Some Basic Concept of Chemistry

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*.

DALTON'S ATOMIC THEORY

- Matter is made up of very small indivisible particles called atoms.
- All the atoms of a given element are identical in all respect i.e. mass, shape, size, etc.
- Atoms cannot be created or destroyed by any chemical process.
- Atoms of different elements are different in nature.



Classification of matter

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

On hydrogen scale :

Relative atomic mass (R.A.M)

Mass of one atom of an element mass of one hydrogen atom

On oxygen scale :

Relative atomic mass (R.A.M)

= Mass of one atom of an element $\frac{1}{16}$ × mass of one oxygen atom

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

Relative atomic mass (R.A.M)

Mass of one atom of an element $\frac{1}{12}$ × mass of one C – 12 atom

Atomic mass unit (or amu) :

The atomic mass unit (amu) is equal to $\left(\frac{1}{12}\right)^{th}$ mass

of one atom of carbon-12 isotope.

- \therefore 1 amu = $\frac{1}{12}$ × mass of one C-12 atom
 - \sim mass of one nucleon in C-12 atom.

=
$$1.66 \times 10^{-24}$$
 gm or 1.66×10^{-27} kg

- **O** one amu is also called one Dalton (Da).
- **O** Today, amu has been replaced by 'u' which is known as unified mass

Atomic & molecular mass :

It is the mass of 1 atom of a substance it is expressed inamu

- \mathbf{O} Atomic mass = $R.A.M \times 1$ amu Relative molecular mass
 - mass of one molecule of the substance

$$\frac{1}{12}$$
 × mass of one – C-12 atom

Molecular mass = Relative molecular mass $\times 1$ amu Ο

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

Solved Examples

- **Ex.-1** 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 = $R.A.M \times 1$ amu

 $= 16 \times 1$ amu = 16 amu

MOLE

The Mass / Number Relationship

Mole is a chemical counting SI unit and defined as follows:

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

From mass spectrometer we found that there are 6.023×10^{23} atoms present in 12 gm 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 also include in this but as this number (N_{λ}) is very large therefore it is used only for very small things.

Note : In modern practice gram-atom and grammolecule are termed as mole.

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 amu × 6.02 × 10²³
= 16 × 1.66 × 10⁻²⁴ g × 6.02 × 10²³
= 16 g
(
$$:: 1.66 \times 10^{-24} \times 6.02 \times 10^{23} \simeq 1$$
)

Solved Examples

- *Ex.-2* How many atoms of oxygen are their in 16 g oxygen.
- Sol. Let x atoms of oxygen are present

So,
$$16 \times 1.66 \times 10^{-24} \times x = 16$$
 g

$$x = \frac{1}{1.66 \text{ x } 10^{-24}} = N_A$$

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 O_2 ' molecule

= mass of one 'O₂' molecule

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= 2 \times \text{mass of one 'O' atom}
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$$= 2 \times 16$$
 amu

= 32 amu

gram molecular mass

= mass of
$$6.02 \times 10^{23}$$
 'O₂' molecules

$$= 32 \text{ amu} \times 6.02 \times 10^{23}$$

$$= 32 \times 1.66 \times 10^{-24} \text{ gm} \times 6.02 \times 10^{23}$$

Solved Examples

Ex.-3 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, moles of

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

H ₂ SO ₄	Η	S	0
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	onemole	4 mole
· 3 mole	6 mole	3 mole	12 mole

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 at the same temperature and pressure

$H_2(g)$	+	$\operatorname{Cl}_2(g)$	\longrightarrow 2HCl
1 vol		1 vol	2 vol

Avogadro's hypothesis :

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

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 experimentally 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.-4 Calculate the volume in litres of 20 g hydrogen gas at STP.

Sol. No. of moles of hydrogen gas

$$= \frac{Mass}{Molecular mass}$$

 $=\frac{20 \text{ gm}}{2 \text{ gm}}$

= 10 mol

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

Y-MAP

Interconversion of mole - volume,

mass and number of particles :



The laws 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.

(i) The law of conservation of mass :

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

Solved Examples

Ex.-5
$$H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(1)$$

 $H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(1)$

Before 1 mole $\frac{1}{2}$ mole 0 reaction initially

After 0 0 1 mole the reaction

mass before reaction

= mass of 1 mole H₂(g) + $\frac{1}{2}$ mole O₂(g) = 2 + 16 = 18 gm

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

(ii) Law of constant or Definite proportion :

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

Example :

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

Solved Examples

- *Ex.-6* 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

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

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 a fixed. Hence, the results follow the law of constant proportion.

(iii) The law of multiple proportion :

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.

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.

See oxidation number of carbon also have same ratio 1 : 2 in both the oxide.

Solved Examples

Ex.-7 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 oxi	de
Carbon	42.9 %	27.3 %	(Given)
Oxygen	57.1%	72.7 %	
(by differe	ence)		

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.

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.

PERCENTAGE COMPOSITION

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

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

Solved Examples

Ex.-8 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 words 17 gm of NH_3 always contains 14 gm of N and 3 gm of H. Now find out % of each element in the compound.

Sol. Mass % of N in NH₃

 $= \frac{\text{Mass of N in 1 mol NH}_3}{\text{Mass of 1 mol of NH}_3} \times 100$

$$= \frac{14 \text{ gm}}{17} \times 100 = 82.35 \%$$

Some Basic Concept of Chemistry

Mass % of H in NH₃

$$= \frac{\text{Mass of H is 1 mol NH}_3}{\text{Mass of 1 mol e of NH}_3} \times 100$$

$$=\frac{3}{17} \times 100 = 17.65 \%$$

EMPIRICALAND MOLECULAR FORMULA

i.e. molecular formula = empirical formula \times n

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

Solved Examples

- *Ex.-9* 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 = $(1 \times 12) + 1 = 13$. 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 \times (Empirical formula of the compound)

 $= 2 \times CH = C_2 H_2$

Thus the molecular formula is $C_2 H_2$

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 $6 \times CH = C_6 H_6$

Ex.-10 An organic substance containing carbon, hydrogen and oxygen gave the following percentage composition.

C = 40.684%; 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 = <u>Percentage</u> At. mass	Simplest atomic ratio	Simplest whole no. atomic ratio
Carbon	С	40.687	12	$\frac{40.687}{12}$ = 3.390	<u>3.390</u> 3.389 =1	2
Hydrogen	н	5.085	1	$\frac{5.085}{1}$ = 5.085	<u>5.085</u> 3.389 =1.5	3
Oxygen	ο	54.228	16	$\frac{54.228}{16}$ = 3.389	<u>3.389</u> 3.389 =1	2

 \therefore Empirical Formula is C₂H₃O₂

Step-2

To calculate the empirical formula mass.

The empirical formula of the compound is $C_2H_3O_2$

... Empirical formula mass

 $= (2 \times 12) + (3 \times 1) + (2 \times 16) = 59.$

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. Molecular formula = $n \times (\text{Empirical formula})$ = $2 \times C_2 H_3 O_2 = C_4 H_6 O_4$ Thus the molecular formula is $C_4 H_6 O_4$

DENSITY

It is of two type. (i) Absolute density, (ii) Relative density.

