NCERT Solutions for 11th Class Chemistry: Chapter 8-Redox Reactions

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Class 11: Chemistry Chapter 8 solutions. Complete Class 11 Chemistry Chapter 8 Notes.

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NCERT 11th Chemistry Chapter 8, class 11 Chemistry Chapter 8 solutions

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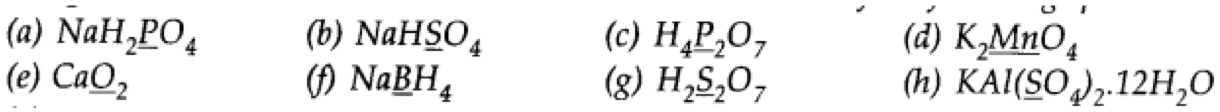
Question 1. Assign oxidation number to the underlined elements in each of the following species:



(a) $NaH_2\underline{P}O_4$ (b) $NaH\underline{S}O_4$ (c) $H_4\underline{P}_2O_7$ (d) $K_2\underline{Mn}O_4$

(e) $Ca\underline{O}_2$ (f) $Na\underline{B}H_4$ (g) $H_2\underline{S}_2O_7$ (h) $KAl(\underline{S}O_4)_2.12H_2O$

Answer:

(a) P in $\overset{+1}{\text{Na}}\,\overset{+1}{\text{H}_2}\,\overset{x}{\text{P}}\,\overset{-2}{\text{O}_4}$

$$\begin{aligned}(+1) + 2(+1) + x + 4\,(-2) &= 0\\ x + 3 - 8 \text{ or } x &= +5\end{aligned}$$

(b) S in NaHSO_4

$\overset{+1}{\text{Na}}\,\overset{+1}{\text{H}}\,\overset{x}{\text{S}}\,\overset{-2}{\text{O}_4}$

$$\begin{aligned}(+1) + (+1) + x + 4\,(-2) &= 0\\ x - 6 &= 0\\ x &= +6\end{aligned}$$

(*c*) P in $H_4P_2O_7$

$$\overset{+1}{H_4}\,\overset{x}{P_2}\,\overset{-2}{O_7}$$

$$\begin{aligned} 4(+1) + 2x + 7(-2) &= 0 \\ 2x - 10 &= 0 \\ x &= +5 \end{aligned}$$

(*d*) Mn in K_2MnO_4

$$\overset{+1}{K_2}\overset{x}{Mn}\overset{-2}{O_4}$$

$$\begin{aligned} 2(+1) + x + 4(-2) &= 0 \\ x - 6 &= 0 \\ x &= +6 \text{ oxygen.} \end{aligned}$$

(*e*) Let the oxidation number of CaO_2 be x.

$$2 + 2x = 0 \qquad (\because \text{ oxy No. of } a = +2)$$

$$x = -1$$

Thus, oxidation number of O in CaO_2 = **–1.**

(*f*) In $NaBH_4$, H is present as hydride ion. Therefore, its oxidation number is –1. Thus,

$$\overset{+1}{Na}\;\overset{x}{B}\;\overset{-1}{H_4} \qquad \therefore \quad 1(+1) + x + 4(-1) = 0 \quad \text{or} \quad x = +3$$

Thus, the oxidation number of B in $NaBH_4$ = **+ 3.**

(*g*)

$$\overset{+1}{H_2}\,\overset{x}{S_2}\,\overset{-2}{O_7} \qquad \therefore \quad 2(+1) + 2(x) + 7(-2) = 0 \quad \text{or} \quad x = +6$$

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

(*h*)

$$\overset{+1}{K}\,\overset{+3}{Al}\,(\overset{x}{S}\,\overset{-2}{O_4})_2\,12\,(\overset{+1}{H_2}\,\overset{-2}{O}) \quad \text{or} \quad +1 + 3 + 2x + 8(-2) + 12(2 \times 1 - 2) \text{ or } x = +6$$

Alternatively, since H_2O is a neutral molecule, therefore, sum of oxidation numbers of all the atoms in H_2O may be taken as zero. As such water molecules may be ignored white computing the oxidation number of S.

$\therefore +1 + 3 + 2x - 16 = 0$ or $x = +6$

Thus, the oxidation number of S in $KAl(SO_4)_2.12H_2O$ = **+6.**

Question 2. What are the oxidation number of the underlined elements in each of the following and how do you rationalise your results ?

(a) $K\underline{I}_3$ (b) $H_2\underline{S}_4O_6$ (c) $\underline{Fe}_3O_4$ (d) $\underline{C}H_3\underline{C}H_2OH$ (e) $\underline{C}H_3\underline{C}OOH$.

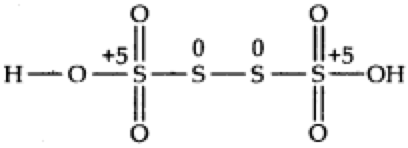
Answer: (a) In Kl_3, since the oxidation number of K is +1, therefore, the average oxidation number of iodine = -1/3. But the oxidation number cannot be fractional. Therefore, we must consider its structure, $K^+[I —I <— I]^-$. Here, a coordinate bond is formed between I_2 molecule and I^- ion. The oxidation number of two iodine atoms forming the I_2 molecule is zero while that of iodine forming the coordinate bond is -1. Thus, the O.N. of three I atoms, atoms in Kl_3 are 0, 0 and -1 respectively.

(b) *By conventional method.* O.N. of S in $H_2S_4O_6 = \overset{+1}{H_2}\,\overset{x}{S_4}\,\overset{-2}{O_6}$

or $2(+1) + 4x + 6(-2) = 0$ or $x = +2.5$ (*wrong*)

But it is wrong because all the four S atoms cannot be in the same oxidation state.

By chemical bonding method. The structure of $H_2S_4O_6$ is shown below:



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) *By conventional method.* O.N. of Fe in $\overset{x}{Fe_3}\,\overset{-2}{O_4}$ or $3x + 4(-2) = 0$ or $x = 8/3$.

By stoichiometry. $Fe_3O_4 \equiv \overset{+2}{Fe_3}\,\overset{-2}{O}\cdot\overset{+3}{Fe_2}\,\overset{-2}{O_3}$.

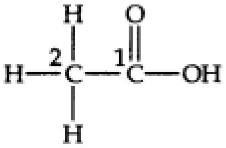
$\therefore$ O.N. of Fe in Fe_3O_4 is + 2 and + 3

(d) *By conventional method.* O.N. of C in $CH_3CH_2OH = \overset{x}{C_2}\,\overset{+1}{H_6}\,\overset{-2}{O}$

or $2x + 6(+1) + 1(-2) = 0$ or $x = -2$.

(e) *By conventional method.* $CH_3COOH = \overset{x}{C_2}\,\overset{+1}{H_4}\,\overset{-2}{O_2}$ or $2x + 4 - 4 = 0$ or $x = 0$

By chemical bonding method, C_2 is attached to three *H*-atoms (less electronegative than carbon) and one—COOH group (more electronegative than carbon).



therefore, O.N. of $C_2 = 3(+1) + x + 1(-1) = 0$ or $x = -2$

C_1 is, however, attached to one oxygen atom by a double bond, one OH (O.N. = −1) and one CH_3 (O.N. = +1) group, therefore, O.N. of $C_1 = +1 + x + 1(-2) + 1(-1) = 0$ or $x = +2$

Question 3. Justify that the following reactions are redox reactions:

(a) $CuO(s) + H_2(g)$ ——> $Cu(s) + H_2O(g)$

(b) $Fe_2O_3(s) + 3CO(g)$ —-> $2Fe(s) + 3CO_2(g)$

(c) $4BCl_3(g) + 3LiAlH_4(s)$ ——> $2B_2H_6(g) + 3LiCl(s) + 3AlCl_3(s)$

(d) 2K(s) +F_2(g)——> 2K+F^-(s)

Answer:

$$(a)\ \overset{+2\,-2}{CuO}(s)+\overset{0}{H_2}(g)\longrightarrow \overset{0}{Cu}(s)+\overset{+1\,-2}{H_2O}(g)$$

Here, O is removed from CuO, therefore, it is reduced to Cu while O is added to H_2 to form H_20, therefore, it is oxidised. Further, 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_20. Therefore, CuO is reduced to Cu but H_2 is oxidised to H_20. Thus, this is a redox reaction.

$$(b)\ \overset{+3}{Fe_2}\overset{-2}{O_3}(s)+3\overset{+2}{C}O(g)\longrightarrow 2\overset{0}{Fe}(s)+3\overset{+4}{C}O_2(g)$$

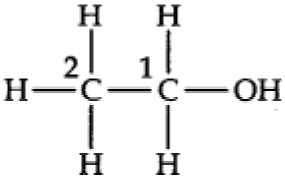
Here O.N. of Fe decreases from +3 if Fe_2O_3 to 0 in Fe while that of C increases from +2 in CO to +4 in CO_2. Further, oxygen is removed from Fe_2O_3 and added to CO, therefore, Fe_2O_3 is reduced while CO is oxidised. Thus, this is a redox reaction.

$$(c)\ 4\overset{+3\,-1}{BCl_3}(g)+\overset{+1\,+3\,-1}{LiAlH_4}(s)\longrightarrow 2\overset{-3}{B_2}\overset{+1}{H_6}(g)+3\overset{+1}{Li}\overset{-1}{Cl}(s)+3\overset{+3}{Al}\overset{-1}{Cl_3}(s)$$

Here, O.N. of B decreases from +3 in $BrCl_3$to -3 in B_2H_6 while that of H increases from -1 in $LiAlH_4$to +1 in B_2H_6. Therefore, BCl_3 is reduced while $LiAlH_4$ is oxidised. Further, H is added to BCl_3 but is removed from $LiAlH_4$, therefore, BC13 is reduced while $LiAlH_4$ is oxidised. Thus, it is a redox reaction.

