Oxidation & Reduction (Redox Chemistry Section III)

⊛ Oxidation :-

According to the electronic concept, oxidation is a process in which an atom, an ion or a molecule losses one or more electrons.

Ex:- $Zn \rightarrow Zn^{2+} + 2e$; $Fe^{2+} \rightarrow Fe^{3+} + e$; $2I^- \rightarrow I_2 + 2e$; $H_2 \rightarrow 2H^+ + 2e$ etc.

⊛ Reduction :-

According to the electronic concept, reduction is a process in which an atom, an ion or a molecule gains one or more electrons,

Ex:- $H + e \rightarrow H^-$; $Fe^{3+} + e \rightarrow Fe^{2+}$, $I_2 + 2e \rightarrow 2I^-$, $2H^+ + 2e \rightarrow H_2$ etc.

⊛ Redox - rxn :-

Redox rxn is a process in which oxidation and reduction takes place simultaneously.

Ex:-

$$\overset{+3}{2FeCl_3} + \overset{+2}{SnCl_2} = \overset{+2}{2FeCl_2} + \overset{+4}{SnCl_4}$$

(oxidation: $Sn^{+2} \rightarrow Sn^{+4}$; reduction: $Fe^{+3} \rightarrow Fe^{+2}$)

⊛ Oxidising agent :-

An oxidising agent is one that gains electrons and is reduced to a lower oxidation state.

⊛ Reducing agent :-

A reducing agent is one that ~~gains~~ losses electrons and is oxidised to a higher oxidation state.

Ex:-

$$\overset{+3}{2FeCl_3} + \overset{+2}{SnCl_2} = \overset{+2}{2FeCl_2} + \overset{+4}{SnCl_4}$$

(oxidation: $Sn^{+2} \rightarrow Sn^{+4}$; reduction: $Fe^{+3} \rightarrow Fe^{+2}$)

On this rxn $FeCl_3$ acts as an oxidising agent and $SnCl_2$ acts as a reducing agent.

⊛ Oxidation number (O.N) :

The oxidation number of an element in a particular comp. is a number which denotes the extent of oxidation or reduction required for conversion from free state into its particular state in the compound.

⊛ Oxidation state :-

Oxidation state of an atom is the oxidation number (O.N) per atom of that element in a given compound or ion.

Ex:- the total O.N of 'Cr' atom in $K_2Cr_2O_7$ molecule is +12.
the oxidation state of 'Cr' atom in $K_2Cr_2O_7$ molecule is $\left(\frac{+12}{2}\right) = +6$

Electrode	Reduction Rxn	Standard redox potential (E°)
(6)		
(5) Mg^{2+}/Mg	(5) $Mg^{2+} + 2e \rightarrow Mg$	(5) -2.36
(4) Mn^{2+}/Mn	(4) $Mn^{2+} + 2e \rightarrow Mn$	(4) -1.18
(3) Zn^{2+}/Zn	(3) $Zn^{2+} + 2e \rightarrow Zn$	(3) -0.76
(2) Fe^{2+}/Fe	(2) $Fe^{2+} + 2e \rightarrow Fe$	(2) -0.44
(1) $2H^+/H_2$	(1) $2H^+ + 2e \rightarrow H_2$	(1) 0.00
(2) Cu^{2+}/Cu	(2) $Cu^{2+} + 2e \rightarrow Cu$	(2) $+0.34$
(3) Cu^{2+}/Cu^+	(3) $Cu^{2+} + e \rightarrow Cu^+$	(3) $+0.15$
(4) Cu^+/Cu	(4) $Cu^+ + e \rightarrow Cu$	(4) $+0.52$
(5) Fe^{3+}/Fe^{2+}	(5) $Fe^{3+} + e \rightarrow Fe^{2+}$	(5) $+0.77$
(6) I_2/I^-	(6) $I_2 + 2e \rightarrow 2I^-$	(6) $+0.54$
(7) Ag^+/Ag	(7) $Ag^+ + e \rightarrow Ag$	(7) $+0.80$.
(8) Ag^{2+}/Ag	(8) $Ag^{2+} + 2e \rightarrow Ag$	(8) $+1.98$
(9) $[Fe(CN)_6]^{3-}$ / $[Fe(CN)_6]^{4-}$	(9) $[Fe(CN)_6]^{3-} + e \rightarrow [Fe(CN)_6]^{4-}$	(9) $+0.36$ V
(10) $^{+5}AsO_4^{3-}/^{+3}AsO_3^{3-}$	(10) $AsO_4^{3-} + 2e \rightarrow AsO_3^{3-}$	(10) $+0.56$ V
(11) MnO_4^-/Mn^{2+}	(11) $MnO_4^- + 5e \rightarrow Mn^{2+}$	(11) $+1.51$ V
(12) Br_2/Br^-	(12) $Br_2 + 2e \rightarrow Br^-$	(12) $+1.07$ V
(13) Cl_2/Cl^-	(13) $Cl_2 + 2e \rightarrow Cl^-$	(13) $+1.36$ V
(14) $Cr_2O_7^{2-}/Cr^{3+}$	(14) $Cr_2O_7^{2-} + 6e \rightarrow Cr^{3+}$	(14) $+1.33$ V

