# **Redox Reactions**

#### INTRODUCTION

The process in which it involves the loss of electrons by the atoms or ions is termed as **Oxidation**.

The process in which it involves the gain of electrons by the atoms or ions is termed as Reduction.

Those reactions, in which reduction and oxidation takes place simultaneously is called a Redox Reaction. The species that lose electrons (i.e., gets oxidised) is known as reducing agent or reductant, the species which accepts electrons from reductant (i.e., gets reduced) is known as oxidising agent or oxidant.

#### Ex.

 $Mg + Zn^{2+} \longrightarrow Mg^{2+} + Zn$  is a redox reaction.

**Oxidation :**  $Mg^{0} \longrightarrow Mg^{2+} + 2e^{-}$ 

**Reduction :**  $Zn^{+2} + 2e^{-} \longrightarrow Zn^{0}$ 

Mg causes reduction of Zn<sup>2+</sup>, so it is Reductant. Zn<sup>2+</sup> causes oxidation of Mg, so it is Oxidant.

Oxidation Number (O.N.) : It refers to the total charge on all atoms of same kind in a compound. Oxidation State (O.S.) : It refers to the charge per atom of all atoms of same kind in a compound. In a compound O.N. of an element is equal to oxidation state of that element multiplied by total atoms of that element in particular compound.

**(i)** In ionic compounds, it is simply the charge on corresponding cation and anion which is expressed as oxidation state of that particular element. For example, oxidation state of potassium and chlorine in potassium chloride (KCl) is simply +1 and -1 respectively as KCl is treated as K<sup>+</sup>Cl<sup>-</sup>.

Refer to following examples where oxidation states are written above the atoms :

#### **Concept Ladder**

**Rack your Brain** 

One of the most important processes in living organisms is photosynthesis, consists of a series of oxidation-reduction reactions.

which

that occurs

Why this reaction is not redox reaction? NaOH +HCl → NaCl +H<sub>2</sub>O

### Previous Year's Questions

Hot concentrated sulphuric acid is a moderately strong oxidizing agent which of the following reactions does not show oxidizing behaviour

#### [NEET]

- (1)  $Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$
- $\begin{array}{l} (2) \quad S+2H_2SO_4 \longrightarrow 3SO_2+2H_2O \\ (3) \quad C+2H_2SO_4 \longrightarrow CO_2+2SO_2+2H_2O \end{array}$
- (4)  $CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$

Mg Cl	+2 - 2 Ca S	+3 - 1 Al Cl <sub>2</sub>	$CaO^{+2}O^{-2}$	+1 -1 Na F	+1 +6 -2 K_SO.
0 2	040	3	040		

(ii) In Covalent Compounds, it is not easy to assign oxidation state of an atom. In order to simplify the concept, we are going to define a set of rules which would enable us to assign oxidation state of every element in any compound.

# Rules for Assigning Oxidation state (O.S.) and Oxidation Number (O.N.)

- (i) Any element in elemental state is assigned an oxidation state of zero. For example: O.S. of H, P, S, O, Fe, Br in H<sub>2</sub>, P<sub>4</sub>, S<sub>8</sub>, O<sub>2</sub>, Fe, Br<sub>2</sub> is equal to 0.
- (ii) The oxidation state of any cation or anion (of form A<sup>+</sup> or B<sup>-</sup>) is equal to the magnitude of its charge. For example: O.S. of Ca in Ca<sup>2+</sup> = +2, O.S. of Al in Al<sup>3+</sup> = +3, O.S. of Cl in Cl<sup>-</sup> = -1 and so on.
- (iii) (a) The algebraic sum of the oxidation number of all atoms in neutral compounds is equal to 0.
  - (b) The algebraic sum of the oxidation numbers of all atoms in an ion (like PO<sub>4</sub><sup>3-</sup> etc.) is equal to the ion's charge.
- (iv) The oxidation state of Alkali Metals (Group IA) is +1 in all of their compounds and that of Alkaline Earth elements (Group IIA) is +2 in all of their compounds.
- (v) Hydrogen in almost all of its compounds is assigned an oxidation state of +1. The exception occurs when hydrogen forms compounds with strong metals (metallic hydrides). For example: KH, NaH, MgH<sub>2</sub>, CaH<sub>2</sub> etc. In all of these, the oxidation state of hydrogen is -1.

# **Concept Ladder**

When a covalent bond forms between two with atoms different electronegativities the shared electrons in the bond lie closer to the more electronegative atom: The oxidation number of an atom is the charge that results.

#### Rack your Brain



Find out the oxidation state of phosphorous in  $H_3PO_4$  and  $H_3PO_3$ ?

- (vi) Oxygen in almost all of its compounds is assigned an oxidation state of -2. In a class of compounds, Peroxides, oxidation state of oxygen is -1, for example :  $H_2O_2$ ,  $Na_2O_2$  etc. Another exception is  $OF_2$ , where O.S. is +2.  $O_2F_2$ , where O.S. is +1 and  $KO_2$  in which O.S. is  $-\frac{1}{2}$ .
- (vii) Fluorine is most electronegative element and is assigned an O.S. of -1, in all its compounds. For other halogens, O.S. is generally -1 except when they are bonded to a more electronegative halogen or oxygen. O.S. of iodine in IF<sub>7</sub> is +7, O.S. of chlorine in KClO<sub>3</sub> is +5.

#### **Concept of Fractional Oxidation State**

Fractional O.S. is the average oxidation state of the element under examination, and it means that the element for which fractional O.S. is realized is present in different oxidation states.

Structure of the species  $C_3O_2$ ,  $Br_3O_8$  and  $S_4O_6^{2-}$  reveal the following bonding situations :



#### **Rack your Brain**



Find the oxidation number of Cl in  $ClO_4^{-?}$ ?

 $^{+2}_{O = C = C} ^{0}_{C = C} ^{+2}_{C = 0} C$ Structure of C<sub>3</sub>O<sub>2</sub> (Carbon suboxide)



Structure of Br<sub>3</sub>O<sub>8</sub> (Tribromoethaoxide)

The elements marked with asterisk in the above examples will exhibit different oxidation state from the remaining atoms of the same element in each of the species. This means that in  $C_3O_2$ , two carbon atoms are present in +2 oxidation state each, whereas the third one is



Structure of  $S_4 O_6^{2-}$  (Tetrathionate ion)

present in 0 oxidation state and the average is 4/3. Likewise in Br3O8, each of the 2 terminal Br atoms are present in +6 O.S. and the middle Br atom is present in +4 O.S. and the average is 16/3. In the same manner, in the species  $S_4O_6^{2-}$  is 2.5,

whereas the reality being +5, 0, 0 and +5 O.N. respectively for each S atom. Some other examples of the compounds are Pb3O4, Fe3O4,  $Mn_3O_4$ , which are mixed oxides having the metal in fractional oxidation state. However, the oxidation states may be in fraction as in  $O_2^+$  and  $O_2^-$ 

where it is +1/2 and -1/2 respectively.

#### **Analysis of a Redox Reaction**

Consider the following Redox Reaction:

 $CusO_4 + Pb \longrightarrow PbSO_4 + Cu$  **1.** Assign oxidation state of each atom.  $\begin{array}{c} +2 +6 -2 & 0 \\ Cu & SO_4 + Pb \longrightarrow Pb & SO_4 + Cu \end{array}$ 

Rewriting the equation as two equations (oxidation and reduction) as follows :

**Reduction :**  $Cu^{2+} + 2e^{-} \longrightarrow Cu^{0}$ 

**Oxidation :**  $Pb^0 \longrightarrow Pb^{2+} + 2e^-$ 

We can now re-define oxidation and reduction as follows :

Oxidation is an increase in oxidation state and reduction is a decrease in oxidation state.

#### **Types of Redox Reaction**

#### 1. Combination reactions

It may be denoted in the manner : A + B  $\longrightarrow$  C

All combustion reactions, which make use of reactions involving elements other than dioxygen as well as elemental dioxygen, are redox reactions. Some important examples of this category are :





Decomposition reactions happen all around us, but we often don't notice them. The decomposition of carbonic acid in soft drinks, which can be represented by the chemical equation  $H_2CO_3 \longrightarrow H_2O + CO_2$ 



 $(gaining 2e^{-})$ 

 $(losing 2e^{-})$ 

The reaction  $2Pb(NO_3)_2 \longrightarrow$ 2PbO +  $4NO_2 + O_2$  is a type of reaction?  $\begin{array}{c} \overset{0}{\operatorname{C}} & \overset{0}{\operatorname{C}} & \overset{0}{\longrightarrow} & \overset{+4}{\operatorname{C}} & \overset{-2}{\operatorname{O}} \\ \overset{0}{\operatorname{C}} & \overset{0}{\longrightarrow} & \overset{0}{\operatorname{C}} & \overset{+2}{\longrightarrow} & \overset{-3}{\operatorname{O}} \\ 3 \operatorname{Mg}(s) + \operatorname{N}_{2}(g) & \overset{\Delta}{\longrightarrow} & \operatorname{Mg}_{3} \operatorname{N}_{2}(s) \\ \overset{-4}{\operatorname{C}} & \overset{+1}{\operatorname{C}} & \overset{0}{\operatorname{C}} & \overset{+4}{\longrightarrow} & \overset{-2}{\operatorname{C}} & \overset{+1}{\operatorname{O}} & \overset{-2}{\operatorname{H}_{2}} \\ \end{array}$ 

#### 2. Decomposition reactions

They are the opposite of combination reactions. Decomposition reactions takes place when there is breakdown of a compound into two or more components in which atleast one must be in the elemental state.

