Equivalent Concept & Titrations

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 32 g

12 g 8 g

$\because$ 32 g of O_2 reacts with 48 g of Mg

$\therefore$ 8 g of $O_2 = \frac{48 \times 8}{32} = 12$ g

$\therefore$ Equivalent weight of Mg = 12

Similarly, $Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$

65.5 g 32.75

$\therefore$ Equivalent weight of Zn $= \frac{65.5}{2} = 32.75$ g

$Al + \frac{3}{2}Cl_2 \longrightarrow AlCl_3$

27 g $\quad \frac{3}{2} \times 71$ g

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 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, $$\text{Eq. wt. (E)} = \frac{\text{Atomic weight or Molecular weight}}{\text{valency factor(v.f)}} = \frac{\text{Mol. wt.}}{\text{n} - \text{factor}} = \frac{M}{x}$$

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

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

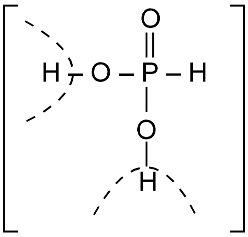
- Equivalent mass is a pure number which, when expressed in gram, is called gram equivalent mass.
- The equivalent mass of a substance may have different values under different conditions.
- There is no hard and fast rule that equivalent weight will be always less than the molecular mass.

Valency factor calculation :

- **For Elements :** Valency factor = valency of the element.
- **For Acids :** Valency factor = number of replaceable H^+ ions per acid molecule.

Solved Examples

Ex.-1 HCl , H_2SO_4 H_3PO_4 H_3PO_3



{see there are only two replaceable H^+ions}

		HCl	H_2SO_4	H_3PO_4	H_3PO_3
Sol.	Valency factor →	1	2	3	2
	Eq. wt. (E) →	M/1	M/2	M/3	M/2

(Assume 100% dissicoiation)

❍ 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 Examples

		NaOH,	KOH
Ex-2.			
Sol.	v .f. →	1	1
	Eq. wt. →	M/1	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

Ex-3. $\underset{\text{Base}}{2NaOH} + \underset{\text{Acid}}{H_2SO_4} \longrightarrow Na_2SO_4 + 2H_2O$

Sol. Valency factor of base = 1

Here, two molecule of NaOH replaced $2H^+$ ion from the H_2SO_4. 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-4. $\underset{\text{Base}}{NaOH} + \underset{\text{Acid}}{H_2SO_4} \longrightarrow NaHSO_4 + H_2O$

Sol. Valency factor of acid = 1

Here, one of molecule of H_2SO_4 replaced one OH^- from NaOH. Therefore, valency factor for H_2SO_4 is one

$$\therefore \quad \text{Eq. wt. of } H_2SO_4 = \frac{\text{Mol.wt}}{1}$$

- **Salts :**

(a) In non-reacting condition

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

Solved Examples

Ex-5.		Na_2CO_3 ,	$Fe_2(SO_4)_3$,	$FeSO_4.7H_2O$
Sol.	V.f.	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. $\underset{\text{Base}}{Na_2CO_3} + \underset{\text{Acid}}{HCl} \longrightarrow NaHCO_3 + NaCl$

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.

Section (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 $KMnO_4 + H_2O_2 \longrightarrow Mn^{2+} + O_2$

Sol. Mn in $KMnO_4$ is going from +7 to +2, so change in oxidation number per molecule of $KMnO_4$ is 5. So the valency factor of $KMnO_4$ 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

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

- **Normality (N) =** $\frac{W \times 1000}{E \times V}$
- **Relations between Normality and Molarity :**

Normality (N) = Molarity x Valency factor

or N × V (in mL) = M × V (in mL) × n

or **milliequivalents = millimoles × n**

Solved Examples

Ex-8. Calculate the normality of a solution containing 15.8 g of $KMnO_4$ in 50 mL acidic solution.

So. **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-9. 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 x 6 = 30 N

Section (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.

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_xN_y ; meq of M_xN_y = meq of M = meq of N

Solved Examples

Ex-10. 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 × v.f. = moles of $kMnO_4$ × v.f.

