} \times 56 = 84 \text{ g}$$

Ex. In a gravimetric determination of P of an aqueous solution of dihydrogen phosphate in $H_2PO_4^-$ is treated with a mixture of ammonium and magnesium ions to precipitate magnesium ammonium phosphate, $Mg(NH_4)PO_4.6H_2O$. This is heated and decomposed to magnesium pyrophosphate, $Mg_2P_2O_7$. A solution of $H_2PO_4^-$ yielded 2.054 g of ($Mg_2P_2O_7$) which is weighed. What weight of NaH_2PO_4 was present originally?

Sol. $NaH_2PO_4 + Mg^{2+} + NH_4^+ \longrightarrow Mg(NH_4)PO_4.6H_2O \xrightarrow{\Delta} Mg_2P_2O_7$

As P atoms are conserved, applying POAC for P atoms, moles of P in NaH_2PO_4 = Moles of P in $Mg_2P_2O_7$

$\Rightarrow$ $1 \times$ Moles of $NaH_2PO_4 = 2 \times$ Moles of $Mg_2P_2O_7$

$$\therefore \quad \frac{W_{NaH_2PO_4}}{M_{NaH_2PO_4}} = 2 \times \frac{W_{Mg_2P_2O_7}}{M_{Mg_2P_2O_7}} \Rightarrow \frac{W_{NaH_2PO_4}}{120} = 2 \times \frac{2.054}{222}$$

$$\therefore \quad W_{NaH_2PO_4} = 2.22 \text{ g}$$

Ex. A solid mixture weighing 5.00 g containing lead nitrate and sodium nitrate was heated below 600°C until the mass of the residue was constant. If the loss of mass is 30 %, find the mass of lead nitrate and sodium nitrate in mixture.

(At. wt. of Pb = 207, Na = 23, N = 14, O = 16)

Sol. $2Pb(NO_3)_2 \xrightarrow{\Delta} 2PbO + 4NO_2\uparrow + O_2\uparrow$

$2 \times 331 \quad\quad 2 \times 223$

$2NaNO_3 \xrightarrow{\Delta} 2NaNO_2 + O_2\uparrow$

$2 \times 85 \quad 2 \times 69$

Let, wt. of $Pb(NO_3)_2$ in mixture = x

wt. of $NaNO_3 = (5 - x)$ g

662 g of $Pb(NO_3)_2$ will give residue = 446

$\therefore$ xg of $Pb(NO_3)_3$ will give residue $= \frac{446}{662} \times (x) = 0.674x$ g

170 g of $NaNO_3$ give residue = 138 g

$\therefore$ (5 – x), g $NaNO_3$ will give residue $= \frac{138}{170} \times (5 - x) = 0.812 \times (5 - x)$

Actual wt. of residue obtained $= \left(5 - 5 \times \frac{30}{100}\right) = 3.5$ g

$\therefore$ $0.674x + 0.812 \times (5 - x) = 3.5 \quad \Rightarrow \quad 0.138\,x = 0.56$

$\Rightarrow$ x = 4.05 g = wt. of $Pb(NO_3)_2$

$\therefore$ wt. of $NaNO_3$ in the mixture = (5 – 4.05) = 0.95 g

Ex. 3.0 g an impure sample of sodium sulphate dissolved in water was treated with excess of barium chloride solution when 1.74 g of **$BaSO_4$** were obtained as dry precipitate. Calculate the percentage purity of sample.

Sol. $Na_2SO_4 + BaCl_2 \longrightarrow BaSO_4 + 2NaCl$

142g $\quad\quad$ 223g

223 g of $BaSO_4$ are produced from 142 g of Na_2SO_4

$\therefore$ 1.74 g of $BaSO_4$ would be produced by $= \frac{142}{233} \times 1.74 = 1.06$ g of Na_2SO_4

% purity of $Na_2SO_4 = \frac{1.06}{3.0} \times 100 = 35.33\ \%$

2. Mass - Volume Analysis

Now again consider decomposition of $KClO_3$

$$2\,KClO_3 \longrightarrow 2KCl + 3\,O_2$$

mass volume ratio : 2×122.5 g : 2×74.5 g : 3×22.4 L at STP

we can use two relation for volume of oxygen

$$\frac{\text{Mass of } KClO_3}{\text{volume of } O_2 \text{ at STP}} = \frac{2 \times 122.5\,g}{3 \times 22.4\,L} \quad ....(i)$$

and $$\frac{\text{Mass of KCl}}{\text{volume of } O_2 \text{ at STP}} = \frac{2 \times 74.5\,g}{3 \times 22.4\,L} \quad ......(ii)$$

Ex. How much marble of 90.5 % purity would be required to prepare 10 litres of CO_2 at STP when the marble is acted upon by dilute HCl ?

Sol. $CaCO_3 + 2HCl \longrightarrow CaCl_2 + H_2O + CO_2$

100 g 22.4litre

22.4 L of CO_2 at STP will be obtained from 100 g of $CaCO_3$

$\therefore$ 10 L of CO_2 at STP will be obtained from pure $CaCO_3 = \frac{100}{22.4} \times 10 = 44.64$ g

$\therefore$ Impure marble required = $\frac{100}{90.5} \times 44.64 = 49.326$ g

3. Mole - Mole Analysis

This analysis is very much important for quantitative analysis point of view.

Now consider again the decomposition of $KClO_3$.

$$2\,KClO_3 \longrightarrow 2\,KCl + 3\,O_2$$

In very first step of mole-mole analysis you should read the balanced chemical equation like **2 moles $KClO_3$ on decomposition gives you 2 moles KCl and 3 moles O_2** and from the stoichiometry of reaction we can write

$$\frac{\text{Moles of } KClO_3}{2} = \frac{\text{Moles of KCl}}{2} = \frac{\text{Moles of } O_2}{3}$$

Now for any general balance chemical equation like

$$a\,A + b\,B \longrightarrow c\,C + d\,D$$

you can write.

$$\frac{\text{Moles of A reacted}}{a} = \frac{\text{Moles of B reacted}}{b} = \frac{\text{Moles of C reacted}}{c} = \frac{\text{Moles of D reacted}}{d}$$

21. PRINCIPLE OF ATOM CONSERVATION (POAC)

Infact POAC is nothing but the conservation of mass, expressed before in the concepts of atomic theory. And if atoms are conserved, moles of atoms shall also be conserved.

The principle is fruitful for the students when they don't get the idea of balanced chemical equation in the problem.

This principle can be under stand by the following example.

Consider The Decomposition of $KClO_3\,(s) \rightarrow KCl\,(s) + O_2\,(g)$ (Unbalanced Chemical Reaction)

Apply the principle of atom conservation (POAC) for K atoms.

Moles of K atoms in reactant = moles of K atoms in products

or moles of K atoms in $KClO_3$ = moles of K atoms in KCl

Now, since 1 molecule of $KClO_3$ contains 1 atom of K

or 1 mole of $KClO_3$ contains 1 mole of K, similarly 1 mole of KCl contains 1 mole of K

Thus, moles of K atoms in $KClO_3 = 1 \times$ moles of $KClO_3$

and moles of K atoms in KCl = 1 × moles of KCl

$\therefore$ moles of $KClO_3$ = moles of KCl

or $$\frac{\text{wt. of } KClO_3 \text{ in g}}{\text{mol. wt. of } KClO_3} = \frac{\text{wt. of KCl in g}}{\text{mol. wt. of KCl}}$$

The above equation gives the mass-mass relationship between $KClO_3$ and KCl which is important in stoichiometric calculations.

Again, applying the principle of atom conservation for O atoms,

moles of O in $KClO_3$ = 3 × moles of $KClO_3$

moles of O in O_2 = 2 × moles of O_2

$\therefore$ 3 × moles of $KClO_3$ = 2 × moles of O_2

or $$3 \times \frac{\text{wt. of } KClO_3}{\text{mol. wt. of } KClO_3} = 2 \times \frac{\text{vol. of } O_2 \text{ at NTP}}{\text{standard molar vol. (22.4 lt)}}$$

The above equations thus gives the mass-volume relationship of reactants and products.

Ex. 27.6 g K_2CO_3 was treated by a series of reagents so as to convert all of its carbon to $K_2Zn_3[Fe(CN)_6]_2$. Calculate the weight of the product.