 $2 \overset{+1}{H_2} \overset{-2}{O}(l) \xrightarrow{\Delta} 2 \overset{0}{H_2}(g) + \overset{0}{O_2}(g)$   $2 \overset{+1}{NaH}(s) \xrightarrow{\Delta} 2 \overset{0}{Na(s)} + \overset{0}{H_2}(g)$   $2 \overset{+1}{K} \overset{+5}{Cl} \overset{-2}{O_3}(s) \xrightarrow{\Delta} 2 \overset{+1}{K} \overset{-1}{Cl}(s) + 3 \overset{0}{O_2}(g)$ 

It can be noted here that there is no change in the oxidation state of H in  $CH_4$  under combination reactions and that of K in KCl in reaction. All decomposition reactions are not redox reactions. For ex., decomposition of CaCO<sub>2</sub> is not a redox reaction.

 $\overset{+2}{\operatorname{Ca}} \overset{+4}{\operatorname{C}} \overset{-2}{\operatorname{O}} \overset{-}{\operatorname{Ca}} \overset{+2}{\operatorname{O}} \overset{-2}{\operatorname{O}} \overset{+4}{\operatorname{C}} \overset{-2}{\operatorname{O}} \overset{+4}{\operatorname{O}} \overset{-2}{\operatorname{O}} \overset{-}{\operatorname{O}} \overset{-}{\operatorname{O}} \overset{+}{\operatorname{O}} \overset{-}{\operatorname{O}} \overset{-}{\operatorname{O$ 

#### 3. Displacement reactions

When in a reaction an atom (or an ion) in a compound is replaced by an atom (or an ion) of another element, then the reaction is defined as displacement reactions. It may be denoted as :

 $X + YZ \longrightarrow XZ + Y$ 

Displacement reactions fit into 2 categories : metal displacement and non- metal displacement.

(a) Metal displacement : When a metal in a compound can be displaced by anothermetal in the uncombined



Rack your Brain

H+ into H<sub>a</sub>.



Why do the displacement reactions of chlorine, bromine and iodine using fluorine not generally carry out in aqueous solution?

#### **Concept Ladder**



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state then the reaction is metal displacement. This reaction have many applications in metallurgical processes in which pure metals are obtained from their compounds in ores. A few such examples are :

$$\begin{array}{c} \overset{+2}{\text{Cu}} \overset{+6}{\text{S}} \overset{-2}{\text{Cu}} \overset{0}{\text{S}} \overset{0}{\text{Cu}} \overset{+2}{\text{S}} \overset{+6}{\text{C}} \overset{-2}{\text{Cu}} \overset{0}{\text{S}} \overset{+2}{\text{Cu}} \overset{+6}{\text{S}} \overset{-2}{\text{Cu}} \overset{0}{\text{S}} \overset{+2}{\text{Cu}} \overset{-2}{\text{S}} \overset{0}{\text{S}} \overset{+2}{\text{Cu}} \overset{-2}{\text{S}} \overset{0}{\text{Cu}} \overset{+2}{\text{S}} \overset{-2}{\text{Cu}} \overset{0}{\text{S}} \overset{+2}{\text{Cu}} \overset{-2}{\text{S}} \overset{0}{\text{Cu}} \overset{+2}{\text{S}} \overset{-2}{\text{Cu}} \overset{0}{\text{S}} \overset{+2}{\text{S}} \overset{-2}{\text{Cu}} \overset{0}{\text{S}} \overset{0}{\text{Cu}} \overset{+2}{\text{S}} \overset{-1}{\text{Cu}} \overset{0}{\text{Cu}} \overset{0}{\text{S}} \overset{+2}{\text{Cu}} \overset{-1}{\text{S}} \overset{0}{\text{Cu}} \overset{0}{\text{Cu}} \overset{+2}{\text{S}} \overset{-1}{\text{Cu}} \overset{0}{\text{Cu}} \overset{0}{\text{Cu}} \overset{+2}{\text{Cu}} \overset{-1}{\text{Cu}} \overset{0}{\text{Cu}} \overset{0}{\text{Cu}} \overset{+2}{\text{Cu}} \overset{-1}{\text{Cu}} \overset{0}{\text{Cu}} \overset{0}{\text{Cu}} \overset{-1}{\text{Cu}} \overset{0}{\text{Cu}} \overset{0}{\text{Cu}}$$

(b) Non-metal displacement : This type of redox reactions include displacement of hydrogen and a rarely occurring reaction displacement, occurring reaction involving oxygen displacement.

> All group 1 elements and some alkaline earth metals (Sr, Ca & Ba) which are very good reductants, will displace hydrogen from cold water.

$$^{0}_{2Na(s) + 2H_{2}O(l)} \longrightarrow ^{+1}_{2NaOH(aq) + H_{2}(g)}$$

$$\overset{0}{\operatorname{Ca}}(s) + 2\overset{+1-2}{\operatorname{H}_2} \overset{0}{\operatorname{O}}(l) \xrightarrow{2} \overset{+2}{\longrightarrow} \overset{-2}{\operatorname{Ca}} \overset{+1}{\operatorname{OH}} \overset{0}{\operatorname{Ca}}(aq) + \overset{0}{\operatorname{H}_2}(g)$$

Less active metals such as Mg and Fe react with steam to produce H<sub>2</sub> as:

$$\stackrel{0}{\text{Mg}(s)} + 2 \stackrel{+1-2}{\text{H}_2O}(l) \xrightarrow{\Delta} \stackrel{+2-2+1}{\text{Mg}(OH)_2(s)} + \stackrel{0}{\text{H}_2(g)}$$

$$\stackrel{0}{2\text{Fe}(s)} + 3 \stackrel{+1-2}{\text{H}_2O}(l) \xrightarrow{\Delta} \stackrel{+3-2}{\text{Fe}_2O_3(s)} + 3 \stackrel{0}{\text{H}_2(g)}$$

From acids hydrogen are displaced by many metals, including those which do not react with cold water. Such metals may produce dihydrogen from acid which do not react with steam. Cd and Pb are the examples

# **Concept Ladder**

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The elements in group one of the periodic table (with the exception of hydrogen - see below) are known as the alkali metals because they form alkaline solutions when they react with water.

#### **Rack your Brain**

Why do the displacement reactions of chlorine, bromine and iodine using fluorine not generally carry out in aqueous solution?

# Concept Ladder

Group two of the periodic table the comprises elements beryllium, calcium, magnesium, strontium, barium and radium. The elements in this group, which are all shiny and silvery-white in appearance, are known as the alkaline earth metals. Like the alkali metals, they form alkaline solutions when they react with water.

of such metals. A few examples for the displacement of hydrogen from acids are:  ${}^{0}$   ${}^{+1}$   ${}^{-1}$   ${}^{+2}$   ${}^{-1}$   ${}^{0}$  $Zn(s) + 2HCl(aq) \longrightarrow ZnCl_2(aq) + H_2(g)$  ${}^{0}$   ${}^{+1}$   ${}^{-1}$   ${}^{+2}$   ${}^{-1}$   ${}^{0}$  $Mg(s) + 2HCl(aq) \longrightarrow MgCl_2(aq) + H_2(g)$  ${}^{0}$   ${}^{+1}$   ${}^{-1}$   ${}^{+2}$   ${}^{-1}$   ${}^{0}$  $Fe(s) + 2HCl(aq) \longrightarrow FeCl_2(aq) + H_2(g)$ 

Here, the reactivity of metals is reflected in the rate of  $H_2$  gas evolution, for the least active metal Fe it is slowest, whereas for for the most reactive metal Mg it is fastest. Very less active metals, which may occur in the native state such as silver and gold do not react even with hydrochloric acid.

Zn > Cu > Ag is the order of reducing activity for the metals — zinc, copper and silver according to the tendency of losing electrons. Like metals, activity series also exists for the halogens. The power of these elements as oxidising agents decreases as we move down from fluorine to iodine in group 17 of the periodic table. This implies that fluorine is so reactive that it can replace chloride, bromide and iodide ions in solution. In fact, fluorine is so reactive that it attacks water and displaces the oxygen of water :

 $2 H_2^{+1} O(l) + 2F_2(g) \longrightarrow 4 HF(aq) + O_2(g)$ 

This is the reason behind not using F for displacement reactions of Cl, Br and I in aqueous solution. On the other hand, Cl can displace Br and I ions in an aqueous solution as shown below.

# Concept Ladder

**Rack your Brain** 

Zinc doesn't react with cold water, so to make the reaction proceed, we must give some external energy so that the reaction mixture can reach the activation energy barrier and allow the reaction to occur.



Find the reason behind Zn reacts with steam but not with cold water?

# Previous Year's Questions



In acidic medium,  $H_2O_2$  changes  $Cr_2O_7^{2-}$  to  $CrO_5$  which has two (-0-0-) bonds. Oxidation state of Cr in  $CrO_5$  is

#### [NEET]

- (1) +5
- (2) +3
- (3) +6
- (4) -10

$$Cl_{2}(g) + 2KBr(aq) \longrightarrow 2KCl(aq) + Br_{2}(l)$$

$$Cl_{2}(g) + 2KI(aq) \longrightarrow 2KCl(aq) + I_{2}(l)$$

By the colour of the solution,  $Br_2$  and  $I_2$  can be easily identified as they are also coloured and can be dissolved in  $CCl_4$ . The given below reactions represents ionic form of above one:

 $Cl_{2}(g) + 2Br^{-}(aq) \longrightarrow 2Cl^{-}(aq) + Br_{2}(l)$  $Cl_{2}(g) + 2I^{-}(aq) \longrightarrow 2Cl^{-}(aq) + I_{2}(l)$ 

Given reactions form the basis of identifying bromide and iodide ions in the laboratory through the test which is popularly known as 'Layer Test'. Also, bromine can displace iodide ion in solution :

 $\operatorname{Br}_{2}^{0}(l) + 2I^{-}(aq) \longrightarrow 2\operatorname{Br}^{-1}(aq) + I_{2}(s)$ 

The displacement reactions for halogens have a direct industrial application. From their halides, halogens can be recovered by oxidation process, which is represented by :

$$2 X^{-} \longrightarrow X_{2} + 2 e^{-}$$

Here X denotes a halogen element. Whereas chemical means are available to oxidise chlorine, bromine and iodide ions, as fluorine is the strongest O.A.; there is no way to convert F<sup>-</sup> ions to F<sub>2</sub> by chemical means. The only way to achieve F<sub>2</sub> form F<sup>-</sup> is to oxidise electrolytically, the details to which you will study at a later stage.

