Oxidation & Reduction

Introduction :-

The concept of oxidation & reduction is very important in our day to day life.

e.g. 1) Rusting of iron
2) Generation of electricity
3) Extraction & purification of metal
4) Digestion of food in our body.

* Classical concept :-

Oxid^{n} :- According classical (earlier) concept oxidation is defined as the addition of oxygen (electronegative elements) or removel of hydrogen.

e.g.
i) $2Mg + O_2 \longrightarrow 2MgO$
ii) $C + O_2 \longrightarrow CO_2$
} Addition of O_2

iii) $H_2S + Cl_2 \longrightarrow 2HCl + S$
iv) $MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$
} Removel of H_2

Oxidising agent :- A substance which can bring about the oxidation called oxidising agent or oxidant.

e.g. In above example 1 & 2 O_2 is an oxidising agent
iii, Cl_2 & MnO_2 act as oxidising agent in reac^{n} ③ & ④ respectively because they remove hydrogen & bring about oxidation.

to be included

Reduction :-

According to classical concept, reduction is defined as the addition of hydrogen or removel of oxygen.

e.g. i) $Cl_2 + H_2 \longrightarrow 2HCl$
ii) $H_2S + Cl_2 \longrightarrow 2HCl + S$
} Addⁿ of Hydrogen

iii) $ZnO + C \longrightarrow Zn + CO$
iv) $Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$
} Removel of oxygen.

Reducing agent :-

A substance which Provides hydrogen or removes oxygen is called as reducing agent.

or

The substance which can bring about reduction called reducing agent or reductant.

eg. In above ex. H_2, H_2S, C & CO are reducing agent because they bring about ~~reduction~~ reaction.

* Electronic concept :-

oxidation & reduction reaction are defined in terms of electron transfer betⁿ the reactants, known as electronic concept of oxidation & reduction.

1) oxidation :- (De-electronation)

According to electronic concept, oxidation is a Process which involves loss of electrons by an atom or group of atoms.

As a result of loss of $\bar{e}$s, there is increase in the positive charge or decrease in negative charge of the atom or ion undergoing oxidation.

e.g. i) Atom $Na \longrightarrow Na^+ + \bar{e}$
$Mg \longrightarrow Mg^{+2} + 2\bar{e}$
} loss of $\bar{e}$ results in increase in

ii) cation

$Sn^{+2} \longrightarrow Sn^{+4} + 2\bar{e}$

$Fe^{+2} \longrightarrow Fe^{+3} + 1\bar{e}$

} loss of $\bar{e}$ increase +ve charge

iii) Anion

$2Cl^{-} \longrightarrow Cl_2 + 2\bar{e}$

$MnO_4^{--} \longrightarrow MnO_4^{-} + \bar{e}$

} loss of $\bar{e}$ results decrease in -ve charge.

2) Reduction :- (Electronation)

According to electronic concept, reduction is a Proce which involves gain of $\bar{e}$ by an atom or group of atoms Due to gain of $\bar{e}$ there is increase of negative charge of an atom or ion undergoing reduction.

e.g. i) $Fe^{+++} + 1\bar{e} \longrightarrow Fe^{++}$

ii) $Sn^{4+} + 2\bar{e} \longrightarrow Sn^{2+}$

} Gain of $\bar{e}$ results in decrease of +ve charge

iii) $MnO_4^{-} + 1\bar{e} \longrightarrow MnO_4^{--}$

iv) $[Fe(CN)_6]^{3-} \xrightarrow{1\bar{e}} [Fe(CN)_6]^{4-}$

} Gain of $\bar{e}$ resulting in increase of -ve charge.

oxidising agent / Reducing agent :-

According to electronic concept, the substance which accept $\bar{e}$ known as oxidising agent. & which gives $\bar{e}$s are known as reducing agent.

e.g. i) $Zn + Cu^{++} \longrightarrow Zn^{++} + Cu$

(R.A.) (O.A.)

ii) $Na + Cl \longrightarrow Na^{+} + Cl^{-}$

(R.A.) (O.A.)

Oxidation state or oxidation number :-

Oxidation number is defined as the charge which an atom appears to have when all other atoms are removed from it as ions.

The sign of charge or numerical value on the element known as oxidat^{n} state or oxid^{n} number.

