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.**	$S + H_2 \rightarrow H_2S$
(3)	Increase in positive charge	(iii)	Decrease in positive charge
e.g.	$Fe^{2+} \rightarrow Fe^{3+} + e^-$	**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.	$Sn^{2+} \rightarrow Sn^{4+} + 2e^-$	**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 $-\frac{1}{2}$
(iii) ozonide (KO_3) 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. $\overset{+5}{KClO_3}\ \ \overset{+5}{HIO_3}\ \ \overset{+7}{HClO_4}\ \ \overset{+5}{KBrO_3}$

- **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. $\overset{0}{O_2},\overset{0}{S_8},\overset{0}{P_4},\overset{0}{O_3}$

- 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 to +5 $(\overset{-3}{N}H_3,\overset{+2}{N}O,\overset{+3}{N_2}O_3,\overset{+4}{N}O_2,\overset{+5}{N_2}O_5)$

Calculation of average oxidation number :

Solved Examples :

Ex. Calculate oxidation number of underlined element $Na_2\underline{S}_2O_3$:

Sol. Let oxidation number of S-atom is x. Now work accordingly with the rules given before.

(+1) 2 + (x) 2 + (–2) 3 = 0

x = + 2

Ex. $Na_2\underline{S}_4O_6$:

Sol. Let oxidation number of S-atom is x

(+1) 2 + (x) 2 + (–2) 6 = 0

x = + 2.5

- It's important to note here that $Na_2S_2O_3$ have two S-atom and there are four S-atom in $Na_2S_4O_6$ 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.

Ex. Calculate the O.S. of all the atoms in the following species :

(i) ClO^-, (ii) NO_2^-, (iii) NO_3^- (iv) CCl_4 (v) K_2CrO_4 and (vi) $KMnO_4$

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.

x is + 1

(ii) NO_2^- : (2 –2) + x = –1 (where 'x' is O.S. of N)

$\therefore$ x = +3

(iii) NO_3^- : x + (3 –2) = –1 (where 'x' is O.S. of N)

x = +5

(iv) In CCl_4, Cl has an O.S. of –1

x + 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,
$2 \quad +1 + x + 4 \quad -2 = 0$

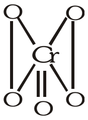
$\therefore\ x = +6$

(vi) $KMnO_4$: $+1 + x + (4 \quad -2) = 0$

$\therefore\ x = +7$ (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 :

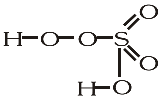
◆ The structure of CrO_5 is 

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 $x = 6$

$\therefore$ O.N. of Cr = +6 **Ans.**

◆ The strcuture of H_2SO_5 is 

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.

$\therefore$ $+1 - 2 + x + (-2)\ 2 + (-2) + 1 = 0$

or $x + 2 - 8 = 0$

or $x - 6 = 0$

or $x = 6$

$\therefore$ O.N. of S in H_2SO_5 is +6 **Ans**

❑ Paradox of fractional oxidation number :

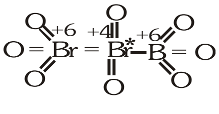
Fractional oxidation state is the average oxidation state of the element under examination and the structural parameters reveal that the element for whom fractional oxidation state is realised is actually present in different oxidation states. Structure of the species C_3O_2, Br_3O_8 and $S_4O_6^{2-}$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

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

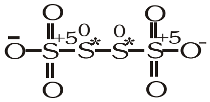
Structure of C_3O_2
(Carbon suboxide)

◆ 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.



Structure of Br_3O_8 (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.



Structure of $S_4O_6^{2-}$ (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. $KMnO_4$, $K_2Cr_2O_7$, HNO_3, conc. H_2SO_4 etc, are powerful oxidising agents.

- **Reducing agent or Reductant :**

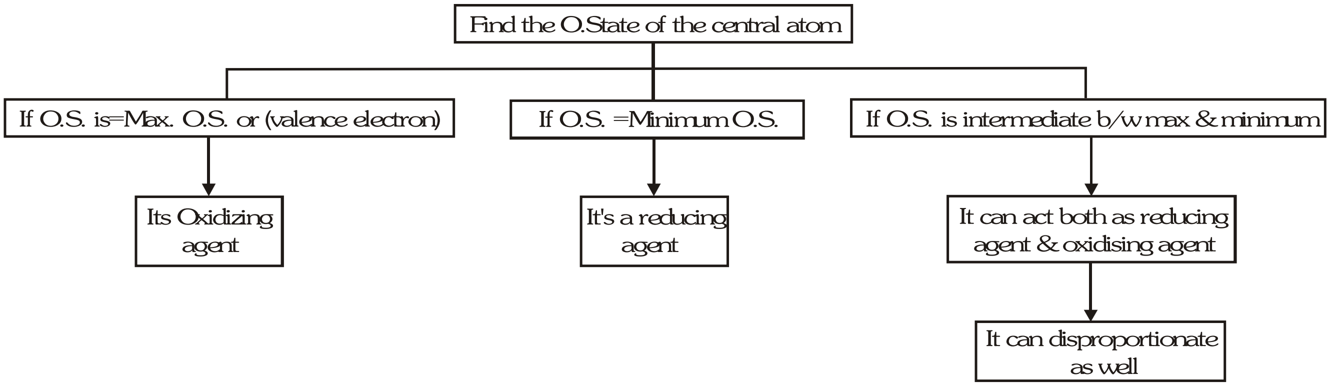
  Redusing agents are those compound which can reduce others and oxidise itself during the chemical reaction. Those reagents whose O.N. increase or which loses electrons in a redox reaction are termed as reductants.

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. $10\overset{+2}{Fe}SO_4 + 2K\overset{+7}{Mn}O_4 + 8H_2SO_4 \longrightarrow 5\overset{+3}{Fe}_2(SO_4)_3 + 2\overset{+2}{Mn}SO_4 + K_2SO_4 + 8H_2O$

- **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.

$\overset{+1}{2H_2}\overset{-1}{O_2}(aq) \longrightarrow \overset{+1}{2H_2}\overset{-2}{O_2}(\ell) + \overset{0}{O}(g)$

$\overset{0}{S_8}(s) + 12OH^-(aq) \longrightarrow 4\overset{-2}{S^{2-}}(aq) + 2\overset{+2}{S_2}O_3^{2-}(aq) + 6H_2O(\ell)$

$\overset{0}{Cl_2}(g) + 2OH^-(aq) \longrightarrow \overset{+1}{ClO^-}(aq) + \overset{-1}{Cl^-}(aq) + H_2O(\ell)$

- Consider following reactions :

(a) $2KClO_3 = 2KCl + 3O_2$

$KClO_3$ plays a role of oxidant and reductant both. Because same element is not oxidised and reduced. Here, Cl present in $KClO_3$ is reduced and O present in $KClO_3$ 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) $4KClO_3 \longrightarrow 3KClO_4 + KCl$

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

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

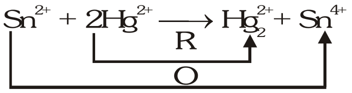
F_2 + NaOH (dil) $\longrightarrow F^- + OF_2$

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

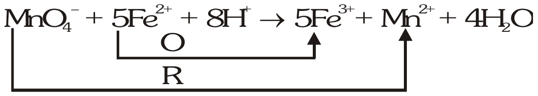
- Reverse of disproportionation is called Comproportionation. In some of the disproportionation reactions by changing the medium (from acidic to basic or reverse) the reaction goes in backward direction and can be taken as an example of Comproportionation.

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

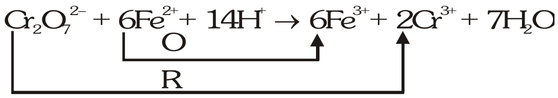
- Some examples of redox reactions are :

- 

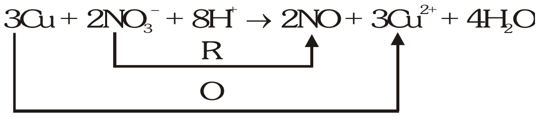
$Sn^{2+} + 2Hg^{2+} \longrightarrow Hg_2^{2+} + Sn^{4+}$

- 

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

- 

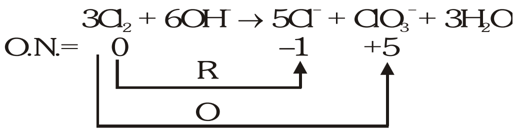
$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$

- 

$3Cu + 2NO_3^- + 8H^+ \rightarrow 2NO + 3Cu^{2+} + 4H_2O$

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

◆

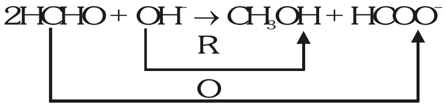


$$3Cl_2 + 6OH^- \rightarrow 5Cl^- + ClO_3^- + 3H_2O$$

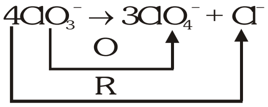
In the above reaction, we can see that Cl_2 has been oxidized as well as reduced. Such type of redox reaction is called **disproportionation** reaction.

