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PRE-MEDICAL

PHYSICAL CHEMISTRY

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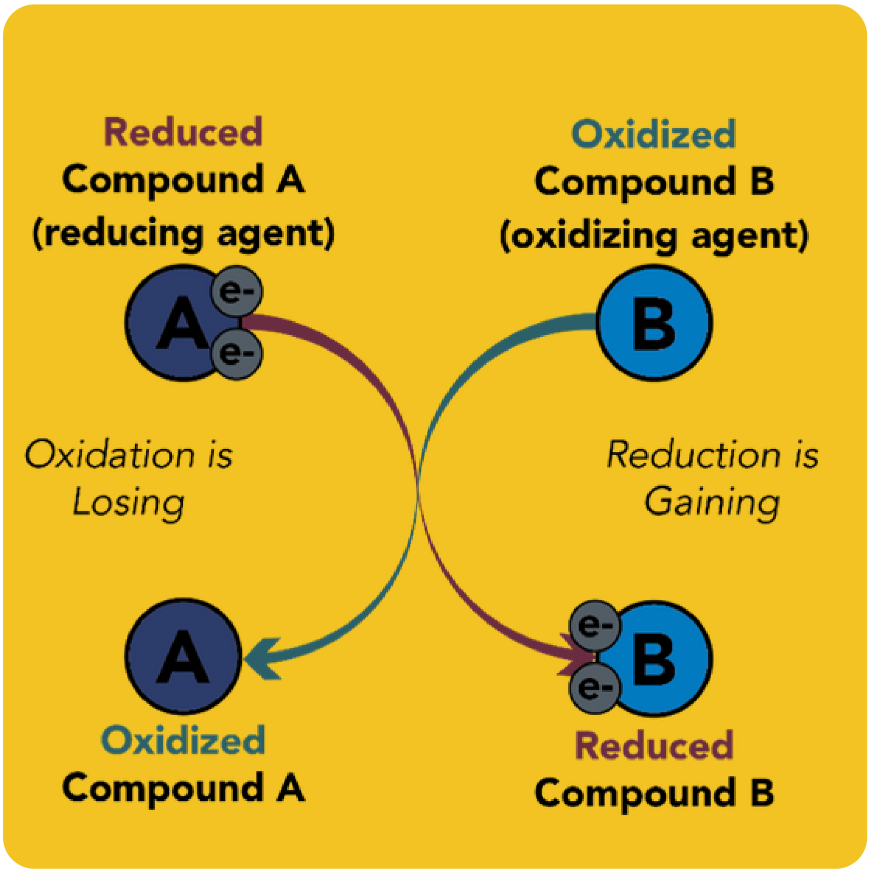

STUDY MATERIAL

Redox Reaction

ENGLISH MEDIUM

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REDOX REACTION

6.0 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.

6.1 Redox Reaction (Oxidation-Reduction) :

Many chemical reactions involve transfer of electrons from one chemical substance to another. These electron-transfer 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.

6.2 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 –

$P > H$ $C > H$ $S > C$ $Cl > N$

(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

$N_3H \Rightarrow$ 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. $H_2S \Rightarrow$ O.S of S = −2

$H_2SO_3 \Rightarrow$ O.S of S = +4

$H_2SO_4 \Rightarrow$ O.S of S = +6

6.3 Some helping rules for calculating oxidation number :

(A) In case of covalent bond :

(i) For homoatomic molecule

$$\begin{array}{lccc} & A - A & A = A & A \equiv A \\ & \downarrow \quad \downarrow & \downarrow \quad \downarrow & \downarrow \quad \downarrow \\ \text{O.N. :} & 0 \quad 0 & 0 \quad 0 & 0 \quad 0 \end{array}$$

(ii) For heteroatomic molecule (EN of B > A)

$$\begin{array}{lccc} & A - B & A = B & A \equiv B \\ & \downarrow \quad \downarrow & \downarrow \quad \downarrow & \downarrow \quad \downarrow \\ \text{O.N. :} & +1 \quad -1 & +2 \quad -2 & +3 \quad -3 \end{array}$$

(iii) The oxidation state of an element in its free state is zero. Example- Oxidation state of Na, Cu, I, Cl, O etc. are zero.