1 × 8 = moles of $KMnO_4$ × 5 ⇒ moles of $KMnO_4$ **= 8/5**

($\therefore$ v.f. of $Cu_2S = 2\,(2 - 1) + 1\,(4 - (-2))) = 8$ and v.f. of $KMnO_4 = 1\,(7 - 2) = 5$)

Ex-11. 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) × 2 = 1 × 5

($\therefore$ v.f. of $C_2O_4^{2-} = 2\,(4 - 3) = 2$ and v.f. of $MnO_4^- = 1\,(7 - 2) = 5$).

$x = \frac{5}{2}$ mole of $C_2O_4^{2-}$ 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 $MnO_4^- = \frac{\text{Mol. wt. of } MnO_4^-}{5}$

  e.g. $3e^- + 2H_2O + MnO_4^- \longrightarrow MnO_2 + 4OH^-$ Eq.wt of $MnO_4^- = \frac{\text{Mol. wt. of } MnO_4^-}{3}$

  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 $KMnO_4$ 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 $KMnO_4$ participates. e.g. if $KMnO_4$ forms Mn^{2+}, normality = 0.1 x 5 = 0.5 N. This *same* sample of $KMnO_4$, if employed in a reaction giving MnO_2 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, KIO_3 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.

  $\because$ v.f. of I_2 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 $KMnO_4$ solution would be required to exactly titrate 25 mL of 0.2 M $Fe(NO_3)_2$ 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 x 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 MnO_4^- = milliequivalents of Fe^{2+}

$M_1 \times vf_1 \times V_1 = M_2 \times vf_2 \times V_2$

$0.02 \times 5 \times V_1 = 0.2 \times 1 \times 25$ $(\because MnO_4^- \longrightarrow Mn^{2+}$; v.f. = 5, $Fe^{2+} \longrightarrow Fe^{3+}$; v.f. = 1)

$\therefore$ V_1 = 50 mL.

Section (D) : Equivalent Concept for Redox reactions, $KMnO_4$ / $K_2Cr_2O_7$ 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, $K_2Cr_2O_7$, $AgNO_3$, $CuSO_4$, 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, $KMnO_4$ 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 studied in Ionic equilibrium)
- **Redox Titrations**

Some Common Redox Titrations

Table of Redox Titrations : (Excluding Iodometric / Iodimetric titrations)

S.No.	Estimation of	By titrating with	Reactions	Relation*between OA and RA
1	Fe^{2+}	MnO_4^-	$Fe^{2+} \longrightarrow Fe^{3+} + e^-$	$5Fe^{2+} \equiv MnO_4^-$
			$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$	Eq. wt. of Fe^{2+} = M/1
2	Fe^{2+}	$Cr_2O_7^{2-}$	$Fe^{2+} \longrightarrow Fe^{3+} + e^-$	$6Fe^{2+} \equiv Cr_2O_7^{2-}$
			$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$	Eq.wt. of $Cr_2O_7^{2-}$ = M/6
3	$C_2O_4^{2-}$	MnO_4^-	$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$	$5C_2O_4^{2-} \equiv 2MnO_4^-$
			$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$	Eq. wt. of $C_2O_4^{2-}$ = M/2
4	H_2O_2	MnO_4^-	$H_2O_2 \longrightarrow 2H^+ + O_2 + 2e^-$	$5H_2O_2 \equiv 2MnO_4^-$
			$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$	Eq.wt. of H_2O_2 = M/2
5	As_2O_3	MnO_4^-	$As_2O_3 + 5H_2O \longrightarrow 2AsO_4^{3-} + 10H^+ + 4e^-$	Eq. wt. of As_2O_3 = M/4
			$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$	
6	AsO_3^{3-}	BrO_3^-	$AsO_3^{3-} + H_2O \longrightarrow AsO_4^{3-} + 2H^+ + 2e^-$	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 :

- $KMnO_4$ is generally used as an oxidising agent in acidic medium generally provided by dilute H_2SO_4 .
- $KMnO_4$ 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.

Solved Examples

Ex-13 Write the balanced reaction of titration of $KMnO_4$ Vs oxalic acid in presence of H_2SO_4.

