Stoichiometry

C1 In this chapter we will discuss the calculations based on chemical equations. It has been classified into two parts :

1. Mole Concept
2. Equivalent Concept

C2 **MOLE CONCEPT :**

In mole concept we deal with different types of relations like weight-weight, weight-volume, or volume-volume relationship between reactants or products of the reaction.

Mole concept is based on balanced chemical chemical reaction. Some basic definitions used in mole concept are as follows :

Limiting Reagent : A reagent which is consumed completely during the chemical reaction.

$$\text{Number of moles of a substance(n)} = \frac{\text{weight of substance}}{\text{atomic or molecular weight}}$$

Also, $$\text{Number of moles of a substance(n)} = \frac{\text{Given number of molecules}}{\text{Avogadro number}}$$

In gas phase reaction number of moles of a gas $(n) = \dfrac{PV}{RT}$,

At STP/NTP one mole of any gas contains 22.4 L i.e. at 273 K and 1 atm pressure.

In aq. solution **n = MV [M - molarity, V - volume of solution]**

Practice Problems :

1. **Chlorine can be produced by reacting H_2SO_4 acid with a mixture of MnO_2 and NaCl. The reactions follows the equation : $2NaCl + MnO_2 + 3H_2SO_4 \rightarrow 2NaHSO_4 + MnSO_4 + Cl_2 + H_2O$ what volume of chlorine at STP can be produced from 100 g of NaCl ? (At. wt. Na = 23, Cl = 35.5)**

    (a) **19.15 lt**   (b) **30 lt**   (c) **29 lt**   (d) **5 lt**

2. **A solution contains 5 g of KOH was poured into a solution containing 6.8 g of $AlCl_3$, find the mass of precipitate formed [At. wt. : H-1, Al-27, Cl-35.5, K-39]**

    (a) **2.3 g**   (b) **23 g**   (c) **32 g**   (d) **0.32 g**

    [Answers : (1) a (2) a]

C3 **DIFFERENT WAYS OF EXPRESSING THE CONCENTRATION TERMS :**

Important Definitions :

$$\text{mass percent} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100$$

$$\text{Molarity(M)} = \frac{\text{No. of moles of solute}}{\text{Vol. of solution in L}}, \text{ unit of molarity are mol/lit., M or molar.}$$

$$\text{Normality(N)} = \frac{\text{No. of gramequivalents of solute}}{\text{Vol. of solution in L}}, \text{ unit of normality are g-eq./lit., N or normal.}$$

$$\text{Molality(m)} = \frac{\text{No. of moles of solute}}{\text{wt. of solvent}}, \text{ unit of molality are mol/kg, m or molal.}$$

$$\text{Mole fraction}(x_A) = \frac{n_A}{n_A + n_B} \cdot$$

$$\text{ppm} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 10^6$$

$$\text{No. of gram equivalents of solute}(n_{eq}) = \frac{\text{Weight of solute}}{\text{Equivalent weight}}$$

$$\text{Equivalent weight} = \frac{\text{Molecular weight (or) Atomic weight (or) Ionic weight}}{n \text{ factor}}$$

The relation between different concentration terms :

1. $n_{eq} = n_{mol} \times$ n-factor
2. n_{eq} = Normality $\times$ Volume (L)
3. Number of moles(n_{mol}) = Molarity $\times$ Volume (L)
4. Normality = Molarity $\times$ n-factor

5. $$M = \frac{10xd}{M'}$$
6. $$m = \frac{M \times 1000}{1000d - MM'}$$

7. $$m = \frac{x_B \times 1000}{(1 - x_B)M_A}$$

(d $\rightarrow$ density of solution in g/ml, $M' \rightarrow$ molar mass of solute, x_B and x_A are mole fraction of solute and solvent respectively, $M_A \rightarrow$ molar mass of solvent)

Calculation of 'n' Factor for Different Compounds :

1. Acids : n = basicity

   H_3PO_4 n = 3 H_3PO_3 n = 2

   H_3PO_2 n = 1 H_3BO_3 n = 1

2. Bases : n = acidity of base

   e.g. Ammonia and all amines are monoacidic bases,

   NaOH(n = 1), Na_2CO_3(aq) n = 2, $NaHCO_3$(n = 1)

3. Salt : (Which does not undergo redox reactions)

   n factor = Total cationic or anionic charge, e.g. Na_3PO_4 n = 3, $Ba_3(PO_4)_2$ n = 6

4. Oxidizing Agents or Reducing Agents : 'n' factor = change in oxidation number Or number of electron lost or gained from one mole of the compound.

C4   EQUIVALENT CONCEPT

It is based on law of equivalence which is explained as follows :

Law of chemical equivalents : In a chemical reaction the equivalents of all the species (reactants or products) are equal to each other provided none of these compounds is in excess.