Some More examples :

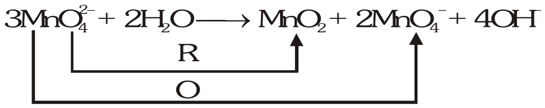
$$2Cu^+ \xrightarrow{\text{Disproportionates}} Cu + Cu^{2+}$$



$$2HCHO + OH^- \rightarrow CH_3OH + HCOO^-$$



$$4ClO_3^- \rightarrow 3ClO_4^- + Cl^-$$



$$3MnO_4^{2-} + 2H_2O \longrightarrow MnO_2 + 2MnO_4^- + 4OH^-$$

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 :

(i) 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.

$$\overset{0}{Cu} + \overset{+1+5-2}{HNO_3} \xrightarrow{\qquad\qquad} \overset{+2+5-2}{Cu(NO_3)_2} + \overset{+4\ -2}{NO_2} + \overset{+1\ -2}{H_2O}$$

There is change in oxidation number of Cu and N.

$$\overset{0}{Cu} \longrightarrow \overset{+2}{Cu(NO_3)_2} \quad ....(1) \qquad \text{(Oxidation no. is increased by 2)}$$

$$\overset{+5}{HNO_3} \longrightarrow \overset{+4}{NO_2} \quad .....(2) \qquad \text{(Oxidation no. is decreased by 1)}$$

To make increase and decrease equal, eq. (2) is multiplied by 2.

$$Cu + 2HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + H_2O$$

Balancing nitrates ions, hydrogen and oxygen, the following equation is obtained.

$$Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

This is the balanced equation.

Ex. Write the skeleton equation for each of the following processes and balance them by ion electron method :

(i) Permagnet ion oxidizes oxalate ions in acidic medium to carbon dioxide and gets reduced itself to Mn^{2+} 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 :

$$MnO_4^- + C_2O_4^{2-} + H^+ \longrightarrow Mn^{2+} + CO_2 + H_2O$$

◆ **Step (1)** : Indicating oxidation number :

$$\overset{+7\ -2}{MnO_4^-} + \overset{+3}{C_2O_4^{2-}} \longrightarrow Mn^{2+} + \overset{+4\ -2}{CO_2} + \overset{+1\ -2}{H_2O}$$

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

$$\overset{+3}{C_2O_4^{2-}} \longrightarrow 2\overset{+4}{CO_2} \qquad \text{(Oxidation half)}$$

$$\overset{+7}{MnO_4^-} \longrightarrow Mn^{2+} \qquad \text{(Reduction half)}$$

◆ **Step (3)** : Adding electrons to make the difference in O.N.

$$\overset{+3}{C_2O_4^{2-}} \longrightarrow 2\overset{+4}{CO_2} + 2e^-$$

$$\overset{+7}{MnO_4^-} + 5e^- \longrightarrow Mn^{2+}$$

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

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

$$MnO_4^- + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

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

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

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

◆ **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.

$[C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-] \quad 5$

$[MnO_4^- + 5e^- + 8H^+ \longrightarrow Mn^{2+} + 4H_2O] \quad 2$

$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$

(ii) The skeleton equation for the given process is

$Br_2 + H_2O_2 \longrightarrow BrO_3^- + H_2O$ (in acidic medium)

◆ **Step (1)** : Indicate the oxidation number of each atom

$\overset{0}{Br_2} + \overset{+1}{H_2}\overset{-2}{O_2} \longrightarrow \overset{+6}{Br}\overset{-2}{O_3^-} + \overset{+1}{H_2}\overset{-2}{O}$

Thus, Br and O changes their oxidation numbers.

◆ **Step (2)** : Write the oxidation and reduction half reaction.

$\overset{0}{Br_2} \longrightarrow 2\left(\overset{+5}{B}rO_3^-\right)$ (Oxidation half)

$H_2\overset{-1}{O_2} \longrightarrow 2H_2\overset{-2}{O}$ (Reduction half)

◆ **Step (3)** : Addition of electrons to make up for the difference in O.N.

$\overset{0}{Br_2} \longrightarrow 2\left(\overset{+5}{B}rO_3^-\right) + 10e^-$

$H_2O_2^{-1} + 2e^- \longrightarrow 2H_2O^{-2}$

◆ **Step (4)** : Balance 'O' atoms by adding H_2O molecules

$Br_2 + 6H_2O \longrightarrow 2BrO_3^- + 10e^-$

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

◆ **Step (5)** : Equalize the electrons by multiplying the reduction half with 5 and add the two half reactions

$Br_2 + 6H_2O \longrightarrow 2BrO_3^- + 10e^- + 12H^+$

$[H_2O_2 + 2e^- + 2H^+ \longrightarrow 2H_2O] \quad 5$

$Br_2 + 5H_2O_2 \longrightarrow 2BrO_3^- + 4H_2O + 2H^+$

(iii) The skeleton equation for the given process :

$Cl_2 + OH^- \longrightarrow Cl^- + ClO_3^- + H_2O$

◆ **Step (1)** : Indicate the oxidation number of each atom

$\overset{0}{Cl_2} + \overset{+2}{O}H^- \longrightarrow Cl^- + \overset{+5}{Cl}O_3^- + \overset{+1}{H_2}\overset{-2}{O}$

Thus, chlorine is the only element which undergoes the change in oxidation number. It decreases its oxidation number from 0 to 1 and also increases its oxidation number from 0 to 5.

◆ **Step (2)** : Write the oxidation and reduction half reactions

$\overset{0}{Cl_2} \longrightarrow 2\overset{+5}{Cl}O_3^-$ (Oxidation half)

$\overset{0}{Cl_2} \longrightarrow 2Cl^-$ (Reduction half)

◆ **Step (3)** : Add electrons to make up for the difference in O.N.

$\overset{0}{Cl_2} \longrightarrow 2\overset{+5}{Cl}O_3^- + 10e^-$

$\overset{0}{Cl_2} + 2e^- \longrightarrow 2Cl^-$

◆ **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.

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

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

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

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.

$\overset{+7\ -2}{MnO_4^-} + Fe^{+2} \xrightarrow{\qquad\qquad} Mn^{+2} + Fe^{+3}$

change in oxidation number has occurred in Mn and Fe.

$\overset{+7}{MnO_4^-} \longrightarrow \overset{+2}{Mn}$ ......(1) (Decrement in oxidation no. by 5)

$Fe^{+2} \longrightarrow Fe^{+3}$ ......(2) (Increment in oxidation no. by 1)

To make increase and decrease equal, eq. (2) is multiplied by 5.

$MnO_4^- + 5Fe^{+2} \longrightarrow Mn^{+2} + 5Fe^{+3}$

To balance oxygen, $4H_2O$ are added to R.H.S. and to balance hydrogen, $8H^+$ are added to L.H.S.

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

This is the balanced equation.

Ex. Balance the following chemical reaction by oxidation number method and write their skeleton equation :

(i) Chloride ions reduce maganese dioxide to manganese (II) ions in acidic medium and get itself oxidized to chlorine gas.

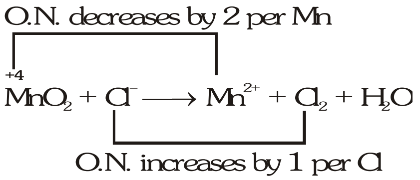
(ii) The nitrate ions in acidic medium oxidize magnesium to Mg^{2+} ions but itself gets reduced to nitrous oxide.

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

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

◆ **Step (1)** : $\overset{+4\ -2}{MnO_2} + Cl^- \longrightarrow Mn^{2+} + \overset{+4}{Cl_2} + \overset{+1\ -2}{H_2O}$

◆ **Step (2)** :



- **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)** : $\overset{0}{Mg} + (\overset{+5}{N}\overset{-2}{O_3})^- \longrightarrow Mg^{2+} + \overset{+1}{N_2}\overset{-2}{O} + \overset{+1}{H_2}\overset{-2}{O}$

  Multiply NO_3^- by 2 to equalize N atoms
- **Step (2)** : O.N. increases by 2 per Mg atom

  $$\overset{0}{Mg} + 2NO_3^- \longrightarrow Mg^{2+} + \overset{+1}{N_2}O + H_2O$$

  4 2 = 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.

$FeSO_4 + KMnO_4 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + MnSO_4 + H_2O$

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

$$\overset{+2}{Fe}\overset{+6}{S}\overset{-2}{O_4} + \overset{+1}{K}\overset{+7}{Mn}\overset{-2}{O_4} + \overset{+1}{H_2}\overset{+6}{S}\overset{-2}{O_4} \longrightarrow \overset{+3}{Fe_2}(\overset{+6}{S}\overset{-2}{O_4})_3 + \overset{+2}{Mn}\overset{+6}{S}\overset{-2}{O_4} + \overset{+1}{H_2}\overset{-2}{O}$$

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

$$Fe^{2+} + \overset{+7}{MnO_4^-} \longrightarrow Fe^{3+} + Mn^{2+}$$

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

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

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

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

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.

$Fe^{2+} \longrightarrow Fe^{3+}$ (no oxygen atom) ……….(i)

$8H^+ + MnO_4^- \longrightarrow Mn^{2+} + 4H_2O$ ………(ii)

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.