So. Reaction : $2KMnO_4 + 3H_2SO_4 + 5H_2C_2O_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2$

Redox Changes : $C_2^{3+} \longrightarrow 2C^{4+} + 2e$ $\left(E_{H_2C_2O_4} = \dfrac{M}{2}\right)$

$5e + Mn^{7+} \longrightarrow Mn^{2+}$ $\left(E_{KMnO_4} = \dfrac{M}{5}\right)$

Indicator : $KMnO_4$ acts as self indicator.

Ex-14 Write the balanced reaction of titration of $KMnO_4$ 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 : $Fe^{2+} \longrightarrow Fe^{3+} + e$ $\left(E_{FeSO_4} = \dfrac{M}{1}\right)$

$Mn^{7+} + 5e \longrightarrow Mn^{2+}$ $\left(E_{KMnO_4} = \dfrac{M}{5}\right)$

Indicator : $KMnO_4$ 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) 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 I_2.

$$IO_3^- (aq) + 5I^- (aq) + 6H^+ (aq) \longrightarrow 3I_2 (s) + 3H_2O (\ell)$$

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

$$\underset{\text{colourless}}{2S_2O_3^{2-} (aq)} + \underset{\text{black}}{I_2 (s)} \longrightarrow \underset{\text{colourless}}{S_4O_6^{2-}} + 2I^-$$

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

S.No.	Estimation of	Reaction	Relation between O.A. and R.A.
1.	I_2	$I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$	$I_2 \equiv 2I \equiv 2Na_2S_2O_3$
		or $I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$	Eq.wt. of $Na_2S_2O_3$ = M/1
2.	$CuSO_4$	$2CuSO_4 + 4KI \longrightarrow 2CuI + 2K_2SO_4 + I_2$	$2CuSO_4 \equiv I_2 \equiv 2I = 2Na_2S_2O_3$
		or $2Cu^{2+} + 4I^- \longrightarrow \underset{\text{white ppt}}{2CuI} + I_2$	Eq.wt.of $CuSO_4$ = M/1
3.	$CaOCl_2$	$CaOCl_2 + H_2O \longrightarrow Ca(OH)_2 + Cl_2$	$CaOCl_2 \equiv Cl_2 \equiv I_2 \equiv 2I \equiv 2Na_2S_2O_3$
		$Cl_2 + 2KI \longrightarrow 2KCl + I_2$	
		$Cl_2 + 2I^- \longrightarrow 2Cl^- + I_2$	Eq.wt. of $CaOCl_2$ = M/2
4.	MnO_2	$MnO_2 + 4HCl(conc.) \xrightarrow{\Delta} MnCl_2 + Cl_2 + 2H_2O$	$MnO_2 \equiv Cl_2 \equiv I_2 \equiv 2Na_2S_2O_3$
		$Cl_2 + 2KI \longrightarrow 2KCl + I_2$	Eq.wt. of MnO_2 = M/2
		or $MnO_2 + 4H^+ + 2Cl^- \longrightarrow Mn^{2+} + 2H_2O + Cl_2$	
		$Cl_2 + 2I^- \longrightarrow I_2 + 2Cl^-$	
5.	IO_3^-	$IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$	$IO_3^- \equiv 3I_2 \equiv 6I \equiv 6Na_2S_2O_3$
			Eq.wt. of IO_3^- = M/6
6.	H_2O_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 = 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
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.	ClO^-	$ClO^- + 2I^- + 2H^+ \longrightarrow H_2O + Cl^- + I_2$	$ClO^- \equiv I_2 \equiv 2I \equiv 2Na_2S_2O_3$
			Eq.wt. of OCl^- = M/2
10.	$Cr_2O_7^{2-}$	$Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 3I_2 + 2Cr^{3+} + 7H_2O$	$Cr_2O_7^{2-} \equiv 3I_2 \equiv 6I$
			Eq.wt. of $Cr_2O_7^{2-}$ = M/6
11.	MnO_4^-	$2MnO_4^- + 10I^- + 16H^+ \longrightarrow 2Mn^{2+} + 5I_2 + 8H_2O$	$2MnO_4^- \equiv 5I_2 \equiv 10I$
			Eq.wt. of MnO_4^- = M/5
12.	BrO_3^-	$BrO_3^- + 6I^- + 6H^+ \longrightarrow Br^- + 3I_2 + 3H_2O$	$BrO_3^- \equiv 3I_2 \equiv 6I$
			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_3AsO_4 = M/2
14.	HNO_2	$2HNO_2 + 2I^- \longrightarrow I_2 + 2NO + H_2O$	$2HNO_2 \equiv I_2 \equiv 2I$
			Eq.wt. of HNO_2 = M/1
15.	HClO	$HClO + 2I^- + H^+ \longrightarrow Cl^- + I_2 + H_2O$	$HClO \equiv I_2 \equiv 2Na_2S_2O_3$
			Eq.wt. of HClO = M/2

