### Section (A) : Classical Concept of Equivalent weight / Mass, Equivalent weight, n-factor and Normality for Acid, Base and Precipitate

### 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. 
$$2Mg + O_2 \longrightarrow 2MgO$$
  
 $48 g \quad 32 g$   
 $12 g \quad 8 g$   
 $\therefore \quad 32 g \text{ of } O_2 \text{ reacts with } 48 g \text{ of } Mg$   
 $\therefore \quad 8 g \text{ of } O_2 = \frac{48 \times 8}{32} = 12 g$   
 $\therefore \quad \text{Equivalent weight of } Mg = 12$   
Similarly,  $Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$   
 $65.5 g \quad 32.75$   
 $\therefore \quad \text{Equivalent weight of } Zn = \frac{65.5}{2} = 32.75 g$   
 $Al \quad + \quad \frac{3}{2} Cl_2 \longrightarrow AlCl_3$   
 $27 g \quad \frac{3}{2} \times 71 g$ 

$$\therefore \qquad 35.5 \text{ chlorine reacts with} = \frac{27 \times 35.5}{111.5} 9.0 \text{ g of Al}$$

$$\therefore$$
 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 in the above three cases is their respective valencies.

### Equivalent weight (E) :

In general, Eq. wt. (E) =  $\frac{\text{Atomic weight or Molecular weight}}{\text{valency factor(v.f)}} = \frac{\text{Mol. wt.}}{n - \text{factor}} = \frac{M}{x}$ 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 a substance may have different values under different conditions.
- There is 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<sup>+</sup> ions per acid molecule.

Lyuiv				
	— Solved Examples ———			
Ex1	HCI, H <sub>2</sub> SO <sub>4</sub> H <sub>3</sub> PO <sub>4</sub> H <sub>3</sub> PO <sub>3</sub> $\begin{bmatrix} \ddots & O \\ H \\ - & O - P - H \\ - & I \\ - &$			
Sol.	Valency factor $\rightarrow$ 1 2 3 2 $\uparrow$ $\uparrow$			
	$\begin{array}{cccc} & (Assume 100\% \ dissicolation) \\ \mbox{Eq. wt. (E)} & \rightarrow & M/1 & M/2 & M/3 & M/2 \\ \mbox{O} & Replaceable hydrogen atoms are those hydrogen atoms which are attached with the atoms of group VI and group VII i.e. O, S, Se, Te & F, Cl, Br, I. \end{array}$			
•	For Bases : Valency factor = number of replacable OH <sup>-</sup> ions per base molecule.			
	Solved Examples			
Ex-2. Sol.	$\begin{array}{cccc} & NaOH, & KOH \\ v.f. \rightarrow & 1 & 1 \\ Eq. wt. \rightarrow & M/1 & M/1 \\ O & Bases may be defined as the substances in which OH group is/are directly attached with group I elements (Li,Na, K,Rb,Cs), group II elements (Be, Mg,Ca,Ba) or group III elements (AI, Ga,In,TI) transition metals, non-metallic cations like PH4+, NH4+ etc. \end{array}$			
•	<ul> <li>Acid-base reaction :</li> <li>In case of acid base reaction, the valence factor is the actual number of H<sup>+</sup> or OH<sup>-</sup> replaced in the reaction. The acid or base may contain more number of replaceble H<sup>+</sup> or OH<sup>-</sup> than actually replaced in reaction.</li> <li>v. f. for base is the number of H<sup>+</sup> ion from the acid replaced by each molecule of the base.</li> </ul>			
Fx-3				
Sol.	Base Acid Valency factor of base = 1 Here, two molecule of NaOH replaced 2H <sup>+</sup> ion from the H <sub>2</sub> SO <sub>4</sub> . Therefore, each molecule of NaOH replaced only one H <sup>+</sup> ion of acid, so v.f. = 1.			
О	<b>v. f.</b> for acid is the number of $OH^-$ replaced from the base by each molecule of acid.			
	Solved Examples			
Ex-4.	$NaOH + H_2SO_4 \longrightarrow NaHSO_4 + H_2O$			
Sol.	Base Acid Valency factor of acid = 1 Here, one of molecule of H <sub>2</sub> SO <sub>4</sub> replaced one OH <sup>-</sup> from NaOH. Therefore, valency factor for H <sub>2</sub> SO <sub>4</sub> is one			
	$\therefore \qquad \text{Eq. wt. of } H_2 \text{SO}_4 = \frac{\text{Horizon}}{1}$			

Salts :

(a) In non-reacting condition
 Valency factor = Total number of positive charge or negative charge present in the compound.