$Fe^{2+} \xrightarrow{\text{oxidation}} Fe^{3+} + e^-$ ……….(1)

$5e^- + 8H^+ + MnO_4^- \xrightarrow{\text{Reduction}} Mn^{2+} + 4H_2O$ ……….(2)

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

$Fe^{2+} \longrightarrow Fe^{3+} + e^-$ ………….(1) 5

$5e^- + 8H^+ + MnO_4^- \rightarrow M^{2+} + 4H_2O$ ………….(2) 1

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

(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

$$5\ FeSO_4 + KMnO_4 + 4H_2SO_4 \rightarrow \frac{5}{2}\ Fe_2(SO_4)_3 + MnSO_4 + 4H_2O \qquad \text{or}$$

$$10\ FeSO_4 + 2KMnO_4 + 8H_2SO_4 \rightarrow 5Fe_2(SO_4)_3 + 2MnSO_4 + 8H_2O + K_2SO_4$$

- **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 : $ClO^- + CrO_2^- + OH^- \longrightarrow Cl^- + CrO_4^{2-} + H_2O$

Sol : By using up to step V we will get

$\overset{+1}{ClO^-} \xrightarrow{\text{Reduction}} Cl^-$ | $\overset{+3}{CrO_2^-} \xrightarrow{\text{Oxidation}} \overset{+6}{CrO_4^{2-}}$

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

$2H^+ + ClO^- \longrightarrow Cl^- + H_2O$ | $2H_2O + CrO^-_2 \longrightarrow CrO_4^{2-} + 4H^+$

- 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.

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

Finally you will get | Finally you will get

$H_2O + ClO^- \longrightarrow Cl^- + 2OH^-$ ....(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) 3

$4OH^- + CrO_2^- \rightarrow CrO_4^{-2} + 2H_2O + 3e^-$ ....(ii) 2

Adding : $3ClO^- + 2CrO_2^- + 2OH^- \rightarrow 3Cl^- + 2CrO_4^{2-} + H_2O$

☐ Equivalent weight (E) :

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

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

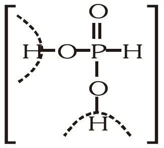
- Equivalent mass is a pure number when expressed in gram, it is called gram equivalent mass.
- The equivalent mass of substance may have different values under different conditions.

☐ Valency factor calculation :

- **For Acids :**

valence factor = number of replaceable H^+ ions

☐ Solved Examples :



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

Ex :	HCl,	H_2SO_4	H_3PO_4	H_3PO_3
Sol : valence→ factor	1	2 (assume 100% dissociation)	3	2
Eq.wt.→	$\frac{M}{1}$	$\frac{M}{2}$	$\frac{M}{3}$	$\frac{M}{2}$

Self practice problems :

1. Find the valence factor for following acids
   (i) CH_3COOH
   (ii) NaH_2PO_4
   (iii) H_3BO_3

Answers :

1. (i) 1 (ii) 2 (iii) 1

◆ **For Base :**

v.f. = number of replicable OH^- ions

❑ **Solved Examples :**

		NaOH,	KOH
Ex :		NaOH,	KOH
Sol :	v.f.→	1	1
	E.→	$\frac{M}{1}$	$\frac{M}{1}$

Self practice problems :

1. Find the valence factor for following bases

(i) $Ca(OH)_2$

(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 H_2SO_4 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

$$E = \frac{\text{mol. wt. of } H_2SO_4}{1}$$

◆ **For Salts :**

(a) In non reacting condition

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

❑ **Solved Examples :**

		Na_2CO_3	$Fe_2(SO_4)_3(2Fe^{3+} + 3SO_4^{2-})$	$FeSO_4.7H_2O$
Sol :	V.f.	2	2 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)

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

Ex: In acidic medium, $C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$

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

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

$(+7)$ $(+6)$

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)

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

- **Questions based on Equivalent weight :**

1. Molecular weight of $KMnO_4$ in acidic medium and neutral medium will be respectively :

(A) 7 equivalent wt. and 2 equivalent wt.

(B) 5 equivalent wt. and 4 equivalent wt.

(C) 4 equivalent wt. and 5 equivalent wt.

(D) 2 equivalent wt. and 4 equivalent wt.

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

$H_3PO_4 + OH^- \longrightarrow H_2PO_4^- + H_2O$

$H_3PO_4 + 2OH^- \longrightarrow HPO_4^{2-} + 2H_2O$

$H_3PO_4 + 3OH^- \longrightarrow PO_4^{3-} + 3H_2O$

(A) 98, 49, 32.67 (B) 49, 98, 32.67 (C) 98, 32.67, 49 (D) 32.67, 49, 98

3. In acidic medium, equivalent weight of $K_2Cr_2O_7$ (Mol. wt. = M) is –

(A) M/3 (B) M/4 (C) M/6 (D) M/2

Answers :

(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.

- No. of equivalent of solute = $\frac{W}{E}$
- V mL of solution have $\frac{W}{E}$ equivalent of solute
- 1000 mL solution have $\frac{W \times 1000}{E \times VmL}$
- **Normality (N) =** $\frac{W \times 1000}{E \times VmL}$
- **Normality (N) = Molarity Valence factor**

Normality (N) = molarity Valence factor (n)

or N V (in mL) = M V (in mL) n

or milli equivalents = millimoles n

❑ Solved Examples :

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

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

where W = 15.8 g, V = 50 mL $E = \frac{\text{molar mass of } KMnO_4}{\text{Valence factor}}$ = 158/5 = 31.6

So, N = 10

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

Sol : Normality (N) = Molarity Valence factor

= 5 6 = 30 N

❑ MOLARITY V/S NORMALITY :

	Molarity (M)		Normality (N)
1.	No. of moles of solute present in one litre of solution.	1.	No. of equivalents of solute present in one litre of solution.
2.	No. of moles $=\frac{W}{M}$	2.	No. of equivalents $=\frac{W}{E}$
3.	$\frac{W}{M}$ 1000 = No. of millimoles	3.	$\frac{W}{E}$ 1000 = No. of equivalance
4.	Molarity V(in mL)=No. of millimoles	4.	Normality V(in mL) = No. of equivalents
5.	Molarity $=\frac{\text{milli moles}}{\text{Volume of solution in mL}}$	5.	Normality $=\frac{\text{milli equivalents}}{\text{Volume of solution in mL}}$

❑ 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 → mM + nN

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

(ii) In a compound M_xN_y

m.eq of M_xN_y = m.eq of M = m.eq of N

❑ Solved Examples :

Ex : 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.

moles of Cu_2S 8 = 1 5 ⇒ 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 MnO_4^-

x (mole) 2 = 1 5

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

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

∴ Volume of 2 M HCl required = (2 – x) L

$M_1V_1 \quad + \quad M_2V_2 \quad = \quad M_3V_3$

6M HCl 2M HCl 3M HCl

6 (x) + 2 (2 – x) = 3 2

⇒ 6x + 4 – 6x = 6 ⇒ 4x = 2

∴ 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 $\quad$ 40 = 6 g

$\therefore$ 1 mL of this solution contain NaOH $= \frac{6}{1000} \quad 10^{-3}$ g

$\therefore$ 1.184 g of NaOH will be present in $= \frac{1}{6 \times 10^{-3}} \quad 1.184 = 197.33$ 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

$= 45.6 \quad 0.235$

$$\therefore \quad \frac{W_{Na_2CO_3}}{E_{Na_2CO_3}} \quad 1000 = 45.6 \quad 0.235$$

$$\Rightarrow \quad \frac{W_{Na_2CO_3}}{106/2} \quad 1000 = 45.6 \quad 0.235$$

$$\therefore \quad W_{Na_2CO_3} = 0.5679 \text{ g}$$

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

$\therefore$ For 0.5679 g of pure Na_2CO_3, 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. $5e^- + 8H^+ + MnO_4^- \rightarrow Mn^{2+} + 2H_2O$

$\therefore$ Eq. wt of $MnO_4^- = \frac{MnO_4^-(\text{mol.wt.})}{5}$

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

$\therefore$ Eq. wt. of $MnO_4^- = \frac{MnO_4^-}{3}$

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 $KMnO_4$ 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 $\quad$ 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 $\quad$ 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 reaction 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^-

$\because$ IO_3^- react with I^- $\Rightarrow$ meq of IO_3^- = meq of I^-

◆ meq of hypo = 2   meq of IO_3^-

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

$\because$ v.f. of I_2 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 $KMnO_4$ solution would be required to exactly titrate 25.00 mL of 0.2000 M $Fe(NO_3)_2$ 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   0.2000

and in volume V (in milliliters of the MnO_4^-)

Millimoles of MnO_4^- = V (0.02000)

The balanced reaction is :

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

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   moles of MnO_4^-

Normality MnO_4^- = 5   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 $V_{MnO_4^-}$ Normality of MnO_4^-

= $V_{Fe^{2+}}$ Normality of Fe^{2+}

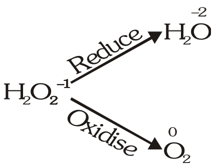
For 0.02000 M MnO_4^- solution

Normality of MnO_4^- = (5) (0.02000) = 0.1 N   and for 0.2000 M Fe^{2+} solution

Normality of Fe^{2+} = 0.2000 N $V_{MnO_4^-} = (25.00\ \text{mL}) \left(\frac{0.2000}{0.1000}\right) = 50.00\,\text{mL}$

❑ HYDROGEN PEROXIDE (H_2O_2) :

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



- Oxidising agent : (H_2O_2)

(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 :

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

v.f. = 2

(b) Basic medium :

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

v.f. = 2

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.**

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

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

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

Strength (in g/L) : Denoted by S

Strength = molarity mol. wt.

= molarity 34

Strength = Normality Eq. weight.