Iodimetric Titrations

S.No.	Estimation of	Reaction	Relation 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)	$SO_3^{2-} + I_2 + H_2O \longrightarrow SO_4^{2-} + 2I^- + 2H^+$	$SO_3^{2-} \equiv I_2 \equiv 2I$ Eq.wt. of SO_3^{2-} = M/2
3.	Sn^{2+} (in acidic medium)	$Sn^{2+} + I_2 \longrightarrow Sn^{4+} + 2I^-$	$Sn^{2+} \equiv I_2 \equiv 2I$ Eq.wt. of Sn^{2+} = M/2
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.	N_2H_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

Solved Examples

Ex-15. 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) – $\dfrac{\text{m.moles of hypo used}}{2}$

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

$= 0.04$ = millimoles of H_2S

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

$CaOCl_2 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + Cl_2$

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

$CaOCl_2 + 2CH_3COOH \longrightarrow Ca(CH_3COO)_2 + H_2O + Cl_2$

$CaOCl_2 + CO_2 \longrightarrow CaCO_3 + Cl_2$

Method of determination :

$$\underset{\text{(Sample of bleaching powder)}}{CaOCl_2} + 2CH_3COOH \longrightarrow Ca(CH_3COO)_2 + H_2O + Cl_2$$

$Cl_2 + 2KI \longrightarrow 2KCl + I_2$

$$\underset{\text{v.f.} = 2}{I_2} + \underset{\text{v.f.} = 1}{2Na_2S_2O_3} \xrightarrow{\text{Starch as indicator}} Na_2S_4O_6 + 2NaI$$

End point is indicated by disappearance of blue colour.

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

∴ millimoles of Cl_2 produced = m.moles of I_2 used by hypo

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

mass of Cl_2 produced $= \dfrac{M \times V \times 10^{-3}}{2} \times 71$

$= 35.5 \times M \times V \times 10^{-3}$

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

where W = amount of belaching powder taken in g.

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

Solved Examples

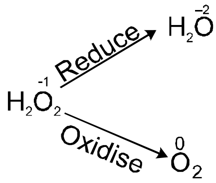
Ex-16 3.55 g sample of bleaching powder suspended in H_2O was treated with enough acetic acid and KI solution. Iodine thus liberated required 80 mL of 0.2 M hypo for titration. Calculate the % of available chlorine.

So. % of Cl_2 = $\dfrac{3.55 \times 0.2 \times 80}{3.55}$ = 16%

Section (F) : Volume strength of H_2O_2, Hardness of water

Hydrogen peroxide (H_2O_2)

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



- **Oxidising agent : ($H_2O_2 \rightarrow H_2O$)**

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

  v.f. = 2

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

  v.f = 2

- **Reducing agent : ($H_2O_2 \rightarrow O_2$)**

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

  v.f = 2

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

  v.f = 2

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

  20V H_2O_2 means **one litre** of this sample of H_2O_2 on decomposition gives **20L of O_2** gas at **STP.**

  Decomposition of H_2O_2 is given as :

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

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

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

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

  Strength (in g/L) : Denoted by S

  Strength = Molarity × Mol. wt = Molarity × 34

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

Temporary hardness - due to bicarbonates of Ca & Mg

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

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

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

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

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

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

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

Measurement of Hardness :

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

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

Solved Examples

Ex-17 0.00012% $MgSO_4$ and 0.000111% $CaCl_2$ is present in water. What is the measured hardness of water and millimoles of washing soda required to purify water 1000 L water ?

