REDOX

1. CLASSICAL CONCEPT OF OXIDATION REDUCTION

A. Oxidation : According to this concept, oxidation is considered as the addition of oxygen or removal of hydrogen in an ion, in a compound or in a species. Or the addition of an electronegative element or removal of electropositive element in a group, in a ion, in a species or in a compound is called oxidation.

For example :

(a) $2Mg + O_2 \rightarrow 2MgO$

$\rightarrow$ Addition of Oxygen.

(b) $C + O_2 \rightarrow CO_2$

(c) $\underline{H_2S} + Cl_2 \rightarrow 2HCl + S$

$\rightarrow$ Removal of Hydrogen

(d) $MnO_2 + 4\underline{HCl} \rightarrow MnCl_2 + Cl_2 + 2H_2O$

B. Reduction : According to this concept, reduction is considered as addition of hydrogen or removal of oxygen in an atom, in a group, in an ion, in a species or in a compound. Or addition of an electropositive element or removal of an electronegative element in a group, in an ion, in a species or in a compound is called reduction.

For example :

(a) $H_2S + \underline{Cl_2} \rightarrow 2HCl + S$

$\rightarrow$ Addition of Hydrogen

(b) $H_2 + \underline{Cl_2} \rightarrow 2HCl$

(C) $\underline{ZnO} + C \rightarrow Zn + CO$

$\rightarrow$ Removal of Oxygen

(d) $\underline{Fe_2O_3} + 3CO \rightarrow 2Fe + 3CO_2$

2. VALENCY CONCEPT OF OXIDATION REDUCTION

A. Oxidation: According to this concept, increase in (+)ve valency or decrease in (–)ve valency in a reaction is called oxidation.

For example :

$$\underset{(0)}{2Mg} + O_2 \rightarrow \underset{(+2)}{2MgO}$$

B. Reduction : According to this concept, It is the process in which (+) ve valency decreases whereas (–)ve valency increases in a reaction is called reduction.

For example :

$$\underset{(+2)}{2HgCl_2} + SnCl_2 \rightarrow \underset{(+1)}{Hg_2Cl_2} + SnCl_4$$

3. OXIDATION NUMBER CONCEPT OF OXIDATION-REDUCTION

A. Oxidation : According to this concept, increase in oxidation no. in an element in a reaction is called oxidation.

B. Reduction : According to this concept, decrease in oxidation no. in an element in a reaction is called reduction.

For example :

$$\underset{+7}{KMnO_4} + \underset{+2}{FeSO_4} \rightarrow \underset{+2}{MnO} + \underset{+3}{Fe_2(SO_4)_3}$$

4. MODERN OR ELECTRONIC CONCEPT OF OXIDATION REDUCTION

A. Oxidation : According to this concept, the process in which involves the loss of e^- in an element or species is called oxidation. It is also called deelectronation.

For example **:**

$Fe \rightarrow Fe^{2+} + 2e^-$ (O.N. of Fe, $0 \rightarrow 2$)

$Fe^{2+} \rightarrow Fe^{3+} + e^-$ (O.N. of Fe, $2 \rightarrow 3$)

$2Cl^- \rightarrow Cl_2 + 2e^-$ (O.N. of Cl, $-1 \rightarrow 0$)

B. Reduction : According to this concept, the process which involves the gain of electrons by an element or an atom or an ion is called reduction. It is also called electronation.

For example :

$I_2 + 2e^- \rightarrow 2I^-$ (O.N. of I,$0 \rightarrow -1$)

$Fe^{3+} + e^- \rightarrow Fe^{+2}$ (O.N. of Fe, $+3 \rightarrow +2$)

$Sn^{+4} + 2e^- \rightarrow Sn^{+2}$ (O.N. of Sn, $+4 \rightarrow +2$)

5. OXIDANT OR OXIDISING AGENT

Species, which oxidise other species, which is present in a reaction and reduce it self. This type of species is called oxidant or oxidising agent. Or species, which accepts electron in a reaction by another species and show decreases in its oxidation no. in the reaction is called oxidant or oxidising agent.

