# **Redox Reactions**

## **NCERT** FOCUS

## ANSWERS

### **TOPIC 1**

**1.** (a)  $\underset{CuO_{(s)}}{\overset{+2-2}{\overset{0}{\underset{(s)}{+}}}} \overset{0}{\overset{+1-2}{\underset{(s)}{+}}} \overset{0}{\overset{+1-2}{\underset{(s)}{+}}} \overset{+1-2}{\overset{+2-2}{\underset{(s)}{+}}}$ 

O.N. of Cu decreases from + 2 in CuO to 0 in Cu but that of H increases from 0 in  $H_2$  to + 1 in  $H_2$ O. Therefore, CuO is reduced to Cu but  $H_2$  is oxidised to  $H_2$ O. Thus, this is a redox reaction.

(b) 
$$\operatorname{Fe}_{2}^{+3} \operatorname{O}_{3(s)}^{+2} + \operatorname{3CO}_{(g)}^{+2} \to \operatorname{2Fe}_{(s)}^{0} + \operatorname{3CO}_{2(g)}^{+4}$$

O.N. of Fe decreases from +3 in  $Fe_2O_3$  to 0 in Fe while that of C increases from +2 in CO to +4 in  $CO_2$ . Therefore,  $Fe_2O_3$  is reduced and CO is oxidised. Thus, this is a redox reaction.

(c) 
$${}^{+3-1}_{4 \text{ BCl}_{3(g)}} + {}^{+1+3-1}_{4 \text{ IAI}} \rightarrow {}^{-3+1}_{2\text{ B}_2\text{ H}_{6(g)}} + {}^{+1-1}_{3 \text{ LiCl}_{(s)}} + {}^{+3-1}_{4 \text{ AICl}_{3(s)}}$$

O.N. of B decreases from +3 in  $BCl_3$  to -3 in  $B_2H_6$  while that of H increases from -1 in LiAlH<sub>4</sub> to + 1 in  $B_2H_6$ . Therefore,  $BCl_3$  is reduced while LiAlH<sub>4</sub> is oxidised. Thus, this is a redox reaction.

(d)  $2K_{(s)} + F_{2(g)} \rightarrow 2K^+F^-_{(s)}$ 

Each K atom has lost one electron to form  $K^+$  while  $F_2$  has gained two electrons to form two  $F^-$  ions. Therefore, K is oxidised while  $F_2$  is reduced. Thus, it is a redox reaction.

(e) 
$${}^{-3+1}_{4\mathrm{NH}_{3(g)}} + {}^{0}_{5\mathrm{O}_{2(g)}} \rightarrow {}^{+2-2}_{4\mathrm{NO}_{(g)}} + {}^{+1-2}_{6\mathrm{H}_{2}\mathrm{O}_{(g)}}$$

O.N. of N increases from -3 in NH<sub>3</sub> to +2 in NO while that of O decreases from 0 in O<sub>2</sub> to -2 in NO or H<sub>2</sub>O. Therefore, NH<sub>3</sub> is oxidised while O<sub>2</sub> is reduced. Thus, it is a redox reaction.

**2.** 
$$H_2^{+1}O^+ + F_2^{-1} \longrightarrow HF^{+1}HOF^{+1}$$

Since fluorine can undergo oxidation as well as reduction hence, it is an example of redox reaction.

**3.** In AgF<sub>2</sub> oxidation state of Ag is +2 which is very unstable. Therefore, it quickly, accepts an electron to form the more stable +1 oxidation state.

$$Ag^{2+} + e^- \rightarrow Ag^+$$

Therefore, AgF<sub>2</sub>, if formed, will act as a strong oxidising agent.

**4.** (i) C is a reducing agent while  $O_2$  is an oxidising agent. If excess of carbon is burnt in a limited supply of  $O_2$ , CO is formed in which oxidation state of C is +2 but when  $O_2$  is in excess CO formed gets oxidised to  $CO_2$  in which oxidation state of C is + 4

(a) 
$$2C_{(s)} + O_{2(g)} \longrightarrow 2CO_{(g)};$$
  
(Excess)

(b) 
$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$$
  
(Excess)

(ii)  $P_4$  is a reducing agent while  $Cl_2$  is an oxidising agent. When excess of  $P_4$  is used,  $PCl_3$  is formed in which the oxidation state of P is +3. When excess of  $Cl_2$  is used, the initially formed  $PCl_3$  reacts further to form  $PCl_5$  in which the oxidation state of P is +5.

(a) 
$$P_{4(s)} + 6Cl_{2(g)} \longrightarrow 4PCl_3$$
  
(Excess)

(b) 
$$P_{4(s)} + \frac{10Cl_{2(g)}}{(Excess)} \rightarrow 4PCl$$

(iii) Na is a reducing agent and  $O_2$  is an oxidising agent. When excess of Na is used, sodium oxide is formed in which the oxidation state of O is -2. If, excess of  $O_2$  is used,  $Na_2O_2$  is formed in which the oxidation state of O is -1.

(a) 
$$4Na_{(s)} + O_{2(g)} \longrightarrow 2Na_2^{-2}O_{(s)}$$

(b) 
$$2\operatorname{Na}_{(s)} + \operatorname{O}_{2(g)} \longrightarrow \operatorname{Na}_2 \operatorname{O}_{2(s)}^{-1}$$
  
(Excess)

5.

	Reducing agent (Substance oxidised)	Oxidising agent (Substance reduced)
(a)	$C_6H_6O_{2(aq)}$	AgBr <sub>(s)</sub>
(b)	HCHO <sub>(/)</sub>	$[Ag(NH_3)_2]^+_{(aq.)}$
(c)	HCHO <sub>(/)</sub>	Cu <sup>2+</sup> ( <i>aq</i> )
(d)	N <sub>2</sub> H <sub>4(/)</sub>	H <sub>2</sub> O <sub>2(/)</sub>
(e)	Pb <sub>(S)</sub>	PbO <sub>2(S)</sub>

6.  $XeO_{6(aq)}^{4-} + 2F_{(aq)}^{-} + 6H_{(aq)}^{+} \rightarrow XeO_{3(g)} + F_{2(g)} + 3H_2O_{(l)}$ In this reaction, O.N. of Xe decreases from +8 in  $XeO_6^{4-}$  to +6 in XeO<sub>3</sub> while that of F increases from -1 in F<sup>-</sup> to 0 in F<sub>2</sub>. Therefore,  $XeO_6^{4-}$  is reduced while F<sup>-</sup> is oxidised. From this reaction it is concluded that Na<sub>4</sub>XeO<sub>6</sub> is a stronger oxidising agent than F<sub>2</sub>.

**7.** Reactions (a) and (b) indicate that both AgNO<sub>3</sub> and CuSO<sub>4</sub> oxidise  $H_3PO_2$  to  $H_3PO_4$ . Hence, both are oxidising agents.