Sol. Basis of calculation = 100 g hard water

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

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

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

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

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

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

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

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

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

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

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

Strength of Oleum :

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

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

Solved Examples

Ex-18 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**

MISCELLANEOUS SOLVED PROBLEMS (MSPS)

1. Find the valency factor for following acids

(i) CH_3COOH	(ii) NaH_2PO_4	(iii) H_3BO_3
Ans. (i) 1	(ii) 2	(iii) 1

2. Find the valency factor for following bases :

(i) $Ca(OH)_2$	(ii) CsOH	(iii) $Al(OH)_3$
Ans. (i) 2	(ii) 1	(iii) 3

3. Find the valence factor for following salts :

(i) $K_2SO_4.Al_2(SO_4)_3.24H_2O$	(ii) $CaCO_3$
Ans. (i) 8	(ii) 2

4. Find the valency factor for following redox reactions :

(i) $$KMnO_4 \begin{cases} \xrightarrow{\text{acidic}} Mn^{2+} \\ \xrightarrow{\text{neutral}} MnO_2 \\ \xrightarrow{\text{alkaline}} K_2MnO_4 \end{cases}$$

(ii) $K_2Cr_2O_7 \xrightarrow{\text{acidic}} Cr^{3+}$

(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 $K_2Cr_2O_7$ and 50 mL of 2 M $K_2Cr_2O_7$ in acidic medium.

Sol. v.f. of $K_2Cr_2O_7$ = 6

so $N_f = \dfrac{N_1V_1 + N_2V_2}{V_1 + V_2} = \dfrac{5 \times 6 \times 50 + 2 \times 6 \times 50}{50 + 50} = 21$ N

6. Calculate the normality of a solution containing 13.4 g of Sodium oxalate in 100 mL Sol.

Sol. Normality = $\dfrac{\text{wt. in g / eq. wt}}{\text{vol. of solution in litre}}$

Here, eq. wt. of $Na_2C_2O_4$ = 134/2 = 67

so $N = \dfrac{13.4/67}{100/1000} = 2N$

7. The number of moles of ferrous oxalate oxidised by one mole of $KMnO_4$ in acidic medium is :

(A) 5/2 (B) 2/5 (C) 3/5 (D) 5/3

Sol. Eq. of FeC_2O_4 = Eq. of $KMnO_4$

moles of FeC_2O_4 × 3 = moles of $KMnO_4$ × 5

so, moles of FeC_2O_4 = 5/3 **Ans. (D)**

8. How many moles of $KMnO_4$ are needed to oxidise a mixture of 1 mole of each $FeSO_4$ & FeC_2O_4 in acidic medium ?

(A) 4/5 (B) 5/4 (C) 3/4 (D) 5/3

Sol. Eq. of $KMnO_4$ = Eq. of $FeSO_4$ + Eq. of FeC_2O_4

moles of $KMnO_4$ × 5 = moles of $FeSO_4$ × 1 + moles of FeC_2O_4 × 3

$\therefore$ moles of $KMnO_4$ = 4/5 **Ans. (A)**

9. A sample of hydrazine sulphate $[N_2H_6SO_4]$ was dissolved in 100 mL water. 10 mL of this solution was treated with excess of $FeCl_3$ Sol. Ferrous ions formed were estimated and it required 20 mL of M/50 $KMnO_4$ 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.

Sol. (a) Given $4Fe^{3+} + N_2H_4 \longrightarrow N_2 + 4Fe^{2+} + 4H^+$

$MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$

(b) In 10 mL solution, eq. of $N_2H_6SO_4$ = Eq. of Fe^{2+} = Eq. of $KMnO_4$

$$= 20 \times \frac{1}{50} \times 5 \times 10^{-3} = 2 \times 10^{-3}$$

v.f. of $N_2H_6SO_4$ = 4

so, weight of $N_2H_6SO_4$ in 1 L solution = $\dfrac{2 \times 10^{-3} \times 1000}{4 \times 10} \times 130 = 6.5$ g.