5.1 Some Important oxidising agent or oxidant

1. All elements with high electronegative character like N, O, F, Cl, etc.

2. All metallic oxides like Li_2O, Na_2O, Na_2O_2, CO_2, CaO, MgO, BaO_2 etc.

3. Some nonmetallic oxides like CO_2, SO_2, H_2O_2, O_3.

4. All neutral compound or ion in which element shows their higher oxidation no. or state are act as oxidant or oxidising agent like $KMnO_4$, H_2SO_4, $SnCl_4$, H_3PO_4, $K_2Cr_2O_7$, $HClO_4$, $CuCl_2$, HNO_3, H_2SO_5, $FeCl_3$, $HgCl_2$, etc.

6. REDUCTANT OR REDUCTION AGENT

Species which reduce other element in a reaction and oxidise itself to donate electrons and show increase in its oxidation no. is called reductant or reducing agent.

6.1 Some Important reducing agent or reductant

1. All metals like, K, Mg, Ca, etc.
2. All metallic hydrides like NaH, CaH_2, $LiAlH_4$, $NaBH_4$, AlH_3, etc.
3. All hydroacids like HF, HCl, HBr, H_2S etc.
4. Some organic compounds like Aldehyde, formic acid, oxalic acid, tartaric acid.
5. All neutral compounds or ions, which show their lower oxidation state.

MnO, $HClO$, $HClO_2$, H_3PO_2, HNO_2, H_2SO_3, $FeCl_2$, $SnCl_2$, Hg_2Cl_2, CH_2Cl_2 etc.

Some Important compound which can act as oxidant and reductant both

HNO_2, SO_2, H_2O_2, O_3, Al_2O_3, CrO_2, MnO_2, ZnO, CuO,

NOTE : Al_2O_3, CrO_2, MnO_2, ZnO, CuO are called as amphoteric oxide.

7. OXIDATION NUMBER

A. Definition : It represents the number of electron gained or lost by atom when it changes in compound from a free state.

(a) If electron are lose by an atom in the formation of compound, oxidation number is given (+)ve sign.

(b) If electrons are gain by an atom in the formation of compound oxidation number given is (–)ve sign.

(c) It represents the real charge in case of ionic compounds and represents the imaginary charge in case of covalent compounds.

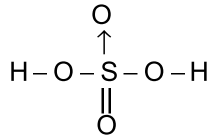
(d) Maximum oxidation no. of an element is equal to group no. in the periodic table

(e) Minimum oxidation no. of an element is equal to group no. – 8.

I group elements always shows +1 oxidation no.
II group elements always shows +2 oxidation no.
III group elements show +3 oxidation no. but +1 becomes more stable going down the group (due to inert pair effect)
IV group shows –4 to +4 oxidation no.
V group shows –3 to +5 oxidation no.
VI group shows –2 to +6 oxidation no.
VII group shows –1 to +7 oxidation no.
Inert gases show zero oxidation no.

7.1 Oxidation no. for Coordinate bond

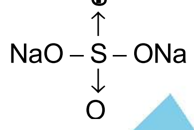
(a) When coordinate bond is formed from low electronegative element to high electronegative element then the e^- donor element shows +2 oxidation number whereas e^- acceptor element shows –2, oxidation no. in this type of bonded compounds. For example in H_2SO_4.



Here 'S' is low electronegative element than O. therefore, number of S = +2 and O. N. of O = –2

(b) When coordinate bond is formed between the two same electronegative elements then the e^- donor element shows +2 oxidation number where e^- acceptor element shows –2 oxidation number in this type of bonded compound.

For example :– In $Na_2S_2O_3$



Here O.N. of 'S' is +2, Because it is e^- donor and the other 'S' is –2, Because it is e^- acceptor.

(c) When coordinate bond is formed from high electronegative element to low electronegative element then no change will be shown by both the elements, which is bonded by coordinate bond. eg. CH_3NC

8. OXIDATION STATE

Oxidation state of an atom is defined as oxidation number per atom for all practical purposes. Oxidation state is often expressed as oxidation number.

8.1 The rules to derive oxidation number or oxidation state

(a) The O.S. of an element in its free state is zero. Example O.S.' s of Na, Cu, I_2, Cl_2, O_2 etc. are zero

(b) Sum of O.S.' s of all the atoms in neutral molecule is zero.

(c) Sum of O.S.' s of all the atoms in a complex ion is equal number of charge present on it.

