REDOX REACTION & EQUIVALENT CONCEPT

□ OXIDATION & REDUCTION :

Let us do a comparative study of oxidation and Reduction ;

	Oxidation		Reduction
(1)	Addition of oxygen	(i)	Removal of oxygen
e.g.	$2Mg + O_2 \rightarrow 2MgO$	e.g.	$CuO + C \rightarrow Cu + CO$
(2)	Removal of Hydrogen	(ii)	Addition of Hydrogen
e.g.	$H_2S + Cl_2 \rightarrow 2HCl + S$	e.g.	$S + H_2 \rightarrow H_2 S$
(3)	Increase in positive charge	(iii)	Decrease in positive charge
e.g.	$\mathrm{Fe}^{2_{+}} \rightarrow \mathrm{Fe}^{3_{+}} + e^{-}$	e.g.	$Fe^{3+} + e \rightarrow Fe^{2+}$
(4)	Increase in oxidation number	(iv)	Decrease in oxidation number
	(+2) (+4)		(+7) (+2)
	$SnCl_2 \rightarrow SnCl_4$		$MnO_4^- \rightarrow Mn^{2+}$
(5)	Removal of electron	(v)	Addition of electron
e.g.	$\operatorname{Sn}^{2_+} \to \operatorname{Sn}^{4_+} + 2e^-$	e.g.	$Fe^{3+} + e^- \rightarrow Fe^{2+}$

Oxidation Number :

- It is an imaginary or apparent charge gained by an element when it goes from its elemental free state to combined state in molecules.
- It is calculated on basis of a arbitrary set of rules.
- It is a relative charge in a particular bonded state.

Rules governing oxidation number :

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

• Fluorine atom :

Fluorine is most electronegativity atom (known). It always has oxidation no. equal to -1 in all its compounds.

• Oxygen atom :

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

In case of :

- (i) peroxide (e.g. H_2O_2 , Na_2O_2) is -1
- (ii) super oxide (e.g. KO_2) is \Box
- (iii) ozonide (KO₃) is $-\frac{1}{3}$
- (iv) oxygen fluoride OF_2 is +2 & in O_2F_2 is +1

• Hydrogen atom :

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

• Halogen atom :

In general, all halogen atom (Cl, Br, I) has oxidation number equal to -1.

But if halogen atom is attached with an more electronegative atom than halogen atom then it will show positive oxidation numbers.

e.g.
$$KCIO_3$$
 HIO_3 $HCIO_4$ $KBrO_3$

Metals :

(a) Alkali metal (Li, Na, K, Rb,) always have oxidation number +1.

(b) Alkaline earth metal (Be, Mg, Ca) always have oxidation number +2.

Note : Metal may have negative or zero oxidation number.

(c) Aluminium always have +3 oxidation number

• Oxidation number of an element in free state or in allotropic forms is always zero.

e.g. $\begin{array}{c} 0 & 0 & 0 \\ O_2, S_8, P_4, O_3 \end{array}$

- Sum of the charges of elements in a molecule is zero.
- Sum of the charges of all elements in an ions is equal to the charge on the ion.
- If the group no. of an element in periodic table is n then its oxidation number may vary from n to n 8 (but it is mainly applicable in p-block elements)
- e.g. N-atom belongs to v group in the periodic table therefore as per rule its oxidation number may vary from $-3 \text{ to } +5 \text{ (NH}_3, \text{NO}, \text{N}_2\text{O}_3, \text{NO}_2, \text{N}_2\text{O}_5)$

Calculation of average oxidation number :

Solved Examples :

- **Ex.** Calculate oxidation number of underlined element $Na_2S_2O_3$:
- Sol. Let oxidation number of S-atom is x. Now work accordingly with the rules given before.

(+1) H 2 + (x) H 2 + (-2) H 3 = 0

x = + 2

- **Ex.** $\operatorname{Na}_2 \underline{S}_4 O_6$:
- Sol. Let oxidation number of S-atom is x

(+1) H 2 + (x) H 2 + (-2) H 6 = 0

- x = + 2.5
- It's important to note here that Na₂S₂O₃ have two S-atom and there are four S-atom in Na₂S₄O₆ but none sulphur atom in both the compound have +2 or +2.5 oxidation number, it is the average charge (O. No.) Which reside on each sulphur atom therefore we should work to calculate the individual oxidation number of each sulphur atom in these compound.
- $\ensuremath{\text{Ex.}}$ Calculate the O.S. of all the atoms in the following species :

(i) ClO⁻, (ii) NO₂⁻, (iii) NO₃⁻ (iv) CCl₄ (v) K_2 CrO₄ and (vi) KMnO₄

Sol. (i) In ClO⁻, the net charge on the species is -1 and therefore the sum of the oxidation states of Cl and O must be equal to -1. Oxygen will have an O.S. of -2 and if the O.S. of Cl is assumed to be 'x' then x - 2 should be equal to -1.

(ii) $NO_2^-: (2 \ 4 \ -2) + x = -1$ (where 'x' is O.S. of N) $\therefore x = +3$ (iii) $NO_3^-: x + (3 \ 4 \ -2) = -1$ (where 'x' is O.S. of N) x = +5(iv) In CCl₄, Cl has an O.S. of -1 $x + 4 \ 4 \ -1 = 0$ $\therefore x = +4$ (where 'x' is O.S. of C)

- (v) K_2CrO_4 : K has O.S. of +1 and O has O.S. of -2 and let Cr has O.S. 'x' then, 2 4 +1 + x + 4 4 -2 = 0 \therefore x = +6
- (vi) $KMnO_4 : +1 + x + (4 \ Y -2) = 0$ $\therefore x = +7$

(where x is O.S. of Mn).

□ MISCELLANEOUS EXAMPLES :

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

• The structure of CrO_5 is

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

$$\therefore$$
 x + (-2)2 + (-2) = 0 or x = 6

$$\therefore \qquad \text{O.N. of } Cr = +6 \text{ Ans.}$$

• The structure of
$$H_2SO_5$$
 is H_0-0-5

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

 $\begin{array}{ll} \therefore & +1-2+x+(-2)\,2+(-2)+1=0\\ \text{or} & x+2-8=0\\ \text{or} & x-6=0\\ \text{or} & x=6 \end{array}$

$$\therefore$$
 O.N. of S in H₂SO₅ is +6 **Ans**

□ Paradox of fractional oxidation number :

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

• The element marked with asterisk in each species is exhibiting the different oxidation state (oxidation number) from rest of the atoms of the same element in each of the species. This reveals that in C₃O₂, two carbon atoms are present in +2 oxidation state each whereas the third one is present in zero oxidation state and the average is 4/3. However the realistic picture is +2 for two terminal carbons and zero for the middle carbon.

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

Structure of C₃O₂
(Carbon suboxide)

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

$$O = Br = Br - B = O$$

Structure of Br₃O₈ (tribromooctaoxide)

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

$$\begin{smallmatrix} 0 & 0 \\ \mathbb{I}_{+5}^{0} & 0 \\ \mathbb{I}_{+5}^{0} & \mathbb{I}_{+5}^{0} \\ \mathbb{S}^{-} \\ \mathbb$$

Structure of $S_4 O_6^{2-}$ (tetrathionate ion)

□ OXIDISING AND REDUCING AGENT :

Oxidising agent or Oxidant :

Oxidising agents are those compound which can oxidise others and reduced itself during the chemical reaction. Those reagents whose O.N. decrease or which gain electrons in a redox reaction are termed as oxidants

e.g. KMnO₄, K₂Cr₂O₇, HNO₃, conc. H₂SO₄ etc, are powerful oxidising agents.

Reducing agent or Reductant :

Redusing agents are those compound which can reduce others and oxidise itself during the chemical reaction. Those reagents whose O.N. increase or which loses electrons in a redox reaction are termed as reductants.

e.g. KI, $Na_2S_2O_3$ are powerful reducing agents.

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

e.g. H_2O_2 , NO_2^-

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



□ REDOX REACTION :

A reaction in which oxidation and reduction simultaneously take place.

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

e.g.
$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 \longrightarrow 5Fe_2(SO_4)_3 + 2MnSO_4 + K_2SO_4 + 8H_2O_4 = 10FeSO_4 + 10F$$

• Disproportionations reactions :

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

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

$$\begin{array}{c} 2\overset{+1}{H_2}\overset{-1}{O_2}(aq) \longrightarrow 2\overset{+1}{H_2}\overset{-2}{O_2}(\ell) + \overset{0}{O}(g) \\ \overset{0}{S_8}(s) + 12OH^{-}(aq) \longrightarrow 4\overset{-2}{S^{2-}}(aq) + 2\overset{+2}{S_2}O_3^{2-}(aq) + 6H_2O(\ell) \\ \overset{0}{Cl_2}(g) + 2OH^{-}(aq) \longrightarrow \overset{+1}{ClO^{-}}(aq) + \overset{-1}{Cl^{-}}(aq) + H_2O(\ell) \end{array}$$

- Consider following reactions :
 - $2\text{KClO}_3 = 2\text{KCl} + 3\text{O}_2$ (a)

KClO₃ plays a role of oxidant and reductant both. Because same element is not oxidised and reduced. Here, Cl present in KClO₃ is reduced and O present in KClO₃ is oxidized. So its not a disproportion reaction although it looks like one.

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

Nitrogen in this compound has -3 and +3 oxidation number so it is not a definite value, so its not a disproportion reaction. Its a example of **comproportionation reaction** which is a class of redox reaction in which a element from two different oxidation state gets converted into a single oxidation state.

(c)
$$4\text{KClO}_3 \longrightarrow 3\text{KClO}_4 + \text{KCl}$$

Its a case of disproportionation reaction in which Cl is the atom disproportionating.

List of some important disproportionation reaction :

1.
$$H_2O_2 \longrightarrow H_2O + O_2$$

- 2. $X_2 + OH^-$ (dil.) $\longrightarrow X^- + XO^-$
- $X_2 + OH^-$ (conc.) $\longrightarrow X^- + XO_3^-$ 3.

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

$$F_2$$
 + NaOH (dil) \longrightarrow F^- + OF_2

 F_2 + NaOH concentration (dil) $\longrightarrow F^- + O_2$

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

$$I^- + IO_3^- + H^+ \longrightarrow I_2 + H_2O$$
 (acidic)

Some examples of redox reactions are :

$$\mathbf{Sn}^{2+} + 2\mathbf{Hg}^{2+} \longrightarrow \mathbf{F}$$

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

$$3Cu + 2NO_{3}^{-} + 8H^{+} \rightarrow 2NO + 3Cu^{2+} + 4H_{2}O$$

If one of the half reactions does not take place, other half will also not take place. We can say oxidation \Rightarrow and reduction go side by side.

$$\bullet \qquad \begin{array}{c} 3\text{Cl}_2 + 6\text{OH} \rightarrow 5\text{Cl}^- + \text{Cl}_3^- + 3\text{H}_2\text{O} \\ \text{O.N} = \begin{array}{c} 0 & -1 & +5 \\ \hline 0 & -1 & +5 \\ \hline 0 & \end{array} \\ \bullet & \bullet \end{array}$$

In the above reaction, we can see that Cl_2 has been oxidized as well as reduced. Such type of redox reaction is called **disproportionation** reaction.

□ Some More examples :



□ BALANCING OF REDOX REACTION :

All balanced equations must satisfy two criteria

1. Atom balance (mass balance) :

That is there should be the same number of atoms of each kind in reactant and products side.

2. Charge balance :

That is the sum of actual charges on both side of the equation must be equal

There are two methods for balancing the redox equations

- (a) Oxidation number change method
- (b) Ion electron method or half cell method

(a) Oxidation number change method :

This method was given by Jonson. In a balanced redox reaction, total increase in oxidation number must be equal to total decreases in oxidation number. This equivalence provides the basis for balancing redox reactions.

The general procedure involves the following steps :

- Select the atom in oxidising agent whose oxidation number decreases and indicate the gain of electrons.
- (ii) Select the atom in reducing agent whose oxidation number increases and write the loss of electrons.
- (iii) Now cross multiply i.e. multiply oxidising agent by the number of loss of electrons and reducing agent by number of gain of electrons.
- (iv) Balance the number of atoms on both sides whose oxidation numbers change in the reaction.
- (v) In order to balance oxygen atoms, add H_2O molecules to the side deficient in oxygen. Then balance the number of H atoms by adding H⁺ ions in the hydrogen.

Ex. Balance the following reaction by the oxidaton number method :

 $Cu + HNO_3 \longrightarrow Cu(NO_3)_2 + NO_2 + H_2O$

Sol. Write the oxidation number of all the atoms.

+1+5-2 +2+5-2+4 -2 +1 -2 0 There is change in oxidation number of Cu and N. 0 +2 $Cu \longrightarrow Cu(NO_3)_2 \dots (1)$ (Oxidation no. is increased by 2) (Oxidation no. is decreased by 1) $Cu + 2HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + H_2O_3$ Balancing nitrates ions, hydrogen and oxygen, the following equation is obtained. $Cu + 4HNO_{3} \longrightarrow Cu(NO_{3})_{2} + 2NO_{2} + 2H_{2}O$ This is the balanced equation. Write the skeleton equation for each of the following processes and balance them by ion electron method : Ex. Permagnet ion oxidizes oxalate ions in acidic medium to carbon dioxide and gets reduced itself to (i) Mn²⁺ ions.

- (ii) Bromine and hydrogen peroxide react to give bromate ions and water.
- (iii) Chlorine reacts with base to form chlorate ion, chloride ion and water in acidic medium.