10. Write the balanced redox reaction and calculate the equivalent weight of oxidising agent and reducing agent for titration of $K_2Cr_2O_7$ Vs Ferrous ammonium sulphate.

Ans. The reaction : $6[FeSO_4(NH_4)_2SO_4.6H_2O] + K_2Cr_2O_7 + 7H_2SO_4 \longrightarrow$

$3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + K_2SO_4 + 6(NH_4)_2SO_4 + 43H_2O$

Redox changes : $\left(E_{FeSO_4} = \dfrac{M}{1}\right)$; $\left(E_{K_2Cr_2O_7} = \dfrac{M}{6}\right)$

11. One litre of acidified $KMnO_4$ solution containing 15.8 g $KMnO_4$ is decolorized by passing sufficient SO_2. If SO_2 is produced by FeS_2, what is the amount of FeS_2 required to give desired SO_2 ?

Ans. 15 g.

Sol. v.f. of $KMnO_4$ = 5 & v.f. of SO_2 = 2

Now, Eq. of $KMnO_4$ = Eq. of SO_2

$$\frac{15.8}{158/5} = \text{moles of } SO_2 \times 2$$

so, moles of SO_2 = 1/4

Now, applying POAC on S, we get :

$2 \times$ mole of FeS_2 = $1 \times$ moles of SO_2

so, moles of FeS_2 = $\frac{1}{4} \times \frac{1}{2} = \frac{1}{8}$

so, weight of FeS_2 = $\frac{1}{8} \times 120 = 15$ g.

12. An aqueous solution containing 0.1 g KIO_3 (formula weight = 214) and an excess of KI was acidified with HCl. The liberated I_2 consumed 45 mL of thiosulphate. The molarity of sodium thiosulphate solution is :

The reaction involved is : $IO_3^- + I^- + H^+ \longrightarrow I_2 + H_2O$

(A) 0.0623 M (B) 0.0313 M (C) 0.126 M (D) 0.252 M

Sol. $IO_3^- + 5I^- + H^+ \longrightarrow 3I_2 + H_2O$

$2Na_2S_2O_3 + I_2 \longrightarrow 2NaI + Na_2S_4O_6$

Now, Moles of KIO_3 = $\frac{0.1}{214}$

So, Moles of I_2 = $3 \times \frac{0.1}{214}$

Now, Moles of $Na_2S_2O_3$ = $2 \times 3 \times \frac{0.1}{214}$

$\therefore$ $M \times V_L = 2 \times 3 \times \frac{0.1}{214}$ $\therefore$ $M \times \frac{45}{1000} = 2 \times 3 \times \frac{0.1}{214}$

Now, Molarity of hypo solution = $2 \times 3 \times \frac{0.1}{214} \times \frac{1000}{45}$ = 0.0623 M **Ans. (A)**

13. Calculate the percentage of available chlorine in a sample of 3.55 g of bleaching powder which was 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. $CaOCl_2 + H_2O \longrightarrow Ca(OH)_2 + Cl_2$

$Cl_2 + 2KI \longrightarrow 2KCl + I_2$

$I_2 + 2Na_2S_2O_3 \longrightarrow Na_2S_2O_6 + 2NaI$

In 25 mL solution, moles of $Na_2S_2O_3$ = $\frac{20}{1000} \times \frac{0.125}{1} = 25 \times 10^{-4}$

So, moles of I_2 = $\frac{1}{2} \times$ moles of $Na_2S_2O_3$

$= \frac{1}{2} \times 25 \times 10^{-4} = 12.5 \times 10^{-4}$

So, in 100 mL solution, moles of Cl_2 = $4 \times 12.5 \times 10^{-4} = 50 \times 10^{-4}$

So, weight of Cl_2 = $50 \times 10^{-4} \times 71$ g

% of available Cl_2 = $\frac{50 \times 10^{-4} \times 71}{3.55} \times 100 = 10\%$