Redox Reactions

Transformation of matter from one kind into another occurs through the various types of reactions. One important category of such reactions is **Redox Reactions**.

OXIDATION :

Oxidation may be defined as any of the following processes

(a) Addition of oxygen.

$2\ Mg + O_2 \rightarrow 2MgO$

(b) Removal of hydrogen

$3O_2 + 4NH_3 \rightarrow 2N_2 + 6H_2O$

(c) Addition of electronegative element

$Cu + Cl_2 \rightarrow CuCl_2$

(d) Removal or decrease in the electropositive element

$H_2S + Cl_2 \rightarrow 2\ HCl + S$

(e) De - electronation

$M \rightarrow M^{n+} + ne-$

REDUCTION :

Reduction may be defined as any of the following processes

(a) Addition of hydrogen

$N_2 + 3H_2 \rightarrow 2NH_3$

(b) Addition of electropositive element

$CuCl_2 + Cu \rightarrow Cu_2Cl_2$

(c) Removal of oxygen

$CuO + H_2 \rightarrow Cu + H2O$

(d) Removal or decrease in the electronegative element

$2HgCl_2 + SnCl_2 \rightarrow Hg_2Cl_2 + SnCl_4$

(e) Electronation

$M^{n+}\ ne^- \rightarrow M$

OXIDANT OR OXIDISING AGENT :

As stated above the oxidising agent may be defined as a substance supplying oxygen or electronegative element, removing hydrogen or electropositive element and can accept electrons. They show decrease in oxidation number.

Examples: $KMnO_4$, H_2O_2, Cl_2

REDUCTANT OR REDUCING AGENT :

A substance supplying hydrogen or electropositive element, removing oxygen or electro negative element and can donateelectrons. They show increase in oxidation number.

Examples: H_2, H_2S, Mg

REDOX REACTIONS :

Reactions comprising of simultaneous oxidation and reduction and called oxidation - reduction or redox reactions.

$SnCl_2 + 2HgCl_2 \rightarrow SnCl_4 + Hg_2Cl_2$

TYPES OF REDOX REACTIONS :

(*i) Intermolecular redox reactions* - In this case one substance is oxidised and another is reduced.
$4\ HCl + MnO_2 \rightarrow MnCl_2 + Cl_2 + 2H_2O$,Here HCl is oxidised and MnO_2 is reduced.

(*ii) Disproportionation* - In this case the same substance is oxidised and reduced eg. $4KClO_3 \rightarrow 3KClO_4 + KCl$

(*iii) Intramolecular redox reactions* - In this case one element of the compound is reduced while another element of the same compound is oxidised
$(NH_4)_2Cr_2O_7 \rightarrow N_2 + Cr_2O_3 + 4H_2O$, Cr is reduced and N is oxidised

OXIDATION NUMBER :
It is the number of electrons lost or gained by an element during its change from free state to a particular compound.
Or
Oxidation numb er denotes the oxidation state of an element in a compound ascertained according to a set of rules formulated on the basis that. electron pair in a covalent bond belongs entirely to more electronegative element.

RULES FOR DETERMINING OXIDATION NUMBER:

1. In elements, in the free or the uncombined state, each atom bears an oxidation number of zero. Evidently each atom in H_2, O_2, O_3, P_4, S_8, Na has the oxidation number zero.

2. For ions composed of only one atom, the oxidation number is equal to the charge on the ion. Thus Na^+ ion has an oxidation number of +1, Mg^{2+} ion of +2 and so on.

3. Oxidation number of oxygen is –2 except in OF_2 where it is + 2 and in peroxides where it is – 1.

4. The oxidation number of hydrogen is +1,except when it is bonded to metals in binary compounds. For example, in LiH, NaH, and CaH_2, its oxidation number is –1.

5. In all its compounds, fluorine has an oxidation number of –1. Other halogens (Cl, Br, and I) also have an oxidation number of –1, when they occur as halide ions in their compounds. Chlorine, bromine and iodine when combined with oxygen, for example in oxoacids and oxoanions, have positive oxidation numbers.

6. The algebraic sum of the oxidation number of all the atoms in a compound must be zero. In polyatomic ion, the algebraic sum of all the oxidation numbers of atoms of the ion must equal the charge on the ion.Thus, the sum of oxidation number of three oxygen atoms and one carbon atom in the carbonate ion, CO_3^{2-} must equal –2.

STOCK NOTATION :

Representation of oxidation state of element by Roman numerals within parenthesis is known as stock notation eg $FeCl_3$ is written as Iron(III) chloride and $FeSO_4$ as Iron(II) sulphate.