$N_1V_1 = N_2V_2$ (when normalities and volumes are given).

If the number of equivalence of both the reactants are different then reactant with the lesser number of equivalence will be the **limiting reagent**.

Application of equivalent concept : It is used in acid base titration, back titration and double titration, similarly in redox titration. Equivalent concepts can be used on all reaction whether they are balanced or not balanced but mole concept is used in solving the problems when the reactions are balanced.

Basic principles of tirations :

In voltmetric analysis, a given amount (weight or volume) of an unknown substance is allowed to react with a known volume of a standard solution slowly. A chemical reaction takes place between the solute of an unknown substance and the solute of the standard solution. The completion of the reaction is indicated by the end point of the reaction, which is observed by the colour change either due to the indicator or due to the solute itself. Whether the reactions during the analysis are either between an acid and or base or between O.A. and R.A., the law of equivalence is used at end point.

Following are the different important points regarding this process :

(i)   In case of acid base titration at the equivalence point

          (n_{eq})acid = (n_{eq})base

(ii)   In case of redox titration

          (n_{eq})oxidant = (n_{eq})reductant

(iii)   If a given volume of solution is diluted then number of moles or number of equivalence of solute remains same but molarity or normality of the solution decreases.

(iv)   If a mixture contains more than one acids and is allowed to react completely with the base then at the equivalence point, (n_{eq}) acid$_1$ + (neq) acid$_2$ + ... = (n_{eq}) base

(v)   Similarly if a mixture contains more than one oxidising agents then at equivalence point,

(n_{eq}) O.A$_1$ + (n_{eq}) O.A$_2$ +... = (n_{eq}) reducing agent.

(vi)   If it is a difficute to solve the problem through equivalence concept then use the mole concept.

Back titration :

This is a method in which a substance is taken in excess and some part of its has to react with another substance and the remaining part has to be titrated against standard reagent.

Double titration :

This is a titration of specific compound using different indicators. Let us consider a solid mixture of NaOH, Na$_2$CO$_3$ and inert impurities.

When the solution containing NaOH and Na$_2$CO$_3$ is titrated using phenolphalein indicator following reaction takes place at the phenolphthalein end point –

NaOH + HCl $\rightarrow$ NaCl + H$_2$O

Na$_2$CO$_3$ + HCl $\rightarrow$ NaHCO$_3$ + H$_2$O
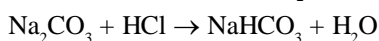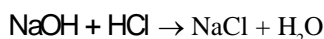
Here, eq. of $\mathbf{NaOH + \dfrac{1}{2} eq.\,of\, Na_2CO_3 = eq.\,of\,HCl}$
$_{(n=2)}$

When methyl orange is used, Na$_2$CO$_3$ is converted into NaCl + CO$_2$ + H$_2$O

Hence, eq. of NaOH + eq. of $\mathbf{Na_2CO_3}$ = eq. of HCl
$_{(n=2)}$

TITRATION OF MIXTURE OF BASES WITH TWO INDICATORS

Every indicator has a working range

Indicator	pH range	Behaving as
Phenolphthalein	8 — 10	weak organic acid
Methyl orange	3 — 4.4	weak organic base

Thus methyl orange with lower pH range can indicate complete neutralisation of all types of bases. Extent of reaction of different bases with acid (HCl) using these two indicators summarised below

	Phenolphthalein	**Methyl Orange**
NaOH	100% reaction is indicated NaOH + HCl $\rightarrow$ NaCl + H$_2$O	100 % reaction is indicated NaOH + HCl $\rightarrow$ NaCl + H$_2$O
Na$_2$CO$_3$	50% reaction upto NaHCO$_3$ stage is indicated Na$_2$CO$_3$ + HCl $\rightarrow$ NaHCO$_3$ + NaCl	100% reaction is indicated Na$_2$CO$_3$ + 2HCl $\rightarrow$ 2NaCl + H$_2$O + CO$_2$
NaHCO$_3$	No reaction is indicated	NaHCO$_3$ + HCl $\rightarrow$ NaCl + H$_2$O + CO$_2$ 100% reaction is indicated