Reactions (c) and (d) suggest that  $[Ag(NH_3)_2]^+$  oxidises  $C_6H_5CHO$  (benzaldehyde) to  $C_6H_5COO^-$  (benzoate ion) but  $Cu^{2+}$  ions cannot oxidise  $C_6H_5CHO$  to  $C_6H_5COO^-$ . Therefore, from the above reactions, we infer that  $Ag^+$  ion is a stronger oxidising agent than  $Cu^{2+}$  ion.

#### **TOPIC 2**

1. Let the oxidation no. of underlined element in all the given compounds = x

(a)  $\begin{array}{c} +1 + 1 x -2 \\ NaH_2 PO_4 \end{array}$ 

Since the sum of oxidation number of various atoms in  $NaH_2PO_4$  (neutral) is zero.

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

$$x - 5 = 0$$
 or  $x = +5$ 

Thus, the oxidation number of P in  $NaH_2PO_4 = +5$ 

Thus, the oxidation number of S in  $NaHSO_4 = +6$ 

(c) 
$$\ln H_4 P_2 O_7 : 4(+1) + 2(x) + 7(-2) = 0$$
  
or  $x = +5$ 

Thus, the oxidation number of P in  $H_4P_2O_7 = +5$ 

(d) 
$$\ln K_2 \operatorname{MnO}_4^{-2} : 2(+1) + 1(x) + 4(-2) = 0$$
  
or  $x = +6$ 

Thus, the oxidation number of Mn in  $K_2MnO_4 = +6$ 

(e)  $\ln \operatorname{CaO}_2^2 : 2 + 2x = 0 \text{ or } x = -1$ 

Thus, the oxidation number of oxygen in  $CaO_2 = -1$ 

(f) In NaBH<sub>4</sub>, hydrogen is present as hydride ion. Therefore, its oxidation number is -1. Thus,

 $^{+1}x - 1$ In NaBH<sub>4</sub> : 1(+1) + x + 4(-1) = 0 or x = +3 Thus, the oxidation number of B in NaBH<sub>4</sub> = +3

(g)  $\ln H_2^{+1} S_2^{-2} O_7^{-2} : 2(+1)+2(x) + 7(-2) = 0$ or x = +6

Thus, the oxidation number of S in  $H_2S_2O_7 = +6$ 

(h) In K AI(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O :

 $+1 + 3 + 2x + 8(-2) + 12 \times 0 = 0$  or x = +6

Thus, the oxidation number of S in KAl(SO<sub>4</sub>)<sub>2</sub>.  $12H_2O = +6$ 

2. (a) In KI<sub>3</sub>, since the oxidation number of K is +1, therefore, the average oxidation number of iodine = -1/3. In the structure, K<sup>+</sup>[I – I ← I]<sup>-</sup>, a coordinate bond is formed between I<sub>2</sub> molecule and I<sup>-</sup> ion. The oxidation number of two iodine atoms forming

the  $I_2$  molecule is zero while that of iodine ion forming the coordinate bond is -1. Thus, the O.N. of three iodine atoms in KI<sub>3</sub> are 0, 0 and -1 respectively.

(b) The structure of  $H_2S_4O_6$  is shown below :

$$\begin{array}{c} & & O \\ H - O \stackrel{+5\parallel}{=} S - S - S - S - S - OH \\ & & & \\ O & & & \\ & & & \\ O & & & \\ \end{array}$$

The O.N. of each of the S atoms linked with each other in the middle is zero while that of each of the remaining two S-atoms is +5.

(c) 
$$Fe_3 O_4^{x -2}$$

Let O.N. of Fe = x, then 3x + 4(-2) = 0

or 
$$X = +\frac{8}{3}$$
 (average)  
By stoichiometry Fe<sub>2</sub>O<sub>4</sub> is Fe

By stoichiometry  $Fe_3O_4$  is  $Fe_3O_2 O_3^{+2-2} O_3^{+3-2}$ . Thus, Fe has O.N. of +2 and +3.

(d) 
$$H = \begin{bmatrix} H & H \\ 2^{l} & 1^{l} \\ H = C - C - OH \\ H & H \end{bmatrix}$$

In this molecule, C-2 is attached to three H-atoms (less electronegative than carbon) and one  $CH_2OH$  group (more electronegativity than carbon).

Therefore O.N. of C-2 = 3(+1) + x + 1(-1) = 0

or x = -2

C-1 is however, attached to one OH (charge = -1) and one CH<sub>3</sub> (charge = +1), and two H-atoms, O.N. of +1.

Therefore, O.N. of C-1 = 1(+1) + 2(+1) + x + 1(-1) = 0 or x = -2

(e) 
$$H = C - C - OH = H$$

In this molecule, C-2 is attached to three H-atoms (less electronegative than carbon) and one -COOH group (more electronegativity than carbon).

Therefore, O.N. of C-2 = 3(+1) + x + 1(-1) = 0

C-1 is, however, attached to one oxygen atom by a double bond, one OH (charge = -1) and one CH<sub>3</sub> (charge = +1) group, therefore, O.N. of C-1 = 1 (+1) + x + 1 (-2) + 1 (-1) = 0 or x = +2

#### 3. Oxidation number of sulphur in H<sub>2</sub>SO<sub>5</sub>:

Let the oxidation number of S = x

then  $(+1) \times 2 + x + (-2) \times 5 = 0$  or 2 + x - 10 = 0

$$\Rightarrow x - 8 = 0$$

 $\therefore X = +8$ 

The maximum O.N. of S cannot be more than 6 since it has only 6 electrons in the valence shell. This fallacy is overcome if we calculate the O.N. of sulphur by chemical bonding method. The structure of  $H_2SO_5$  is

It has two peroxide oxygen with O.N. = -1 and three oxygens with O.N. = -2

Thus,  $2 \times (+1) + x + 2(-1) + 3 \times (-2) = 0$ +  $2 + x - 2 - 6 = 0 \implies x - 6 = 0 \implies x = +6$ Thus,  $2 \ge 0$  of subcharging  $||| \le 0$  and x = +6

Thus, O.N. of sulphur in  $H_2SO_5 = +6$ 

#### Oxidtion number of chromium in $Cr_2O_7^{2-}$ :

Let the oxidation number of chromium = x

- $\therefore \quad 2x + 7(-2) = -2 \quad \Longrightarrow \quad 2x 14 = -2$
- $\Rightarrow 2x = -2 + 14$
- $\Rightarrow$  2x = + 12  $\Rightarrow$  x = + 6

Thus, the oxidation number of chromium = + 6

#### Oxidation number of nitrogen in $NO_3^-$ :

Let the oxidation number of nitrogen = xthen  $x + (-2) \times 3 = -1 \implies x - 6 = -1$  $\implies x = -1 + 6 \implies x = + 5$ Thus, the oxidation number of nitrogen = + 5