(iv) Oxidation state of atoms present in homoatomic molecules is zero.

Ex. H_2 , O_2 , N_2 , P_4 , S_8 = zero

(v) Oxidation state of an element in any of its allotropic form is zero.

Ex. $C_{Diamond}$, $C_{Graphite}$, $S_{Monoclinic}$, $S_{Rhombic}$ = 0

(vi) Oxidation state of all the components of an alloy are zero.

Ex. $\underset{0}{\overset{\downarrow}{(Na}} - \underset{0}{\overset{\downarrow}{Hg)}}$

(vii) In complex compounds, oxidation state of some neutral molecules (ligands) is zero.

Ex. CO, NO, NH_3, H_2O.

(viii) Oxidation state of fluorine in all its compounds is –1.

(ix) Oxidation state of IA & II A group elements are +1 and +2 respectively.

(x) Oxidation state of hydrogen in most of its compounds is +1 except in metal hydrides (-1)

Ex.	NaH	LiH	CaH_2	MgH_2
	↓ ↓	↓ ↓	↓ ↓	↓ ↓
O.S. :	+1 –1	+1 –1	+2 –1	+2 –1

(xi) Oxidation state of oxygen in most of its compounds is -2 except in -

(a) Peroxides $(O_2^{-2}) \rightarrow$ Oxidation state (O) = -1

Ex. H_2O_2 , BaO_2

(b) Super Oxides $(O_2^{-1}) \rightarrow$ Oxidation state (O) = -1/2

Ex. $\underset{-1/2}{\overset{}{KO_2}}$ ↓ –1/2

(c) Ozonide $(O_3^{-1}) \rightarrow$ Oxidation state (O) = –1/3

Ex. KO_3 ↓ –1/3

(d) OF_2 (Oxygen difluoride)

F – O – F
↓
Oxidation state (O) = + 2

(e) O_2F_2 (dioxygen difluoride)
↓
Oxidation state (O) = + 1

(xii) Oxidation state of monoatomic ions is equal to the charge present on the ion.

Ex. $Mg^{+2} \rightarrow$ Oxidation state = +2

(xiii) The algebric sum of oxidation state of all the atoms present in a polyatomic neutral molecule is 0.

Ex. $H_2\underline{S}O_4$

If O.S of S is x then

2 (+1) + x + 4 (-2) = 0

x - 6 = 0

x = +6

Ex. $H_2\underline{S}O_3$

If O.S of S is x then

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

$x - 4 = 0$

$x = +4$

(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. $\underline{S}O_4^{-2}$

If O.S of S is x then

$x + 4(-2) = -2$

$x - 6 = 0$

$x = +6$

Ex. $H\underline{C}O_3^-$

If O.S of C is x then

$+1 + x + 3(-2) = -1$

$x - 4 = 0$

$x = +4$

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

$$\begin{array}{lcccccccc} & A & \rightarrow A & B & \rightarrow B & A & \rightarrow B & B & \rightarrow A \\ & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow \\ \text{O.S.:} & +2 & -2 & +2 & -2 & +2 & -2 & O & O \end{array}$$

(C) In case of Ionic bond :

Charge on cation = O.S of cation

Charge on anion = O.S of anion

Ex.

$$\begin{array}{lcccc} NaCl \rightarrow & Na^+ & + & Cl^- \\ & \downarrow & & \downarrow \\ & +1 & & -1 \\ MgCl_2 \rightarrow & Mg^{+2} & + & 2Cl^- \\ & \downarrow & & \downarrow \\ & +2 & & -1 \end{array}$$

Illustrations

Illustration 1. Oxidation number of cobalt in $[Co(NH_3)_6]\,Cl_2Br$ is –

(1) +6 (2) Zero (3) +3 (4) +2

Solution. Let the oxidation number of Co be x

Oxidation number of NH_3 is zero

Oxidation number of Cl is –1

Oxidation number of Br is –1

Hence, $x + 6(0) - (1 \times 2) - 1 = 0$

$\therefore \quad x = +3$

So, the oxidation number of cobalt in the given complex compound is +3.