Sol. (i) The skeleton equation for the process :

$$MnO_4^- + C_2O_4^{2-} + H^+ \longrightarrow Mn^{2+} + CO_2 + H_2O_4^{2-}$$

• Step (1) : Indicating oxidation number :

$$\overset{+7}{\text{MnO}_{4}^{-}} + \overset{+3}{\text{C}_{2}^{2}} \overset{-2}{\longrightarrow} \text{Mn}^{2+} + \overset{+4}{\text{C}_{2}^{-2}} + \overset{+1}{\text{H}_{2}^{-2}} \overset{-2}{\longrightarrow}$$

Step (2) : Writing oxidation and reduction half reaction :

$$\overset{+3}{C}_{2}O_{4}^{2-} \longrightarrow 2\overset{+4}{C}O_{2}$$
 (Oxidation half)

$$MnO_4^- \longrightarrow Mn^{2+}$$
 (Reduction half)

• Step (3) : Adding electrons to make the difference in O.N. +3 +4

$$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^{-1}$$

 $\stackrel{^{+7}}{\text{MnO}_4^-}$ + 5e⁻ \longrightarrow Mn²⁺

• Step (4) : Balancing 'O' atom by adding H_2O molecules

$$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$$

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

• Step (5) : Balancing H atom by adding H^+ ions

$$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$$

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

Step (6) : Multiply the oxidation half reaction by 2 and reduction half reaction by 5 to equalize the electrons lost and gained and add the two half reactions.

• Step (3) : Add electrons to make up for the difference in O.N. $\overset{0}{\text{Cl}_2} \longrightarrow 2 \overset{+5}{\text{ClO}_3^-} + 10e^ \overset{0}{\text{Cl}_2} + 2e^- \longrightarrow 2\text{Cl}^-$ • Step (4) : Balance O atoms by adding H_2O molecules $Cl_2 + 6H_2O \longrightarrow 2(ClO_3)^- + 10e^-$

 $Cl_2 + 2e^- \longrightarrow Cl^-$

• Step (5) : Since medium is basic, balance H atoms by adding H_2O molecules to the side falling short of H atoms and equal number of OH^- ions to the other side.

$$Cl_2 + 6H_2O + 12OH^- \longrightarrow 2ClO_3^- + 10e^- + 12H_2O$$

 $Cl_2 + 2e^- \longrightarrow 2Cl^-$

• Step (6) : Multiply the reduction half reaction by 5 and add two half reactions.

 $Cl_2 + 5H_2O + 2OH^- \longrightarrow 2ClO_3^- + 10e^- + 12H_2O$

 $[Cl_2 + 2e^- \longrightarrow 2Cl^-] \ 4 \ 5$

$$Cl_2 + 5Cl_2 + 12OH^- \longrightarrow 2ClO_3^- + 10Cl^- + 6H_2O$$

or,
$$6Cl_2 + 12OH^- \longrightarrow 2ClO_3^- + 10Cl^- + 6H_2O$$

or, $3Cl_2 + 6OH^- \longrightarrow ClO_3^- + 5Cl^- + 3H_2O$

Ex : Balance the following reaction by the oxidation number method :

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

Sol : Write the oxidation number of all the atoms.

 $\begin{array}{rcl} +7&-2\\ MnO_4^- &+& Fe^{+2} &\longrightarrow Mn^{+2} + Fe^{+3}\\ \text{change in oxidation number has occurred in Mn and Fe.}\\ +7&&+2\\ MnO_4^- &\longrightarrow Mn & \dots\dots(1) & (\text{Decrement in oxidation no. by 5})\\ Fe^{+2} &\longrightarrow Fe^{+3} & \dots\dots(2) & (\text{Increment in oxidation no. by 1})\\ \text{To make increase and decrease equal, eq. (2) is multiplied by 5.}\\ MnO_4^- + 5Fe^{+2} &\longrightarrow Mn^{+2} + 5Fe^{+3}\\ \text{To balance oxygen, } 4H_2O \text{ are added to R.H.S. and to balance hydrogen, }8H^+ \text{ are added to L.H.S.}\\ MnO_4^- + 5Fe^{+2} + 8H^+ &\longrightarrow Mn^{+2} + 5Fe^{+3} + 4H_2O\end{array}$

This is the balanced equation.

- Ex. Balance the following chemical reaction by oxidation number method and write their skeleton equation :
 - Chloride ions reduce maganese dioxide to manganese (II) ions in acidic medium and get itself oxidized to chlorine gas.
 - (ii) The nitrate ions in acidic medium oxidize magnesium to Mg^{2+} ions but itself gets reduced to nitrous oxide.

Sol. (i) The skeleton equation for the given process is

 $MnO_2 + Cl^- \longrightarrow Mn^{2+} + Cl_2 + H_2O$

 $\bullet \qquad \text{Step (1)} : \qquad \overset{^{+4}}{\text{MnO}}_2 + \text{Cl}^- \longrightarrow \text{Mn}^{2+} + \overset{^{+4}}{\text{Cl}}_2 + \overset{^{+1}}{\text{H}}_2 \overset{^{-2}}{\text{O}}$

• Step (2) : O.N. decreases by 2 per Mn

$$\downarrow^{44}$$

MnO₂ + $\square^{-} \longrightarrow Mn^{2+} + \square_2 + H_2O$
O.N. increases by 1 per \square

- Step (3) : Equalize the increase/decrease in O.N. by multiplying MnO_2 by 1 and Cl^- by 2 $MnO_2 + 2Cl^- \longrightarrow Mn^{2+} + Cl_2 + H_2O$
- Step (4) : Balance other atoms except H and O. Here they are all balanced.
- Step (5) : Balance O atoms by adding H_2O molecules to the side falling short of O atoms. $MnO_2 + 2Cl^- \longrightarrow Mn^{2+} + Cl_2 + H_2O + H_2O$
- Step (6) : Balance H atoms by adding H⁺ ions to the side falling short of H atoms. $MnO_2 + 2Cl^- + 4H^+ \longrightarrow Mn^{2+} + Cl_2 + 2H_2O$
- (ii) The skeleton equation for the given process is

 $Mg + NO_3^- \longrightarrow Mg^{2+} + N_2O + H_2O$

• Step (1) : $\stackrel{0}{Mg} + (\stackrel{+5}{NO_3})^- \longrightarrow Mg^{2+} + \stackrel{+1}{N_2O}^{-2} + \stackrel{+1}{H_2O}^{-2}$

Multiply NO_3^- by 2 to equalize N atoms

- Step (2) : O.N. increases by 2 per Mg atom $\int_{0}^{+1} Mg + 2NO_{3}^{-} \longrightarrow Mg^{2+} + N_{2}O + H_{2}O$ $\downarrow \underline{4 \ 42 = 8}$ O.N. decreases by 4 per N atom
- Step (3) : Equalize increase/decrease in O.N. by multiplying Mg by 4 and $2NO_3^-$ by 1. $4Mg + 2NO_3^- \longrightarrow Mg^{2+} + N_2O + H_2O$
- Step (4) : Balance atoms other than O and H
 - $4Mg + 2NO_3^- \longrightarrow 4Mg^{2+} + N_2O + H_2O$
- Step (5) : Balance O atoms

 $4Mg + 2NO_3^- \longrightarrow 4Mg^{2+} + N_2O + H_2O + 4H_2O$

• Step (6) : Balance H atoms as is done in acidic medium.

 $4Mg + 2NO_3^- + 10H^+ \longrightarrow 4Mg^{2+} + N_2O + 5H_2O$

(b) Ion electron method or half cell method :

By this method redox equation are balanced in two different medium

(a) Acidic medium (b) Basic medium

Balancing in acidic medium

Students are advised to follow the following steps to balance the redox reactions by ion electron method in acidic medium.

□ Solved Examples :

Ex : Balance the following redox reaction.

 $FeSO_4 + KMnO_4 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + MnSO_4 + H_2O_4$

Sol : Step-I assign the oxidation No. to each elements present in the reaction.

$$\overset{_{+2}}{\text{Fe}} \overset{_{+6}-_2}{\text{O}_4} + \overset{_{+1}}{\text{KMnO}_4} + \overset{_{+1}}{\text{H}_2} \overset{_{+2}}{\text{SO}_4} \longrightarrow \overset{_{+3}}{\text{Fe}_2} \overset{_{+6}-_2}{(\text{SO}_4)_3} + \overset{_{+2}}{\text{MnSO}_4} \overset{_{+2}}{\text{H}_2} \overset{_{+6}-_2}{\text{O}_4} + \overset{_{+1}}{\text{H}_2} \overset{_{-2}}{\text{O}_4}$$

Step-II Now convert the reaction in ionic form by eliminating the elements or species which are not going either oxidation or reduction

$$\operatorname{Fe}^{2+} + \operatorname{MnO}_{4}^{-} \longrightarrow \operatorname{Fe}^{3+} + \operatorname{Mn}^{2+}$$

Step-III Now identify the oxidation / reduction occurring into the reaction.

undergoes reduction

$$Fe^{2+} + MnO_4 \rightarrow Fe^{3+} + Mn^{2+}$$

undergoes oxidation

Step-IV Split the ionic reaction in two half one for oxidation and other for reduction

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

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

$$Fe^{2+} \rightarrow Fe^{3+}$$
 $MnO_4^- \rightarrow Mn^{2+}$

Fe & Mn atom are balanced in both side.

Step-VI Now balance O & H atom by H_2O & H⁺ respectively by the following way for one excess oxygen atom add one H_2O on the other side and two H⁺ on the same side.

Step VII Now see equation (i) & (ii) is balanced atomwise. Now balance both equations chargewise to balance the charge add electrons to the electrically positive side.

Step VIII The number of electrons gained and lost in each half-reaction are equalised by multiply suitable factor in both the half reaction and finally the half reactions are added to give the over all balanced reaction.

Here we multiply equation (i) by 5 and (ii) by one

(Here at this stage you will get balanced redox reaction in ionic form)

Step IX Now convert the ionic reaction in to molecular form by adding the elements or species which are removed instep (II).

Now by some manipulation you will get

$$5 \operatorname{FeSO}_4 + \operatorname{KMnO}_4 + 4\operatorname{H}_2\operatorname{SO}_4 \rightarrow \frac{5}{2} \operatorname{Fe}_2(\operatorname{SO}_4)_3 + \operatorname{MnSO}_4 + 4\operatorname{H}_2\operatorname{O} \quad \text{or}$$

$$10 \operatorname{FeSO}_4 + 2\operatorname{KMnO}_4 + 8\operatorname{H}_2\operatorname{SO}_4 \rightarrow 5\operatorname{Fe}_2(\operatorname{SO}_4)_3 + 2\operatorname{MnSO}_4 + 8\operatorname{H}_2\operatorname{O} + \operatorname{K}_2\operatorname{SO}_4$$

Balancing in basic medium :

In this case except step VI all the steps are same. We can understand it by following example balance the redox reaction in basic medium

Ex :
$$\text{ClO}^- + \text{CrO}_2^- + \text{OH}^- \longrightarrow \text{Cl}^- + \text{CrO}_4^{2-} + \text{H}_2\text{O}$$

Sol : By using up to step V we will get

$$\begin{array}{c|c} & & & \\ & & \\ ClO^{-} & \underline{\text{Reduction}} & Cl^{-} \end{array} \end{array} \xrightarrow{+3} CrO_{2}^{-} & \underline{\text{Oxidation}} & \overset{+6}{\text{CrO}}_{4}^{2-} \end{array}$$

Now student are advised to follow step VI to balance 'O' and 'H' atom

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

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

$$2OH^{-} + 2H^{+} + CIO^{-} \longrightarrow CI^{-} + H_{2}O + 2OH^{-} \qquad 4OH^{-} + 2H_{2}O + CrO_{2}^{-} \rightarrow CrO_{4}^{2-} + 4H^{+} + 2H_{2}O + CrO_{2}^{-} \rightarrow CrO_{4}^{2-} + 2H^{+} +$$

Finally you will get

 $40H^2 + 2H_2O^2 + Crossing Finally you will get$

 $40H^{-}$

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

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

Now from step VIII

$$2e^{-} + H_2O + ClO^{-} \rightarrow Cl^{-} + 2OH^{-}$$
(i) $\Psi = 3$
 $4OH^{-} + CrO_2^{-} \rightarrow CrO_2^{-2} + 2H_2O + 3e^{-}$ (ii) $\Psi = 2$

 $\frac{40\Pi + \text{CrO}_2 \rightarrow \text{CrO}_4^- + 2\text{H}_2\text{O} + 3\text{e}^-}{\text{Adding}: 3\text{ClO}^- + 2\text{CrO}_2^- + 2\text{OH}^- \rightarrow 3\text{Cl}^- + 2\text{CrO}_4^{-2-} + \text{H}_2\text{O}}$

□ Equivalent weight (E) :

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

no of Equivalents = $\frac{\text{mass of a sample}}{\text{eq.wt. of that species}}$

- Equivalent mass is a pure number when expressed in gram, it is called gram equivalent mass.
- The equivalent mass of substance may have different values under different conditions.
- □ Valency factor calculation :
 - For Acids :

valence factor = number of replaceable H^+ ions

□ Solved Examples :

HCl,
$$H_2SO_4$$
 H_3PO_4

 $\frac{M}{2}$

(see there are only two replaceable $H^{\scriptscriptstyle +}$ ions) 2

Sol :	valence \rightarrow	1	2	3	
	factor		(assume 100%		
			dissociation)		
	Eq.wt.→	$\frac{M}{1}$	$\frac{M}{2}$	$\frac{M}{3}$	

Self practice problems :

- 1. Find the valence factor for following acids
 - (i) CH₃COOH

Answers :

- **1**. (i) 1 (ii) 2 (iii) 1
 - For Base :
 - v.f. = number of replicable OH^- ions

□ Solved Examples :

Ex :		NaOH	[,	KOH	
Sol :	v.f.→	1		1	
	E.→	$\frac{M}{1}$		$\frac{M}{1}$	
	Self p	practice	proble	ems :	
-	D		<i>c</i> .	c c 11	

1. Find the valence factor for following bases

- (ii) CsOH
- (iii) Al(OH)₃

Answers :

- **1**. (i) 2 (ii) 1 (iii) 3
 - 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 replaceable H⁺ or OH⁻ than actually replaced in reaction.

v.f. for base is the number of H^+ ion form the acid replaced by per molecule of the base.

