Chemistry

(Chapter 8)(Redox Reactions)

XI

Question 8.1:

Assign oxidation numbers 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) $KAl(\underline{S}O_4)_2.12\ H_2O$

Answer

(a) $NaH_2\underline{P}O_4$

Let the oxidation number of P be *x*.

We know that,

Oxidation number of Na = +1

Oxidation number of H = +1

Oxidation number of O = –2

$$\Rightarrow \overset{+1}{Na}\,\overset{+1}{H_2}\,\overset{x}{P}\,\overset{-2}{O_4}$$

Then, we have

$$1(+1)+2(+1)+1(x)+4(-2)=0$$
$$\Rightarrow 1+2+x-8=0$$
$$\Rightarrow x=+5$$

Hence, the oxidation number of P is +5.

(b) $NaH\underline{S}O_4$

$$\overset{+1}{Na}\,\overset{+1}{H}\,\overset{x}{S}\,\overset{-2}{O_4}$$

Then, we have

$$1(+1)+1(+1)+1(x)+4(-2)=0$$
$$\Rightarrow 1+1+x-8=0$$
$$\Rightarrow x=+6$$

Hence, the oxidation number of S is + 6.

(c) $H_4\underline{P}_2O_7$

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

Then, we have

$$4(+1)+2(x)+7(-2)=0$$
$$\Rightarrow 4+2x-14=0$$
$$\Rightarrow 2x=+10$$
$$\Rightarrow x=+5$$

Hence, the oxidation number of P is + 5.

(d) $K_2\underline{Mn}O_4$

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

Then, we have

$$2(+1)+x+4(-2)=0$$
$$\Rightarrow 2+x-8=0$$
$$\Rightarrow x=+6$$

Hence, the oxidation number of Mn is + 6.

(e) $Ca\underline{O_2}$

$$\overset{+2}{Ca}\overset{x}{O_2}$$

Then, we have

$$(+2)+2(x)=0$$
$$\Rightarrow 2+2x=0$$
$$\Rightarrow x=-1$$

Hence, the oxidation number of O is – 1.

(f) $Na\underline{B}H_4$

$$\overset{+1}{Na}\overset{x}{B}\overset{-1}{H_4}$$

Then, we have

$$1(+1)+1(x)+4(-1)=0$$
$$\Rightarrow 1+x-4=0$$
$$\Rightarrow x=+3$$

Hence, the oxidation number of B is + 3.

(g) $H_2\underline{S_2}O_7$

$$\overset{+1}{H_2}\overset{x}{S_2}\overset{-2}{O_7}$$

Then, we have

$$2(+1)+2(x)+7(-2)=0$$
$$\Rightarrow 2+2x-14=0$$
$$\Rightarrow 2x=12$$
$$\Rightarrow x=+6$$

Hence, the oxidation number of S is + 6.

(h) $KAl(\underline{S}O_4)_2.12H_2O$

$$\overset{+1}{K}\overset{3+}{Al}\left(\overset{x}{S}\overset{2-}{O_4}\right)_2.12\overset{+1}{H_2}\overset{-2}{O}$$

Then, we have

$$1(+1)+1(+3)+2(x)+8(-2)+24(+1)+12(-2)=0$$
$$\Rightarrow 1+3+2x-16+24-24=0$$
$$\Rightarrow 2x=12$$
$$\Rightarrow x=+6$$

Or,

We can ignore the water molecule as it is a neutral molecule. Then, the sum of the oxidation numbers of all atoms of the water molecule may be taken as zero. Therefore, after ignoring the water molecule, we have

$$1(+1)+1(+3)+2(x)+8(-2)=0$$
$$\Rightarrow 1+3+2x-16=0$$
$$\Rightarrow 2x=12$$
$$\Rightarrow x=+6$$

Hence, the oxidation number of S is + 6.

Question 8.2:

What are the oxidation numbers 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) $K\underline{I}_3$

In KI_3, the oxidation number (O.N.) of K is +1. Hence, the average oxidation number of I is $-\frac{1}{3}$. However, O.N. cannot be fractional. Therefore, we will have to consider the structure of KI_3 to find the oxidation states.

In a KI_3 molecule, an atom of iodine forms a coordinate covalent bond with an iodine molecule.