[mol. wt. of K_2CO_3 = 138 and mol. wt. of $K_2Zn_3[Fe(CN)_6]_2$ = 698]

Sol. Here we have not knowledge about series of chemical reactions but we known about initial reactant and final product accordingly

$$K_2CO_3 \xrightarrow[\text{Steps}]{\text{Several}} K_2Zn_3[Fe(CN)_6]_2$$

Since C atoms are conserved, applying POAC for C atoms,

moles of C in K_2CO_3 = moles of C in $K_2Zn_3[Fe(CN)_6]_2$

1 × moles of K_2CO_3 = 12 × moles of $K_2Zn_3[Fe(CN)_6]_2$

(✈ 1 mole of K_2CO_3 contains 1 moles of C)

$$\frac{\text{wt. of } K_2CO_3}{\text{mol. wt. of } K_2CO_3} = 12 \times \frac{\text{wt. of the product}}{\text{mol. wt. of product}}$$

$$\text{wt. of } K_2Zn_3[Fe(CN)_6]_2 = \frac{27.6}{138} \times \frac{698}{12} = 11.6 \text{ g}$$

Ex. A sample of 3 g containing Na_2CO_3 and $NaHCO_3$ loses 0.248 g when heated to 300°C, the tempera ture at which $NaHCO_3$ decomposes to Na_2CO_3, CO_2 and H_2O. What is the percentage of Na_2CO_3 in the given mixture?

Sol. The loss in weight is due to removal of CO_2 and H_2O which escape out on heating.

wt. of Na_2CO_3 in the product = 3.00 – 0.248 = 2.752 g

Let wt. of Na_2CO_3 in the mixture be x g

$\therefore$ wt. of $NaHCO_3$ = (3.00 – x) g

Since Na_2CO_3 in the products contains x g of unchanged reactant Na_2CO_3 and rest produced from $NaHCO_3$.

The wt. of Na_2CO_3 produced by $NaHCO_3$ = (2.752 – x)g

$NaHCO_3 \longrightarrow Na_2CO_3 + (H_2O + CO_2)\uparrow$

(3.0 – x) (2.752 – x)

Applying POAC for Na atom

$$1 \times \text{moles of } NaHCO_3 = 2 \times \text{moles of } Na_2CO_3 \Rightarrow \frac{(3-x)}{84} = 2x\frac{(2.752-x)}{106}$$

$\therefore$ x = 2.3244 g

$$\therefore \% \text{ of } Na_2CO_3 = \frac{2.3244}{3} \times 100 = 77.48\ \%$$

22. LIMITING REAGENT

The reactant which consumed first into the reaction

When we are dealing with balance chemical equation then if number of moles of reactants are not in the ratio of stoichiometric coefficient of balanced chemical equation, then there should be one reactant which should be limiting reactant.

Ex. Three mole of Na_2CO_3 is reacted with 6 moles of HCl solution. Find the volume of CO_2 gas produced at STP. The reaction is

$$Na_2CO_3 + 2\,HCl \longrightarrow 2\,NaCl + CO_2 + H_2O$$

Sol. From the reaction : $Na_2CO_3 + 2\,HCl \longrightarrow 2\,NaCl + CO_2 + H_2O$

gives moles 3 mol 6 mol

given mole ratio 1 : 2

Stoichiometric coefficient ratio 1 : 2

See here given moles of reactant are in stoichiometric coefficient ratio therefore non reactant left over.

Now use Mole-mole analysis to calculate volume of CO_2 produced at STP

$$\frac{\text{Moles of } Na_2CO_3}{1} = \frac{\text{Mole of } CO_2 \text{ produced}}{1}$$

Moles of CO_2 produced = 3

volume of CO_2 produced at STP = 3 × 22.4 L = 67.2 L

Ex. 6 moles of Na_2CO_3 is reacted with 4 moles of HCl solution. Find the volume of CO_2 gas produced at STP. The reaction is

$$Na_2CO_3 + 2\,HCl \longrightarrow 2\,NaCl + CO_2 + H_2O$$

Sol. From the reaction : $Na_2CO_3 + 2\,HCl \longrightarrow 2\,NaCl + CO_2 + H_2O$

gives moles of reactant 6 : 4

given molar ratio 3 : 2

Stoichiometric coefficient ratio 1 : 2

See here given number of moles of reactants are not in stoichiometric coefficient ratio. Therefore there should be one reactant which consumed first and becomes limiting reagent.

But the question is how to find which reactant is limiting, it is not very difficult you can easily find it. According to the following method.

23. HOW TO FIND LIMITING REAGENT

Step : I

Divided the given moles of reactant by the respective stoichiometric coefficient of that reactant.

Step : II

See for which reactant this division come out to be minimum. The reactant having minimum value is limiting reagent for you.

Step : III

Now once you find limiting reagent then your focus should be on limiting reagent

From	Step I & II	Na_2CO_3	HCl
		$\frac{6}{1} = 6$	$\frac{4}{2} = 2$ (division in minimum)

∴ **HCl is Limiting Reagent**

From Step III

From $\frac{\text{Mole of HCl}}{2} = \frac{\text{Mole of } CO_2 \text{ produced}}{1}$

∴ mole of CO_2 produced = 2 moles

∴ volume of CO_2 produced at S.T.P. = 2 × 22.4 = 44.8 L

Ex. Calculate the weight of FeO from 4 g VO and 5.75 g of Fe_2O_3. Also report the limiting reactant.

$VO + Fe_2O_3 \longrightarrow FeO + V_2O_5$

Sol.

Balanced equation	$2VO$	+	$3Fe_2O_3$	$\longrightarrow$	$6FeO$	+	V_2O_5
Moles before reaction	$\frac{4}{67}$		$\frac{5.75}{160}$		0		0
	= 0.05970		0.03590				
Moles after reaction	(0.05970–0.0359)		0		$\left(\frac{6}{3}\times 0.0359\right)$		$\left(\frac{1}{3}\times 0.0359\right)$

As 2 moles of VO react with 3 moles of Fe_2O_3

∴ 0.05970 g moles of VO = $\frac{3}{2}$ × 0.05970 = 0.08955 moles of Fe_2O_3

Moles of Fe_2O_3 available = 0.0359 only

Hence, Fe_2O_3 is the limiting reagent.

Moles of FeO formed = $\frac{6}{3}$ × 0.0359

∴ Weight of FeO formed = 0.0359 × 2 × 72 = 5.17 g

$$\left(\frac{n_{FeO}}{n_{Fe_2O_3}} = \frac{6}{3}\right) \Rightarrow n_{FeO} = \frac{6}{3} \times n_{Fe_2O_3}$$

$$W_{FeO} = \frac{6}{3} \times n_{Fe_2O_3} \times M_{Fe_2O_3}$$

Ex. A mixture of KBr, NaBr weighing 0.56 g was treated with aqueous solution of Ag^+ and the bromide ion was recovered as 0.97 g of pure AgBr. What was the weight of KBr in the sample ?

Sol.

KBr	+	NaBr	+	Ag^+	$\longrightarrow$	AgBr
a g		(0.56 – a)g				0.97 g

Applying POAC for Br atoms,

Moles of Br in KBr + Moles of Br in NaBr = Moles of Br in AgBr

or 1 × Moles of KBr + 1 × Moles of NaBr = 1 × Moles of AgBr

⇒ $\frac{a}{119} + \frac{(0.56 - a)}{103} = \frac{0.97}{188}$ $(M_{KBr} = 199,\ M_{NaBr} = 103,\ M_{AgBr} = 188)$

∴ a = 0.2124 g

Percentage of KBr in the sample = $\frac{0.2124}{0.560} \times 100 = 37.93$

Ex. The reaction

$2C + O_2 \longrightarrow 2CO$

is carried out by taking 24 g of carbon and 128 g of O_2.

Find out :

(i) Which reactant is left in excess ?

(ii) How much of it is left ?

(iii) How many moles of CO are formed ?

(iv) How many grams of other reactant should be taken so that nothing is left at the end of reaction ?

Sol.

	$2C$	+	O_2	$\longrightarrow$	$2CO$
Mole before reaction	$\frac{24}{12}$		$\frac{128}{32}$		
Mole after reaction	0		3		2

✈ Mole ratio of C : O_2 : CO : : 2 : 1 : 2

(i) O_2 is left in excess.

(ii) 3 moles of O_2 or 96 g of O_2 is left.

(iii) 2 moles of CO or 56 g of CO is formed.

(iv) To use O_2 completely, total 8 moles of carbon or 96 g of carbon is needed.

PERCENTAGE YIELD : The percentage yield of product $= \dfrac{\text{actual yield}}{\text{the theoretical maximum yield}} \times 100$

AVERAGE / MEAN ATOMIC MASS

The weighted average of the isotopic masses of the element's naturally occuring isotopes.