Here, each K atom as 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.

By chemical bonding, C_2 is attached to three H-atoms (less electronegative than carbon) and one CH_2OH group (more electronegative than carbon), therefore,



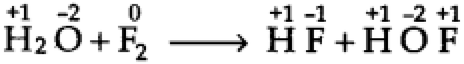
O.N. of C_2 = 3 (+1) + x + 1 (-1) = 0 or x = -2 C_2 is, however, attached to one OH (O.N. = -1) and one CH_3 (O.N. = +1) group, therefore, O.N. of C_4 = + 1 + 2 (+1) + x + 1 (-1) = 0 or x = -2

Question 4. Fluorine reacts with ice and results in the change:

$H_2O(S) + F_2(g)$ ——-> $HF(g) + HOF(g)$

Justify that this reaction is a redox reaction.

Answer: Writing the O.N. of each atom above its symbol, we have,

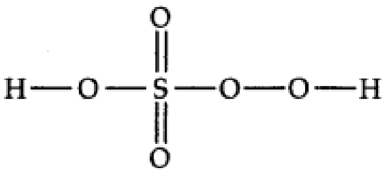


$$\overset{+1}{H_2}\overset{-2}{O} + \overset{0}{F_2} \longrightarrow \overset{+1}{H}\overset{-1}{F} + \overset{+1}{H}\overset{-2}{O}\overset{+1}{F}$$

Here, the O.N. of F decreases from 0 in F_2 to -1 in HF and increases from 0 in F_2 to +1 in HOF. Therefore, F_2 is both reduced as well as oxidised. Thus, it is a redox reaction and more specifically, it is a disproportionation reaction.

Question 5. Calculate the oxidation number of sulphur, chromium and nitrogen in H_2SO_5, Cr_2O_2 and NOT. Suggest structure of these compounds. Count for the fallacy.

Answer: O.N. of S in H_2SO_5. By conventional method, the O.N. of S in H_2SO_5 is $2(+1) + x + 5(-2) = 0$ or $x = +8$ This is impossible because the maximum O.N. of S cannot be more than six since it has only six electrons in the valence shell. This fallacy is overcome if we calculate the O.N. of S by chemical bonding method. The structure of H_2SO_5 is



$$H-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-O-O-H$$

$$\underset{\text{(for H)}}{2 \times (+1)} + \underset{\text{(for S)}}{x} + \underset{\text{for (O – O)}}{2(-1)} + \underset{\substack{\text{(for other O)}\\ \text{atoms}}}{3 \times (-2)} = 0 \text{ or } x = +6$$

Cr in $Cr_2O_7^{2-}$

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

$$2x - 14 = -2$$

$$2x = -2 + 14 \qquad x = +6$$

$$x + \underset{\text{(for O}^-\text{)}}{1(-1)} + \underset{\text{(for = O)}}{1(-2)} + \underset{\text{for} \rightarrow \text{O}}{1(-2)} = 0 \text{ or } x + 5$$

Thus, there is no fallacy about the O.N. of N in No_3^- whether one calculates by conventional method or by chemical bonding method.

Question 6.Write formulas for the following compounds:

(a) Mercury (II) chloride, (b) Nickel (II) sulphate, (c) Tin (IV) oxide, (d) Thallium

(I) sulphate, (e) Iron (III) sulphate, (f) Chromium (III) oxide.

Answer: (a) $Hg(II)Cl_2$, (b) $Ni(II)SO_4$, (c)$S_n(IV)O_2$ (d) $T_{12}(I)SO_4$, (e) $Fe_2(III)(So_4)_3$, (f) $Cr_2(III)O_3$.

Question 7. Suggest a list of substances where carbon can exhibit oxidation states from -4 to +4 and nitrogen from -3 to +5.

Answer:

Compound	O.N. of Carbon	Compound	O.N. of Nitrogen
CH_4	−4	NH_3	−3
CH_3CH_3	−3	NH_2-NH_2	−2
$CH_2=CH_2$ or CH_3Cl	−2	$NH=NH$	−1
$CH\equiv CH$	−1	$N\equiv N$	0
CH_2Cl_2 or $C_6H_{12}O_6$	0	N_2O	+1
C_2Cl_2 or C_6Cl_6	+1	NO	+2
CO or $CHCl_3$	+2	N_2O_3	+3
C_2Cl_6 or $(COOH)_2$	+3	N_2O_4	+4
CO_2 or CCl_4	+4	N_2O_5	+5

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Question 8. While sulphur dioxide and hydrogen peroxide can act as an oxidising as well as reducing agents in their reactions, ozone and nitric acid act only as oxidants. Why?

Answer: (i) In So_2 , O.N. of S is +4. In principle, S can have a minimum O.N. of -2 and maximum of +6. Therefore, S in So_2 can either decrease or increase its O.N. and hence can act both as an oxidising as well as a reducing agent.

(ii) In H_2O_2, the O.N. of O is -1. In principle, O can have a minimum O.N. of -2 and maximum of zero (+1 is possible in $O_2F_2$and +2 in OF_2).

Therefore, O in H_2O_2 can either decrease its O.N. from -1 to -2 or can increase its O.N. from -1 to zero. Therefore, H_2O_2 acts both as an oxidising as well as a reducing agent.

(iii) In O_3, the O.N. of O is zero. It can only decrease its O.N. from zero to -1 or -2, but cannot increase to +2. Therefore, O_3 acts only as an oxidant.

(iv) In HNO_3, O.N. of N is +5 which is maximum. Therefore, it can only decrease its O.N. and hence it acts as an oxidant only.

Question 9. Consider the reactions:

(a) $6CO_2(g)\ 6H_2O(l)$ ———> $C_6H_{12}O_6(s) + 6O_6(g)$ (b) $O_3(g) + H_2O_2(l)\ H_2O(l) + 2O_2(g)$

Why it is more appropriate to write these reactions as:

(a) $6CO_2(g) + 12H_2O(l)$ ————-> $C_6H_{12}O_6(s) + 6H_2O(l) + 6O_2(g)$

(b) $O_3(g) + H_2O_2\ (l)$ ————> $H_2O(l) + O_2(g) + O_2(g)$

Also suggest a technique to investigate the path of above (a) and (b) redox reactions.

Answer:

$$\begin{array}{rcll} 12H_2O(l) & \longrightarrow & 12H_2(g) + 6O_2(g) & \ldots(i) \\ 6CO_2(g) + 12H_2(g) & \longrightarrow & C_6H_{12}O_6(s) + 6H_2O(l) & \ldots(ii) \\ \hline 6CO_2(g) + 12H_2O(l) & \longrightarrow & C_6H_{12}O_6(s) + 6H_2O(l) + 6O_2(g) & \ldots(iii) \end{array}$$

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

$$\begin{array}{rcl} O_3(g) & \longrightarrow & O_2(g) + O(g) \\ H_2O_2 + O(g) & \longrightarrow & H_2O(l) + O_2(g) \\ \hline O_3(g) + H_2O_2(l) & \longrightarrow & H_2O(l) + O_2(g) + O_2(g) \end{array}$$

The path of reactions (a) and (b) can be determined by using $H_20_2^{18}$ or D_20 in reaction

(a) or by using $H_20_2^{18}$ or O_3^{18}in reaction

Question 10. The compound AgF_2 is unstable. However, if formed, the compound acts as a very strong oxidising agent. Why?

Answer: In AgF_2 oxidation state of Ag is +2 which is very very unstable. Therefore, it quickly accepts an electron to form the more stable +1 oxidation state.

$Ag^{2+} + e^{-}$ ———–> Ag^{+}

Therefore, AgF_2, if formed, will act as a strong oxidising agent.

Question 11. Whenever a reaction between an oxidising agent and a reducing agent is carried out, a compound of

lower oxidation state is formed if the reducing agent is in excess and a compound of higher oxidation state is formed if oxidising agent is in excess. Justify this statement giving three illustrations.

Answer: (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 the oxidation state of C is +2. If, however, excess of O_2 is used, the initially formed CO gets oxidised to CO_2 in which oxidation state of C is + 4.

$$\underset{\text{(Excess)}}{2C(s)} + O_2(g) \longrightarrow 2\overset{+2}{C}O(g)\,; \qquad C(s) + \underset{\text{(Excess)}}{O_2(g)} \longrightarrow \overset{+4}{C}O_2(g)$$

(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. If, however, 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

$$\underset{\text{(Excess)}}{P_4(s)} + 6Cl_2(g) \longrightarrow 4\overset{+3}{P}Cl_3\,; \qquad P_4(s) + \underset{\text{(Excess)}}{10Cl_2} \longrightarrow 4\overset{+5}{P}Cl_5$$

(iii) Na is a reducing agent while 02 is an oxidising agent. When excess of Na is used, sodium oxide is formed in which the oxidation state of O is -2. If, however, excess of 02 is used, Na_2O_2 is formed in which the oxidation state of O is -1 which is higher than -2.

$$\underset{\text{(Excess)}}{4Na(s)} + O_2(g) \longrightarrow Na_2\overset{-2}{O}(s)\,; \quad 2Na(s) + \underset{\text{(Excess)}}{2O_2(g)} \longrightarrow Na_2\overset{-1}{O_2}(s)$$

