REDOX REACTIONS
OXIDATION NUMBER

❖ 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, another 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, intermolecular 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

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

(ii) Intramolecular redox reaction

$$2K\overset{+5}{Cl}\overset{-2}{O}_3 \rightarrow 2KCl + 3O_2$$

+5 −2 −10

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

$$\overset{0}{Cl_2} + H_2O \rightarrow \overset{+1}{HClO} + \overset{-1}{HCl}$$

S.No.	Reaction	Oxidant (Getting Reduced)	Reductant (Getting Oxidised)
1.	$C + O_2 \rightarrow CO_2$	O $[0 \rightarrow -2]$	C $[0 \rightarrow +4]$
2.	$PbS + 4O_3 \rightarrow PbSO_4 + 4O_2$	O $[+2 \rightarrow 0]$	S $[-2 \rightarrow +6]$
3.	$PbS + 4H_2O_2 \rightarrow PbSO_4 + 4H_2O$	O $[-1 \rightarrow -2]$	S $[-2 \rightarrow +6]$
4.	$Sn + 2F_2 \rightarrow SnF_4$	F $[0 \rightarrow -1]$	Sn $[0 \rightarrow +4]$
5.	$SO_2 + 2H_2O + Cl_2 \rightarrow 2HCl + H_2SO_4$	Cl $[0 \rightarrow -1]$	S $[+4 \rightarrow +6]$
6.	$I_2 + 10HNO_3 \rightarrow 2HIO_3 + 10NO_2 + 4H_2O$	N $[+5 \rightarrow +4]$	I $[0 \rightarrow +5]$
7.	$CuO + H_2 \rightarrow Cu + H_2O$	Cu $[+2 \rightarrow 0]$	H $[0 \rightarrow +1]$
8.	$2KMnO_4 + 3H_2SO_4 + 5H_2S \rightarrow SO_4 + 2MnSO_4 + 8H_2O + 5S$	Mn $[+7 \rightarrow +2]$	S $[-2 \rightarrow 0]$
9.	$H_2O_2 + Ag_2O \rightarrow 2Ag + H_2O + O_2$ (Oxygen of H_2O_2)	Ag $[+1 \rightarrow 0]$	O $[-1 \rightarrow 0]$
10	$H_2SO_4 + 2HI \rightarrow SO_2 + I_2 + 2H_2O$	S $[+6 \rightarrow +4]$	I $[-1 \rightarrow 0]$

Types of Redox Reactions

(a) Intermolecular redox reaction: When oxidation and reduction takes place separate in different compounds, then the reaction is called intermolecular redox reaction

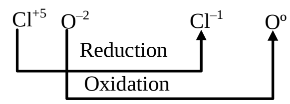
$$SnCl_2 + 2FeCl_3 \rightarrow SnCl_4 + 2FeCl_2$$

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

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

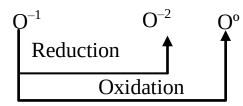
(b) Intramolecular redox reaction: During the chemical reaction if oxidation and reduction takes place in single compound then the reaction is called intramolecular redox reaction

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



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

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



- **Balance 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 increases in oxidation number must be equal to total decreases in oxidation number. This equivalence provides the basic for balancing redox reactions.

(i) Select the atom in oxidizing 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 electrons.

(iii) Now cross multiply i.e., multiply oxidizing agent by the number of loss of electrons and reducing agent 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, and 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.

Example: Balance the following reaction by oxidation number method -

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

Solution: Writer the oxidation number of all the atoms

$$\overset{0}{Cu} + \overset{+1}{H}\overset{+5}{N}\overset{-2}{O_3} \longrightarrow \overset{+2}{Cu}(\overset{+5}{N}\overset{-2}{O_3})_2 + \overset{+4}{N}\overset{-2}{O_2} + \overset{+1}{H_2}\overset{-2}{O}$$

There is change in oxidation number of Cu and N.

$$\overset{0}{Cu} \rightarrow \overset{+2}{Cu}(NO_3)_2 \quad \text{.........(1)}$$