Equiv	valent Concept & Titration		
	— Solved Examples ———		
Ex-5.	Na <sub>2</sub> CO <sub>3</sub> , Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> , FeSO <sub>4</sub> .7H <sub>2</sub> O		
501.	V.I. 2 2×3=6 2 Eq.wt. M/2 M/6 M/2		
	Note : In case of hydrated salt, positive/negative charge of water molecule is not counted.		
	(b) In reacting condition		
	— Solved Examples ———		
Ex-6.	$Na_2CO_3 + HCI \longrightarrow NaHCO_3 + NaCI$		
Sol.	It is an acid base reaction, therefore valency factor for Na <sub>2</sub> CO <sub>3</sub> is one while in non-reacting condition, it will be two.		
Secti	on (B) : Equivalent weight, n-factor and Normality for Oxidant and Reductant (c) Equivalent weight of oxidising / reducing agents in a redox reaction In case of redox change , v.f. = Total change in oxidation number per molecule .		
	— Solved Examples ———		
Ex-7 Sol.	KMnO <sub>4</sub> + H <sub>2</sub> O <sub>2</sub> $\longrightarrow$ Mn <sup>2+</sup> + O <sub>2</sub> Mn in KMnO <sub>4</sub> is going from +7 to +2, so change in exidation number per molecule of KMnO <sub>4</sub> is 5. So the		
valency factor of KMnO <sub>4</sub> 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 = $\frac{W}{E}$ VmL of solution contain $\frac{W}{E}$ equivalents of solute $\therefore$ 1000 mL solution will contain $\frac{W \times 1000}{E \times V}$ equivalents of solute.		
•	Normality (N) = $\frac{W \times 1000}{W \times 1000}$		
•	Relations between Normality and Molarity : Normality (N) = Molarity x Valency factor or $N \times V$ (in mL) = M x V (in mL) x n or milliequivalents = millimoles x n		
	Solved Examples		
Ex-8. So.	Calculate the normality of a solution containing 15.8 g of KMnO <sub>4</sub> in 50 mL acidic solution. Normality (N) = $\frac{W \times 1000}{E \times V}$		
	Here $W = 15.8 \text{ g}$ , $V = 50 \text{ mL}$ $E = \frac{\text{molar mass of KMnO}_4}{\text{Valency factor}} = 158/5 = 31.6$		
<b>F ^</b>	So, normality = $10 \text{ N}$		
Ex-9. Sol.	Calculate the normality of a solution containing 50 mL of 5 M solution of $K_2Cr_2O_7$ in acidic medium. Normality (N) = Molarity × valency factor = 5 x 6 = 30 N		
Secti	on (C) : Equivalent Concept for Acid Base Titration and Precipitation Reactions		

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.

Equivalent Concept & Titration / Accordingly (i)  $aA + bB \rightarrow mM + nN$ ; (ii) In a compound M<sub>2</sub>N<sub>2</sub>: meg of A = meg of B = meg of M = m.eg. of N (ii) In a compound  $M_x N_y$ ; meg of  $M_x N_y =$  meg of M = meg of N Solved Examples — **Ex-10.** Find the number of moles of KMnO<sub>4</sub> needed to oxidise one mole Cu<sub>2</sub>S in acidic medium. The reaction is KMnO<sub>4</sub> + Cu<sub>2</sub>S  $\longrightarrow$  Mn<sup>2+</sup> + Cu<sup>2+</sup> + SO<sub>2</sub> Sol. From law of equivalence, equivalents of  $Cu_2S$  = equivalents of KMnO<sub>4</sub> moles of  $Cu_2S \times v.f. =$  moles of kMnO<sub>4</sub> × v.f.  $1 \times 8 = \text{moles of KMnO}_4 \times 5$ moles of KMnO<sub>4</sub> = 8/5  $\Rightarrow$ (∴ v.f. of  $Cu_2S = 2(2-1) + 1(4 - (-2))) = 8$  and v.f. of KMnO<sub>4</sub> = 1(7 - 2) = 5) **Ex-11.** The number of moles of oxalate ions oxidized by one mole of MnO<sub>4</sub><sup>-</sup> ion in acidic medium are : (A)  $\frac{5}{2}$  (B)  $\frac{2}{5}$ Equivalents of C<sub>2</sub>O<sub>4</sub><sup>2-</sup> = equivalents of MnO<sub>4</sub><sup>-</sup> (C)  $\frac{3}{5}$ (D)  $\frac{5}{3}$ Sol.  $x(mole) \times 2 = 1 \times 5$ ( $\therefore$  v.f. of C<sub>2</sub>O<sub>4</sub><sup>2-</sup> = 2 (4 - 3) = 2 and v.f. of MnO<sub>4</sub><sup>-</sup> = 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.  $5e^- + 8H^+ + MnO_4^- \longrightarrow Mn^{2+} + 2H_2O$   $\therefore$  Eq.wt of  $MnO_4^- = \frac{Mol. wt. of MnO_4^-}{5}$ e.g.  $3e^- + 2H_2O + MnO_4^- \longrightarrow MnO_2 + 4OH^-$  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 0.1mol KMnO<sub>4</sub> 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 KMnO<sub>4</sub> participates. e.g. if KMnO<sub>4</sub> forms  $Mn^{2+}$ , normality = 0.1 x 5 = 0.5 N. This *same* sample of KMnO<sub>4</sub>, if employed in a reaction giving MnO<sub>2</sub> as product (Mn in +4 state), will have normality 0.1 x 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, KIO<sub>3</sub> reacts with KI to liberate iodine and liberated lodine is titrated with standard hypo solution. The reactions are :
  - (i)  $IO_3^- + I^- \longrightarrow I_2$  (ii)  $I_2 + S_2O_3^{2-}$ 
    - meq of hypo = meq of  $I_2$  = meq of  $IO_3^-$  = meq of  $I^-$
- (ii)  $I_2 + S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + I^-$ 
  - $\therefore$  meq of hypo = meq of IO<sub>3</sub><sup>-</sup>.
  - This is wrong. Note that  $I_2$  formed by equation (i) has v.f. = 5/3 & in equation (ii) has v.f. = 2.
  - □ 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.