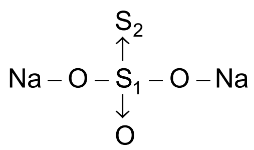
(d) In complex compounds, O.S. of some neutral molecules (ligands) is zero. Example CO, NO, NH_3, H_2O.

(e) Generally O.S. of oxygen is –2 but in H_2O_2 it is –1 and in OF_2 it is +2.

(f) Generally O.S. of Hydrogen is +1 but in metallic hydrides it is –1.

(g) Generally O.S. of halogen atoms is –1 but in interhalogen compounds it changes.

NOTE : Some times same atom in a compound has different O.S. For example, structure of $Na_2S_2O_3$ is



Here S_1 and S_2 both are sulphur atoms but they have different O.S.

O.S. of S_1 = 6

O.S. of S_2 = –2 (it is accepting two electrons from S_1)

Average O.S. of S = $\frac{6-2}{2}$ = 2

(h) Generally, O.S. of alkali metals is +1 and that of alkaline earth metals is +2.

(i) O.S. of transition elements very high from compound to compound. Mn has O.S. from +1 to +7.

$Mn_2O \rightarrow +1$, $MnO \rightarrow +2$, $Mn_3O_4 \rightarrow 8/3$, $MnO_2 \rightarrow +4$, $Mn_2O_5 \rightarrow +5$, $MnO_4^{2-} \rightarrow +6$, $MnO_4^{-} \rightarrow +7$

(j) O.S. of an atom may be fractional, negative, zero as well as Positive.

8.2 Oxidation State As A periodic Property

Oxidation state of an atom depends upon the electronic configuration of atom it is periodic properties.

(a) I A group or alkali metals shows +1 oxidation state.

(b) II A group or alkaline earth metals show +2 O.S.

(c) The maximum normal oxidation state, show by III A group elements is +3. These elements also show +2 to +1 oxidation states also.

(d) Elements of IVA group show their max & min. oxidation states +4 & - 4 respectively.

(e) Non metals shows number of oxidation states, the relation between max & min. oxidation states for non metals is equal to maximum O.S. –minimum O.S. = 8

For example sulphur has maximum oxidation number +6 as being in VI A group element.

8.3 Fractional Oxidation States

Lot of elements shows fractional oxidation states. For example oxidation state of oxygen in superoxides of alkali metals (KO_2, SO_2, RbO_2) is -1/2.

eg. In Fe_3O_4, Fe shows its oxidation state as 8/3 as it is a mixed oxide and can be written as $Fe^{II}\ Fe_2^{III}O_4$.

Oxidation number and oxidation state

S.No.	Reaction	Oxidant (Getting Reduced)	Reductant (Getting Oxidised)
1.	$C + O_2 \rightarrow CO_2$	O [0 → – 2]	C [0 → + 4]
2.	$PbS + 4O_3 \rightarrow PbSO_4 + 4O_2$	O [+ 2 → 0]	S [– 2 → + 6]
3.	$PbS + 4H_2O_2 \rightarrow PbSO_4 + 4H_2O$	O [–1 → –2]	S [– 2 → + 6]
4.	$Sn + 2F_2 \rightarrow SnF_4$	F [0 → –1]	Sn [0 →+ 4]
5.	$SO_2 + 2H_2O + Cl_2 \rightarrow 2HCl + H_2SO_4$	Cl [0 → –1]	S [+ 4 → + 6]
6.	$I_2 + 10HNO_3 \rightarrow 2HIO_3 + 10NO_2 + 4H_2O$	N [+ 5 → + 4]	I [0 → + 5]
7.	$CuO + H_2 \rightarrow Cu + H_2O$	Cu [+ 2 → 0]	H [0 → + 1]
8.	$2KMnO_4 + 3H_2SO_4 + 5H_2S \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5S$	Mn [+ 7 → + 2]	S [–2 → 0]
9.	$H_2O_2 + Ag_2O \rightarrow 2Ag + H_2O + O_2$ (Oxygen of H_2O_2)	Ag [+ 1 → 0]	O [–1 → 0]
10.	$H_2SO_4 + 2HI \rightarrow SO_2 + I_2 + 2H_2O$	S [+6 → +4]	I [–1 → 0]

9. REDOX REACTIONS

(a) The reactions in which oxidation and reduction both occur simultaneously are called redox reactions.