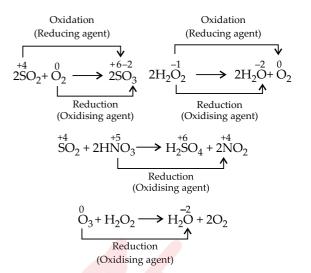
4.	(a) HgCl <sub>2</sub>	(b)	NiSO <sub>4</sub>
(c)	SnO <sub>2</sub>	(d)	Tl <sub>2</sub> SO <sub>4</sub>
(e)	$Fe_2(SO_4)_3$	(f)	$Cr_2O_3$

#### 5.

Compound	O.N. of Carbon	Compound	O.N. of Nitrogen
CH <sub>4</sub>	-4	NH <sub>3</sub> , NH <sub>4</sub> Cl	-3
$CH_3 - CH_3$	-3	$NH_2 - NH_2$	-2
$CH_2 = CH_2$ or $CH_3CI$	-2	NH <del>==</del> NH, NH <sub>2</sub> OH	-1
СНЩСН	-1	N=N	0
C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>	0	N <sub>2</sub> O	+1
C <sub>6</sub> Cl <sub>6</sub>	+1	NO	+2
CHCl <sub>3</sub>	+2	N <sub>2</sub> O <sub>3</sub> , HNO <sub>2</sub>	+3
(COOH) <sub>2</sub>	+3	N <sub>2</sub> O <sub>4</sub>	+4
CCl <sub>4</sub> , CO <sub>2</sub>	+4	N <sub>2</sub> O <sub>5</sub> , HNO <sub>3</sub>	+5

**6.** The oxidation state of sulphur in sulphur dioxide is +4. It can be oxidised to +6 oxidation state or reduced to +2. Therefore, sulphur dioxide acts as a reducing agent as well as oxidising agent. Similarly, the oxidation state of oxygen in hydrogen peroxide is -1. It can be oxidised to  $O_2$  (zero oxidation state) or reduced to  $H_2O$  or  $OH^-$  (-2 oxidation state) and therefore, acts as reducing as well as oxidising agents.

However, both ozone and nitric acid can only decrease their oxidation number and therefore, act only as oxidising agents.



7. (a) Most accepted mechanism of photosynthesis is supposed to occur in two steps. In the first step,  $H_2O$  decomposes to give  $H_2$  and  $O_2$  in presence of chlorophyll and the  $H_2$  thus produced reduces  $CO_2$  to  $C_6H_{12}O_6$  and  $H_2O$  molecules are also produced as shown below :

$$12H_2O_{(l)} \rightarrow 12H_{2(g)} + 6O_{2(g)}$$
 ... (i)

$$6CO_{2(g)} + 12H_{2(g)} \rightarrow C_6H_{12}O_{6(s)} + 6H_2O_{(l)} \qquad \dots (ii)$$

$$6CO_{2(g)} + 12H_2O_{(l)} \rightarrow C_6H_{12}O_{6(s)} + 6H_2O_{(l)} + 6O_{2(g)} \dots (iii)$$

Therefore, it is more appropriate to write the equation for photosynthesis as (iii) because it emphasises that 12 molecules of  $H_2O$  are used per molecule of carbohydrate formed and 6 molecules of  $H_2O$  are produced during the process.

(b) The purpose of writing  $O_2$  two times suggests that  $O_2$  is being obtained from each of the two reactants.

$$\begin{array}{c} O_{3(g)} \longrightarrow O_{2(g)} + O_{(g)} \\ H_2O_{2(g)} + O_{(g)} \longrightarrow H_2O_{(l)} + O_{2(g)} \\ \hline O_{3(g)} + H_2O_{2(l)} \longrightarrow H_2O_{(l)} + O_{2(g)} + O_{2(g)} \end{array}$$

The path of reactions (a) and (b) can be determined by tracer technique method using labelled H or O,  $H_2O^{18}$  or  $D_2O$  in reaction (a) or by using  $H_2O_2^{18}$  or  $O_3^{18}$  in reaction (b).

**8.** (a) In neutral medium,  $KMnO_4$  acts as an oxidant as follows :

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

In laboratory, alkaline  $KMnO_4$  is used to oxidise toluene to benzoic acid.

$$\underbrace{\bigcirc}_{\text{Tolugne}}^{\text{CH}_3} + 2\text{MnO}_{4(aq.)}^- \rightarrow \underbrace{\bigcirc}_{\text{H}_2\text{O}}^+ + \text{H}_2\text{O} + 2\text{MnO}_2 + \text{OH}_{(aq.)}^-$$

In industry alcoholic  ${\rm KMnO}_4$  is preferred due to following reasons :

1. Cost of adding a base or an acid is avoided as a base  $(OH^{-} \text{ ions})$  is produced during the reaction itself.

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An organic polar solvent, ethyl alcohol, helps in mixing 2. of two reactants KMnO<sub>4</sub> (due to its polar nature) and toluene (because, an organic compound).

(b) When a chloride such as NaCl is heated with conc.  $H_2SO_4$ , HCl is evolved which is not a good reducing agent and is not oxidised with conc.  $H_2SO_4$ .

$$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HC$$

But when NaBr is heated with conc. H<sub>2</sub>SO<sub>4</sub>, HBr produced being a good reducing agent is oxidised by conc.  $H_2SO_4$  to give Br<sub>2</sub> (red vapours).

$$\begin{array}{l} H_2 SO_{4(aq)} \xrightarrow{\text{heat}} SO_{2(g)} + H_2 O_{(l)} + [O] \\ NaBr_{(s)} + H_2 SO_{4(aq)} \xrightarrow{\text{heat}} NaHSO_{4(aq)} + HBr_{(g)} \\ 2HBr_{(g)} + [O] \longrightarrow H_2 O_{(l)} + Br_{2(g)} \end{array}$$

9. The average O.N. of S in  $S_2O_3^{2-}$  is +2 while in  $S_4O_6^{2-}$  it is +2.5. The O.N. of S in  $SO_4^{2-}$  is +6. Since Br<sub>2</sub> is a stronger oxidising agent, it oxidises S of  $S_2O_3^{2-}$  to a higher oxidation state of +6 and hence forms  $SO_4^{2-}$  ion. I<sub>2</sub>, however, being a weaker oxidising agent oxidises S of  $S_2O_3^{2-}$  ion to a lower oxidation state of + 2.5 in  $S_4O_6^{2-}$  ion.

**10.** The halogens  $(X_2)$  have strong electron accepting tendency and have positive standard oxidation potential values. They are therefore, powerful oxidising agents. The decreasing order of oxidising powers of halogens is :

 $X_2: F_2 > Cl_2 > Br_2 > l_2$  $E^\circ: +2.87V +1.36V +1.09V +0.54V$ 

Fluorine is the strongest oxidising agent (oxidant) because it can liberate the other halogens from their respective compounds. For example,

 $2\text{KCI} + \text{F}_2 \longrightarrow 2\text{KF} + \text{CI}_2$  $2KBr + F_2 \longrightarrow 2KF + Br_2$  $2KI + F_2 \longrightarrow 2KF + I_2$ 

Among halogen acids (HX), the HI is the strongest reducing agent or reductant because it has minimum bond dissociation energy.