# .Solved Examples –

- Ex-12 How many millilitres of 0.02 M KMnO<sub>4</sub> solution would be required to exactly titrate 25 mL of 0.2 M Fe(NO<sub>3</sub>)<sub>2</sub> solution in acidic medium ?
- Sol.Method -1 : Mole concept methodStarting with 25 mL of 0.2 M Fe2+, we can write :Millimoles of  $Fe^{2+} = 25 \times 0.2$ and in volume V (in milliliters) of the KMnO4,

Equivalent Concept & Titration 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,  $\frac{\text{m.moles of MnO}_{4}^{-}}{=} \frac{\text{m.moles of Fe}^{2+}}{\text{m.moles of Fe}^{2+}}$  $\frac{V(0.02)}{1} = \frac{(25)(0.2)}{5} \quad (\text{from (1) \& (2)})$ *.*.. V = 50 mL.*.*.. Method -2 : Equivalent Method : At the equivalence point, milliequivalents of  $MnO_4^-$  = milliequivalents of Fe<sup>2+</sup>  $M_1 \times Vf_1 \times V_1 = M_2 \times Vf_2 \times V_2$  $(\Box MnO_{4^{-}} \longrightarrow Mn^{2+}; v.f. = 5, Fe^{2+} \longrightarrow Fe^{3+}; v.f. = 1)$  $0.02 \times 5 \times V_1 = 0.2 \times 1 \times 25$  $V_1 = 50 \text{ mL}.$ *.*..

# Section (D) : Equivalent Concept for Redox reactions, KMnO<sub>4</sub> / K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> v/s Reducing Agents & their Redox Titration

### **Titrations :**

Titration is a procedure for determining the concentration of a solution by allowing its 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<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, AgNO<sub>3</sub>, CuSO<sub>4</sub>, 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, HCI, H<sub>2</sub>SO<sub>4</sub>, I<sub>2</sub>, KMnO<sub>4</sub> etc.

Titrate : Solution consisting of substance to be estimated, its 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 :

 $n_1V_1M_1 = n_2V_2M_2$ 

**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 lodometric / lodimetric titrations)

S.No.	Estimation of	By titrating with	Reactions	Relation*between OA and RA
1	Fo <sup>2+</sup>	MpO	$Fe^{2+} \longrightarrow Fe^{3+} + e^{-}$	$5Fe^{2+} \equiv MnO_4^-$
•	16	WITIO4	$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$	Eq. wt. of $Fe^{2+} = M/1$
2	Fe <sup>2+</sup>	$Cr_2O_7^{2-}$	$Fe^{2+} \longrightarrow Fe^{3+} + e^{-}$	$6Fe^{2+} \equiv Cr_2O_7^{2-}$
			$Cr_2O_7^{2-}$ + 14H <sup>+</sup> + 6e <sup>-</sup> $\longrightarrow$ 2Cr <sup>3+</sup> + 7H <sub>2</sub> O	Eq.wt. of $Cr_2O_7^{2-} = M/6$
3	$C_2O_4^{2-}$	MnO₄ <sup>−</sup>	$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$	$5C_2O_4^{2-} \equiv 2MnO_4^{-1}$
			$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$	Eq. wt. of $C_2O_4^{2-} = M/2$
Α	H <sub>2</sub> O <sub>2</sub>	MpO.=	$H_2O_2 \longrightarrow 2H^+ + O_2 + 2e^-$	$5H_2O_2 \equiv 2MnO_4^-$
4		IVINO4	$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$	Eq.wt. of $H_2O_2 = M/2$
5	As <sub>2</sub> O <sub>3</sub>	MpO -	$As_2O_3 + 5H_2O \longrightarrow 2AsO_4^{3-} + 10H^+ + 4e^-$	Eq. w/t, of $A = M/4$
		IVITIO4	$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$	$Eq. wi. 01 AS_2O_3 = 10/4$
6	AsO <sub>3</sub> <sup>3–</sup>	AsO <sub>3</sub> <sup>3-</sup> BrO <sub>3</sub> <sup>-</sup>	$AsO_3^{3-} + H_2O \longrightarrow AsO_4^{3-} + 2H^+ + 2e^-$	Eq. wt. of $AsO_3^{3-} = M/2$
			$BrO_3^- + 6H^+ + 6e^- \longrightarrow Br^- + 3H_2O$	Eq.wt. of $BrO_3^- = M/6$

#### **Permanganate Titrations :**

- KMnO<sub>4</sub> is generally used as an oxidising agent in acidic medium generally provided by dilute H<sub>2</sub>SO<sub>4</sub>.
- KMnO<sub>4</sub> works as self indicator persistent pink color is the indication of end point.
- Mainly used for estimation of  $Fe^{2+}$ , oxalic acid ,oxalates,  $H_2O_2$  etc.