(b) Most of the chemical reactions are redox because if one element is there to lose electrons, other element has to be there to accept them.

(c) Any redox reaction may be divided in two parts:

(i) Oxidation half reaction

(ii) Reduction half reaction

Now, we will study some reaction.

NOTE : In reaction 2 oxygens of ozone have different OS.

Structure of ozone is

$O_3 \leftarrow O_1{=}O_2$

OS of O_1 = + 2

OS of O_2 = 0

Here O_1 is getting reduced in reaction 2

OS of O_3 = - 2

(d) Redox reactions may be intramolecular or disproportionation reactions. It depends upon whether the migration of electron takes place in the atoms of the same compound or different compounds .

(i) Intermolecular redox reaction

$$2H_2\overset{+6}{S}O_4(conc.) + Cu \rightarrow \overset{+2}{Cu}SO_4 + \overset{+4}{S}O_2 + 2H_2O$$

(ii) Intramolecular redox reaction

$$2K\overset{+5}{Cl}\overset{-2}{O_3} \rightarrow 2K\overset{-1}{Cl} + 3\overset{0}{O_2}$$

(iii) Disproportions Redox Reaction : In this type of redox reactions same element acts as both oxidsing & reducing agent.

$$\overset{0}{Cl_2} + H_2O \rightarrow H\overset{+1}{Cl}O + H\overset{-}{Cl}$$

10. BALANCING OF REDOX EQUATIONS BY ION ELECTRON METHOD

10.1 Acidic Medium

(a) consider the example,

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

(b) Write both the half reactions.

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

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

(c) Atoms other than H and O are balanced

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

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

(d) Balance O–atoms by the addition of H_2O to another side

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

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

(e) Balance H–atoms by the addition of H^+ ions to another side

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

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

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

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

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

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

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

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

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

10.2 Alkaline Medium

(a) Consider the reaction

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

(b) Separate the two half reactions.

$Cr(OH)_3 \rightarrow CrO_4^{2-}$ (Oxidation half reaction)

$IO_3^- \rightarrow I^-$ (Reduction half reaction)

(c) Balance O– atoms by adding H_2O.

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

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

(d) Balance H–atoms by adding H_2O to side having deficiency and OH^- to side having deficiency of H–atoms.

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

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

$IO_3^- + 6H_2O \rightarrow I^- + 3H_2O + 6OH^-$

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

(e) Balance the charges by electrons

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

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

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

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

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

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

11. EQUIVALENT WEIGHT

(a) Equivalent wt. of an oxidant (get reduced)

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

$$= \frac{\text{Mol. wt.}}{\text{Decrease in O.S.} \times \text{No. of atom undergoing reduction}}$$

Example :

In acidic medium

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

Here atoms undergoing reduction is Cr its O.S. is decreasing from 6 to 3

$$\text{Eq. wt. of } K_2Cr_2O_7 = \frac{\text{Mol. wt. of } K_2Cr_2O_7}{3 \times 2}$$

$$= \frac{\text{Mol. wt.}}{6}$$

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)

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

$$= \frac{\text{Mol. wt.}}{\text{increase in O.S.} \times \text{No. of atom undergoing oxidation}}$$

Example :

In acidic medium, $C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-$

Here, O.S. of carbon is changing from +1 to

+2 i.e. each carbon atom is losing one electron and there are 2 atoms of carbon so total electrons lost = 2 so, eq. wt = $\frac{\text{Mol.wt}}{2}$

(c) In different condition a compound may have different equivalent wts. Because, it depends upon the number of electrons gained or lost by that compound in that reaction.

Example :

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

So, Here 5 electrons are taken so eq. wt

$$= \frac{\text{Mol. wt. of } KMnO_4}{5} = \frac{158}{5} = 31.6$$

(ii) $MnO_4^- \rightarrow MnO_2$ (neutral medium)
(+7) (+4)

Here, only 3 electrons are gained

$$\text{so, eq. wt} = \frac{\text{Mol. wt. of } KMnO_4}{3}$$

$$= \frac{158}{3} = 52.7$$

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

Here, only one electron is gained

$$\text{so, eq. wt} = \frac{\text{Mol. wt. of } KMnO_4}{1} = 158$$

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 med. > Alkaline medium

while, $K_2Cr_2O_7$ acts as an oxidant only in acidic medium as follows

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

Here, 6 electrons are gained

so eq. wt

$$= \frac{\text{Mol. wt. of } K_2Cr_2O_7}{6}$$

$$= \frac{294.21}{6} = 49.03$$

(d) It is clear that $KMnO_4$ is better oxidant than $K_2Cr_2O_7$.