Halogen acid : HF HCI HBr HI Bond dissociation : 566 431 366 299 enthalpy (kJ mol<sup>-1</sup>)

The iodination of methane is of reversible nature because HI produced in the reaction being a reducing agent converts iodomethane back to methane.

$$CH_4 + I_2 \longrightarrow CH_3I + HI$$

$$CH_3I + HI \longrightarrow CH_4 + I_2$$
Net reaction : 
$$CH_4 + I_2 \implies CH_3I + HI$$

**11.** (a) The skeleton equation is :

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

The O.N. of the atoms involved in the equation is : (i)

$$\overset{+7}{\text{MnO}_4^-} \overset{-2}{+} \overset{-1}{\text{I}^-} \overset{+4}{\longrightarrow} \overset{-2}{\text{MnO}_2^-} \overset{0}{+} \overset{0}{\text{I}_2}$$

(ii) The species involved in the oxidation and reduction half reaction : Increase in O.N. (Oxidation)

$$\stackrel{+7}{\text{MnO}_{4}^{-}} + \stackrel{-1}{\text{I}^{-}} \longrightarrow \stackrel{+4}{\text{MnO}_{2}} \stackrel{0}{\text{MnO}_{2}} + \stackrel{1}{\text{I}_{2}}$$

$$\stackrel{(-3)}{\square}$$
Decrease in O.N. (reduction)

(iii) Oxidation half reaction :  $I^- \longrightarrow I_2$ 

Reduction half reaction :  $MnO_4^- \longrightarrow MnO_2$ 

- (iv) Balancing the oxidation half reaction  $2l^- \longrightarrow l_2 + 2e^-$ ...(i)
- (v) Balancing the reduction half reaction

(1) As the decrease in O.N. is 3, therefore, adding  $3e^-$  on the reactant side

$$MnO_4^- + 3e^- \longrightarrow MnO_2$$

(2) To balance the oxygen atoms, add two H<sub>2</sub>O molecules on the product side

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

(3) To balance the charges, add 4 OH<sup>-</sup> on the product side. Then to balance H atoms, add four H<sub>2</sub>O molecules on the reactant side.

(vi) Adding the two half reactions

In order to equate the electrons, multiply eqn. (i) by 3 and eqn. (ii) by 2. Add the two equations.

$$[21^{-} \longrightarrow I_{2} + 2e^{-}] \times 3$$

$$[MnO_{4}^{-} + 3e^{-} + 2H_{2}O \longrightarrow MnO_{2} + 4OH^{-}] \times 2$$

$$2MnO_{4}^{-} + 6I^{-} + 4H_{2}O \longrightarrow 3I_{2} + 2MnO_{2} + 8OH^{-}$$
or
$$2MnO_{4}^{-}(aq) + 6I^{-}(aq) + 4H_{2}O_{(l)} \longrightarrow 3I_{2(s)} + 2MnO_{2(s)} + 8OH^{-}_{(aq)}$$
(b) The skeleton equation is:

(b) The skeleton equation is :

$$MnO_{4(aq)}^{-} + SO_{2(g)} \longrightarrow Mn_{(aq)}^{2+} + HSO_{4(aq)}^{-}$$

(i) The O.N. of atoms involved in the equation is :

 $\stackrel{+7}{\text{MnO}_4^-} \stackrel{+4}{+} \stackrel{-2}{\text{SO}_2} \xrightarrow{+2} \stackrel{+2}{\text{Mn}^{2+}} \stackrel{+1+6-2}{+} \stackrel{+2}{\text{HSO}_4^-}$ 

(ii) The species involved in the oxidation and reduction half reactions : \_ \_ \_ \_ \_

Increase in O.N. (Oxidation)  

$$(+2)$$
  
 $+7$   
 $MnO_4^- + SO_2 \longrightarrow Mn^{2+} + HSO_4^-$   
 $(-5)$   
Decrease in O.N. (reduction)

(iii) Oxidation half reaction :  $SO_2 \longrightarrow HSO_4^-$ Reduction half reaction :  $MnO_4^- \longrightarrow Mn^{2+}$ 

- (iv) Balancing the oxidation half reaction
- (1) As the increase in O.N. is 2, therefore, add two electrons on the product side to balance change in O.N.

$$50_2 \longrightarrow HSO_4^- + 2e^2$$

(2) In order to balance the number of oxygen atoms, add two  $H_2O$  molecules on the reactant side and then to balance H atoms add  $3H^+$  on the product side.

$$SO_2 + 2H_2O \longrightarrow HSO_4^- + 3H^+ + 2e^- \qquad \dots (i)$$

(v) Balancing the reduction half reaction

The reduction half reaction is :

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

(1) As the decrease in O.N. is 5, therefore add  $5e^-$  on the reactant side,

$$MnO_4^- + 5e^- \longrightarrow Mn^{2+}$$

(2) In order to balance the no. of oxygen atoms, add four  $H_2O$  molecules on the product side and then to balance H atoms add 8 H<sup>+</sup> on the reactant side.

$$MnO_{4}^{-} + 8H^{+} + 5e^{-} \longrightarrow Mn^{2+} + 4H_{2}O \qquad \dots (ii)$$

(vi) Adding the two half, reactions

In order to equate the electrons, multiply eqn. (i) by 5 and eqn. (ii) by 2. Add the two eqns.

$$[SO_2 + 2H_2O \longrightarrow HSO_4^- + 3H^+ + 2e^-] \times 5 
[MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O] \times 2 
2MnO_4^-(aq) + 5SO_2(g) + 2H_2O_{(l)} + H^+_{(aq)} \longrightarrow 5HSO_4^-(aq) + 2Mn^{2+}_{(aq)}$$

(c) Oxidation half equation :  $Fe_{(aq)}^{2+} \longrightarrow Fe_{(aq)}^{3+} + e^{-}$ 

Reduction half equation :  $H_{-}O_{-} + 2H^{+} + 2e^{-}$ 

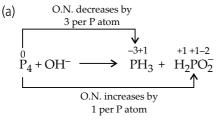
$$H_2 U_{2(aq)} + 2Fe_{(aq)} + 2H_{(aq)} \longrightarrow 2Fe_{(aq)} + 2H_2 U_{(aq)}$$

(d) Oxidation half equation :  $SO_{2(g)} + 2H_2O_{(f)} \longrightarrow SO_4^{2-}(aq) + 4H_{(aq)}^+ + 2e^-$  ...(i) Reduction half equation :

