CHAPTER 6

REDOX

❑ 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 :**

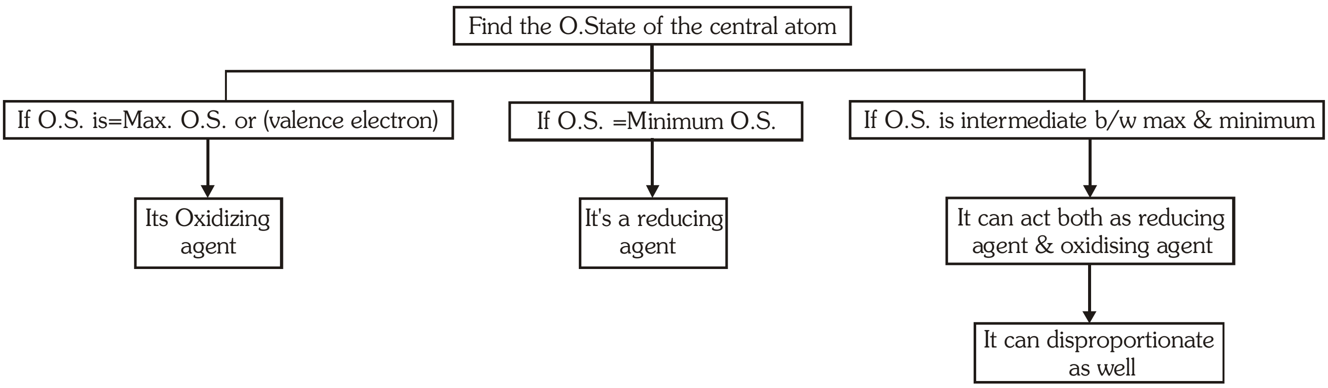
  Redusing agents are those compound which can reduce others and oxidise itself during the chemical reaction. Those reagents whose O.N. increase or which loses electrons in a redox reaction are termed as reductants.

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. $10\overset{+2}{Fe}SO_4 + 2K\overset{+7}{Mn}O_4 + 8H_2SO_4 \longrightarrow 5\overset{+3}{Fe_2}(SO_4)_3 + 2\overset{+2}{Mn}SO_4 + K_2SO_4 + 8H_2O$

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.

(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)

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

❑ 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	$E = \frac{M}{1}$

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

LAW OF EQUIVALENCE

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

According :

(i) $aA + bB \rightarrow mM + nN$

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

(ii) In a compound M_xN_y

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

Solved Examples :

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	$I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$	$I_2 = 2I \equiv 2Na_2S_2O_3$
	or	Eq. wt. of $Na_2S_2O_3 = M/1$
	$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$	
$CuSO_4$	$2CuSO_4 + 4KI \longrightarrow 2Cu_2I_2 + 2K_2SO_4 + I_2$	$2CuSO_4 \equiv I_2 \equiv 2I \equiv 2Na_2S_2O_3$
	$Cu^{2+} + 4I^- \longrightarrow Cu_2I_2 + I_2$	Eq. wt. of $CuSO_4 = M/1$
	(White ppt.)	
	$CaOCl_2 + H_2O \longrightarrow Ca(OH)_2 + Cl_2$	
$CaOCl_2$	$Cl_2 + 2KI \longrightarrow 2KCl + I_2$	
	$CaOCl_2 \equiv Cl_2 \equiv I_2 \equiv 2I \equiv 2Na_2S_2O_3$	
	$Cl_2 + 2I^- \longrightarrow 2Cl^- + I_2$	Eq. wt. of $CaOCl_2 = M/2$
	$MnO_2 + 4HCl\,(conc) \xrightarrow{\Delta} MnCl_2 + Cl_2 + 2H_2O$	
	$Cl_2 + 2KI \longrightarrow 2KCl + I_2$	
MnO_2	or	$MnO_2 \equiv Cl_2 \equiv I_2 \equiv 2I \equiv 2Na_2S_2O_3$
	$MnO_2 + 4H^+ + 2Cl^- \longrightarrow Mn^{2+} + 2H_2O + Cl_2$	Eq. wt. of $MnO_2 = M/2$
	$Cl_2 + 2I^- \longrightarrow I_2 + 2Cl^-$	
IO_3^-	$IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$	$IO_3^- \equiv 3I_2 \equiv 6I \equiv 6Na_2S_2O_3$
		Eq. wt. of $IO_3^- = M/6$