(Oxidation no. is increased by 2)

$$H\overset{+5}{N}O_3 \rightarrow \overset{+4}{N}O_2 \quad \text{......(2)}$$

(Oxidation no. is decreased by 1)

To make increases and decrease equal, eq. (2) is multiplied by 2.

$$Cu + 2HNO_3 \rightarrow Cu(NO_3)_2 + 2NO_2 + H_2O$$

Balancing nitrates ions, hydrogen and oxygen,

the following equation is obtained.

$$Cu + 4HNO_3 \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

This is the balanced equation

Example: Balance the following reaction by the oxidation number method

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

Solution: Write the oxidation number of all the atoms.

$$\overset{+7}{Mn}\overset{-2}{O_4^-} + Fe^{+2} \longrightarrow Mn^{+2} + Fe^{+3}$$

Change in oxidation number has occurred in Mn and Fe

$$\overset{+7}{Mn}O_4^- \rightarrow \quad \text{..........(1)}$$

(Decrement in oxidation no. by 5)

$$Fe^{+2} \rightarrow Fe^{+3} \quad \text{...........(2)}$$

(Increment in oxidation no. by 1)

To make increase and decrease equal, eq. (2) is multiplied by 5.

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

To balance oxygen, $4H_2O$ are added to R.H.S. and to balance hydrogen,

$8H^+$ are added to L.H.S.

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

This is the balanced equation

(b) Ion- Electrom method:

This method was given by Jette and La mew 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 sub steps.

  (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^+ ions equal to the deficiency in the side which is deficient in hydrogen atoms

  (d) Balance the charge by adding electron to the side which is 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 added is equal to the deficiency.

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

Example:

(A) Acidic Medium

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

(b) Write both the half reaction

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

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

$C_2O_4^{2-} \rightarrow CO_2$

(e) Balance H-atoms by the addition of H^+ 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 electron (e^-)

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

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

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

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

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

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

(B) 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^+ to side having deficiency and add equal no. of OH^- ions to the side

($\because$ medium is known)

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

$5OH^- + H_2O + Cr(OH)_3$

$\rightarrow CrO_4^{2-} + 5H^+ + 5OH^-$

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

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

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

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

(e) Balance the charges by adding electrons

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

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

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

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

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

Add there balanced half reaction to give complete balanced reaction.

$4OH^- + 2Cr(OH)_3 + IO_3^-$

$\rightarrow 5H_2O + 2CrO_4^{2-} + I^-$

◆ **Type of redox reactions**

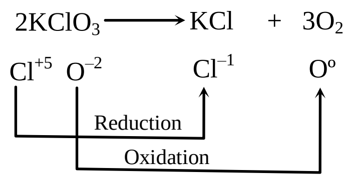
(1) Intermolecular redox reaction: When oxidation and reduction take place separately in different compounds, then the reaction is called intermolecular redox reaction.

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

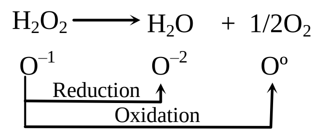
$Sn^{+2} \longrightarrow Sn^{+4}$ (Oxidation)

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

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



(3) Disproportioning reaction: When reeducation and oxidation take place in the same element to the same compound then the reaction is called disproportionation reaction.



Equivalent weight

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

$$=\frac{\text{Mol.wt.}}{\text{No.ofelectronsgainedbyonemole}}$$

$$=\frac{\text{Mol.wt.}}{\text{DecreaseinO.S.}\times\text{NO.ofatomundergoingreduction}}$$

Example: In acidic medium

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

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

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

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

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)

$$=\frac{\text{Mol.wt.}}{\text{No.ofelectronslostbyonemole}}$$

$$=\frac{\text{Mol.wt.}}{\text{increaseinO.S.}\times\text{No.ofatomundergoingoxidation}}$$

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 wets. 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

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

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 $= \frac{\text{Mol.wt.of} K_2Cr_2O_7}{1}$

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

(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)