 $\operatorname{Cr}_2\operatorname{O}_{7(aq)}^{2-} + 14\operatorname{H}_{(aq)}^+ + 6e^- \longrightarrow 2\operatorname{Cr}_{(aq)}^{3+} + 7\operatorname{H}_2\operatorname{O}_{(l)} \quad \dots \text{(ii)}$ Multiplying eqn. (i) by 3 and adding to eqn. (ii) we get,

$$Cr_2O_7^{2-}_{(aq)} + 3SO_{2(g)} + 2H^+_{(aq)} \longrightarrow 2Cr^{3+}_{(aq)} + 3SO_4^{2-}_{(aq)} + H_2O_{(f)}$$

#### 12. Oxidation number method :



Total increase in O.N. of P from  $P_4$  to  $H_2PO_2^- = 1 \times 4 = 4$ Total decrease in O.N. of P from  $P_4$  to  $PH_3 = 3 \times 4 = 12$ 

Therefore, to balance increase/decrease in O.N. multiply PH<sub>3</sub>

by 1 and  $H_2PO_2^-$  by 3, we have

 $\mathsf{P}_{4(s)} \longrightarrow \mathsf{PH}_{3(g)} + \mathsf{3H}_2\mathsf{PO}_{2(aq)}^-$ 

To balance O atoms, add  $60H^-$  on the left side

 $P_{4(s)} + 6OH_{(aq)}^{-} \longrightarrow PH_{3(g)} + 3H_2PO_{2(aq)}^{-}$ To balance H atoms, add  $3H_2O$  to L.H.S. and  $3OH^{-}$  to the R.H.S.  $P_{4(s)} + 6OH_{(aq)}^{-} + 3H_2O_{(l)}^{-} \longrightarrow PH_{3(g)} + 3H_2PO_{2(aq)}^{-} + 3OH_{(aq)}^{-}$ or,  $P_{4(s)} + 3OH_{(aq)}^{-} + 3H_2O_{(l)}^{-} \longrightarrow PH_{3(g)} + 3H_2PO_{2(aq)}^{-}$ Ion electron method : The two half reactions are :

Oxidation half reaction :

$$P_{4(s)} + 8OH_{(aq)}^{-} \longrightarrow 4H_2PO_{2(aq)}^{-} + 4e^{-}$$
 ... (i)  
Reduction half reaction :

 $P_{4(s)} + 12H_2O_{(l)} + 12e^- \longrightarrow 4PH_{3(g)} + 12OH_{(aq)} \qquad \dots (ii)$ Multiply eq. (i) by 3 and add it to eq. (ii), we get

 $4P_{4(s)} + 24OH_{\overline{(aq)}} + 12H_2O_{(l)} \longrightarrow 4PH_{3(g)} + 12H_2PO_{\overline{2}(aq)} + 12OH_{\overline{(aq)}}$ 

or,  $P_{4(s)} + 3OH_{(aq)}^{-} + 3H_2O_{(l)} \longrightarrow PH_{3(g)} + 3H_2PO_{2(aq)}^{-}$ Reductant - phosphorus; oxidant-phosphorus (b) N H =  $1 CIO^{-}$  (CIC - 1)

$$(D) \qquad \mathsf{N}_2\mathsf{H}_{4(I)} + \mathsf{CIO}_{3(aq)} \longrightarrow \mathsf{NO}_{(g)} + \mathsf{CI}_{(aq)}$$

Oxidation number method :

$$^{-2}$$
  $^{+5}$   $^{+2}$   $^{-1}$   $^{-1}$   $^{-1}$   $^{-1}$   $^{-1}$ 

Net reaction is

. (i)

$$6N_2H_4 + 8CIO_3^- \longrightarrow 12NO + 8CI^- + 12H_2O$$
$$3N_2H_4 + 4CIO_3^- \longrightarrow 6NO + 4CI^- + 6H_2O$$

#### Ion-electron method :

Oxidation half-reaction :

 $[N_2H_4 + 80H^- \longrightarrow 2NO + 8e^- + 6H_2O] \times 6$ Reduction half-reaction :

$$[\mathsf{CIO}_3^- + 6e^- + 3\mathsf{H}_2\mathsf{O} \longrightarrow \mathsf{CI}^- + 6\mathsf{OH}^-] \times 8$$

Net reaction is

$$6N_2H_4 + 8CIO_3^- \longrightarrow 12NO + 8CI^- + 12H_2O$$

$$3N_2H_4 + 4CIO_3^- \longrightarrow 6NO + 4CI^- + 6H_2O$$

Reductant :  $N_2H_4$ ; Oxidant :  $CIO_3^-$ 

(c)  $Cl_2O_{7(g)} + H_2O_{2(aq)} \longrightarrow ClO_{2(aq)} + O_{2(g)} + H_{(aq)}^+$ Oxidation number method :

$$\overset{8e^{-}}{\underset{l_2O_7}{\overset{+7}{\underset{l_2O_2}{\overset{-1}{\underset{l_2O_2}{\overset{+3}{\atop\\+3}{\atop\\+3}}}}}}}}}}}}}}}}}}}}}$$

Net reaction is

$$Cl_2O_7 + 4H_2O_2 + 20H^- \longrightarrow 2ClO_2^- + 5H_2O_2 + 4O_2$$

#### MtG100PERCENT Chemistry Class-11

Ion-electron method :

Oxidation half-reaction :  $[H_2O_2 + 2OH^- \longrightarrow O_2 + 2e^- + 2H_2O] \times 4$ Reduction half-reaction :  $CI_2O_7 + 8e^- + 3H_2O \longrightarrow 2CIO_2^- + 6OH^-$ Net reaction is

 $\begin{array}{l} \mathsf{Cl}_2\mathsf{O}_7 + 4\mathsf{H}_2\mathsf{O}_2 + 2\mathsf{O}\mathsf{H}^- \longrightarrow 2\mathsf{Cl}\mathsf{O}_2^- + 5\mathsf{H}_2\mathsf{O} + 4\mathsf{O}_2\\ \mathsf{Reductant}: \mathsf{H}_2\mathsf{O}_2; \qquad \mathsf{Oxidant}: \mathsf{Cl}_2\mathsf{O}_7 \end{array}$ 

**13.** Let *x* be the oxidation number of C.

 $\therefore$  0.N. of C in cyanogen,  $(CN)_2 = 2(x - 3) = 0$ 

or *x* = +3

O.N. of C in cyanide ion,  $CN^- = x - 3 = -1$ 

or *x* = +2

O.N. of C in cyanate ion,  $CNO^- = x - 3 - 2 = -1$ 

or *x* = +4

The four informations about the reaction are :

(i) The reaction involves decomposition of cyanogen,  $(CN)_2$  in the alkaline medium to cyanide ion,  $CN^-$  and cyanate ion,  $CNO^-$ .

(ii) The O.N. of C decreases from +3 in  $(CN)_2$  to +2 in  $CN^-$  ion and increases from +3 in  $(CN)_2$  to +4 in  $CNO^-$  ion. Thus, cyanogen is simultaneously reduced to cyanide ion and oxidised to cyanate ion.