Illustration 2. The order of increasing oxidation numbers of S in S_8, $S_2O_8^{-2}$, $S_2O_3^{-2}$, $S_4O_6^{-2}$ is given below –

(1) $S_8 < S_2O_8^{-2} < S_2O_3^{-2} < S_4O_6^{-2}$ (2) $S_2O_8^{-2} < S_2O_3^{-2} < S_4O_6^{-2} < S_8$

(3) $S_2O_8^{-2} < S_8 < S_4O_6^{-2} < S_2O_3^{-2}$ (4) $S_8 < S_2O_3^{-2} < S_4O_6^{-2} < S_2O_8^{-2}$

Solution. The oxidation number of S are shown below along with the compounds

S_8	$S_2O_8^{-2}$	$S_2O_3^{-2}$	$S_4O_6^{-2}$
0	+6	+2	+2.5

Hence the order of increasing oxidation state of S is –

$S_8 < S_2O_3^{-2} < S_4O_6^{-2} < S_2O_8^{-2}$

Illustration 3. The oxidation number of Cl in $NOClO_4$ is –

(1) +11 (2) +9 (3) +7 (4) +5

Solution. The compound may be written as $NO^+ \, ClO_4^-$.

For ClO_4^-, Let oxidation number of Cl = a

$$a + 4 \times (-2) = -1$$

$$a = +7$$

Hence, the oxidation number of Cl in $NOClO_4$ is + 7

Illustration 4. The two possible oxidation states of N atoms in NH_4NO_3 are respectively –

(1) +3, +5 (2) +3, –5 (3) –3, +5 (4) –3, –5

Solution. There are two N atoms in NH_4NO_3, but one N atom has negative oxidation states (attached to H) and the other has positive oxidation states (attached to O). Therefore evaluation should be made separately as –

Oxidation states of N is NH_4^+

$a + 4 \times (+1) = +1$

$\therefore\ a = -3$

Oxidation states of N in NO_3^-

and $a + 3(-2) = -1$

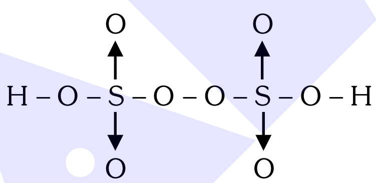
$\therefore\ a = +5$

Here the two oxidation states are –3 and +5 respectively.

Illustration 5. The oxidation states of S in $H_2S_2O_8$ is –

(1) +8 (2) –8 (3) +6 (4) +4

Solution. In $H_2S_2O_8$, two O atoms form peroxide linkage i.e.



$$2 \times 1 + 2a + 6(-2) + 2(-1) = 0$$

$$\therefore\ a = +6$$

Thus the oxidation states of S in $H_2S_2O_8$ is +6

Illustration 6. The oxidation number of S in $(CH_3)_2SO$ is –

(1) 1 (2) 2 (3) 0 (4) 3

Solution. Let the oxidation number of S is 'a'

Oxidation number of $CH_3 = +1$

Oxidation number of O = –2

$2(+1) + a + (-2) = 0$

$$a = 0$$

Hence the oxidation no. of S in dimethyl sulphoxide is zero.

BEGINNER'S BOX-1

1. In which of the following compounds, the oxidation state of I-atom is highest ?
(1) KI_3 (2) KIO_4 (3) KIO_3 (4) IF_5

2. The oxidation number of phosphorus in $Ba(H_2PO_2)_2$ is –
(1) +3 (2) +2 (3) +1 (4) –1

3. Oxidation number of Ni in $Ni(CO)_4$ is –
(1) 0 (2) 4 (3) 8 (4) 2

4. Positive oxidation state of an element indicates that it is –
(1) Elementary form (2) Oxidised (3) Reduced (4) Only reductant

5. Predict the highest and lowest oxidation state of (a) Ti and (b) Tl in combined state.
(1) a[0, +3] b[0, +2] (2) a[+3, 0] b[+4, 0] (3) a[+4, 0] b[+4, 0] (4) a[+4. +2] b[+3, +1]

6. The oxidation state of oxygen atom in potassium superoxide is –
(1) Zero (2) –1/2 (3) –1 (4) –2

6.4 APPLICATIONS OF OXIDATION NUMBER :

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

Strength of acid $\propto$ Oxidation Number

Strength of base $\propto$ $\dfrac{1}{\text{Oxidation Number}}$

Example : Decreasing order of acidic strength in HClO, $HClO_2$, $HClO_3$, $HClO_4$ will be.