Solved Examples :

Ex : $2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$

Base acid

Sol : valency factor of base = 1

valency factor of acid = 2

Here two molecule of NaOH replaced 2H⁺ ion from the H₂SO₄ therefore per molecule of NaOH replaced only one H^+ ion of acid so v.f. = 1

v.f. for acid is number of OH⁻ replaced for the base by per molecule of acid

Ex :
$$NaOH + H_2SO_4 \rightarrow NaHSO_4 + H_2O$$

Base acid

Sol : valence factor of acid = 1

here one of molecule of H_2SO_4 replaced one OH^- from NaOH therefore v.f. for H_2SO_4 is = 1

$$E = \frac{\text{mol. wt. of } H_2 SO_4}{1}$$

For Salts : ٠

(a) In non reacting condition

v.f. = Total number of positive charge or negative charge present into the compound.

Solved Examples :

Ex :	Na_2CO_3	Fe ₂ (SO ₄) ₃ (2Fe ³⁺ + 3SO ₄ ²⁻)	$FeSO_4.7H_2O$
Sol : V.f.	2	2 Y 3 = 6	2
E.	$\frac{M}{2}$	$\frac{M}{6}$	$\frac{M}{2}$

(b) Salt in reacting condition :

Solved Examples :

Ex :
$$Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$$

Base Acid

Sol : It is a acid base reaction therefore v.f. for Na_2CO_3 is one while in non reaction condition it will be two.

(c) Eq. wt. of oxidising / reducing agents in redox reaction :

The equivalent weight of an oxidising agent is that weight which accepts one mole electron in a chemical reaction.

(a) Equivalent wt. of an oxidant (get reduced)

 $= \frac{\text{Mol.wt.}}{\text{No. of electrons gained by one mole}}$

Ex : In acidic medium

 $6e^- + Cr_2O_7^{2-} + 14H^+ \longrightarrow 2Cr^{3+} + 7H_2O$

Eq. wt. of
$$K_2Cr_2O_7 = \frac{\text{Mol. wt of } K_2Cr_2O_7}{6} = \frac{\text{Mol. wt.}}{6}$$

Note : [6 in denominator indicates that 6 electrons were gained by $Cr_2O_7^{2-}$ as it is clear from the given balanced equation]

(b) Similarly equivalent wt. of a reductant (gets oxidised)

$$= \frac{\text{Mol. wt.}}{\text{No. of electrons lost by one mole}}$$
$$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^{-}$$

Ex: In acidic medium,

Here, Total electrons lost = 2 So, eq. wt. = $\frac{\text{Mol. wt.}}{2}$

 In different condition a compound may have different equivalent weights. Because, it depends upon the number of electrons gained or lost by that compound in that reaction.

Ex : (i)

$$MnO_4^{-} \longrightarrow Mn^{2+} \text{ (acidic medium)}$$

(+7) (+2)

Here 5 electrons are taken so eq. wt. = $\frac{\text{Mol.wt.of KMnO}_4}{5} = \frac{158}{5} = 31.6$

(ii)
$$MnO_4^- \longrightarrow Mn^{+4}$$
 (neutral medium)
(+7) (+4)

Here, only 3 electrons are gained, so eq. wt. = $\frac{\text{Mol.wt.of KMnO}_4}{3} = \frac{158}{3} = 52.7$

(iii)
$$MnO_4^- \longrightarrow MnO_4^{-2}$$
 (alkaline to $(+7)$ $(+6)$

Here, only one electron is gained, so eq. wt. = $\frac{\text{Mol.wt.of KMnO}_4}{1} = 158$

Note : It is important to note that $KMnO_4$ acts as an oxidant in every medium although with different strength which follows the order.

acidic medium > neutral medium > alkaline medium

Ex :

$$2S_2O_3^{--} \longrightarrow S_4O_6^{--} + 2e^-$$

(Reducing agent)

Answers :

equivalent weight of $S_2O_3^{--} = \frac{2M}{2} = M$

• Questions based on Equivalent weight :

- 1. Molecular weight of KMnO₄ in acidic medium and neutral medium will be respectively :
 - (A) 7 Y equivalent wt. and 2 Y equivalent wt.
 - (B) 5 Y equivalent wt. and 4 Y equivalent wt.
 - (C) 4 Y equivalent wt. and 5 Y equivalent wt.
 - (D) 2 Y equivalent wt. and 4 Y equivalent wt.

2. Equivalent wt. of H_3PO_4 in each of the reaction will be respectively :

(1) B	(2) A	(3) C
--------------	--------------	--------------

□ NORMALITY :

Normality of solution is defined as the number of equivalent of solute present in one litre (1000 mL) solutions. Let a solution is prepared by dissolving W g of solute of eq. wt. E in V mL water.



• Normality (N) = Molarity 4 Valence factor

Normality (N) = molarity 4 Valence factor (n) or N 4 V (in mL) = M 4 V (in mL) 4 n or milli equivalents = millimoles 4 n

□ Solved Examples :

Ex : Calculate the normality of a solution containing 15.8 g of KMnO₄ in 50 mL acidic solution.

Sol : Normality (N) =
$$\frac{W \times 1000}{E \times VmL}$$

where
$$W = 15.8 \text{ g}$$
, $V = 50 \text{ mL}$

So, N = 10

Ex : Calculate the normality of a solution containing 50 mL of 5 M solution $K_2Cr_2O_7$ in acidic medium.

1.

Sol : Normality (N) = Molarity 4 Valence factor

= 5 H 6 = 30 N

□ MOLARITY V/S NORMALITY :

Molarity (M)

- 1. No. of moles of solute present in one litre of solution.
- 2. No. of moles $=\frac{W}{M}$

3.
$$\frac{W}{M}$$
 4 1000 = No. of millimoles

Normality (N)

2. No. of equivalents
$$=\frac{W}{E}$$

$$\frac{W}{E}$$
 Y 1000 = No. of equivalance

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

No. of equivalents of solute present in one litre

W

4. Molarity 4 V(in mL)=No. of millimoles 4. Normality 4 V(in mL) = No. of equivalents

5. Molarity =
$$\frac{\text{min moles}}{\text{Volume of solution in mL}}$$
 5. Normality = $\frac{\text{min equivalents}}{\text{Volume of solution in mL}}$

3.

□ LAW OF EQUIVALENCE :

The law states that one equivalent of an element combine with one equivalent of the other, and in a chemical reaction equivalent and mill equivalent of reactants react in equal amount to give same no. of equivalent or milli equivalents of products separately.

According :

- (i) $aA + bB \rightarrow mM + nN$ m.eq of A = m.eq of B = m.eq of M = m.eq of N
- (ii) In a compound $M_v N_u$

m.eq of $M_x N_y = m.eq$ of M = m.eq of N

□ Solved Examples :

- **Sol** : From law of equivalence

equivalents of $Cu_2S =$ equivalents of $KMnO_4$ moles of $Cu_2S \lor v.f =$ moles of $KMnO_4 \lor v.f$. moles of $Cu_2S \lor 8 = 1 \lor 5 \Rightarrow$ moles of $Cu_2S = 5/8$

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

(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 MnO₄⁻ x (mole) 42 = 145

$$x = \frac{5}{2}$$

Ex. What volume of 6 M HCl and 2 M HCl should be mixed to get two litre of 3 M HCl ?

Sol. Let, the volume of 6 M HCl required to obtain 2 L of 3M HCl = x L

 $\therefore \text{ Volume of 2 M HCl required} = (2 - x) L$ $M_1V_1 + M_2V_2 = M_3V_3$ 6M HCl 2M HCl 3M HCl 6 H (x) + 2 H (2 - x) = 3 H 2 $\Rightarrow 6x + 4 - 6x = 6 \Rightarrow 4x = 2$ $\therefore x = 0.5 L$ Hence, volume of 6 M HCl required = 0.5 L Volume of 2M HCl required = 1.5 L

- **Ex.** In a reaction vessel, 1.184 g of NaOH is required to be added for completing the reaction. How many millilitre of 0.15 M NaOH should be added for this requirement ?
- Sol. Amount of NaOH present in 1000 mL of 0.15 M NaOH = 0.15 Y 40 = 6 g

 \therefore 1 mL of this solution contain NaOH = $\frac{6}{1000}$ 4 10⁻³ g

:. 1.184 g of NaOH will be present in $=\frac{1}{6 \times 10^{-3}}$ 4 1.184 = 197.33 mL

Ex. What weight of Na_2CO_3 of 85% purity would be required to prepare 45.6 mL of 0.235N H_2SO_4 ?

Sol. Meq. of $Na_2CO_3 = Meq.$ of H_2SO_4

= 45.6 Ч 0.235
∴
$$\frac{W_{Na_2CO_3}}{E_{Na_2CO_3}}$$
 Ч 1000 = 45.6 Ч 0.235
⇒ $\frac{W_{Na_2CO_3}}{106/2}$ Ч 1000 = 45.6 Ч 0.235

 $\therefore \qquad \qquad W_{Na_2CO_3}=~0.5679~g$

For 85 g of pure Na_2CO_3 , weighed sample = 100 g

 $\therefore \quad \text{For } 0.5679 \text{ g of pure } \text{Na}_2\text{CO}_3, \text{ weighed sample } = \frac{100}{85} \times 0.5679$ = 0.6681 g

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

$$\therefore \qquad \text{Eq. wt of } \text{MnO}_4^- = \frac{\text{MnO}_4^-(\text{mol.wt.})}{5}$$

e.g.
$$3e^- + 2H_2O + MnO_4^- \rightarrow MnO_2 + 4OH^-$$

$$\therefore \qquad \text{Eq. wt. of } \text{MnO}_4^- = \frac{\text{MnO}_4^-}{3}$$

Thus the no. of equivalents of MnO_4^- will be different in the above two cases but no. 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 $\mbox{ H}$ 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 $\mbox{ H}$ 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 reaction are

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

(ii)
$$I_2 + S_2 O_3^{2-} \longrightarrow S_4 O_6^{2-} + I^-$$

meq of hypo = meq of I_2 = meq of IO_3^- + meq of I^-

$$\therefore$$
 IO₃⁻ react with I⁻ \Rightarrow meq of IO₃⁻ = meq of I⁻

meq of hypo = 2 Y meq of IO₃⁻
 This is wrong. Note that I₂ formed by (i) have v.f. = 5/3 & reacted in equation (ii) have v.f. = 2.
 v.f. of I₂ in both the equation are different therefore we cannot equate m.eq is sequence. In this type of case students are advised to use mole concept.

□ Solved Example :

Ex : How many milliliters of 0.02000 M KMnO₄ solution would be required to exactly titrate 25.00 mL of 0.2000 M Fe(NO₃)₂ solution.

Sol : Method - 1 : Mole concept method

Starting with 25.00 mL of $0.2000MFe^{2+}$, we can write. Millimoles of $Fe^{2+} = 25.00$ Y 0.2000 and in volume V (in milliliters of the MnO₄⁻) Millimoles of MnO₄⁻ = V (0.02000) The balanced reaction is : MnO₄⁻ + 5Fe²⁺ + 8H⁺ \longrightarrow Mn²⁺ + 5 Fe³⁺ + 4H₂O This requires that at the equivalent point, $\frac{V(0.02000)}{1} = \frac{(25.00)(0.2000)}{5} \qquad V = 50.00 \text{ mL}$

Method - 2 : Equivalent Method :

Equivalents of $MnO_4^- = 5 \text{ Y}$ moles of MnO_4^- Normality $MnO_4^- = 5 \text{ Y}$ molarity of MnO_4^- For Fe^{2+} , moles and equivalents are equal, At the equivalence point, Equivalents of $MnO_4^- =$ Equivalents of Fe^{2+} or $V_{MnO_4^-}$ Y Normality of $MnO_4^ = V_{Fe}^{2+}$ Y Normality of Fe^{2+} For 0.02000 M MnO_4^- solution Normality of MnO_4^- = (5) (0.02000) = 0.1 N and for 0.2000 M Fe^{2+} solution

Normality of $Fe^{2+} = 0.2000 \text{ N}$

$$V_{MnO_{4}^{-}} = (25.00 \text{ mL}) \left(\frac{0.2000}{0.1000}\right) = 50.00 \text{ mL}$$

\Box HYDROGEN PEROXIDE (H₂O₂) :

 H_2O_2 can behave both like oxidising and reducing agents in both the medium (acidic and basic).



Oxidising agent : (H₂O₂)
 (a) Acidic medium :

$$2e^{-} + 2H^{+} + H_2O_2 \xrightarrow{\frac{3}{4}(R)} 2H_2O$$

v.f. = 2

(b) Basic medium :

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

v.f. = 2

• Reducing agent : (H_2O_2) :

(a) Acidic medium :

$$\begin{array}{l} H_2O_2 \longrightarrow O_2 + \ 2H^+ + \ 2e^- \\ v.f. \ = \ 2 \end{array}$$

(b) Basic medium :

 $2OH^{-} + H_2O_2 \longrightarrow O_2 + 2H_2O + 2e^{-}$ v.f. = 2

Note : Valency factor of H_2O_2 is always equal to 2.

Volume strength of H_2O_2 : Strength of H_2O_2 is represented as 10 V, 20 V, 30 V etc. 20V H_2O_2 means one litre of this sample of H_2O_2 on decomposition gives 20 L of O_2 gas at S.T.P.