Write the balanced reaction of titration of KMnO<sub>4</sub> Vs oxalic acid in presence of H<sub>2</sub>SO<sub>4</sub>. Ex-13  $2KMnO_4 + 3H_2SO_4 + 5H_2C_2O_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2$ So. Reaction :

Redox Changes :

 $C_2^{3+} \longrightarrow 2C^{4+} + 2e$ 

 $5e + Mn^{7+} \longrightarrow Mn^{2+}$ 

 $Mn^{7+}$  + 5e  $\longrightarrow Mn^{2+}$ 

 $\begin{pmatrix} \mathsf{E}_{\mathsf{H}_2\mathsf{C}_2\mathsf{O}_4} = \frac{\mathsf{M}}{2} \\ \\ \mathsf{E}_{\mathsf{K}\mathsf{M}\mathsf{n}\mathsf{O}_4} = \frac{\mathsf{M}}{5} \end{pmatrix}$ 

Indicator : KMnO<sub>4</sub> acts as self indicator.

Write the balanced reaction of titration of  $KMnO_4$  vs ferrous ammonium sulphate in presence of  $H_2SO_4$ . Ex-14 Sol.  $2KMnO_4 + 10[FeSO_4(NH_4)_2SO_4.6H_2O] + 8H_2SO_4 \longrightarrow$ Reaction :

5Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> + 10(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> + K<sub>2</sub>SO<sub>4</sub> + 2MnSO<sub>4</sub> + 68H<sub>2</sub>O  $\left(\mathsf{E}_{\mathsf{FeSO}_4} = \frac{\mathsf{M}}{\mathsf{1}}\right)$  $Fe^{2+} \longrightarrow Fe^{3+} + e$ Redox Changes :  $\left(\mathsf{E}_{\mathsf{KMnO}_4} = \frac{\mathsf{M}}{5}\right)$ 

Indicator : KMnO4 acts as self indicator

### Section (E) : Iodometric/Iodimetric Titration, Calculation of Available Chlorine from a sample of bleaching powder

Iodometric/Iodimetric Titrations :

Compound containing iodine are widely used in titrations. (i) lodide ions can be oxidised to  $I_2$  by suitable oxidising agent.  $2I^{-}(aq) \longrightarrow I_{2}(s) + 2e^{-}$ (ii) lodine (V) ions,  $IO_3^-$ , will oxidise  $I^-$  to  $I_2$ .  $IO_3^-$  (aq) + 5I<sup>-</sup> (aq) + 6H<sup>+</sup> (aq)  $\longrightarrow$  3I<sub>2</sub> (s) + 3H<sub>2</sub>O ( $\Box$ ) (iii) Thiosulphate ions,  $S_2O_3^{2-}$ , can reduce iodine to iodide ions.  $2S_2O_3^{2-}$  (ag) + I<sub>2</sub> (s)  $\longrightarrow$  S<sub>4</sub> O<sub>6</sub><sup>2-</sup> + 2I<sup>-</sup> colourless black colourless

