# **REDOX REACTION**

#### Introduction :

Redox reactions shows vital role in non renewable energy sources. In cell reactions where oxidation and reduction both occurs simultaneously will have redox reaction for interconversion of energy.

#### **Redox Reaction (Oxidation-Reduction) :**

Many chemical reactions involve transfer of electrons from one chemical substance to another. These electrontransfer reactions are termed as **oxidation-reduction** or **redox reactions**.

Or

Those reactions which involve oxidation and reduction both simultaneously are known as oxidation reduction or redox reactions.

Or

Those reactions in which increase and decrease in oxidation number of same or different atoms occurs are known as redox reactions.

#### **Oxidation State :**

Oxidation state of an atom in a molecule or ion is the hypothetical or real charge present on an atom due to electronegativity difference.

Or

Oxidation state of an element in a compound represents the number of electrons lost or gained during its change from free state into that compound.

#### Some important points concerning oxidation number :

(1) Electronegativity values of no two elements are same –

P > H C > H S > C C | > N

(2) Oxidation number of an element may be positive or negative.

(3) Oxidation number can be zero, whole number or a fractional value.

Ex.	$Ni(CO)_4$	$\Rightarrow$	O.S  of  Ni = 0
	$N_{3}H$	$\Rightarrow$	O.S of N = $-1/3$
	HCl	$\Rightarrow$	O.S of Cl = $-1$

(4) Oxidation state of same element can be different in same or different compounds.

Ex.  $H_2S \implies O.S \text{ of } S = -2$  $H_2SO_3 \implies O.S \text{ of } S = +4$  $H_2SO_4 \implies O.S \text{ of } S = +6$ 

#### Some helping rules for calculating oxidation number :

#### (A) In case of covalent bond :

(i) For homoatomic molecule  $A - A \qquad A = A$  $A \equiv A$  $\downarrow$  $\downarrow \downarrow$  $\downarrow$  $\downarrow$  $\downarrow$ 0 0 O.N. : 0 0 0 0 (ii) For heteroatomic molecule (EN of B > A) A – B A = B $A \equiv B$  $\downarrow \downarrow$  $\downarrow \downarrow$  $\downarrow \downarrow$ +2 -2 +3 -3 O.N. : +1 -1

(iii)			te of an elemer etc. are zero.	t in its free state	is zero. Example- Oxidation state of	
(iv)	Oxid	ation state of	f atoms present	in homoatomic	molecules is zero.	
	Ex. H	$H_2$ , $O_2$ , $N_2$ ,	$P_4$ , $S_8$ = zero			
(v)				any of its allotro	ppic form is zero.	
	Ex.	C <sub>Diamond</sub> , C	C <sub>Graphite</sub> , S <sub>Monoclin</sub>	$_{\rm ic}$ , S <sub>Rhombic</sub> = 0		
(vi)	Oxid		•	nents of an alloy	are 0.	
	Ex.	(Na – Hg)				
		$\downarrow \downarrow \downarrow$ 0 0				
(vii)	In co	mplex comp	ounds, oxidatio	n state of some	neutral molecules (ligands) is zero.	
	Ex. C	CO, NO, NH	I <sub>3</sub> , H <sub>2</sub> O.			
(viii)	Oxid	ation state of	f fluorine in all i	ts compounds is	-1.	
(ix)	Oxid	ation state o	of IA & II A grou	p elements are -	+1 and +2 respectively.	
(x)	Oxid	ation state o	f hydrogen in n	nost of its compo	bunds is $+1$ except in metal hydrides (-2	L)
	Ex.	NaH	H LiH	$CaH_2$	MgH <sub>2</sub>	
				$\downarrow \downarrow$		
	O.S.	: +1-	-1 +1 -1	+2-1	+2 -1	
(xi)	Oxid	ation state o	f oxygen in mo	st of its compou	nds is -2 except in -	
	(a)	Peroxides	$(O_2^{-2}) \rightarrow Oxic$	lation state (O) =	= -1	
		Ex.	$H_2O_2$ , $BaO_2$			
	(b)	Super Oxic		idation state (O)	) = -1/2	
		Ex.	KO <sub>2</sub>			
			$\downarrow$			
		- ·	-1/2	. (2)		
	(c)	Ozonide -	0	dation state (O)	= -1/3	
		Ex.	KO <sub>3</sub>			
			↓ 1./0			
	(1)		-1/3			
	(d)	$OF_2 (Oxyge F - O - F$	en difluoride)			
		$\downarrow$				
	(e)		state (O) = + 2 sygen difluoride)			
	(0)	$\downarrow$				
	0.11		state (O) = $+1$			
(xii)					ne charge present on the ion.	
(_····)	Ex.	0	xidation state =			1 : 0
(xiii)	_		of oxidation sta	te of all the atom	ns present in a polyatomic neutral mole	cule is U.
	Ex.	H <sub>2</sub> SO <sub>4</sub> If O.S of S	icy than			
			+ 4 (-2) = 0			
		2(+1) + x x - 6 = 0	+ + (-2) = 0			
		$\begin{array}{l} x - 0 = 0 \\ x = +6 \end{array}$				
		$\Lambda \rightarrow 10$				