	Species	Changed to	Reactions	Electron exchanged or change in O.N.	Eq. wt.
1.	MnO_4^- (O.A.)	Mn^{2+} in acidic medium	$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	5	$E = \dfrac{M}{5}$
2.	MnO_4^- (O.A.)	MnO_2 in basic medium	$MnO_4^- + 3e^- + 2H_2O \rightarrow MnO_2 + 4OH^-$	3	$E = \dfrac{M}{3}$
3.	MnO_4^- (O.A.)	MnO_4^{2-} in neutral medium	$MnO_4^- + e^- + 2H_2O \rightarrow MnO_2^{2-}$	1	$E = \dfrac{M}{1}$
4.	$Cr_2O_7^{2-}$ (O.A.)	Cr^{3+} in acidic medium	$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	6	$E = \dfrac{M}{6}$
5.	MnO_2 (O.A.)	Mn^{2+} in acidic medium	$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	2	$E = \dfrac{M}{2}$
6.	Cl_2 (O.A.) (in bleaching powder)	Cl^-	$Cl_2 + 2e^- \rightarrow 2Cl^-$	2	$E = \dfrac{M}{2}$
7.	$CuSO_4$ (O.A.) (in iodometric titration)	Cu^+	$Cu^{2+} + e^- \rightarrow Cu^+$	1	$E = \dfrac{M}{1}$
8.	$S_2O_3^{2-}$ (R.A.)	$S_4O_6^{2-}$	$2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^-$	2 (for two molecules)	$E = \dfrac{M}{5} = M$
9.	H_2O_2 (O.A.)	H_2O	$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	2	$E = \dfrac{M}{2}$
10.	H_2O_2 (R.A.)	O_2	$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$ (O.N. of oxygen in H_2O_2 is (–1) per atom)	2	$E = \dfrac{M}{2}$
11.	Fe^{2+} (R.A.)	Fe^{3+}	$Fe^{2+} \rightarrow Fe^{3+} + e^-$	1	$E = \dfrac{M}{1}$

	Estimation of	Reaction	Relation between O.A. and R.A.
1.	I_2	$I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6^{2-}$ $I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$	$I_2 \equiv 2I^- \equiv 2Na_2S_2O_3$ Eq. wt. $(Na_2S_2O_3) = E = \dfrac{M}{1}$
2.	$CuSO_4$	$2CuSO_4 + 4KI \rightarrow Cu_2I_2 + 2K_2SO_4 + I_2$ or $2Cu^{2+} + 4I^- \rightarrow Cu_2I_2 + I_2$ white ppt.	$2CuSO_4 \equiv I_2 \equiv 2Na_2S_2O_3$ Eq. wt. of $CuSO_4 = \dfrac{M}{1}$
3.	$CaOCl_2$	$CaOCl_2 + H_2O \rightarrow Ca(OH)_2 + Cl_2$ $Cl_2 + 2KI \rightarrow 2KCl + I_2$ $Cl_2 + 2I^- \rightarrow 2Cl^- + I_2$	$CaOCl_2 \equiv Cl_2 \equiv I_2 \equiv 2I^- \equiv 2Na_2S_2O_3$ Eq. wt. of $CaOCl_2 = \dfrac{M}{2}$
4.	MnO_2	$MnO_2 + 4HCl$ (conc.) $\xrightarrow{\Delta}$ $MnCl_2 + Cl_2 + 2H_2O$ $Cl_2 + 2KI \rightarrow 2KCl + I_2$ or $MnO_2 + 4H^+ + 2Cl^- \rightarrow Mn^{2+} + 2H_2O + Cl_2$ $Cl_2 + 2I^- \rightarrow I_2 + 2Cl^-$	$MnO_2 \equiv Cl_2 \equiv I_2 \equiv 2I^- \equiv 2Na_2S_2O_3$ Eq. wt. of $MnO_2 = \dfrac{M}{2}$
5.	IO_3^-	$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$	$IO_3^- \equiv 3I_2 \equiv 6I \equiv 6Na_2S_2O_3$ Eq. wt. $IO_3^- = \dfrac{M}{6}$

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6.	H_2O_2	$H_2O_2 + 2I^- + 2H^+ \rightarrow I_2 + 2H_2O$	$H_2O_2 \equiv I_2 \equiv 2I^- \equiv 2Na_2S_2O_3$ Eq. wt. $H_2O_2 = \dfrac{M}{2}$
7.	Cl_2	$Cl_2 + 2I^- \rightarrow 2Cl^- + I_2$	$Cl_2 \equiv I_2 \equiv 2I^- \equiv 2Na_2S_2O_3$ Eq. wt. of $Cl_2 = \dfrac{M}{2}$
8.	O_3	$O_3 + 6I^- + 6H^+ \rightarrow 3I_2 + 3H_2O + O_2$	$O_3 \equiv 3I_2$ Eq. wt. of $O_3 = \dfrac{M}{2}$
9.	ClO^-	$ClO^- + 2I^- + 2H^+ \rightarrow H_2O + Cl^- + I_2$	$ClO^- \equiv I_2 \equiv 2I \equiv 2Na_2S_2O_3$ Eq. wt. of $ClO^- = \dfrac{M}{2}$
10.	$Cr_2O_7^{2-}$	$Cr_2O_7^{2-} + 14H^+ + 6I^- \rightarrow 3I_2 + 2Cr^{3+} + 7H_2O$	$Cr_2O_7^{2-} \equiv 3I_2 \equiv 6I^-$ Eq. wt. of $Cr_2O_7^{2-} = \dfrac{M}{6}$