(e) Try to balance reaction (a) (b) (c) of reduction of $KMnO_4$ by ion electron method as you should get following –

(i) $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$
(acidic medium)

(ii) $MnO_4^- + e^- \rightarrow MnO_4^{2-}$
(alkaline medium)

12. EQUIVALENT WEIGHT IN DISPROPORTION REACTION

The equivalent weight of the substance undergoing disproportion can be determined by the following method.

Consider the substance 'X' is undergoing disproportionation reaction.

(i) Find out the equivalent weight of 'X' for oxidation reaction, say it is E_1.

(ii) Also find out the equivalent weight of 'X' for reduction reaction, say it is E_2.

(iii) The equivalent weight of 'X' = $E_1 + E_2$ for example, Cl_2 disproportionate in Cl^- & ClO_3^-

reduction

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

oxidation

The X factor for oxidation = 2
The X factor for reduction = 10

$$\text{The equivalent wt of } Cl_2 = \frac{71}{2} + \frac{71}{10}$$

$$= 35.5 + 7.1$$

$$= 42.6 \textbf{ Ans.2}$$

SOLVED PROBLEMS

Ex.1 Which of the following acts as both oxidant and reductant –

(A) HNO_3

(B) HNO_2

(C) Both HNO_3 & HNO_2

(D) Neither HNO_3 nor HNO_2 ***(Ans. B)***

Sol. O.N. of N in HNO_2 is + 3

Max. O.N. of N is + 5

Min. O.N. of N is – 3

Thus O.N. of N in HNO_2 can show an increase or decrease as the case may be. That is why HNO_2 acts as oxidant and reductant both.

O.N. of N in HNO_3 is + 5, Hence it can act only as an oxidant.

Ex.2 State which of the following reactions is neither oxidation nor reduction –

(A) $Na \rightarrow NaOH$

(B) $Cl_2 \rightarrow Cl^- + ClO^-_3$

(C) $P_2O_5 \rightarrow H_4P_2O_7$

(D) $Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$ ***(Ans. C)***

Sol. In the reaction $P_2O_5 \rightarrow H_4P_2O_7$

The O.N. of P in P_2O_5 is

$2x + 5(-2) = 0$ or $x = +5$

The O.N. of P in $H_4P_2O_7$ is

$4(+1) + 2(x) + 7(-2) = 0$

$2x = 10$ or $x = +5$

Since there is no change in O.N. of P, hence the above reaction is neither oxidation nor reduction.

Ex.3 In the reaction

$C_2O_4^{-2} + MnO^-_4 + H^+ \rightarrow Mn^{+2} + CO_2$ the reductants is –

(A) $C_2O_4^{-2}$ ***(B) H^+***

(C) MnO^-_4 ***(D) None of the above***

(Ans. A)

Sol. In the above reaction $C_2O_4^{-2}$ acts as a reductant because it is oxidised to CO_2 as :

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

$C_2O_4^{-2}$ reduces MnO_4^- to Mn^{+2} ion in solution.

Ex.4 Oxidation number of cobalt in $[Co(NH_3)_6]Cl_2Br$ is –

(A) + 6 ***(B) Zero*** ***(C) + 3*** ***(D) + 2***

(Ans. C)

Sol. Let the O.N.of Co be x

O.N. of NH_3 is zero

O.N. of Cl is –1

O.N. of Br is –1

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

$\therefore$ $x = +3$

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

Ex.5 The order of increasing O.N. of S in S_8, $S_2O_8^{-2}$, $S_2O_3^{-2}$, $S_4O_6^{-2}$ is given below –

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

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

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

(D) $S_8 < S_2O_3^{-2} < S_4O_6^{-2} < S_2O_8^{-2}$ ***(Ans. D)***

Sol. The O.Ns. of S are shown below along with the compounds

$S_8, S_2O_8^{-2}, S_2O_3^{-2}, \quad S_4O_6^{-2}$

$0 \quad +6 \quad +2 \quad +2.5$

Hence the order of increasing O.N. of S is

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

Ex.6 The composition of a sample of wustite is $Fe_{0.93}O_{1.00}$. What percentage of iron is present in the form of Fe (III)