Mathematically, average atomic mass of X $(A_x) = \dfrac{a_1x_1 + a_2x_2 + ... + a_nx_n}{100}$

Where :

a_1, a_2, a_3 .... atomic mass of isotopes.

and x_1, x_2, x_3 .... mole % of isotopes.

Ex. Naturally occuring chlorine is 75% Cl^{35} which has an atomic mass of 35 amu and 25% Cl^{37} which has a mass of 37 amu. Calculate the average atomic mass of chlorine -

(A) 35.5 amu (B) 36.5 amu (C) 71 amu (D) 72 amu

Sol. (A) Average atomic mass $= \dfrac{\text{\% of I isotope x its atoms mass + \% of II isotope x its atomic mass}}{100}$

$$= \frac{75 \times 35 + 25 \times 37}{100} = 35.5 \text{ amu}$$

Note : **(a)** In all calculations we use this mass. **(b)** In periodic table we report this mass only.

MEAN MOLAR MASS OR MOLECULAR MASS

The average molar mass of the different substance present in the container = $\frac{n_1M_1 + n_2M_2 + ...n_nM_n}{n_1 + n_2 + ...n_n}$.

Where :

M_1, M_2, M_3 .... are molar masses.
n_1, n_2, n_3 .... moles of substances.

Ex. The molar composition of polluted air is as follows :

Gas	At. wt.	mole percentage composition
Oxygen	16	16%
Nitrogen	14	80%
Carbon dioxide	-	03%
Sulphurdioxide	-	01%

What is the average molecular weight of the given polluted air ? (Given, atomic weights of C and S are 12 and 32 respectively.

Sol. $M_{avg} = \frac{\sum_{j=1}^{j=n} n_j M_j}{\sum_{j=1}^{j=n} n_j}$ Here $\sum_{j=1}^{j=n} n_j = 100$

$$\therefore M_{avg} = \frac{16 \text{ x } 32 + 80 \text{ x } 28 + 44 \text{ x } 3 + 64 \text{ x } 1}{100} = \frac{512 + 2240 + 132 + 64}{100} = \frac{2948}{100} = \textbf{29.48 Ans.}$$

Oxidation & Reduction

Let us do a comparative study of oxidation and reduction :

	Oxidation		**Reduction**
1.	Addition of Oxygen	**1.**	Removal of Oxygen
Ex.	$2Mg + O_2 \rightarrow 2MgO$	**Ex.**	$CuO + C \rightarrow Cu + CO$
2.	Removal of Hydrogen	**2.**	Addition of Hydrogen
Ex.	$H_2S + Cl_2 \rightarrow 2HCl + S$	**Ex.**	$S + H_2 \rightarrow H_2S$
3.	Increase in positive charge	**3.**	Decrease in positive charge
Ex.	$Fe^{2+} \rightarrow Fe^{3+} + e^-$	**Ex.**	$Fe^{3+} + e^- \rightarrow Fe^{2+}$
4.	Increase in oxidation number	**4.**	Decrease in oxidation number
Ex.	$\overset{(+2)}{SnCl_2} \rightarrow \overset{(+4)}{SnCl_4}$	**Ex.**	$\overset{(+7)}{MnO_4^-} \rightarrow \overset{(+2)}{Mn^{2+}}$
5.	Removal of electron	**5.**	Addition of electron
Ex.	$Sn^{2+} \rightarrow Sn^{4+} + 2e^-$	**Ex.**	$Fe^{3+} + e^- \rightarrow Fe^{2+}$

Oxidation Number

- It is an imaginary or apparent charge developed over atom of an element when it goes from its elemental free state to combined state in molecules.
- It is calculated on basis of an arbitrary set of rules.
- It is a relative charge in a particular bonded state.
- In order to keep track of electron-shifts in chemical reactions involving formation of compounds, a more practical method of using oxidation number has been developed.
- In this method, it is always assumed that there is a complete transfer of electron from a less electronegative atom to a more electronegative atom.

Rules Governing Oxidation Number

The following rules are helpful in calculating oxidation number of the elements in their different compounds. It is to be remembered that the basis of these rule is the electronegativity of the element .

Fluorine Atom

Fluorine is most electronegative atom (known). It always has oxidation number equal to –1 in all its compounds

Oxygen Atom

In general and as well as in its oxides , oxygen atom has oxidation number equal to –2.

In case of (i) peroxide (e.g. H_2O_2 , Na_2O_2) is –1,
(ii) super oxide (e.g. KO_2) is –1/2
(iii) ozonide (e.g. KO_3) is –1/3
(iv) in OF_2 is + 2 & in O_2F_2 is +1

Hydrogen Atom

In general, H atom has oxidation number equal to +1. But in metallic hydrides (e.g. NaH, KH), it is –1.

Halogen Atom

In general, all halogen atoms (Cl, Br , I) have oxidation number equal to –1.
But if halogen atom is attached with a more electronegative atom than halogen atom, then it will show positive oxidation numbers.

Ex. $K\overset{+5}{Cl}O_3$, $H\overset{+5}{I}O_3$, $H\overset{+7}{Cl}O_4$, $K\overset{+5}{Br}O_3$

Metals

(a) Alkali metal (Li , Na, K, Rb, ...) always have oxidation number +1
(b) Alkaline earth metal (Be , Mg , Ca ....) always have oxidation number +2.
(c) Aluminium always has +3 oxidation number

Note : Metal may have negative or zero oxidation number
Oxidation number of an element in free state or in allotropic forms is always zero

Ex. $\overset{0}{O_2}$, $\overset{0}{S_8}$, $\overset{0}{P_4}$, $\overset{0}{O_3}$

Sum of the oxidation numbers of atoms of all elements in a molecule is zero.
Sum of the oxidation numbers of atoms of all elements in an ion is equal to the charge on the ion .
If the group number of an element in modern periodic table is **n,** then its oxidation number may vary from **(n – 10)** to **(n – 18)** (but it is mainly applicable for p-block elements)
Ex. N- atom belongs to 15th group in the periodic table, therefore as per rule, its oxidation number may vary from

$$-3 \text{ to } +5 \; (\overset{-3}{N}H_3, \overset{+2}{N}O, \overset{+3}{N_2}O_3, \overset{+4}{N}O_2, \overset{+5}{N_2}O_5)$$

The maximum possible oxidation number of any element in a compound is never more than the number of electrons in valence shell.(but it is mainly applicable for p-block elements)

Calculation of Average Oxidation Number

Ex. Calculate oxidation number of underlined element :

(a) $Na_2\underline{S}_2O_3$ (b) $Na_2\underline{S}_4O_6$

Sol. **(a)** Let oxidation number of S-atom is x. Now work accordingly with the rules given before .

$(+1) \times 2 + (x) \times 2 + (-2) \times 3 = 0$

$x = +2$

(b) Let oxidation number of S-atom is x

$\therefore \quad (+1) \times 2 + (x) \times 4 + (-2) \times 6 = 0$

$x = +2.5$

It is important to note here that $Na_2S_2O_3$ have two S-atoms and there are four S-atom in $Na_2S_4O_6$. However none of the sulphur atoms in both the compounds have + 2 or + 2.5 oxidation number, it is the average of oxidation number, which reside on each sulphur atom. Therefore, we should work to calculate the individual oxidation number of each sulphur atom in these compounds.

Calculation of Individual Oxidation Number

It is important to note that to calculate individual oxidation number of the element in its compound one should know the structure of the compound and use the following guidelines.

Formula

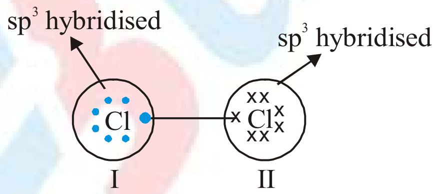
Oxidation Number = Number of electrons in the valence shell – Number of electrons taken up after bonding

Guidelines : It is based on electronegativity of elements.

1. If there is a bond between similar type of atom and each atom has same type of hybridisation, then bonded pair electrons are equally shared by each element.

Ex. Calculate oxidation number of each Cl-atom in Cl_2 molecule

Structure :



I : Number of electrons in the valence shell = 7.

Number of electrons taken up after bonding = 7.

$\therefore$ oxidation number = 7 – 7 = 0.

II : similarly, oxidation number = 7 – 7 = 0

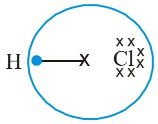
2. If there is a bond between different type of atoms :

Ex. A – B (if B is more electronegative than A)

Then after bonding, bonded pair of electrons are counted with B - atom .