#### 4. Disproportionation reactions

They are special type of redox reactions, in which an element in one oxidation state is simultaneously oxidised and reduced. One of the reacting substances in a this reaction always contains an element that can exist

#### Concept Ladder

For the recovery of halogens from their halides requires an oxidation process, so we need such element which has more oxidising strength than that halogen

# Rack your Brain



How do bleaching agents decolourise the colour of stains of colourless substances?



# Concept Ladder

The reverse of disproportionation reaction is called comproportionation reaction. In a c o m p r o p o r t i o n a t i o n reaction, a compound in an intermediate oxidation state is formed from the lower or higher oxidation state in at least three oxidation states. The decomposition of H<sub>2</sub>O<sub>2</sub> is a familiar example of the reaction, where O<sub>2</sub> experiences disproportionation.

$$^{+1}_{2} \overset{-1}{O}_{2}(aq) \longrightarrow ^{+1}_{2} \overset{-2}{O}(l) + \overset{0}{O}_{2}(g)$$

Here the  $O_2$  of peroxide, which is present in -1 state, is converted to 0 oxidation state in oxygen and decreases to -2 oxidation state in water.

Below reactions shows disproportionation of P, S & Cl in the alkaline medium :

$$\overset{0}{P_{4}(s)} + 3 OH^{-}(aq) + 3H_{2}O(l) \xrightarrow{-3}{P} \overset{-3}{H_{3}(g)} + 3H_{2} \overset{+1}{P} O_{2}^{-}(aq)$$

$$\overset{0}{S_{8}(s)} + 12 OH^{-}(aq) \xrightarrow{-2}{4} \overset{-2}{S^{2-}(g)} + 2 \overset{+2}{S_{2}} O_{3}^{2-}(aq) + 6H_{2}O(l)$$

$$\overset{0}{Cl_{2}(g)} + 2 OH^{-}(aq) \xrightarrow{+1}{Cl} O^{-}(aq) + \overset{-1}{Cl^{-}(aq)} + H_{2}O(l)$$

The formation of household bleaching agents are shown by the above reactions. The colour-bearing stains of the substances are changed to colourless compounds by the hypochlorite ion (ClO<sup>-</sup>) formed in the reaction oxidises. Whereas Br and I follow the same trend as exhibited by Clin reaction, F shows deviation from this behaviour when it reacts with group 1 elements. Below reaction shows the reaction takes place in case of flourine :

 $2F_2(g) + 2OH^-(aq) \longrightarrow 2F^-(aq) + OF_2(g) + H_2O(l)$ 

Being the most electronegative element, F cannot exhibit any positive oxidation state as it has certain limitations.



# **Previous Year's Questions**

Thecorrect order of acidic strength is

#### [AIPMT]

(1)  $HClO_4 < HClO_3 < HClO_2 < HClO$ (2)  $HClO_2 < HClO_3 < HClO_4 < HClO$ (3)  $HClO_4 < HClO < HClO_2 < HClO_3$ (4)  $HClO < HClO_2 < HClO_3 < HClO_4$ 

#### **Rack your Brain**

In this reaction which has more reducing power F<sup>-</sup> or OH<sup>-</sup>?

This means that among halogens, fluorine does not show a disproportionation tendency.

#### **Balancing of Redox Reactions**

For balancing of Redox Reactions, two methods are generally adopted :

- (1) Oxidation Number Method
- (2) Ion Electron (Half-Reaction) Method

#### (1) Oxidation Number Method

While balancing a given reaction by this method, following steps are to be followed ;

- (i) Assign oxidation state to each element (atom) on both sides of the equation and identify which element has been oxidised and which element has been oxidised and which reduced.
- (ii) Write two oxidation and reduction reactions (two half reactions) separately involving only atoms. Now balance the atoms on both sides of equation in each half reaction.
- (iii) Balance charge on both sides by adding electrons to whichever side is deficient in electrons. (i.e., negative charge)
- (iv) Add two half reactions together. How? In doing this we want electrons to cancel from both sides. For this, multiply the equations by appropriate coefficients so that number of electrons produced in oxidation reaction equals to that used up in reduction reaction.
- (v) Now compare this balanced equation with original unbalanced equation. Here, notice whether the given equation is a molecular equation or an ionic equation.

#### Concept Ladder



Ion electron method is most used methodology to balance redox reaction.

#### **Rack your Brain**



One mole of ferrous oxalate requires\_\_\_\_ moles of  $MnO_4^-$  to get oxidised completely in an acidic medium.



# [AIPMT]

- (1) Reduction
- (2) Oxidation
- (3) Both oxidation and reduction
- (4) None of these

- (vi) For molecular equation, to balance Oxygen (O) and Hydrogen (H), add required water to the side deficient in H and check for Oxygen atoms on both sides. (They will be equal on both sides)
- (vii) For ionic equation, apart form balancing O and H atoms, charge needs to be balanced. It depends upon the medium in which the reaction is taking place : Acidic (containing H<sup>+</sup> ions or any acid) or Alkaline (containing OH<sup>-</sup> ions or any base).
- (a) In Acidic medium, count total charge on both sides and balance it by adding H<sup>+</sup> ions to the required side (i.e., to the side deficient in +ve charge). Finally add enough water molecules to balance H and O atoms to the required side.
- (b) In Basic medium, balance the charge by adding OH<sup>-</sup> ions to the side with excess of +ve charge and finally add required number of H<sub>2</sub>O molecules to the appropriate side to balance O and Η.

#### (2) Ion Electron (Half-Reaction) Method

- Find the reduction and oxidation half (i) reactions and write them separately in ionic form. Note that, write whole of ion in half reaction (unlike the oxidation number method where only atoms undergoing the change of state were taken).
- **Ex.** Mn in  $MnO_4^-$  in acidic medium generally

goes to  $MnSO_4$  or  $Mn^{2+}$ . Write it like this :

 $MnO_4^- \longrightarrow Mn^{2+}$ 

# **Previous Year's Questions**

If in a chemical reaction, Fe<sup>+2</sup> is converted into Fe<sup>+3</sup>, then Fe<sup>+2</sup> -

# [AIPMT]

- (1) Gains one electron
- (2) Loses one electron
- (3) Gains one proton
- (4) Loses one proton



The oxidation number of atom in a neutral free elements is zero.

**Previous Year's Questions** 

The reaction of aqueous KMnO, with H<sub>2</sub>O<sub>2</sub> in acidic conditions given.

[AIPMT]

- (1)  $Mn^{4+}$  and  $O_2$
- (2)  $Mn^{2+}$  and  $O_2$
- (3)  $Mn^{2+}$  and  $O_3$

 $(and not as Mn^{7+} \longrightarrow Mn^{2+})$ 

(4)  $Mn^{4+}$  and  $MnO_{2}$ 

- (ii) Balance each half reaction separately. This is done accordingly to the following procedure.
- (iii) Balance all the atoms of both reactions except O and H.
- (iv) Now first balance O and H atoms (unlike in first method) depending upon the medium of reaction.

#### **Acidic Medium**

To balance O atoms add same number of water ( $\rm H_2O$ ) molecules to the side deficient in O atoms.

 $\begin{array}{ll} MnO_{4}^{-} & \longrightarrow & Mn^{2+} & \left( acidic \ medium \right) \\ MnO_{4}^{-} & \longrightarrow & Mn^{2+} + 4 H_{2}O \end{array}$ 

Now to balance H atoms, add as many H<sup>+</sup> ions required to the side deficient in H atoms (generally it is equal to double the number of water molecules added to the other side while balancing O atoms).

 $MnO_{4}^{-} + 8H^{+} \longrightarrow Mn^{2+} + 4H_{2}O$ 

#### **Basic Medium**

To balance O atoms, add same number of  $H_2O$  molecules to the side having excess of O atoms and add the number of  $OH^-$  ions to the other side (i.e., to the side deficient in O atoms).

 $MnO_{4}^{-} + 8H^{+} \longrightarrow Mn^{2+} + 4H_{2}O$ 

Now to balance H atoms (if required), add same number of OH– ions to the side in excess of H atoms and then add same number of water molecules to the other side (i.e., the side deficient in H atoms).

$$NO_{3}^{-} + 3 H_{2}O + 4 H_{2}O \longrightarrow NH_{4}^{+} + 6 OH^{-} + 4 OH^{-}$$
$$NO_{3}^{-} + 7 H_{2}O \longrightarrow NH_{4}^{+} + 10 OH^{-}$$

(v) Now add electrons to the side deficient in negative charge in order to balance the charge on both sides.



Redox reactions are carried out in aqueous solutions. When the concentration of H<sup>+</sup> is more in the solution i.e. it is acidic in nature, we call it acidic medium.



In weak alkaline medium  $MnO_4$  converted in to

(2) K<sub>2</sub>MnO<sub>4</sub>

(4) MnO



When the concentration of OH<sup>-</sup> is more in the solution i.e. it is basic in nature, we call it basic medium.  $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$ 

 $NO_{3}^{-} + 7H_{2}O + 8e^{-} \longrightarrow NH_{4}^{+} + 10OH^{-}$ 

These are balanced half reactions in acidic and basic medium respectively.