Iodometric Titrations (Titration Solution is of Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> .5H <sub>2</sub> O)				
S.No.	Estimation of	Reaction	Relation between O.A. and R.A.	
4	T	$I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$	$I_2 \equiv 2I \equiv 2Na_2S_2O_3$	
1.	12	or $I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$	Eq.wt. of $Na_2S_2O_3 = M/1$	
		$2CuSO_4 + 4KI \longrightarrow 2CuI + 2K_2SO_4 + I_2$	$2CuSO_{4} = I_{2} = 2I = 2Na_{2}S_{2}O_{3}$	
2.	CuSO₄	or $2Cu^{2+} + 4I^- \longrightarrow 2CuI + I_2$ white ppt	Eq.wt.of CuSO <sub>4</sub> = M/1	
0		$CaOCl_2 + H_2O \longrightarrow Ca(OH)_2 + Cl_2$	$CaOCI_2 = CI_2 = I_2 = 2I = 2Na_2S_2O_3$	
3.	CaOCl <sub>2</sub>	$CI_2 + 2KI \longrightarrow 2KCI + I_2$		
		$CI_2 + 2I^- \longrightarrow 2CI^- + I_2$	Eq.wt. of $CaOCI_2 = M/2$	
		$MnO_2 + 4HCl(conc.) \xrightarrow{\Delta} MnCl_2 + Cl_2 + 2H_2O$	$MnO_2 = CI_2 = I_2 = 2Na_2S_2O_3$	
1	MpO	$CI_2 + 2KI \longrightarrow 2KCI + I_2$	Eq.wt. of $MnO_2 = M/2$	
4.		or MnO <sub>2</sub> + 4H <sup>+</sup> + 2Cl <sup>-</sup> $\longrightarrow$ Mn <sup>2+</sup> + 2H <sub>2</sub> O + Cl <sub>2</sub>		
		$Cl_2 + 2l^- \longrightarrow l_2 + 2Cl^-$		
_	IO <sub>3</sub> <sup>-</sup>		$IO_3^- \equiv 3I_2 \equiv 6I \equiv 6Na_2S_2O_3$	
5.		$1O_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$	Eq.wt. of $IO_3^- = M/6$	
6.	H <sub>2</sub> O <sub>2</sub>	$H_2O_2 + 2I^- + 2H^+ \longrightarrow I_2 + 2H_2O$	$H_2O_2 \equiv I_2 \equiv 2I \equiv 2Na_2S_2O_3$	
			Eq.wt. of $H_2O_2 = M/2$	
7	Cl <sub>2</sub>	$CI_2 + 2I^- \longrightarrow 2CI^- + I_2$	$CI_2\equiv I_2\equiv 2I\equiv 2Na_2S_2O_3$	
1.			Eq.wt. of $CI_2 = M/2$	
8.	03	$O_2 + 6I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O_1$	$O_3 \equiv 3I_2 \equiv 6I \equiv 6Na_2S_2O_3$	
<u>.</u>			Eq.wt. of $O_3 = M/6$	
9.	CIO⁻	$CIO^- + 2I^- + 2H^+ \longrightarrow H_2O + CI^- + I_2$	$CIO^{-} \equiv I_2 \equiv 2I \equiv 2Na_2S_2O_3$	
			Eq.wt. of OCI <sup>-</sup> = $M/2$	
10.	Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup> MnO <sub>4</sub> <sup>-</sup>	$Dr^{2-} \qquad Cr_2Or^{2-} + 14H^+ + 6I^- \longrightarrow 3I_2 + 2Cr^{3+} + 7H_2O$ $Dq^{-} \qquad 2MnO_4^- + 10I^- + 16H^+ \longrightarrow 2Mn^{2+} + 5I_2 + 8H_2O$	$Cf_2 O_7^{2-1} \equiv 3I_2 \equiv 6I$	
-			$Eq.WI. Of Cl_2Or^2 = W/6$	
11.			2WI104 = 512 = 101	
			$BrO_{0}^{-} = 3I_{0} = 6I$	
12.	BrO₃ <sup>−</sup>	$BrO_3^- + 6I^- + 6H^+ \longrightarrow Br^- + 3I_2 + 3H_2O$	Eq. wt. of $BrO_3^- = M/6$	
10	As(V)	$H_2AsO_4 + 2I^- + 3H^+ \longrightarrow H_3AsO_3 + H_2O + I_2$	$H_3AsO_4 \equiv I_2 \equiv 2I$	
13.			Eq.wt. of $H_3AsO_4 = M/2$	
4.4	HNO <sub>2</sub>	$2HNO_2 + 2I^- \longrightarrow I_2 + 2NO + H_2O$	$2HNO_2 \equiv I_2 \equiv 2I$	
14.			Eq.wt. of $HNO_2 = M/1$	
15	HCIO	$HCIO + 2\mathrm{I}^- + \mathrm{H}^+ \longrightarrow \mathrm{CI}^- + \mathrm{I}_2 + \mathrm{H}_2\mathrm{O}$	$HCIO = I_2 = 2Na_2S_2O_3$	
15.			Eq.wt. of HCIO = M/2	

### **Iodimetric Titrations**

S.No.	Estimation of	Reaction	Relation between O.A. and R.A.
1.	H <sub>2</sub> S (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 <sub>3</sub> <sup>2–</sup> (in acidic medium)	$SO_3^{2-} + I_2 + H_2O \longrightarrow SO_4^{2-} + 2I^- + 2H^+$	$SO_3^{2-} \equiv I_2 \equiv 2I$ Eq.wt. of $SO_3^{2-} = M/2$
3.	Sn <sup>2+</sup> (in acidic medium)	$Sn^{2+} + I_2 \longrightarrow Sn^{4+} + 2I^-$	$ \begin{aligned} Sn^{2+} &\equiv I_2 \equiv 2I \\ Eq.wt. \text{ of } Sn^{2+} = M/2 \end{aligned} $
4.	As(III) (at pH 8)	$H_2AsO_3^- + I_2 + H_2O \longrightarrow HAsO_4^{2-} + 2I^- + 3H^+$	$H_2AsO_3^- \equiv I_2 \equiv 2I$ Eq.wt. of $H_2AsO_3^- = M/2$
5.	N2H4	$N_2H_4 + 2I_2 \longrightarrow N_2 + 4H^+ + 4I^-$	$N_2H_4 = 2I_2 \equiv 4I$ Eq.wt. of $N_2H_4 = M/4$

Solved Examples

*Ex-15.* The sulphur content of a steel sample is determined by converting it to H<sub>2</sub>S gas, absorbing the H<sub>2</sub>S in 10 mL of 0.005 M I<sub>2</sub> and then back titrating the excess I<sub>2</sub> with 0.002 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. If 10 mL Na<sub>2</sub> S<sub>2</sub>O<sub>3</sub> is required for the titration, how many milligrams of sulphur are contained in the sample? **Reactions :** H<sub>2</sub>S + I<sub>2</sub>  $\longrightarrow$  S + 2I<sup>-</sup> + 2H<sup>+</sup> ; I<sub>2</sub> + 2S<sub>2</sub>O<sub>3</sub><sup>2-</sup>  $\longrightarrow$  2I<sup>-</sup> + S<sub>4</sub>O<sub>6</sub><sup>2-</sup>

**Sol.** Used millimoles of  $I_2 = (m.moles of I_2 taken initially) - \frac{m.moles of hypo used$ 

= 0.005 × 10 - 0.002 × 
$$\frac{10}{2}$$
  
= 0.04 = millimoles of H<sub>2</sub>S

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

### Calculation of available chlorine from a sample of bleaching powder :

The weight of available  $CI_2$  released from the given sample of bleaching powder on reaction with dilute acids or  $CO_2$  is called available chlorine.