Ex.  $H_2 \underline{S} O_3$ 

If O.S of S is x then 2(+1) + x + 3(-2) = 0 x - 4 = 0x = +4

- (xiv) The algebric sum of oxidation state of all the atoms in a polyatomic ion is equal to the charge present on the ion.
  - Ex. <u>S</u>O<sub>4</sub>-2

If O.S of S is x then x + 4(-2) = -2 x - 6 = 0 x = +6Ex. HQO<sub>3</sub><sup>-</sup> If O.S of C is x then +1 + x + 3(-2) = -1 x - 4 = 0x = +4

### (B) In case of co-ordinate bond (EN of B > A):

	А-	$  AB \to B \\ \downarrow \qquad \downarrow $		$A \rightarrow B$			$B \rightarrow A$		
	$\downarrow$	$\downarrow$	$\downarrow$	$\downarrow$	$\downarrow$	$\downarrow$		$\downarrow$	$\downarrow$
O.S.:	+2	-2	+2	-2	+2	-2		0	0

### (C) In case of Ionic bond :

Charge on cation = O.S of cation

Charge on anion = O.S of anion

## **APPLICATIONS OF OXIDATION NUMBER :**

## (A) To compare the strength of acid and base :

Strength of acid	α Oxidation Number	
Strength of base	$\alpha \qquad \frac{1}{\text{Oxidation Number}}$	
Example :	Order of acidic strength in $\mathrm{HClO}_2,\mathrm{HClO}_2,\mathrm{HClO}_3,\mathrm{HClO}_4$ will be	2.
Solution :	Oxidation Number of chlorine	:
	HClO (Hypo chlorous acid) +1	
	$HCIO_2$ (Chlorous acid) +3	
	$HCIO_{3}$ (Chloric acid) +5	
	$HClO_4$ (Perchloric acid) +7	
	Strength of acid $\alpha$ Oxidation Number	
So the orde	will be -	
	$HCIO_4 > HCIO_3 > HCIO_2 > HCIO$	

### (B) To determine the oxidising and reducing nature of the substances :

**Oxidising agents** are the substances which accept electrons in a chemical reaction i.e., electron acceptors are oxidising agent.

**Reducing agents** are the substances which donate electrons in a chemical reaction i.e., electron donors are reducing agent.

Highest O.S.	+4	+5	+5	+6	+7	+6	+7	+8	+8	+2	+1
Elements	С	Ν	Р	S	Cl	Cr	Mn	Os	Ru	0	Н
Lowest O.S.	-4	-3	-3	-2	-1	0	0	0	0	-2	-1

(a) If effective element in a compound is present in maximum oxidation state then the compound acts as oxidising agent.
 Ex. KMnO<sub>4</sub>, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, H<sub>2</sub>SO<sub>4</sub>, SO<sub>2</sub>, H<sub>2</sub>PO<sub>4</sub>, HNO<sub>2</sub>, HClO<sub>4</sub>

$\underset{\downarrow}{KMnO_4}$	$K_2 C_2 O_7$	$H_{2}SO_{4}SO_{3}$	$\downarrow^{\text{H}_3\text{PO}_4}$	↓	1NO <sub>3</sub> F	+CIO <sub>4</sub> ↓
+7	+6	+6	+6	+5	+5	+7

(b) If effective element in a compound is present in minimum oxidation state then the compound acts as reducing agent.