Ex. Calculate oxidation number of each atom in HCl molecule

Structure :

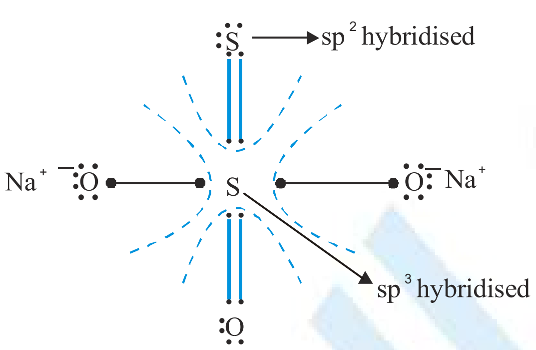


Note : Electron of H-atom is now counted with Cl-atom, because Cl-atom is more electronegative than H-atom

H : Number of electrons in the valence shell = 1
Number of electrons taken up after bonding = 0
Oxidation number of H = 1 – 0 = + 1
Cl : Number of electrons in the valence shell = 7
Number of electrons taken up after bonding = 8
Oxidation number of Cl = 7 – 8 = – 1

Ex. Calculate individual oxidation number of each S-atom in $Na_2S_2O_3$ (sodium thiosulphate) with the help of its structure

Sol. **Structure :**



EDUBULL KEY POINTS

I (central S-atom) is sp^3 hybridised (25% s-character) and II (terminal S-atom) is sp^2 hydbridised (33% s character). Therefore, terminal sulphur atom is more electronegative than central sulphur atom. Now, the shared pair of electrons are counted with terminal S-atom.

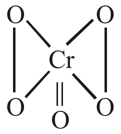
∴ I, S-atom : Number of electrons in the valence shell = 6
Number of electrons left after bonding = 0
Oxidation number of central S-atom = 6 – 0 = + 6

II, S-atom : Number of electrons in the valence shell = 6
Number of electrons left after bonding = 8
Oxidation number of terminal S-atom = 6 – 8 = – 2

Now, you can also calculate Average Oxidation number of S = $\frac{6+(-2)}{2}$ = + 2 (as we have calculated before)

Miscellaneous Examples

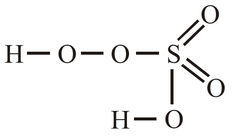
In order to determine the exact or individual oxidation number we need to take help from the structures of the molecules.
Some special cases are discussed as follows:

- The structure of CrO_5 is 

From the structure, it is evident that in CrO_5 there are two peroxide linkages and one double bond. The contribution of each peroxide linkage is –2. Let the oxidation number of Cr is x.

∴ $x + (-2)2 + (-2) = 0$ or $x = 6$
∴ Oxidation number of Cr = + 6 **Ans**

- The structure of H_2SO_5 is



From the structure, it is evident that in H_2SO_5, there is one peroxide linkage, two sulphur-oxygen double bonds and one OH group. Let the oxidation number of S = x.

∴ $(+1) + (-2) + x + (-2)2 + (-2) + 1 = 0$

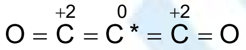
or $x + 2 - 8 = 0$ or $x - 6 = 0$ or $x = 6$

∴ Oxidation number of S in H_2SO_5 is $+6$ **Ans.**

Paradox of Fractional Oxidation Number

Fractional oxidation number is the average of oxidation state of all atoms of element under examination and the structural parameters reveal that the atoms of element for whom fractional oxidation state is realised a actually present in different oxidation states. Structure of the species C_3O_2, Br_3O_8 and $S_4O_6^{2-}$ reveal the following bonding situations :

The element marked with asterisk (*) in each species is exhibiting different oxidation number from rest of the atoms of the same element in each of the species. This reveals that in C_3O_2, two carbon atoms are present in +2 oxidation state each whereas the third one is present in zero oxidation state and the average is +4/3. However, the realistic picture is +2 for two terminal carbons and zero for the middle carbon.

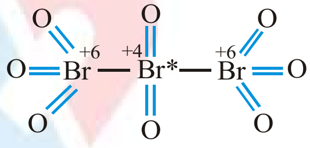


$$O = \overset{+2}{C} = \overset{0}{C}{}^{*} = \overset{+2}{C} = O$$

Structure of C_3O_2

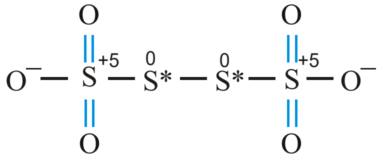
(Carbon suboxide)

Likewise in Br_3O_8, each of the two terminal bromine atoms are present in +6 oxidation state and the middle bromine is present in +4 oxidation state. Once again the average, that is different from reality, is + 16/3.



Structure of Br_3O_8 (Tribromooctaoxide)

In the same fashion, in the species $S_4O_6^{2-}$, average oxidation number of S is + 2.5, whereas the reality being +5,0,0 and +5 oxidation number respectively for respective sulphur atoms.



Structure of $S_4O_6^{2-}$ (tetrathionate ion)

In general, the conclusion is that the idea of fractional oxidation state should be taken with care and the reality is revealed by the structures only.

Oxidising And Reducing Agent

Oxidising Agent or Oxidant

Oxidising agents are those compounds which can oxidise others and reduce itself during the chemical reaction. Those reagents in which for an element, oxidation number decreases or which undergoes gain of electrons in a redox reaction are termed as oxidants.

Ex. $KMnO_4$, $K_2Cr_2O_7$, HNO_3, conc.H_2SO_4 etc are powerful oxidising agents .

Reducing Agent or Reductant

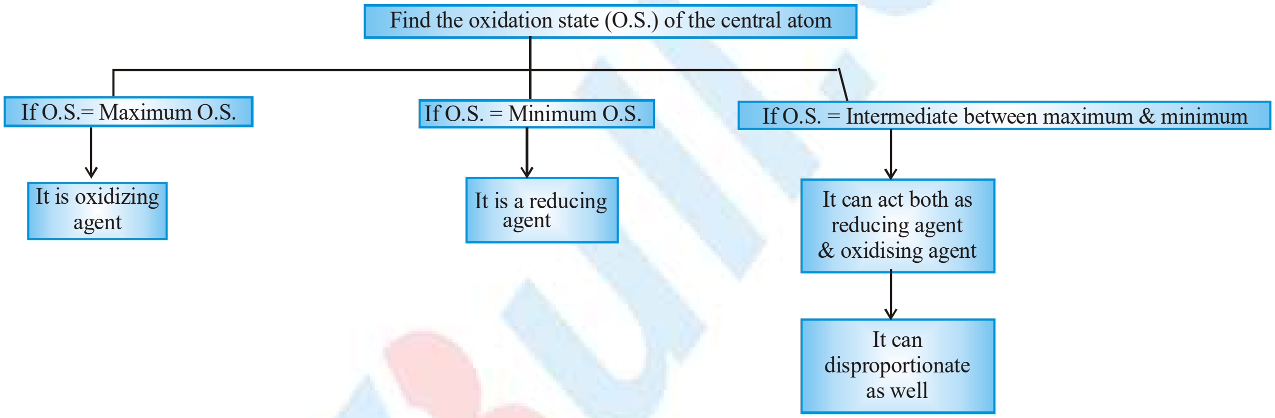
Reducing agents are those compounds which can reduce other and oxidise itself during the chemical reaction. Those reagents in which for an element, oxidation number increases or which undergoes loss of electrons in a redox reaction are termed as reductants.

Ex. KI , $Na_2S_2O_3$ etc are the powerful reducing agents.

Note : There are some compounds also which can work both as oxidising agent and reducing agent

Ex. H_2O_2, NO_2^-

HOW TO IDENTIFY WHETHER A PARTICULAR SUBSTANCE IS AN OXIDISING OR A REDUCING AGENT



Redox Reaction

A reaction in which oxidation and reduction simultaneously take place is called a redox reaction

In all redox reactions, the total increase in oxidation number must be equal to the total decrease in oxidation number.

Ex. $10\,\overset{+2}{Fe}SO_4 + 2K\overset{+5}{Mn}O_4 + 8H_2SO_4 \longrightarrow 5\,\overset{+3}{Fe_2}(SO_4)_3 + 2\,\overset{+2}{Mn}SO_4 + K_2SO_4 + 8H_2O$

Disproportionation Reaction

A redox reaction in which same element present in a particular compound in a definite oxidation state is oxidized as well as reduced simultaneously is a disproportionation reaction.