Solution :

	Oxidation Number of chlorine
HClO (Hypo chlorous acid)	+1
$HClO_2$ (Chlorous acid)	+3
$HClO_3$ (Chloric acid)	+5
$HClO_4$ (Perchloric acid)	+7

$\because$ Strength of acid α Oxidation Number

So the order will be -

$HClO_4 > HClO_3 > HClO_2 > HClO$

(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	C	N	P	S	Cl	Cr	Mn	Os	Ru	O	H
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. $KMnO_4 \downarrow +7$, $K_2Cr_2O_7 \downarrow +6$, $H_2SO_4 \downarrow +6$, $SO_3 \downarrow +6$, $H_3PO_4 \downarrow +5$, $HNO_3 \downarrow +5$, $HClO_4 \downarrow +7$

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

PH_3	NH_3	CH_4
$\downarrow$	$\downarrow$	$\downarrow$
–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 = $\dfrac{\text{Molecular weight}}{\text{No. of electrons gained by one mole of oxidant}}$

Example : In acidic medium

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

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

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

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

(b) Equivalent weight of a reductant = $\dfrac{\text{Molecular weight}}{\text{No. of electrons lost by one mole of reductant}}$

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 $C_2O_4^{-2} = \dfrac{M}{2}$

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

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

(ii) $\underset{(+7)}{MnO_4^-} \longrightarrow \underset{(+4)}{MnO_2}$ (neutral medium) or (Weak alkaline medium)

Here, only 3 electrons are gained by MnO_4^- so its equivalent weight = $\dfrac{M}{3} = \dfrac{158}{3} = 52.7$

Note : When only alkaline medium is given consider it as weak alkaline medium.

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

Here, only one electron is gained by MnO_4^- so its equivalent weight = $\dfrac{M}{1}$ = 158

Note :- $KMnO_4$ 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

$$Cr_2O_7^{2-} \longrightarrow 2Cr^{3+}$$
$$(2 \times 6) \longrightarrow (2 \times 3)$$

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

(D) 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 formula can be confirmed.

GOLDEN KEY POINTS

SOME OXIDIZING AGENTS/REDUCING AGENTS WITH EQUIVALENT WEIGHT :

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 or in weak alkaline medium	$MnO_4^- + 3e^- + 2H_2O \longrightarrow MnO_2 + 4OH^-$	3	$E = \frac{M}{3}$
MnO_4^- (O.A.)	MnO_4^{2-} in strong alkaline medium	$MnO_4^- + e^- \longrightarrow MnO_4^{2-}$	1	$E = \frac{M}{1}$
$Cr_2O_7^{2-}$(O.A.)	Cr^{3+} in acidic medium	$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$	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 moles)	$E = \frac{2M}{2} = M$
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	$E = \frac{M}{1}$
I^- (R.A)	I_2 (in acidic medium)	$2I^- \longrightarrow I_2 + 2e^-$	2 (for two moles)	$E = \frac{M}{1}$
I^- (R.A)	IO_3^- (in basic medium)	$I^- + 6OH^- \longrightarrow IO_3^- + 3H_2O + 6e^-$	6	$E = \frac{M}{6}$

Illustrations

Illustration 7. Find the n-factor of reactant in the following chemical changes.

(i) $KMnO_4 \xrightarrow{H^+} Mn^{2+}$ (ii) $KMnO_4 \xrightarrow{H_2O} Mn^{4+}$

(iii) $KMnO_4 \xrightarrow{OH^- \text{(concentrated basic medium)}} Mn^{6+}$ (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) $Fe_2O_3 \rightarrow FeSO_4$

Solution (i) In this reaction, $KMnO_4$ which is an oxidizing agent, itself gets reduced to Mn^{2+} under acidic conditions.

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

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

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

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

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

(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.)

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

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

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

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

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

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

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

Illustration 8. Suppose that there are three atoms A, B, C and their oxidation numbers are 6, –1, –2, respectively. Then the molecular formula of compound will be.