 $\begin{array}{l} \mathsf{CaOCl}_2 + \mathsf{H}_2\mathsf{SO}_4 \longrightarrow \mathsf{CaSO}_4 + \mathsf{H}_2\mathsf{O} + \mathsf{Cl}_2\\ \mathsf{CaOCl}_2 + 2\mathsf{HCI} \longrightarrow \mathsf{CaCl}_2 + \mathsf{H}_2\mathsf{O} + \mathsf{Cl}_2\\ \mathsf{CaOCl}_2 + 2\mathsf{CH}_3\mathsf{COOH} \longrightarrow \mathsf{Ca}(\mathsf{CH}_3\mathsf{COO})_2 + \mathsf{H}_2\mathsf{O} + \mathsf{Cl}_2\\ \mathsf{CaOCl}_2 + \mathsf{CO}_2 \longrightarrow \mathsf{CaCO}_3 + \mathsf{Cl}_2 \end{array}$ 

### Method of determination :

 $\begin{array}{rcl} CaOCl_2 & + & 2CH_3COOH \longrightarrow Ca(CH_3COO)_2 + H_2O + Cl_2 \\ (\text{Sample of bleaching powder}) \\ Cl_2 + 2KI & \longrightarrow 2KCI + I_2 \\ I_2 & + & 2Na_2S_2O_3 \xrightarrow{\text{Starch as indicator}} Na_2S_4O_6 + 2Nal \\ \text{v.f.} = 2 & \text{v.f.} = 1 \end{array}$ 

End point is indicated by disappearance of blue colour.

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

 $\therefore$  millimoles of Cl<sub>2</sub> produced = m.moles of l<sub>2</sub> used by hypo

 $= \frac{M \times V}{2} \text{ where } V = \text{vol of hypo solution used in ml.}$ mass of Cl<sub>2</sub> produced  $= \frac{M \times V \times 10^{-3}}{2} \times 71$  $= 35.5 \times M \times V \times 10^{-3}$ % 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-16 3.55 g sample of bleaching powder suspended in H<sub>2</sub>O 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.

**So.** % of  $CI_2 = \frac{3.55 \times 0.2 \times 80}{3.55} = 16\%$ 

*.*..

### Section (F) : Volume strength of H<sub>2</sub>O<sub>2</sub>, Hardness of water Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>)

H<sub>2</sub>O<sub>2</sub> 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 :  $2e^- + 2H^+ + H_2O_2 \longrightarrow 2H_2O_2$ 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 $2OH^- + H_2O_2 \longrightarrow O_2 + 2H_2O + 2e^-$ (b) Basic medium :

Volume strength of H<sub>2</sub>O<sub>2</sub>: Strength of H<sub>2</sub>O<sub>2</sub> is represented as 10V, 20 V, 30 V etc. 20V H<sub>2</sub>O<sub>2</sub> means one litre of this sample of H<sub>2</sub>O<sub>2</sub> on decomposition gives 20L of O<sub>2</sub> gas at STP. Decomposition of H<sub>2</sub>O<sub>2</sub> is given as :

 $H_2O_2 \longrightarrow H_2O + \frac{1}{2}O_2$  $\frac{1}{2}$  × 22.4 L O<sub>2</sub> at STP 1 mole = 34g = 11

Molarity of  $H_2O_2(M) = \frac{Volume strength of H_2O_2}{Volume strength of H_2O_2}$ 

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		(PO₃ <sup>-</sup> )₃ etc.	

### **Measurement of Hardness :**

Hardness is measured in terms of ppm (parts per million) of CaCO<sub>3</sub> or equivalent to it.

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

Solved Examples Ex-17 0.00012% MgSO<sub>4</sub> and 0.000111% CaCl<sub>2</sub> 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<sub>4</sub> = 0.00012 g =  $\frac{0.00012}{120}$  mole  $CaCl_2 = 0.000111 \text{ g} = \frac{0.000111}{111} \text{ mole}$ equivalent moles of CaCO<sub>3</sub> =  $\left(\frac{0.00012}{120} + \frac{0.000111}{111}\right)$  mole *.*.. mass of CaCO<sub>3</sub> =  $\left(\frac{0.00012}{120} + \frac{0.000111}{111}\right) \times 100 = 2 \times 10^{-4} \text{ g}$ ÷. Hardness (in terms of ppm of CaCO<sub>3</sub>) =  $\frac{2 \times 10^{-4}}{100} \times 10^{6}$  = 2 ppm  $CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 + 2NaCl$  $NaSO_4 + Na_2CO_3 \longrightarrow MgCO_3 + Na_2SO_4$ Required Na<sub>2</sub>CO<sub>3</sub> for 100g of water =  $\left(\frac{0.00012}{120} + \frac{0.000111}{111}\right)$  mole ÷. = 2 × 10<sup>-6</sup> mole Required Na<sub>2</sub>CO<sub>3</sub> for 1000 litre water =  $\frac{2 \times 10^{-6}}{100} \times 10^{6} = \frac{2}{100}$  mole ( $\Box$  d = 1g/mL) ÷.  $=\frac{20}{1000}$  mole = 20 m mole