CALCULATION/ DETERMINATION OF OXIDATION NUMBER OF UNDERLINED ELEMENT IN SOME COMPOUNDS:

(a) $K_2\underline{Cr}_2O_7$ -

Let the O.N. of Cr be x then

$2\times(+1)+2\times(x)+7\times(-2)=0$

$2+2x-14=0 \quad \therefore x=+6$

(b) $K\underline{Mn}O_4$ -

Let the O.N. of Mn be x then

$1\times(+1)+1\times(x)+4\times(-2)=0$

$1+1x-8=0 \quad \therefore x=+7$

(c) $H_2\underline{S}O_4$ -

Let the O.N. of S be x then

$2\times(+1)+1\times(x)+4\times(-2)=0$

$2+x-8=0 \quad \therefore x=+6$

(d) $\underline{N}H_4\underline{N}O_3$ - Split into two ions NH_4^+ and NO_3^-

Let O.N. of N be x in NH_4^+ ion then

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

$x+4=+1 \quad \therefore x=-3$

Let the O.N. of N be x in NO_3^- ion then

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

$x-6=-1 \quad \therefore x=+5$

(e) $\underline{P}O_4^{3-}$ -

Let the O. N. of P be x then

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

$x-8=-3 \quad \therefore x=+5$

(e) $\underline{P}O_4^{3-}$ -

Let the O. N. of P be x then

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

$x-8=-3 \quad \therefore x=+5$

(f) $H\underline{N}O_3$ -

Let the O.N. of N be x then

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

$1+x-6=0 \quad \therefore x=5$

(g) $K\underline{I}_3$ -

Let the O.N. of I be x then

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

$\therefore 1+3x=0 \quad \therefore x=-1/3$

(h) $Na\underline{O}_2$ - It is super oxide.

Let O.N. of O be x then

$1\times(+1)+2\times(x)=0 \therefore 1+2x=0 \quad \therefore x=-1/2$

(i) $\underline{Fe}_3O_4$ - It is mixed oxide $FeO.Fe_2O_3$ and Fe has O.N and +3 respectively.

(j) $\underline{Fe}_{0.96}O$

Let O.N. of Fe be x then $0.96x+(-2)=0$

$\therefore 0.96x-2=0$

$\therefore x=\dfrac{+2}{0.96}$

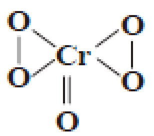
(i)

$\underline{Cr}O_5$ - Let the O.N. of Cr be x then

$1\times(x)+5\times(-2)=0$

$x-10=0 \quad \therefore x=10$ **(wrong)**

Apply chemical bond method



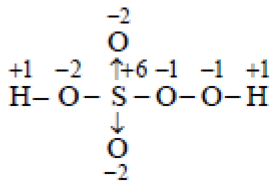
$x \quad + \quad 1\times(-2) \quad + \quad 4\times(-1) \quad =0$

(for Cr) (one=O) (four O – O)

$\therefore x=+6$

(j)

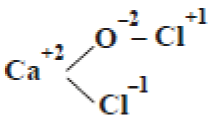
$H_2\underline{S}O_5$ (Caro acid) - Write structure and apply chemical bond method



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

for H for S for O for O – O $\therefore x = +6$

(k)

$CaO\underline{Cl}_2$ - Its structure is 

$\therefore$ O.N. of Cl is –1 and +1.

OXIDATION NUMBER CONCEPT OF OXIDANT (OXIDISING AGENT) AND REDUCTANT (REDUCING AGENT) :

(i) Oxidising agent : A substance can act as oxidising agent if the oxidation number of one of its element is maximum eg HNO_3 (O.N. of N = 5 which is maximum value) The more the electronegativity of element and the more is O.N., the more is the oxidising power eg $KClO_4$

(ii) Reducing agent : A substance can act as reducing agent if the oxidation number of one of its element is **minimum** eg $SnCl_2$ (O.N. of Sn = 2 which is minimum value

(iii) Reducing as well as oxidising agent : A substance that can act as both, reducing as well as oxidising agent if O.N. of one of its element is in between the maximum and the minimum value
eg HNO_2 (O.N. of N = +3 which is intermediate of +5 and 0)

OXIDATION NUMBER AND ACID STRENGTH :
The greater the O.N. of the element in oxyacids, the greater is the acid strength.
$HClO_4 > HClO_3 > HClO_2 > HClO$.

EQUIVALENT WEIGHT OF AN OXIDISING AGENT

It can be obtained by dividing the molecular weight by the number of electrons gained represented in a chemical balanced equation.

eg. $$2K\overset{+7}{Mn}O_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2\overset{+2}{Mn}SO_4 + 3H_2O + 5O$$

Equivalent wt. of $KMnO_4$ in acid medium

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

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

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

EQUIVALENT WEIGHT OF REDUCING AGENT :

It can be obtained by dividing the molecular weight by the number of electrons lost as represented by a chemical balanced equation.

$$\overset{+2}{H_2}\overset{+6}{C_2}\overset{-8}{O_4} + O \longrightarrow 2\overset{+4}{C}\overset{-4}{O_2} + H_2O$$

The change in O.N. of two atoms of carbon is +2. Hence

$$\text{Equivalent weight of oxalic acid} = \frac{\text{Mol.wt of Oxalic acid}}{2}$$

BALANCING OF CHEMICAL EQUATIONS :

(a) Oxidation Number Method:

Step 1: Write the correct formula for each reactant and product.