(A) 13.05 ***(B) 14.05***

(C) 15.05 ***(D) 16.05***

(Ans. C)

Sol. O.N. of. Fe in wustite is $= \frac{200}{93} = 2.15$

It is an intermediate value in between Fe (II) & Fe (III)

Let % of Fe (III) be a, then

$2 \times (100 - a) + 3 \times a = 2.15 \times 100$

$a = 15.05$

$\therefore$ % of Fe (III) = 15.05%

Ex.7 The oxid.no. of Cl in $NOClO_4$ is –

(A) + 11 (B) + 9 (C) + 7 (D) + 5

(Ans. C)

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

For ClO_4^-, Let Ox. No.of Cl = a

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

$a = +7$

Hence, the oxidation no. of Cl in $NOClO_4$ is +7.

Ex.8 The two possible oxidation numbers of N atoms in NH_4NO_3 are respectively –

(A) +3, +5 (B) +3, –5

(C) –3, +5 (D) –3, –5

(Ans. C)

Sol. There are two N atoms in NH_4NO_3, but one N atom has negative oxidation number (attached to H) and the other has positive oxid.no. (attached to O). Therefore evaluation should be made separately as –

O.N. of N is NH_4^+ O.N. of N in NO_3^-

$a + 4 \times (+1) = +1$ and $a + 3(-2) = -1$

$\therefore a = -3$ $\therefore a = +5$

Here the two O.N. are –3 and +5 respectivley.

Ex.9 The oxidation number of S in $H_2S_2O_8$ is –

(A) +8 (B) –8 (C) +6 (D) +4

(Ans. C)

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

$$\begin{array}{ccccccccccccc} & & & O & & & & & O & & & & \\ & & & \uparrow & & & & & \uparrow & & & & \\ H & - & O & - & S & - & O & - & O & - & S & - & O & - & H \\ & & & \downarrow & & & & & \downarrow & & & & \\ & & & O & & & & & O & & & & \end{array}$$

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

$\therefore a = +6$

Thus the O.N. of S in $H_2S_2O_8$ is + 6

Ex.10 When $K_2Cr_2O_7$ is converted into K_2CrO_4 the change in oxidation number of Cr is –

(A) 0 (B) 3 (C) 4 (D) 6

(Ans. A)

Sol. When $Cr_2O_7^{-2}$ is converted into CrO_4^{-2} the change in oxidation number of Cr is zero

$$\underset{+6}{Cr_2O_7^{-2}} \rightarrow \underset{+6}{CrO_4^{-2}}$$

There is no change in oxidation state of Cr, hence it is neither oxidised nor reduced and remains in the same oxidation state.

Ex.11 The oxidation number of S in $(CH_3)_2\,SO$ is

(A) 1 (B) 2 (B) 0 (D) 3

(Ans. C)

Sol. Let the oxidation no. of S is 'a'

O.N. of CH_3 = +1

O.N. of O = –2

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

$a = 0$

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

Ex.12 What will be the oxidation number of I in the KI_3 –

(A) $-\frac{1}{3}$ (B) $-\frac{1}{4}$ (C) + 4 (D) + 3

(Ans. A)

Sol. In KI_3 $1 + 3 \times (a) = 0$

$a = -\frac{1}{3}$

or KI_3 is $KI + I_2$

$\therefore$ I has two oxidation no. –1 and 0 respectively. However factually speaking oxidation number of I in KI_3 is on average of two values – 1 and 0.

Average O.N. $= \dfrac{-1 + 2 \times (0)}{3} = -\dfrac{1}{3}.$

Ex.13 Oxidation number of Fe in $[Fe(CN)_6]^{-3}$, $[Fe(CN)_6]^{-4}$, $[Fe(SCN)]^{+2}$ and $[Fe(H_2O)_6]^{+3}$ respectively would be–

(A) +3, +2, +3 and +3

(B) +3, +3, +3 and +3

(C) +3, +2, +2 and +2

(D) +2, +2, +2 and +2 (Ans. A)