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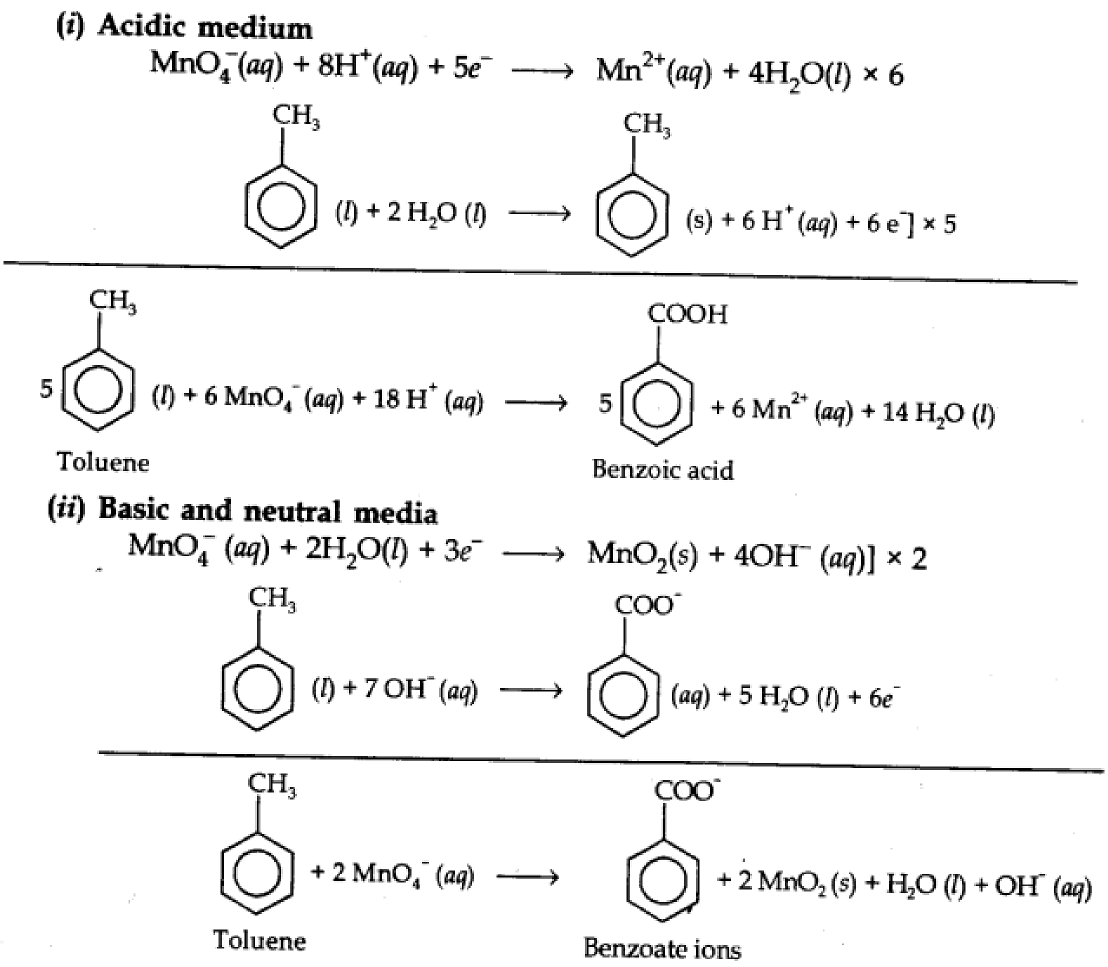
Question 12. How do you account for the following observations?

(a) Though alkaline potassium permanganate and acidic potassium permanganate both are used as oxidants, yet in the manufacture of benzoic acid from toluene we use alcoholic potassium permanganate as an oxidant. Why? Write a balanced redox equation for the reaction.

(b) When concentrated sulphuric acid is added to an inorganic mixture containing chloride, we get colourless pungent smelling gas HCl, but if the mixture contains bromide then we get red vapour of bromine. Why?

Answer: (a) Toluene can be oxidised to benzoic acid in acidic, basic and neutral media according to the following redox equations:



In the laboratory, benzoic acid is usually prepared by alkaline $KMnO_4$ oxidation of toluene. However, in industry alcoholic $KMnO_4$ is preferred over acidic or alkaline $KMnO_4$ because of the following reasons:

(i) The cost of adding an acid or the base is avoided because in the neutral medium, the base (OH- ions) are produced in the reaction itself.

(ii) Since reactions occur faster in homogeneous medium than in heterogeneous medium, therefore, alcohol helps in mixing the two reactants, i.e., $KMnO_4$ (due to its polar nature) and toluene (because of its being an organic compound).

(b) When cone. H_2So_4 is added to an inorganic mixture containing chloride, a pungent smelling gas HCl is produced because a stronger acid displaces a weaker acid from its salt.

$$2NaCl + \underset{\text{Stronger acid}}{2H_2SO_4} \longrightarrow 2NaHSO_4 + \underset{\text{Weaker acid}}{2HCl}$$

$$HCl + H_2SO_4 \longrightarrow Cl_2 + SO_2 + 2H_2O$$

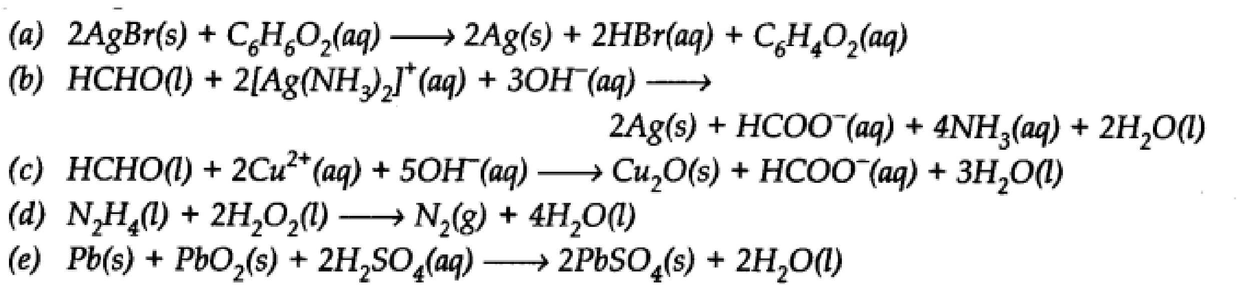
Since HCl is a very weak reducing agent, it can not reduce H_2So_4 to So_2 and hence HCl is not oxidised to Cl_2.

However, when the mixture contains bromide ion, the initially produced HB_r being a strong reducing agent than HCl reduces $H_2So_4$to So_2 and is itself oxidised to produce red vapour of Br_2.

$$2NaBr + 2H_2SO_4 \longrightarrow 2NaHSO_4 + 2HBr$$

$$2HBr + H_2SO_4 \longrightarrow Br_2 + SO_2 + 2H_2O$$

Question 13. Identify the substance oxidised, reduced, oxidising agent and reducing agent for each of the following reactions.



(a) $2AgBr(s) + C_6H_6O_2(aq) \longrightarrow 2Ag(s) + 2HBr(aq) + C_6H_4O_2(aq)$

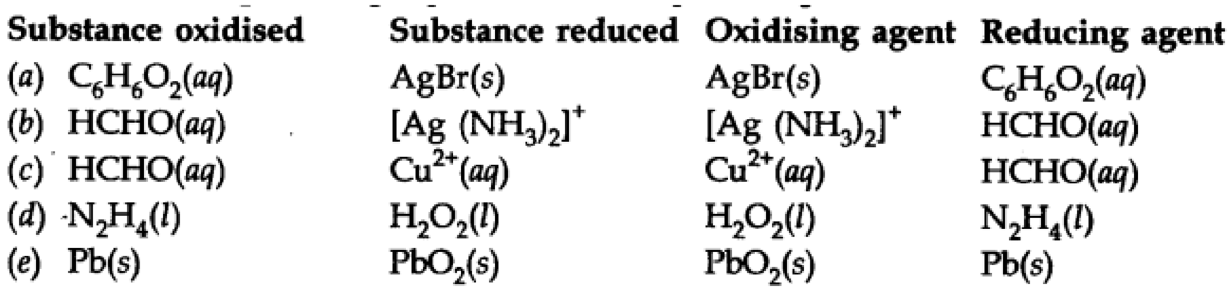
(b) $HCHO(l) + 2[Ag(NH_3)_2]^+(aq) + 3OH^-(aq) \longrightarrow 2Ag(s) + HCOO^-(aq) + 4NH_3(aq) + 2H_2O(l)$

(c) $HCHO(l) + 2Cu^{2+}(aq) + 5OH^-(aq) \longrightarrow Cu_2O(s) + HCOO^-(aq) + 3H_2O(l)$

(d) $N_2H_4(l) + 2H_2O_2(l) \longrightarrow N_2(g) + 4H_2O(l)$

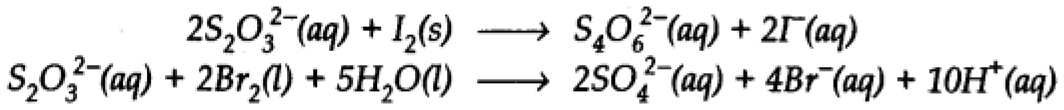
(e) $Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \longrightarrow 2PbSO_4(s) + 2H_2O(l)$

Answer:



Substance oxidised	**Substance reduced**	**Oxidising agent**	**Reducing agent**
(a) $C_6H_6O_2(aq)$	$AgBr(s)$	$AgBr(s)$	$C_6H_6O_2(aq)$
(b) $HCHO(aq)$	$[Ag(NH_3)_2]^+$	$[Ag(NH_3)_2]^+$	$HCHO(aq)$
(c) $HCHO(aq)$	$Cu^{2+}(aq)$	$Cu^{2+}(aq)$	$HCHO(aq)$
(d) $N_2H_4(l)$	$H_2O_2(l)$	$H_2O_2(l)$	$N_2H_4(l)$
(e) $Pb(s)$	$PbO_2(s)$	$PbO_2(s)$	$Pb(s)$

Question 14. Consider the reactions:



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

$$S_2O_3^{2-}(aq) + 2Br_2(l) + 5H_2O(l) \longrightarrow 2SO_4^{2-}(aq) + 4Br^-(aq) + 10H^+(aq)$$

Why does the same reductant, thiosulphate react difforerently with iodine and bromine?