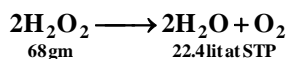**Practice Problems :**

1. [Na^+] in a solution prepared by mixing 30.00 mL of 0.12 M NaCl with 70 mL of 0.15 M Na_2SO_4 is
   (a)   0.135 M   (b)   0.141 M   (c)   0.210 M   (d)   0.246 M

2. The equivalent mass of $MnSO_4$ is half of its molar mass when it is converted to
   (a) Mn_2O_3 (b) MnO_2 (c) MnO_4^- (d) MnO_4^{2-}

3. The anion nitrate can be converted into ammonium ion. The equivalent mass of NO_3^- ion in this reaction would be
   (a)   6.20 g   (b)   7.75 g   (c)   10.5 g   (d)   21.0 g

4. When BrO_3^- ion reacts with Br^- ion in acid solution Br_2 is liberated. The equivalent weight of $KBrO_3$ in this reaction is
   (a)   M/8   (b)   M/3   (c)   M/5   (d)   M/6

5. The number of moles of $KMnO_4$ that will be needed to react completely with one mole of ferrous oxalate in acidic solution is
   (a)   3/5   (b)   2/5   (c)   4/5   (d)   1

6. 5 ml of N-HCl, 20 ml of $N/2$-H_2SO_4 and 30 ml of $N/3$ – HNO_3 are mixed together and the volume made to 1 litre.
   (i)   The normality of the resulting solution is
   (a)   N/5   (b)   N/10   (c)   N/20   (d)   N/40
   (d)
   (ii)   The wt. of pure NaOH required to neutralize the above solution is
   (a)   10 g   (b)   2 g   (c)   1 g   (d)   2.5 g

7. 0.7 g of a sample of $Na_2CO_3.xH_2O$ were dissolved in water and the volume was made to 100 ml, 20 ml of this solution required 19.8 ml of N/10 HCl for complete neutralization. The value of x is
   (a)   7   (b)   3   (c)   2   (d)   5

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8. 100 mL of 1 M $KMnO_4$ oxidised 100 mL of H_2O_2 in acidic medium (when MnO_4^- is reduced to Mn^{2+}); volume of same $KMnO_4$ required to oxidise 100 mL of H_2O_2 in basic medium (when MnO_4^- is reduced to MnO_2) will be

(a) $\dfrac{100}{3}$ mL   (b) $\dfrac{500}{3}$ mL   (c) $\dfrac{300}{3}$ mL   (d) 100 mL

9. 100 mL of a mixture of NaOH and Na_2SO_4 is neutralised by 100 mL of 0.5 M H_2SO_4. Hence amount of NaOH in 100 mL mixture is

(a) 0.2 g   (b) 0.4 g   (c) 0.6 g   (d) 1.0 g

10. 3 mol of a mixture of $FeSO_4$ and $Fe_2(SO_4)_3$ required 100 mL of 2 M $KMnO_4$ solution is acidic medium. Hence mol fraction of $FeSO_4$ in the mixture is

(a) $\dfrac{1}{3}$ (b) $\dfrac{2}{3}$ (c) $\dfrac{2}{5}$ (d) $\dfrac{3}{5}$

11. 5.3 g of M_2CO_3 is dissolved in 150 mL of 1 N HCl. Unused acid required 100 mL of 0.5 N NaOH. Hence equivalent weight of M is

(a) 23   (b) 12   (c) 24   (d) 13

[Answers : (1) d (2) b (3) b (4) c (5) a (6) (i) d (ii) c (7) c (8) b (9) b (10) a (11) a]

C5   VOLUME STRENGTH OF H_2O_2

x volume of H_2O_2 means x litre of O_2 is liberated by 1 volume of H_2O_2 on decomposition

$$\underset{68\,gm}{2H_2O_2} \longrightarrow 2H_2O + \underset{22.4\,lit\,at\,STP}{O_2}$$

Volume strength of H_2O_2 solution = $N \times 5.6$...... (where N is the normality of the H_2O_2 solution

Practice Problems :

1. (a) Calculate the strength of '20 V' of H_2O_2 in terms of :

     (i) normality (ii) grams per litre (iii) molarity and (iv) percentage

(b) Calculate the volume strength of 2.0 N H_2O_2 solution.

2. In a 50 ml solution of H_2O_2 an excess of KI and dilute H_2SO_4 were added. The I_2 so liberated required 20 ml of 0.1 N $Na_2S_2O_3$ for complete reaction. Calculate the strength of H_2O_2 in grams per litre.

[Answers : (a) (i) 3.58 N (ii) 60.86 g/lit. (iii) 1.79 M (iv) 6.086% (W/V) (b) 11.2 V (2) 0.68 g/litre]