Solution Since, the charge on a free compound is zero. So

$$+6 = (-1 \times 4) + (-2)$$
$$+6 = -6$$
$$\text{or} \quad +6 = (-1 \times 2) + (-2 \times 2)$$
$$= -2 + (-4) = -6$$

So molecular formula, AB_4C or AB_2C_2.

BEGINNER'S BOX-2

1. Molecular weight of $KMnO_4$ in acidic medium and neutral medium will be respecitvely –

(1) 7 × equivalent weight and 2 × equivalent weight

(2) 5 × equivalent weight and 3 × equivalent weight

(3) 4 × equivalent weight and 5 × equivalent weight

(4) 2 × equivalent weight and 4 × equivalent weight

2. In acidic medium, equivalent weight of $K_2Cr_2O_7$ (Molecular weight = M) is –

(1) M/3 (2) M/4 (3) M/6 (4) M/2

6.5 OXIDATION AND REDUCTION :

There are two concepts of oxidation and reduction.

(A) Classical/old concept :

	OXIDATION	REDUCTION
(1)	Addition of O_2 $2Mg + O_2 \rightarrow 2MgO$ $C + O_2 \rightarrow CO_2$	Addition of H_2 $N_2 + 3H_2 \rightarrow 2NH_3$ $H_2 + Cl_2 \rightarrow 2HCl$
(2)	Removal of H_2 $H_2S + Cl_2 \rightarrow 2HCl + S$ (oxidation of H_2S) $4HI + O_2 \rightarrow 2I_2 + 2H_2O$ (oxidation of HI)	Removal of O_2 $CuO + C \rightarrow Cu + CO$ (reduction of CuO) $H_2O + C \rightarrow CO + H_2$ (reduction of H_2O)
(3)	Addition of electronegative element $Fe + S \rightarrow FeS$ (oxidation of Fe) $SnCl_2 + Cl_2 \rightarrow SnCl_4$ (oxidation of $SnCl_2$)	Addition of electropositive element $CuCl_2 + Cu \rightarrow Cu_2Cl_2$ (reduction of $CuCl_2$) $HgCl_2 + Hg \rightarrow Hg_2Cl_2$ (reduction of $HgCl_2$)
(4)	Removal of electropositive element $2NaI + H_2O_2 \rightarrow 2NaOH + I_2$ (oxidation of NaI)	Removal of electronegative element $2FeCl_3 + H_2 \rightarrow 2FeCl_2 + 2HCl$ (reduction of $FeCl_3$)

(B) Electronic/Modern Concept :

	OXIDATION	REDUCTION
(1)	De-electronation	Electronation
(2)	Oxidation process are those process in which one or more e^-s are lost by an atom, ion or molecule.	Reduction process are those process in which one or more e^-s are gained by an atom, ion or molecule.
(3)	Example -	
	(a) $Zn \rightarrow Zn^{+2} + 2e^-$ $M \rightarrow M^{n+} + ne^-$	$Cu^{+2} + 2e^- \rightarrow Cu$ $M^{n+} + ne^- \rightarrow M$
	(b) $Sn^{+2} \rightarrow Sn^{+4} + (4-2)\ e^-$ $M^{+n_1} \rightarrow M^{+n_2} + (n_2-n_1)e^-$	$Fe^{+3} + (3-2)\ e^- \rightarrow Fe^{+2}$ $M^{+x_1} + (x_1-x_2)e^- \rightarrow M^{+x_2}$
	(c) $Cl^- \rightarrow Cl + e^-$ $A^{-n} \rightarrow A + ne^-$	$O + 2e^- \rightarrow O^{2-}$ $A + xe^- \rightarrow A^{-x}$
	(d) $MnO^{-2}_4 \rightarrow MnO_4^- + (2-1)e^-$ $A^{-n_1} \rightarrow A^{-n_2} + (n_1-n_2)e^-$	$[Fe(CN)_4]^{3-} + (4-3)e^- \rightarrow [Fe(CN)_4]^{-4}$ $A^{-n_1} + (n_2-n_1)e^- \rightarrow A^{-n_2}$

6.6 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.