Sol. Oxidation number of Fe in–

First	Second	Third	Fourth
$x - 6 = -3$	$x - 6 = -4$	$x - 1 = +2$	$x + 6 \times 0 = +3$
$x = +3$	$x = +2$	$x = +3$	$x = +3$

Ex.14 Which of the following is not a redox reaction–

(A) $\frac{1}{2}H_2 + \frac{1}{2}I_2 \Leftrightarrow HI$

(B) $PCl_5 \Leftrightarrow PCl_3 + Cl_2$

(C) $2CuSO_4 + 4KI \Leftrightarrow Cu_2I_2 + 2K_2SO_4 + I_2$

(D) $CaOCl_2 \Leftrightarrow Ca^{+2} + OCl^{-} + Cl^{-}$ **(Ans. D)**

Sol. In all the above reaction except (D) there is change in oxidation states of reactant and product atoms, hence they are all redox reactions. In reaction (D) the oxidation states of the atoms of the reactants and products remain unchanged hence, it is not a redox reaction.

Ex.15 In the reaction $Al + Fe_3O_4 \rightarrow Al_2O_3 + Fe$ – what is the total no. of electrons transferred during the change –

(A) 16 (B) 24 (C) 8 (D) 12

(Ans. B)

Sol. $2Al^o \rightarrow Al_2^{+3} + 6e^{-}$ .... (A)

$8e + Fe_3^{+8/3} \rightarrow 3Fe^o$ .... (B)

Multiplying Eq. (A) by 4 and Eq. (B) by 3, then on addition

$8Al^o \rightarrow 4Al_2^{+3} + 24e$

$24e + 3Fe_3^{+8/3} \rightarrow 9Fe^o$

$8Al^o + 3Fe_3^{+8/3} \rightarrow 9Fe^o + 4Al_2^{+3}$

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or $8Al + 3Fe_3O_4 \rightarrow 4Al_2O_3 + 9Fe$

Therefore, it is clear that total no. of electrons transferred during change = 24

Ex.16 In the redox reaction –

$10FeC_2O_4 + x\ KMnO_4 + 24H_2SO_4 \rightarrow 5Fe_2(SO_4)_3 + 20CO_2 + y\ MnSO_4 + 3K_2SO_4 + 24H_2O$. The values of x and y are respectively –

(A) 6, 3 (B) 3, 6 (C) 3, 3 (D) 6, 6

(Ans. D)

Sol. The balanced redox reaction given above can be written as :

$10FeC_2O_4 + 6KMnO_4 + 24H_2SO_4 \rightarrow 5Fe_2(SO_4)_3 + 20CO_2 + 6\ MnSO_4 + 3\ K_2SO_4 + 24H_2O$

so the value of x = 6 and y = 6

Ex.17 A solution containing 2.68×10^{-3} mol of A^{+n} ions requires 1.61×10^{-3} mole of MnO^{-}_4 for the oxidation of A^{+n} to AO^{-}_3 in acidic medium. What is the value of n –

(A) 1 (B) 2 (C) 3 (D) 4

(Ans. B)

Sol. The reaction are

$MnO^{-}_4 + 8H^+ + 5e^- \rightarrow Mn^{+2} + 4H_2O$

$A^{+n} + 3H_2O \rightarrow AO_3^- + 6H^+ + (5-n)\ e^-$

Amount of electrons involved in the given amount of $MnO_4^- = 5 \times 1.61 \times 10^{-3}$ mol.

Equating these two we get

$5 \times 1.61 \times 10^{-3} = (5-n)\ 2.68 \times 10^{-3}$

$\therefore$ n = 2 (approx.)

Ex.18 Which of the following is correctly balanced half reaction –

(A) $AsO_3^{-3} + H_2O \rightarrow AsO_4^{-3} + 2H^+ - 2e^-$

(B) $H_2O_2 + 2e \rightarrow O_2 + 2H^+$

(C) $Cr_2O_7^{-2} + 14H^+ \rightarrow 2Cr^{+3} + 7H_2O - 6e^-$

(D) $IO^{-}_3 + 6H^+ \rightarrow I_2 + 3H_2O + 5e^-$

(Ans. C)

Sol. The correctly balanced half reaction is –

$Cr_2O_7^{-2} + 14H^+ \rightarrow 2Cr^{+3} + 7H_2O - 6e^-$ It is a reduction half reaction in balancing the equation by ion–electron method.