⊛ General rules for calculating the oxidation state (O.N/atom) of elements:-

(1) $\overset{0}{Cl_2}$, $\overset{0}{Br_2}$

(2) In Na_2SO_4, the sum of the O.N's $= 2\times(+1) + 1\times(+6) + 4\times(-2)$
$= 0$

(3) In $Cr_2O_7^{=}$, the sum of the O.N's $= 2\times(+6) + 7\times(-2)$
$= -2$

(4) In Ca_3N_2 and NH_3, the O.N of 'N' is (-3).

(5) O.N of 'H' atom is (a) zero (0) in H_2 molecule.
(b) (+1) in NH_3, PH_3, H_2O_2
(c) (-1) in metallic hydrides - NAH, $LiAlH_4$, CaH_2

(6) O.N of 'O' atom is (a) (-2) in H_2O, SO_2, Cl_2O etc.
(b) (-I) in peroxide (H_2O_2, BaO_2, Na_2O_2)
(c) $(-\frac{1}{2})$ in KO_2 (Superoxide)
(d) (+I) in O_2F_2
(e) (+2) in OF_2
(f) zero (0) in O_2 molecule.

(7) O.N of 'H' atom in all the compounds is (-1)

(8) O.N of all the hallogen is (-1)

Balance the redox-rxn by O.N method :-

Q. (1) $MnO_4^- + C_2O_4^{=} \longrightarrow Mn^{2+} + CO_2$ (in acid medium)

(a) The given equⁿ is

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

(Reduction: $+7 \to +2$; Oxidation: $+3 \to +4$)

MnO_4^- acts as an oxidising agent and $C_2O_4^{=}$ acts as a reducing agent.

(b) Increase of O.N in one 'C' atom $= (+4) - (+3) = +1$.
Increase of O.N in two 'C' atoms $= 2\times(+1) = +2$.
Decrease of O.N in one Mn atom $= (+7) - (+2) = +5$.
In order to make the total increase in O.N equal to the total decrease in O.N.
The oxidising agent (MnO_4^-) should be multiplied by 2 and

reducing agent should by multiplied by 5. Thus the given eqn should be written as

$2MnO_4^- + 5C_2O_4^{=} \rightarrow 2Mn^{2+} + 10CO_2$

(c) In order to balance O atom, $8H_2O$ is added to the R.H.S of the above rxn

$2MnO_4^- + 5C_2O_4^{=} \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$

(d) In order to show the acidic medium and to balance H atoms adding $16H^+$ to the L.H.S of the rxn.

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

This is the balanced eqn (since electrical charges on both sides are equal).

5. (a) $As_2S_3 + NO_3^- \rightarrow H_3AsO_4 + NO + SO_4^{=}$ (in acid medium)

(a) The given eqn is redox reaction.

$\overset{+3}{As_2}\overset{-2}{S_3} + \overset{+5}{N}O_3^- \rightarrow H_3\overset{+5}{As}O_4 + \overset{+2}{N}O + \overset{+6}{S}O_4^{=}$

(oxidation)

NO_3^- acts as a oxidising agent and As_2S_3 acts as a reducing agent.

(b) Increase in O.N in one 'As' atom = $(+5) - (+3) = +2$

Increase in O.N in two 'As' atoms = $2 \times (+2) = +4$

Increase in O.N in three 'S' atoms = $3 \times [(+6) - (-2)] = 3 \times (+8) = +24$

Decrease in O.N in one N atom = $(+5) - (+2) = +3$

→ total increase in O.N in two As atoms and three S atoms = $(+4) + (+24) = +28$

In order to make the total increase in O.N equal to the total decrease in O.N

The oxidising agent (NO_3^-) should be multiplied by 28 and the reducing agent (As_2S_3) should be multiplied by 3

Thus the given eqn should be written as

$3As_2S_3 + 28NO_3^- \rightarrow 6H_3AsO_4 + 28NO + 9SO_4^{=}$

(c) In order to balance 'O' atom, $4H_2O$ is added to the R.H.S of the above rxn.

$3As_2S_3 + 28NO_3^- + 4H_2O \rightarrow 6H_3AsO_4 + 28NO + 9SO_4^{=}$

(d) In order to show the acidic medium of the rxn and to balance H atom, added $10H^+$ to the L.H.S of the rxn.

$3As_2S_3 + 28NO_3^- + 4H_2O \xrightarrow{+10H^+} 6H_3AsO_4 + 28NO + 9SO_4^{=}$

This is the balanced eqn (since the electrical charges on both sides are equal).