$$SnCl_2 + 2FeCl_3 \longrightarrow SnCl_4 + 2FeCl_2$$

$$Sn^{+2} \longrightarrow Sn^{+4} \text{ (Oxidation)}$$

$$Fe^{+3} \longrightarrow Fe^{+2} \text{ (Reduction)}$$

(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.

$$2KClO_3 \longrightarrow 2KCl + 3O_2$$

$$Cl^{+5}O^{-2} \qquad Cl^{-1} \qquad O^{\circ}$$

Reduction

Oxidation

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

$$H_2O_2 \longrightarrow H_2O + 1/2\, O_2$$

$$O^{-1} \qquad O^{-2} \qquad O^{\circ}$$

Reduction

Oxidation

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

BEGINNER'S BOX-3

1. Oxidation is defined as –

(1) Gain of electrons
(2) Decrease in positive valency
(3) Loss of electrons
(4) Addition of electropositive element

2. Reduction is defined as –

(1) Increase in positive valency
(2) Gain of electrons
(3) Loss of protons
(4) Decrease in negative valency

3. In the reaction $MnO_4^- + SO_3^{-2} + H^+ \longrightarrow SO_4^{-2} + Mn^{2+} + H_2O$

(1) MnO_4^- and H^+ both are reduced
(2) MnO_4^- is reduced and H^+ is oxidised
(3) MnO_4^- is reduced and SO_3^{2-} is oxidised
(4) MnO_4^- is oxidised and SO_3^{2-} is reduced

4. The charge on cobalt in $[Co(CN)_6]^{-3}$ is –

(1) –6 (2) –3 (3) +3 (4) +6

5. Which of the following halogen always show only one oxidating state in its compounds?

(1) Cl (2) F (3) Br (4) I

6. Which of the following reactions do not involve oxidation-reduction ?

(1) $2Rb + 2H_2O \longrightarrow 2RbOH + H_2$ (2) $2CuI_2 \longrightarrow 2CuI + I_2$

(3) $NH_4Cl + NaOH \longrightarrow NaCl + NH_3 + H_2O$ (4) $3Mg + N_2 \longrightarrow Mg_3N_2$

7. The fast reaction between water and sodium is the example of –

(1) Oxidation (2) Reduction (3) Intermolecular redox (4) Intramolecular redox

8. Choose the redox reaction from the following–

(1) $Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$ (2) $BaCl_2 + H_2SO_4 \longrightarrow BaSO_4 + 2HCl$

(3) $2NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2O$ (4) $KNO_3 + H_2SO_4 \longrightarrow 2HNO_3 + K_2SO_4$

9. Which of the following is not a redox reaction ?

(1) $MnO_4^- \longrightarrow MnO_2 + O_2$ (2) $Cl_2 + H_2O \longrightarrow HCl + HClO$

(3) $2CrO_4^{2-} + 2H^+ \longrightarrow Cr_2O_7^{2-} + H_2O$ (4) $MnO_4^- + 8H^+ + 5Ag \longrightarrow Mn^{+2} + 4H_2O + 5Ag^+$

10. In the reaction $6Li + N_2 \longrightarrow 2Li_3N$

(1) Li undergoes reduction (2) Li undergoes oxidation

(3) N undergoes oxidation (4) Li is oxidant

11. $H_2O_2 + H_2O_2 \longrightarrow 2H_2O + O_2$ is an example of dispropotionation because –

(1) Oxidation number of oxygen only decreases

(2) Oxidation number of oxygen only increases

(3) Oxidation number of oxygen decreases as well as increase

(4) Oxidation number of oxygen neither decreases nor increases

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6.7 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 :

(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 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_2O 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 9. Balance the following reaction by the oxidation number method –

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

Solution Write the oxidation number of all the atoms.

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

There is change in oxidation number of Cu and N.

$$\overset{0}{Cu} \longrightarrow \overset{+2+5-2}{Cu(NO_3)_2} \quad ....(1) \text{ (Oxidation no. is increased by 2)}$$

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

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.

Illustration 10. 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.

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

change in oxidation number has occured in Mn and Fe.

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

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

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.

(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 equation 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 in both half reactions.

(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^+ 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^- ions are added to both sides of balanced equation, which is equal to number of H^+ ions in Balanced Equation.