Normality of
$$H_2O_2$$
 (N) = $\frac{\text{Volume, strength of } H_2O_2}{5.6}$

÷

$$M_{H_2O_2} = \frac{N_{H_2O_2}}{v.f} = \frac{N_{H_2O_2}}{2}$$

• Molarity of
$$H_2O_2$$
 (M) = $\frac{\text{Volume, strength of } H_2O_2}{11.2}$

Strength (in g,	/L) : Denoted by S
Strength	= molarity Y mol. wt.
	= molarity 4 34
Strength	= Normality Y Eq. weight.
	= Normality Y 17

□ Solved Example :

Ex : 20 mL of H_2O_2 after acidification with dil H_2SO_4 required 30 mL of $\frac{N}{12}$ KMnO₄ for complete oxidation. The strength of H_2O_2 solution is [Molar mass of $H_2O_2 = 34$]

Sol :

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

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

strengt

...

th = N' Y equivalent mass =
$$\frac{1}{8}$$
 Y 17 = 2.12 g/L

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

Temporary hardness - due to bicarbonates of Ca & Mg

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

(a)	by boiling	:	$2HCO_{3}^{-} \rightarrow H_{2}O + CO_{2} + CO_{3}^{2-} \text{ or }$
	by slaked lime	:	$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow CaCO_3 + 2H_2O$
			$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3$
(b)	By Washing Soda	:	$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaCl$
(c)	By ion exchange resins	:	$Na_2R + Ca^{2+} \rightarrow CaR + 2Na^+$

□ 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 are present in every 1000000 g of solution.

$$ppm_{A} = \frac{mass \, of \, A}{Total \, mass} \, \, \Psi \, 10^{6} = mass \, fraction \, \Psi \, 10^{6}$$

• Measurement of Hardness :

Hardness is measured in terms of ppm (parts per million) of CaCO3 or equivalent to it.

□ Solved Example :

- **Ex** : 0.00012% MgSO₄ and 0.000111% CaCl₂ is present in water. What is the measured hardness of water and millimoles of washing soda requires to purify 1000 litre water.
- $\begin{array}{l} \mbox{Sol}\ :\ 0.00012\%\ \mbox{MgSO}_4 = 1\ \mbox{mg}\ \mbox{CaCO}_3\ \mbox{1 L water} \\ 0.000111\%\ \mbox{CaCl}_2 = 1\ \mbox{mg}\ \mbox{CaCO}_3\ \mbox{1 L water} \\ \mbox{hardness} = 2\ \mbox{ppm}\ \mbox{and}\ \mbox{mm}\ \mbox{of}\ \mbox{Na}_2\mbox{CO}_3\ \mbox{require}\ \mbox{is 20} \end{array}$

• 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

□ CALCULATION OF AVAILABLE CHLORINE FROM A SAMPLE OF BLEACHING POWDER :

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

$$\begin{split} & \text{CaOCl}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{CaSO}_4 + \text{H}_2\text{O} + \text{Cl}_2 \\ & \text{CaOCl}_2 + 2\text{HCl} \rightarrow \text{CaCl}_2 + \text{H}_2\text{O} + \text{Cl}_2 \\ & \text{CaOCl}_2 + 2\text{H}_3\text{CCOOH} \rightarrow \text{Ca(CH}_3\text{COO)}_2 + \text{H}_2\text{O} + \text{Cl}_2 \\ & \text{CaOCl}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{Cl}_2 \end{split}$$

• Method of determination :

Bleaching powder + $CH_3COOH + KI \xrightarrow{\text{or } KI_3} KI_3 \xrightarrow{\text{starch}} Hypo$ end point (Blue \rightarrow colourless) % of $Cl_2 = \frac{3.55 \times x \times V(mL)}{W(g)}$ where x = molarity of hypo solution

v = mL of hypo solution used in titration.

□ Solved Example :

Ex : 3.55 g sample of bleaching powder suspended in H₂O was treated with enough acetic acid and KI solution. Iodine thus liberated requires 80 mL of 0.2 M hypo for titration. Calculate the % of available chlorine. [Available Chlorine = mass of chlorine liberated / mass of bleaching powder Y 100]

Sol : moles of iodine = moles of chlorine =
$$\frac{80 \times 0.2}{2}$$
 4 $10^{-3} = 8$ 4 10^{-5}
so required % = $\frac{8 \times 71 \times 10^{-3}}{4}$ 4 $100\% = 16\%$

FOR ACID-BASE (NEUTRALIZATION REACTION) OR REDOX REACTION : $N_1V_1 = N_2V_2$ is always true. But $M_1V_1 = M_2V_2$ (may or may not be true) But $M_1 H n_1 HV_1 = M_2 H n_2 HV_2$ (always true where n terms represent n factor). 'n' FACTOR : FACTOR RELATING MOLECULAR WEIGHT AND EQUIVALENT WEIGHT : n-factor = $\frac{M}{E}$ E = $\frac{M}{n-factor}$ n-FACTOR IN VARIOUS CASES In Non Redox Change • n-factor for element : Valency of the element • For acids : Acids will be treated as species which furnish H⁺ ions when dissolved in a solvent. The

n-factor	of an acid is t	he no. of acidic $\boldsymbol{H}^{\scriptscriptstyle +}$ ions that a molecule of	the acid would give w	nen dissolved in
a solver	at (Basicity).			
For exa	mple, for HC	$(n = 1), HNO_3 (n = 1), H_2SO_4 (n = 2), H_3$	PO_4 (n = 3) and H_3P	D ₃ (n = 2)
 For bas 	es : Bases will	be treated as species which furnish $OH^{\scriptscriptstyle -}~$ i	ons when dissolved in	a solvent . The
n-factor	r of a base is t	he no. of OH^- ions that a molecule of the	base would give whe	n dissolved in a
solvent	(Acidity).			
For exa	mple, NaOH	$(n = 1), Ba(OH)_2 (n = 2), Al(OH)_3 (n = 3),$	etc.	
♦ For salt	s : A salt read	ting such that no atom of the salt underg	pes any change in ox	dation state.
For exa	mple, 2AgNC	$_{3} + MgCl_{2} \rightarrow Mg(NO_{3})_{2} + 2AgCl_{3}$		
In this r	eaction, it can	be seen that the oxidation state of Ag, N,	O, Mg and Cl remains	the same even
in the j	product. The 1	n-factor for such a salt is the total charge	on cation or anion.	
In Redox Cha	nge			
For oxidizing a	gent or redu	cing agent n-factor is the change in o	xidation number pe	r mole of the
substance.				

□ SOME OXIDIZING AGENTS/REDUCING AGENTS WITH EQ. WT.

Species	Changed to	Reaction	Electrons exchanged or change in O.N.	Eq. wt.
MnO ₄ ⁻ (O.A.)	$Mn^{+2}_{\text{in acidic medium}}$	$MnO_{4}^{-} + 8H^{+} + 5e^{-} \longrightarrow Mn^{2+} + 4H_{2}O$	5	$E = \frac{M}{5}$
MnO ₄ ⁻ (O.A.)	MnO_2 in neutral medium	$MnO_4^- + 3e^- + 2H_2O \longrightarrow MnO_2 + 4OH^-$	3	$E = \frac{M}{3}$
MnO ₄ ⁻ (O.A.)	MnO_4^{2-} in basic medium	$MnO_4^- + e^- \longrightarrow MnO_4^{2-}$	1	$E = \frac{M}{1}$
Cr ₂ O ₇ ^{2–} (O.A.)	${\rm Cr}^{3_+}$ in acidic medium	$\operatorname{CrO}_7^{2-} + 14\mathrm{H}^+ + 6\mathrm{e}^- \longrightarrow 2\mathrm{Cr}^{3+} + 7\mathrm{H}_2\mathrm{O}$	6	$E = \frac{M}{6}$
MnO ₂ (O.A.)	$Mn^{2+} \\ {}_{\text{in acidic medium}}$	$MnO_2 + 4H^+ + 2e^- \longrightarrow Mn^{2+} + 2H_2O$	2	$E = \frac{M}{2}$
Cl ₂ (O.A.) in bleaching powder	Cl⁻	$Cl_2 + 2e^- \longrightarrow 2Cl^-$	2	$E = \frac{M}{2}$
CuSO ₄ (O.A.)	Cu^+	$Cu^{2+} + e^- \longrightarrow Cu^+$	1	$E = \frac{M}{1}$
S ₂ O ₃ ²⁻ (R.A.)	S406 ²⁻	$2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2e^-$	2	$E = \frac{2M}{2} = M$
		(for	r two molecules)	
H ₂ O ₂ (O.A.)	H ₂ O	$\mathrm{H_2O_2} + 2\mathrm{H^+} + 2\mathrm{e^-} \longrightarrow 2\mathrm{H_2O}$	2	$E = \frac{M}{2}$
H ₂ O ₂ (R.A.)	O ₂	$H_2O_2 \longrightarrow O_2 + 2H^+ + 2e^-$ (O.N. of	2	$E = \frac{M}{2}$
		oxygen in H_2O_2 is –1 per atom)		١v
Fe ²⁺ (R.A.)	Fe ³⁺	$Fe^{2+} \longrightarrow Fe^{3+} + e^{-}$	1	$E = \frac{WI}{1}$

Ex. To find the n-factor in the following chemical changes.

	(i)	$KMnO_4 \xrightarrow{H^+} Mn^{2+}$	(ii)	$KMnO_4 \xrightarrow{H_2O} Mn^{4+}$				
	(iii)	$KMnO_4 \longrightarrow Mn^{6+}$	(iv)	$K_2Cr_2O_7 \xrightarrow{H^+} Cr^{3+}$				
	(v)	$C_2O_4^{2-} \rightarrow CO_2$	(vi)	$FeSO_4 \rightarrow Fe_2O_3$				
	(vii)	$Fe_2O_3 \rightarrow FeSO_4$						
Sol.	(i)	In this reaction, $\rm KMnO_4$ which is a conditions.	in oxi	dizing agent, itself gets reduced to Mn^{2+} under acidic				
		$n = 1 \ 4 \ (+7) - 1 \ 4 \ (+2) = 5$						
	(ii)	In this reaction, $KMnO_4$ gets reduce	d to I	Mn ⁴⁺ under neutral or slightly (weakly) basic conditions.				
		$n = 1 \ 4 \ (+7) - 1 \ 4 \ (+4) = 3$						
	(iii)	In this reaction, KMnO ₄ gets reduce	d to	Mn ⁶⁺ under basic conditions.				
		$n = 1 \ Y (+7) - 1 \ Y (+6) = 1$						
	(iv)	In this reaction, $\mathrm{K_2Cr_2O_7}$ which acts a	as an	oxidizing agent reduced to Cr ³⁺ under acidic conditions.				
		(It does not react under basic condit	ions.)					
		$n = 2 \ Y (+6) - 2 \ Y (+3) = 6$						
	(v)	In this reaction, $C_2O_4^{2-}$ (oxalate ion) g n = $ 2 \ Y (+3) - 2 \ Y (+4) = 2$	ets ox	xidized to CO_2 when it is reacted with an oxidizing agent.				
	(vi)	In this reaction, ferrous ions get oxi	dized	to ferric ions.				
		$n = 1 \ Y (+2) - 1 \ Y (+3) = 1$						
	(vi)	In this reaction, ferric ions are gettin	ng rea	duced to ferrous ions.				
		$n = 2 \ 4 \ (+3) - 2 \ 4 \ (+2) = 2$						
Ex.	Calculat	te the molar ratio in which the follow	ving t	wo substances would react ?				
	Ba ₃ (PO	$_{4})_{2}$ and AlCl ₃						
Sol.	n-factor	$f \text{ of } Ba_3(PO_4)_2 = 3 4 (+2) = 6 = n_1$						
	While n-factor of $AlCl_3 = 1$ 4 (+3) = 3 = n_2							

$$\frac{n_1}{n_2} = \frac{6}{3}$$
 If $\frac{n_1}{n_2} = \frac{x}{y}$

Molar ratio $=\frac{y}{x}$ (inverse of equivalent ratio)

 \therefore Molar ratio in which Ba₃(PO₄)₂ and AlCl₃ will react = 3 : 6 = 1 : 2

□ APPLICATIONS OF THE LAW OF EQUIVALENCE

Simple Titration

In this, we can find the concentration of unknown solution by reacting it with solution of known concentration (standard solution).

For example, let there be a solution of substance A of unknown concentration. We are given solution of another substance B whose concentration is known (N_1). We take a certain known volume of A in a flask (V_2) and then we add B to A slowly till all the A is consumed by B (this can be known with the help of indicators). Let us, assume that the volume of B consumed is V_1 . According to the law of equivalence, the number of g equivalents of B at the end point.

 $\therefore N_1 V_1 = N_2 V_2, \text{ where } N_2 \text{ is the conc. of A.}$ From this we can calculate the value of N₂.

Ex. 0.4 M KMnO₄ solution completely reacts with 0.05 M FeSO₄ solution under acidic conditions. The volume of FeSO₄ used is 50 mL. What volume of KMnO₄ was used ?

Sol. 0.4 454 V = 0.05450

 $V = 1.25 \ mL$

Ex. 1.20 g sample of Na_2CO_3 and K_2CO_3 was dissolved in water to form 100 mL of a Solution. 20 mL of this solution required 40 mL of 0.1 N HCl for complete neutralization. Calculate the weight of Na_2CO_3 in the mixture. If another 20 mL of this solution is treated with excess of $BaCl_2$ what will be the weight of the precipitate ?