Answer: 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_2 is a stronger oxidising agent that I_2, it oxidises S of $S_2O_3^{2-}$ to a higher oxidation state of +6 and hence forms SO_4^{2-} ion. I_2, however, being weaker oxidising agent oxidises S of $S_2O_3^{2-}$ ion to a lower oxidation of +2.5 in $S_4O_6^{2-}$ ion. It is because of this reason that thiosulphate reacts differently with Br_2 and I_2.

Question 15. Justify-giving reactions that among halogens, fluorine is the best oxidant and among hydrohalic compounds, hydroiodic add is the best reductant.

Answer: Halogens have a strong tendency to accept electrons. Therefore, they are strong oxidising agents. Their relative oxidising power is, however, measured in terms of their electrode potentials. Since the electrode potentials of halogens decrease in the order: F_2 (+2.87V) > Cl_2 (+1.36V) > Br_2 (+1.09V) > I_2 (+0.54V), therefore, their oxidising power decreases in the same order.

This is evident from the observation that F_2 oxidises Cl^- to Cl_2, $Br^-$to Br_2, I – to I_2 ; Cl_2 oxidises $Br^-$to Br_2 and F to I_2 but not F^- to F_2. Br_2, however, oxidises F to I_2 but not F^- to F_2 , and Cl^- to Cl_2.

$F_2(g) + 2Cr(aq)$ ————> $2F^-(aq) + Cl_2(g)$; F2(g) + $2Br^-(aq)$ ———-> $2F^-(aq) + Br_2$ (Z)

$F_2(g) + 2I^-(aq)$ ———-> $2F^-(aq) + I_2(s)$; Cl2 (g) + $2Br^-(aq)$ ————> $2Cl^-(aq) + Br_2$ (Z)

$Cl_2(g) + 2I^-(aq)$ ————> $2Cl^-$ (aq) + $I_2(s)$ and Br_2 (Z) + 2F ———> $2Br^-$ (aq) + $I_2(s)$

Thus, F_2 is the best oxidant.

Conversely, halide ions have a tendency to lose electrons and hence can act as reducing agents. Since the electrode potentials of halide ions decreases in the order: I^-(-0.54 V) > Br^- (-1.09 V) > Cl^-(-1.36 V) > I_2 (-2.87 V), therefore, the reducing power of the halide ions or their corresponding hydrohalic acids decreases in the same order: HI > HBr > HCl > HF. Thus, hydroiodic acid is the best reductant. This is supported by the following reactions. For example, HI and HBr reduce H_2So_4 to So_2 while HCl and HF do not.

$2HBr + H_2So_4$ ——> $Br_2 + So_2 + 2H_2O$; $2HI + H_2So_4$ ——> $I_2 + So_2 + 2H_2O$

Further F reduces Cu^{2+} to Cu^+ but Br does not.

$2Cu^{2+}(aq) + 4I^-(aq) > Cu_2I_2(s) + I_2(aq)$; Cu2+(aq) + $2Br^-$> No reaction.

Thus, HI is a stronger reductant than HB_r.

Further among HCl and HF, HCl is a stronger reducing agent than HF because HCl reduces MnO_2 to Mn^{2+} but HF does not.

$MnO_2(s) + 4HCl(aq)$ ——-> $MnCl_2(aq) + Cl_2(aq) + 2H_2O$

$MnO_2(s) + 4HF(l)$ ————> No reaction.

Thus, the reducing character of hydrohalic acids decreases in the order: HI > HBr > HCl > HF.

Question 16. Why does the following reaction occur?

$$XeO_6^{4-}(aq) + 2F^-(aq) + 6H^+(aq) \longrightarrow XeO_3(s) + F_2(g) + 3H_2O(l)$$

What conclusion about the compound Na_4XeO_6 (of which XeO_6^{4-} is a part) can be drawn from the reaction?

Answer:

$$\overset{+8}{Xe}O_6^{4-}(aq) + 2\overset{-1}{F^-}(aq) + 6H^+(aq) \longrightarrow \overset{+6}{Xe}O_3(s) + \overset{0}{F_2}(g) + 3H_2O(l)$$

Here, O.N. of Xe decreases from +8 in XeO_6^{4-} to +6 in XeO_3 while that of F increases from –I in F^- to 0 in F_2. Therefore, XeO_6^{4-} is reduced while F^- is oxidised. This reaction occurs because $Na_2XeO_6^{4-}$ (or XeO_6^{4-}) is a stronger oxidising agent than F_2.

Question 17. Consider the reactions:

(a) H_3Po_2(aq) + 4$AgNO_3$(aq) + 2H_2O(l) ————->H_3PO_4(aq) + 4Ag(s) + 4HNO_3(aq)

(b) H_3Po_2(aq) + 2$CuSo_4$(aq) + 2H_2O(l) ————->H_3Po_4(aq) + 2Cu(s) + H_2So_4(aq)

(c) C_6H_5CHO(l) + 2$[Ag(NH_3)_2]^+$(aq) + 3OH^-(aq)————> $C_6H_5COO^-$(aq) + 2Ag(s) + 4NH_3(aq) + 2H_2o(l)

(d) C_6H_5CHO(l) + 2Cu^{2+}(aq) + 5OH^-(aq) ————> No change observed

What inference do you draw about the behaviour of Ag^+ and Cu^{2+} from these reactions?

Answer: Reactions (a) and (b) indicate that H_3Po_2 (hypophosphorous acid) is a reducing agent and thus reduces both $AgNO_3$ and $CuSo_4$ to Ag and Cu respectively. Conversely, both $AgNO_3$ and $CuSo_4$ act as oxidising agent and thus oxidise $H_3Po_2$to H_3Po_4 (orthophosphoric acid) Reaction (c) suggests that $[Ag(NH_3)_2]^+$ oxidises C_6H_5CHO (benzaldehyde) to $C_6H_5COO^-$ (benzoate ion) but reaction (d) indicates that Cu^{2+} ions cannot oxidise C_6H_5CHO to $C_6H_5COO^-$. Therefore, from the above reactions, we conclude that Ag^+ ion is a strong deoxidising agent than Cu^{2+} ion.

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Question 18. Balance the following redox reactions by ion-electron method.

(a) MnO_4^-(aq) +I^-(aq) ———>Mno_2(s) + I_2 (s) (in basic medium)

(b) MnO_4^-(aq) + So2(g) ——-> Mn^{2+}(aq) +$H_2So_4^-$(in acidic solution)

(c) H_2O_2(aq) + Fe2+(aq) ———-> Fe^3+(aq) + H_2O(l) (in acidic solution)

(d) $Cr_2O_7^{2-}$(aq) + So_2 (g)——> Cr^{3+}(aq) + SO_4^{2-}(aq) (in acidic solution)

Answer: (a) Do it yourself.

(b) The balanced half reaction equations are:

Oxidation half equation:

So_2(g) + $2H_2O$(l) ———> HSo_4^- (aq) + $3H^+$(aq) +$2e^-$ ...(i)

Reduction half equation:

MnO_4^-(aq) + $8H^+$(aq) + $5e^-$ ———> Mn^{2+}(aq) + $4H_2O$(l) ....(ii)

Multiply Eq. (i) by 3 and Eq. (ii) by 2 and add, we have,

$2MnO_4^-$(aq) + $5So_2$(g) + $2H_2o$(l) + H^+(aq) —————> $2Mn^{2+}$(aq) + $5HSO_4^-$(aq)

(c) Oxidation half equation: Fe^{2+}(aq) ———> Fe^{3+}(aq) + e^- ...(i)

Reduction half equation: H_2O_2(aq) + $2H^+$(aq) + $2e^-$ ———> $2H_2O$(l) ...(ii)

Multiply Eq. (i) by 2 and add it to Eq. (ii), we have,

$H_2O_2(aq) + 2Fe^{2+}(aq) + 2H^+(aq)$ ——-> $2Fe^{3+}(aq) + 2H_2O(l)$

(d) Following the procedure detailed on page 8/23, the balanced half reaction equations are:

Oxidation half equation:

$SO_2(g) + 2H_2O(l)$ ————> $SO_4^{2-}(aq) + 4H^+(aq) + 2\ e^-$ ...(i)

Reduction half equation:

$Cr_2O_72^-(aq) + 14H^+(aq) + 6e^-$ ————> $2Cr^{3+}(aq) + 7H_2o(l)$ ...(ii)

Multiply Eq. (i) by 3 and add it to Eq. (ii), we have,

$Cr_2O_72^-(aq) + 3SO_2(q) + 2H^+(aq)$ ————> $2Cr^{3+}(aq) + 3SO_4^{2-}(aq) + H_2o(l)$

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Question 19. Balance the following equation in basic medium by ion electron method and oxidation number method and identify the oxidising agent and the reducing agent.

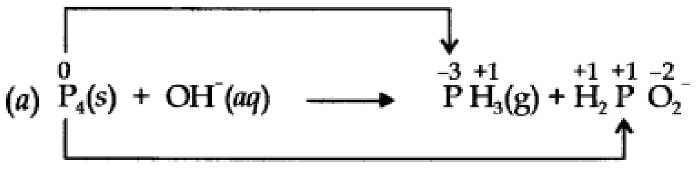
(a) $P_4(s) + OH^-(aq)$ ———> $PH_3(g) + H_2PO_2^-(aq)$

(b) $N_2H_4(l) + ClO^-(aq)$ ———> $NO(g) + CV(aq)$

(c) $Cl_2O_7(g) + H_2O_2(aq)$ ———-> $ClO_2^-(aq) + O_2(g) + H^+$

P_4 acts both as an oxidising as well as a reducing agent.