(vi) Now add two half reactions together in such a manner that electrons from both sides cancel. So multiply by coefficients so that number of electrons produced in oxidation equals the number of electrons used in reduction (as done in oxidation number method step – 4).

#### **CONCEPT OF GRAM EQUIVALENTS**

In the method of gram-equivalents (milliequivalents), there is no need to balance a redox reaction. For example, let us consider a typical redox reaction (consisting of two reactants and two main products) :

 $\begin{array}{ccc} X &+ & Y \\ \begin{array}{c} \text{Reducing} & \text{Oxidising} \\ \begin{array}{c} \text{agent} \end{array} & \begin{array}{c} \text{agent} \end{array} & A &+ & B \end{array}$ 

According to concept of gram equivalent (or meq); 1 gm eq. of X = 1 gm eq. of Y = 1 gm eq. of A = 1 gm eq. of B

or meq. of an oxidising agent = meq. of a reducing agent

#### Equivalent Weight (E) of Oxidant and Reductant

The equivalent weight of an oxidizing or reducing agent is defined as :

Equivalent weight = E =  $\frac{M_0}{x}$ 

where  $M_0$  = molecular mass; x = number of electrons transferred (loss or gain) by one mole of oxidising or reducing agent as given by their balanced ionic half reaction.

# **Concept Ladder**

Equivalent weight, in chemistry, the quantity of a substance that exactly reacts with, or is equal to the combining value of, an arbitrarily fixed quantity of another substance in a particular reaction.

Rack your Brain



What will be normality of 2M H<sub>2</sub>SO<sub>4</sub> aq. solution?



#### Examples :

#### (i) **FeSO**<sub>4</sub> (Ferrous Sulphate)

As reducing agent :  $Fe^{2+} \longrightarrow Fe^{3+} + 1e^{-1}$ 1 mole of e's are transferred/mole of  $FeSO_4$ , so x = 1

$$\Rightarrow \quad \mathsf{E}_{\mathsf{FeSO}_4} = \frac{\mathsf{M}_0}{\mathsf{x}} = \frac{152}{1} = 152$$

As an oxidising agent:  $Fe^{2+} + 2e^{-} \longrightarrow Fe + 1e^{-}$ 

$$\Rightarrow x = 2$$
  
$$\Rightarrow E_{FeSO_4} = \frac{M_0}{x} = \frac{152}{2}$$

 ${\rm FeSO}_{\scriptscriptstyle 4}$  (ferrous sulphate) acts both as an oxidant and as a reductant.

(ii)  $H_2C_2O_4$  (Oxalic acid) or  $C_2O_4^{2-}$  (Oxalate ion) As reducing agent only :

$$C_2 O_4^{2-} \longrightarrow 2 CO_2 + 2 e^{-}$$

or  $H_2C_2O_4 \longrightarrow 2CO_2 + 2H^+ + 2e^-$ 

x = 2 or 
$$E_{H_2C_2O_4} = \frac{90}{2}$$

(iii) **SO**<sub>2</sub> (Sulphur Dioxide) As reducing agent :

 $SO_2 + 2H_2O \longrightarrow SO_4^{2-} + 4H^+ + 2e^-$ 

$$x = 2 \Longrightarrow E_{SO_2} = \frac{64}{2}$$

(iv) HI (Hydrogen lodide) As reducing agent only :  $2HI \longrightarrow I_2 + 2H^+ + 2e^-$ 

2 mole of e⁻/2 mole of HI

$$x = \frac{2}{2} = 1$$
 (for 1 mole of HI)  
128

$$E_{HI} = \frac{120}{1}$$

# (v) $\operatorname{Fe}_2(\operatorname{SO}_4)_3$ (Ferric sulphate)

As oxidising agent only:  $Fe^{3+} + 1e^{-} \longrightarrow Fe^{2+}$ 

Since 1 mole of  $Fe_2(SO_4)_3 = 2$  moles of  $Fe^{3+}$ x = 2 for 1 mole of  $Fe_2(SO_4)_3$ - 400

$$\Rightarrow E_{Fe_2(SO_4)_3} = \frac{400}{2}$$

### Concept Ladder

Hydrogen iodide is a diatomic molecule and hydrogen halide. Aqueous solutions of HI are known as hydroiodic acid or hydriodic acid, a strong acid.





In this reaction find out the oxidation state of sulphur in  $SO_2$  and  $SO_4^{-2}$ ?



Oxalic acid, also called ethanedioic acid, a colourless, crystalline, toxic organic compound belonging to the family of carboxylic acids. (vi) Na,S,O, (Sodium Thiosulphate) As reducing agent in acidic medium :  $2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2e^{-}$  $x = \frac{2}{2} = 1$  for 1 mole of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>  $\Rightarrow \quad \mathsf{E}_{\mathsf{Na}_2\mathsf{S}_2\mathsf{O}_3/\mathsf{H}^+} = \frac{158}{1}$ 

# (vii) KMnO<sub>4</sub> (Potassium Permanganate)

As oxidising agent in acidic medium :

 $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$ 

 $\Rightarrow \quad \mathsf{E}_{\mathsf{KMnO}_4/\mathsf{H}^+} = \frac{158}{\texttt{F}}$ 

As oxidising agent in strong alkaline medium

$$: MnO_4^- + 1e^- \longrightarrow MnO_4^2$$
$$x = 1$$
$$\Rightarrow E_{KMnO_4} = \frac{158}{1}$$

(viii) K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (Potassium Dichromate) As oxidising agent only :

 $Cr_2O_7^{2-} + 6e^- + 14H^+ \longrightarrow 2Cr^{3+} + 7H_2O^{-}$ x = 6  $\Rightarrow E_{K_2Cr_2O_7} = \frac{294}{6}$ 

# (ix) MnO<sub>2</sub> (Manganese dioxide)

As oxidising agent in acidic medium :

 $MnO_4 + 4H^+ + 2e^- \longrightarrow Mn^{2+} + 2H_2O$ 

$$\Rightarrow E_{MnO_2} = \frac{87}{2}$$

As oxidising agent in dilute alkaline medium :

$$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-$$

$$\Rightarrow \quad \mathsf{E}_{\mathsf{KMnO}_4/\mathsf{OH}^-} = \frac{158}{3}$$

As reducing agent in alkaline medium :

# **Concept Ladder**

KMnO<sub>4</sub> was first developed as a disinfectant in 1857. Since then, it's been widely used to treat a variety of skin conditions, including fungal infections.



Number of moles of MnO<sub>4</sub>required to oxidize one mole of ferrous oxalate completely in acidic medium will be [AIPMT]

(1) 7.5 moles (2) 0.2 moles (4) 0.4 moles (3) 0.6 moles

# **Concept Ladder**





Potassium dichromate K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, common inorganic reagent, most commonly used as an oxidizing agent in various laboratory and industrial applications. As with all hexavalent chromium compounds, it is acutely and chronically harmful to health.

$$S_2O_3^{2^-} + 10 \text{ OH}^- \longrightarrow 2 \text{ SO}_4^{2^-} + 5 \text{ H}_2\text{ O} + 8 \text{ e}^2$$
  
 $x = 8$   
 $\Rightarrow \quad \text{E}_{\text{Na}_2S_2O_3/\text{OH}^-} = \frac{158}{8}$ 

# Equivalent weight of a compound undergoing disproportion

8

Let a compound 'A' contains an ion 'X' undergoing disproportionation.

Then,  $E_A = Equivalent$  weight of A

Effective molecular weight of A

Number of e<sup>-</sup> transfer

Where Effective molecular weight of A

 $= \begin{pmatrix} \text{Total weight of A in} \\ \text{Oxidation half reaction} \end{pmatrix} + \begin{pmatrix} \text{Total weight of A in} \\ \text{Reduction half reaction} \end{pmatrix}$ 

When number of e<sup>-</sup> transfer are in oxidation and reduction half reactions

H<sub>2</sub>O<sub>2</sub> undergoes disproportionation in acidic medium given by the following reaction :

 $H_2O_2 \longrightarrow H_2O + O_2$ 

(1)

**Oxidation half reaction :** 

(2e<sup>-</sup> transfer)  $H_2O_2 \longrightarrow O_2 + 2H^+ + 2e^-$ ...(i)

**Reduction half reaction :** 

$$H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$$
 (2e<sup>-</sup> transfer)

Thus, Effective molecular mass of

 $\begin{array}{l} {{H_2}{O_2}} \ = \ {{M_{{H_2}{O_2}}}} + \ {M_{{H_2}{O_2}}} \\ {\text{from (i)}} \ \ \text{from (ii)} \end{array} = 2 \, {M_{{H_2}{O_2}}} \end{array}$ 

$$\Rightarrow \quad \mathsf{E}_{\mathsf{H}_2\mathsf{O}_2} = \frac{2\mathsf{M}_{\mathsf{H}_2\mathsf{O}_2}}{2} = 34$$

When number of e<sup>-</sup> transfer are different in (2) oxidation and reduction half reactions

Br, undergoes disproportionation in basic medium given by the following reaction :

 $Br_2 + OH^- \longrightarrow Br^- + BrO_3^- + H_2O$ 

#### **Oxidation half reaction :**

$$Br_2 + 12 OH^- \longrightarrow 2 BrO_3^- + 6 H_2 O + 10 e^-$$
 (10e<sup>-</sup> transfer) ....(i)





In disproportionation reaction to find out the equivalent weight we should firstly split the reaction into oxidation and reduction reaction. By it we can easily find out the number of envolved electrons by one one mole of that substance.

...(ii)



 $Br_2 + 2e^- \longrightarrow 2Br$  (2e<sup>-</sup> transfer) Now, effective molecular mass of  $Br_2 = M_{Br_2} + 5 M_{Br_2} = 6 M_{Br_2}$ Here,  $5M_{Br_2}$  is taken because we have to

equalize the number of electrons in both oxidation reduction.