 <u>W</u>			
$\frac{M_{BaCO_3}}{M_{BaCO_3}} \text{ I 1000}$	= 40 Y 0.1 = 4		
- W _{BaCO3} Ч 2 Ч 1 197	000 = 4		
$\cdot W_{BaCO_3} = 0.3$	94 g		
BACK TITRATI	ON		
Back titration is u	ised to calculate	% purity of a sample. Let us assume th	at we are given an impure solid
substance C weig	ning w gs and w	e are asked to calculate the percentage o	f pure C in the sample. We will
assume that the in	npurities are iner	t. We are provided with two solutions A a	nd B, where the concentration of
B is known (N ₁) a	nd that of A is n	ot known. This type of titration will work	only if the following condition is
satisfied, i.e. the n	ature of compou	nds A, B and C should be such that A and B	can react with each other. A and
 C can react with e	ach other but th	e product of A and C should not react wit	h B.
Now, we take a c	ertain volume of	A in a flask (the g equivalents of A taken	should be \geq g equivalents of C in
the sample and th	iis can be done b	y taking A in excess). Now, we perform	a simple titration using B. Let us
assume that the v	volume of B use	d is $V_{_1}$. In another beaker, we again tak	e the solution of A in the same
volume as taken	earlier. Now, C	is added to this and after the reaction is	completed, the solution is being
titrated with B. L	et us assume tha	it the volume of B used up is V_2 . Gram	equivalents of B used in the first
titration = N_1V_1 .			
∴ gm. equivalents	of A initially $=$ 1	N ₁ V ₁	

gm. equivalents of B used in the second titration = N_1V_2

- ∴ gm. equivalents of A left in excess after reacting with $C = N_1 V_2$ gm. equivalents of A that reacted with $C = N_1 V_1 - N_1 V_2$ If the n-factor of C is x, then the moles of pure $C = \frac{N_1 V_1 - N_1 V_2}{v}$
- $\therefore \text{ The weight of } C = \frac{N_1V_1 N_1V_2}{x} \text{ W} \text{ Molecular weight of } C$ $\therefore \text{ Percentage of } C = \frac{N_1V_1 N_1V_2}{x} \text{ W} \frac{\text{Molecular wt. of } C}{w} \times 100$

SOME REDOX TITRATIONS (EXCLUDING IODOMETRIC / IODIMETRIC)

Estimation of	By titrating with	Reactions	Relation *between O.A. and R.A.
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. $Fe^{2+} = M/1$
			Eq. wt. $MnO_4^- = M/5$
Fe ²⁺	Cr ₂ O ₇ ²⁻	$Fe^{2+} \longrightarrow Fe^{3+} + e^{-}$	$6Fe^{2+} \equiv Cr_2O_7^{2-}$
		$\operatorname{Cr}_2\operatorname{O}_7^{2-}$ + 14H ⁺ + 6e ⁻ \longrightarrow 2Cr ³⁺ +7H ₂ O	Eq. wt. $Cr_2O_7^{2-} = M/6$
C ₂ O ₄ ²⁻	MnO_4^-	$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$	$5C_2O_4^{2-} \equiv 2MnO_4^{-}$
		$MnO_4^{-} + 8H^+ + 5e^- \longrightarrow Mn^{+2} + 4H_2O$	Eq. wt. $C_2 O_4^{2-} = M/2$
			Eq. wt. $MnO_4^- = M/5$
H_2O_2	MnO_4^-	$H_2O_2 \longrightarrow 2H^+ + O_2 + 2e^-$	$5H_2O_2 = 2MnO_4^-$
		$MnO_4^{-} + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$	Eq. wt. $H_2O_2 = M/2$
			Eq. wt. $MnO_4^- = M/5$
As_2O_3	MnO_4^-	$As_2O_3 + 5H_2O \rightarrow 2AsO_4^{3-} + 10H^+ + 4e^-$	Eq. wt. $As_2O_3 = M/4$
AsO_3^{3-}	BrO_3^-	$AsO_3^{3-} + H_2O \longrightarrow AsO_4^{3-} + 2H^+ + 2e^-$	Eq. wt. $AsO_3^{3-} = M/2$
		$BrO_3^- + 6H^+ + 6e^- \longrightarrow Br^- + 3H_2O$	Eq. wt. $BrO_3^- = M/6$
20σ of a comple	of Ro(OH) is di	esolution 10 mL of 0.5 N HCl solution	. The evenes of HCl was titrate

Ex. 20 g of a sample of Ba(OH)₂ is dissolved in 10 mL of 0.5 N HCl solution : The excess of HCl was titrated with 0.2 N NaOH. The volume of NaOH used was 20 cc. Calculate the percentage of Ba(OH)₂ in the sample.

Sol. Milli eq. of HCl initially = 10 4 0.5 = 5 Milli eq. of NaOH consumed = Milli eq. of HCl in excess = 10 4 0.2 = 2 ∴ Milli eq. of HCl consumed = Milli eq. of Ba(OH)₂ = 5 - 2 = 3 ∴ Eq. of Ba(OH)₂ = 3/1000 = 3 4 10⁻³ Mass of Ba(OH)₂ = 3 4 10⁻³ 4 (171/2) = 0.2565 g % Ba(OH)₂ = (0.2565 / 20) 4 100 = 1.28 %

- **Ex.** 3.2 g of pyrolusite was treated with 50 mL of 0.5 M oxalic acid and some sulphuric acid. The oxalic acid left undecomposed was raised to 250 mL in a flask. 25 mL of this solution when treated with 0.02 M $KMnO_4$ required 32 mL of the solution : Find the % of MnO_2 in the sample and also the percentage of available oxygen.
- **Sol.** Redox changes are $C_2O_4^{2-} \longrightarrow 2CO_2$ (n-factor = 2)

$$MnO_4^- \longrightarrow Mn^{2+}$$
 (n-factor = 5)
 $MnO_2 \longrightarrow Mn^{2+}$ (n-factor = 2)

Meq. of $MnO_2 = Meq$. of oxalic acid taken - Meq. of oxalic acid left = 50 4 0.5 4 2 - 32 4 0.02 4 5 4 10 (in 250 mL) = 18

 $\begin{array}{l} \frac{W_{MnO_2}}{M_{MnO_2}} \lor 2 \lor 1000 = 18 \Rightarrow \frac{W_{MnO_2}}{87} \lor 2 \lor 1000 = 18, \\ \therefore \qquad W_{MnO_2} = 0.7821 \text{ g} \\ \therefore \qquad \% \text{ of } MnO_2 = \frac{0.7821}{3.2} \times 100 = 24.44 \ \% \\ \text{Meq. of } MnO_2 = \text{Meq. of } O_2 \\ \frac{W_{O_2}}{16} \lor 2 \lor 1000 = 18, \ \therefore \ W_{O_2} = 0.144 \text{ g} \\ \% \text{ of available } O_2 = \frac{0.144}{3.2} \ \lor 100 = 4.5 \end{array}$

DOUBLE TITRATION

The method involves two indicators (Indicators are substances that change their colour when a reaction is complete) phenolphthalein and methyl orange. This is a titration of specific compounds. Let us consider a solid mixture of NaOH, Na_2CO_3 and inert impurities weighing w g. You are asked to find out the % composition of mixture. You are also given a reagent that can react with the sample say, HCl along with its concentration (M₁)

We first dissolve the mixture in water to make a solution and then we add two indicators in it, namely, phenolphthalein and methyl orange, Now, we titrate this solution with HCl.

NaOH is a strong base while Na_2CO_3 is a weak base. So, it is safe to assume that NaOH reacts completely and only then Na_2CO_3 reacts.

 $NaOH + HCl \rightarrow NaCl + H_2O$

Once NaOH has reacted, it is the turn of Na2CO3 to react. It reacts with HCl in two steps :

 $Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl and then,$

 $NaHCO_3 + HCl \rightarrow NaCl + CO_2 + H_2O$

As can be seen, when we go on adding more and more of HCl, the pH of the solution keeps on falling. When Na_2CO_3 is converted to $NaHCO_3$, completely, the solution is weakly basic due to presence of $NaHCO_3$ (which is a weaker base as compared to Na_2CO_3). At this instant phenolphthalein changes colour since it requires this weakly basic solution to change its colour. Therefore, remember that **phenolphthalein changes colour only when the weakly basic NaHCO_3 is present.** As we keep adding HCl, the pH again falls and when all the NaHCO_3 reacts to form NaCl, CO_2 and H_2O , the solution becomes weakly acidic due to the presence of the weak acid H_2CO_3 ($CO_2 + H_2O$). At this instance, methyl orange changes colour since it requires this weakly acidic solution to do so. Therefore, remember methyl orange changes colour only when H_2CO_3 is present.

Now, let us assume that the volume of HCl used up for the first and the second reaction, i.e., $NaOH + HCl \rightarrow NaCl + H_2O$ and $Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$ be V_1 (this is the volume of HCl from the begining of the titation up to the point when phenolphthalein changes colour).

Let, the volume of HCl required for the last reacton, i.e. $NaHCO_3 + HCl \rightarrow NaCl + CO_2 + H_2O$ be V_2 (this is the volume of HCl from the point where phenolphthalein had changed colour up to the point when methyl orange changes colour). Then,

Moles of HCl used for reacting with $NaHCO_3 = Moles$ of $NaHCO_3$ reacted = M_1V_2

Moles of NaHCO₃ produced by the Na₂CO₃ = M_1V_2

Moles of Na_2CO_3 that gave M_1V_2 moles of $NaHCO_3 = M_1V_2$

Mass of $Na_2CO_3 = M_1V_2$ 4 106

$$\% \text{ Na}_2 \text{CO}_3 = \frac{M_1 V_2 \times 106}{W} \times 100$$

Moles of HCl used for the first two reactions = M_1V_1 Moles of $Na_2CO_3 = M_1V_2$ Moles of HCl used for reacting with $Na_2CO_3 = M_1V_2$ Moles of HCl used for reacting with only $NaOH = M_1V_1 - M_1V_2$ \therefore Moles of NaOH = M₁V₁ - M₁V₂ Mass of NaOH = $(M_1V_1 - M_1V_2) 40$

% NaOH = $\frac{(M_1V_1 - M_1V_2) \times 40}{w} \times 100$

WORKING RANGE OF FEW INDICATORS

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 neutralization of all types of bases. Extent of reaction for different bases with acid (HCI) using these two indicators is summarized below :

	Phenolphthalein	Methyl orange
NaOH	100% reaction is indicated	100% reaction is indicated
	$NaOH + HCl \longrightarrow NaCl + H_2O$	$NaOH + HCl \longrightarrow NaCl + H_2O$
Na ₂ CO ₃	50% reaction upto $NaHCO_3$	100% reaction is indicated
	stage is indicated	$Na_2CO_3 + 2HCI \longrightarrow 2NaCl + H_2O + CO_2$
	$Na_2CO_3 + HCl \longrightarrow NaHCO_3 + NaCl$	
NaHCO ₃	No reaction is indicated	100% reaction is indicated
		$NaHCO_3 + HCl \longrightarrow NaCl + H_2O + CO_2$

- Ex. 0.4 g of a mixture of NaOH and Na_2CO_3 and inert impurities was first titrated with phenolphthalein and N/10 HCl, 17.5 mL of HCl was required at the end point. After this methyl orange was added and 1.5 mL of same HCl was again required for next end point. Find out percentage of NaOH and Na_2CO_3 in the mixture.
- Sol. Let W_1 g NaOH and W_2 g Na₂CO₃ was present in mixture. At phenolphthalein end point,

At second end point following reaction takes place

Eq. of $NaHCO_3$ = Eq. of HCl used (in second titration)

=
$$\frac{1}{2}$$
Eq. of Na₂CO₃
 $\frac{1}{2} \times \frac{W_2}{53} = 1.5 \text{ Y} \frac{1}{10} \text{ Y} 10^{-3}$
W₂ = 0.01590 g

١

Putting the value of W_2 in Eq. (1) we get

$W_1 = 0.064 \text{ g}$	2				
1	0.064				
Percentage of Na	$OH = -0.4$ $ 4 \ 100 = 16\%$				
Percentage of Na	$a_2 CO_3 = \frac{0.01590}{0.4}$ 4 100 = 3.975 %				
Iodometric and	Iodimetric Titration :				
The reduction of f	ree iodine to iodide ions and oxidation of iodide ions to	free iodine occurs in these titrations.			
$I_2 + 2e^- \longrightarrow 2I^-$ (r	eduction)				
$2I^- \longrightarrow I_2 + 2e^-$ (c	xidation)				
These are divided	into two types :				
Iodometic Titrat	on :				
In iodometric titrat	ions, an oxidizing agent is allowed to react in neutral m	edium or in acidic medium with excess			
of potassium iodic	e to liberate free iodine.				
KI + oxidizing age	$nt \longrightarrow I_2$				
Free iodine is titrat	ed against a standard reducing agent usually with sodiur	n thiosulphate. Halogen, dichromates,			
cupric ion, peroxi	les etc., can be estimated by this method.				
 $I_2 + 2NaS_2O_3$ —	$aS_2O_3 \longrightarrow 2Nal + Na_2S_4O_6$				
$2CuSO_4 + 4KI -$	4 KI \longrightarrow Cu ₂ I ₂ + 2K ₂ SO ₄ + I ₂				
$K_4 Cr_2 O_7 + 6KI +$	$+7H_2SO_4 \longrightarrow Cr_2(SO_4)_3 + 4K_2SO_4 + 7H_2O + 3I_2$				
Iodimetric Titra	tion				
These are the titra	titrations in which free iodine is used as it is difficult to prepare the solution of iodine (volatile and				
less soluble in wat	Juble in water), it is dissolved in KI solution :				
 $\underline{\mathrm{KI}} + \underline{\mathrm{I}}_2 \longrightarrow \underline{\mathrm{KI}}_3(\mathrm{P})$	otassium triiodide)				
This solution is first	standardized before using with the standard solution of s	ubstance such as sulphite, thiosulphate,			
arsenite etc, are e	stimated.				
In iodimetric and i	odometric titration, starch solution is used as an indica	or. Starch solution gives blue or violet			
changed to jodide	buille. At the end point, the blue of violet colour d	isappears when roune is completely			
SOME IODOME	RIC TITRATIONS (TITRATING SOLUTIONS IS	Na _S_O5H_O)			
Estimation of	Prostion	$\begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} $			
	Neaction	Relation between O.A. and R.A.			
l ₂	$I_2 + 2Na_2S_2O_3 \longrightarrow 2Nal + Na_2S_4O_6$	$l_2 = 2l \equiv 2Na_2S_2O_3$			
	or	Eq. wt. of $Na_2S_2O_3 = M/1$			
	$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$				
CuSO ₄	$2\text{CuSO}_4 + 4\text{KI} \longrightarrow 2\text{Cu}_2\text{I}_2 + 2\text{K}_2\text{SO}_4 + \text{I}_2$	$2CuSO_4 \equiv I_2 \equiv 2I \equiv 2Na_2S_2O_3$			
	$Cu^{2+} + 4I^- \longrightarrow Cu_2I_2 + I_2$	Eq. wt. of $CuSO_4 = M/1$			
	(White ppt.)				
	$CaOCl_2 + H_2O \longrightarrow Ca(OH)_2 + Cl_2$				
CaOCl ₂	$Cl_2 + 2KI \longrightarrow 2KCl + I_2$	$CaOCl_2 = Cl_2 = I_2 = 2I = 2Na_2S_2O_3$			