= Normality 17

❑ **Solved Example :**

Ex : 20 mL of H_2O_2 after acidification with dil H_2SO_4 required 30 mL of $\frac{N}{12}$ $KMnO_4$ for complete oxidation. The strength of H_2O_2 solution is [Molar mass of H_2O_2 = 34]

Sol :

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

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

$$\therefore \quad \text{strength} = N' \quad \text{equivalent mass} = \frac{1}{8} \quad 17 = 2.12 \text{ g/L}$$

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 : $2HCO_3^- \rightarrow H_2O + CO_2 + CO_3^{2-}$ 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.

$$ppm_A = \frac{\text{mass of A}}{\text{Total mass}} \quad 10^6 = \text{mass fraction} \quad 10^6$$

◆ **Measurement of Hardness :**

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

❑ **Solved Example :**

Ex : 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 requires to purify 1000 litre water.

Sol : 0.00012% $MgSO_4$ = 1 mg $CaCO_3$ 1 L water

0.000111% $CaCl_2$ = 1 mg $CaCO_3$ 1 L water

hardness = 2 ppm and mm of Na_2CO_3 require is 20

◆ **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

❑ **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.

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

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

$CaOCl_2 + 2H_3CCOOH \rightarrow Ca(CH_3COO)_2 + H_2O + Cl_2$

$CaOCl_2 + CO_2 \rightarrow CaCO_3 + Cl_2$

◆ **Method of determination :**

Bleaching powder + CH_3COOH + KI $\xrightarrow{\text{or } KI_3}$ KI_3 $\frac{\text{starch}}{\text{Hypo}}$ end point (Blue → colourless)

$$\% \text{ of } Cl_2 = \frac{3.55 \times x \times V(mL)}{W(g)}$$

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 H_2O 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 100]

Sol : moles of iodine = moles of chlorine = $\frac{80 \times 0.2}{2} \quad 10^{-3} = 8 \quad 10^{-3}$

so required % = $\frac{8 \times 71 \times 10^{-3}}{3.55} \quad 100\% = 16\%$

❑ 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 $M_1 \quad n_1 \quad V_1 = M_2 \quad n_2 \quad V_2$ (always true where n terms represent n-factor).

❑ 'n' FACTOR : FACTOR RELATING MOLECULAR WEIGHT AND EQUIVALENT WEIGHT :

$$\text{n-factor} = \frac{M}{E}$$

$$E = \frac{M}{n - \text{factor}}$$

❑ 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 the no. of acidic H^+ ions that a molecule of the acid would give when dissolved in a solvent (Basicity).

  For example, for HCl (n = 1), HNO_3 (n = 1), H_2SO_4 (n = 2), H_3PO_4 (n = 3) and H_3PO_3 (n = 2)
- **For bases** : Bases will be treated as species which furnish OH^- ions when dissolved in a solvent . The n-factor of a base is the no. of OH^- ions that a molecule of the base would give when dissolved in a solvent **(Acidity)**.

  For example, NaOH (n = 1), $Ba(OH)_2$ (n = 2), $Al(OH)_3$ (n = 3), etc.
- **For salts** : A salt reacting such that no atom of the salt undergoes any change in oxidation state.

  For example, $2AgNO_3 + MgCl_2 \rightarrow Mg(NO_3)_2 + 2AgCl$

  In this reaction, it can be seen that the oxidation state of Ag, N, O, Mg and Cl remains the same even in the product. The n-factor for such a salt is the total **charge on cation or anion.**

In Redox Change

For oxidizing agent or reducing agent n-factor is the **change in oxidation number per 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} in acidic medium	$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$	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	$E = \frac{M}{1}$
$Cr_2O_7^{2-}$(O.A.)	Cr^{3+} in acidic medium	$CrO_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$	6	$E = \frac{M}{6}$
MnO_2(O.A.)	Mn^{2+} 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.) in iodometric titration	Cu^+	$Cu^{2+} + e^- \longrightarrow Cu^+$	1	$E = \frac{M}{1}$
$S_2O_3^{2-}$ (R.A.)	$S_4O_6^{2-}$	$2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2e^-$	2 (for two molecules)	$E = \frac{2M}{2} = M$
H_2O_2(O.A.)	H_2O	$H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$	2	$E = \frac{M}{2}$
H_2O_2(R.A.)	O_2	$H_2O_2 \longrightarrow O_2 + 2H^+ + 2e^-$ (O.N. of oxygen in H_2O_2 is –1 per atom)	2	$E = \frac{M}{2}$
Fe^{2+}(R.A.)	Fe^{3+}	$Fe^{2+} \longrightarrow Fe^{3+} + e^-$	1	$E = \frac{M}{1}$

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) $KMnO_4 \xrightarrow{OH^-} Mn^{6+}$ (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, $KMnO_4$ which is an oxidizing agent, itself gets reduced to Mn^{2+} under acidic conditions.

$n = |1\ (+7) - 1\ (+2)| = 5$

(ii) In this reaction, $KMnO_4$ gets reduced to Mn^{4+} under neutral or slightly (weakly) basic conditions.

$n = |1\ (+7) - 1\ (+4)| = 3$

(iii) In this reaction, $KMnO_4$ gets reduced to Mn^{6+} under basic conditions.

$n = |1\ (+7) - 1\ (+6)| = 1$

(iv) In this reaction, $K_2Cr_2O_7$ which acts as an oxidizing agent reduced to Cr^{3+} under acidic conditions. (It does not react under basic conditions.)

$n = |2\ (+6) - 2\ (+3)| = 6$

(v) In this reaction, $C_2O_4^{2-}$ (oxalate ion) gets oxidized to CO_2 when it is reacted with an oxidizing agent.

$n = |2\ (+3) - 2\ (+4)| = 2$

(vi) In this reaction, ferrous ions get oxidized to ferric ions.

$n = |1\ (+2) - 1\ (+3)| = 1$

(vi) In this reaction, ferric ions are getting reduced to ferrous ions.

$n = |2\ (+3) - 2\ (+2)| = 2$

Ex. Calculate the molar ratio in which the following two substances would react ?

$Ba_3(PO_4)_2$ and $AlCl_3$

Sol. n-factor of $Ba_3(PO_4)_2 = 3\ (+2) = 6 = n_1$

While n-factor of $AlCl_3 = 1\ (+3) = 3 = n_2$

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

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

∴ Molar ratio in which $Ba_3(PO_4)_2$ and $AlCl_3$ 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.

$\therefore$ $N_1V_1 = N_2V_2$, where N_2 is the conc. of A.

From this we can calculate the value of N_2.

Ex. 0.4 M $KMnO_4$ solution completely reacts with 0.05 M $FeSO_4$ solution under acidic conditions. The volume of $FeSO_4$ used is 50 mL. What volume of $KMnO_4$ was used ?

Sol. $0.4 \quad 5 \quad V = 0.05 \quad 50$

$V = 1.25$ 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 ?

Sol. Let, weight of Na_2CO_3 = x g

Weight of K_2CO_3 = y g

$\therefore$ $x + y = 1.20$ g ....(i)

For neutralization reaction of 100 mL

Meq. of Na_2CO_3 + Meq. of K_2CO_3 = Meq. of HCl

$\Rightarrow \frac{x}{106} \quad 2 \quad 1000 + \frac{y}{138} \quad 2 \quad 1000 = \frac{40\times0.1\times100}{20}$

$\therefore$ $69\,x + 53\,y = 73.14$ ....(ii)

From Eqs. (i) and (ii), we get

$x = 0.5962$ g

$y = 0.604$ g

Solution of Na_2CO_3 and K_2CO_3 gives ppt. of $BaCO_3$ with $BaCl_2$

(Meq. of Na_2CO_3 + Meq. of K_2CO_3) in 20 mL = Meq. of $BaCO_3$

$\Rightarrow$ Meq. of HCl for 20 mL mixture = Meq. of $BaCO_3$

$\Rightarrow$ Meq. of $BaCO_3$ = $40 \quad 0.1 = 4$

$$\frac{W_{BaCO_3}}{M_{BaCO_3}} \quad 1000 = 40 \quad 0.1 = 4$$

$$\frac{W_{BaCO_3}}{197} \quad 2 \quad 1000 = 4$$

$\therefore$ $W_{BaCO_3} = 0.394$ g

❑ BACK TITRATION

Back titration is used to calculate % purity of a sample. Let us assume that we are given an impure solid substance C weighing w gs and we are asked to calculate the percentage of pure C in the sample. We will assume that the impurities are inert. We are provided with two solutions A and B, where the concentration of B is known (N_1) and that of A is not known. This type of titration will work only if the following condition is satisfied, i.e. the nature of compounds A, B and C should be such that A and B can react with each other. A and C can react with each other but the product of A and C should not react with B.

Now, we take a certain volume of A in a flask (the g equivalents of A taken should be ≥ g equivalents of C in the sample and this can be done by taking A in excess). Now, we perform a simple titration using B. Let us assume that the volume of B used is V_1. In another beaker, we again take 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. Let us assume that the volume of B used up is V_2. Gram equivalents of B used in the first titration = N_1V_1.