Answer:



(a) $\overset{0}{P_4}(s) + OH^-(aq) \longrightarrow \overset{-3}{P}\overset{+1}{H_3}(g) + \overset{+1}{H_2}\overset{+1}{P}\overset{-2}{O_2^-}$

O.N. increases by 1 per P atom.

P_4 acts both as an oxidising as well as a reducing agent.

Oxidation number method:

Total decrease in O.N. of P_4 in $PH_3 = 3 \times 4 = 12$

Total increase in O.N. of P_4 in $H_2PO_2^- = 1 \times 4 = 4$

Therefore, to balance increases decreases in O.N. multiply PH_3 by 1 and $H_2PO_2^-$ by 3, we have,

$$P_4(s) + OH^-(aq) \longrightarrow PH_3(g) + 3H_2PO_2^-(aq)$$

To balance O atoms, multiply OH^- by 6, we have,

$$P_4(s) + 6OH^-(aq) \longrightarrow PH_3(g) + 3H_2PO_2^-(aq)$$

To balance H atoms, add $3H_2O$ to L.H.S. and $3OH^-$ to the R.H.S., we have,

$$P_4(s) + 6OH^-(aq) + 3H_2O(l) \longrightarrow PH_3(g) + 3H_2PO_2^-(aq) + 3OH^-(aq)$$

or $$P_4(s) + 3OH^-(aq) + 3H_2O(l) \longrightarrow PH_3(g) + 3H_2PO_2^-(aq) \quad ...(i)$$

Thus, Eq. (*i*) represents the correct balanced equation.

Ion electron method. The two half reactions are:

Oxidation half reaction:

$$P_4(s) \longrightarrow H_2PO_2^-(aq) \qquad ...(ii)$$

Balancing *P* atoms, we have,

$$\overset{0}{P}_4(s) \longrightarrow 4H_2\overset{+1}{P}O_2^-(aq)$$

Balance O.N. by adding electrons,

$$P_4(s) \longrightarrow 4H_2PO_2^-(aq) + 4e^-$$

Balance charge by adding 8 OH^- ions,

$$P_4(s) + 8OH^-(aq) \longrightarrow 4H_2PO_2^-(aq) + 4e^- \qquad ...(iii)$$

O and H get automatically balanced. Thus, Eq. (*iii*) represents the balanced oxidation half reaction.

Reduction half reaction:

$$\overset{0}{P}_4(s) \longrightarrow \overset{-3}{P}H_3(g) \qquad ...(iv)$$

Balancing P atoms, we have,

$$P_4(s) \longrightarrow 4PH_3(g)$$

Balance O.N. by adding electrons,

$$P_4(s) + 12e^- \longrightarrow 4PH_3(g)$$

Balance charge by adding $12OH^-$ ions,

$$P_4(s) + 12e^- \longrightarrow 4PH_3(g) + 12OH^-(aq)$$

Balance *O* atoms, by adding $12H_2O$ to L.H.S. of above equation.

$$P_4(s) + 12H_2O(l) + 12e^- \longrightarrow 4PH_3(g) + 12OH^-(aq) \qquad ...(v)$$

To cancel out electrons, multiply Eq. (*iii*) by 3 and add it to Eq. (*v*), we have,

$$4P_4(s) + 24OH^-(aq) + 12H_2O(l) \longrightarrow 4PH_3(aq) + 12H_2PO_2^-(aq) + 12H_2O(l) + 12OH^-(aq)$$

or $$P_4(g) + 3OH^-(aq) + 3H_2O(l) \longrightarrow PH_3(aq) + 3H_2PO_2^-(aq) \qquad \text{...}(vi)$$

Thus, Eq. (*vi*) represents the correct balanced equation.

(*b*) $N_2H_4(l) + ClO_3^-(aq) \longrightarrow NO(g) + Cl^-(aq)$

Oxidation number method

Total increase in O.N. of N = 2 × 4 = 8

Total decreases in O.N. of Cl = 1 × 6 = 6

Therefore, to balance increase/decrease in O.N. multiply N_2H_4 by 3 and ClO_3^- by 4, we have,

$$3N_2H_4(l) + 4ClO_3^-(aq) \longrightarrow NO(g) + Cl^-(aq)$$

To balance *N* and Cl atoms, multiply NO by 6 and Cl^- by 4, we have,

$$3N_2H_4(l) + 4ClO_3^-(aq) \longrightarrow 6NO(g) + 4Cl^-(aq)$$

Balance O atoms by adding $6H_2O$,

$$3N_2H_4(l) + 4ClO_3^-(aq) \longrightarrow 6NO(g) + 4Cl^-(aq) + 6H_2O(l) \qquad \text{...}(i)$$

H atoms get automatically balanced and thus Eq. (*i*) represents the correct balanced equation.

Ion electron method.

Oxidation half reaction: $\overset{-2}{N_2}H_4(l) \longrightarrow \overset{+2}{N}O(g)$

Balance *N* atoms, $N_2H_4(l) \longrightarrow 2NO(g)$

Balance O.N. by adding electrons,

$$N_2H_4(l) \longrightarrow 2NO(g) + 8e^-$$

Balance charge by adding $8OH^-$ ions,

$$N_2H_4(l) + 8OH^-(aq) \longrightarrow 2NO(g) + 8e^-$$

Balance O atoms by adding 6 H_2O,

$$N_2H_4(l) + 8OH^-(aq) \longrightarrow 2NO(g) + 6H_2O(l) + 8e^- \qquad \text{...}(ii)$$

Thus, Eq. (*ii*) represents the correct balanced oxidation half equation.

Reduction half reaction

$$\overset{+5}{\mathrm{ClO_3^-}}(aq) \longrightarrow \overset{-1}{\mathrm{Cl^-}}(aq)$$

Balance O.N. by adding electrons,

$$\mathrm{ClO_3^-}(aq) + 6e^- \longrightarrow \mathrm{Cl^-}(aq)$$

Balance charge by adding OH⁻ ions,

$$\mathrm{ClO_3^-}(aq) + 6e^- \longrightarrow \mathrm{Cl^-}(aq) + 6\mathrm{OH^-}(aq)$$

Balance O atoms by adding $3H_2O$,

$$\mathrm{ClO_3^-}(aq) + 3\mathrm{H_2O}(l) + 6e^- \longrightarrow \mathrm{Cl^-}(aq) + 6\mathrm{OH^-}(aq) \qquad ...(iii)$$

Thus, Eq. (*iii*) represents the correct balanced reduction half equation.

To cancel out electrons gained and lost, multiply Eq. (*ii*) by 3 and Eq. (*iii*) by 4 and add, we have,

$$3\mathrm{N_2H_4}(l) + 4\mathrm{ClO_3^-}(aq) \longrightarrow 6\mathrm{NO}(g) + 4\mathrm{Cl^-}(aq) + 6\mathrm{H_2O}(l) \qquad ...(iv)$$

Thus, Eq. (*iv*) represents the correct balanced equation

O.N. decreases by 4 per Cl aton

(*c*) $\overset{+7}{Cl}_2O_7(g) + H_2\overset{-1}{O}_2(aq) \longrightarrow \overset{+3}{Cl}O_2^-(aq) + \overset{0}{O}_2(g) + H^+$

O.N. increases by 1 per O atom

Thus, $Cl_2O_7(g)$ acts an oxidising agent while $H_2O_2(aq)$ as the reducing agent.

Oxidation number method

Total decrease in O.N. of $Cl_2O_7 = 4 \times 2 = 8$

Total increase in O.N. of $H_2O_2 = 2 \times 1 = 2$

$\therefore$ To balance increase/decrease in O.N. multiply H_2O_2 and O_2 by 4, we have,

$$Cl_2O_7(g) + 4H_2O_2(aq) \longrightarrow ClO_2^-(aq) + 4O_2(g)$$

To balance Cl atoms, multiply ClO_2^- by 2, we have,

$$Cl_2O_7(g) + 4H_2O_2(aq) \longrightarrow 2ClO_2^-(aq) + 4O_2(g)$$

To balance O atoms, add $3H_2O$ R.H.S., we have,

$$Cl_2O_7(g) + 4H_2O_2(aq) \longrightarrow 2ClO_2^-(aq) + 4O_2(g) + 3H_2O(l)$$

To balance H atoms, add $2H_2O$ to R.H.S. and $2OH^-$ to L.H.S., we have,

$$Cl_2O_7(g) + 4H_2O_2(g) + 2OH^-(aq) \longrightarrow 2ClO_2^-(aq) + 4O_2(g) + 5H_2O$$

This represents the balanced redox equation.