Step 2: Identify atoms which undergo change in oxidation number in the reaction by assigning the oxidation number to all elements in the reaction.

Step 3: Calculate the increase or decrease in the oxidation number per atom and for the entire molecule/ion in which it occurs. If these are not equal then multiply by suitable number so that these become equal.

Step 4: Ascertain the involvement of ions if the reaction is taking place in water, add H^+ or OH^- ions to the expression on the appropriate side so that the total ionic charges of reactants and products are equal. If the reaction is carried out in acidic solution, use H^+ ions in the equation; if in basic solution, use OH^- ions.

Step 5 : Make the numbers of hydrogen atoms in the expression on the two sides equal by adding water (H_2O) molecules to the reactants or products. Now, also check the number of oxygen atoms. If there are the same number of oxygen atoms in the reactants and products, the equation then represents the balanced redox reaction.

Example 1 :

Balance the equation involving oxidation of ammonia by copper oxide to give Cu, N_2 and H_2O

Solution - $$\underset{\underset{3\times 2 = 6\bar{e}}{\uparrow}}{\overset{+2}{Cu}O} + 2\underset{\underset{6\bar{e}}{\downarrow}}{\overset{-3}{N}H_3} \rightarrow Cu^0 + N_2^0 + H_2O$$

$$\therefore 3CuO + 2NH_3 \rightarrow 3Cu + N_2 + H_2O$$

Balance O by adding H_2O to RHS

$$3\,CuO + 2NH_3 \rightarrow 3Cu + N_2 + 3H_2O$$

Example 2 :

The reduction of permanganate ion by ferrous ion in presence of a dilute acid

$$MnO_4^- + Fe^{2+} + H^+ \rightarrow Mn^{2+} + Fe^{3+} + H_2O$$

Solution =

$$\overset{+7}{Mn}O_4^- + Fe^{2+} + H^+ \rightarrow Mn^{2+} + Fe^{3+} + H_2O$$

$\uparrow 5\bar{e}$ $\quad \downarrow 5\times1\bar{e}$

$$MnO_4^- + 5Fe^{2+} + H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + H_2O$$

Balance O and H by adding H_2O and H^+; $3H_2O$ on RHS and $7H^+$ on LHS

$$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

Example 3 :

The reduction of dichromate ion by an iodide in presence of a dilute acid

$$Cr_2O_7^{2-} + \bar{I} + H^+ \rightarrow Cr^{3+} + I_2 + H_2O$$

Solution - Balancing atoms

$$\overset{+12}{Cr_2}O_7^{2-} + 2\bar{I} + H^+ \rightarrow 2Cr^{3+} + I_2 + H_2O$$

$\uparrow 6\bar{e}$ $\quad \downarrow 3\times2\bar{e}$

$$\therefore Cr_2O_7^{2-} + 6I^- + H^+ \rightarrow 2Cr^{3+} + 3I_2 + H_2O$$

Balance O by adding $6H_2O$ on RHS and balance H^+ by adding $13H^+$ on LHS

$$\therefore Cr_2O_7^{2-} + 6I^- + 14H^+ \rightarrow 2Cr^{3+} + 3I_2 + 7H_2O$$

(b) Half Reaction Method: In this method,the two half equations are balanced separately and then added together to give balanced equation.

The rules are as follows:

(a) Split up the reaction into two half reactions showing oxidation and reduction separately.

(b) Balance number of atoms undergoing the change of oxidation state.

(c) Balance O on both sides by adding H2O.

(d) Balance H atoms by adding H+ ions.

(e) Balance charge by adding required number of electrons

(f) Make the number of electrons equal in two half reactions by multiplying with suitable coefficient.

(g) Add the two half reactions

Example 1 :

Oxidation of ferrous salt by potassium dichromate in acid solution.

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

Solution - (i) Reduction|half reactions

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

Equalize Cr atoms

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

Balance O and H atoms on both sides by adding H_2O and H^+ ions.

$$\underset{}{Cr_2O_7^{2-}} + \underset{+13H^+}{H^+} \rightarrow 2Cr^{3+} + \underset{+6H_2O}{H_2O}$$

Balance charge on both sides by adding electrons

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

(ii) Oxidation half-reaction

$Fe^{2+} - e^- \rightarrow Fe^{3+}$

Balance electrons of two half reactions

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

Adding two half reaction (electrons are cancelled)

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

Example 2 :

Balance the equation

$H_2C_2O_4 + H_2O_2 \rightarrow CO_2 + H_2O$

Solution (i) Oxidation half - reaction

$H_2C_2O_4 \rightarrow CO_2$

Balance C, O, H atoms and charge

$H_2C_2O_4 \rightarrow 2CO_2 + 2H^+ + 2e^-$ .... (i)

(ii) Reduction half reactions

$H_2O_2 \rightarrow H_2O$

Balance O, H atoms and charge

$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ .... (ii)

Add two balanced half reactions (i) and (ii)

$H_2C_2O_4 + H_2O_2 \rightarrow 2CO_2 + 2H_2O$