$\stackrel{\text{PH}_3}{\downarrow}$	$\stackrel{NH_3}{\downarrow}$	$\overset{\mathrm{CH}_4}{\downarrow}$
-3	-3	-4

(c) If effective element in a compound is present in intermediate oxidation state then the compound can act as oxidising agent as well as reducing agent.

$HNO_2$	$H_3PO_3$	$SO_2$	$H_2O_2$
$\downarrow$	$\downarrow$	$\downarrow$	$\downarrow$
+3	+3	+4	-1

#### (C) To calculate the equivalent weight of compounds :

The equivalent weight of an oxidising agent or reducing agent is that weight which accepts or loses one mole electrons in a chemical reaction.

(a) Equivalent weight of oxidant =  $\frac{\text{Molecular weight}}{\text{No. of electrons gained by one mole}}$ 

**Example :** In acidic medium

(b)

 $6e^{-} + Cr_{2}O_{7}^{2-} + 14H^{+} \longrightarrow 2Cr^{3+} + 7H_{2}O$ 

Here atoms which undergoes reduction is Cr. Its O. S. is decreasing from +6 to +3

Equivalent weight of 
$$K_2Cr_2O_7 = \frac{\text{Molecular weight of } K_2Cr_2O_7}{3 \times 2} = \frac{M}{6}$$

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

Molecular weight	t
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Equivalent weight of a reducant = 
$$\frac{1}{N_{0}}$$
 No. of electrons lost by one mole

In acidic medium,  $C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$ Here, atoms which undergoes oxidation is C. Its oxidation state is increasing from +3 to +4.

Here, Total electrons lost in  $C_2O_4^{-2} = 2$  So, equivalent weight of  $C_2O_4^{-2} = \frac{M}{2}$ 

(c) In different conditions a compound may have different equivalent weight because, it depends upon the number of electrons gained or lost by that compound in that reaction. Example :

(i)  $MnO_4^- \longrightarrow Mn^{+2}$  (acidic medium) (+7) (+2)

Here 5 electrons are taken by  $MnO_4^-$  so its equivalent weight =  $\frac{M}{5} = \frac{158}{5} = 31.6$ 

 $\begin{array}{ccc} MnO_{4}^{-} & \longrightarrow & MnO_{2} \\ (+7) & & (+4)^{2} \end{array}$  (neutral medium) or (Weak alkaline medium) (ii)

Here, only 3 electrons are gained by  $MnO_4^-$  so its equivalent weight =  $\frac{M}{3} = \frac{158}{3} = 52.7$  **Note :** When only alkaline medium is given consider it as weak alkaline medium.  $MnO_4^- \longrightarrow MnO_4^{-2}$  (strong alkaline medium) (+7)

(iii)

Here, only one electron is gained by MnO<sub>4</sub><sup>-</sup> equivalent weight =  $\frac{M}{1}$  = 158

Note :- KMnO<sub>4</sub> acts as an oxidant in every medium although with different strength which follows the order -

acidic medium > neutral medium > alkaline medium while,  $K_2Cr_2O_7$  acts as an oxidant only in acidic medium as follows  $Cr_2O_7^{2-7} \longrightarrow 2Cr^{3+}$   $(2 \times 6) \longrightarrow (2 \times 3)$ 

Here, 6 electrons are gained by  $K_2Cr_2O_7$  equivalent weight =  $\frac{M}{6} = \frac{294}{6} = 49$ 

- To determine the possible molecular formula of compound : Since the sum of oxidation number of all the atoms present in a compound is zero, so the validity of the **(D)** 
  - formula can be confirmed.