$\therefore$ gm. equivalents of A initially = N_1V_1

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

$\therefore$ gm. equivalents of A left in excess after reacting with C = N_1V_2

gm. equivalents of A that reacted with C = $N_1V_1 - N_1V_2$

If the n-factor of C is x, then the moles of pure C = $\frac{N_1V_1 - N_1V_2}{x}$

$\therefore$ The weight of C = $\frac{N_1V_1 - N_1V_2}{x}$ Molecular weight of C

$\therefore$ Percentage of C = $\frac{N_1V_1 - N_1V_2}{x} \quad \frac{\text{Molecular wt. of C}}{w} \times 100$

❑ SOME REDOX TITRATIONS (EXCLUDING IODOMETRIC / IODIMETRIC)

Estimation of	By titrating with	Reactions	Relation *between O.A. and R.A.
Fe^{2+}	MnO_4^-	$Fe^{2+} \longrightarrow Fe^{3+} + e^-$ $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$	$5Fe^{2+} \equiv MnO_4^-$ Eq. wt. Fe^{2+} = M/1 Eq. wt. MnO_4^- = M/5
Fe^{2+}	$Cr_2O_7^{2-}$	$Fe^{2+} \longrightarrow Fe^{3+} + e^-$ $Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$	$6Fe^{2+} \equiv Cr_2O_7^{2-}$ Eq. wt. $Cr_2O_7^{2-}$ = M/6
$C_2O_4^{2-}$	MnO_4^-	$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$ $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{+2} + 4H_2O$	$5C_2O_4^{2-} \equiv 2MnO_4^-$ Eq. wt. $C_2O_4^{2-}$ = M/2 Eq. wt. MnO_4^- = M/5
H_2O_2	MnO_4^-	$H_2O_2 \longrightarrow 2H^+ + O_2 + 2e^-$ $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$	$5H_2O_2 \equiv 2MnO_4^-$ Eq. wt. H_2O_2 = M/2 Eq. wt. MnO_4^- = M/5
As_2O_3 AsO_3^{3-}	MnO_4^- BrO_3^-	$As_2O_3 + 5H_2O \rightarrow 2AsO_4^{3-} + 10H^+ + 4e^-$ $AsO_3^{3-} + H_2O \longrightarrow AsO_4^{3-} + 2H^+ + 2e^-$ $BrO_3^- + 6H^+ + 6e^- \longrightarrow Br^- + 3H_2O$	Eq. wt. As_2O_3 = M/4 Eq. wt. AsO_3^{3-} = M/2 Eq. wt. BrO_3^- = M/6

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 = $10 \quad 0.5 = 5$

Milli eq. of NaOH consumed = Milli eq. of HCl in excess = $10 \quad 0.2 = 2$

$\therefore$ Milli eq. of HCl consumed = Milli eq. of $Ba(OH)_2 = 5 - 2 = 3$

$\therefore$ Eq. of $Ba(OH)_2 = 3/1000 = 3 \quad 10^{-3}$

Mass of $Ba(OH)_2 = 3 \quad 10^{-3} \quad (171/2) = 0.2565$ g

% $Ba(OH)_2 = (0.2565\ /\ 20) \quad 100 = 1.28$ %

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

$= 50 \quad 0.5 \quad 2 - 32 \quad 0.02 \quad 5 \quad 10$ (in 250 mL) = 18

$$\frac{W_{MnO_2}}{M_{MnO_2}} \quad 2 \quad 1000 = 18 \Rightarrow \frac{W_{MnO_2}}{87} \quad 2 \quad 1000 = 18,$$

$\therefore \quad W_{MnO_2} = 0.7821$ g

$\therefore \quad$ % of $MnO_2 = \dfrac{0.7821}{3.2} \times 100 = 24.44$ %

Meq. of MnO_2 = Meq. of O_2

$$\frac{W_{O_2}}{16} \quad 2 \quad 1000 = 18, \therefore W_{O_2} = 0.144 \text{ g}$$

% of available $O_2 = \dfrac{0.144}{3.2} \quad 100 = 4.5$

❑ 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 (M_1)

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 Na_2CO_3 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 $NaHCO_3$ produced by the Na_2CO_3 = 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 = $M_1V_2 \quad 106$

$$\% \ Na_2CO_3 = \frac{M_1V_2 \times 106}{w} \times 100$$

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 = $M_1V_1 - M_1V_2$

Mass of NaOH = $(M_1V_1 - M_1V_2) \quad 40$

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

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 (HCl) using these two indicators is summarized below :

	Phenolphthalein	Methyl orange
NaOH	100% reaction is indicated $NaOH + HCl \longrightarrow NaCl + H_2O$	100% reaction is indicated $NaOH + HCl \longrightarrow NaCl + H_2O$
Na_2CO_3	50% reaction upto $NaHCO_3$ stage is indicated $Na_2CO_3 + HCl \longrightarrow NaHCO_3 + NaCl$	100% reaction is indicated $Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2$
$NaHCO_3$	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 Na_2CO_3 was present in mixture. At phenolphthalein end point,

$$\left(\frac{W_1}{40}+\frac{1}{2}\times\frac{W_2}{53}\right)=\frac{1}{10} \quad 17.5 \quad 10^{-3} \qquad \text{.........(1)}$$

At second end point following reaction takes place

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

$= \frac{1}{2}$ Eq. of Na_2CO_3

$$\frac{1}{2}\times\frac{W_2}{53} = 1.5 \quad \frac{1}{10} \quad 10^{-3}$$

W_2 = 0.01590 g

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

W_1 = 0.064 g

Percentage of NaOH $=\frac{0.064}{0.4} \quad 100 = 16\%$

Percentage of Na_2CO_3 $= \frac{0.01590}{0.4} \quad 100 = 3.975\ \%$

Iodometric and Iodimetric Titration :

The reduction of free iodine to iodide ions and oxidation of iodide ions to free iodine occurs in these titrations.

$I_2 + 2e^- \longrightarrow 2I^-$ (reduction)

$2I^- \longrightarrow I_2 + 2e^-$ (oxidation)

These are divided into two types :

Iodometic Titration :

In iodometric titrations, an oxidizing agent is allowed to react in neutral medium or in acidic medium with excess of potassium iodide to liberate free iodine.

KI + oxidizing agent $\longrightarrow I_2$

Free iodine is titrated against a standard reducing agent usually with sodium thiosulphate. Halogen, dichromates, cupric ion, peroxides etc., can be estimated by this method.

$I_2 + 2NaS_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$

$2CuSO_4 + 4KI \longrightarrow Cu_2I_2 + 2K_2SO_4 + I_2$

$K_4Cr_2O_7 + 6KI + 7H_2SO_4 \longrightarrow Cr_2(SO_4)_3 + 4K_2SO_4 + 7H_2O + 3I_2$

Iodimetric Titration

These are the titrations in which free iodine is used as it is difficult to prepare the solution of iodine (volatile and less soluble in water), it is dissolved in KI solution :

$KI + I_2 \longrightarrow KI_3$ (Potassium triiodide)

This solution is first standardized before using with the standard solution of substance such as sulphite, thiosulphate, arsenite etc, are estimated.

In iodimetric and iodometric titration, starch solution is used as an indicator. Starch solution gives blue or violet colour with free iodine. At the end point, the blue or violet colour disappears when iodine is completely changed to iodide.

❑ SOME IODOMETRIC TITRATIONS (TITRATING SOLUTIONS IS $Na_2S_2O_3.5H_2O$)

Estimation of	Reaction	Relation between O.A. and R.A.
I_2	$I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$ or $I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$	$I_2 = 2I \equiv 2Na_2S_2O_3$ Eq. wt. of $Na_2S_2O_3 = M/1$
$CuSO_4$	$2CuSO_4 + 4KI \longrightarrow 2Cu_2I_2 + 2K_2SO_4 + I_2$ $Cu^{2+} + 4I^- \longrightarrow \underset{\text{(White ppt.)}}{Cu_2I_2} + I_2$ $CaOCl_2 + H_2O \longrightarrow Ca(OH)_2 + Cl_2$	$2CuSO_4 \equiv I_2 \equiv 2I \equiv 2Na_2S_2O_3$ Eq. wt. of $CuSO_4 = M/1$
$CaOCl_2$	$Cl_2 + 2KI \longrightarrow 2KCl + I_2$ $Cl_2 + 2I^- \longrightarrow 2Cl^- + I_2$ $MnO_2 + 4HCl\ (conc) \xrightarrow{\Delta} MnCl_2 + Cl_2 + 2H_2O$ $Cl_2 + 2KI \longrightarrow 2KCl + I_2$	$CaOCl_2 \equiv Cl_2 \equiv I_2 \equiv 2I \equiv 2Na_2S_2O_3$ Eq. wt. of $CaOCl_2 = M/2$
MnO_2	or $MnO_2 + 4H^+ + 2Cl^- \longrightarrow Mn^{2+} + 2H_2O + Cl_2$ $Cl_2 + 2I^- \longrightarrow I_2 + 2Cl^-$	$MnO_2 \equiv Cl_2 \equiv I_2 \equiv 2I \equiv 2Na_2S_2O_3$ Eq. wt. of $MnO_2 = M/2$
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_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 $H_2O_2 = M/2$
Cl_2	$Cl_2 + 2I^- \longrightarrow 2Cl^- + I_2$	$Cl_2 \equiv I_2 \equiv 2I \equiv 2Na_2S_2O_3$ Eq. wt. of $Cl_2 = M/2$
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 $O_3 = M/6$
$Cr_2O_7^{2-}$	$Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 3I_2 + 2Cr^{3+} + 7H_2O$	$Cr_2O_7^{2-} \equiv 3I_2 \equiv 6I$ Eq. wt. of $Cr_2O_7^{2-}$
MnO_4^-	$2MnO_4^- + 10I^- + 16H^+ \longrightarrow 2MnO_4^- + 5I_2 + 8H_2O$	$2MnO_4^- \equiv 5I_2 \equiv 10I$ Eq. wt. of $MnO_4^- = M/5$
BrO_3^-	$BrO_3^- + 6I^- + 6H^+ \longrightarrow Br^- + 3I_2 + 3H_2O$	$BrO_3^- \equiv 3I_2 \equiv I_2$ Eq. wt. of $BrO_3^- = M/6$
As(V)	$H_3AsO_4 + 2I^- + 2H^+ \longrightarrow H_3AsO_3 + H_2O + I_2$	$H_3AsO_4 \equiv I_2 \equiv 2I$ Eq. wt. of $H_3AsO_4 = M/2$