For Liquid and Solids

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

We know that density of water at $4^{\circ}C = 1$ g/ml.

For Gases :

 Absolute density (mass/volume) = Molar mass Molar volume

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.

Vapour density =
$$\frac{d_{gas}}{d_{H_2}}$$

$$V.D. = \frac{M_{gas}}{M_{H_2}} = \frac{M_{gas}}{2}$$

 $M_{gas} = 2$ V.D.

Relative density can be calculated w.r.t. to other gases also.

Solved Examples

Ex.-11 What is the V.D. of SO₂ with respect to CH_4

Sol. V.D. =
$$\frac{\text{M.W. SO}_2}{\text{M.W. CH}_4}$$
 V.D = $\frac{64}{16}$ = 4

Ex.-12 7.5 litre of the particular gas at S.T.P. weighs 16 gram. What is the V.D. of gas

Sol. 7.5 litre = 16 gram

moles =
$$\frac{7.5}{22.4} = \frac{16}{M}$$

M = 48 gram

$$V.D = \frac{48}{2} = 24$$

INTERPRETATION OF BALANCED CHEMICALEQUATIONS

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

- Mass mass analysis
- Mass volume analysis
- Mole mole analysis
- Vol-Volanalysis (separately discussed as eudiometry or gas analysis)

Now you can understand the above analysis by following example

• Mass-mass analysis :

Consider the reaction

 $2\text{KClO}_3 \longrightarrow 2\text{KCl} + 3\text{O}_2$

According to stoichiometry of the reaction

mass-mass ratio :

$$2 \times 122.5$$
 : 2×74.5 : 3×32

or
$$\frac{\text{Mass of KCIO}_3}{\text{Mass of KCI}} = \frac{2 \times 122.5}{2 \times 74.5}$$

 $\frac{\text{Mass of KCIO}_3}{\text{Mass of O}_2} = \frac{2 \times 122.5}{3 \times 32}$

- *Ex.-14* 367.5 gram $KClO_3$ (M = 122.5) when heated. How many gram KCl and oxygen is produced.
- Sol. Balance chemical equation for heating of KClO₃ is

 $2\text{KClO}_{3} \longrightarrow 2\text{KCl} + 3\text{O}_{2}$ mass-mass ratio : $2 \times 122.5 \text{ gm} : 2 \times 74.5 \text{ gm} : 3 \times 32 \text{ gm}$ $\frac{\text{mass of KClO}_{3}}{\text{mass of KCl}} = \frac{2 \times 122.5}{2 \times 74.5}$ $\Rightarrow \frac{367.5}{\text{W}} = \frac{122.5}{74.5} \text{ W} = 3 \times 74.5 = 223.5 \text{ gm}$ $\frac{\text{Mass of KClO}_{3}}{\text{Mass of O}_{2}} = \frac{2 \times 122.5}{3 \times 32}$ $\Rightarrow \frac{367.5}{\text{W}} = \frac{2 \times 122.5}{3 \times 32} \text{ W} = 144 \text{ gm}$

• Mass - volume analysis :

Now again consider decomposition of KClO₃

 $2\text{KClO}_3 \longrightarrow 2\text{KCl} + 3\text{O}_2$

mass volume ratio :

 $2\times 122.5~gm$: $2\times 74.5~gm$:

 3×22.4 lt. at STP

we can use two relation for volume of oxygen

 $\frac{\text{Mass of KCIO}_3}{\text{volume of O}_2 \text{ at STP}} = \frac{2 \times 122.5}{3 \times 22.4 \text{ lt}} \quad ...(i)$

and

$$\frac{\text{Mass of KCI}}{\text{volume of }O_2 \text{ at STP}} = \frac{2 \times 74.5}{3 \times 22.4 \text{ It}} \qquad ...(ii)$$

Solved Examples

Ex.-15 367.5 gm KClO₃ (M = 122.5) when heated, how many litre of oxygen gas is produced at STP.

Sol. You can use here equation (1)

$$\frac{\text{massof KCIO}_3}{\text{volume of O}_2 \text{ at STP}} = \frac{2 \times 122.5}{3 \times 22.4 \text{ It}}$$

$$\Rightarrow \frac{367.5}{V} = \frac{2 \times 122.5}{3 \times 22.4 \text{ lt}}$$

$$V = 3 \times 3 \times 11.2 \implies V = 100.8 \text{ lt}$$

• Mole-mole analysis :

$$2\text{KClO}_3 \longrightarrow 2\text{KCl} + 3\text{O}_2$$

 $\frac{\text{Moles of KCIO}_3}{2} = \frac{\text{Moles of KCI}}{2}$

$$=\frac{\text{Moles of O}_2}{3}$$

Now for any general balance chemical equation like

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

you can write.

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

Note : In fact mass-mass and mass-vol analysis are also interpreted in terms of mole-mole analysis you can use following chart also.



LIMITING REAGENT

The reactant which is consumed first and limits the amount of product formed in the reaction, and is therefore, called limiting reagent.

Limiting reagent is present in least stoichiometric amount and therefore, controls amount of product.

The remaining or left out reactant is called the excess reagent.

When you 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 is limiting reactant.

Solved Examples

Ex.-16 Three mole of $Na_2 CO_3$ is reacted with 6 moles of HCl solution. Find the volume of CO_2 gas produced at STP. The reaction is

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

Sol. From the reaction :

$Na_2CO_3 + 2HCl \longrightarrow$	2 NaCl + C	O ₂ -	$+ H_2O$
given moles	3 mol		6 mol
given mole ratio	1	:	2
Stoichiometric coefficien	ntratio 1	:	2

See here given moles of reactant are in stoichiometric coefficient ratio therefore none reactant left over.

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

 $\frac{\text{Moles of Na}_2\text{CO}_3}{1} = \frac{\text{Mole of CO}_2 \text{Produced}}{1}$

Moles of CO_2 produced = 3

volume of CO_2 produced at STP = 3 × 22.4 L

Ex.-17 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

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

Sol. From the reaction :

$Na_2CO_3 + 2HCl \longrightarrow 2 NaCl$	Cl + CC	$D_{2} + 1$	H ₂ O
given mole 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.

How to find limiting reagent :

Step : I

Divide 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, CO₃ HCl

$$=6$$
 $\frac{4}{2}=2$

(division is minimum)

∴ HCl is limiting reagent

6 1

From Step III

From
$$\frac{\text{Mole of HCl}}{2} = \frac{\text{Moles of CO}_2 \text{ produced}}{1}$$

- \therefore mole of CO₂ produced = 2 moles
- $\therefore \text{ volume of CO}_2 \text{ produced at S.T.P.} = 2 \times 22.4$ = 44.8 lt.

PRINCIPLE OF ATOM CONSERVATION (POAC)

POAC is conservation of mass. Atoms are conserved, moles of atoms shall also be conserved in a chemical reaction (but not in nuclear reactions.)

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

The strategy here will be around a particular atom. We focus on a atom and conserve it in that reaction. This principle can be understand by the following example.