Thus, 
$$E_{Br_2} = \frac{6M_{Br_2}}{10} = 0.6$$
;  $M_{Br_2} = 96$   
This means n-factor of  $Br_2$  is  $\frac{10}{6}$ .

#### **Redox reactions as the basis for Titrations**

The strength of one solution against the other can be find out by titration method using pH sensitive indicator in acid-base systems. Similarly, in redox systems, the method of titration can be adopted for determining the strength of oxidant/reductant using a redox sensitive indicator.

The usage of indicators in redox titration is illustrated below :

- (i) The reagent itself is intensely colored, e.g.,  $MnO_4^-$  ion. Here  $MnO_4^-$  acts as the selfindicator. After oxidising the last reductant (Fe<sup>2+</sup> or  $C_2O_4^{2-}$ ), the visible end point is achived for this case and then at  $MnO_4^$ pink colour appears for low concentration value as 10<sup>-6</sup> mol dm<sup>-3</sup> (10<sup>-6</sup> mol L<sup>-1</sup>). This ensures the point where the reductant and the oxidant are equal in terms of their mole stoichiometry or a minimal 'overshoot' in colour beyond the equivalence point.
- (ii) There are some indicators which oxidised immediately after the consumption of last bit of the reactant by producing a dramatic colour change, it occurs when there is no dramatic auto-colour change (as with MnO<sub>4</sub><sup>-</sup> titration).

# **Concept Ladder**

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...(ii)

Titration is a method or process of determining the concentration of a dissolved substance in terms of the smallest amount of reagent of known concentration required to bring about a given effect in reaction with a known volume of the test solution.

#### **Rack your Brain**



What is the purpose of titration in chemistry?

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The best example is afforded by  $Cr_2O_7^{2-}$ , which is not a self-indicator, but produces an intense blue color (signalling the end point) just after achieving equivalence point by oxidising the indicator substace diphenylamine.

(iii) The reagents which can oxidise I<sup>-</sup> ions are restricted to be used by this method. It is quite common method.

**Ex.** Cu(II):  $2Cu^{2+}(aq) + 4I^{-}(aq) \longrightarrow Cu_{2}I_{2}(s) + I_{2}(aq)$ The given method relies on the facts that iodine itself gives an intense blue color with starch and has a very specific reaction with  $(S_{2}O_{3}^{2-})$ , which too is a redox reaction:

 $I_2(aq) + 2S_2O_3^{2-}(aq) \longrightarrow 2I^{-}(aq) + S_4O_6^{2-}(aq)$ 

 $\rm I_2$  remains in solution containing KI as  $\rm KI_3$  though insoluble in water.

An intense blue color appears on adding starch to the reaction of  $Cu^{2+}$  ion on iodide ions, after the libration of iodine. Iodine is consumed by the  $S_2O_3^{2-}$  ions then the colour is disappeared. Thus, the end-point can easily be tracked and the rest is the stoichiometric calculation only.

#### Limitations of Concept of Oxidation Number

The concept of redox processes has been evolving with time. This process of evolution is continuing. In fact, in recent past the oxidation process is visualised as a decrease in electron density and reduction process as an increase in electron density around the atom(s) involved in the reaction.

#### **Redox Reaction and Electrode Process**

The experiment corresponding to reaction, can also be observed if zinc rod is dipped in copper sulphate solution. The redox reaction takes place

# Rack your Brain

Find out the equivalent weight of  $I_2$  in the following reaction  $2Cu^{2+}(aq) + 4I^{-}(aq) \longrightarrow Cu_2I_2(s)$  $+ I_2(aq)$ 

#### **Concept Ladder**

I<sub>2</sub> exists as a semi-lustrous, non-metallic solid at standard conditions that melts to form a deep violet liquid at 114 degrees Celsius, and boils to a violet gas at 184 degrees Celsius. and during the reaction, Zn is oxidised to Zn+ ions and Cu2+ ions are reduced to metallic Cu due to direct transfer of electrons from Zn to Cu ion. Heat is also evolved during the reaction. Now, we modify the exp. in such a manner that transfer of electrons takes place indirectly for the same redox reaction. This necessitates the separation of Zn metal from CuSO4 solution. We take CuSO4 solution in a beaker and put a Cu rod in it. We also take ZnSO4 solution in another beaker and put a Zn rod in it. Now reaction takes place at either the interface of the metal & of the beakers and its salt solution in each beaker both the oxidized and reduced forms of the same species are present. These represent the species in the oxidation and reduction half reactions. A redox couple is termed as having together the reduced and oxidised forms of a substance taking part in an reduction or oxidation half reaction.

#### **Rack your Brain**



Write down the redox reaction which is occuring in this voltalic cell.

# **Rack your Brain**



Tell about which substance is behaving like reducing and oxidising agent in this volatalic cell?



By separating the reduced form from the oxidised form by a slash or vertical line representing an interface (e.g. solid/solution), it represents redox couple. For example in above experiment the two redox couples are represented as Cu2+/ Cu and Zn2+/ Zn. In both cases, the reduced form is put after the oxidised form. Now, we put the beaker containing CuSO4 solution and the beaker containing ZnSO4 solution side by side. We connect solutions of both beakers by a U-tube (a U-tube/salt bridge contains a solution of KCl or ammonium nitrate usually solidified by boiling with agar-agar and later cooling to a jelly like substance). This provides an electric contact between the both solutions without mixing them with each other. The Zn and Cu rods are connected by a metallic wire with a provision for an ammeter and a switch. The setup as shown in is known as Daniell cell. No reaction takes place when the switch is in the off position, and current not flows through the metallic wire.

The following observations are made when the switch is in the on position:

- (i) The transfer of electrons now take place through the metallic wire connecting the two rods but not directly Zn to Cu2+ ion..
- (ii) The electricity flowing due to migration of ions through the salt bridge will flow from solution in one beaker to other. Due to the potential difference between the copper and zinc rods there is flow of current. These rods are known as electrodes.

Electrode potential is defined as the potential associated with each electrode. Standard Electrode Potential (SEP) is the potential of each electrode when the concentration of each species is unity which takes part in the electrode reaction and further the reaction is carried out

#### **Rack your Brain**



Find the equivalent weight in terms of molecular weight for  $Zn^{+2}$  in the reaction which is occuring in that voltalic cell.

#### **Concept Ladder**



The cathode is where reduction takes place and oxidation takes place at the anode.

# **Rack your Brain**



What is purpose of salt bridge in that voltalic cell?

at 298K. By convention, the standard electrode potential EO of H electrode is 0.00 volts. The value of relative tendency of the active species in the process to remain in the reduced or oxidised form is measured as the electrode potential value for each electrode. A negative EO means that the redox couple is a stronger reducing agent than the H+/H2 couple. If H+/H2 is stronger reducing agent than redox couple, this implies positive EO. We can get a large number of other useful information from SEP, hence it is very important.

The values of SEPs for some selected electrode processes (reduction reactions) are given below.

#### **Concept Ladder**

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By the basis of the below table, we can decide which substance can reduce or oxidise another substance in redox reaction.

		Electrode	Reaction	SRP(at 298K)		
		Li	$Li^{_{^+}}$ + e $^{}$ $ ightarrow$ Li(s)	–3.05 V		
		к	$K^{\scriptscriptstyle +}$ + $e^{\scriptscriptstyle -}$ $ ightarrow$ K(s)	–2.93 V		
		Ва	$Ba^{{}^{\scriptscriptstyle+2}}$ + 2e <sup>-</sup> $\to$ Ba	–2.91 V		
		Ca	$Ca^{\scriptscriptstyle{+2}}$ + 2e <sup>-</sup> $ ightarrow$ Ca(s)	–2.87 V		
		Na	$Na^{\scriptscriptstyle +}$ + e <sup>-</sup> $ ightarrow$ Na(s)	–2.71 V		
	1	Mg	$Mg^{\scriptscriptstyle{+2}}$ + 2e <sup>-</sup> $ ightarrow$ Mg(s)	-2.36 V		
		Al	$Al^{\scriptscriptstyle 3+}$ + $3e^- \to Al$	–1.66 V		
		Mn	$Mn^{{}^{*2}}$ + 2e $^{-} \to Mn$	–1.18 V		
ł		$H_2O$	$H_2O(\ell)$ +e <sup>-</sup> $\rightarrow \frac{1}{2}H_2$ + $OH^-$	-0.828 V		
	ų	Zn	$\operatorname{Zn}^{{}^{\scriptscriptstyle+\!2}}$ + 2e <sup>-</sup> $ ightarrow$ Zn(s)	-0.76 V		
	gen	Cr	$Cr^{ extsf{+3}}$ + 3e $^{ imes}$ $ ightarrow$ Cr(s)	-0.74 V	gent	
	л В Ц	Fe	$Fe^{^{2^+}}$ + 2e <sup>-</sup> $ ightarrow$ Fe	-0.44V	ាទ a	
	duci	Cd	$Cd^{\scriptscriptstyle{+3}}$ + 2e <sup>-</sup> $ ightarrow$ Cd(s)	-0.40 V	lasir	
	free	Co	$ extsf{Co}^{ imes 2}$ + 2 $ extsf{e}^{ o}$ $ ightarrow$ Co	-0.28 V	oxid	
	th o	Ni	$Ni^{\scriptscriptstyle +}$ + 2e $^{\scriptscriptstyle -}$ $ ightarrow$ Ni(s)	-0.25 V	ו of	
	eng	Sn	$Sn^{{}^{\scriptscriptstyle+\!2}}$ + 2e $^{\scriptscriptstyle-}$ $ ightarrow$ Sn(s)	-0.14 V	ngth	
	str	Pb	$Pb^{{}^{+2}}$ + 2e $^{-} \rightarrow Pb(s)$	-0.13 V	stre	
	sing	H <sub>2</sub>	$2H^{*} + 2e^{-} \rightarrow H_{2}(s)$	0.00 V	ы Л	
	crea	Cu	$Cu^{^{2+}}$ + 2e <sup>-</sup> $ ightarrow$ Cu(s)	0.34 V	easi	
	Inc	$I_2$	$I_2 + 2e^- \rightarrow 2I^-$	0.54 V	Incr	
		Fe	$Fe^{^{3^+}} + e^- \rightarrow Fe^{^{2^+}}$	0.77 V		
		Hg	$Hg_{^{2^{+}}}$ + 2e $\rightarrow$ 2Hg( $\ell$ )	0.79 V		
		Ag	$Ag^{\scriptscriptstyle +} + e^{\scriptscriptstyle -} \to Ag$	0.80 V		
		Hg	$Hg^{^{2+}}$ + 2e <sup>-</sup> $\rightarrow$ Hg( $\ell$ )	0.85 V		
		Br <sub>2</sub>	$Br_{_2}$ + 2e <sup>-</sup> $ ightarrow$ 2Br <sup>-</sup>	1.09 V		
		Pt	$Pt^{^{+2}}$ + 2e <sup>-</sup> $ ightarrow$ Pt	1.20 V		
		O <sub>2</sub>	1/2 $O_2$ +2H <sup>+</sup> +2e <sup>-</sup> →H <sub>2</sub> O( $\ell$ )	1.23 V		
		Cl <sub>2</sub>	$\operatorname{Cl}_{\scriptscriptstyle 2}$ + 2e <sup>-</sup> $ ightarrow$ 2 $\operatorname{Cl}^-$	1.36 V		
		Au	$\operatorname{Au}^{_{+3}}$ + $\operatorname{3e}^{_{-}} \to \operatorname{Au}(s)$	1.40 V		
		F <sub>2</sub>	$F_{_2}$ + 2 $e^-  ightarrow 2F^-$	2.87 V		