(iii) It is an example of disproportionation redox reaction.

(iv) Cyanogen is a pseudohalogen while cyanide ion is a pseudohalide ion.

14. The skeletal equation is :

 $Mn^{3+}_{(aq)} \longrightarrow Mn^{2+}_{(aq)} + MnO_{2(s)} + H^+_{(aq)}$ Oxidation half equation :

$$Mn^{3+}_{(aq)} \longrightarrow MnO_{2(s)}$$

or,  $\operatorname{Mn}_{(aq)}^{+3} + 2\operatorname{H}_2\operatorname{O}_{(l)} \longrightarrow \operatorname{MnO}_{2(s)} + 4\operatorname{H}_{(aq)}^+ + e^-$ 

Reduction half equation :  $Mn^{3+}_{(aq)} \longrightarrow Mn^{2+}_{(aq)}$ 

or, 
$$\operatorname{Mn}^{3+}_{(aq)} + e^{-} \longrightarrow \operatorname{Mn}^{2+}_{(aq)}$$
 ...(ii)

Adding Eq. (i) and Eq. (ii), the balanced equation for the disproportionation reaction is

 $2\mathsf{Mn}^{3+}_{(aq)} + 2\mathsf{H}_2\mathsf{O}_{(l)} \longrightarrow \mathsf{MnO}_{2(s)} + \mathsf{Mn}^{2+}_{(aq)} + 4\mathsf{H}^+_{(aq)}$ 

**15.** (a) F : Fluorine is the most electronegative element and shows only -1 oxidation state.

(b) Cs : Because of the presence of single electron in the valence shell, (alkali metals) Cs exhibits an oxidation state of +1 only.

(c) I : Because of the presence of seven electrons in the valence shell, I shows an oxidation state of -1 in compounds with more electropositive elements (such as H, Na, K, Ca, etc.)

and oxidation states of +3, +5, +7 in compounds of I with more electronegative elements (such as, O, F, etc.)

(d) Ne : It is an inert gas (with high ionization enthalpy and highly positive electron gain enthalpy) and hence, it exhibits neither negative nor positive oxidation states.

**16.** The skeletal equation is :

$$Cl_{2(g)} + SO_{2(g)} + H_2O_{(l)} \longrightarrow Cl^{-}_{(aq)} + SO_4^{2-}_{(aq)}$$
  
Reduction half equation :

$$Cl_{2(g)} + 2e^- \longrightarrow 2Cl_{(aq)}^- \qquad \dots (i)$$

Oxidation half equation :

 $SO_{2(g)} + 2H_2O_{(l)} \longrightarrow SO_{4(aq)}^{2-} + 4H_{(aq)}^+ + 2e^-$  ...(ii) Adding Eq. (i) and Eq. (ii), we get,

 $Cl_{2(g)} + SO_{2(g)} + 2H_2O_{(j)} \longrightarrow 2Cl_{(aq)}^- + SO_{4(aq)}^2 + 4H_{(aq)}^+$ This represents the balanced redox reaction.

**17.** (a) The non-metals which show disproportionation reaction are N, P, S, Cl, Br and I.

(i)  $P_{4(s)} + 3OH_{(aq)}^{-} + 3H_2O_{(l)} \longrightarrow PH_{3(g)} + 3H_2PO_{2(aq)}^{-}$ 

(ii) 
$$S_{8(s)} + 120H_{(aq)} \longrightarrow 4S_{(aq)}^{2-} + 2S_2O_3^{2-} + 6H_2O_{(f)}$$

(iii) 
$$Cl_{2(q)} + 2OH_{(aq)} \longrightarrow Cl_{(aq)} + CIO_{(aq)} + H_2O_{(l)}$$

Bromine and iodine give similar reactions as chlorine.

(b) The metals which undergo disproportionation reaction are :

(

...(i)

(i) 
$$2Cu_{(aq)}^+ \longrightarrow Cu_{(aq)}^{2+} + Cu_{(s)}$$

ii) 
$$3Ga^+_{(aq)} \longrightarrow Ga^{3+}_{(aq)} + 2Ga_{(s)}$$

(iii)  $3\ln^+_{(aq)} \longrightarrow \ln^{3+}_{(aq)} + 2\ln_{(s)}$ 

18. The reaction involved in the manufacturing process is :

 $\therefore$  68 g of NH<sub>3</sub> will react with 160 g of O<sub>2</sub> to produce 120 g of NO<sub>(*a*)</sub>

But oxygen which is actually available (20.0 g) is less than the amount which is required. Therefore, oxygen is the limiting reactant.

Now 160 g of  $O_2$  will form NO = 120 g

:. 20 g of O<sub>2</sub> will form NO = 
$$\frac{(120)}{(160)} \times (20) = 15$$
 g

#### **TOPIC 3**

1. (a) The possible reaction between  $\operatorname{Fe}_{(aq)}^{3+}$  and  $\operatorname{I}_{(aq)}^{-}$  is  $2\operatorname{Fe}_{(aq)}^{3+} + 2\operatorname{I}_{(aq)}^{-} \longrightarrow 2\operatorname{Fe}_{(aq)}^{2+} + \operatorname{I}_{2(s)}$ 

The above redox reaction can be split into the following two half reactions,

#### **Oxidation**:

$$2I_{(aq)}^{-} \longrightarrow I_{2(s)} + 2e^{-}; E_{oxi}^{\circ} = -0.54 \text{ V}$$
 ...(i)

#### **Reduction** :

 $[\operatorname{Fe}_{(aq)}^{3+} + e^{-} \longrightarrow \operatorname{Fe}_{(aq)}^{2+}] \times 2; E_{\operatorname{red}}^{\circ} = +0.77 \text{ V} \qquad \dots \text{(ii)}$ 

### Overall reaction :

 $2Fe^{3+}_{(aq)} + 2I^{-}_{(aq)} \longrightarrow 2Fe^{2+}_{(aq)} + I_{2(s)}; E^{\circ} = + 0.23 V$ Since the EMF for the above reaction is positive, therefore, the

above reaction is feasible.

(b) The possible reaction between  $Ag^+_{(aq)}$  and  $Cu_{(s)}$  is

 $Cu_{(s)} + 2Ag^+_{(aq)} \longrightarrow Cu^{2+}_{(aq)} + 2Ag_{(s)}$ 

The above redox reaction can be split into the following two half reactions,

#### Oxidation :

 $Cu_{(s)} \longrightarrow Cu_{(aq)}^{2+} + 2e^{-} ; E_{oxi}^{\circ} = -0.34 V$ **Reduction :** 

 $[\operatorname{Ag}_{(aq)}^{+} + e^{-} \longrightarrow \operatorname{Ag}_{(s)}] \times 2 \quad ; \quad E_{\operatorname{red}}^{\circ} = + \ 0.80 \ V$ 

#### Overall reaction :

 $Cu_{(s)} + 2Ag^+_{(aq)} \longrightarrow Cu^{2+}_{(aq)} + 2Ag_{(s)}; E^\circ = + 0.46 V$ 

Since the EMF for the above reaction comes out to be positive, therefore, the above reaction is feasible.