Rules to assign the oxidation number :-

1) The oxidation number of an element in the free or elementary state is always zero.

e.g. He, H_2, O_2, Fe, Br_2, P_4, Cl_2, S_8 etc have zero oxid^{n} state

2) The oxidation number of an element in a single (mono atomic) ion is the same as the charge on the ion.

e.g. $K^{+1} = +1$; $Al^{+3} = +3$; $SO_4^{2-} = -2$

~~Ca^{+2}~~ $= +2$; $Cl^{-} = -1$; $PO_4^{3-} = -3$

3) In binary compounds of metals & non-metals the oxidation number of metal is always +ve, while that of the non-metal is -ve.

e.g. $NaCl \Longrightarrow Na = +1$, $Cl = -1$.

4) In compounds formed by the combination of non-metallic atoms, the atom with higher electronegativity is given negative oxidation number.

e.g. $HCl \Longrightarrow Cl = -1$, $H = +1$

$NaF \Longrightarrow Na = +1$, $F = -1$

5) The oxidation number of hydrogen is +1, except in hydrides of active metal

e.g. LiH, NaH, KH, MgH_2, CaH_2 where hydrogen has

The oxidation number of oxygen is -2 except in peroxides in which it is -1. & in the compound OF_2 is +2.

e.g. i) CuO $\quad Cu = +2$, $O = -2$.

ii) H_2O_2 $\quad H = +1$, $O = -1$

iii) BaO_2 $\quad Ba = +2$, $O = -1$

7) For neutral molecule the sum of the oxidation numbers of all the atoms is equal to zero.

e.g. In NH_3 the sum of oxid^n numbers of nitrogen & hydrogen atom is equal to zero.

8) For a complex ion, the sum of the oxidation numbers of all the atoms is equal to charge on the ion.

e.g. $SO_4^{2-} = S + (4 \times -2) = -2$

$S - 8 = -2$

$\therefore \underline{S = +6}$

Q. Calculate the oxid^n number of an underline element

1) $H_2\underline{S}$

$\Rightarrow +1 \times 2 + x = 0$

$+2 + x = 0$

$\therefore \underline{x = -2}$

O.N. of S in H_2S is -2.

2) $H_2\underline{S}O_3$

$\Rightarrow +1 \times 2 + x + (-2 \times 3) = 0$

$+2 + x - 6 = 0$

$\underline{x = +4}$

3) $\underline{S_2}O_7^{2-}$

$\Rightarrow 2 \times x + (-2 \times 7) = -2$

$2x - 14 = -2$

$2x = +12$

$\therefore \underline{x = +6}$

4) $Na_2\underline{S_2}O_3$

$\Rightarrow +1 \times 2 + 2x - 6 = 0$

$2x - 4 = 0$

5) $\underline{Cl}O_3^-$

$x - 6 = -1$

$\underline{x = +5}$

6) $\underline{Br}F_3$

$x + (-1 \times 3) = 0$

$\underline{x = +3}$

7) CH_4

$x + 4 = 0$

$x = -4$

8) $C_6H_{12}O_6$

$6x + 12 - 12 = 0$

$x = 0$

9) $Na_2B_4O_7$

$+2 + 4x - 14 = 0$

$4x = 12$

$x = +3$

10) CO_2

$x - 4 = 0$

$x = +4$

11) SiO_2

$x - 4 = 0$

$x = +4$

12) $PbSO_4$

$x - 2 = 0$

$x = +2$

13) ClO_4^-

$x - 8 = -1$

$x = +7$

14) PO_4^{3-}

$x - 8 = -3$

$x = +5$

15) CCl_4

$x - 4 = 0$

$x = +4$

16) HNO_3

$+1 + x - 6 = 0$

$x = +5$

17) HNO_2

$+1 + x - 4 = 0$

$x = +3$

18) $NO = +2$

19) $N_2O = +1$

20) $N_2 = 0$

21) $K_2Cr_2O_7$

$+2 + 2x - 14 = 0$

$2x = +12$

$x = +6$

22) H_3PO_4

$+3 + x - 8 = 0$

$x = +5$

23) $K_2S_2O_8$

$+2 + 2x - 16 = 0$

$2x = +14$

$x = +7$

24) SiO_4^-

$x - 8 = -1$

$x = +7$

25) $Na_2S_4O_6$

$+2 + 4x - 12 = 0$

$4x = 10$

$x = +2.5$

26) Fe_3O_4

$3x - 8 = 0$

$x = +8/3$

27) $C_2O_4^{-2} = +3$

28) $NH_4^+ = -3$

29) $N_3H = -1/3$

30) $S_2Cl_2 = +1$

Oxidation :-

According to oxidⁿ number concept, to increase the O.N. of an element is known as oxidation.