Ion electron method

Oxidation half reaction:

$$H_2\overset{-1}{O}_2(aq) \longrightarrow \overset{0}{O}_2(g)$$

Balance O.N. by adding electrons,

$$H_2O_2(aq) \longrightarrow O_2(g) + 2e^-$$

Balance charge by adding $2OH^-$ ions,

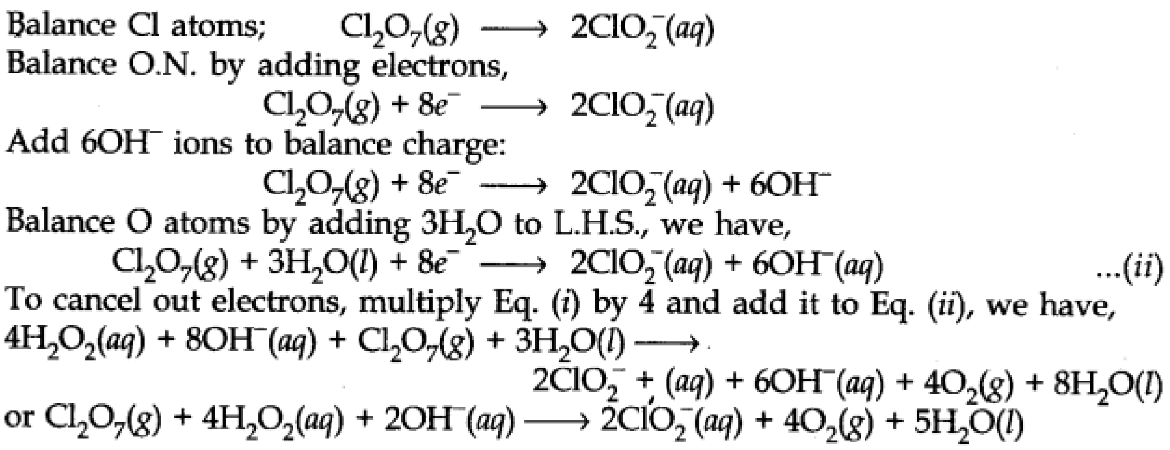
$$H_2O_2(aq) + 2OH^-(aq) \longrightarrow O_2(g) + 2e^-$$

Balance O atoms by adding $2H_2O$,

$$H_2O_2(aq) + 2OH^-(aq) \longrightarrow O_2(g) + 2H_2O(l) + 2e^- \quad ...(i)$$

Reduction half reaction:

$$\overset{+7}{Cl}_2O_7(g) \longrightarrow \overset{+3}{Cl}O_2^-(aq)$$



Balance Cl atoms; $Cl_2O_7(g) \longrightarrow 2ClO_2^-(aq)$

Balance O.N. by adding electrons,

$$Cl_2O_7(g) + 8e^- \longrightarrow 2ClO_2^-(aq)$$

Add $6OH^-$ ions to balance charge:

$$Cl_2O_7(g) + 8e^- \longrightarrow 2ClO_2^-(aq) + 6OH^-$$

Balance O atoms by adding $3H_2O$ to L.H.S., we have,

$$Cl_2O_7(g) + 3H_2O(l) + 8e^- \longrightarrow 2ClO_2^-(aq) + 6OH^-(aq) \quad ...(ii)$$

To cancel out electrons, multiply Eq. (i) by 4 and add it to Eq. (ii), we have,

$$4H_2O_2(aq) + 8OH^-(aq) + Cl_2O_7(g) + 3H_2O(l) \longrightarrow 2ClO_2^- + (aq) + 6OH^-(aq) + 4O_2(g) + 8H_2O(l)$$

or $Cl_2O_7(g) + 4H_2O_2(aq) + 2OH^-(aq) \longrightarrow 2ClO_2^-(aq) + 4O_2(g) + 5H_2O(l)$

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Question 20. Write Jour informations about the reaction:

$(CN)_2(g) + 2OH^-(aq)$ —–> $CN^-(aq) + CNO^-(aq) + H_2O(l)$

Answer: Let x be the O.N. of C.

O.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 = -lora: = +4 The four information 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^-.

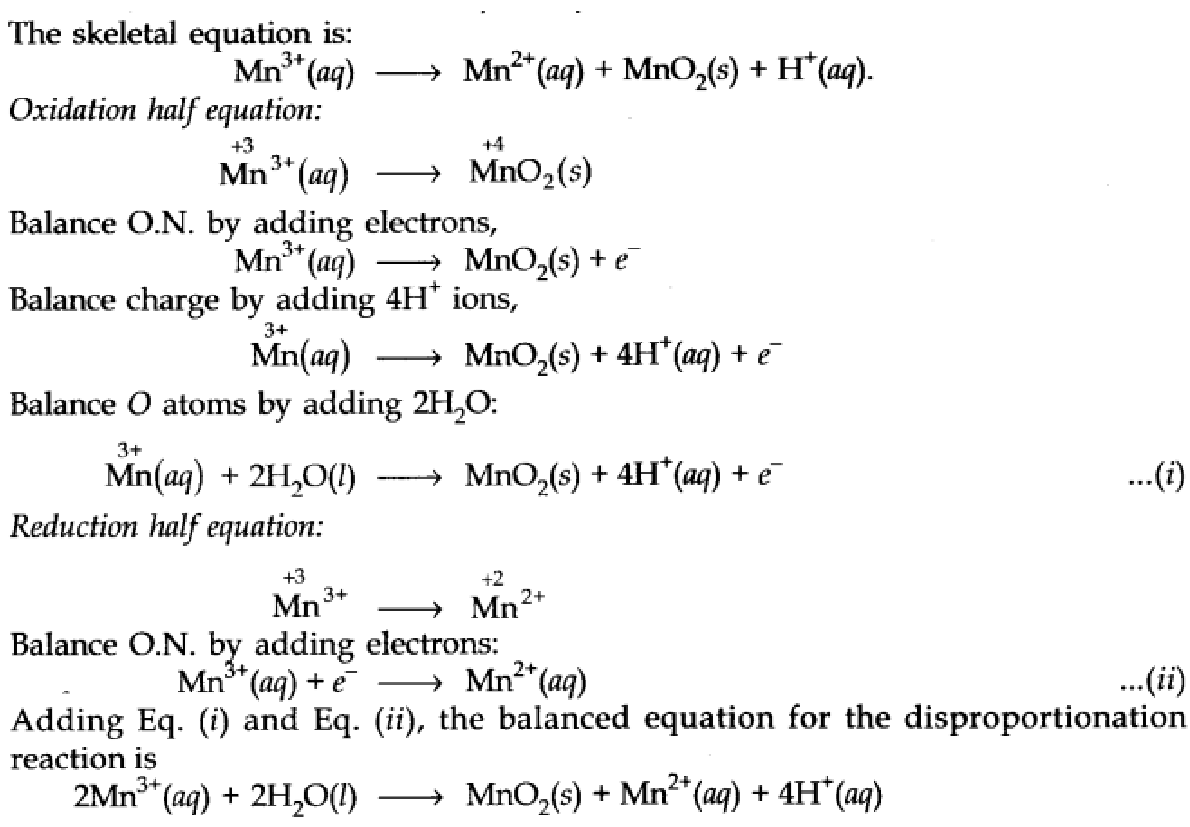
(ii) The O.N. of C decreases from +3 in $(CN)_2$ to +2 in CN^-ion and increases from +3 in$(CN)_2$ to +4 in CNO^- ion. Thus, cyanogen is simultaneously reduced to cyanide ion and oxidised to cyanate ion.

(iii) It is an example of a redox reaction in general and a disproportionation reaction in particular.

(iv) Cyanogen is a pseudohalogen (behaves like halogens) while cyanide ion is a pseudohalide ion (behaves like halide ion).

Question 21. The Mn^{3+} ion is unstable in solution and undergoes disproportionation to give Mn^{2+}, MnO_2 and H^+ ion. Write a balanced ionic equation for the reaction.

Answer:



The skeletal equation is:

$$Mn^{3+}(aq) \longrightarrow Mn^{2+}(aq) + MnO_2(s) + H^+(aq).$$

Oxidation half equation:

$$\overset{+3}{Mn}{}^{3+}(aq) \longrightarrow \overset{+4}{Mn}O_2(s)$$

Balance O.N. by adding electrons,

$$Mn^{3+}(aq) \longrightarrow MnO_2(s) + e^-$$

Balance charge by adding $4H^+$ ions,

$$\overset{3+}{Mn}(aq) \longrightarrow MnO_2(s) + 4H^+(aq) + e^-$$

Balance *O* atoms by adding $2H_2O$:

$$\overset{3+}{Mn}(aq) + 2H_2O(l) \longrightarrow MnO_2(s) + 4H^+(aq) + e^- \quad ...(i)$$

Reduction half equation:

$$\overset{+3}{Mn}{}^{3+} \longrightarrow \overset{+2}{Mn}{}^{2+}$$

Balance O.N. by adding electrons:

$$Mn^{3+}(aq) + e^- \longrightarrow Mn^{2+}(aq) \quad ...(ii)$$

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

$$2Mn^{3+}(aq) + 2H_2O(l) \longrightarrow MnO_2(s) + Mn^{2+}(aq) + 4H^+(aq)$$

Question 22. Consider the elements: Cs, Ne, I, F

(a) Identify the element that exhibits -ve oxidation state.

(b) Identify the element that exhibits +ve oxidation state.

(c) Identify the element that exhibits both +ve and -ve oxidation states.

(d) Identify the element which neither exhibits -ve nor +ve oxidation state.

Answer: (a) F. Fluorine being the most electronegative element shows only a -ve oxidation state of -1.

(b) Cs. Alkali metals because of the presence of a single electron in the valence shell, exhibit an oxidation state of +1.

(c) I. Because of the presence of seven electrons in the valence shell, I shows an oxidation state of -1 (in compounds of I with more electropositive elements such as H, Na, K, Ca, etc.) or an oxidation state of +1 compounds of I with more electronegative elements, i.e., O, F, etc.) and because of the presence of d-orbitals it also exhibits +ve oxidation states of +3, +5 and +7.

(d) Ne. It is an inert gas (with high ionization enthalpy and high positive electron gain enthalpy) and hence it neither exhibits -ve nor +ve oxidation states.

Question 23. Chlorine is used to purify drinking water. Excess of chlorine is harmful. The excess chlorine is removed by treating with sulphur dioxide. Present a balanced equation for the reaction for this redox change taking place in water.