❑ SOME IODIMETRIC TITRATION (TITRATING SOLUTIONS IS I_2 IN KI)

Estimation of	Reaction	Relation between O.A. and R.A.
H_2S (in acidic medium)	$H_2S + I_2 \longrightarrow S + 2I^- + 2H^+$	$H_2S \equiv I_2 \equiv 2I$ Eq. wt. of $H_2S = M/2$
SO_3^{2-} (in acidic medium)	$SO_3^{2-} + I_2 + H_2O \longrightarrow SO_3^{2-} + 2I^- + 2H^+$	$SO_3^{2-} \equiv I_2 \equiv 2I$ Eq. wt. of $SO_3^{2-} = M/2$
Sn^{2+} (in acidic medium)	$Sn^{2+} + I_2 \longrightarrow Sn^{4+} + 2I^-$	$Sn^{2+} \equiv I_2 \equiv 2I$ Eq. wt. of $Sn^{2+} = M/2$
As(III) (at pH = 8)	$H_2AsO_3^- + I_2 + H_2O \longrightarrow HAsO_4^{2-} + 2I^- + 2H^+$	$H_2AsO_3^- \equiv I_2 \equiv 2I$ Eq. wt. of $H_2AsO_3^- = M/2$
N_2H_4	$N_2H_4 + 2I_2 \longrightarrow N_2 + 4H^+ + 4I^-$	$N_2H_4 \equiv 2I_2 \equiv 4I$ Eq. wt. of $N_2H_4 = M/4$

❑ CONCEPTS AND FORMULA AT A GLANCE

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

Number of moles of atoms $= \dfrac{\text{wt. in g}}{\text{Atomic mass}}$

Number of moles of gases $= \dfrac{\text{Volume at STP}}{\text{Standard molar volume}}$

Number of moles of particles, e.g. atoms, molecular ions etc. $= \dfrac{\text{Number of particles}}{\text{Avogadro No.}}$

Moles of solute in solution = M V(L)

2. Equivalent wt. of element $= \dfrac{\text{Atomic wt.}}{\text{Valence}}$

Equivalent wt. of compound $= \dfrac{\text{Mol. wt.}}{\text{Total charge on cation or anion}}$

Equivalent wt. of acid $= \dfrac{\text{Mol wt.}}{\text{Basicity}}$

Equivalent wt. of base $= \dfrac{\text{Mol wt.}}{\text{Acidity}}$

Equivalent wt. of an ion $= \dfrac{\text{Formula wt.}}{\text{Charge on ion}}$

Equivalent wt. of acid salt $= \dfrac{\text{Molecular wt.}}{\text{Replaceable H atom in acid salt}}$

Equivalent wt. of oxidizing or reducing agent $= \dfrac{\text{Mol. wt.}}{\text{Change in oxidation number per mole}}$

No. of equivalent = N V(L) $= \dfrac{\text{wt. in g}}{\text{Eq. wt.}}$

3. Molarity (M) = $\frac{W_s \times 1000}{M_s \times V} = \frac{x \times d \times 10}{M_s}$

where

W_s = wt. of solute in g

M_s = Mol. wt. of solute

x = % by mass of solute

d = density of solution in g/ml

V = volume of solution in ml

4. Normality (N) = $\frac{W_s \times 1000}{E_s \times V} = \frac{x \times d \times 1000}{E_s}$

W_s = wt. of solute in g.

E_s = eqv. wt. of solute

V = volume of solution in ml

x = % by mass of solute

d = density of solution in g/ml

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

Millimoles = M V(ml) = $\frac{\text{wt. of solute}}{\text{Mol.wt.}} \times 1000$

Equivalents of solute = N 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.

$M_1V_1 = M_2V_2$

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

$$\frac{M_1V_1}{n_1} = \frac{M_2V_2}{n_2}$$

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 = $\frac{N_B V_B}{1000}$

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

$\Rightarrow$ $N_A \quad V_B = N_B \quad V_B$

The above equation is called normality equation.

7. Normality (N) = Molarity (M) $\quad$ n

(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) = $\dfrac{\text{Moles of solute}}{\text{wt. of solvent (in kg)}}$

9. Strength of solution (S) = N $\quad$ Eq.wt.

= M $\quad$ mol. wt.

SOLVED PROBLEMS (SUBJECTIVE)

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

$0.40 \quad V_{H_2SO_4} = 5$

$\therefore\ V_{H_2SO_4} = \dfrac{5}{0.40} = 12.5$ litre

Ex 2. To 50 L of 0.2 N NaOH, 2.5 L of 2N HCl and 15 L of 0.1 N $FeCl_3$ 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 $\quad$ 0.2 = 10

Eq. of HCl = 2.5 $\quad$ 2 = 5

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

$FeCl_3 + NaOH \rightarrow Fe\ (OH)_3 \downarrow \xrightarrow{\Delta} Fe_2O_3$

$FeCl_3$ reacts with NaOH to give $Fe(OH)_3$ which on ignition gives Fe_2O_3

$\therefore$ Eq. of NaOH used for $FeCl_3$ = Eq. of $Fe(OH)_3$

= Eq. of Fe_2O_3

= 15 $\quad$ 0.1 = 3.5

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

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

$\dfrac{W_{Fe_2O_3}}{M_{Fe_2O_3}} \quad 6 = 1.5$ $\qquad$ (n-factor for Fe_2O_3 = 6)

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

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 $Na_2S_2O_3$ 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?

Sol. $O_3 + 2\ KI + H_2O \rightarrow 2KOH + I_2 + O_2$

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

Millimoles of O_3 = Millimoles of I_2 = ½ Millimoles of $Na_2S_2O_3$

= ½ 30 1/10 = 1.5 millimoles

= 0.0015 moles

Total moles of O_3 and O_2 in the mixture

PV = n RT

1 1 = n 0.0821 273

∴ n = 0.044

Moles of O_2 = 0.044 – 0.0015 = 0.0425

W_{O_2} = 0.0425 32 g = 1.36 g

W_{O_3} = 0.0015 48 g = 0.072 g

$$\therefore \ \%\ \text{of}\ O_3 = \frac{0.072}{1.432}\quad 100 = 5.028\ \%$$

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

Ex 4. A 20 g sample of only CuS and Cu_2S was treated with 100 mL of 1.25 M $K_2Cr_2O_7$. The products obtained were Cr^{3+}, Cu^{2+} and SO_2. The excess oxidant was reacted with 50 mL of Fe^{2+} Solution : 25 mL of the same Fe^{2+} solution required 0.875 M $KMnO_4$ under acidic condition, the volume of $KMnO_4$ used was 20 mL. Find the % of CuS and Cu_2S in the sample.

Sol. Equivalents of dichromate initially = $\dfrac{1.25 \times 6 \times 100}{1000}$ = 0.75

Equivalents of Fe^{2+} in 25 mL = $\dfrac{0.875 \times 5 \times 5 \times 20}{1000}$ = 0.0875

Equivalents of Fe^{2+} in 50 mL = 0.0875 2 = 0.175

Equivalents of excess dichromate = 0.175

∴ Equivalents of dichromate consumed by (CuS and Cu_2S)

= 0.75 – 0.175 = 0.575

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

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

∴ x = 5.74 g

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

% Cu_2S = 71.3 %

Ex 5. 2.249 g of a sample of pure $BaCO_3$ and impure $CaCO_3$ containing some CaO was treated with dil. HCl and it evolved 168 mL of CO_2 at N.T.P. From this solution, $BaCrO_4$ was precipitated filtered and washed. The precipitate was dissolved in dil. H_2SO_4 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 $Na_2S_2O_3$. Calculate the percentage of CaO in the sample.

Sol. Let, weight of $BaCO_3$, $CaCO_3$ and CaO are x,y and z respectively.