(c) There are two probabilities for reaction between Cu and  $Fe^{3+}$ . The reaction between  $Fe^{3+}_{(aq)}$  and  $Cu_{(s)}$  occurs according to the following equation :

(i)  $Cu_{(s)} + 2Fe^{3+}_{(aq)} \longrightarrow Cu^{2+}_{(aq)} + 2Fe^{2+}_{(aq)}$ The above reaction can be split into the following two half reactions,

#### Oxidation :

 $Cu_{(s)} \longrightarrow Cu_{(aq)}^{2+} + 2e^-$ ;  $E_{oxi}^{\circ} = -0.34 \text{ V}$ Reduction :

 $[\operatorname{Fe}_{(aq)}^{3+} + e^{-} \longrightarrow \operatorname{Fe}_{(aq)}^{2+}] \times 2 ; E_{\operatorname{red}}^{\circ} = +0.77 \,\mathrm{V}$ 

#### **Overall reaction :**

 $Cu_{(s)} + 2Fe_{(aq)}^{3+} \longrightarrow Cu_{(aq)}^{2+} + 2Fe_{(aq)}^{2+}$ ;  $E^{\circ} = + 0.43$  V

Since the EMF for the above reaction is positive, therefore, the above reaction is feasible.

(ii) If the reaction between  $Fe_{(aq)}^{3+}$  and  $Cu_{(s)}$  occurs according to the following equation,

 $3Cu_{(s)} + 2Fe_{(aq)}^{3+} \longrightarrow 3Cu_{(aq)}^{2+} + 2Fe_{(s)}$ 

The EMF of the reaction comes out to be negative, *i.e.*, -0.376 V(-0.34 V -0.036 V) and hence, this reaction is not feasible. (d) There are two possibilities for reaction between Ag and Fe<sup>3+</sup> ion.

(i) If the reaction occurs by following equation,

$$Ag_{(s)} + Fe_{(aq)}^{3+} \longrightarrow Ag_{(aq)}^{+} + Fe_{(aq)}^{2+}$$

The reaction can be split into the following two half reactions, **Oxidation :** 

$$Ag_{(s)} \longrightarrow Ag^+_{(aq)} + e^-$$
;  $E^{\circ}_{oxi} = -0.80 V$ 

Reduction :

$$\operatorname{Fe}_{(aq)}^{3+} + e^{-} \longrightarrow \operatorname{Fe}_{(aq)}^{2+}$$
;  $E_{\mathrm{red}}^{\circ} = + 0.77 \,\mathrm{V}$ 

#### **Overall reaction :**

 $Ag_{(s)} + Fe^{3+}_{(aq)} \longrightarrow Ag^+_{(aq)} + Fe^{2+}_{(aq)}$ ;  $E^\circ = -0.03 \text{ V}$ 

Since the EMF for the above reaction is negative, therefore, the above reaction is not feasible.

(ii) The reaction between  $Ag_{(s)}$  and  $Fe_{(aq)}^{3+}$  may occur according to the following equation,

 $3Ag_{(s)} + Fe_{(aq)}^{3+} \longrightarrow 3Ag_{(aq)}^{+} + Fe_{(s)}$ 

EMF of this reaction comes to be even more negative *i.e.*, -0.836 V, and hence this redox reaction is also not feasible.

(e) The reaction between  $Br_{2(aq)}$  and  $Fe_{(aq)}^{2+}$  occurs according to the following equation :

$$Br_{2(aq)} + 2Fe_{(aq)}^{2+} \longrightarrow 2Br_{(aq)}^{-} + 2Fe_{(aq)}^{3+}$$

The above reaction can be split into the following two half reactions.

Oxidation :

$$[Fe_{(aq)}^{2+} \longrightarrow Fe_{(aq)}^{3+} + e^{-}] \times 2 ; E_{oxi}^{\circ} = -0.77 V$$

Reduction :

$$Br_{2(aq)} + 2e^- \longrightarrow 2Br_{(aq)}^-$$
;  $E_{red}^\circ = + 1.09 V$ 

Overall reaction :

 $2Fe_{(aq)}^{2+} + Br_{2(aq)} \longrightarrow 2Fe_{(aq)}^{3+} + 2Br_{(aq)}^{-}$ ;  $E^{\circ} = + 0.32 V$ 

Since the EMF for the above reaction is positive, therefore, the above reaction is feasible.

**2.** (i) In aqueous solution, AgNO<sub>3</sub> ionises to give Ag<sup>+</sup><sub>(aq)</sub> and NO<sup>-</sup><sub>3(aq)</sub> ions.

 $AgNO_{3(aq)} \longrightarrow Ag^{+}_{(aq)} + NO^{-}_{3(aq)}$ 

Thus, when electricity is passed  $Ag^+_{(aq)}$  ions move towards the cathode while  $NO_3^-$  ions move towards the anode.

$$Ag^{+}_{(aq)} + e^{-} \longrightarrow Ag_{(s)} ; E^{\circ} = + 0.80 V \qquad ...(i)$$

$$2H_2O_{(l)} + 2e^- \longrightarrow H_{2(g)} + 2OH_{(aq)}^-$$
;  $E^\circ = -0.83 V$  ...(ii)

Since the electrode potential (*i.e.*, reduction potential of  $Ag^+_{(aq)}$  ions is higher than that of  $H_2O$  molecules, therefore, at the cathode,  $Ag^+_{(aq)}$  ions (rather than  $H_2O$  molecules) are reduced. Similarly, at the anode, either Aq metal of the anode or  $H_2O$ 

molecules may be oxidised. Their electrode potentials are :

$$Ag_{(s)} \longrightarrow Ag^{+}_{(aq)} + e^{-}; \quad E^{\circ} = -0.80 V \qquad ...(iii)$$

$$2H_2O_{(l)} \longrightarrow O_{2(g)} + 4H_{(aq)}^+ + 4e^-; \quad E^\circ = -1.23 V \qquad \dots (iv)$$

Since the oxidation potential of Ag is much higher than that of  $H_2O$  therefore, at the anode, Ag of the silver anode gets oxidised and not the  $H_2O$  molecules. It may, however, be mentioned here that the oxidation potential of  $NO_3^-$  ions is even lower than that of  $H_2O$  since more bonds are to be broken during reduction of  $NO_3^-$  ions than those in  $H_2O$ .

Thus, when an aqueous solution of  $AgNO_3$  is electrolysed, Ag from Ag anode dissolves while  $Ag^+_{(aq)}$  ions present in the solution gets reduced and gets deposited on the cathode.