## POINTS TO REVISE

#### SOME OXIDIZING AGENTS/REDUCING AGENTS WITH EQUIVALENT WEIGHT :

Species	Changed to	Reaction	Electrons exchanged or change in O.N.	Eq. wt.
MnO <sub>4</sub> <sup>-</sup> (O.A.)	Mn <sup>+2</sup> in acidic medium	$MnO_{4}^{-} + 8H^{+} + 5e^{-} \longrightarrow Mn^{2+} + 4H_{2}O$	5	$E = \frac{M}{5}$
MnO <sub>4</sub> <sup>-</sup> (O.A.)	MnO <sub>2</sub> in neutral medium or in weak alkaline medium	$MnO_{4}^{-} + 3e^{-} + 2H_{2}O \longrightarrow MnO_{2} + 4OH^{-}$	3	$E = \frac{M}{3}$
MnO <sub>4</sub> <sup>-</sup> (O.A.)	$MnO_4^{2-}$ in strong alkaline medium	$MnO_4^- + e^- \longrightarrow MnO_4^{-2-}$	1	$E = \frac{M}{1}$
Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup> (O.A.)	$Cr^{3+}$ in acidic medium	$\mathrm{Cr}_{2}\mathrm{O}_{7}^{2^{-}} + 14\mathrm{H}^{+} + 6\mathrm{e}^{-} \longrightarrow 2\mathrm{Cr}^{3^{+}} + 7\mathrm{H}_{2}\mathrm{O}$	6	$E = \frac{M}{6}$
MnO <sub>2</sub> (O.A.)	Mn <sup>2+</sup> in acidic medium	$MnO_2 + 4H^+ + 2e^- \longrightarrow Mn^{2+} + 2H_2O$	2	$E = \frac{M}{2}$
Cl <sub>2</sub> (O.A.) in bleaching powder	Cl-	$Cl_2 + 2e^- \longrightarrow 2Cl^-$	2	$E = \frac{M}{2}$
CuSO <sub>4</sub> (O.A.) in iodometric titration	Cu+	$Cu^{2+} + e^- \longrightarrow Cu^+$	1	$E = \frac{M}{1}$
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> (R.A.)	S4062-	$2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2e^{-}$	2 (for two moles)	$E = \frac{2M}{2} = M$
H <sub>2</sub> O <sub>2</sub> (O.A.)	H <sub>2</sub> O	$H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$	2	$E = \frac{M}{2}$ $E = \frac{M}{2}$
H <sub>2</sub> O <sub>2</sub> (R.A.)	0 <sub>2</sub>	$H_2O_2$ → $O_2 + 2H^+ + 2e^-$ (O.N. of oxygen in $H_2O_2$ is -1 per atom)	2	$E = \frac{M}{2}$
Fe <sup>2+</sup> (R.A.) (R.A)	Fe <sup>3+</sup> (in acidic medium)	$Fe^{2+} \longrightarrow Fe^{3+} + e^{-}$	1 (for two moles)	$E = \frac{M}{1}$
ŀ	$I_2$	$2I^{-} \longrightarrow I_{2} + 2e^{-}$	2	$E = \frac{M}{1}$
I⁻ (R.A)	$IO_3^-$ (in basic medium)	$I^- + 6OH^- \longrightarrow IO_3^- + 3H_2O + 6e^-$	6	$E = \frac{M}{6}$

#### **OXIDATION AND REDUCTION :**

There are two concepts of oxidation and reduction.

## (A) Classical/old concept :

	OXIDATION	REDUCTION
(1)	Addition of $O_2$	Addition of H <sub>2</sub>
	$2Mg + O_2 \rightarrow 2MgO$	$N_2 + 3H_2 \rightarrow 2NH_3$
	$C + O_2 \rightarrow CO_2$	$H_2 + Cl_2 \rightarrow 2HCl$
(2)	Removal of H <sub>2</sub>	Removal of O <sub>2</sub>
	$H_2S + Cl_2 \rightarrow 2HCl + S$ (oxidation of $H_2S$ )	$CuO + C \rightarrow Cu + CO$ (reduction of CuO)
	$4\text{HI} + \text{O}_2 \rightarrow 2\text{I}_2 + 2\text{H}_2\text{O}$ (oxidation of HI)	$H_2O + C \rightarrow CO + H_2$ (reduction of $H_2O$ )
(3)	Addition of electronegative element	Addition of electropositive element
	$Fe + S \rightarrow FeS$ (oxidation of Fe)	$CuCl_2 + Cu \rightarrow Cu_2Cl_2$ (reduction of $CuCl_2$ )
	$SnCl_2 + Cl_2 \rightarrow SnCl_4$ (oxidation of $SnCl_2$ )	$HgCl_2 + Hg \rightarrow Hg_2Cl_2$ (reduction of $HgCl_2$ )
(4)	Removal of electropositive element	Removal of electronegative element
	$2NaI + H_2O_2 \rightarrow 2NaOH + I_2$ (oxidation of NaI)	$2\text{FeCl}_3 + \text{H}_2 \rightarrow 2\text{FeCl}_2 + 2\text{HCl} \text{ (reduction of FeCl}_3)$