Consider the decomposition of $\text{KClO}_3(s) \rightarrow \text{KCl}(s) + \text{O}_2(g)$ (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 KClO₃

= moles of K atoms in KCl.

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

or 1 mole of KClO₃ contains 1 mole of K, similarly,1 mole of KCl contains 1 mole of K.

Thus, moles of K atoms in KClO₃

= $1 \times \text{moles of KClO}_3$

and moles of K atoms in $KCl = 1 \times moles$ of KCl.

 \therefore moles of KClO₃ = 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 KClO₃ = $3 \times$ moles of KClO₃ moles of O in O₂ = $2 \times$ moles of O₂

 \therefore 3 × moles of KClO₃ = 2 × moles of O₂

or
$$3 \times \frac{\text{wt. of KClO}_3}{\text{mol. wt. of KClO}_3}$$

$$= 2 \times \frac{\text{vol. of O}_2 \text{ at NTP}}{\text{stan dard molar vol. (22.4 lt.)}}$$

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

Solved Examples

- *Ex.-18* 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 know about initial reactant and final product accordingly

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

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

moles of C in K_2CO_3

= moles of C in $K_2 Zn_3 [Fe(CN)_6]_2$

 $1 \times \text{moles of } K_2 \text{CO}_3$

=
$$12 \times \text{moles of } K_2 Zn_3 [Fe(CN)_6]_2$$

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

 $\frac{\text{wt. of } \text{K}_2\text{CO}_3}{\text{mol. wt.of } \text{K}_2\text{CO}_3} = 12 \times \frac{\text{wt. of the product}}{\text{mol. wt.of product}}$

wt. of K₂Zn₃ [Fe(CN)₆]₂ =
$$\frac{27.6}{138} \times \frac{698}{12} = 11.6 \text{ g}$$

Concentration terms :

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

- Molarity (M)
- Molality (m)
- Mole fraction (x)
- % calculation

- Normality (N)
- 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.

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

= number of moles of solute volume of solution in litre

 $Molarity (M) = \frac{w \times 1000}{(Mol. wt of solute) \times V_{ml}}$

Some other relations may also useful.

• Molarity of solution may also given as :

Number of millimole of solute Total volume of solution in ml

• Molarity is a unit that depends upon temperature. It varies inversely with temperature.

Molarity $\propto \frac{1}{\text{temperature}} \propto \frac{1}{\text{volume}}$

• If a particular solution having volume V_1 and molarity = M_1 is diluted upto volume V_2 mL than $M_1V_1 = M_2V_2$

M₂: Resultant molarity

• If a solution having volume V_1 and molarity M_1 is mixed with another solution of same solute having volume V_2 mL & molarity M_2

then

$$M_1V_1 + M_2V_2 = M_R(V_1 + V_2)$$

$$M_{R} = \text{Resultant molarity} = \frac{M_{1}V_{1} + M_{2}V_{2}}{V_{1} + V_{2}}$$

Solved Examples

Ex.-19 149 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

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

:. Molarity of the solution = $\frac{2}{10} = 0.2 \text{ M}$

MOLALITY(m):

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

i.e., molality = $\frac{\text{number of moles of solute}}{\text{mass of solvent in gram}} \times 1000$

Let Y gm of a solute is dissolved in X gm of a solvent. The molecular mass of the solute is M_0 . Then Y/M₀ mole of the solute are dissolved in X gm of the solvent. Hence

Molality =
$$\frac{Y}{M_0 \times X} \times 1000$$

• Molality is independent of temperature changes.

Solved Examples

Ex.-20 225 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

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

Mass of solvent = (255-5) = 250 gm

... Molality of the solution

$$= \frac{\text{Number of moles of solute}}{\text{Mass of solvent in gram}} \times 1000$$

$$=\frac{0.083}{250}\times 1000 = 0.332.$$

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 Mole fraction of solute $(x_1) = \frac{n}{n+N}$
- $\therefore \quad \text{Mole fraction of solvent}(\mathbf{x}_2) = \frac{\mathsf{N}}{\mathsf{n} + \mathsf{N}}$

also $x_1 + x_2 = 1$

• Mole fraction is a pure number. It will remain independent of temperature changes.

% calculation :

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

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

i.e. % $_{W/W} = \frac{mass \text{ of solute in gm}}{mass \text{ of solution in gm}} \times 100$

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

i.e., % $_W/_V = \frac{\text{mass of solute in gm}}{\text{volume of solution in mI}} \times 100$

c. % volume by volume (v/v) : It is given as volume of solute present in per 100 ml solution.

i.e., % v/v = $\frac{\text{volume of solute in ml}}{\text{volume of solution in ml}} \times 100$

Solved Examples

Ex.-21 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 percentage of the substance (w/w)

$$= \frac{0.5}{0.5 + 25} \times 100 = 1.96$$

- *Ex.-22* 20 cm³ of an alcohol is dissolved in80 cm³ of water. Calculate the percentage of alcohol in solution.
- **Sol.** Volume of alcohol = 20 cm^3

Volume of water = 80 cm^3

: Percentage of alcohol

$$= \frac{20}{20+80} \times 100 = 20.$$

MISCELLANEOUS

• AVERAGE/ MEAN ATOMIC MASS :

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

M athematically, average atomic mass of X (A_x) =

 $\frac{a_1x_1 + a_2x_2 + \dots + a_nx_n}{100}$

Where :

a₁, a₂, a₃ atomic mass of isotopes.

and x_1, x_2, x_3 mole % of isotopes.

Solved Examples

Ex.-23 Naturally occuring chlorine is 75% Cl³⁵ which has an atomic mass of 35 amu and 25% Cl³⁷ 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 =

 $\underline{\% \, of \, I \, isotope \, its atoms mass} + \% \, of \, Il \, isotope \, its atom is atom is a top of \, Il \, isotope \, its atom is a top of \, Il \, isotope \, Il \, isotope \, its atom is a top of \, Il \, isotope \, its atom is a top of \, Il \, isotope \, its atom is a top of \, Il \, isotope \, its atom is a top of \, Il \, isotope \, its atom is a top of \, Il \, isotope \, its atom is a top of \, Il \, isotope \, its atom is a top of \, Il \, isotope \, its atom is a top of \, Il \, isotope \, its atom is a top of \, Il \, isotope \, its atom is a top of \, Il \, isotope \, its atom is a top of \, Il \, isotope \, Il \, isotope \, its atom is atom is atom is atom is ato$

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

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

$$= \frac{n_1 M_1 + n_2 M_2 + \dots + n_n M_n}{n_1 + n_2 + \dots + n_n}$$

Where :

 M_1, M_2, M_3 are molar masses.

 n_1, n_2, n_3 moles of substances.