- Q.1 In the reactions given below, identify the species undergoing oxidation and reduction :
  - (i)  $H_2S(g) + Cl_2(g) \longrightarrow 2HCl(g) + S(s)$
  - (ii)  $3Fe_3O_4(s) + 8Al(s) \longrightarrow 9Fe(s) + 4Al_2O_3(s)$
  - (iii)  $2Na(s) + H_2(g) \longrightarrow 2NaH(s)$
- **Sol.** (i) H<sub>2</sub>S is oxidised because a more electronegative element, Cl is added to H (or a more electropositive element, H has been removed from S). Cl is reduced due to addition of H to it.
  - (ii) Al is oxidised because O is added to it. Fe<sub>3</sub>O<sub>4</sub> is reduced because O has been removed from it.
  - (iii) With the application of the concept of E.N. only we may infer that Na is oxidised and H is reduced.

**2** Justify that the reaction :  $2Na(s) + H_2(g) \longrightarrow 2NaH(s)$  is a redox change.

**Sol.** In the given reaction the product formed is an ionic compound. The product may also be represented as Na<sup>+</sup>H<sup>-</sup>(s), this suggests that one half reaction in this process is :

 $2Na(s) \longrightarrow 2Na^+(g) + 2e^-$ 

and the other half reaction is :

 $H_2(g) + 2e^- \longrightarrow 2H^-(g)$ 

The splitting of the reaction under examination into two half reactions automatcally reveals that here Na is oxidised, and  $H_2$  is reduced, therefore the complete reaction is a redox change.

A polyvalent metal weighing 0.1 gm and having atomic weight of 50 reacted with dilute H<sub>2</sub>SO<sub>4</sub> to give 44.8 mL of hydrogen at STP. The solution containing the metal in this Lower oxidation state, was found to require 60 mL of 0.1 N KMnO<sub>4</sub> solution for complete oxidation. What are valencies of metal? **Sol.** Metal (M) + H<sub>2</sub>SO<sub>4</sub>  $\longrightarrow$  H<sub>2</sub> 44.8 mL H<sub>2</sub> at STP =  $\frac{44.8}{22400}$  moles of H<sub>2</sub> Now, meq of M = meq of H<sub>2</sub> For Hydrogen 2H<sup>+</sup> + 2e<sup>-</sup>  $\longrightarrow$  H<sub>2</sub> meq of H<sub>2</sub> = 2 × m. moles of H<sub>2</sub>  $\Rightarrow \frac{0.1}{50 / x} = \left(\frac{44.8}{22400}\right) \times 2 \Rightarrow x = 2$ Thus, M  $\longrightarrow$  M<sup>x+</sup> + xe<sup>-</sup>, i.e., oxidation state is +2. Now, M<sup>2+</sup> will acquire higher oxidation state when oxidized by KMnO<sub>4</sub> M<sup>2+</sup>  $\longrightarrow$  M<sup>2+n</sup> + ne<sup>-</sup> meq of M<sup>2+</sup> = meq of KMnO<sub>4</sub>  $\frac{0.1}{50 / n} \times 1000 = 0.1 \times 60 \Rightarrow n = 3$ So oxidation state of M is M<sup>2+n</sup> = M<sup>+5</sup> Hence, the possible valencies are +2, +5.

# 25 ml solution containing (6.35 g/L of K H<sub>3</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>.2H<sub>2</sub>O required V<sub>1</sub> ml of 0.1 N NaOH and V<sub>2</sub> ml of 0.1 N KMnO<sub>4</sub> in two separate titrations. Calculate V<sub>1</sub> and V<sub>2</sub>.

**Sol.** KH<sub>3</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>.2H<sub>2</sub>O ; M<sub>0</sub> = 254 gm/mol

(a) meq of compound (as acid) = meq of NaOH 25 × N<sub>a</sub> = V<sub>1</sub> × 0.1

$$\Rightarrow$$
 where N<sub>a</sub> =  $\frac{S}{E} = \frac{6.35}{254/3} = 0.075$ 

$$\Rightarrow V_1 = \frac{25 \times 0.075}{0.1} = 18.75 \text{ ml}$$

(b) meq of compound (as RA) = meq of KMnO<sub>4</sub>  
25 × N<sub>RA</sub> = V<sub>2</sub> × 0.1  
where N<sub>RA</sub> = 
$$\frac{S}{E} = \frac{6.35}{254/4} = 0.10$$

$$\Rightarrow V_2 = \frac{25 \times 0.1}{0.1} = 25 \text{ ml}$$

Redox Reactions



**OI.** In In reaction (a), the compound NO is formed by the combination of the elemental substances,  $N_2$  and  $O_2$ ; therefore, this is an example of combination redox reaction. The reaction (b), the compound  $Pb(NO_3)_2$  break down into three components, therefore this is categorised under decomposition redox reaction. In reaction (c), H of H<sub>2</sub>O has been displaced by hydride ion into H<sub>2</sub> gas. Therefore, it is called displacement redox reaction. The reaction (d), the compound NO<sub>2</sub> (+4 state) disproportnate into  $NO_2^-$  (+3 state) and  $NO_3^-$  (+5 state). Therefore

reaction (d) is an example of disproportionation redox reaction.





**Sol.** Pb<sub>3</sub>O<sub>4</sub> is actually a stoichiometric mixture of 2 mol of PbO and 1 mol of PbO<sub>2</sub>. In PbO<sub>2</sub>, Pb is present in +4 O.S., whereas the stable O.S. of Pb in PbO is +2. PbO<sub>2</sub> thus can act as an oxidant (O.A.) and, therefore can oxidise Cl<sup>-</sup> ion of HCl into Cl. As PbO is a basic oxide. Therefore, the reaction

$$Pb_{3}O_{4} + 8HCl \longrightarrow 3PbCl_{2} + Cl_{2} + 4H_{2}O$$

can be splitted into two reactions namely :

 $2PbO + 4HCl \longrightarrow 2PbCl_2 + 2H_2O$  (acid-base reaction)

 $PbO_2^{+4} + 4HCl \longrightarrow PbCl_2^{-1} + Cl_2^{-1} + Cl_2^{$ 

Since HNO3 itself is an O.A. therefore, the reaction may not occur between  $PbO_2$ and  $HNO_3$ . However, the acid-base reaction occurs :  $2PbO + 4HNO_3 \longrightarrow 2Pb(NO_3)_2 + 2H_2O$ 

**Q.8** Balance the following by ion-electron method. (Acidic medium)  $Mn^{2+} + S_2O_8^{2-} \longrightarrow MnO_4^- + HSO_4^-$ 

**Sol.** Two half reactions are :

(a)  $Mn^{2+} \longrightarrow MnO_4^-$ 

Balancing these two half reactions :  $Mn^{2+} + 4H_2O \longrightarrow MnO_4^- + 5e^- + 8H^+$ 

(b)  $S_2O_8^{2-} \longrightarrow HSO_4^{-}$ 

 $S_2O_8^{2-} + 2H^+ + 2e^- \longrightarrow 2HSO_4^-$ 

Adding the above two half reactions, we have the balanced equation.

 $2 \operatorname{Mn}^{2+} + 5 \operatorname{S}_2 \operatorname{O}_8^{2-} + 8 \operatorname{H}_2 \operatorname{O} \longrightarrow 2 \operatorname{MnO}_4^- + 6 \operatorname{H}^+ + 10 \operatorname{HSO}_4^-$ 

# 50 ml of an aqueous solution of H<sub>2</sub>O<sub>2</sub> was titrated with an excess of KI solution in dilute H<sub>2</sub>SO<sub>4</sub>, the liberated iodine required 20 ml of 0.1 N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution for complete reaction. Calculate volume strength of H<sub>2</sub>O<sub>2</sub> solution.