#### (B) Electronic/Modern Concept :

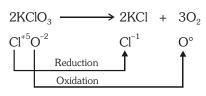
(D)	Liethonic/Modern Concept.				
	OXIDAT	TION	REDUCTION		
(1)	De-electr	onation	Electronation		
(2)	Oxidatio	n process are those process in	Reduction process are those process in which		
	which or	ne or more e⁻s are lost by an atom,	one or more e⁻s are gained by an atom, ion or		
	ion or me	olecule.	molecule.		
(3)	Example	-			
	(a)	$Zn \rightarrow Zn^{+2} + 2e^{-}$	$Cu^{+2} + 2e^{-} \rightarrow Cu$		
		$M \rightarrow M^{n_+} + ne^-$	$M^{n_{+}} + ne^{-} \rightarrow M$		
	(b)	${\rm Sn^{+2}} \rightarrow {\rm Sn^{+4}}$ + (4–2) $e^-$	$Fe^{+3} + (3 - 2) e^{-} \rightarrow Fe^{+2}$		
		$M^{+n_1} \rightarrow M^{+n_2} + (n_2 - n_1)e^-$	$M^{+x_1} \mathrel{+} (x_1 - x_2) e^{-} \rightarrow M^{+x_2}$		
	(c)	$Cl^- \rightarrow Cl + e^-$	$O + 2e^- \rightarrow O^{2-}$		
		$A^{-n} \rightarrow A + ne^{-}$	$A + xe^{-} \rightarrow A^{-x}$		
	(d)	$MnO_4^{-2} \rightarrow MnO_4^{-} + (2-1)e^{-}$	$[Fe(CN)_4]^{3-} + (4-3)e^- \rightarrow [Fe(CN)_4]^{-4}$		
		$A^{-n_1} \rightarrow A^{-n_2} + (n_1 - n_2)e^{-n_2}$	$\mathbf{A}^{-\mathbf{n}_1} + (\mathbf{n}_2 - \mathbf{n}_1) e^- \rightarrow \mathbf{A}^{-\mathbf{n}_2}$		

### **TYPES OF REDOX REACTIONS :**

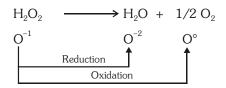
(A) Intermolecular redox reaction :- When oxidation and reduction takes place separately in different compounds, then the reaction is called intermolecular redox reaction.

$$\begin{array}{l} SnCl_{2} + 2FeCl_{3} \longrightarrow SnCl_{4} + 2FeCl_{2} \\ Sn^{+2} \longrightarrow Sn^{+4} (Oxidation) \\ Fe^{+3} \longrightarrow Fe^{+2} (Reduction) \end{array}$$

**(B)** Intramolecular redox reaction :- During the chemical reaction, if oxidation and reduction takes place in single compound then the reaction is called intramolecular redox reaction.



**(C) Disproportionation reaction :-** When reduction and oxidation takes place in the same element of the same compound then the reaction is called disproportionation reaction.



(D) Comproportionation reaction: Reverse of disproportionation reaction known as comproportionation reaction. Ex.  $HCIO + Cl^- \rightarrow Cl_2 + OH^-$ 

#### **BALANCING OF REDOX REACTION :**

- (A) Oxidation number change method.
- (B) Ion electron method.

#### (A) Oxidation number change method :

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

The general procedure involves the following steps :

- Select the atom in oxidising agent whose oxidation number decreases and indicate the gain of electrons.
- (ii) Select the atom in reducing agent whose oxidation number increases and indicate 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<sub>2</sub>O molecules to the side deficient in oxygen.
- (vi) Then balance the number of H atoms by adding  $H^+$  ions to the side deficient in hydrogen.