Solved Examples

Ex.-24 The molar composition of polluted air is as follows

At. wt.	mole % composition
16	16%
14	80%
-	03%
-	01%
	At. wt. 16 14 -

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
$$\sum_{j=1}^{j=n} n_j = 100$$

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

CONCEPT OF EQUIVALENTS

Equivalent mass of element

Number of parts by mass of an element which reacts or displaces from a compound 1.008 parts by mass of hydrogen, 8 parts by mass of oxygen and 35.5 parts by mass of chlorine, is known as the equivalent weight of that element.

e.g.
$$2Mg + O_2 \longrightarrow 2MgO$$

 $48g \quad 32g$
 $12g \quad 8g$
 $\therefore \quad 32 \text{ g of } O_2 \text{ reacts with } 48 \text{ g of } Mg$
 $\therefore \quad 8 \text{ g of } O_2 = \frac{48 \times 8}{32} = 12 \text{ g}$
 $\therefore \quad \text{Equivalent weight of } Mg = 12$
Similarly, $Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$
 $65.5 \text{ g} \qquad 32.75$
 $\therefore \quad \text{Equivalent weight of } Zn = \frac{65.5}{2} = 32.75 \text{ g}$

Al +
$$\frac{1}{2}$$
Cl₂ \longrightarrow AlCl₃
27 g $\frac{3}{2} \times 71$ g

- \therefore 111.5 g chlorine reacts with 27 g of Al.
- \therefore 35.5 chlorine reacts with $\frac{27 \times 35.5}{111.5}$

$$= 9.0 \text{ g of Al}$$

 \therefore Equivalent weight of aluminium = $\frac{27}{3}$ = 9.0

As we can see from the above examples that equivalent weight is the ratio of atomic weight and a factor (say n- factor or valency factor) which is in above three cases is their respective valencies.

Equivalent weight (E) :

In general, Eq. wt. (E)

Atomic weight or Molecular weight

valency factor(v.f)

 $=\frac{Mol.wt.}{n-factor} = \frac{M}{x}$

Number of Equivalents

= $\frac{\text{mass of species}}{\text{eq. wt. of that species}}$

For a solution, Number of equivalents = N_1V_1 , where N is the normality and V is the volume in litres

- Equivalent mass is a pure number which, when expressed in gram, is called gram equivalent mass.
- The equivalent mass of substance may have different values under different conditions.
- There in no hard and fast rule that equivalent weight will be always less than the molecular mass.

Valency factor calculation

• For Elements :

Valency factor = valency of the element.

• For Acids :

Valency factor = number of replaceable H^+ ions per acid molecule

Solved Examples

{see there are only two replaceable H⁺ions}

Sol. Valency factor $\rightarrow 1$ 2 3 2 (assume 100% dissicolation)

Eq. wt. (E) $\rightarrow \frac{M}{1} = \frac{M}{2} = \frac{M}{3} = \frac{M}{2}$

• Replaceable hydrogen atoms are those hydrogen atoms which are attached with the atoms of group VI and group VII i.e. O,S,Se,Te, & F, Cl,Br,I. For Bases :

Valency factor = number of replacable OH⁻ions per base molecule.

Solved E	Examples
-----------------	----------

Ex30	NaOH,	KOH
<i>Sol.</i> v .f. →	1	1
Eq. wt. \rightarrow	$\frac{M}{1}$	$\frac{M}{1}$

• Bases may be defined as the substances in which OH group is/are directly attached with group I elements (Li,Na, K,Rb,Cs), group II elements (Be, Mg,Ca,Ba) or group III elements (Al, Ga,In,Tl), transition metals, non-metallic cations like PH_4^+ , NH_4^+ etc.

• Acid - base reaction :

In case of acid base reaction, the valence factor is the actual number of H^+ or OH^- replaced in the reaction. The acid or base may contain more number of replaceble H^+ or OH^- than actually replaced in reaction.

• v. f. for base is the number of H⁺ ion from the acid replaced by each molecule of the base

Solved Examples

 $\begin{array}{cc} \textbf{\textit{Ex.-31}} & 2\text{NaOH} + \text{H}_2 & \text{SO}_4 & \longrightarrow \text{Na}_2 & \text{SO}_4 + 2\text{H}_2\text{O} \\ & \text{Base} & \text{Acid} \end{array}$

Sol. Valency factor of base = 1 Here, two molecule of NaOH replaced $2H^+$ ion from the H₂ SO₄. Therefore, each molecule of NaOH replaced only one H⁺ ion of acid, so v.f. = 1.

• v. f. for acid is the number of OH⁻ replaced from the base by each molecule of acid

Solved Examples

 $Ex.-32 \text{ NaOH} + \text{H}_2\text{SO}_4 \longrightarrow \text{NaHSO}_4 + \text{H}_2\text{O}$ Base Acid

Sol. Valency factor of acid = 1

Here, one of molecule of H_2SO_4 replaced one OHfrom NaOH. Therefore, valency factor for H_2SO_4

is one \therefore Eq. wt. of $H_2SO_4 = \frac{Mol.wt}{1}$

• Salts :

(a) In non-reacting condition

• Valency factor = Total number of positive charge or negative charge present in the compound.

Solved Examples

Ex33	$Na_2 CO_3$,	$\operatorname{Fe}_{2}(\operatorname{SO}_{4})_{3}$	$FeSO_4.7H_2O$
<i>Sol.</i> V.f.	2	$2 \times 3 = 6$	2
Eq.w	rt. $\frac{M}{2}$	<u>M</u> 6	<u>M</u> 2

Note : In case of hydrated salt, positive/ negative charge of water molecule is not counted.

(b) In reacting condition

Solved Examples

 $Ex.-34 \operatorname{Na}_{2} \operatorname{CO}_{3} + \operatorname{HCl} \longrightarrow \operatorname{NaHCO}_{3} + \operatorname{NaCl}$ Base Acid

Sol. It is an acid base reaction, therefore valency factor for Na_2CO_3 is one while in non-reacting condition, it will be two.

(c) Equivalent weight of oxidising / reducing agents in a redox reaction

In case of redox change , $\mathbf{v.f.} = \text{Total change in}$ oxidation number per molecule .

Solved Examples

Ex.-35 KMnO₄ + H₂O₂ \longrightarrow Mn²⁺ + O₂

Sol. Mn in KMnO₄ is going from +7 to +2, so change in oxidation number per molecule of KMnO₄ is 5. So the valency factor of KMnO₄ is 5 and equivalent weight is $\frac{M}{5}$.

NORMALITY

Normality of a solution is defined as the number of equivalents of solute present in one litre (1000 mL) solution.

Let V mL of a solution is prepared by dissolving W g of solute of equivalent weight E in water.

• Number of equivalents of solute =
$$\frac{W}{F}$$

VmL of solution contain $\frac{W}{F}$ equivalents of solute

 $\therefore 1000 \text{ mL solution will contain}$ $\frac{W \times 1000}{E \times V} \text{ equivalents of solute.}$

• Normality (N) =
$$\frac{W \times 1000}{E \times V}$$

• Normality (N) = Molarity x Valency factor

$$N \times V(in mL) = M \times V(in mL) \times n$$

or

• milliequivalents = millimoles × n

Solved Examples

Ex.-36 Calculate the normality of a solution containing 15.8 g of KMnO_4 in 50 mL acidic solution.