$\therefore$ x + y + z = 2.249

$BaCO_3 \longrightarrow BaCrO_4$

Redox change $\quad Cr^{6+} + 3e^- \longrightarrow Cr^{3+}$

$\quad 2I^- \longrightarrow I_2 + 2e^-$

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

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

$\therefore$ x = 0.657 g ....(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

$$\therefore \quad \frac{x}{197} + \frac{y}{100} = \frac{168}{22400}$$

$\Rightarrow$ 200 x + 294 y = 295.5 ....(2)

From equation (1) and (2)

y = 0.416 g

$\therefore$ 0.657 + 0.416 + z = 2.249

z = 1.176

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

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 $\quad$ 0.02 = 3 $\quad 10^{-2}$

Millimoles of iodine $= \dfrac{3 \times 10^{-2}}{2} = 1.5 \quad 10^{-2}$ $\quad$ [$\because$ n-factor for iodine = 2]

Millimoles of ozone = 1.5 $\quad 10^{-2}$

$$\text{Volume of ozone} = \frac{nRT}{P} = \frac{1.5 \times 10^{-5} \times 0.0821 \times 300}{1} = 36.945 \quad 10^{-5} \text{ litre}$$

$$\text{Volume percent of ozone} = \frac{36.945 \times 10^{-5}}{10} \quad 100 = 3.6945 \quad 10^{-3}$$

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   6

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

$$\text{Equivalents of } X_2O_3 = \frac{2.18 - x}{2x+48} \times 8$$

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

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

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

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 I_2 consumed 55 mL of thiosulphate solution to decolourize the blue starch-iodine complex. Calculate molarity of the sodium thiosulphate solution :

Sol. $\text{Moles of } KIO_3 = \dfrac{0.1}{214} = 0.00047$

$\therefore$ Moles of I_2 liberated from $KIO_3 = \dfrac{0.00047}{2} = 0.000235$

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 KI $= \dfrac{0.00235}{2} = 0.001175$

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 :

$\text{Molarity} = \dfrac{0.00282 \times 1000}{55} = 0.0512$ M (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   0.15 – 32.10   0.10

= 11.79

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

For redox change,

$$\overset{+5}{NO_3^-} \xrightarrow{+8e^-} \overset{-3}{NH_3} \quad \text{(n - factor = 8)}$$

$\therefore$ Meq. of NH_3 for n-factor 8 = 8   11.79

$\therefore$ Normality of $NO_3^- = \dfrac{94.32}{25} = 3.77$

$\text{Molarity of } NO_3^- = \dfrac{3.77}{8} = 0.47125$

Ex10. 30 mL of a solution containing 9.15 g/litre of an oxalate $K_xH_y\ (C_2O_4)_z.nH_2O$ are required for titrating 27 mL of 0.12 N NaOH and 36 mL of 0.12 N $KMnO_4$ separately. Calculate x,y,z and n. Assume all H atoms (except H_2O) 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 z

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

∴ Meq. of acid in 30 mL = Meq. of NaOH used

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

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

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

∴ $x + y = 2z$ ...(4)

By equations (3) and (4)

$x : y : z :: 1 : 3 : 2$

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), $M = \frac{30 \times 9.15 \times 3}{27 \times 0.12} = 254.16$

∴ 218 + 18n = 254.15

∴ n = 2

∴ **Oxalate salt is $KH_3(C_2O_4)_2.2H_2O$**

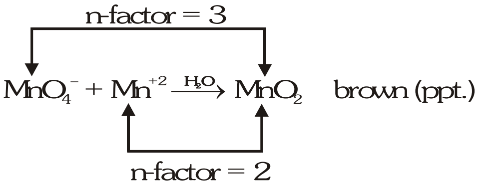
Ex11. Hydrogen peroxide solution (20 mL) reacts quantitatively with a solution of $KMnO_4$ (20 mL) acidified with dilute H_2SO_4. The same volume of the $KMnO_4$ solution is just decolourized by 10 mL of $MnSO_4$ in neutral medium simultaneously forming a dark brown precipitate of hydrated MnO_2. The 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 MnO_2 = Meq. of $Na_2C_2O_4$

= 20 0.2 2 = 8

$(C_2O_4^{2-} \rightarrow 2CO_2$, n-factor = 2)

Millimoles of $MnO_2 = \frac{8}{2} = 4$



or $2MnO_4^- + 3Mn^{2+} \rightarrow 5MnO_2$ (Mole ratio is reciprocal of n-factor ratio)

$$\frac{\text{Millimoles of } MnO_4^-}{\text{Millimoles of } MnO_2} = \frac{2}{5}$$

Millimoles MnO_4^- = $\frac{2}{5}$ Millimoles of MnO_2

= $\frac{2}{5}$ 4 = $\frac{8}{5}$

$2KMnO_4 + 5H_2O_2 + 3H_2SO_4 \rightarrow 2\ MnSO_4 + K_2SO_4 + 8H_2O + 5O_2$

$$\frac{\text{Millimoles of } H_2O_2}{\text{Millimoles of } MnO_4^-} = \frac{5}{2}$$

$\therefore$ Millimoles of H_2O_2 = $\frac{5}{2} \times \frac{8}{5}$ = 4

$N_{H_2O_2}$ 20 = 4 2 (n-factor for H_2O_2 = 2)

$\therefore$ $N_{H_2O_2}$ = 0.4

Volume strength of H_2O_2 = 5.6 $N_{H_2O_2}$

= 5.6 0.4 = 2.24

Ex12. 1.0 g of moist sample of mixture of potassium chlorate ($KClO_3$) and potassium chloride (KCl) was dissolved in water and solution made upto 250 mL. This solution was treated with SO_2 to reduce all ClO_3^- to Cl^- and excess of SO_2 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 $FeSO_4$ and unused $FeSO_4$ required 37.5 mL of 0.08 N $KMnO_4$ solutions.

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

Given that, $ClO_3^- + 6Fe^{2+} + 6H^+ \longrightarrow Cl^- + 6Fe^{3+} + 3H_2O$

$3SO_2 + ClO_3^- + 3H_2O \longrightarrow Cl^- + 3SO_4^{2-} + 6H^+$

Sol. ClO_3^- is reduced to Cl^- by SO_2 and ClO_3^- is also reduced to Cl^- by Fe^{2+}, hence AgCl is formed due to total Cl^-

Meq. of Fe^{2+} initially taken = 30 0.2 = 6

Meq. of Fe^{2+} unused = 37.5 0.08 = 3

$\therefore$ Meq. of Fe^{2+} = 6.0 – 3.0 = 3.0

Thus, Meq. of ClO_3^- in 25 mL = 3.0

Moles of ClO_3^- in 25 mL = $\frac{3.0}{1000 \times 6}$ = 0.0005

$\overset{+5}{Cl}O_3^- \longrightarrow \overset{-1}{Cl^-}$ (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 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 $NaNO_3$ also contains $NaIO_3$. The $NaIO_3$ 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 g $NaIO_3$, is treated with stoichiometric quantity of $NaHSO_3$. Now additional amount of same solution is added to the reaction mixture to bring about the second reaction. How many grams of $NaHSO_3$ 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 I_2 ?

Sol. Meq. of $NaHSO_3$ = Meq. of $NaIO_3$ = $N \quad V = \frac{6.8}{198} \quad 6 \quad 1000$

$I^{5+} + 6e^- \longrightarrow I^-$ (For KIO_3, n-factor = 6)

$\therefore$ Meq. of $NaHSO_3$ = 206.06

$$\frac{W_{NaHSO_3}}{M/2} \quad 1000 = 206.06$$

$$\Rightarrow W_{NaHSO_3} = \frac{206.06 \times 104}{2 \times 1000} = 10.715 \text{ g}$$

Also, Meq. of I^- formed using n-factor 6 = 206.06

In step 2, n-factor I^- is 1 and n-factor for IO_3^- is 5

Meq. of I^- formed using n-factor 1 $= \frac{206.06}{6}$

Meq. of $NaIO_3$ used in 2nd step $= \frac{206.06}{6}$

$$\Rightarrow \frac{6.8}{198} \quad 5 \quad V = \frac{206.06}{6}$$

$\therefore V_{NaIO_3}$ = 199.99 mL

Ex14. 1 g sample of $AgNO_3$ 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 KIO_3 in presence of 6 M HCl till all I^- converted into ICl. It requires 50 ml of M/10 KIO_3 Solution : 20 mL of the same stock solution of KI require 30 mL of M/10 KIO_3 under similar conditions. Calculate % of $AgNO_3$ in the sample. The reaction is :

$KIO_3 + 2KI + 6HCl \longrightarrow 3ICl + 3KCl + 3H_2O$.

Sol. $AgNO_3 + KI \longrightarrow AgI \downarrow + KNO_3$

As present in $AgNO_3$ is removed as AgI by adding 50 mL of KI solution of which 20 mL requires 30 mL of M/10 KIO_3

Meq. of KI in 20 mL = Meq. of KIO_3 = $30 \quad \frac{1}{10} \times 4$

For KIO_3, $I^{5+} + 4e^- \rightarrow I^+$

$I_- \rightarrow I^{1+} + 2e^-$

$\therefore$ Eq. wt. of KI = $\frac{M}{2}$

$\therefore$ Meq. of KI in 50 mL added to $AgNO_3$ $= \frac{30 \times 4 \times 50}{10 \times 20} = 30$

Meq. of KI left unused by $AgNO_3$ = $50 \quad \frac{1}{10} \times 4 = 20$

$\therefore$ Meq. of KI used for $AgNO_3$ = 30 – 20 = 10

$\therefore$ Meq. of $AgNO_3$ = 10

$$\frac{W_{AgNO_3}}{170} \quad 2 \quad 1000 = 10$$

$\therefore$ W_{AgNO_3} = 0.85 g = 85%

$$\frac{\text{Mole of } AgNO_3}{\text{Mole of KI}} = \frac{1}{1}$$

$\therefore$ If equivalent weight of KI = $\frac{M}{2}$

Equivalent weight of $AgNO_3$ = $\frac{M}{2}$

Ex15. A sample of Mg was burnt in air to give a mixture of MgO and Mg_3N_2. The ash was dissolved in 60 Meq. of HCl and the resulting solution was back titration with NaOH. 12 Meq. of NaOH were required to reach the end point. An excess of NaOH was then added and the solution was distilled. The ammonia released was then trapped in 10 Meq. of acid. Back titration of this solution required 6 Meq. of base. Calculate the % of Mg burnt to the nitride.