# Illustrations ——

**Illustration** Balance the following reaction by the oxidation number method –

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Solution  

$$Cu + HNO_{3} \longrightarrow Cu(NO_{3})_{2} + NO_{2} + H_{2}O$$
Write the oxidation number of all the atoms.  

$$0 + 1+5-2 + 2+5-2 + 4-2 + 1-2$$

$$Gu + HNO_{3} \longrightarrow Cu(NO_{3})_{2} + NO_{2} + H_{2}O$$
There is change in oxidation number of Cu and N.  

$$0 + 2+5-2$$

$$Gu \longrightarrow Cu(NO_{3})_{2} \qquad .....(1) (Oxidation no. is increased by 2)$$

$$+5 + 4$$

$$HNO_{3} \longrightarrow NO_{2} \qquad .....(2) (Oxidation no. is decreased by 1)$$
To make increase and decrease equal, eq. (2) is multiplied by 2.  

$$Cu + 2HNO_{3} \longrightarrow Cu(NO_{3})_{2} + 2NO_{3} + H_{2}O$$

Balancing nitrates ions, hydrogen and oxygen, the following equation is obtained.  $Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O_3$ This is the balanced equation. **Illustration** Balance the following reaction by the oxidation number method –  $MnO_4^- + Fe^{+2} \longrightarrow Mn^{+2} + Fe^{+3}$ Solution Write the oxidation number of all the atoms. +7 - 2 $Fe^{+2} \longrightarrow Mn^{+2} + Fe^{+3}$ MnO,⁻+ change in oxidation number has occured in Mn and Fe. +7  $MnO_4^- \longrightarrow Mn^{+2}$  .....(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<sub>2</sub>O are added to R.H.S. and to balance hydrogen, 8H<sup>+</sup> are added to L.H.S.  $MnO_4^{-} + 5Fe^{+2} + 8H^{+} \longrightarrow Mn^{+2} + 5Fe^{+3} + 4H_2O$ This is the balanced equation.

#### (B) Ion-Electron method :-

This method was given by Jette and La Mev in 1972.

The following steps are followed while balancing redox reaction (equations) by this method.

- (i) Write the equation in ionic form.
- (ii) Split the redox equation into two half reactions, one representing oxidation and the other representing reduction.
- (iii) Balance these half reactions separately and then add by multiplying with suitable coefficients so that the electrons are cancelled. Balancing is done using following substeps.
- (a) Balance all other atoms except H and O.
- (b) Then balance oxygen atoms by adding  $H_2O$  molecules to the side deficient in oxygen. The number of  $H_2O$  molecules added is equal to the deficiency of oxygen atoms.
- (c) Balance hydrogen atoms by adding H<sup>+</sup> ions equal to the deficiency in the side which is deficient in hydrogen atoms.
- (d) Balance the charge by adding electrons to the side which is rich in +ve charge. i.e. deficient in electrons. Number of electrons added is equal to the deficiency.
- (e) Multiply the half equations with suitable coefficients to equalize the number of electrons.
- (iv) Add these half equations to get an equation which is balanced with respect to charge and atoms.

(v) If the medium of reaction is basic, OH<sup>-</sup> ions are added to both sides of balanced equation, which is equal to number of H<sup>+</sup> ions in Balanced Equation.

# Illustrations -

Illustration Balance the following reaction by ion-electron method in acidic medium :

 $\operatorname{Cr}_{2}O_{7}^{2-} + C_{2}O_{4}^{2-} \longrightarrow \operatorname{Cr}^{3+} + CO_{2}$ 

$$\operatorname{Cr}_2O_7^{2-} + \operatorname{C}_2O_4^{2-} \longrightarrow \operatorname{Cr}^{3+} + \operatorname{CO}_2$$