Disproportionation reactions are a special type of redox reactions. One of the reactants in a disproportionation reaction always contains **an element that can exist in at least three oxidation states**. The element in the form of reacting substance is in the intermediate oxidation state and both higher and lower oxidation states of that element are formed in the reaction. For example :

$$2H_2\overset{-1}{O_2}(aq) \longrightarrow 2H_2\overset{-2}{O}(l) + \overset{0}{O_2}(g)$$

$$\overset{0}{S_8}(s) + 12OH^-(aq) \longrightarrow 4\overset{-2}{S^{2-}}(aq) + 2\overset{+2}{S_2}O_3^{2-}(aq) + 6H_2O(\bullet)$$

$$\overset{0}{Cl_2}(g) + 2OH^-(aq) \longrightarrow \overset{+1}{Cl}O^-(aq) + \overset{-1}{Cl^-}(aq) + H_2O(\bullet)$$

Consider The Following Reactions

(a) $2KClO_3 \longrightarrow 2KCl + 3O_2$

$KClO_3$ plays a role of oxidant and reductant both. Here, Cl present in $KClO_3$ is reduced and O present in $KClO_3$ is oxidized. Since same element is not oxidized and reduced, so **it is not a disproportionation reaction,** although it looks like one.

(b) $NH_4NO_2 \longrightarrow N_2 + 2H_2O$

Nitrogen in this compound has -3 and +3 oxidation number, which is not a definite value. So it is not a disproportionation reaction. It is an example of comproportionation reaction, which is a class of redox reaction in which an element from two different oxidation state gets converted into a single oxidation state.

(c) $4K\overset{+5}{Cl}O_3 \longrightarrow 3K\overset{+7}{Cl}O_4 + K\overset{-1}{Cl}$

It is a case of disproportionation reaction and Cl atom is disproportionating.

List of Some Important Disproportionation Reactions

1. $H_2O_2 \longrightarrow H_2O + O_2$
2. $X_2 + OH^-(\text{dil.}) \longrightarrow X^- + XO^-$ $(X = Cl, Br, I)$
3. $X_2 + OH^-(\text{conc.}) \longrightarrow X^- + XO_3^-$

F_2 does not undergo disproportionation as it is the most electronegative element.

$F_2 + NaOH(\text{dil.}) \longrightarrow F^- + OF_2$

$F_2 + NaOH(\text{conc.}) \longrightarrow F^- + O_2$

4. $(CN)_2 + OH^- \longrightarrow CN^- + OCN^-$
5. $P_4 + OH^- \longrightarrow PH_3 + H_2PO_2^-$
6. $S_8 + OH^- \longrightarrow S^{2-} + S_2O_3^{2-}$
7. $MnO_4^{2-} \longrightarrow MnO_4^- + MnO_2$
8. $NH_2OH \longrightarrow N_2O + NH_3$

   $NH_2OH \longrightarrow N_2 + NH_3$
9. Oxyacids of Phosphorus (+1, +3 oxidation number)

   $H_3PO_2 \longrightarrow PH_3 + H_3PO_3$

   $H_3PO_3 \longrightarrow PH_3 + H_3PO_4$
10. Oxyacids of Chlorine(Halogens)(+1, +3, +5 Oxidation number)

    $ClO^- \longrightarrow Cl^- + ClO_2^-$

    $ClO_2^- \longrightarrow Cl^- + ClO_3^-$

    $ClO_3^- \longrightarrow Cl^- + ClO_4^-$
11. $HNO_2 \longrightarrow NO + HNO_3$

- Reverse of disproportionation is called **Comproportionation.** In some of the disproportionation reactions, by changing the medium (from acidic to basic or reverse), the reaction goes in backward direction and can be taken as an example of **Comproportionation reaction.**

$$I^- + IO_3^- + H^+ \longrightarrow I_2 + H_2O$$

BALANCING OF REDOX REACTIONS

All balanced equations must satisfy two criteria.

1. **Atom Balance (Mass Balance)**

There should be the same number of atoms of each kind on reactant and product side.

2. **Charge Balance**

The sum of actual charges on both sides of the equation must be equal.

There are two methods for balancing the redox equations :

1. Oxidation - number change method
2. Ion electron method or half cell method

– Since First method is not very much fruitful for the balancing of redox reactions, students are advised to use second method (Ion electron method) to balance the redox reactions

Ion electron method : By this method redox equations are balanced in two different medium.

(a) Acidic medium (b) Basic medium

– **Balancing in Acidic Medium**

Students are adviced to follow the following steps to balance the redox reactions by Ion electron method in acidic medium

Ex. Balance the following redox reaction :

$$FeSO_4 + KMnO_4 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + MnSO_4 + H_2O + K_2SO_4$$

Sol. **Step–I** Assign the oxidation number to each element present in the reaction.

$$\overset{+2}{Fe}\overset{+6}{S}\overset{-2}{O_4} + \overset{+1}{K}\overset{+7}{Mn}\overset{-2}{O_4} + \overset{+1}{H_2}\overset{+6}{S}\overset{-2}{O_4} \longrightarrow \overset{+3}{Fe_2}(\overset{+6}{S}\overset{-2}{O_4})_3 + \overset{+2}{Mn}\overset{+6}{S}\overset{-2}{O_4} + \overset{+1}{H_2}\overset{-2}{O}$$

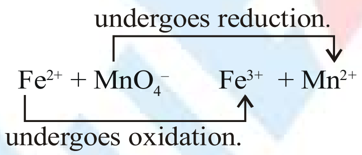
Step II :

Now convert the reaction in Ionic form by eliminating the elements or species, which are not undergoing either oxidation or reduction.

$$Fe^{2+} + \overset{+7}{Mn}O_4^- \longrightarrow Fe^{3+} + Mn^{2+}$$

Step III :

Now identify the oxidation / reduction occuring in the reaction



Step IV : Spilt the Ionic reaction in two half, one for oxidation and other for reduction.

$$Fe^{2+} \xrightarrow{\text{oxidation}} Fe^{3+} \quad \Big| \quad MnO_4^- \xrightarrow{\text{Reduction}} Mn^{2+}$$

Step V :

Balance the atom other than oxygen and hydrogen atom in both half reactions

$$Fe^{2+} \longrightarrow Fe^{3+} \quad \Big| \quad MnO_4^- \longrightarrow Mn^{2+}$$

Fe & Mn atoms are balanced on both side.

Step VI :

Now balance O & H atom by H_2O & H^+ respectively by the following way : For one excess oxygen atom, add one H_2O on the other side and two H^+ on the same side.

$Fe^{2+} \longrightarrow Fe^{3+}$ (no oxygen atom) ....(i)

$8H^+ + MnO_4^- \longrightarrow Mn^{2+} + 4H_2O$ ....(ii)

Step VII :

Equation (i) & (ii) are balanced atomwise. Now balance both equations chargewise. To balance the charge, add electrons to the electrically positive side.

$Fe^{2+} \xrightarrow{\text{oxidation}} Fe^{3+} + e^-$ ....(1)

$5e^- + 8H^+ + MnO_4^- \xrightarrow{\text{Reduction}} Mn^{2+} + 4H_2O$ ....(2)

Step VIII :

The number of electrons gained and lost in each half -reaction are equalised by multiplying both the half reactions with a suitable factor and finally the half reactions are added to give the overall balanced reaction.
Here, we multiply equation (1) by 5 and (2) by 1 and add them :

$Fe^{2+} \longrightarrow Fe^{3+} + e^-$ ....(1) × 5

$$\frac{5e^- + 8H^+ + MnO_4^- \longrightarrow Mn^{2+} + 4H_2O \quad ....(2)\times 1}{5Fe^{2+} + 8H^+ + MnO_4^- \longrightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O}$$

(Here, at his stage, you will get balanced redox reaction in Ionic form)

Step IX :

Now convert the Ionic reaction into molecular form by adding the elements or species, which are removed in step (2). Now, by some manipulation, you will get :

$$5\,FeSO_4 + KMnO_4 + 4H_2SO_4 \longrightarrow \frac{5}{2}\,Fe_2(SO_4)_3 + MnSO_4 + 4H_2O + \frac{1}{2}\,K_2SO_4 \quad \text{or}$$

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 \longrightarrow 5Fe_2(SO_4)_3 + 2MnSO_4 + 8H_2O + K_2SO_4.$$

Balancing in Basic Medium

In this case, except step VI, all the steps are same. We can understand it by the following example:

Ex. Balance the following redox reaction in basic medium :

$ClO^- + CrO_2^- + OH^- \longrightarrow Cl^- + CrO_4^{2-} + H_2O$

Sol. By using upto step V, we will get :

$\overset{+1}{Cl}O^- \xrightarrow{\text{Reduction}} Cl^-$ | $\overset{+3}{Cr}O_2^- \xrightarrow{\text{Oxidation}} \overset{+6}{Cr}O_4^{2-}$

Now, students are advised to follow step VI to balance 'O' and 'H' atom.