Sol. Both chemical equations involved in the problem are typical redox reactions.  $H_2O_2 + KI + H_2SO_4 \longrightarrow I_2 + H_2O + K_2SO_4$ ...(i) and  $I_2 + 2Na_2S_2O_3 \longrightarrow 2Nal + Na_2S_4O_6$ ...(ii) Now, meq. of  $I_2 = meq.$  of  $Na_2S_2O_3$  (in eq. (ii))  $\Rightarrow$  meq. of  $I_{22}^2 = 20 \times 0.1 = 2$ meq. of  $H_2O_2$  = meq. of  $I_2$  (in eq. (i)) and  $N_{H_2O_2} \times V_{H_2O_{12}} = 2 \Longrightarrow N_{H_2O_2} = \frac{2}{50} = \frac{1}{25}$ Now,  $1 \text{ N H}_2\text{O}_2$  solution = 5.6 vol. of  $\text{O}_2$  $\Rightarrow \frac{1}{25} \text{N H}_2\text{O}_2 \text{ solution} = 5.6 \times \frac{1}{25} = 0.224 \text{ vol of O}_2$  $\Rightarrow$  Volume Strength of H<sub>2</sub>O<sub>2</sub> solution = 0.224 vol. Which of the following are examples of disproportionation reactions? (a)  $Ag(NH_2)^+_2 + 2H^+ \longrightarrow Ag^+ + 2NH_4^+$ (b)  $Cl_2 + 2OH^- \longrightarrow ClO^- + Cl^- + H_2O$ (c)  $CaCO_3 \longrightarrow CaO + CO_2$ (d)  $2HgO \longrightarrow 2Hg + O_{2}$ (e)  $Cu_2O + 2H^+ \longrightarrow Cu + Cu^{2+} + H_2O$ (f)  $CuS + O_2 \longrightarrow Cu + SO_2$ (g)  $2HCuCl_{0} + dil.H_{0}O \longrightarrow Cu + Cu^{2+} + 4Cl^{-} + 2H^{+}$ 

- (h)  $2H_2O_2 \longrightarrow 2H_2O + O_2$
- **Sol.** A reaction in which same atom is oxidised and reduced at the same time is called as a disproportionation reaction. Observing very carefully among the above reactions, we note that (b), (e), (g) and (h) are disproportionation reactions.

# Write the net ionic equation for the reaction f potassium dichromate (VI). K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> with sodium sulphite, Na<sub>2</sub>SO<sub>3</sub>, in an acid solution to give chromium (III) ion and the sulphate ion.

**Sol.** Step 1: The skeletal ionic equation is :  $Cr_2O_7^{2-}(aq) + SO_3^{2-}(aq) \longrightarrow Cr^{3+}(aq) + SO_4^{2-}(aq)$ 

> **Step 2 :** Find oxidation numbers for Cr and S  $_{+6}^{+6} \stackrel{-2}{\longrightarrow} _{+4}^{+4} \stackrel{-2}{\longrightarrow} \stackrel{+3}{\longrightarrow} \stackrel{+6}{\longrightarrow} \stackrel{-2}{\xrightarrow} _{+6}^{-2}$ Cr<sub>2</sub> O<sub>7</sub><sup>2-</sup>(aq) + S O<sub>3</sub><sup>2-</sup>(aq)  $\longrightarrow$  Cr<sup>3+</sup>(aq) + S O<sub>4</sub><sup>2-</sup>(aq)

This indicates that the  $\rm Cr_2O_7^{2-}$  ion is the oxidant and the  $\rm SO_3^{2-}$  ion is the reductant.

**Step 3 :** Calculate the increase and decrease of oxidation number, and make them equal: from step 2 we can notice that there is change in oxidation state of Cr and S. Oxidation state of Cr changes to +3 from +6.

There is decrease in oxidation state of +3 in Cr atom on R.H.S. of the equation. Oxidation state of S changes to +6 from +4. There is increase in oxidation state of +2 in S atom on R.H.S. To make the increase and decrease of O.S. equal, place value 2 before Cr3+ ion on R.H.S. and value 3 before SO42- ion on R.H.S. and balance the Cr and S atoms on both the sides of the equation. Thus we get

 $\overset{+6}{\text{Cr}_{2}} \overset{-2}{\text{O}_{7}^{2-}}(aq) + 3 \overset{+4}{\text{S}} \overset{-2}{\text{O}_{3}^{2-}}(aq) \longrightarrow 2 \overset{+3}{\text{Cr}^{3+}}(aq) + 3 \overset{+6}{\text{S}} \overset{-2}{\text{O}_{4}^{2-}}(aq)$ 

**Step 4 :** For the reaction to be occurs in acidic medium, and to make ionic charges equal on both the sides, add 8H+ on the left side of the equation.  $Cr_2O_7^{2-}(aq) + 3SO_3^{2-}(aq) + 8H^+ \longrightarrow 2Cr^{3+}(aq) + 3SO_4^{2-}(aq)$ 

**Step 5 :** Finally, count the H atoms, and add appropriate number of  $H_2O$  molecules (i.e.,  $4H_2O$ ) on the right to achieve balanced redox change.  $Cr_2O_7^{2-}(aq) + 3SO_3^{2-}(aq) + 8H^+(aq) \longrightarrow 2Cr^{3+}(aq) + 3SO_4^{2-}(aq) + 4H_2O(l)$ 

12 20 mL of a solution containing oxalic acid and sulphuric acid on titration with 0.05 N NaOH required 40 mL of the base. 20 mL of same solution on titration with 0.02 N KMnO<sub>4</sub> required 50 mL of KMnO<sub>4</sub>. Determine the strength of oxalic acid and H<sub>2</sub>SO<sub>4</sub>.

**Sol.** In this problem, two type of titrations viz : Neutralisation and Redox are involved. Note that in both cases, the volume of sample is same, i.e., moles of two

constituent are same in both.

Let x = m moles of  $H_2C_2O_4$  and y = m moles of  $H_2SO_4$  in first titration, both  $H_2C_2O_4$  and  $H_2SO_4$  react with base (as acids). [n-factor of both being 2 due to  $2H^+$  per mole in each].

$$\Rightarrow$$
 2 × x + 2 × y = meq of NaOH = 40 × 0.05 = 2

 $\Rightarrow$  x + y = 1

In second titration, only  $H_2C_2O_4$  (being reducing agent) reacts with  $KMnO_4$ .

 $\Rightarrow 2 \times x = \text{meq of } KMnO_4 = 50 \times 0.02 = 1$  $\left[H_2C_2O_4 \longrightarrow CO_2 + 2H^+ + 2e^-\right]$ 

Using Stock notation, represent the following compound : HAuCl<sub>4</sub>, Tl<sub>2</sub>O, FeO, Fe<sub>2</sub>O<sub>3</sub>, CuI, CuO, MnO and MnO<sub>2</sub>.

**Sol.** The O.N. of each metallic element in its compound can be find out by applying various rules of calculating the O.N. of the desired element in a compound, is as follows:

$$HAuCl_4$$
 — Au has 3  
 $Tl_2O$  — Tl has 1  
FeO — Fe has 2  
 $Fe_2O_3$  — Fe has 3  
Cul — Cu has 1  
CuO — Cu has 2  
MnO — Mn has 2  
MnO<sub>2</sub> — Mn has 4

Therefore, the above compounds may be written as :  $HAu(III)Cl_4$ ,  $Tl_2(I)O$ , Fe(II)O,  $Fe_2(III)O_3$ , Cu(I)I, Cu(II)O, Mn(II)O,  $Mn(IV)O_2$ .

#### **14** Justify that the reaction :

 $2 \operatorname{Cu}_2 O(s) + \operatorname{Cu}_2 S(s) \longrightarrow 6 \operatorname{Cu}(s) + \operatorname{SO}_2(g)$ 

is a redox reaction. Identify the species oxidised/reduced, which acts as an oxidant, and which acts as a reductant.

**Sol.** Let us mark oxidation number on each of the species in the given reaction under ex amination. This results into :

 $2Cu_{2}^{+1} \xrightarrow{-2}{O(s)} + Cu_{2}^{+1} \xrightarrow{-2}{S(s)} \longrightarrow 6Cu(s) + SO_{2}^{+4} \xrightarrow{-2}{O(s)}$ 

Therefore, conclude that in this reaction Cu is reduced form +1 state to 0 oxidation state and S is oxidised to +4 from -2 state. Thus, the above reaction is a redox reaction.

Further,  $Cu_2O$  helps S in  $Cu_2S$  to increase its O.N., therefore Cu(I) is an oxidizing agent; and S of  $Cu_2S$  helps Cu both in  $Cu_2S$  itself and  $Cu_2O$  to decrease its O.N.; therefore, S of  $Cu_2S$  is reducing agent.

#### 15 Permanganate(VII) ion, MnO $_4^-$ in basic solution oxidises iodide ion, $\vdash$ to pro-

duce molecular iodine (I<sub>2</sub>) and manganese(IV) oxide (MnO<sub>2</sub>). Write a balanced ionic equation to represent this redox reaction.