### Strength of Oleum :

Oleum is SO<sub>3</sub> dissolved in 100% H<sub>2</sub>SO<sub>4</sub>. 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<sub>3</sub> in the oleum to give 100% sulphuric acid. Hence, weight % of free SO<sub>3</sub> in oleum = 80(y - 100)/18

# Solved Examples

- **Ex-18** What volume of water is required (in mL) to prepare 1 L of 1 M solution of H<sub>2</sub>SO<sub>4</sub> (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 x 98 = 8.09 g.

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

### **MISCELLANEOUS SOLVED PROBLEMS (MSPS)**

1.	Find the valency factor for following acids			
	(i) CH₃COOH	(ii) NaH <sub>2</sub> PO <sub>4</sub>	(iii) H₃BO₃	
Ans.	(i) 1	(ii) 2	(iii) 1	
2.	Find the valency factor for following bases : (i) Ca(OH) <sub>2</sub> (ii) CsOH (iii) Al(OH) <sub>2</sub>			
Ans.	(i) 2	(ii) 1	(iii) 3	
3.	Find the valence factor for following salts : (i) $K_2SO_4$ Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> .24H <sub>2</sub> O (ii) CaCO <sub>3</sub>			
Ans.	(i) 8	(ii) 2		

Equivalent Concept & Titration Find the valency factor for following redox reactions : acidic > Mn<sup>2+</sup> neutral > MnO<sub>2</sub> (ii)  $K_2Cr_2O_7 \xrightarrow{\text{acidic}} Cr^{3+}$ (i) KMnO<sub>4</sub>alkaline → K₂MnO₄ (iii)  $C_2O_4^{2-} \longrightarrow CO_2$ (iv)  $Fe^{2+} \longrightarrow Fe^{3+}$ Ans. (i) 5, 3, 1; (ii) 6; (iii) 2 ; (iv) 1 5. Calculate the normality of a solution obtained by mixing 50 mL of 5 M solution of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and 50 mL of 2 M K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in acidic medium. Sol. v.f. of  $K_2Cr_2O_7 = 6$  $N_{f} = \frac{N_{1}V_{1} + N_{2}V_{2}}{V_{1} + V_{2}} = \frac{5 \times 6 \times 50 + 2 \times 6 \times 50}{50 + 50} = 21 N$ so 6. Calculate the normality of a solution containing 13.4 g of Sodium oxalate in 100 mL Sol. Normality =  $\frac{\text{vol. in S}}{\text{vol. of solution in litre}}$ wt. in g/eq. wt Sol. Here, eq. wt. of  $Na_2C_2O_4 = 134/2 = 67$  $N = \frac{13.4/67}{100/1000} = 2N$ so 7. The number of moles of ferrous oxalate oxidised by one mole of KMnO4 in acidic medium is : (C) 3/5 (A) 5/2 (B) 2/5 (D) 5/3 Eq. of  $FeC_2O_4 = Eq.$  of KMnO<sub>4</sub> Sol. moles of  $FeC_2O_4 \times 3 =$  moles of KMnO<sub>4</sub> × 5 moles of  $FeC_2O_4 = 5/3$  Ans. (D) SO. How many moles of KMnO<sub>4</sub> are needed to oxidise a mixture of 1 mole of each FeSO<sub>4</sub> & FeC<sub>2</sub>O<sub>4</sub> in 8. acidic medium? (A) 4/5 (D) 5/3 (B) 5/4 (C) 3/4 Sol. Eq. of  $KMnO_4 = Eq.$  of  $FeSO_4 + Eq.$  of  $FeC_2O_4$ moles of KMnO<sub>4</sub>  $\times$  5 = moles of FeSO<sub>4</sub>  $\times$  1 + moles of FeC<sub>2</sub>O<sub>4</sub>  $\times$  3  $\therefore$  moles of KMnO<sub>4</sub> = 4/5 Ans. (A) 9. A sample of hydrazine sulphate [N<sub>2</sub>H<sub>6</sub>SO<sub>4</sub>] was dissolved in 100 mL water. 10 mL of this solution was treated with excess of FeCl<sub>3</sub> Sol. Ferrous ions formed were estimated and it required 20 mL of M/50 KMnO<sub>4</sub> solution in acidic medium.  $Fe^{3+} + N_2H_4 \longrightarrow N_2 + Fe^{2+} + H^+$  $MnO_4^- + Fe^{2+} + H^+ \longrightarrow Mn^{2+} + Fe^{3+} + H_2O$ (a) Write the balanced redox reactions. (b) Estimate the amount of hydrazine sulphate in one litre of Sol.  $4Fe^{3+} + N_2H_4 \longrightarrow N_2 + 4Fe^{2+} + 4H^+$ Sol. (a) Given  $MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$ (b) In 10 mL solution, eq. of  $N_2H_6SO_4 = Eq.$  of  $Fe^{2+} = Eq.$  of KMnO<sub>4</sub>  $= 20 \times \frac{1}{50} \times 5 \times 10^{-3} = 2 \times 10^{-3}$ v.f. of  $N_2H_6SO_4 = 4$ weight of N<sub>2</sub>H<sub>6</sub>SO<sub>4</sub> in 1 L solution =  $\frac{2 \times 10^{-3} \times 1000}{4 \times 10}$  × 130 = 6.5 g. SO. 10. Write the balanced redox reaction and calculate the equivalent weight of oxidising agent and reducing agent for titration of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> Vs Ferrous ammonium sulphate. The reaction :  $6[FeSO_4(NH_4)_2SO_4.6H_2O] + K_2Cr_2O_7 + 7H_2SO_4 -$ Ans. 3Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> + Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> + K<sub>2</sub>SO<sub>4</sub> + 6(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> + 43H<sub>2</sub>O Redox changes :  $\left(\mathsf{E}_{\mathsf{FeSO}_4} = \frac{\mathsf{M}}{\mathsf{1}}\right)$ ;  $\left(\mathsf{E}_{\mathsf{K}_2\mathsf{Cr}_2\mathsf{O}_7} = \frac{\mathsf{M}}{\mathsf{6}}\right)$ 11. One litre of acidified KMnO<sub>4</sub> solution containing 15.8 g KMnO<sub>4</sub> is decolorized by passing sufficient SO<sub>2</sub>. If SO<sub>2</sub> is produced by FeS<sub>2</sub>, what is the amount of FeS<sub>2</sub> required to give desired SO<sub>2</sub>?