$2H^+ + ClO^- \longrightarrow Cl^- + H_2O$ | $2H_2O + CrO_2^- \longrightarrow CrO_4^{2-} + 4H^+$

– Now, since we are balancing in basic medium, therefore add as many as OH^- on both side of equation as there are H^+ ions in the equation.

$2OH^- + 2H^+ + ClO^- \longrightarrow Cl^- + H_2O + 2OH^-$ | $4OH^- + 2H_2O + CrO_2^- \longrightarrow CrO_4^{2-} + 4H^+ + 4OH^-$

Finally you will get | Finally you will get

$H_2O + ClO^- \longrightarrow Cl^- + 2OH^-$ ....(i) $4OH^- + CrO_2^- \longrightarrow CrO_4^{2-} + 2H_2O$ .... (ii)

Now see equation (i) and (ii) in which O and H atoms are balanced by OH^- and H_2O

Now from step VIII

$2e^- + H_2O + ClO^- \longrightarrow Cl^- + 2OH^-$ .... (i) ×3

$4OH^- + CrO_2^- \longrightarrow CrO_4^{2-} + 2H_2O + 3e^-$ .... (ii) ×2

Adding : $3ClO^- + 2CrO_2^- + 2OH^- \longrightarrow 3Cl^- + 2CrO_4^{2-} + H_2O$

24. SOLUTIONS

A mixture of two or more substances can be a solution. We can also say that a solution is a homogeneous mixture of two or more substances 'Homogeneous' means 'uniform throughout'. Thus a homogeneous mixture, i.e., a solution, will have uniform composition throughout.

25. CONCENTRATION TERMS

The following concentration terms are used to expressed the concentration of a solution. These are :

1. Molarity (M)
2. Molality (m)
3. Mole fraction (x)
4. % calculation
5. ppm

Remember that all of these concentration terms are related to one another. By knowing one concentration term you can also find the other concentration terms. Let us discuss all of them one by one.

1. **Molarity (M) : The number of moles of a solute dissolved in 1 L (1000 ml) of the solution is known as the molarity of the solution.**

i.e., Molarity of solution = $\dfrac{\text{number of moles}}{\text{volume of solution in litre}}$

Let a solution is prepared by dissolving w g of solute of mol. wt. M in V mL water.

$\therefore$ Number of moles of solute dissolved = $\dfrac{w}{M}$

$\therefore$ V mL water have $\dfrac{w}{M}$ mole of solute

$\therefore$ 1000 mL water have $\dfrac{w \times 1000}{M \times V(\text{in mL})}$ $\Rightarrow$ $\therefore$ Molarity (M) = $\dfrac{w \times 1000}{(\text{Mol. wt of solute}) \times V(\text{in mL})}$

Ex. 149 gm of potassium chloride (KCl) is dissolved in 10 Lt of an aqueous solution. Determine the molarity of the solution (K = 39, Cl = 35.5)

Sol. Molecular mass of KCl = 39 + 35.5 = 74.5 gm

$\therefore$ Moles of KCl = $\dfrac{149\text{ gm}}{74.5\text{ gm}} = 2$

$\therefore$ Molarity of the solution = $\dfrac{2}{10} = 0.2$ M

2. **Molality (m) :** The number of moles of solute dissolved in 1000 g (1 kg) of a solvent is known as the molality of the solution.

i.e., $$\text{molality} = \frac{\text{number of moles of solute}}{\text{mass of solvent in gram}} \times 100$$

Let y g of a solute is dissolved in x g of a solvent. The molecular mass of the solute is m. Then y/m mole of the solute are dissolved in x g of the solvent. Hence

$$\text{Molality} = \frac{y}{m \times x} \times 1000$$

Ex. 225 gm of an aqueous solution contains 5 gm of urea. What is the concentration of the solution in terms of molality. (Mol. wt. of urea = 60)

Sol. Mass of urea = 5 gm

Molecular mass of urea = 60

$$\text{Number of moles of urea} = \frac{5}{60} = 0.083$$

Mass of solvent = (255 – 5) = 250 gm

$$\therefore \quad \text{Molality of the solution} = \frac{\text{Number of moles of solute}}{\text{Mass of solvent in gram}} \times 1000 = \frac{0.083}{250} \times 1000 = 0.332.$$

3. **Mole Fraction (x) :** The ratio of number of moles of the solute or solvent present in the solution and the total number of moles present in the solution is known as the mole fraction of substances concerned.

Let number of moles of solute in solution = n

Number of moles of solvent in solution = N

$$\therefore \quad \text{Mole fraction of solute } (x_1) = \frac{n}{n+N}$$

$$\therefore \quad \text{Mole fraction of solvent } (x_2) = \frac{N}{n+N} \quad \Rightarrow \quad \text{also} \quad x_1 + x_2 = 1$$

Ex. 0.5 g of a substance is dissolved in 25 g of a solvent. Calculate the percentage amount of the substance in the solution.

Sol. Mass of substance = 0.5 g

Mass of solvent = 25 g

$$\therefore \quad \text{percentage of the substance (w/w)} = \frac{0.5}{0.5+25} \times 100 = 1.96$$

Ex. 20 cm^3 of an alcohol is dissolved in80 cm^3 of water. Calculate the percentage of alcohol in solution.

Sol. Volume of alcohol = 20 cm^3

Volume of water = 80 cm^3

$$\therefore \quad \text{Percentage of alcohol} = \frac{20}{20+80} \times 100 = 20.$$

4. **% Calculation :** The concentration of a solution may also expressed in terms of percentage in the following way.

(i) % weight by weight (w/w) : It is given as mass of solute present in per 100 g of solution.

i.e. $$\% \text{ w/w} = \frac{\text{mass of solute in g}}{\text{mass of solution in g}} \times 100$$

[X % by mass means 100 g solution contains X g solute ; $\therefore$ (100 – X) g solvent]

(ii) % weight by volume (w/v) : It is given as mass of solute present in per 100 mL of solution.

i.e. $$\% \text{ w/v} = \frac{\text{mass of solute in g}}{\text{volume of solution in mL}} \times 100$$

[X % $\left(\frac{w}{V}\right)$ means 100 mL solution contains X g solute]

(iii) % volume by volume (V/V) : It is given as volume of solute present in per 100 mL solution.

Ex. $$\% \text{ V/V} = \frac{\text{Volume of solute}}{\text{Volume of solution in mL}} \times 100$$

5. **Parts Per Million (ppm) :** $\frac{\text{Mass of solute}}{\text{Mass of solvent}} \times 10^6 \cong \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^6$

26. EUDIOMETRY OR GAS ANALYSIS

Gaseous reactions are carried out in a special type of tube known as eudiometer tube. The tube is graduated in millimeters for volume measurement. The reacting gases taken in the eudiometer tube are exploded by sparks. The volumes of the products of a gases are determined by absorbing them in suitable reagents,

Ex.

Solvent	Gas (es) Absorb
KOH	CO_2, SO_2, Cl_2
Ammonical Cu_2Cl_2	CO
Turpentine oil	O_3
Alkaline pyrogallol	O_2
Water	NH_3, HCl
$CuSO_4$	H_2O

Eudiometry is mainly bases on Avogadro's law i.e. $V \propto n$ at the same temperature and pressure.

$\therefore$ The mole concept may be applied in solving the problems, keeping in mind that in a gaseous reaction the relative volumes (measured under identical conditions) of each reactant and product represent their relative numbers of moles.

Ex. $$A(g) + B(g) \rightarrow C(g) + D(g)$$

a volumes b volumes c volumes d volumes

a moles b moles c moles d moles

Generally, explosions are carried out at STP and H_2O is assumed to be in liquid state, means its volume is negligible as compared to product gases.

Burning of Hydrocarbon

1. Hydrocarbon containing carbon and hydrogen only.

$$C_xH_y(g) + \left(x + \frac{y}{4}\right)O_2(g) \longrightarrow xCO_2(g) + \frac{y}{2}H_2O(\bullet)$$

2. Hydrocarbon containing carbon and hydrogen and oxygen.

$$C_xH_yO_z(g) + \left(x + \frac{y}{2} - \frac{z}{2}\right)O_2(g) \longrightarrow xCO_2(g) + \frac{y}{2}H_2O(\bullet)$$

Ex. What volume of oxygen at STP is required to effect complete combustion of 400 cm^3 of acetylene and what would be the volume of carbon dioxide formed?