Sol. Let, total moles of Mg used for MgO and Mg_3N_2 be a and b respectively

$2Mg + O_2 \longrightarrow 2MgO$

a 0

0 a

$3Mg + N_2 \longrightarrow Mg_3N_2$

b 0

0 b/3

Now a, $\frac{b}{3}$ moles respectively of MgO and Mg_3N_2 are present in the mixture.

$MgO + 2HCl \longrightarrow MgCl_2 + H_2O$

$Mg_3N_2 + 8HCl \longrightarrow 3MgCl_2 + 2NH_4Cl$

or solution contains (a) moles of $MgCl_2$ from MgO and (b) moles of $MgCl_2$ from Mg_3N_2 and $\frac{2b}{3}$ moles of NH_4Cl.

Now, moles of HCl or Meq. of HCl (monobasic) = 30 – 12 = 48

$$2a + \frac{8b}{3} = 48 \qquad \text{..........(1)}$$

Moles of NH_4Cl formed = Moles of NH_3 liberated = Moles of HCl used for absorbing NH_3.

$$\frac{2b}{3} = (10 - 6) = 4 \qquad \text{..........(2)}$$

From (1), $2a + \frac{8 \times 6}{3} = 48$ or a = 16

$\therefore$ % of Mg used for Mg_3N_2 = $\frac{6}{(6+16)} \quad 100 = 27.27\%$

SOLVED PROBLEMS (OBJECTIVE)

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.

(A) 0.02 (B) 0.04 (C) 0.0122 (D) 0.3

Sol.

n-factor = 5

$$As_2O_3 + MnO_4^- \longrightarrow 2AsO_4^{3-} + Mn^{2+}$$

n-factor = 4

Let, molarity of $KMnO_4$ solution be M

$\therefore$ Eq. of As_2O_3 = Eq. of $KMnO_4$ solution

$$\frac{0.1097}{198} \quad 4 = \frac{36.10 \times M \times 5}{1000} \quad (\text{Equivalent weight } As_2O_3 = \frac{198}{4})$$

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 $S_2O_3^{2-}$?

(A) 200 mL (B) 156.4 mL (C) 170.4 mL (D) 190.4 mL

Sol. $40 \quad 0.246 \quad 8 = V \quad 0.154 \quad 3$ (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 (D) 0.25 M

Sol.

	$Al_2(SO_4)_3$	+	$BaCl_2$	$\longrightarrow$	$BaSO_4 \downarrow$	+	$AlCl_3$
Initial Meq.	$10 \quad 0.4 \quad 6$ = 24		$20 \quad 0.6 \quad 2$ = 24		0		0
Final Meq.	0		0		24		24

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

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,

$BrO_3^- + 6H^+ + 6e^- \longrightarrow Br^- + 3H_2O$, is

(A) 1.56 g (B) 0.9386 g (C) 1.23 g (D) 1.32 g

Sol. Meq. of $NaBrO_3$ = $55.5 \quad 0.672$ = 37.296

Let weight of $NaBrO_3$ = W

$\therefore \frac{W}{M_{NaBrO_3}} \quad 6 \quad 1000 = 37.296$ (equivalent weight = M/6) of n-factor = 6

$\therefore \frac{M}{151} \quad 6 \quad 1000 = 37.296$

$\therefore$ W = 0.9386 g

Hence, (B) is the correct answer.

Ex 5. $NaIO_3$ reacts with $NaHSO_3$ according to equation

$IO_3^- + 3HSO_3^- \longrightarrow I^- + 3H^+ + 3SO_4^{2-}$

The weight of $NaHSO_3$ required to react with 100 mL of solution containing 0.68 g of $NaIO_3$ is

(A) 5.2 g (B) 0.2143 g (C) 2.3 g (D) none of the above

Sol. Meq. of $NaHSO_3$ = Meq. of $NaIO_3$ = $N \quad V = \frac{0.68}{198} \quad 6 \quad 1000$ $(I^{5+} + 6e^- \rightarrow I^-)$

$$\therefore \frac{W_{NaHSO_3}}{M_{NaHSO_3}} \quad 2 \quad 1000 = \frac{0.68}{198} \quad 6 \quad 100$$

$$W_{NaHSO_3} = \frac{0.68 \times 6 \times 100 \times 104}{198 \times 1000} = 0.2143$$

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

(A) 0.7 mol (B) 0.5 mol (C) 0.2 mol (D) 0.05 mol

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 $0.1 \quad \frac{3}{2} = 0.15$. 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 $0.1 \quad \frac{1}{2} = 0.05$ 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

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

$\therefore E = 26$

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

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

34 g of H_2O_2 gives 11200 mL of O_2 at STP

$$\therefore \frac{34}{1120} \text{ g of } H_2O_2 \equiv \frac{11200}{34} \quad \frac{34}{1120} = 10 \text{ mL of } O_2 \text{ at STP.}$$

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. $Mn^{7+} + 5\,e^- \rightarrow Mn^{2+}$] 3

$Fe^{2+} \rightarrow Fe^{3+} + e^-$

$C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-$]

3 moles of $KMnO_4$ = 5 moles of FeC_2O_4

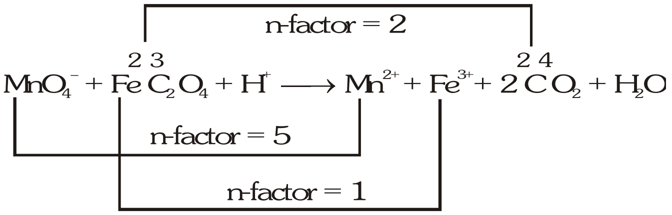
$\therefore$ 2 mol of ferrous oxalate $\equiv \frac{6}{5}$ mole of $KMnO_4$

Hence, (A) is the correct answer.

Ex10. What volume of 0.1 M $KMnO_4$ is needed to oxidize 100 mg of FeC_2O_4 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



$$MnO_4^- + \overset{2}{Fe}\overset{3}{C_2}O_4 + H^+ \longrightarrow Mn^{2+} + Fe^{3+} + 2\overset{4}{C}O_2 + H_2O$$

$\therefore$ V = 4.1 mL

Hence, (A) is the correct answer.

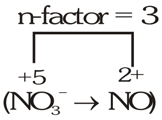
Ex11. What volume of 6 M HNO_3 is needed to oxidize 8 g of Fe^{2+} to Fe^{3+}, HNO_3 gets converted to NO?

(A) 8 mL (B) 7.936 mL (C) 32 mL (D) 64 mL

Sol. Meq. of HNO_3 = Meq. of Fe^{2+}

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

V = 7.936 mL



$$(\overset{+5}{N}O_3^- \rightarrow \overset{2+}{N}O)$$

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

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

$\therefore$ x = 0.103

$\therefore$ % of $SO_3 = \frac{0.103}{0.5}$ 100 = 20.6%

Hence, (C) is the correct answer.

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+}

$$\therefore \ \frac{W_{H_2S}}{34/2} \quad 1000 = \frac{63.5}{63.5/2}\times 1000$$

$$\therefore \ W_{H_2S} = 34\,g$$

Hence, (C) is the correct answer.

Ex14. Which of the following is / are correct?

(A) g mole wt. = mol. wt. in g = wt. of 6.02 10^{23} molecules

(B) mole = N molecule = 6.02 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 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 substance is the weight which either 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 V mL of H_2 at NTP. Eq. wt of metal E is / are :

(A) $E = \dfrac{A}{\text{Wt. of } H_2 \text{ displaced}}$ Eq. wt. of H (B) $E = \dfrac{A \times 1.008 \times 22400}{\text{Volume of } H_2 \text{ displaced} \times 2}$ Eq. wt. of H

(C) $E = \dfrac{A \times 1.008}{\text{Volume of } H_2 \text{ displaced} \times 0.0000897}$ (D) none of the above

Sol. (A), (B) and (C)

Ex18. Which of the following is/are redox reaction (s)?

(A) $BaO_2 + H_2SO_4 \rightarrow BaSO_4 + H_2O_2$ (B) $2BaO + O_2 \rightarrow 2BaO_2$

(C) $2KClO_3 \rightarrow 2KCl + 3O_2$ (D) $SO_2 + 2H_2S \rightarrow 2H_2O + 3S$

Sol. (B), (C) and (D)

Ex19. In the reaction,

$3Br_2 + 6CO_3^{2-} + 3H_2O \rightarrow 5Br^- + BrO_3^- + 6HCO_3^-$

(A) bromine is oxidized and carbonate is reduced (B) bromine is oxidized

(C) bromine is reduced (D) it is disproportionation reaction or autoredox change

Sol. (B), (C) and (D)

Ex20. Which of the following statements is/are true if 1 mol of H_3PO_x is completely neutralized by 40 g of NaOH?

(A) x = 2 and acid is monobasic (B) x = 3 and acid is dibasic

(C) x = 4 and acid is tribasic (D) x = 2 and acid does not form acid salt

Sol. (A) and (D).