Sol. Normality (N) =
$$\frac{W \times 1000}{E \times V}$$

Here W = 15.8 g, V = 50 mL

$$E = \frac{\text{molar mass of KMnO}_4}{\text{Valency factor}} = 158/5 = 31.6$$

So, normality = 10 N

- *Ex.-37* Calculate the normality of a solution containing 50 mL of 5 M solution of $K_2Cr_2O_7$ in acidic medium.
- **Sol.** Normality (N) = Molarity × valency factor = $5 \times 6 = 30 \text{ N}$

LAW OF EQUIVALENCE

The law states that one equivalent of an element combine with one equivalent of the other. In a chemical reaction, equivalents and milli equivalents of reactants react in equal amount to give same number of equivalents or milli equivalents of products separately.

Accordingly

(i) $aA + bB \rightarrow mM + nN$

meq of A = meq of B = meq of M = m.eq. of N

(ii) In a compound $M_x N_y$

meq of $M_x N_y =$ meq of M = meq of N

Solved Examples

Ex.-38 Find the number of moles of $KMnO_4$ needed to oxidise one mole Cu_2S in acidic medium.

The reaction is $KMnO_4 + Cu_2S \longrightarrow$

$$Mn^{2+} + Cu^{2+} + SO_2$$

Sol. From law of equivalence,

equivalents of Cu_2S = equivalents of $KMnO_4$ moles of $Cu_2S \times v.f.$ = moles of $kMnO_4 \times v.f.$

$$1 \times 8 = \text{moles of KMnO}_4 \times 5$$

$$\Rightarrow$$
 moles of KMnO₄ = 8/5

(:. v.f. of
$$Cu_2 S = 2(2-1) + 1(4-(-2)))$$

= 8 and v.f. of
$$KMnO_4 = 1 (7-2) = 5$$
)

Ex.-39 The number of moles of oxalate ions oxidized by one mole of MnO_4^- ion in acidic medium are :

(A)
$$\frac{5}{2}$$
 (B) $\frac{2}{5}$
(C) $\frac{3}{5}$ (D) $\frac{5}{3}$

Sol. Equivalents of
$$C_2O_4^{2-}$$
 = equivalents of MnO_4^{-}
 $x(mole) \times 2 = 1 \times 5$
(\therefore v.f. of $C_2O_4^{2-} = 2 (4-3)$
 $= 2$ and v.f. of $MnO_4^{-} = 1 (7-2) = 5$).

$$x = \frac{5}{2} \text{ mole of } C_2 O_4^{2-} \text{ ions.}$$

DRAWBACKS OF EQUIVALENT

CONCEPT

• Since equivalent weight of a substance (for example oxidising or reducing agent) may be variable hence it is better to use mole concept.

e.g.
$$5e^{-} + 8H^{+} + MnO_{4}^{-} \longrightarrow Mn^{2+} + 2H_{2}O$$

 \therefore Eq.wt of $MnO_{4}^{-} = \frac{Mol.wt.of MnO_{4}^{-}}{5}$
e.g. $3e^{-} + 2H_{2}O + MnO_{4}^{-} \longrightarrow MnO_{2} + 4OH^{-}$
 \therefore Eq.wt of $MnO_{4}^{-} = \frac{Mol. wt.of MnO_{4}^{-}}{3}$

Thus, the number of equivalents of MnO_4^- will be different in the above two cases but number of moles will be same.

• Normality of any solution depends on reaction while molarity does not.

For example :

Consider 0.1 mol KMnO₄ dissolved in water to make 1L solution. Molarity of this solution is 0.1 M. However, its normality is NOT fixed. It will depend upon the reaction in which KMnO₄ participates. e.g. if KMnO₄ forms Mn²⁺, normality = 0.1 x 5 = 0.5 N. This *same* sample of KMnO₄, if employed in a reaction giving MnO₂ as product (Mn in +4 state), will have normality 0.1 × 3 = 0.3 N.

• The concept of equivalents is handy, but it should be used with care. One must never equate equivalents in a sequence which involves same element in more than two oxidation states. Consider an example, KIO₃ reacts with KI to liberate iodine and liberated Iodine is titrated with standard hypo solution. The reactions are :

(i)
$$IO_3^- + I^- \longrightarrow I_2$$

(ii)
$$I_2 + S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + I^-$$

meq of hypo = meq of I_2 = meq of IO_3^- = meq of $I^ \therefore$ meq of hypo = meq of IO_3^- .

This is wrong. Note that I_2 formed by equation (i) has v.f. = 5/3 & in equation (ii) has v.f. = 2.

 \therefore v.f. of I₂ in both the equation are different, therefore we cannot equate milli equivalents in sequence.

In this type of case, students are advised to use mole concept.

Ex.-40 How many millilitres of 0.02 M KMnO_4 solution would be required to exactly titrate 25 mL of 0.2 M Fe(NO₃)₂ solution in acidic medium ?

Sol. Method -1 : Mole concept method

Starting with 25 mL of 0.2 M Fe^{2+} , we can write :

Millimoles of $Fe^{2+} = 25 \times 0.2$ (1)

and in volume V (in milliliters) of the $KMnO_4$,

Millimoles of $MnO_4^- = V(0.02)$ (2)

The balanced reaction is :

$$MnO_4^{-} + 5Fe^{2+} + 8H^{+} \longrightarrow$$

$$Mn^{2+} + 5Fe^{3+} + 4H_2O$$

This requires that at the equivalent point,

$$\frac{\text{m.moles of MnO}_4^-}{1} = \frac{\text{m.moles of Fe}^{2+}}{5}$$

$$\therefore \quad \frac{V(0.02)}{1} = \frac{(25)(0.2)}{5} \quad (\text{from}(1)\&(2))$$

 \therefore V = 50 mL.

Method -2 : Equivalent Method :

At the equivalence point,

milliequivalents of MnO₄⁻ = milliequivalents of Fe²⁺ $M_1 \times vf_1 \times V_1 = M_2 \times vf_2 \times V_2$ $0.02 \times 5 \times V_1 = 0.2 \times 1 \times 25$ ($:: MnO_4^- \longrightarrow Mn^{2+}$; v.f. = 5, Fe²⁺ $\longrightarrow Fe^{3+}$; v.f. = 1)

:. $V_1 = 50 \text{ mL}.$

TITRATIONS

Titration is a procedure for determining the concentration of a solution by allowing a carefully measured volume to react with a standard solution of another substance, whose concentration is known.

Standard solution - It is a solution whose concentration is known and is taken in burette. It is also called **Titrant**.

There are two type of titrants :

Primary titrants/standard - These reagents can be accurately weighed and their solutions are not to be standardised before use.

Ex : Oxalic acid, $K_2Cr_2O_7$, AgNO₃, CuSO₄, ferrous ammonium sulphate, hypo etc.

• Secondary titrants/standard : These reagents cannot be accurately weighed and their solutions are to be standardised before use.

Ex : NaOH, KOH, HCl, H_2SO_4 , I_2 , KMn O_4 etc.

Titrate : Solution consisting of substance to be estimated, generally taken in a beaker .

Equivalence point : It is the point when number of equivalents of titrant added becomes equal to number of equivalents of titrate.