Sol. $2C_2H_2 + 5O_2 \longrightarrow 4CO_2 + 2H_2O$

2 volume of C_2H_2 require O_2 for complete combustion = 5 vol.

$\therefore$ 400 cm^3 of C_2H_2 will require O_2 for complete combustion = $\frac{5}{2} \times 400$

= 1000 cm^3 at STP

2 volume of C_2H_2 produce CO_2 = 4 volume

$\therefore$ 400 cm^3 of C_2H_2 at STP will produce $CO_2 = \frac{4}{2} \times 400 = 800$ cm^3

Thus, volume of CO_2 produced = 800 cm^3 at STP.

Ex. A gaseous hydrocarbon requires 6 times its own volume of O_2 for complete oxidation and produces 4 times its volume of CO_2. What is its formula ?

Sol. The balanced equation for combustion

$$C_xH_y + \left(x + \frac{y}{4}\right) O_2 \longrightarrow xCO_2 + \frac{y}{2} H_2O$$

$$1 \text{ volume} \left(x + \frac{y}{4}\right) \text{volume}$$

$\therefore$ $x + \frac{y}{4} = 6$ (by equation)

or $4x + y = 24$ ....(1)

Again x = 4 since evolved CO_2 is 4 times that of hydrocarbon

$\therefore$ 16 + y = 24 or y = 8 $\therefore$ formula of hydrocarbon C_4H_8

Ex. A 30 c.c. mixture of CO, CH_4 and He gases is exploded by an electric discharge at room temperature with excess of oxygen. The decrease in volume is found to be 13 c.c. A further contraction of 14 c.c. occurs when the residual gas is treated with KOH solution. Find out the composition of the gaseous mixture in terms of volume percentage.

Sol. Let the volume of CO be 'a' c.c. and CH_4 be 'b' c.c

$\therefore$ Volume of He = (30 – a – b)

on explosion with oxygen

$$CO\,(g) + \frac{1}{2}\,O_2\,(g) \longrightarrow CO_2\,(g)$$

$$CH_4\,(g) + 2O_2\,(g) \longrightarrow CO_2\,(g) + 2H_2O\,(\bullet)$$

'a' c.c. of CO give 'a' c.c. of CO_2 and 'b' c.c. of CH_4 gives 'b' c.c. of CO_2.

Therefore the volume decrease is due to the consumption of O_2. O_2 consumed for 'a' c.c. of CO is $\frac{a}{2}$ c.c. and O_2 consumed for 'b' c.c. of CH_4 is '2b' c.c.

$\therefore$ $\frac{a}{2} + 2b = 13$

The further contraction occurs because of the absorption of CO_2 by KOH, a + b = 14

$\therefore$ b = 4 c.c.

$\therefore$ a = 10 c.c.

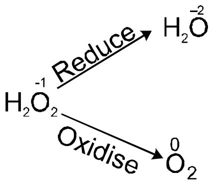
$\therefore$ Percentage composition of CO $= \frac{10}{30} \times 100 = 33.33$ %

Percentage composition of $CH_4 = \frac{4}{30} \times 100 = 13.33$ %

Percentage composition of He $= \frac{(30 - 10 - 4)}{30} \times 100 = 53.33$ %

Hydrogen Peroxide (H_2O_2)

H_2O_2 can behave both like oxidising and reducing agent in both the mediums (acidic and basic).



– **Oxidising Agent :** **($H_2O_2 \rightarrow H_2O$)**

(a) Acidic Medium : $2e^- + 2H^+ + H_2O_2 \longrightarrow 2H_2O$

v.f. = 2

(b) Basic Medium : $2e^- + H_2O_2 \longrightarrow 2OH^-$

v.f = 2

– **Reducing Agent :** **($H_2O_2 \rightarrow O_2$)**

(a) Acidic Medium : $H_2O_2 \longrightarrow O_2 + 2H^+ + 2e^-$

v.f = 2

(b) Basic Medium : $2OH^- + H_2O_2 \longrightarrow O_2 + 2H_2O + 2e^-$

v.f = 2

Volume Strength of H_2O_2 : Strength of H_2O_2 is represented as 10V , 20 V , 30 V etc.

20V H_2O_2 means **one litre** of this sample of H_2O_2 on decomposition gives **20L of O_2** gas at **STP.**
Decomposition of H_2O_2 is given as :

$$H_2O_2 \longrightarrow H_2O + \frac{1}{2}O_2$$

1 mole $\qquad \frac{1}{2} \times 22.4$ L O_2 at STP

= 34g $\qquad$ = 11.2 L O_2 at STP

– **Molarity of H_2O_2 (M) = $\dfrac{\textbf{Volume strength of } H_2O_2}{11.2}$**

Strength (in g/L) : Denoted by S

Strength = Molarity × Mol. wt = Molarity × 34

Hardness of Water (Hard water does not give lather with soap)

Temporary hardness - due to bicarbonates of Ca & Mg

Permanent hardness - due to chlorides & sulphates of Ca & Mg. There are some method by which we can soften the water sample.

(a) By boiling : $2HCO_3^- \longrightarrow H_2O + CO_2 + CO_3^{2-}$ **or**

By Slaked lime : $Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow CaCO_3 + 2H_2O$

$Ca^{2+} + CO_3^{2-} \longrightarrow CaCO_3$

(b) By Washing Soda : $CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 + 2NaCl$

(c) By ion exchange resins : $Na_2R + Ca^{2+} \longrightarrow CaR + 2Na^+$

(d) By adding chelating agents like $(PO_3^-)_3$ etc.

Parts Per Million (ppm)

When the solute is present in very less amount, then this concentration term is used. It is defined as the number of parts of the solute present in every 1 million parts of the solution. ppm can both be in terms of mass or in terms of moles. If nothing has been specified, we take ppm to be in terms of mass. Hence, a 100 ppm solution means that 100 g of solute is present in every 1000000 g of solution.

$$ppm_A = \frac{\text{mass of A}}{\text{Total mass}} \times 10^6 = \text{mass fraction} \times 10^6$$

Measurement of Hardness

Hardness is measured in terms of ppm (parts per million) of $CaCO_3$ or equivalent to it.

$$\text{Hardness in ppm} = \frac{\text{mass of } CaCO_3}{\text{Total mass of solution}} \times 10^6$$

Ex. 0.00012% $MgSO_4$ and 0.000111% $CaCl_2$ is present in water. What is the measured hardness of water and millimoles of washing soda required to purify water 1000 L water ?

Sol. Basis of calculation = 100 g hard water

$$MgSO_4 = 0.00012 g = \frac{0.00012}{120} \text{ mole}$$

$$CaCl_2 = 0.000111 g = \frac{0.000111}{111} \text{ mole}$$

$$\therefore \quad \text{equivalent moles of } CaCO_3 = \left(\frac{0.00012}{120} + \frac{0.000111}{111}\right) \text{mole}$$

$$\therefore \quad \text{mass of } CaCO_3 = \left(\frac{0.00012}{120} + \frac{0.000111}{111}\right) \times 100 = 2 \times 10^{-4} \text{ g}$$

$$\text{Hardness (in terms of ppm of } CaCO_3) = \frac{2 \times 10^{-4}}{100} \times 10^6 = 2 \text{ ppm}$$

$$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 + 2NaCl$$

$$NaSO_4 + Na_2CO_3 \longrightarrow MgCO_3 + Na_2SO_4$$

$$\therefore \quad \text{Required } Na_2CO_3 \text{ for 100g of water} = \left(\frac{0.00012}{120} + \frac{0.000111}{111}\right) \text{mole}$$

$$= 2 \times 10^{-6} \text{ mole}$$

$$\therefore \quad \text{Required } Na_2CO_3 \text{ for 1000 litre water} = \frac{2 \times 10^{-6}}{100} \times 10^6 = \frac{2}{100} \text{ mole} \qquad (\because d = 1 g/mL)$$

$$= \frac{20}{1000} \text{ mole} = 20 \text{ m mole}$$

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.

Hence, weight % of free SO_3 in oleum $= 80(y - 100)/18$

Ex. What volume of water is required (in mL) to prepare 1 L of 1 M solution of H_2SO_4 (density = 1.5g/mL) by using 109% oleum and water only (Take density of pure water = 1 g/mL).

Sol. 1 mole H_2SO_4 in 1L solution = 98 g H_2SO_4 in 1500 g solution = 98 g H_2SO_4 in 1402 g water.