(ii) When electrolysis of AgNO<sub>3</sub> solution is carried out using platinum electrodes, instead of silver electrodes, oxidation of water occurs at the anode since Pt being a noble metal does

not undergo oxidation easily. As a result,  $O_2$  is liberated at the anode according to equation (iv).

(iii) In aqueous solution,  $H_2SO_4$  ionises to give  $H^+_{(aq)}$  and  $SO^{2-}_{4(aq)}$  ions.

 $H_2SO_{4(aq)} \longrightarrow 2H^+_{(aq)} + SO^{2-}_{4(aq)}$ 

Thus, when electricity is passed,  $H^+_{(aq)}$  ions move towards cathode while  $SO_4^{2-}_{(aq)}$  ions move towards anode.

$$\begin{array}{l} 2\mathsf{H}^+_{(aq)}+2e^- \longrightarrow \mathsf{H}_{2(g)}; \quad E^\circ=0.0 \ \mathsf{V} \\ 2\mathsf{H}_2\mathsf{O}_{(l)}+2e^- \longrightarrow \mathsf{H}_{2(g)}+2\mathsf{O}\mathsf{H}^-_{(aq)}; \quad E^\circ=-0.83 \ \mathsf{V} \end{array}$$

Since the electrode potential (*i.e.* reduction potential) of  $H^+_{(aq)}$  ions is higher than that of  $H_2O$ , therefore, at the cathode,  $H^+_{(aq)}$  ions (rather than  $H_2O$  molecules) are reduced to evolve  $H_2$  gas. Similarly at the anode, either  $SO^{2-}_{4(aq)}$  ions or  $H_2O$  molecules are oxidised. Since the oxidation potential of  $SO^{2-}_4$  is expected to be much lower (since it involves cleavage of many bonds as compared to those in  $H_2O$ ) than that of  $H_2O$  molecules, therefore, at the anode, it is  $H_2O$  molecules (rather than  $SO^{2-}_4$  ions) which are oxidised to evolve  $O_2$  gas.

From the above discussion, it follows that during electrolysis of an aqueous solution of  $H_2SO_4$  only the electrolysis of  $H_2O$  occurs liberating  $H_2$  at the cathode and  $O_2$  at the anode.

(iv) In aqueous solution, CuCl<sub>2</sub> ionises as follows :

$$\operatorname{CuCl}_{2(aq)} \longrightarrow \operatorname{Cu}_{(aq)}^{2+} + 2\operatorname{Cl}_{(aq)}^{-}$$

On passing electricity,  $Cu^{2+}_{(aq)}$  ions move towards cathode and  $Cl^-_{(aq)}$  ions move towards anode. Thus, at cathode, either  $Cu^{2+}_{(aq)}$  or  $H_2O$  molecules are reduced. Their electrode potentials are :

 $Cu_{(aq)}^{2+} + 2e^{-} \longrightarrow Cu_{(s)}; E^{\circ} = + 0.34 V$  $2H_2O_{(l)} + 2e^{-} \longrightarrow H_{2(g)} + 2OH_{(aq)}^{-}; E^{\circ} = -0.83 V$ 

Since the electrode potential of  $Cu_{(aq)}^{2+}$  ions is much higher than that of H<sub>2</sub>O, therefore, at the cathode,  $Cu_{(aq)}^{2+}$  ions are reduced and not H<sub>2</sub>O molecules. Similarly, at the anode, either  $Cl_{(aq)}^{-}$  ions or H<sub>2</sub>O molecules are oxidized. Their oxidation potentials are :

$$2\mathsf{Cl}_{(aq)}^{-} \longrightarrow \mathsf{Cl}_{2(g)} + 2e^{-}; E^{\circ} = -1.36 \text{ V}$$
  
$$2\mathsf{H}_{2}\mathsf{O}_{(l)} \longrightarrow \mathsf{O}_{2(g)} + 4\mathsf{H}_{(aq)}^{+} + 4e^{-}; E^{\circ} = -1.23 \text{ V}$$

Although oxidation potential of  $H_2O$  molecules is higher than that of Cl<sup>-</sup> ions, nevertheless, oxidation of Cl<sup>-</sup><sub>(a0)</sub> ions occurs

in preference to  $H_2O$  since due to overvoltage of  $O_2$ , much more potential than -1.36 V is required for the oxidation of chloride ions.

Thus, when an aqueous solution of  $CuCl_2$  is electrolysed, Cu metal is liberated at the cathode while  $Cl_2$  gas is evolved at the anode.

3. We know that,  

$$E_{A|^{3+}/A|}^{\circ} = -1.66 \text{ V}, E_{Cu^{2+}/Cu}^{\circ} = +0.34 \text{ V},$$
  
 $E_{Fe^{2+}/Fe}^{\circ} = -0.44 \text{ V}, E_{Mg^{2+}/Mg}^{\circ} = -2.36 \text{ V} \text{ and } E_{Zn^{2+}/Zn}^{\circ}$   
 $= -0.76 \text{ V}.$ 

Since a metal with lower electrode potential is a stronger reducing agent, therefore, Mg can displace all the above metals from their aqueous solutions, Al can displace all metals except Mg from the aqueous solutions of their salts. Zn can displace all metals except Mg and Al from the aqueous solutions of their salts while Fe can displace only Cu from the aqueous solution of its salts. Thus, the order in which they can displace each other from the solution of their salts is Mg, Al, Zn, Fe, Cu.

4. Lower the electrode potential, better is the reducing power. Since the electrode potentials increase in the order;  $K^+/K(-2.93 \text{ V})$ ,  $Mg^{2+}/Mg(-2.37 \text{ V})$ ,  $Cr^{3+}/Cr(-0.74 \text{ V})$ ,  $Hg^{2+}/Hg(0.79 \text{ V})$ ,  $Ag^+/Ag$  (0.80 V), therefore, reducing power of metals increases in the order, *i.e.*, Ag < Hg < Cr < Mg < K.

5. The given redox reaction is

 $Zn_{(s)} + 2Ag^+_{(aq)} \rightarrow Zn^{2+}_{(aq)} + 2Ag_{(s)}$ 

Since Zn gets oxidized to  $Zn^{2+}$  ions, and  $Ag^+$  gets reduced to Ag metal, therefore, oxidation occurs at zinc electrode and reduction occurs at the silver electrode.

Thus, galvanic cell corresponding to the above redox reaction may be depicted as :  $Zn | Zn^{2+}_{(aq)} || Ag^+_{(aq)} | Ag$ 

(i) Since oxidation occurs at the zinc electrode, therefore, electrons accumulate on the zinc electrode and hence, zinc electrode is negatively charged.

(ii) The ions carry current. The electrons flow from Zn to Ag electrode while the current flows from Ag to Zn electrode.

(iii) The reactions occurring at the two electrodes are :

At anode :  $Zn_{(s)} \longrightarrow Zn_{(aq)}^{2+} + 2e^{-}$ At cathode :  $Ag_{(aq)}^{+} + e^{-} \longrightarrow Ag_{(s)}$ 

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