Illustrations

Illustration 11. Balance the following reaction by ion-electron method in acidic medium :

$$Cr_2O_7^{2-} + C_2O_4^{2-} \longrightarrow Cr^{3+} + CO_2$$

Solution $Cr_2O_7^{2-} + C_2O_4^{2-} \longrightarrow Cr^{3+} + CO_2$

(a) Write both the half reaction.

$Cr_2O_7^{2-} \longrightarrow Cr^{3+}$ (Reduction half reaction)

$C_2O_4^{2-} \longrightarrow CO_2$ (Oxidation half reaction)

(b) Atoms other than H and O are balanced.

$Cr_2O_7^{2-} \longrightarrow 2Cr^{3+}$

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

(c) Balance O-atoms by the addition of H_2O to another side

$Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$

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

(d) Balance H-atoms by the addition of H^+ to another side

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

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

(e) Now, balance the charge by the addition of electron (e^-).

$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$ ....(1)

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

(f) Multiply equations by a constant number to get the same number of electrons on both side. In the above case second equation is multiplied by 3 and then added to first equation.

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

$3C_2O_4^{2-} \longrightarrow 6CO_2 + 6e^-$

$Cr_2O_7^{2-} + 3C_2O_4^{2-} + 14H^+ \longrightarrow 2Cr^{3+} + 6CO_2 + 7H_2O$

Illustration 12. Balance the following reaction by ion-electron method in basic medium :

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

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_2O.

$H_2O + Cr(OH)_3 \longrightarrow CrO_4^{2-}$

$IO_3^- \longrightarrow I^- + 3H_2O$

(c) Balance H-atoms by adding H^+ to side having deficiency and add equal no. of OH^- ions to both side ($\because$ medium is known)

$H_2O + Cr(OH)_3 \longrightarrow CrO_4^{-2} + 5H^+$

$5OH^- + H_2O + Cr(OH)_3 \longrightarrow CrO_4^{2-} + 5H^+ + 5OH^-$

or $5OH^- + Cr(OH)_3 \longrightarrow CrO_4^{2-} + 4H_2O$

$IO_3^- + 6H^+ \longrightarrow I^- + 3H_2O$

$IO_3^- + 6H^+ + 6OH^- \longrightarrow I^- + 3H_2O + 6OH^-$

or $IO_3^- + 3H_2O \longrightarrow I^- + 6OH^-$

(d) Balance the charges by adding electrons

$5OH^- + Cr(OH)_3 \longrightarrow CrO_4^{2-} + 4H_2O + 3e^-$

$IO_3^- + 3H_2O + 6e^- \longrightarrow I^- + 6OH^-$

(e) Multiply first equation by 2 and add to second to give

$10OH^- + 2Cr(OH)_3 \longrightarrow 2CrO_4^{2-} + 8H_2O + 6e^-$

$IO_3^- + 3H_2O + 6e^- \longrightarrow I^- + 6OH^-$

$4OH^- + 2Cr(OH)_3 + IO_3^- \longrightarrow 5H_2O + 2CrO_4^{2-} + I^-$

6.8 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_xN_y

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

GOLDEN KEY POINTS

- **FOR REDOX REACTIONS :**

  Number of m. eq. of oxidant = Number of m. eq. of reductant

  $N_1V_1 = N_2V_2$ 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).

Illustrations

Illustration 13 Calculate the normality of a solution containing 15.8 g of $KMnO_4$ in 50 mL acidic solution.

Solution Normality (N) = $\frac{W \times 1000}{E \times V(mL)}$

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

Illustration 14 Calculate the normality of a solution containing 50 mL of 5 M solution $K_2Cr_2O_7$ in acidic medium.

Solution Normality (N) = Molarity × Valency factor = 5 × 6 = 30 N

Illustration 15 Find the number of moles of $KMnO_4$ needed to oxidise one mole Cu_2S in acidic medium.

The reaction is $KMnO_4 + Cu_2S \longrightarrow Mn^{2+} + Cu^{2+} + SO_2$

Solution From law of equivalence

equivalents of Cu_2S = equivalents of $KMnO_4$

moles of Cu_2S × v.f = moles of $KMnO_4$ × v.f.