Answer: The skeletal equation is:

$$Cl_2(aq) + SO_2(aq) + H_2O(l) \longrightarrow Cl^-(aq) + SO_4^{2-}(aq)$$

Reduction half equation:

$$Cl_2(aq) \longrightarrow Cl^-(aq)$$

Balance Cl atoms, $\overset{0}{Cl_2}(aq) \longrightarrow 2\overset{-1}{Cl^-}(aq)$

Balance O.N. by adding electrons:

$$Cl_2(aq) + 2e^- \longrightarrow 2Cl^-(aq) \qquad ...(i)$$

Oxidation half equation:

$$\overset{+4}{S}O_2(aq) \longrightarrow \overset{+6}{S}O_4^{2-}(aq) + 2e^-$$

Balance O.N. by adding electrons:

$$SO_2(aq) \longrightarrow SO_4^{2-}(aq) + 2e^-$$

Balance charge by adding $4H^+$ ions:

$$SO_2(aq) \longrightarrow SO_4^{2-}(aq) + 4H^+(aq) + 2e-$$

Balance *O* atoms by adding $2H_2O$,

$$SO_2(aq) + 2H_2O(l) \longrightarrow SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \qquad ...(ii)$$

Adding Eq. (*i*) and Eq. (*ii*), we have,

$$Cl_2(aq) + SO_2(aq) + 2H_2O(l) \longrightarrow 2Cl^-(aq) + SO_4^{2-}(aq) + 4H^+(aq)$$

This represents the balanced redox reaction.

Question 24. Refer to the periodic table given in your book and now answer the following questions.

(a) Select the possible non-metals that can show disproportionation reaction.

(b) Select three metals that show disproportionation reaction.

Answer:

(*a*) The non-metals are: P_4, Cl_2 and S_8.

(*i*) $P_4(s) + 3OH^-(aq) + 3H_2O(l) \longrightarrow PH_3(g) + 3H_2PO_2^-(aq)$

(*ii*) $Cl_2(g) + 2OH^-(aq) \xrightarrow{\text{cold}} Cl^-(aq) + ClO^-(aq) + H_2O(l)$

or $3Cl_2(g) + 6OH^-(aq) \xrightarrow{\text{hot}} 5Cl^-(aq) + ClO_3^-(aq) + 3H_2O(l)$

(*iii*) $S_8(s) + 12OH^- \longrightarrow 4S^{2-}(aq) + 2S_2O_3^{2-}(aq) + 6H_2O(l)$

(*b*) The metals are: Cu^+, Ga^+, In^+, Mn^{3+}, etc.

$$2Cu^+(aq) \longrightarrow Cu^{2+}(aq) + \overset{0}{Cu}(s)$$

$$3Ga^+(aq) \longrightarrow Ga^{3+}(aq) + 2\overset{0}{Ga}(s)$$

$$3In^+(aq) \longrightarrow In^{3+}(aq) + 2\overset{0}{In}(s)$$

$$2\overset{3+}{Mn}(aq) + 2H_2O(l) \longrightarrow \overset{4+}{Mn}O_2(s) + \overset{2+}{Mn}(aq) + 4H^+(aq)$$

Question 25. In Ostwald's process for the manufacture of nitric add, the first step involves the oxidation of ammonia gas by oxygen gas to give nitric oxide gas and steam. What is the maximum wight of nitric oxide that can be obtained starting only with 10.0 g of ammonia and 20.0 g of oxygen?

Answer: The balanced equation for the reaction is:

$$\underset{\substack{4 \times 17 \\ = 68\text{ g}}}{4NH_3(g)} + \underset{\substack{5 \times 32 \\ = 160\text{ g}}}{5O_2(g)} \longrightarrow \underset{\substack{4 \times 30 \\ = 120\text{ g}}}{4NO(g)} + 6H_2O(g)$$

Here, 68 g of NH_3 will react will O_2 = 160 g

$$\therefore 10\text{ g of } NH_3 \text{ will react with } O_2 = \frac{160\text{ g}}{68\text{g}} \times 10\text{g} = 23.6\text{ g}$$

But the amount of O_2 which is actually available is 20.0 g which is less than the amount which is needed. Therefore, 02 is the limiting reagent and hence calculations must be based upon the amount of 02 taken and not on the amount of NH_3 taken. From the equation,

160 g of 02 produce NO = 120 g

.•. 20 g of 02 will produce NO =120/160 x 20 = 15 g

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Question 26. Using the standard electrode potentials given in Table 8.1, predict if the reaction between the following is feasible:

(a) Fe^{3+}(aq) and I-(aq) (b) Ag^+ (aq) and Cu(s)

(c) Fe^{3+}(aq) and Cu(s) (d)Ag(s) and Fe^{3+}(aq)

(e) Br_2 (aq) and Fe^{3+} (aq).

Answer: (a) It may be noted that for oxidation reactions, i.e., Eq. (i), the sign of the electrode potential as given in Table 8.1 is reversed. To get the equation for the overall reaction, the number of electrons lost in Eq. (i) and gained in Eq. (ii) must be cancelled. To do so, Eq. (ii) is multiplied by 2 and added to Eq. (i). Further, it may be noted that whenever any half reaction equation is multiplied by any integer, its electrode potential is not multiplied by that integer. Thus,

Overall reaction: $2Fe^{3+}$ (aq) + $2I^-$(aq) ——-> $2Fe^{2+}$ (aq) + I_2(s); E° = + 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. Writing electrode potential for each half reaction from Table 8.1, we have,

Oxidation: $Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-$; $E^\circ = -0.34$ V

Reduction: $Ag^+(aq) + e^- \longrightarrow Ag(s)] \times 2$; $E^\circ = +0.80$ V

Overall reaction: $Cu(s) + 2Ag^+(aq) \longrightarrow Cu^{2+}(aq) + 2Ag(s)$; $E^\circ = \mathbf{+0.46\ V}$

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

(*c*) Suppose the reaction between $Fe^{3+}(aq)$ and $Cu(s)$ occurs according to the following equation.

$$Cu(s) + 2Fe^{3+}(aq) \longrightarrow 3Cu^{2+}(aq) + 2Fe^{2+}(aq)$$

The above reaction can be split into the following two half reactions. Writing electrode potential for each half reaction from Table **8.1,** we have,

Oxidation: $Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-$; $E^\circ = -0.34$ V

Reduction: $Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)] \times 2$; $E^\circ = +0.77$ V

Overall reaction: $Cu(s) + 2Fe^{3+}(aq) \longrightarrow Cu^{2+}(aq) + 2Fe^{2+}(aq)$; $E^\circ = \mathbf{+0.43\ V}$

Since the EMF of the reaction is positive, therefore, *the above reaction is feasible.*

Alternatively, if the reaction between $Fe^{3+}(aq)$ and $Cu(s)$ occurs according to the following equation.

$$3Cu(s) + 2Fe^{3+}(aq) \longrightarrow 3Cu^{2+}(aq) + 2Fe(s)$$

The EMF of the reaction comes out to be –ve, *i.e.,* –0.376 V (–0.34 V – 0.036 V) and hence this reaction is not feasible.

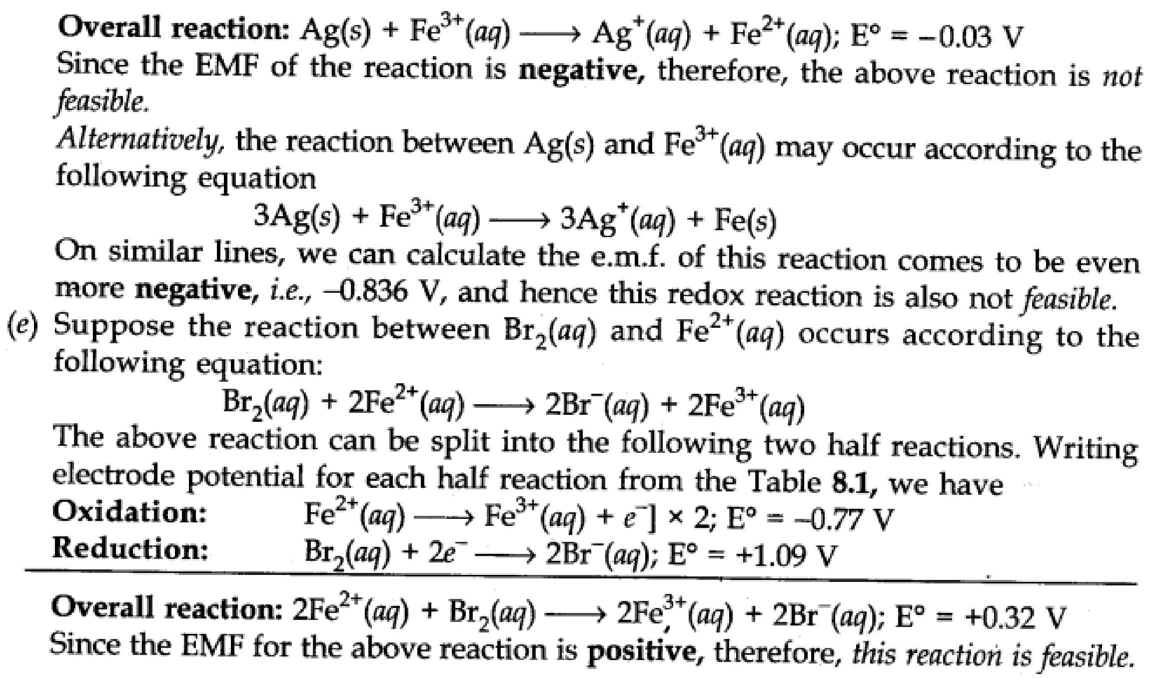
(*d*) Suppose the reaction between $Ag(s)$ and $Fe^{3+}(aq)$ occurs according to the following equation:

$$Ag(s) + Fe^{3+}(aq) \longrightarrow Ag^+(aq) + Fe^{2+}(aq)$$

The above reaction can be split into the following two half reactions. Writing electrode potential for each half reaction from Table **8.1,** we have,