e.g.

$$\overset{+2}{ZnCl_2} + Cl_2 \longrightarrow \overset{+4}{ZnCl_4}$$

$$\overset{+2}{SnCl_2} + Cl_2 \longrightarrow \overset{+4}{SnCl_4}$$

2) Reduction :-

According to oxidation number concept, to decrease the oxidation number of an element is known as reduction

e.g. $2\,\overset{+3}{FeCl_3} + H_2 \longrightarrow 2\,\overset{+2}{FeCl_2} + HCl$

oxidising agent (oxidant) / Reducing agent (Reductant)

According to oxidⁿ number concept, oxidising agent is a substance, whose O.N. decreases & Reducing agent is a substance whose O.N. increases.

e.g. 1) $Fe^{+2} + Ce^{4+} \longrightarrow Fe^{3+} + Ce^{3+}$

R.A. O.A.

2) $Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$

R.A. O.A.

3) $2Na + Cl_2 \longrightarrow 2Na^{+} + 2Cl^{-}$

R.A. O.A.

4) $2Ag + Zn^{2+} \longrightarrow 2Ag^{+} + Zn$

R.A O.A.

5) $2Na_2S_2O_3 + I_2 \longrightarrow 2NaI + Na_2S_4O_6$

Sod. tetrathionate

R.A. O.A.

Balancing of oxidation-Reduction reaction :-

There are two important methods for the balancing redox reaction

1) oxidation number method
2) Ion electron method.

1) oxidation number method :-

This method was developed by Jonson in 1880 for balancing the redox reacⁿ. This method is based on the fact that the increasing & decreasing the o.N. of one or more elements.

In this method increased o.N. should be balanced by decreased o.N. There are several rules to balance the redox reacⁿ by o.N. method & these are as follows

1) Write complete redox reaction.
2) Write o.N. of each element in compound.
3) Find out the element whose o.N. is change, in which one element show increase in o.N. & other element show decrease in o.N.
4) Balance both these elements separately by adding $\bar{e}$ to the deficient side.
5) multiply both eqⁿ by a suitable number for balancing equation
6) Add both these eqⁿ & cancell the common term from both side.
7) Balance the remaining atom by adding oxygen and hydrogen atom.

Consider the following reac^{n} in acidic soln as

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

Soln ⟹ Step-I Write down the oxid^{n} number of various atom.

$$\underset{+6}{Cr_2}\ \underset{-2}{O_7^{2-}} + \underset{+2}{Fe^{2+}} + \underset{+1}{H^+} \longrightarrow \underset{+3}{Cr^{3+}} + \underset{+3}{Fe^{3+}} + H_2O$$

Step-II Write seperate eq^{n} for oxid^{n} & red^{n}

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

$$Cr_2O_7^{2-} \longrightarrow Cr^{3+} \quad \text{(Reduction)}$$

Step-III Balance each half reac^{n} separately

$$Fe^{2+} \longrightarrow Fe^{3+}$$

$$Fe^{2+} \longrightarrow Fe^{3+} + \bar{e} \quad \text{—①}$$

Now, multiply eq^{n} ① by 6 so that $\bar{e}$ are balanced

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

$$Cr_2O_7^{2-} + 6\bar{e} \longrightarrow 2Cr^{3+}$$

∵ Reac^{n} is in acidic medium add $14H^+$ on the left side

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

Balance H-atom, add H_2O

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

$$6Fe^{2+} \longrightarrow 6Fe^{3+} + 6\bar{e}$$

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

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

∴ The balanced eq^{n} is

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

2) $P + HNO_3 \longrightarrow HPO_3 + NO + H_2O$

Soln

$$\overset{0}{P} + \overset{+1\ +5\ -6}{HNO_3} \longrightarrow \overset{+1+5-6}{HPO_3} + \overset{+2\ -2}{NO} + H_2O$$