	$Cl_2 + 2l^- \longrightarrow 2Cl^- + l_2$	Eq. wt. of $CaOCl_2 = M/2$		
	$MnO_2 + 4HCl (conc) \xrightarrow{\Lambda} MnCl_2 + Cl_2 + 2H_2O$			
	$Cl_2 + 2KI \longrightarrow 2KCl + I_2$			
MnO ₂	or	$MnO_2 \equiv Cl_2 \equiv I_2 \equiv 2I \equiv 2Na_2S_2O_3$		
	$MnO_2 + 4H^+ + 2C\Gamma \longrightarrow Mn^{2+} + 2H_2O + Cl_2$	Eq. wt. of $MnO_2 = M/2$		
	$Cl_2 + 2l^- \longrightarrow l_2 + 2Cl^-$			
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 $IO_3^- = M/6$		
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 $H_2O_2 = M/2$		
Cl_2	$Cl_2 + 2I^- \longrightarrow 2CI^- + I_2$	$Cl_2 \equiv I_2 \equiv 2I \equiv 2Na_2S_2O_3$		
		Eq. wt. of $Cl_2 = M/2$		
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 $O_3 = M/6$		
Cr ₂ O ₇ ²⁻	$Cr_2O_7^{2-}+14H^++6I^-\longrightarrow 3I_2+2Cr^{3+}+7H_2O$	$\operatorname{Cr}_2\operatorname{O}_7^{2-} \equiv \operatorname{3I}_2 \equiv \operatorname{6I}$		
		Eq. wt. of $\operatorname{Cr}_2O_7^{2-}$		
MnO_4^-	$2MnO_4^{-}+10I^{-}+16H^{+}\longrightarrow 2MnO_4^{-}+5I_2^{}+8H_2^{}O$	$2MnO_4^- \equiv 5I_2 \equiv 10I$		
		Eq. wt. of $MnO_4^- = M/5$		
BrO_3^-	$BrO_{3}^{-}+6I^{-}+6H^{+}\longrightarrow Br^{-}+3I_{2}+3H_{2}O$	$BrO_3^{-} \equiv 3I_2 \equiv I_2$		
		Eq. wt. of $BrO_3^- = M/6$		
As(V)	$\mathrm{H_{3}AsO_{4}+2I^{-}+2H^{+}\longrightarrow H_{3}AsO_{3}+H_{2}O+I_{2}}$	$H_3AsO_4 \equiv I_2 \equiv 2I$		
		Eq. wt. of $H_3AsO_4 = M/2$		
SOME IODIMETRIC	C TITRATION (TITRATING SOLUTIONS IS I_2	2 IN KI)		
Estimation of	Reaction	Relation between O.A. and R.A.		
H_2S	$\mathrm{H}_{2}\mathrm{S} + \mathrm{I}_{2} \longrightarrow \mathrm{S} + 2\mathrm{I}^{-} + 2\mathrm{H}^{+}$	$H_2S \equiv I_2 \equiv 2I$		
(in acidic medium)		Eq. wt. of $H_2S = M/2$		
SO ₃ ²⁻	$SO_3^{2-} + I_2 + H_2O \longrightarrow SO_3^{2-} + 2I^- + 2H^+$	$SO_3^{2-} \equiv I_2 \equiv 2I$		
(in acidic medium)		Eq. wt. of $SO_3^{2-} = M/2$		
Sn ²⁺	$\mathrm{Sn}^{2+} + \mathrm{I_2} \longrightarrow \mathrm{Sn}^{4+} + 2\mathrm{I^-}$	$\operatorname{Sn}^{2+} \equiv \operatorname{I}_2 \equiv 2\operatorname{I}$		
(in acidic medium)		Eq. wt. of $Sn^{2+} = M/2$		
As(III) (at pH = 8)	$H_2AsO_3^- + I_2 + H_2O \longrightarrow HAsO_4^{2-} + 2I^- + 2H^+$	$H_2AsO_3^- \equiv I_2 \equiv 2I$		

 $N_2H_4 + 2I_2 \longrightarrow N_2 + 4H^+ + 4I^-$

Eq. wt. of $H_2AsO_3^- = M/2$

 $N_2H_4 \equiv 2I_2 \equiv 4I$

CONCEPTS AND FORMULA AT A GLANCE

1. Number of moles of molecules =
$$\frac{\text{wt. in g}}{\text{Mol. wt.}}$$

Number of moles of atoms = $\frac{\text{Atomic mass}}{\text{Atomic mass}}$
Number of moles of gases = $\frac{\text{Volume at STP}}{\text{Standard molar volume}}$
Number of moles of particles, e.g. atoms, molecular ions etc. = $\frac{\text{Number of particles}}{\text{Avogadro No.}}$
Moles of solute in solution = M 4 V(L)
2. Equivalent wt. of element = $\frac{\text{Atomic wt.}}{\text{Valence}}$
Equivalent wt. of compound = $\frac{\text{Mol. wt.}}{\text{Total charge on cation or anion}}$
Equivalent wt. of acid = $\frac{\text{Mol. wt.}}{\text{Basicity}}$
Equivalent wt. of acid = $\frac{\text{Mol. wt.}}{\text{Charge on ion}}$
Equivalent wt. of ase = $\frac{\text{Mol. wt.}}{\text{Charge on ion}}$
Equivalent wt. of acid salt = $\frac{\text{Molecular wt.}}{\text{Replaceable H atomin acid salt}}$
Equivalent wt. of oxidizing or reducing agent = $\frac{\text{Mol. wt.}}{\text{Charge in oxidation number per mole}}$
No. of equivalent = N 4 V(L) = $\frac{\text{wt. in g}}{\text{Eq. wt.}}$
3. Molarity (M) = $\frac{W_{1} \times 1000}{M_{1} \times V}$ = $\frac{\text{xt} \times 10}{M_{2}}$
where
 W_{1} = wt. of solute in g
 M_{1} = Mol. wt. of solute in g
 M_{2} = Mol. wt. of solute in g
 M_{3} = Mol. wt. of solute in g
 M_{4} = Mol. wt. of solute in g.
 W_{4} = wt. of solution in mI
4. Normality (N) = $\frac{W_{1} \times 1000}{E_{1} \times V}$ = $\frac{\text{xt} \times 1000}{E_{1}}$
 W_{2} = wt. of solute in g.
 W_{2} = wt. of solute in g.
 W_{4} = wt. wt. solution in mI

x = % by mass of solute

d = density of solution in g/ml

5. Moles = M Y V(L) =
$$\frac{\text{wt.of solute}}{\text{Mol.wt.}}$$

Millimoles = M Y V(ml) = $\frac{\text{wt.of solute}}{\text{Mol.wt.}} \times 1000$
Equivalents of solute = N Y V(L)
Meq. of solute $\frac{\text{wt.}}{\text{Eq.wt.}} \times 1000$

6. Molarity equation :

If a solution having molarity M_1 and volume V_1 is diluted to volume V_2 so that new molarity is M_2 then total number of moles remains the same.

 $M^{}_{1}V^{}_{1} = M^{}_{2}V^{}_{2}$

For a balanced equation involving n_1 moles of reactant 1 and n_2 moles of reactant 2.

$$\frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2}$$

Normality equation : According to the law of equivalence, the substances combine together in the ratio

of their equivalent masses
$$\frac{\text{wt. of }A}{\text{wt. of }B} = \frac{\text{Eq. wt. of }A}{\text{Eq. wt. of }B}$$

 \Rightarrow

$$\frac{\text{wt.of A}}{\text{Eq.wt.of A}} = \frac{\text{wt.of B}}{\text{Eq.wt.of B}}$$

Number of gram equivalents of A = Number of gram equivalents of B

Number of gram equivalents of A =
$$\frac{N_A \times V_A}{1000}$$

Number of gram equivalents of B = $\frac{N_B V_B}{1000}$

$$\Rightarrow \qquad \frac{N_A V_A}{1000} = \frac{N_B V_B}{1000}$$

 \Rightarrow N_A Y V_B = N_B Y V_B

The above equation is called normality equation.

(where n = n-factor)

For acid-base (neutralization reaction or redox reaction)

 $N_1V_1 = N_2V_2$ always true

But $M_1V_1 = M_2V_2$ (may or may not be true)

But $M_1n_1V_1 = M_2n_2V_2$ (always true where n-terms represent n-factor)

8. Molality (m) =
$$\frac{\text{Moles of solute}}{\text{wt. of solvent (in kg)}}$$

- 9. Strength of solution (S) = N Y Eq.wt. = M Y mol. wt.
- **Ex 1.** What volume of 0.40 M H_2SO_4 is required to produce 34.0 g of H_2S by the reaction,

8 KI + 5
$$H_2SO_4 \rightarrow 4 K_2SO_4 + 4 I_2 + H_2S + 4 H_2O$$
?

Sol. 1 mole of $H_2S \equiv 5$ moles of H_2SO_4 34 g of $H_2S \equiv 5$ moles of H_2SO_4

 $0.40 \text{ U} \text{ V}_{\text{H}_2\text{SO}_4} = 5$

:
$$V_{H_2SO_4} = \frac{5}{0.40} = 12.5$$
 litre

- **Ex 2.** To 50 L of 0.2 N NaOH, 2.5 L of 2N HCl and 15 L of 0.1 N FeCl₃ solutions are added. What weight of Fe_2O_3 can be obtained from the precipitate? Also report the normality of NaOH left in resultant solution :
- **Sol.** Eq. of NaOH = 50 H 0.2 = 10

Eq. of HCl = 2.5 H 2 = 5

Eq. of NaOH left after reaction with HCl = 10 - 5 = 5

 $\text{FeCl}_3 + \text{NaOH} \rightarrow \text{Fe}(\text{OH})_3 \downarrow \xrightarrow{\Lambda} \text{Fe}_2\text{O}_3$

FeCl₃ reacts with NaOH to give Fe(OH)₃ which on ignition gives Fe₂O₃

 \therefore Eq. of NaOH used for FeCl₃ = Eq. of Fe(OH)₃

= Eq. of Fe_2O_3 = 15 4 0.1 = 3.5

 \therefore Eq. of NaOH left finally = 5 - 1.5 = 3.5

Normality of NaOH in the resultant solution = $\frac{3.5}{70}$ = 0.05

 $\frac{W_{Fe_2O_3}}{M_{Fe_2O_3}} \mbox{ } 4 \mbox{ } 6 = 1.5 \mbox{ (n-factor for } Fe_2O_3 = 6) \label{eq:Fe_2O_3}$

$$W_{Fe_2O_3} = \frac{1.5 \times 160}{6} = 40g$$

Ex 3. One litre of a mixture of O_2 and O_3 at NTP was allowed to react with an excess of acidified solution of KI. The iodine liberated required 30 mL of M/10 Na₂S₂O₃ solution for titration. What is the weight percent of ozone in the mixture ?

Ultraviolet radiation of wavelength 300 mm can decompose ozone. Assuming that one photon can decompose one ozone molecule, how many photons would have been required for the complete decomposition of ozone in the original mixture?

1 Ч 1 = n Ч 0.0821 Ч 273 ∴ n = 0.044 Moles of O₂ = 0.044 - 0.0015 = 0.0425 W_{O2} = 0.0425 Ч 32 g = 1.36 g W_{O3} = 0.0015 Ч 48 g = 0.072 g ∴ % of O₃ = $\frac{0.072}{1.432}$ Ч 100 = 5.028 %

No. of photons required for decomposition of Ozone molecules = $0.0015 \text{ H} 6.023 \text{ H} 10^{23}$ = $0.90 \text{ H} 10^{21}$

Ex 4. A 20 g sample of only CuS and Cu₂S was treated with 100 mL of 1.25 M K₂Cr₂O₇. The products obtained were Cr^{3+} , Cu^{2+} and SO_2 . The excess oxidant was reacted with 50 mL of Fe²⁺ Solution : 25 mL of the same Fe²⁺ solution required 0.875 M KMnO₄ under acidic condition, the volume of KMnO₄ used was 20 mL. Find

the % of CuS and Cu_2S in the sample.