At equivalence point :

 $n_1 V_1 M_1 = n_2 V_2 M_2$

Indicator : An auxiliary substance added for physical detection of completion of titration at equivalence point. It generally show colour change on completion of titration.

Type of Titrations :

- Acid-base titrations (to be studided in Ionic equilibrium)
- Redox Titrations

Some Common Redox Titrations

Table of Redox Titrations :

(Excluding Iodometric / Iodimetric titrations)

	Estimation of	By titrating wi	th Reactions	Relation*between OA and
1.	Fe ²⁺	MnO_4^{-}	$Fe^{2+} \longrightarrow Fe^{3+} + e^{-}$	$5 \text{Fe}^{2+} \equiv \text{MnO}_4^-$
			$MnO_4^- + 8H^+ + 5e^- \longrightarrow$	Eq. wt. of $Fe^{2+} = M/1$
			$Mn^{2+} + 4H_2O$	
2.	Fe^{2^+}	Cr ₂ O ₇ ²⁻	$Fe^{2+} \longrightarrow Fe^{3+} + e^{-}$	$6\mathrm{F}\mathrm{e}^{2+} \equiv \mathrm{Cr}_{2}\mathrm{O}_{7}^{2-}$
			$\operatorname{Cr}_{2}\operatorname{O}_{7}^{2-} + 14\operatorname{H}^{+} + 6e^{-} \longrightarrow$	Eq.wt. of $Cr_2O_7^{2-} = M/6$
			$2Cr^{3+} + 7H_{2}O$	
3.	$C_{2}O_{4}^{2-}$	MnO_4^{-}	$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$	$5C_2O_4^{2-} \equiv 2MnO_4^{-}$
			$MnO_4^- + 8H^+ + 5e^- \longrightarrow$	Eq. wt. of $C_2 O_4^{2-} = M/2$
			$Mn^{2+} + 4H_2O$	
4.	H_2O_2	MnO_4^{-}	$H_2O_2 \longrightarrow 2H^+ + O_2 + 2e^-$	$5H_2O_2 \equiv 2MnO_4^{-1}$
			$nO_4^- + 8H^+ + 5e^- \longrightarrow$	Eq.wt. of $H_2O_2 = M/2$
			$Mn^{2+} + 4H_2O$	
5.	As_2O_3	MnO_4^{-}	$As_2O_3 + 5H_2O \longrightarrow$	Eq. wt. of $As_2O_3 = M/4$
			$2AsO_4^{3-} + 10H^+ + 4e^-$	
			$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn$	$^{2+} + 4H_{2}O$
6.	AsO ₃ ³⁻	BrO ₃ ⁻	$AsO_{3}^{3-} + H_{2}O \longrightarrow$	Eq. wt. of $AsO_{3}^{3-} = M/2$
			$AsO_4^{3-} + 2H^+ + 2e^-$	
			$\text{BrO}_3^- + 6\text{H}^+ + 6\text{e}^- \longrightarrow$	Eq.wt. of $BrO_3^- = M/6$
			$Br^- + 3H_2O$	

Permanganate Titrations :

- KMnO₄ is generally used as oxidising agent in acidic 0 medium, generally provided by dilute H₂SO₄.
- KMnO₄ works as self indicator persistent pink color is indication of end point.
- Mainly used for estimation of Fe²⁺, oxalic acid 0 ,oxalates, H₂O₂ etc.

Solved Examples

Ex.-41 Write the balanced reaction of titration of KMnO₄ Vs oxalic acid in presence of H₂SO₄.

Sol. Reaction: $2KMnO_4 + 3H_2SO_4 + 5H_2C_2O_4$ $\longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2$ Redox Changes : $C_2^{3+} \longrightarrow 2C^{4+} + 2e$

$$\left(\mathsf{E}_{\mathsf{H}_2\mathsf{C}_2\mathsf{O}_4}=\frac{\mathsf{M}}{2}\right)$$

• •

$$5e + Mn^{7+} \longrightarrow Mn^{2+} \left(\mathsf{E}_{\mathsf{KMnO}_4} = \frac{\mathsf{M}}{5}\right)$$

Indicator: KMnO₄ acts as self indicator.

- *Ex.-42* Write the balanced reaction of titration of KMnO₄ Vs ferrous ammonium sulphate in presence of H_2SO_4 .
- **Sol.** Reaction: $2KMnO_4 + 10[FeSO_4(NH_4)_2SO_4$.
 - $6H_2O] + 8H_2SO_4 \longrightarrow$ $5Fe_2(SO_4)_3 + 10(NH_4)_2SO_4 + K_2SO_4$ $+ 2MnSO_4 + 68H_2O$ Redox Changes :

 $Fe^{2+} \longrightarrow Fe^{3+} + e \qquad \left(E_{FeSO_4} = \frac{M}{1} \right)$

$$Mn^{7+} + 5e \longrightarrow Mn^{2+} \left(\mathsf{E}_{\mathsf{KMnO}_4} = \frac{\mathsf{M}}{\mathsf{5}} \right)$$

Indicator: KMnO₄ acts as self indicator

IODOMETRIC/IODIMETRIC

TITRATIONS

Compound containing iodine are widely used in titrations.

(i) Iodide ions can be oxidised to I_2 by suitable oxidising agent

 $2I^{-}(aq) \longrightarrow I_{2}(s) + 2e^{-}$

(ii) Iodine (V) ions,
$$IO_3^-$$
, will oxidise I⁻ to I₂
 $IO_3^-(aq) + 5I^-(aq) + 6H^+(aq) \longrightarrow 3I_2(s) + 3H_2O(\ell)$

(iii) Thiosulphate ions, $S_2O_3^{2-}$, can reduce iodine to iodide ions.

Iodometric Titrations (Titration Solution is of $Na_2S_2O_3 . 5H_2O$)