Also, in 109% oleum, 9 g H_2O is required to form 109 g pure H_2SO_4 & so, to prepare 98 g H_2SO_4, water needed is $9/109 \times 98 = 8.09$ g.

Total water needed = 1402 + 8.09 = 1410.09 g = **1410.09 mL**

1. ATOMIC MASS UNIT (OR AMU)

The atomic mass unit (amu) is equal to one twelvth $\left(\frac{1}{12}\right)$ the mass of one atom of carbon-12 isotope.

$\therefore$ 1 amu = $\frac{1}{12}$ × mass of one C-12 atom = 1.66×10^{-24} g or 1.66×10^{-27} kg

2. MOLE

A mole is the amount of a substance that contains as many entities (atoms, molecules or other particles) as there are atoms exactly in 0.012 kg (or 12 g) of the carbon - 12 isotope.

1 mole of atom is also termed as 1 g – atom

1 mole of ions is also termed as 1 g – ion

1 mole of molecule is also termed as 1 g – 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).

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

where R = 0.0821 lit-atm/mol-K (when P is in atmosphere and V is in litre)

1 mole of any gas at STP occupies 22.4 litre.

3. GRAM ATOMIC MASS

The atomic mass of an element expressed in gram is called gram atomic mass of the element.

or

It is also defined as mass of 6.02×10^{23} atoms.

or

It is also defined as the mass of one mole atoms.

4. GRAM MOLECULAR MASS

The molecular mass of a substance expressed in gram is called the gram-molecular mass of the substance.

or

It is also defined as mass of 6.02×10^{23} molecules

or

It is also defined as the mass of one mole molecules.

Average molecule wt. $= \frac{\Sigma n_i M_i}{\Sigma n_i}$ where n_i = no. of moles of compound, m_i = molecular mass of compound

5. PERCENTAGE COMPOSITION AND MOLECULAR FORMULA

$$\text{Mass \% of N in } NH_3 = \frac{\text{Mass of N in 1 mol } NH_3}{\text{Mass of 1 mol of } NH_3} \times 100$$

$$\text{Mass \% of H in } NH_3 = \frac{\text{Mass of H is 1 mol } NH_3}{\text{Mass of 1 mol of } NH_3} \times 100$$

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

Molecular Formula : Formula depicting actual number of atom in onemolecule of the compound.

The molecular formula is generally an integral multiple of the empirical formula.

i.e. molecular formula = empirical formula × n

$$\text{where } n = \frac{\text{molecular formula mass}}{\text{empirical formula mass}}$$

Density

For Liquid and Solids

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

$$\text{Relative density or specific gravity} = \frac{\text{density of the substance}}{\text{density of water at } 4°C}$$

For Gases

$$\text{Absolute density (mass / volume)} = \frac{PM}{RT}$$

where P is pressure of gas, M = mol. wt. of gas, R is the gas constant, T is the temperature.

6. RELATIVE DENSITY OR VAPOUR DENSITY

Vapour density is defined as the density of the gas with respect to hydrogen gas at the same temperature and pressure.

$$\text{Vapour density} = \frac{d_{gas}}{d_{H_2}} = \frac{PM_{gas/RT}}{PM_{H_2/RT}}$$

$$\text{V.D.} = \frac{M_{gas}}{M_{H_2}} = \frac{M_{gas}}{2} \Rightarrow \boxed{M_{gas} = 2\,\text{V.D.}}$$

Gravimetric Analysis

Once we get a balanced chemical equation then we can interpret a chemical equation by following ways

1. Mass - mass analysis
2. Mass - volume analysis
3. Mole - mole analysis
4. Vol - Vol analysis (separately discussed as eudiometry or gas analysis)

Principle of Atom Conservation (poac)

Consider the Dcomposition of $KClO_3$ (s) → KCl (s) + O_2 (g) (unbalanced chemical reaction)

Apply the principle of atom conservation (POAC) for K atoms.

Moles of K atoms in reactant = moles of K atoms in products

or moles of K atoms in $KClO_3$ = moles of K atoms in KCl

Now, since 1 molecule of $KClO_3$ contains 1 atom of K

or 1 mole of $KClO_3$ contains 1 mole of K, similarly 1 mole of KCl contains 1 mole of K

Thus, moles of K atoms in $KClO_3$ = 1 × moles of $KClO_3$

and moles of K atoms in KCl = 1 × moles of KCl

$\therefore$ moles of $KClO_3$ = moles of KCl

or $$\frac{\text{wt. of } KClO_3 \text{ in g}}{\text{mol. wt. of } KClO_3} = \frac{\text{wt. of KCl in g}}{\text{mol. wt. of KCl}}$$

7. LIMITING REAGENT

The reactant which consumed first into the reaction

When we are dealing with balance chemical equation then if number of moles of reactants are not in the ratio of stoichiometric coefficient of balanced chemical equation, then there should be one reactant which should be limiting reactant.

8. AVERAGE/ MEAN ATOMIC MASS

The weighted average of the isotopic masses of the element's naturally occuring isotopes.

Mathematically, average atomic mass of X (A_x) = $$\frac{a_1x_1 + a_2x_2 + ... + a_nx_n}{100}$$

Where :

a_1, a_2, a_3 .... atomic mass of isotopes.

and x_1, x_2, x_3 .... mole % of isotopes.

9. MEAN MOLAR MASS OR MOLECULAR MASS

The average molar mass of the different substance present in the container = $$\frac{n_1M_1 + n_2M_2 + ...n_nM_n}{n_1 + n_2 + ...n_n}.$$

Where :

M_1, M_2, M_3 .... are molar masses.

n_1, n_2, n_3 .... moles of substances.

10. CONCENTRATION TERMS

The following concentration terms are used to expressed the concentration of a solution. These are :

1. Molarity (M)
2. Molality (m)
3. Mole fraction (x)
4. % calculation
5. ppm

Molarity (M) : The number of moles of a solute dissolved in 1 L (1000 ml) of the solution is known as the molarity of the solution.

i.e., Molarity of solution = $$\frac{\text{number of moles}}{\text{volume of solution in litre}}$$

Molality (m) : The number of moles of solute dissolved in 1000 g (1 kg) of a solvent is known as the molality of the solution.

i.e., $\text{molality} = \dfrac{\text{number of moles of solute}}{\text{mass of solvent in gram}} \times 100$

Mole Fraction (x) : The ratio of number of moles of the solute or solvent present in the solution and the total number of moles present in the solution is known as the mole fraction of substances concerned.

Let number of moles of solute in solution = n

Number of moles of solvent in solution = N

∴ Mole fraction of solute $(x_1) = \dfrac{n}{n+N}$

∴ Mole fraction of solvent $(x_2) = \dfrac{N}{n+N}$ ⇒ also $x_1 + x_2 = 1$

% Calculation : The concentration of a solution may also expressed in terms of percentage in the following way.

(i) % weight by weight (w/w) : It is given as mass of solute present in per 100 g of solution.

i.e. $\%\ w/w = \dfrac{\text{mass of solute in g}}{\text{mass of solution in g}} \times 100$

[X % by mass means 100 g solution contains X g solute ; ∴ (100 – X) g solvent]

(ii) % weight by volume (w/v) : It is given as mass of solute present in per 100 mL of solution.

i.e. $\%\ w/v = \dfrac{\text{mass of solute in g}}{\text{volume of solution in mL}} \times 100$

[X % $\left(\dfrac{w}{V}\right)$ means 100 mL solution contains X g solute]

(iii) % volume by volume (V/V) : It is given as volume of solute present in per 100 mL solution.

i.e. $\%\ V/V = \dfrac{\text{Volume of solute}}{\text{Volume of solution in mL}} \times 100$

Parts Per Million (ppm) : $\dfrac{\text{Mass of solute}}{\text{Mass of solvent}} \times 10^6 \cong \dfrac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^6$

Molarity of H_2O_2 (M) $= \dfrac{\text{Volume strength of } H_2O_2}{11.2}$

Strength (in g/L) : Denoted by S

Strength = Molarity × Mol. wt = Molarity × 34

11. BURNING OF HYDROCARBON

Hydrocarbon containing carbon and hydrogen only.

$$C_xH_y\,(g) + \left(x + \frac{y}{4}\right) O_2\,(g) \longrightarrow xCO_2\,(g) + \frac{y}{2} H_2O\,(\bullet)$$

Hydrocarbon containing carbon and hydrogen and oxygen.

$$C_xH_yO_z\,(g) + \left(x + \frac{y}{2} - \frac{z}{2}\right) O_2\,(g) \longrightarrow xCO_2\,(g) + \frac{y}{2} H_2O\,(\bullet)$$