Equivalents of dichromate initially = $\frac{1.25 \times 6 \times 100}{1000} = 0.75$ Sol. Equivalents of Fe²⁺ in 25 mL = $\frac{0.875 \times 5 \times 20}{1000} = 0.0875$ Equivalents of Fe^{2+} in 50 mL = 0.0875 42 = 0.175Equivalents of excess dichromate = 0.175: Equivalents of dichromate consumed by (CuS and Cu₂S) = 0.75 - 0.175 = 0.575

If x g is the mass of CuS, the mass of Cu_2S is (10 - x) g

$$\frac{x}{95.5} \ \text{Y} \ 6 + \frac{(10 - x)}{159} \ \text{Y} \ 8 = 0.575$$

$$\therefore \ x = 5.74 \text{ g}$$

$$\% \ \text{CuS} = \frac{5.74}{20} \ \text{Y} \ 100 = 28.7 \ \%$$

$$\% Cu_2 S = 71.3 \%$$

- Ex 5. 2.249 g of a sample of pure BaCO₃ and impure CaCO₃ containing some CaO was treated with dil. HCl and it evolved 168 mL of CO2 at N.T.P. From this solution, BaCrO4 was precipitated filtered and washed. The precipitate was dissolved in dil. H₂SO₄ and diluted to 100 mL. 10 mL of this solution when treated with KI solution liberated iodine which required exactly 20 mL of 0.05 N Na₂S₂O₃. Calculate the percentage of CaO in the sample.
- Let, weight of BaCO₃, CaCO₃ and CaO are x,y and z respectively. Sol.

$$\therefore x + y + z = 2.249$$
BaCO₃ \longrightarrow BaCrO₄
Redox change
$$Cr^{6+} + 3e^{-} \longrightarrow Cr^{3+}$$
2I⁻ \longrightarrow I₂ + 2e⁻

Meq. of $BaCO_3 = Meq.$ of $BaCrO_4 = Meq.$ of I_2

$$\therefore \frac{x}{197/3} \ \text{Y} \ 1000 = 20 \ \text{Y} \ 0.05 \ \text{Y} \ \frac{100}{10}$$

....(1)

The equivalent weight of $BaCrO_4$ is M/3, therefore for $BaCO_3$, it should be M/3 also because mole ratio of $BaCO_3$ and $BaCrO_4$ is 1:1.

Applying POAC for C atom,

Moles of C in $BaCO_3$ + Moles of C in $CaCO_3$ = Moles of C in CO_2

10

$$\therefore \quad \frac{x}{197} + \frac{y}{100} = \frac{168}{22400} \Rightarrow \quad 200 \text{ x} + 294 \text{ y} = 295.5 \qquad \dots (2) From equation (1) and (2) y = 0.416 \text{ g} \therefore \quad 0.657 + 0.416 + z = 2.249$$

z = 1.176% of CaO = $\frac{1.176}{2.249} = 52.29$ %

Ex 6. For estimating ozone in the air, a certain volume of air is passed through an alkaline KI solution when O_2 is evolved and iodide is oxidized to iodine. When such a solution is acidified, free iodine is evolved which can be titrated with standard $Na_2S_2O_3$ Solution : In an experiment, 10 L of air at 1 atm and 27°C were passed through an alkaline KI solution, and at the end, the iodine was entrapped in a solution which on titration as above required 1.5 mL of 0.02 N $Na_2S_2O_3$ solution. Calculate volume percentage of ozone in the sample.

Sol. The chemical reaction is,
$$H_2O + KI + O_3 \longrightarrow I_2 + O_2 + KOH$$

Milliequivalents of iodine = Milliequivalents of KI = Milliequivalents of O_3 reacted
Milliequivalents of $Na_2S_2O_3 = 1.5 \ \text{U} \ 0.02 = 3 \ \text{U} \ 10^{-2}$
Millimoles of iodine = $\frac{3 \times 10^{-2}}{2} = 1.5 \ \text{U} \ 10^{-2}$ [\because n-factor for iodine = 2]
Millimoles of ozone = $1.5 \ \text{U} \ 10^{-2}$
Volume of ozone = $\frac{nRT}{P} = \frac{1.5 \times 10^{-5} \times 0.0821 \times 300}{1} = 36.945 \ \text{U} \ 10^{-5}$ litre
Volume percent of ozone = $\frac{36.945 \times 10^{-5}}{10} \ \text{U} \ 100 = 3.6945 \ \text{U} \ 10^{-3}$
Fx 7 A 2 18 a sample contains a mixture of XO and XO. It reacts with 0.015 moles of K Cr O

Ex 7. A 2.18 g sample contains a mixture of XO and X_2O_3 . It reacts with 0.015 moles of $K_2Cr_2O_7$ to oxidize the sample completely to form XO_4^- and Cr^{3+} . If 0.0187 mole of XO_4^- is formed, what is the atomic mass of X ?

Sol.
$$XO + K_2Cr_2O_7 \longrightarrow Cr^{3+} + XO_4^{-}$$

 $X_2O_3 + K_2Cr_2O_7 \longrightarrow Cr^{3+} + XO_4^{-}$
Let, wt. of XO in the mixture be x g
Equivalent of $K_2Cr_2O_7$ consumed by the mixture = 0.015 Y 6

Equivalents of XO =
$$\frac{\times 5}{x+16} \times 5$$

Equivalents of X₂O₃ = $\frac{2.18 - x}{2x+48} \times 8$

$$\therefore \frac{x}{x+16} \times 5 + \frac{2.18 - x}{2x - 148} \times 8 = 0.015 \, \text{Y} \, 6$$

Since 1 mole of XO gives 1 mole XO_4^- and 1 mole of $X_2O_3^-$ gives 2 moles of XO_4^- ,

$$\therefore \frac{x}{x+16} + \frac{2x(2.18 - x)}{2x + 48} = 0.0187$$

On solving, x = 99

- **Ex 8**. An aqueous solution containing 0.10 g KIO_3 (formula wt. = 214.0) was treated with an excess of KI Solution : The solution was acidified with HCl. The liberated I₂ consumed 55 mL of thiosulphate solution to decolourize the blue starch-iodine complex. Calculate molarity of the sodium thiosulphate solution :
- Sol. Moles of $\text{KIO}_3 = \frac{0.1}{214} = 0.00047$ \therefore Moles of I_2 liberated from $\text{KIO}_3 = \frac{0.00047}{2} = 0.000235$ Moles of KI reacting = 0.00047 + 5 = 0.00235 (\because n-factor for KIO_3 and KI are 5 and 1 respectively) Moles of I_2 produced from $\text{KI} = \frac{0.00235}{2} = 0.001175$ Total moles of I_2 produced and reacted = 0.000235 + 0.001175 = 0.00141 equivalents of I_2 reacted = 0.00141 + 2 = 0.00282 = equivalents of thiosulphate Solution :

 $Molarity = \frac{0.00282 \times 1000}{55} = 0.0512 \text{ M} \text{ (For thiosulphate n-factor} = 1)$

Ex 9. Mg can reduce NO_3^- to NH_3 in basic medium.

 $NO_3^- + Mg (s) + H_2O \rightarrow Mg (OH)_2 (s) + OH^- (aq.) + NH_3(g)$ A 25.0 mL sample of NO_3^- solution was treated with Mg. The $NH_3 (g)$ was passed into 100 mL of 0.15 N HCl. The excess of HCl required 32.10 mL of 0.10 N NaOH for neutralization. What was the molarity of NO_3^- ions in the original sample ?

Sol. Meq. of NH_3 formed = Meq. of HCl used = $100 \ 4 \ 0.15 - 32.10 \ 4 \ 0.10$ = 11.79

Here, n-factor of NH_3 is 1 (acid - base reaction)

For redox change,

$$\begin{array}{c} \downarrow_{3} \\ NO_{3}^{-} \xrightarrow{+8e^{-}} NH_{3} \\ NH_{3} \\ (n - factor = 8) \\ \therefore \\ Meq. of NH_{3} \\ for n-factor 8 = 8 \\ 411.79 \\ \therefore \\ Normality of NO_{3}^{-} = \frac{94.32}{25} = 3.77 \\ Molarity of NO_{3}^{-} = \frac{3.77}{8} = 0.47125 \\ 30 \\ mL \\ of a solution containing 9.15 \\ g/lit \\ g/$$

- **Ex10**. 30 mL of a solution containing 9.15 g/litre of an oxalate $K_x H_y (C_2 O_4)_z \cdot nH_2 O$ are required for titrating 27 mL of 0.12 N NaOH and 36 mL of 0.12 N KMnO₄ separately. Calculate x,y,z and n. Assume all H atoms (except $H_2 O$) are replaceable and x,y,z are in the simple ratio of g atoms.
- Sol. Let molecular weight of oxalate salt is M
 - (i) n factor in acid base reaction = 2
 - (ii) n factor in redox titration = 2 H z

$$(C_2O_4^{2-} \longrightarrow 2CO_2 + 2e)$$

 \therefore Meq. of acid in 30 mL = Meq. of NaOH used

$$30 \text{ Y} \frac{9.15}{\text{M}} \times \text{y} = 27 \text{ Y} 0.12 \qquad \dots (1)$$

Also,
$$30 \text{ H} \frac{9.15}{\text{M}} \times (2z) = 36 \text{ H} 0.12$$
 ...(2)

From equations (1) and (2) $\frac{y}{2z} = \frac{27}{36} \Rightarrow \frac{y}{z} = \frac{3}{2}$...(3)

Also, total cationic charge = total anionic charge

$$\therefore x + y = 2z \qquad \dots (4)$$

By equations (3) and (4)

These are in simplest ratio and molecular formula is $KH_3 (C_2O_4)_2 .nH_2O$

Molecular weight of salt = 39 + 3 + 176 + 18n = 218 + 18n

From equation (1), $M = \frac{30 \times 9.15 \times 3}{27 \times 0.12} = 254.16$ $\therefore 218 + 18n = 254.15$ $\therefore n = 2$ \therefore Oxalate salt is $KH_3(C_2O_4)_2.2H_2O$ **Ex11**. Hydrogen peroxide solution (20 mL) reacts quantitatively with a solution of KMnO_4 (20 mL) acidified with dilute H_2SO_4 . The same volume of the KMnO_4 solution is just decolourized by 10 mL of MnSO_4 in neutral medium simultaneously forming a dark brown precipitate of hydrated MnO_2 . The brown precipitate is dissolved in 20 mL of 0.2 M sodium oxalate under boiling condition in the presence of dilute H_2SO_4 . Write the balanced equations involved in the reactions and calculate the volume strength of H_2O_2 .

Sol. Meq. of MnO₂ = Meq. of Na₂C₂O₄
= 20 4 0.2 4 2 = 8
(C₂O₄^{2²}
$$\rightarrow$$
 2CO₂, n-factor = 2)
Millimoles of MnO₂ = $\frac{8}{2}$ = 4
 $factor = 3$
MnO₄⁻ + Mn² \xrightarrow{HO} MnO₂ brown (ppt.)
 $n-factor = 2$
or 2MnO₄⁻ + 3Mn²⁺ \rightarrow 5MnO₂ (Mole ratio is reciprocal of n-factor ratio)
 $\frac{Millimoles of MnO_4}{Millimoles of MnO_2} = \frac{2}{5}$
Millimoles of MnO₄⁻ = $\frac{2}{5}$ 4 Millimoles of MnO₂
= $\frac{2}{5}$ 4 4 = $\frac{8}{5}$
2KMnO₄ + 5H₂O₂ + 3H₂SO₄ \rightarrow 2 MnSO₄ + K₂SO₄ + 8H₂O + 5O₂
 $\frac{Millimoles of H_2O_2}{Millimoles of MnO_4} = \frac{5}{2}$
 \therefore Millimoles of H₂O₂ = $\frac{5}{2} \times \frac{8}{5} = 4$
N<sub>H₄O₂ 4 20 = 4 4 2 (n-factor for H₂O₂ = 2)
 \therefore N<sub>H₄O₂ = 0.4
Volume strength of H₂O₂ = 56 U N₁.</sub></sub>

= 5.6 U 0.4 = 2.24

Ex12. 1.0 g of moist sample of mixture of potassium chlorate (KClO₃) and potassium chloride (KCl) was dissolved in water and solution made upto 250 mL. This solution was treated with SO₂ to reduce all ClO₃⁻ to Cl⁻ and excess of SO₂ was removed by boiling. The total chloride was precipitated as silver chloride. The weight of precipitate was found to be 1.435 g. In another experiment, 25 mL of the original solution was heated with 30 ml 0.2 N FeSO₄ and unused FeSO₄ required 37.5 mL of 0.08 N KMnO₄ solutions.

Calculate the molar ratio of the ClO_3^- to the given mixture.

- Given that, $ClO_{3}^{-} + 6Fe^{2+} + 6H^{+} \longrightarrow Cl^{-} + 6Fe^{3+} + 3H_{2}O$ $3SO_{2} + ClO_{3}^{-} + 3H_{2}O \longrightarrow Cl^{-} + 3SO_{4}^{2-} + 6H^{+}$
- **Sol.** CIO_3^- is reduced to CI^- by SO_2^- and CIO_3^- is also reduced to CI^- by Fe^{2+} , hence AgCl is formed due to total CI^-

Meq. of Fe²⁺ initially taken = $30 \ 4 \ 0.2 = 6$ Meq. of Fe²⁺ unused = $37.5 \ 4 \ 0.08 = 3$ \therefore Meq. of Fe²⁺ = 6.0 - 3.0 = 3.0Thus, Meq. of ClO₃⁻ in 25 mL = 3.0Moles of ClO₃⁻ in 25 mL = $\frac{3.0}{1000 \times 6} = 0.0005$ $^{+5}$ ClO₃⁻ $\longrightarrow ^{-1}$ Cl⁻ (n-factor = 6) O.N. 5 -1

Thus, moles of ClO_3^- in 25 mL solution = 0.0005

 ClO_3^- is also reduced to Cl^- by SO_2 in first experiment and precipitated as AgCl.

Thus, Cl^{-} formed from $ClO_{3}^{-} = AgCl$ from $ClO_{3}^{-} = 1.435$ g

Total AgCl formed both from actual and Cl⁻ from $ClO_3^- = 1.435$ g

$$= \frac{1.435}{143.5} = 0.01 \text{ mol}$$

Thus, AgCl formed due to Cl^- only = 0.01 - 0.0005 = 0.0095 mol

Thus, ClO_3^- and Cl^- are in molar ratio = 1 : 19

- **Ex13**. Chile salt peter a source of NaNO₃ also contains NaIO₃. The NaIO₃ can be used as a source of iodine produced in the following reactions :
 - Step 1 : $IO_3^- + 3HSO_3^- \longrightarrow I^- + 3H^+ + 3SO_4^{-2-}$ Step 2 : $5I^- + IO_3^- + 6H^+ \longrightarrow 3I_2 + 3H_4O$

One litre of chile salt peter solution containing $6.80 \text{ g} \text{ NaIO}_3$, is treated with stoichiometric quantity of NaHSO₃. Now additional amount of same solution is added to the reaction mixture to bring about the second reaction. How many grams of NaHSO₃ are required in step 1 and what additional volume of chile salt peter must be added in step 2 to bring in complete conversion of I⁻ to I₂?