Sol. Step 1: Firstly write the skeletal ionic equation, which is

 $MnO_{4}^{-}(aq) + I^{-}(aq) \longrightarrow MnO_{2}(s) + I_{2}(s)$ 

Step 2: The two half-reactions are :

Oxidation half :  $I^{-1}(aq) \longrightarrow I_{2}(s)$ 

+7 +4

Reduction half :  $MnO_4^{-}(aq) \longrightarrow MnO_2(s)$ 

**Step 3 :** For balancing the iodine atoms in the oxidation half reaction, we rewrite it as :

 $2I^{-}(aq) \longrightarrow I_{2}(s)$ 

**Step 4 :** For balancing the oxygen atoms in the reduction half reaction, we add two  $H_2O$  molecules on the right :

 $MnO_{4}^{-}(aq) \longrightarrow MnO_{2}(s) + 2H_{2}O(l)$ 

For balancing the hydrogen atoms, we add 4  $\rm H^{\scriptscriptstyle +}$  ions on the left :

 $MnO_{4}^{-}(aq) + 4H^{+}(aq) \longrightarrow MnO_{2}(s) + 2H_{2}O(l)$ 

Here the reaction takes place in a basic solution, therefore, for 4  $H^+$  ions, we add 4  $OH^-$  ions to both sides of the equation :

 $MnO_{4}^{-}(aq) + 4H^{+}(aq) + 4OH^{-}(aq) \longrightarrow MnO_{2}(s) + 2H_{2}O(l) + 4OH^{-}(aq)$ 

Replacing the  $H^+$  and  $OH^-$  ions with  $H_2O$ , the resultant equation is :

 $MnO_{4}^{-}(aq) + 2H_{2}O(l) \longrightarrow MnO_{2}(s) + 4OH^{-}(aq)$ 

**Step 5 :** By balancing the charges of the two half-reactions in the manner we get:

 $2I^{-}(aq) \longrightarrow I_{2}(s) + 2e^{-}$ 

 $MnO_{4}^{-}(aq) + 2H_{2}O(l) + 3e^{-} \longrightarrow MnO_{2}(s) + 4OH^{-}(aq)$ 

Now to equalise the no. of electrons, we multiply the oxidation half-reaction by three and the reduction half-reaction by two.

 $6l^{-}(aq) \longrightarrow 3l_{2}(s) + 6e^{-}$ 

 $2MnO_4^{-}(aq) + 4H_2O(l) + 6e^{-} \longrightarrow 2MnO_2(s) + 8OH^{-}(aq)$ 

**Step 6 :** Adding both half-reactions to obtain the net reaction after cancelling elec trons on both sides.

 $6l^{-}(aq) + 2MnO_{4}^{-}(aq) + 4H_{2}O(l) \longrightarrow 3l_{2}(s) + 2MnO_{2}(s) + 8OH^{-}(aq)$ 

20 mL of a solution containing 0.2 gm of impure sample of H<sub>2</sub>O<sub>2</sub> reacts with
 0.316 gm of KMnO<sub>4</sub> in presence of H<sub>2</sub>SO<sub>4</sub> as per following reaction.
 KMnO<sub>4</sub> + H<sub>2</sub>O<sub>2</sub> + H<sub>2</sub>SO<sub>4</sub> -----> MnSO<sub>4</sub> + O<sub>2</sub> + H<sub>2</sub>O

- (a) Find the purity of H<sub>2</sub>O<sub>2</sub> solution mm Hg.
- (b) Calculate the volume of dry oxygen evolved at 27°C and at 750 mm Hg.

**Sol.** First write a complete balanced the reaction :  $2KMnO_4 + 5H_2O_2 + 3H_2SO_4 \longrightarrow 2MnSO_4 + K_2SO_4 + 5O_2 + 8H_2O$ From the balanced reaction, we have :  $5 \text{ moles of } H_2O_2 \circ 2 \text{ moles of } KMnO_4$ Moles of  $KMnO_4 = \frac{0.316}{158}$   $\Rightarrow \text{ Moles of } H_2O_2 \text{ required} = \frac{5}{2} \times \frac{0.316}{158}$   $\Rightarrow \text{ Grams of } H_2O_2 = \frac{5}{2} \times \frac{0.316}{158} \times 34 = 0.17 \text{ gm}$   $\Rightarrow \text{ Percentage purity of } H_2O_2 = \frac{0.17}{0.2} \times 100 = 85\%$ Now, 2 moles of  $KMnO_4 \circ 5$  moles of  $O_2$ Moles of  $O_2$  produced  $= \frac{5}{2} \times \frac{0.316}{158} = 5 \times 10^{-3}$ Using PV = nRT we have,  $V = \frac{nRT}{P} = \frac{5 \times 10^{-3} \times 0.0821 \times 300}{760 / 760} = 0.123 \text{ L} = 123 \text{ mL}$ 

# Permanganate ion reacts with bromide ion in basic medium to give manganese dioxide and bromate ion. Write the balanced ionic equation for the reaction.

Sol. Step 1: The skeletal ionic equation is :

 $MnO_{4}^{-}(aq) + Br^{-}(aq) \longrightarrow MnO_{2}(s) + BrO_{3}^{-}(aq)$ 

Step 2: Mark oxidation numbers for Mn and Br  $\stackrel{+7}{\text{Mn}} \stackrel{-1}{\text{O}_4^-}(aq) + \text{Br}^-(aq) \xrightarrow{+4} \text{Mn} \text{O}_2(s) + \stackrel{+5}{\text{Br}} \stackrel{+5}{\text{O}_3^-}(aq)$ 

this indicates that  $MnO_4^-$  ion is the oxidant and Br<sup>-</sup> ion is the re ductant. Step 3 : Calculate the increase and decrease in O.N., and make the increase equal to the decrease.

 $2 \operatorname{Mn} O_4^{-1}(aq) + \operatorname{Br}^{-1}(aq) \longrightarrow 2 \operatorname{Mn} O_2(s) + \operatorname{Br}^{+5}O_3^{-}(aq)$ 

Step 4: Here, the reaction occurs in the basic medium, and for making ionic charges equal on both sides, add 20H<sup>-</sup> ions on R.H.S.

 $2MnO_{4}^{-}(aq) + Br^{-}(aq) \longrightarrow 2MnO_{2}(s) + BrO_{3}^{-}(aq) + 2OH^{-}(aq)$ 

Step 5 : Finally, count the H atoms and add appropriate number of H<sub>2</sub>O molecules (i.e. one water molecule) on L.H.S. to achieve balanced redox change.  $2MnO_4^{-}(aq) + Br^{-}(aq) + H_2O(l) \longrightarrow 2MnO_2(s) + BrO_3^{-}(aq) + 2OH^{-}(aq)$ 

# Complete and balance the following.

- (a)  $H_2O_2 + I_2 \longrightarrow I^- + ??$
- **(b)**  $MnO_{4}^{2-} + H^{+} \longrightarrow Mn^{2+} + ??$

**Sol.** (a)  $I_2$  is reduced to  $I^-$ , so  $H_2O_2$  must be oxidised, i.e., it acts as a reducing agent. Hence final product will be  $O_2$  gas. The complete chemical equation is :

$$\mathsf{H}_2\mathsf{O}_2 + \mathsf{I}_2 \longrightarrow \mathsf{I}^- + \mathsf{O}_2$$

The balanced equation will be :

$$H_2O_2 + I_2 \longrightarrow 2I^- + O_2 + 2H^+$$

(b)  $MnO_4^{2-}$  is reduced to  $Mn^{2+}$ , i.e., it is acting as an oxidising agent. Now H<sup>+</sup> is already in the maximum oxidation state, so  $MnO_4^{2-}$  must also be reduced to  $\mathsf{Mn}^{\scriptscriptstyle 7+}$  state i.e.  $\mathsf{MnO}_4^{\scriptscriptstyle -}$  will be formed. hence it is a case of disproportionation reaction.

 $MnO_4^{2-} + H^+ \longrightarrow Mn^{2+} + MnO_4^-$ 

The balanced equation will be :  $5MnO_4^{2-} + 8H^+ \longrightarrow Mn^{2+} + 4MnO_4^- + 4H_2O$ 

# **Chapter Summary**

1. In a typical redox reaction :  $X + Y \longrightarrow A + B$ 

meq. of an oxidising agent = meq. of a reducing agent

2. From definition of gram-equivalents  $\left(\text{gmeq.} = \frac{g}{E} = NV_L\right)$ , it is very clear that, we

must be very confident about the concept of equivalent weight (E), for an oxidizing or reducing agent.

The equivalent weight of an oxidising or reducing agent is defined as :

Equivalent weight = E = 
$$\frac{M_0}{x}$$

where  $M_0$  = molecular mass; x = number of electrons transferred (loss or gain) by one mole of oxidising or reducing agent as given by their balanced ionic half reaction.

- **3. Variable equivalent weight :** Equivalent weight may be variable in many cases. it may depend upon the medium (acidic/basic); dilute/concentrated solution; whether a reagent is acting as an oxidant or reductant; whether a reagent is acting as an oxidant or an acid, whether a reagent is acting reductant or an acid.
- **4.** A reaction in which same atom is oxidised and reduced at the same time is called as a disproportionation reaction. And the equivalent weight of a compound undergoing disproportionation is :

 $E = \frac{Effective molecular weight of compound}{E}$ 

### Number of e<sup>-</sup> transfer

where Effective molecular weight

_ (	Total weight in		(Total weight in	
= (	Oxidation half reaction		Reduciton half reaction	

- 5. Volume strength is the volume of  $O_2$  given out at S.T.P. by 1 volume solution of  $H_2O_2$ . 1 M  $H_2O_2$  = 11.2 vol of  $O_2$  at STP or 1 N  $H_2O_2$  = 5.6 vol of  $O_2$
- 6. Avoid use of concept of meq in following cases. (Non-typical Redox reactions).
   (i) KMnO<sub>4</sub> + HCl → Cl<sub>2</sub> + MnCl<sub>2</sub> + KCl
  - (ii)  $KIO_3 + KI \longrightarrow I_2$
  - (iii)  $KMnO_4 \longrightarrow KMnO_4 + MnO_2$
- **7.** If a reagent (oxidant or reductant) shows different equivalent weights in two different redox reactions in a given problem then apply concept of meq carefully. In fact it is advised to use the mole concept in such cases.