Solution

Write both the half reaction. (a)  $\operatorname{Cr}_{2}O_{7}^{2-} \longrightarrow \operatorname{Cr}^{3+}$  (Reduction half reaction)  $C_2O_4^{2-} \longrightarrow CO_2$  (Oxidation half reaction) Atoms other than H and O are balanced. (b)  $Cr_{0}O_{7}^{2-} \longrightarrow 2Cr^{3+}$  $C_2 O_4^{2-} \longrightarrow 2CO_2$ Balance O-atoms by the addition of  $H_0O$  to another side (c)  $Cr_{a}O_{7}^{2-} \longrightarrow 2Cr^{3+} + 7H_{a}O$  $C_{2}O_{4}^{2-} \longrightarrow 2CO_{2}$ Balance H-atoms by the addition of H<sup>+</sup> to another side (d)  $Cr_2O_7^{2-}$  + 14 H<sup>+</sup>  $\longrightarrow$  2Cr<sup>3+</sup> + 7H<sub>2</sub>O  $C_{2}O_{4}^{2} \longrightarrow 2CO_{2}$ Now, balance the charge by the addition of electron (e<sup>-</sup>). (e)  $Cr_2O_7^{2-}$  + 14 H<sup>+</sup> + 6e<sup>-</sup>  $\longrightarrow$  2Cr<sup>3+</sup> + 7H<sub>2</sub>O .....(1)  $C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$ .....(2) Multiply equations by a constant to get the same number of electrons on both side. In the (f) above case second equation is multiplied by 3 and then added to first equation.  $Cr_{2}O_{7}^{2-} + 14 H^{+} + 6e^{-} \longrightarrow 2Cr^{3+} + 7H_{2}O$  $3C_2O_4^{2-} \longrightarrow 6CO_2 + 6e^ Cr_{2}O_{7}^{2-} + 3C_{2}O_{4}^{2-} + 14 H^{+} \longrightarrow 2Cr^{3+} + 6CO_{2} + 7H_{2}O_{2}$ **Illustration** Balance the following reaction by ion-electron method :  $Cr(OH)_3 + IO_3^- \xrightarrow{OH^-} I^- + CrO_4^{2-}$ 

Solution

 $Cr(OH)_3 + IO_3^- \xrightarrow{OH^-} I^- + CrO_4^{2-}$ 

(a) Separate the two half reactions.  $Cr(OH)_3 \longrightarrow CrO_4^{2^-}$  (Oxidation half reaction)  $IO_3^- \longrightarrow I^-$  (Reduction half reaction) (b) Balance O-atoms by adding H<sub>2</sub>O. H<sub>2</sub>O + Cr(OH)<sub>3</sub>  $\longrightarrow CrO_4^{2^-}$  $IO_3^- \longrightarrow I^- + 3H_2O$  (c) Balance H-atoms by adding H<sup>+</sup> to side having deficiency and add equal no. of OH<sup>−</sup> ions to the side (··· medium is known)

$$H_{2}O + Cr (OH)_{3} \longrightarrow CrO_{4}^{-2} + 5H^{+}$$

$$5OH^{-} + H_{2}O + Cr(OH)_{3} \longrightarrow CrO_{4}^{2-} + 5H^{+} + 5OH^{-}$$
or
$$5OH^{-} + Cr(OH)_{3} \longrightarrow CrO_{4}^{2-} + 4H_{2}O$$

$$IO_{3}^{-} + 6H^{+} \longrightarrow \Gamma + 3H_{2}O$$

$$IO_{3}^{-} + 6H^{+} + 6OH^{-} \longrightarrow \Gamma + 3H_{2}O + 6OH^{-}$$
or
$$IO_{3}^{-} + 3H_{2}O \longrightarrow \Gamma + 6OH^{-}$$
(d)
Balance the charges by adding electrons
$$5OH^{-} + Cr(OH)_{3} \longrightarrow CrO_{4}^{2-} + 4H_{2}O + 3e^{-}$$

$$IO_{3}^{-} + 3H_{2}O + 6e^{-} \longrightarrow \Gamma + 6OH^{-}$$
(e)
Multiply first equation by 2 and add to second to give
$$10OH^{-} + 2Cr(OH)_{3} \longrightarrow 2CrO_{4}^{2-} + 8H_{2}O + 6e^{-}$$

$$IO_{3}^{-} + 3H_{2}O + 6e^{-} \longrightarrow \Gamma + 6OH^{-}$$

#### LAW OF EQUIVALENCE

The law states that one equivalent of an element combine with one equivalent of the other, and in a chemical reaction equal number of equivalents or milli equivalents of reactants react to give equal number of equivalents or milli equivalents of products separately.

#### According :

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

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

(ii) In a compound M<sub>x</sub>N<sub>y</sub>

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

# POINTS TO REVISE

#### FOR REDOX REACTIONS :

 $N_1V_1 = N_2V_2$  is always true.

But  $(M_1 \times V_1) \times n_1 = (M_2 \times V_2) \times n_2$  (always true where n term represents valency factor).