S.No.	Estimation of	of Reaction	Relation between O.A. and R.A.
1.	I ₂	$I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$ or $I_1 + 2S_2O_2^{} \longrightarrow 2I_1^{} + S_2O_2^{}$	$I_2 = 2I = 2Na_2S_2O_3$
2.	CuSO ₄	$0II_{2} + 2S_{2}O_{3} \longrightarrow 2I + S_{4}O_{6}$ $2CuSO_{4} + 4KI \longrightarrow 2CuI + 2K_{2}SO_{4} + I_{2}$ $0II_{2} + 2K_{2}SO_{4} + I_{2}$ $0II_{2} + 2K_{2}SO_{4} + I_{2}$	Eq. wt. of $\operatorname{Na}_2 \operatorname{S}_2 \operatorname{O}_3 = \operatorname{N/T}$ $2\operatorname{CuSO}_4 \equiv \operatorname{I}_2 \equiv 2\operatorname{I} = 2\operatorname{Na}_2 \operatorname{S}_2 \operatorname{O}_3$ Eq. wt. of $\operatorname{CuSO}_2 = M/1$
		white ppt	Eq. wt.of $CuSO_4 - W/1$
3.	CaOCl ₂	$CaOCl_{2} + H_{2}O \longrightarrow Ca(OH)_{2} + Cl_{2}$ $Cl_{2} + 2KI \longrightarrow 2KCl + I_{2}$	$CaOCl_2 \equiv Cl_2 \equiv I_2 \equiv 2I \equiv 2Na_2S_2O_3$
		$Cl_2 + 2I^- \longrightarrow 2Cl^- + I_2$	Eq.wt. of $CaOCl_2 = M/2$
4.	MnO ₂	$MnO_2 + 4HCl(conc.) \xrightarrow{\Lambda} MnCl_2 + Cl_2 + 2H_2$ $Cl_2 + 2KI \longrightarrow 2KCl + I_2$	$MnO_2 \equiv Cl_2 \equiv I_2 \equiv 2Na_2S_2O_3$ Eq.wt. of $MnO_2 = M/2$
		or $MnO_2 + 4H^+ + 2Cl^- \longrightarrow Mn^{2+} + 2H_2O + Cl_2 + 2I^- \longrightarrow I_2 + 2Cl^-$	Cl ₂
5.	IO_3^{-}	$IO_3^{2-} + 5I^{-} + 6H^{+} \longrightarrow 3I_2 + 3H_2O$	$IO_3^- \equiv 3I_2 \equiv 6I \equiv 6Na_2S_2O_3$ Eq.wt. of $IO_3^- = M/6$
6.	H ₂ O ₂	$H_2O_2 + 2I^- + 2H^+ \longrightarrow I_2 + 2H_2O$	$H_2O_2 \equiv I_2 \equiv 2I \equiv 2Na_2S_2O_3$ Eq.wt. of $H_2O_2 \equiv M/2$
7.	Cl ₂	$Cl_2 + 2I^- \longrightarrow 2Cl^- + I_2$	$Cl_2 \equiv I_2 \equiv 2I \equiv 2Na_2S_2O_3$ Eq.wt. of $Cl_2 = M/2$

		So	me Basic Concept of Chemistry
8.	O ₃	$O_3 + 6I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$	$O_3 \equiv 3I_2 \equiv 6I \equiv 6Na_2S_2O_3$
			Eq.wt. of $O_3 = M/6$
9.	C10 ⁻	$\text{ClO}^- + 2\text{I}^- + 2\text{H}^+ \longrightarrow \text{H}_2\text{O} + \text{Cl}^- + \text{I}_2$	$\text{ClO}^- \equiv \text{I}_2 \equiv 2\text{I} \equiv 2\text{Na}_2\text{S}_2\text{O}_3$
			Eq.wt. of $OCl^- = M/2$
10.	Cr ₂ O ₇ ²⁻	$\operatorname{Cr}_{2}\operatorname{O}_{7}^{2-} + 14\operatorname{H}^{+} + 6\operatorname{I}^{-} \longrightarrow 3\operatorname{I}_{2} + 2\operatorname{Cr}^{3+} + 7\operatorname{H}_{2}\operatorname{O}$	$\mathrm{Cr}_{2}\mathrm{O}_{7}^{2-} \equiv 3\mathrm{I}_{2} \equiv 6\mathrm{I}$
			Eq.wt. of $Cr_2O_7^{2-} = M/6$
11.	MnO_4^-	$2MnO_4^{-} + 10I^{-} + 16H^+ \longrightarrow 2MnO_4^{-} + 5I_2 + 8H_2O$	$2MnO_4^- \equiv 5I_2 \equiv 10I$
			Eq.wt. of $MnO_4^- = M/5$
12.	BrO ₃ ⁻	$\operatorname{BrO}_3^- + 6\overline{I}^- + 6\overline{H}^+ \longrightarrow \overline{Br}^- + 3\overline{I}_2 + 3\overline{H}_2O$	$BrO_3^- \equiv 3I_2 \equiv 6I$
			Eq.wt. of $BrO_3^- = M/6$
13.	As(V)	$H_2AsO_4 + 2I^+ 3H^+ \longrightarrow H_3AsO_3 + H_2O + I_2$	$H_3AsO_4 \equiv I_2 \equiv 2I$
			Eq.wt. of H_3 As $O_4 = M/2$
14.	HNO ₂	$2HNO_2 + 2I^- \longrightarrow I_2 + 2NO + H_2O$	$2\text{HNO}_2 \equiv \text{I}_2 \equiv 2\text{I}$
			Eq.wt. of $HNO_2 = M/1$
15.	HClO	$HClO + 2I^{-} + H^{+} \longrightarrow Cl^{-} + I_{a} + H_{a}O$	$HClO = I_a = 2Na_a S_a O_a$
- /			Eq wt of HClO = $M/2$

Iodimetric Titrations

S.No.	Estimation of	Reaction Re	elation between O.A. and R.A.
1.	H_2S (in acidic medium)	$H_2S + I_2 \longrightarrow S + 2I^- + 2H^+$	$H_2S \equiv I_2 \equiv 2I$ Eq.wt. of $H_2S = M/2$
2.	SO_3^{2-} (in acidic medium)	$SO_3^{2-} + I_2 + H_2O \longrightarrow SO_4^{2-} + 2I^- + 2I_2$	H ⁺ $SO_{3}^{2-} \equiv I_{2} \equiv 2I$ Eq.wt. of $SO_{3}^{2-} \equiv M/2$
3.	Sn ²⁺ (in acidic medium)	$\operatorname{Sn}^{2+} + \operatorname{I}_2 \longrightarrow \operatorname{Sn}^{4+} + 2\operatorname{I}^-$	$\operatorname{Sn}^{2+} \equiv \operatorname{I}_2 \equiv 2\operatorname{I}$ Eq.wt. of $\operatorname{Sn}^{2+} = M/2$
4.	As(III) (at pH 8)	$H_2AsO_3^- + I_2 + H_2O \longrightarrow HAsO_4^{2-} + 2I^{-}$	$^{-}$ + 3H ⁺ H ₂ AsO ₃ ⁻ = I ₂ = 2I Eq.wt. of H ₂ AsO ₂ ⁻ = M/2
5.	N ₂ H ₄	$N_2H_4 + 2I_2 \longrightarrow N_2 + 4H^+ + 4I^-$	$N_2H_4 = 2I_2 \equiv 4I$ Eq.wt. of $N_2H_4 = M/4$

Ex.-43 The sulphur content of a steel sample is determined by converting it to H_2S gas, absorbing the H_2S in 10 mL of 0.005 M I_2 and then back titrating the excess I_2 with 0.002 M $Na_2S_2O_3$. If 10 mL $Na_2S_2O_3$ is required for the titration, how many milligrams of sulphur are contained in the sample? **Reactions :**

$$H_2S + I_2 \longrightarrow S + 2I^- + 2H^-$$

$$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$$

Sol. Used millimoles of $I_2 = (m.moles of I_2 taken initially)$

$$\frac{\text{m.moles of hypo used}}{2}$$

$$= 0.005 \times 10 - 0.002 \times \frac{10}{2}$$

= 0.04 = millimoles of H₂S

:. weight of sulphur = $0.04 \times 10^{-3} \times 32 \times 10^{3}$ mg = 1.28 mg.