**Ans.** 15 g.

Sol. v.f. of KMnO<sub>4</sub> = 5 & v.f. of  $SO_2 = 2$ Now, Eq. of  $KMnO_4 = Eq. of SO_2$  $\frac{15.8}{15.8} = \text{moles of SO}_2 \times 2$ 158/5SO, moles of  $SO_2 = 1/4$ Now, applying POAC on S, we get :  $2 \times \text{mole of FeS}_2 = 1 \times \text{moles of SO}_2$ moles of FeS<sub>2</sub> =  $\frac{1}{4} \times \frac{1}{2} = \frac{1}{8}$ so. weight of  $\text{FeS}_2 = \frac{1}{2} \times 120 = 15 \text{ g}.$ SO, An aqueous solution containing 0.1 g KIO<sub>3</sub> (formula weight = 214) and an excess of KI was acidified 12. with HCI. The liberated I2 consumed 45 mL of thiosulphate. The molarity of sodium thiosulphate solution is : The reaction involved is :  $IO_3^- + I^- + H^+ \longrightarrow I_2 + H_2O_3^-$ (C) 0.126 M (D) 0.252 M (A) 0.0623 M (B) 0.0313 M  $IO_3^- + 5I^- + H^+ \longrightarrow 3I_2 + H_2O$ Sol.  $2Na_2S_2O_3 + I_2 \longrightarrow 2NaI + Na_2S_4O_6$ Moles of KIO<sub>3</sub> =  $\frac{0.1}{214}$ Now, Moles of I<sub>2</sub> = 3 ×  $\frac{0.1}{214}$ So, Moles of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> = 2 × 3 ×  $\frac{0.1}{214}$ Now,  $M \times V_L = 2 \times 3 \times \frac{0.1}{214}$   $\therefore$   $M \times \frac{45}{1000} = 2 \times 3 \times \frac{0.1}{214}$ *.*.. Molarity of hypo solution =  $2 \times 3 \times \frac{0.1}{214} \times \frac{1000}{45} = 0.0623 \text{ M}$ Ans. (A) Now, Calculate the percentage of available chlorine in a sample of 3.55 g of bleaching powder which was 13. dissolved in 100 mL of water. 25 mL of this solution, on treatment with KI and dilute acid, required 20 mL of 0.125 N sodium thiosulphate Sol. Ans. 10 % Sol.  $CaOCl_2 + H_2O \longrightarrow Ca(OH)_2 + Cl_2$  $CI_2 + 2KI \longrightarrow 2KCI + I_2$  $I_2 + 2Na_2S_2O_3 \longrightarrow Na_2S_2O_6 + 2NaI$ moles of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> =  $\frac{20}{1000} \times \frac{0.125}{1} = 25 \times 10^{-4}$ In 25 mL solution, moles of I<sub>2</sub> =  $\frac{1}{2}$  x moles of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> So,  $=\frac{1}{2} \times 25 \times 10^{-4} = 12.5 \times 10^{-4}$ in 100 mL solution, moles of  $CI_2 = 4 \times 12.5 \times 10^{-4} = 50 \times 10^{-4}$ So, weight of  $CI_2 = 50 \times 10^{-4} \times 71 \text{ g}$ So, % of available  $Cl_2 = \frac{50 \times 10^{-4} \times 71}{3.55} \times 100 = 10\%$