Step-II

$P^0 \longrightarrow P^{+5}$ | $N^{+5} \longrightarrow N^{+2}$

$P^0 \longrightarrow P + 5\bar{e}$ —① | $N^{+5} + 3\bar{e} \longrightarrow N^{+2}$ —②

multiply eqn ① by 3 & eqn ② by 5 & add

$3P^0 \longrightarrow 3P^{+5} + 15\bar{e}$ —

$5N^{+5} + 15\bar{e} \longrightarrow 5N^{+2}$

$3P^0 + 5N^{+5} \longrightarrow 3P^{+5} + 5N^{+2}$ —③

Substitute the coefficient from 3 in the skeleton eqn

$3P + 5HNO_3 \longrightarrow 3HPO_3 + 5NO + H_2O$

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e.g. 3) $P + HNO_3 \longrightarrow H_3PO_4 + NO_2 + H_2O$

Ans: $P + 5HNO_3 \longrightarrow H_3PO_4 + H_2O + 5NO_2$.

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4) $Cr_2O_7^{2-} + H_2SO_3 \longrightarrow Cr^{3+} + HSO_4^-$ (in acidic medium)

Ans:- $Cr_2O_7^{2-} + 3H_2SO_3 + 5H^+ \longrightarrow 2Cr^{3+} + 3HSO_4^- + 4H_2O$

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5) $CuO + NH_3 \longrightarrow Cu + N_2 + H_2O$

Ans: $2NH_3 + 3CuO \longrightarrow 3Cu + N_2 + 3H_2O$

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6) $HNO_3 + H_2S \longrightarrow NO + S + H_2O$

Ans $2HNO_3 + 3H_2S \longrightarrow 2NO + 3S + 4H_2O$

Ion - Electron method :- (Half reac^{n} method)

This method was developed by Jette & Lamer in 1927 for balancing the redox reaction. The rules are as follows

1) Write complete reaction using ionic form of reactant & Product.

2) Split the complete reaction into two half reac^{n} on the basis of pairing of ion or molecule appears in reactant or Product. In which one half reac^{n} is of oxidation & another half reac^{n} is of reduction.

3) Balance each half reac^{n} seperately.

4) Balance the oxygen atom by adding water molecule to deficient side.

5) Balance the hydrogen atom by adding H^{+} to the deficient side.

6) Balance the charges by adding $\bar{e}$s to the deficient side.

7) multiply both these reac^{n} by suitable number to balance the reac^{n}.

8) Add both these reac^{n} & cancell the common term from both side.

e.g. ① $Cu + HNO_3 \longrightarrow Cu^{2+} + NO$

$3Cu + 2HNO_3 + 6H^+ \rightleftharpoons 3Cu^{2+} + 2NO + 4H_2O$

② $Cr_2O_7^{2-} + (COOH)_2 \longrightarrow Cr^{3+} + CO_2$.

$Cr_2O_7^{2-} + 3(COOH)_2 + 8H^+ \rightleftharpoons 2Cr^{3+} + 6CO_2 + 7H_2O$

③ $Mn^{2+} + S_2O_8^{2-} + H_2O \longrightarrow MnO_4^- + HSO_4^-$

$2Mn^{2+} + 5S_2O_8^{2-} + 8H_2O \rightleftharpoons 2MnO_4^- + 6H^+ + 10HSO_4^-$

4) $Cr_2O_7^{2-} + SO_3^{2-} \longrightarrow Cu^{3+} + SO_4^{--}$

Ans:- $Cr_2O_7^{2-} + 3SO_3^{--} + 8H^+ \longrightarrow 2Cr^{3+} + 3SO_4^{--} + 4H_2O$

O by H_2O

H by H^+

Charge by e^-

Add & cancell e^-

change $H^+ \longrightarrow H_2O$

by adding $\bar{O}H$

to both side

5) $Zn^{2+} + Al \longrightarrow Zn + Al^{3+}$

$2Al + 3Zn^{2+} \longrightarrow 2Al^{3+} + 3Zn$

6) $Cr + IO_3^- \longrightarrow Cr^{3+} + I^-$

$2Cr + IO_3^- + 6H^+ \longrightarrow 2Cr^{3+} + I^- + 3H_2O$

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