Oxidation: $Ag(s) \longrightarrow Ag^+(aq) + e^-$; $E^\circ = -0.80$ V

Reduction: $Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$; $E^\circ = +0.77$ V



Overall reaction: $Ag(s) + Fe^{3+}(aq) \longrightarrow Ag^+(aq) + Fe^{2+}(aq)$; E° = –0.03 V
Since the EMF of the reaction is **negative,** therefore, the above reaction is *not feasible.*

Alternatively, the reaction between $Ag(s)$ and $Fe^{3+}(aq)$ may occur according to the following equation

$$3Ag(s) + Fe^{3+}(aq) \longrightarrow 3Ag^+(aq) + Fe(s)$$

On similar lines, we can calculate the e.m.f. of this reaction comes to be even more **negative,** *i.e.,* –0.836 V, and hence this redox reaction is also not *feasible.*

(*e*) Suppose the reaction between $Br_2(aq)$ and $Fe^{2+}(aq)$ occurs according to the following equation:

$$Br_2(aq) + 2Fe^{2+}(aq) \longrightarrow 2Br^-(aq) + 2Fe^{3+}(aq)$$

The above reaction can be split into the following two half reactions. Writing electrode potential for each half reaction from the Table **8.1,** we have

Oxidation: $Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq) + e^-] \times 2$; E° = –0.77 V
Reduction: $Br_2(aq) + 2e^- \longrightarrow 2Br^-(aq)$; E° = +1.09 V

Overall reaction: $2Fe^{2+}(aq) + Br_2(aq) \longrightarrow 2Fe^{3+}(aq) + 2Br^-(aq)$; E° = +0.32 V
Since the EMF for the above reaction is **positive,** therefore, *this reaction is feasible.*

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Question 27. Predict the products of electrolysis in each of the following:

(i) An aqueous solution of $AgNO_3$ with silver electrodes.

(ii) An aqueous solution of silver nitrate with platinum electrodes.

(iii) A dilute solution of $H_2So_4$with platinum electrodes.

(iv) An aqueous solution of $CuCl_2$ with platinum electrodes.

Answer: (i) In aqueous solution, $AgNO_3$ ionises to give Ag^+(aq) and NO_3^- (aq) ions.

$AgNo_3$(aq) ———> 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. In other words, at the cathode, either $Ag^+(aq)$ ions or H_2O molecules may be reduced. Which of these will actually get discharged would depend upon their electrode potentials which are given below:

$Ag^+(aq) + e^-$———-> $Ag(s)$; E° = +0.80 V ...(i)

$2H_2O(Z) + 2e^-$ ————> $H_2(g) + 2OH^-(aq)$; E° = -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, it is the $Ag^+(aq)$ ions (rather than H_2O molecules) which are reduced.

Similarly, at the anode, either Ag metal of the anode or H_2O molecules may be oxidised. Their electrode potentials are:

$Ag(s)$ ————> $Ag^+(aq) + e^-$; E° = -0.80 V ...(iii)

$2H_2O(l)$ —————> o2(g) +4H+(aq)+4e^- ; E° = -1.23 V ...(iv)

Since the oxidation potential of Ag is much higher than that of H_2O, therefore,

at the anode, it is the Ag of the silver anode which 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 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 get reduced and get deposited on the cathode.

(ii) If, however, electrolysis of $AgNo_3$ 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).

Thus, when an aqueous solution of $AgNO_3$ is electrolysed using platinum electrodes, Ag^+ ions from the solution get deposited on the cathode while 02 is liberated at the anode.

(iii) In aqueous solution, H_2So_4ionises to give H^+(aq) and SO_4^{2-}(aq) ions.

H_2So_4(aq) ——> $2H^+$(aq) +So_4^-(aq)

Thus, when electricity is passed, H^+ (aq) ions move towards cathode while SO_4^{2-}(aq) ions move towards anode. In other wode either H^+(aq) ions or H_2O molecules are reduced. Their electrode potentials are:$2H^+$(aq)$2e^-$ ——-> H_2(g); E° = 0.0 V

H_2O(aq) + $2e^-$ ——-> H_2(g) + $2OH^-$((aq); E° = -0.83 V

Since the electron potential (i.e., reduction potential) of H^+(aq) ions is higher than that of H_2O, therefore, at the cathode, it is H^+(aq) ions (rather than H_2O molecules) which are reduced to evolve H_2 gas.

Similarly at the anode, either SO_4^{2-}(aq) ions or H_2O molecules are oxidised. Since the oxidation potential of SO_4 is expected to be much lower (since it involved cleavage of many bonds as compared to those in H20) than that of HjO molecules, therefore, at the anode, it is H_2O molecules (rather than SO_4^{2-} 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, $CuCl_2$ ionises as follows:

$CuCl_2(aq)$ ——-> $CU^{2+}(aq) + 2Cl^-(aq)$

On passing electricity, $CU^{2+}(aq)$ ions move towards cathode and $CU^{2+}(aq)$ ions move towards anode.

Thus, at cathode, either $CU^{2+}(aq)$ or H_2O molecules are reduced. Their electrode potentials are:

$CU^{2+} + 2e^-$ ———> $Cu(s)$; $E^o = +0.34$ V

$H_2O(l) + 2e^-$ ———> $H_2(g) + 2OH^-$; $E^o = -0.83$ V

Since the electrode potential of $CU^{2+}(aq)$ ions is much higher than that of H_2O, therefore, at the cathode, it is $CU^{2+}(aq)$ ions which are reduced and not H_2Omolecules.

Similarly, at the anode, either $Cl^-(aq)$ ions or H_2O molecules are oxidised. Their oxidation potentials

$2Cl^-(aq)$ ——> $Cl_2(g) + 2e^-$; $AE^o = -1.36$ V

$2H_2O(l)$ ——>$O_2(g) + 4H^+(aq) + 4e^-$; $\Delta E^o = -1.23$ V

Although oxidation potential of H_2O molecules is higher than that of Cl^- ions, nevertheless, oxidation of $Cl^-(aq)$ ions occurs in preference to H_2O since due to overvoltage much lower potential than -1.36 V is needed for the oxidation of H_2O molecules.

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.

Question 28. Arrange the following metals in the order in which they displace each other from the solution of their salts.Al, Cu, Fe, Mg and Zn.

Answer: It is based upon the relative positions of these metals in the activity series. The correct order is Mg, Al, Zn, Fe, Cu .

Question 29. Given the standard electrode potentials,

K^+/K = -2.93 V, Ag^+/Ag = 0.80 V, Hg^{2+}/Hg = 0.79 V, Mg^{2+}/Mg = -2.37 V,

Cr^{3+}/Cr = -0.74 V. Arrange these metals in increasing order of their reducing power.

Answer: Lower the electrode potential, better is the reducing agent. Since the electrode potentials increase in the oder; K^+/K (-2.93 V), Mg^{2+}/Mg (-2.37 V), Cr^{3+}/Cr (-0.74 V), Hg^{2+}/Hg (0.79 V), Ag^+/Ag (0.80 V), therefore, reducing power of metals decreases in the same order, i.e., K, Mg, Cr, Hg, Ag.

Question 30. Depict the galvanic cell in which the reaction, $Zn(s) + 2Ag^+(aq) \longrightarrow Zn^{2+}(aq) + 2Ag(s)$

takes place. Further show:

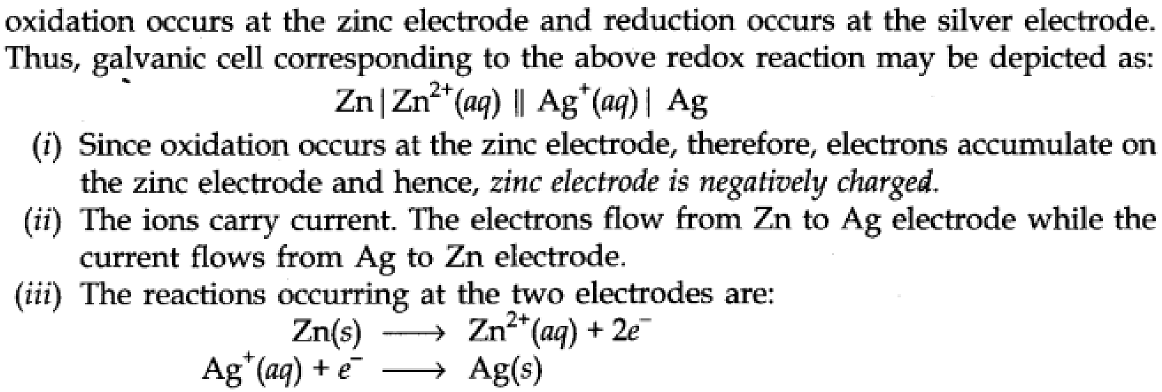
(i) which of the electrode is negatively charged.

(ii) the carriers of current in the cell and

(iii) individual reaction at each electrode.

Answer: The given redox reaction is $Zn(s) + 2Ag^{+}(aq)$ ———————> $Zn^{2+}(aq) + 2Ag(s)$

Since Zn gets oxidised to Zn^{2+} ions, and Ag^{+} gets reduced to Ag metal, therefore,



oxidation occurs at the 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:

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^{-}$$
$$Ag^{+}(aq) + e^{-} \longrightarrow Ag(s)$$

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Chapterwise NCERT Solutions for Class 11 Chemistry:

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