	Oxidation state			
1.	Hydrogen peroxide	H <sub>2</sub> O <sub>2</sub>	H-0-0-H	O =
2.	Nitrous acid	HNO <sub>2</sub>	H—O—N=O	N =
3.	Nitric acid	HNO <sub>3</sub>	H—O—N O	N =
4.	Hypo chlorous acid	HCIO	HOCl	Cl =
5.	Chlorous acid	HClO <sub>2</sub>	H—O—Cl→O	Cl =
6.	Chloric acid	HCIO <sub>3</sub>	H-O-CI	Cl =
7.	Perchloric acid	HClO <sub>4</sub>	H—O—CI→O O	Cl =
8.	Hydrazine	N <sub>2</sub> H <sub>4</sub>	H H     H—N—N—H	N =
9.	Carbonic acid	H <sub>2</sub> CO <sub>3</sub>	H—O—C—O—H ∥ O	C=
10.	Chromium pentoxide	CrO <sub>5</sub>		Cr =
11.	Nitrosyl chloride/ Tilden's reagent	NOCI	Cl—N=O	N =
12.	Chromyl chloride	CrO <sub>2</sub> Cl <sub>2</sub>	O Cl−Cr−Cl O	Cr =
13.	Perchloric anhydride	Cl <sub>2</sub> O <sub>7</sub>		Cl =
14.	Calcium oxy-chloride/ Bleaching powder	CaOCl <sub>2</sub>	Ca(O*Cl)**Cl	*Cl = **Cl =

	O.S. of central Sulphur atom			
1.	Sulphoxilic acid	$H_2SO_2$	HOSOH	
2.	Sulphurous acid	H <sub>2</sub> SO <sub>3</sub>	0 ↑ H—O—S—O—H	
3.	Sulphuric acid	H <sub>2</sub> SO <sub>4</sub>	0 ↑ H—O—S—O—H ↓ O	
4.	Peroxymonosulphuric acid (Caro's acid)	H <sub>2</sub> SO <sub>5</sub>	0 ↑ H—O—S—O—O—H ↓ O	
5.	Thiosulphurous acid	$H_2S_2O_2$	S ↑ H—O—S—O—H	
6.	Thiosulphuric acid	$H_2S_2O_3$	S H—O—S—O—H V	
7.	Dithionous acid	$H_2S_2O_4$	0 0 ↑ ↑ H—O—S—S —O—H	
8.	Pyrosulphurous acid	$H_2S_2O_5$	0 0 ↑ ↑ H—O—S—S —O—H	
9.	Dithionic acid	$H_2S_2O_6$	0 0 ↑ ↑ H—0—S—S—0—H ↓ ↓ 0 0	
10.	Pyrosulphuric acid/ Fuming sulphuric acid/ Oleum	$H_2S_2O_7$	0 ← H0S0H ↓ 0 0	
11.	Peroxydisulphuric acid (Marshal's acid)	$H_2S_2O_8$	0 0 ↑ 1 H—0—\$—0—0—5—0—Н ↓ 0 0	

	O.S. of central P atom			
1.	Hypophophorous acid	H <sub>3</sub> PO <sub>2</sub>	О Н—Р—О—Н Н	
2.	Orthophosphorous acid/ Phophorous acid	H <sub>3</sub> PO <sub>3</sub>	0 ↑ H—O—P—O—H H	
3.	Orthophosphoric acid/ Phophoric acid	H <sub>3</sub> PO <sub>4</sub>	0 ↑ H—O—P—O—H O H H	
4.	Hypophosphoric acid	$H_4P_2O_6$	0 0 ↑ ↑ H—O—P—P—O—H I I 0 0 H H	
5.	Pyrophosphoric acid	H <sub>4</sub> P <sub>2</sub> O <sub>7</sub>	0 0 H-0-P-0-P-0-H 1 0 0 H H H	
6.	Metaphosphoric acid	HPO <sub>3</sub>	0 ↑ 0=P0H	
7.	Peroxymonophosphoric acid	H <sub>3</sub> PO <sub>5</sub>	0 ↑ H—O—P— O—O—H I H	
8.	Peroxydiphosphoric acid	H <sub>4</sub> P <sub>2</sub> O <sub>8</sub>	0 0 ↑ ↑ H-O-P-O-O-P-O-H 0 0 H H H	