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 : (H₂O₂→ H₂O)
 (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 : (H₂O₂ → O₂)
 (a) Acidic medium :

$$H_2O_2 \longrightarrow O_2 + 2H^+ + 2e^-$$

v.f=2

$$2OH^- + H_2O_2 \longrightarrow O_2 + 2H_2O + 2e^-$$

v.f=2

Note : Valency factor of H₂O₂ is always equal to 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 $\frac{1}{2} \times 22.4 \text{ L } O_2 \text{ at STP}$
= 34g = 11.2 L O_2 \text{ at STP}

To obtain 11.2 litre O_2 at STP, at least 34 g H_2O_2 must be decomposed.

For 20 L O₂, we should decompose at least $\frac{34}{11.2} \times 20$ g H₂O₂

. 1 L solution of
$$H_2O_2$$
 contains $\frac{34}{11.2} \times 20 \text{ g H}_2O_2$

$$1 \text{ L solution of H}_2\text{O}_2 \text{ contains } \frac{34}{11.2} \times \frac{20}{17}$$

equivalents of H_2O_2 ($E_{H_2O_2} = \frac{M}{2} = \frac{34}{2} = 17$)

Normality of $H_2O_2 = \frac{34}{11.2} \times \frac{20}{17} = \frac{20}{5.6}$

• Normality of $H_2O_2(N) =$ <u>Volume strength of H_2O_2 </u> 5.6

$$\label{eq:MH2O2} \cdots \ \ M_{H_2O_2} = \frac{N_{H_2O_2}}{v.f.} = \frac{N_{H_2O_2}}{2}$$

• Molarity of $H_2O_2(M) =$ <u>Volume strength of H_2O_2 </u> 11.2

> Strength (in g/L) : Denoted by S Strength = Molarity \times Mol. wt = Molarity \times 34 Strength = Normality \times Eq. weight = Normality \times 17

Ex.-44 20 mL of H_2O_2 after acidification with dilute H_2SO_4 required 30 mL of $\frac{N}{12}$ KMnO₄ for complete oxidation. Final the strength of H_2O_2 solution. [Molar mass of $H_2O_2 = 34$]

Sol. meq. of $KMnO_4 = meq.$ of H_2O_2

$$30 \times \frac{1}{12} = 20 \times N'$$

N' = $\frac{30}{12 \times 20} = \frac{1}{8}N$

 \therefore strength = N' × equivalent mass = $\frac{1}{8}$ × 17

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:
 - $2\text{HCO}_{3}^{-} \longrightarrow \text{H}_{2}\text{O} + \text{CO}_{2} + \text{CO}_{3}^{2-} \text{ or}$ By Slaked lime : $Ca(\text{HCO}_{3})_{2} + Ca(\text{OH})_{2} \longrightarrow CaCO_{3} + 2\text{H}_{2}\text{O}$ $Ca^{2+} + CO_{3}^{2-} \longrightarrow CaCO_{3}$
- (b) By Washing Soda :

$$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 + 2NaCl_3$$

- (c) By ion exchange resins : $Na_{2}R + Ca^{2+} \longrightarrow CaR + 2Na^{+}$
- (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.

Hardness in ppm =
$$\frac{\text{mass of CaCO}_3}{\text{Total mass of solution}} \times 10^6$$

- *Ex.-45* 0.00012% MgSO₄ and 0.000111% CaCl₂ 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

MgSO₄ = 0.00012g =
$$\frac{0.00012}{120}$$
 mole

 $CaCl_2 = 0.000111g = \frac{0.000111}{111}$ mole ∴ equivalent moles of $CaCO_3 =$

$$\left(\frac{0.00012}{120} + \frac{0.000111}{111}\right)$$
mole

$$\therefore$$
 mass of CaCO₃

$$= \left(\frac{0.00012}{120} + \frac{0.000111}{111}\right) \times 100$$

$$= 2 \times 10^{-4} \text{ g}$$

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 Required Na₂CO₃ for 100g of water

$$= \left(\frac{0.00012}{120} + \frac{0.000111}{111}\right)$$
mole

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

: Required Na₂CO₃ for 1000 litre water

$$= \frac{2 \times 10^{-6}}{100} \times 10^{6} = \frac{2}{100} \text{ mole} \qquad (\because d = 1 \text{g/mL})$$
$$= \frac{20}{1000} \text{ mole} = 20 \text{ m mole}$$

STRENGTH OF OLEUM

Oleum is SO₃ 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 SO₃ in the oleum to give 100% sulphuric acid.

Hence, weight % of free SO₃ in oleum = 80(y-100)/18

Solved Examples

- *Ex.-46* 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 × 98 = 8.09 g. Total water needed = 1402 + 8.09 = 1410.09 g = 1410.09 mL

CALCULATION OF AVAILABLE CHLORINE FROM A SAMPLE OF BLEACHING POWDER

The weight of available Cl_2 released from the given sample of bleaching powder on reaction with dilute acids or CO_2 is called available chlorine.

$$CaOCI_2 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + CI_2$$

$$CaOCl_2 + 2HCl \longrightarrow CaCl_2 + H_2O + Cl_2$$

$$Ca(CH_{3}COO)_{2} + H_{2}O + Cl_{2}$$

 $\text{CaOCl}_2 + \text{CO}_2 \longrightarrow \text{CaCO}_3 + \text{Cl}_2$

Method of determination :

$$CaOCl_{2} + 2CH_{3}COOH$$

$$\longrightarrow Ca(CH_{3}COO)_{2} + H_{2}O + Cl_{2}$$
(Sample of bleaching powder)

(Sample of bleaching powder)

$$\begin{array}{rcl} Cl_2 + 2KI & \longrightarrow & 2KCl + I_2 \\ I_2 & + & & 2Na_2S_2O_3 \\ & & & & \underbrace{ & & \\ \text{Starch as indicator} & Na_2S_4O_6 + 2Nal \\ \text{v.f.} = 2 & & & \text{v.f.} = 1 \end{array}$$

End point is indicated by disappearance of blue colour.

Let

$$M = Molarity of hypo (Na_2S_2O_3) solution$$

 \therefore millimoles of Cl₂ produced = m.moles of I₂ used by

hypo $= \frac{M \times V}{2}$ where V = vol of hypo solution used in ml.

mass of Cl₂ produced =
$$\frac{M \times V \times 10^{-3}}{2} \times 71$$

= 35.5 × M × V × 10⁻³

: % of available chlorine = $\frac{35.5 \times M \times V \times 10^{-3}}{W} \times 100$

where W = amount of belaching powder taken in g.

or % of available
$$Cl_2 = \frac{3.55 \times M \times V}{W}$$

Solved Examples

Ex.-47 3.55 g sample of bleaching powder suspended in H_2O was treated with enough acetic acid and KI solution. Iodine thus liberated required 80 mL of 0.2 M hypo for titration. Calculate the % of available chlorine.

Sol. % of
$$Cl_2 = \frac{3.55 \times 0.2 \times 80}{3.55} = 16\%$$