Sol. Meq. of NaHSO₃ = Meq. of NaIO₃ = N 4 V = $\frac{6.8}{198}$ 4 6 4 1000 I⁵⁺ + 6e⁻ → I⁻ (For KIO₃, n-factor = 6) ∴ Meq. of NaHSO₃ = 206.06 $\frac{W_{NaHSO_3}}{M/2}$ 4 1000 = 206.06 $\Rightarrow W_{NaHSO_3} = \frac{206.06 \times 104}{2 \times 1000}$ = 10.715 g Also, Meq. of I⁻ formed using n-factor 6 = 206.06 In step 2, n-factor I⁻ is 1 and n-factor for IO₃⁻ is 5 Meq. of I⁻ formed using n-factor 1 = $\frac{206.06}{6}$ Meq. of NaIO₃ used in 2nd step = $\frac{206.06}{6}$ $\Rightarrow \frac{6.8}{198}$ 4 5 4 V = $\frac{206.06}{6}$

$$\therefore V_{\text{NaIO}_3} = 199.99 \text{ mL}$$

Ex14. 1 g sample of AgNO₃ is dissolved in 50 mL of water. It is titrated with 50 mL of KI Solution : The AgI precipitated is filtered off. Excess of KI in filtrate is titrated with M/10 KIO₃ in presence of 6 M HCl till all I⁻ converted into ICI. It requires 50 ml of M/10 KIO₃ Solution : 20 mL of the same stock solution of KI require

SOLVED PROBLEMS (OBJECTIVE)

(D) 0.3

Ex 1. A 0.1097 g sample of As_2O_3 required 36.10 mL of $KMnO_4$ solution for its titration. The molarity of $KMnO_4$ solution is.

Sol.

(A) 0.02 (B) 0.04 (C) 0.0122

$$n \text{-factor} = 5$$

 $As_2O_3 + MnO_4^- \longrightarrow 2AsO_4^{3-} + Mn^{2+}$
 $n \text{-factor} = 4$

Let, molarity of KMnO₄ solution be M

 \therefore Eq. of As₂O₃ = Eq. of KMnO₄ solution

$$\frac{0.1097}{198} \text{ Y } 4 = \frac{36.10 \times \text{M} \times 5}{1000} \text{ (Equivalent weight As}_2\text{O}_3 = \frac{198}{4}\text{)}$$

Molarity = 0.0122 M

Hence, (C) is the correct answer.

Ex 2. In basic medium, CrO_4^{2-} oxidize $S_2O_3^{2-}$ to form SO_4^{2-} and itself changes to $Cr(OH)_4^{-}$. How many mL of 0.154 M $CrO_4^{\ 2-} are$ required to react with 40 mL of 0.246 M $S_2O_3^{\ 2-}$?

Sol. 40 4 0.246 4 8 = V 4 0.154 4 3 (Meq. of $S_2O_3^{2-}$ = Meq. of CrO_4^{2-})

 \therefore V = 170.4 mL

Hence, (C) is the correct answer.

Ex 3. 10 mL of 0.4 M $Al_2(SO_4)_3$ is mixed with 20 mL of 0.6 M $BaCl_2$. Concentration of Al^{3+} ion in the solution will be.

	(A) 0.266 M	(B) 10.3 M	(C) 0.1 M	1	(D) 0.25 M
Sol.		Al ₂ (SO ₄) ₃ +	$BaCl_2 \longrightarrow$	$BaSO_4 \downarrow +$	AlCl ₃
	Initial Meq.	10Ч0.4Ч6	20 4 0.6 4 2	0	0
		= 24	= 24		
	Final Meq.	0	0	24	24

$$[\mathrm{Al}^{3+}] = \frac{24}{30 \times 3} = 0.266 \mathrm{M}$$

Hence (A) is the correct answer.

Ex 4. The weight of sodium bromate required to prepare 55.5 mL of 0.672 N solution for cell reaction,

BrO₃⁻ + 6H⁺ + 6e⁻
$$\longrightarrow$$
 Br⁻ + 3H₂O, is
(A) 1.56 g (B) 0.9386 g (C) 1.23 g (D) 1.32 g

Sol. Meq. of $NaBrO_3 = 55.5 \text{ } 40.672 = 37.296$

Let weight of $NaBrO_3 = W$ $\therefore \frac{W}{M_{\text{NaBrO}_3}} \text{ Y 6 Y 1000} = 37.296 \text{ (equivalent weight = M/6) of n-factor = 6}$ $\therefore \frac{M}{151} \vee 6 \vee 1000 = 37.296$ ∴ W = 0.9386 g

Hence, (B) is the correct answer.

Ex 5. NalO₃ reacts with NaHSO₃ according to equation $IO_3^- + 3HSO_3^- \longrightarrow I^- + 3H^+ + 3SO_4^{2-}$ The weight of NaHSO₃ required to react with 100 mL of solution containing 0.68 g of NaIO₃ is (A) 5.2 g (B) 0.2143 g (C) 2.3 g (D) none of the above

Sol. Meq. of NaHSO₃ = Meq. of NaIO₃ = N 4 V =
$$\frac{0.68}{198}$$
 4 6 4 1000 (I⁵⁺ + 6e⁻ \rightarrow I⁻)

$$\therefore \frac{W_{\text{NaHSO}_3}}{M_{\text{NaHSO}_3}} \Psi 2 \Psi 1000 = \frac{0.68}{198} \Psi 6 \Psi 100$$
$$W_{\text{NaHSO}_3} = \frac{0.68 \times 6 \times 100 \times 104}{198 \times 1000} = 0.2143$$

Hence (B) is the correct answer.

Ex 6. If 0.5 moles of $BaCl_2$ is mixed with 0.1 moles of Na_3PO_4 , the maximum amount of $Ba_3(PO_4)_2$ that can be formed is

Sol. Let us first solve this problem by writing the complete balanced reaction. $3BaCl_2 + 2Na_3PO_4 \longrightarrow Ba_3(PO_4)_2 \downarrow + 6NaCl$

We can see that the moles of $BaCl_2$ used are $\frac{3}{2}$ times the moles of Na_3PO_4 . Therefore, to react with 0.1 mol of Na_3PO_4 , the moles of $BaCl_2$ required would be 0.1 $\P \frac{3}{2} = 0.15$. Since $BaCl_2$ is 0.5 mol, we can conclude that Na_3PO_4 is the limiting reagent. Therefore, moles of $Ba_3(PO_4)_2$ formed is 0.1 $\P \frac{1}{2} = 0.05$ mol. Hence, (D) is the correct answer.

- Ex 7. 0.52 g of a dibasic acid required 100 mL of 0.2 N NaOH for complete neutralization.
 - The equivalent weight of acid is
 - (A) 26 (B) 52 (C) 104 (D) 156
- **Sol.** Meq. of Acid = Meq. of NaOH

$$\frac{0.52}{E} \times 1000 = 100 \text{ H} 0.2$$

∴ E = 26

Hence (A) is the correct answer.

- Ex 8. 34 g hydrogen peroxide is present in 1120 mL of Solution : This solution is called
 - (A) 10 volume (B) 20 volume (C) 30 volume (D) 32 volume

Sol. Wt. of
$$H_2O_2$$
 in 1 mL = $\frac{34}{1120}$ g

$$\mathrm{H_2O_2} \rightarrow \mathrm{H_2O} + \frac{1}{2}\mathrm{O_2}$$

34 g of H_2O_2 gives 11200 mL of O_2 at STP

$$\therefore \frac{34}{1120} \text{ g of } \text{H}_2\text{O}_2 \equiv \frac{11200}{34} \text{ Y } \frac{34}{1120} = 10 \text{ mL of } \text{O}_2 \text{ at STP.}$$

Hence, (A) is the correct answer.

Ex 9. The number of moles of $KMnO_4$ that will be required to react with 2 mol of ferrous oxalate is

(A)
$$\frac{6}{5}$$
 (B) $\frac{2}{5}$ (C) $\frac{4}{5}$ (D) 1
Sol. $Mn^{7+} + 5e^{-} \rightarrow Mn^{2+}] \lor 3$
 $Fe^{2+} \rightarrow Fe^{3+} + e^{-}$
 $C_2O_4^{2-} \rightarrow 2CO_2 + 2e^{-}$
 $3 \text{ moles of KMnO}_4 = 5 \text{ moles of FeC}_2O_4$
 $\therefore 2 \text{ mol of ferrous oxalate} = \frac{6}{5} \text{ mole of KMnO}_4$
Hence, (A) is the correct answer.
Ex10. What volume of 0.1 M KMnO₄ is needed to oxidize 100 mg of FeC₂O₄ in acid solution ?

(A) 4.1 mL (B) 8.2 mL (C) 10.2 mL (D) 4.6 mL

Sol. Meq. of $KMnO_4 = Meq.$ of FeC_2O_4



 \therefore V = 4.1 mL

Hence, (A) is the correct answer.

- **Ex11**. What volume of 6 M HNO₃ is needed to oxidize 8 g of Fe^{2+} to Fe^{3+} , HNO₃ gets converted to NO?
- (A) 8 mL (B) 7.936 mL (C) 32 mL (D) 64 mL **Sol.** Meq. of $HNO_3 = Meq.$ of Fe^{2+}

or
$$6 \ \text{V} \ 3 \ \text{V} \ \text{V} = \frac{8}{56} \ \text{V} \ 1000$$

V = 7.936 mL

$$n-factor = 3$$

$$| -5 = 2+$$

$$(NO_3^- \rightarrow NO)$$

Hence, (B) is the correct answer.

Ex12. 0.5 g of fuming H_2SO_4 (oleum) is diluted with water. This solution is completely neutralized by 26.7 mL of 0.4 N KOH. The percentage of free SO_3 in the sample is

(A) 30.6% (B) 40.6% C) 20.6% (D) 50%

Sol. Meq. of
$$H_2SO_4$$
 + Meq.of SO_3 = Meq. of KOH

$$\therefore \frac{(0.5 - x)}{98/2} \vee 1000 + \frac{x}{80/2} \vee 1000 = 26.7 \vee 0.4$$

$$\therefore x = 0.103$$

$$\therefore \% \text{ of SO}_3 = \frac{0.103}{0.5} \vee 100 = 20.6\%$$

Hence, (C) is the correct answer.

Ex13	Ex13 . The minimum quantity of H_2S needed to precipitate 63.5 g of Cu^{2+} will be nearly.					
	(A) 63.5 g	(B) 31.75 g	(C) 34 g	(D) 2.0 g		
Sol.	Meq. of $H_2S = Meq.$ of Cu^{2+}					
	$\therefore \frac{W_{H_2S}}{34/2} \ \text{Y} \ 1000 = \frac{63.5}{63.5/2} \times 1000$					
	$\therefore W_{H_2S} = 34 g$					
	Hence, (C) is the correct	answer.				
Ex14	. Which of the following is	s / are correct?				
	(A) g mole wt. $=$ mol. wt	$f: in g = wt. of 6.02 \text{ H} 10^{23}$	molecules			
	(B) mole = N molecule =	6.02 4 10 ²³ molecules				
	(C) mole $=$ g molecules					
	(D) none of the above					
Sol.	(A), (B) and (C)					
Ex15	. 8 g of O_2 has the same i	number of molecules as				
	(A) 7 g of CO	(B) 14 g of CO	(C) 28 g of CO	(D) 11 g of CO ₂		
Sol.	(A) and (D)					
Ex16	. The eq. wt. of a substan	ce is the weight which eith	er combines or displaces.			
	(A) 8 part of O	(B) 2 part of H	(C) 35.5 part of Cl	(D) none of the above		
Sol.	(A) and (C)					
Ex17	. 'A' g of a metal displaces	s V mL of H ₂ at NTP. Eq. v	vt of metal E is / are :			
	(A) $E = \frac{A}{Wt. of H_2 \text{ displace}}$	eed ^H Eq. wt. of H	(B) $E = \frac{A \times 1.008 \times 22400}{\text{Volume of } H_2 \text{ displaced} \times 2} \text{ U} \text{ Eq. wt. of H}$			
S al	(C) $E = \frac{A}{Volume of H_2 di}$	× 1.008 isplaced × 0.0000897	(D) none of the above			
501. E10	(A), (D) and (C)	a long modely modeling (a)?				
LXIO	$(A) B_{2}O + H SO > B_{2}$		(\mathbf{R}) $2\mathbf{R}_{2}\mathbf{O} + \mathbf{O} \rightarrow 2\mathbf{R}_{2}\mathbf{O}$			
	(A) $BaU_2 + \Pi_2 SU_4 \rightarrow BaSU_4 + \Pi_2 U_2$ (C) $2KCIO_2 + 2KCI + 2O_2$		(D) SO + $2HS > 2HO + 3S$			
Sol	(B) (C) and (D)		$(D) OO_2 + 2II_2 O \rightarrow 2II_2 O$			
Fx19	In the reaction					
LAIJ	$_{3}Br + 6CO^{2-} + 3HO$	$\rightarrow 5Br^{-} + BrO^{-} + 6HCO$	-			
	(A) bromine is oxidized a	and carbonate is reduced	(B) bromine is oxidized			
	(C) bromine is reduced		(D) it is disproportionation	n reaction or autoredox change		
Sol.	(B), (C) and (D)					
Ex20	. Which of the following s	tatements is/are true if 1 r	nol of H_PO_is completely	neutralized by 40 g of NaOH?		
22 0	(A) $x = 2$ and acid is mo	nobasic	(B) $x = 3$ and acid is dibat	sic		
	(C) $x = 4$ and acid is trib	asic	(D) $x = 2$ and acid does n	ot form acid salt		
Sol.	(A) and (D).					