$1 \times 8 = n_2 \times 5$

$n_2 = \frac{8}{5} = 1.6$

Illustration 16 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) $\frac{5}{3}$

Solution Equivalents of $C_2O_4^{2-}$ = equivalents of MnO_4^-

x (mole) × 2 = 1 × 5 ; x = $\frac{5}{2}$

Illustration 17 What volume of 6 M HCl and 2 M HCl should be mixed to get two litre of 3 M HCl ?

Solution 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 + M_2V_2 = M_3V_3

6M HCl 2M HCl 3M HCl

$6 \times (x) + 2 \times (2 - x) = 3 \times 2$

$\Rightarrow 6x + 4 - 6x = 6 \Rightarrow 4x = 2$

∴ x = 0.5 L

Hence, volume of 6 M HCl required = 0.5 L

Volume of 2M HCl required = 1.5 L

Illustration 18 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 ?

Solution Amount of NaOH present in 1000 mL of 0.15 M NaOH = $0.15 \times 40 = 6$ g

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

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

Illustration 19 What weight of Na_2CO_3 of 85% purity would be required to prepare 45.6 mL of 0.235N H_2SO_4 ?

Solution Meq. of Na_2CO_3 = Meq. of H_2SO_4 = 45.6×0.235

$$\therefore \frac{W_{Na_2CO_3}}{E_{Na_2CO_3}} \times 1000 = 45.6 \times 0.235 \Rightarrow \frac{W_{Na_2CO_3}}{106/2} \times 1000 = 45.6 \times 0.235$$

$\therefore W_{Na_2CO_3} = 0.5679$ g

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

$\therefore$ For 0.5679 g of pure Na_2CO_3, weight of sample = $\frac{100}{85} \times 0.5679 = 0.6681$ g

Illustration 20 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

Solution $Mn^{7+} + 5e^- \rightarrow Mn^{2+}] \times 3$

$$\left.\begin{array}{l} Fe^{2+} \rightarrow Fe^{3+} + e^- \\ C_2O_4^{2-} \rightarrow 2CO_2 + 2e^- \end{array}\right] \times 5$$

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.

Illustration 21 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

Solution valency factor = 3

$$\overset{+5}{NO_3^-} \rightarrow \overset{2+}{NO}$$

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

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

V = 7.936 mL

Hence, (B) is the correct answer.

Illustration 22 Which of the following is / are correct?

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

(B) mole = N_A molecule = 6.02×10^{23} molecules

(C) mole = g molecules

(D) none of the above

Solution **Ans.** (A), (B) and (C)

BEGINNER'S BOX-4

1. In the half reaction : $2ClO_3^- \longrightarrow Cl_2$

(1) 5 electrons are gained

(2) 5 electrons are liberated

(3) 10 electrons are gained

(4) 10 electrons are liberated

2. The number of electrons required to balance the following equation –

$NO_3^- + 4H^+ + e^- \longrightarrow 2H_2O + NO$ are –

(1) 5 (2) 4 (3) 3 (4) 2

3. Which of the following equations is a balanced one –

(1) $5BiO_3^- + 22H^+ + Mn^{2+} \longrightarrow 5Bi^{3+} + 7H_2O + MnO_4^-$

(2) $5BiO_3^- + 14H^+ + 2Mn^{2+} \longrightarrow 5Bi^{3+} + 7H_2O + 2MnO_4^-$

(3) $2BiO_3^- + 4H^+ + Mn^{2+} \longrightarrow 2Bi^{3+} + 2H_2O + MnO_4^-$

(4) $6BiO_3^- + 12H^+ + 3Mn^{2+} \longrightarrow 6Bi^{3+} + 6H_2O + 3MnO_4^-$

ANSWER KEY

BEGINNER'S BOX-1	Que.	1	2	3	4	5	6				
	Ans.	2	3	1	2	4	2				
BEGINNER'S BOX-2	Que.	1	2								
	Ans.	2	3								
BEGINNER'S BOX-3	Que.	1	2	3	4	5	6	7	8	9	10
	Ans.	3	2	3	3	2	3	3	1	3	2
	Que.	11									
	Ans.	3									
BEGINNER'S BOX-4	Que.	1	2	3							
	Ans.	3	3	2							