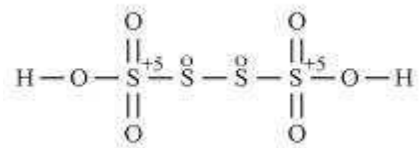
$$\overset{+1}{K^+}\left[\overset{0}{\mathrm{I}}-\overset{0}{\mathrm{I}}\leftarrow\overset{-1}{\mathrm{I}}\right]^-$$

Hence, in a KI_3 molecule, the O.N. of the two I atoms forming the I_2 molecule is 0, whereas the O.N. of the I atom forming the coordinate bond is −1. **(b)** $H_2\underline{S}_4O_6$

$$\overset{+1}{H_2}\overset{x}{S}O_4\overset{-2}{O_6}$$

$$\text{Now, } 2(+1)+4(x)+6(-2)=0$$
$$\Rightarrow 2+4x-12=0$$
$$\Rightarrow 4x=10$$
$$\Rightarrow x=+2\frac{1}{2}$$

However, O.N. cannot be fractional. Hence, S must be present in different oxidation states in the molecule.



The O.N. of two of the four S atoms is +5 and the O.N. of the other two S atoms is 0.

(c) $\underline{Fe}_3O_4$

On taking the O.N. of O as −2, the O.N. of Fe is found to be $+2\frac{2}{3}$. However, O.N. cannot be fractional.

Here, one of the three Fe atoms exhibits the O.N. of +2 and the other two Fe atoms exhibit the O.N. of +3.

$\overset{+2}{Fe}O, \overset{+3}{Fe}_2O_3$

(d) $\underline{C}H_3\underline{C}H_2OH$

$\overset{x}{C}_2\overset{+1}{H}_6\overset{-2}{O}$

$$2(x) + 4(+1) + 1(-2) = 0$$
$$\Rightarrow 2x + 6 - 2 = 0$$
$$\Rightarrow x = -2$$

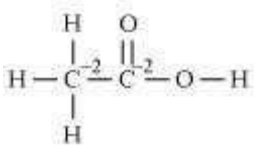
Hence, the O.N. of C is −2.

(e) $\underline{C}H_3\underline{C}OOH$

$\overset{x}{C}_2\overset{+1}{H}_4\overset{-2}{O}_2$

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

However, 0 is average O.N. of C. The two carbon atoms present in this molecule are present in different environments. Hence, they cannot have the same oxidation number. Thus, C exhibits the oxidation states of +2 and −2 in CH_3COOH.



Question 8.3:

Justify that the following reactions are redox reactions:

(a) $CuO(s) + H_2(g) \rightarrow Cu(s) + H_2O(g)$

(b) $Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g)$

(c) $4BCl_3(g) + 3LiAlH_4(s) \rightarrow 2B_2H_6(g) + 3LiCl(s) + 3\ AlCl_3\ (s)$

(d) $2K(s) + F_2(g) \rightarrow 2K^+F^-\ (s)$

(e) $4\ NH_3(g) + 5\ O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$

Answer

(a) $CuO_{(s)} + H_{2(g)} \longrightarrow Cu_{(s)} + H_2O_{(g)}$

Let us write the oxidation number of each element involved in the given reaction as:

$$\overset{+2}{Cu}\overset{-2}{O}_{(s)} + \overset{0}{H}_{2(g)} \longrightarrow \overset{0}{Cu}_{(s)} + \overset{+1}{H}_2\overset{-2}{O}_{(g)}$$

Here, the oxidation number of Cu decreases from +2 in CuO to 0 in Cu i.e., CuO is reduced to Cu. Also, the oxidation number of H increases from 0 in H_2 to +1 in H_2O i.e., H_2 is oxidized to H_2O. Hence, this reaction is a redox reaction.

(b) $Fe_2O_{3(s)} + 3CO_{(g)} \longrightarrow 2Fe_{(s)} + 3CO_{2(g)}$

Let us write the oxidation number of each element in the given reaction as:

$$\overset{+3}{Fe}_2\overset{-2}{O}_{3(s)} + 3\overset{+2}{C}\overset{-2}{O}_{(g)} \longrightarrow 2\overset{0}{Fe}_{(s)} + 3\overset{+4}{C}\overset{-2}{O}_{2(g)}$$

Here, the oxidation number of Fe decreases from +3 in Fe_2O_3 to 0 in Fe i.e., Fe_2O_3 is reduced to Fe. On the other hand, the oxidation number of C increases from +2 in CO to +4 in CO_2 i.e., CO is oxidized to CO_2. Hence, the given reaction is a redox reaction.

(c) $4BCl_{3(g)} + 3LiAlH_{4(s)} \longrightarrow 2B_2H_{6(g)} + 3LiCl_{(s)} + 3AlCl_{3(s)}$

The oxidation number of each element in the given reaction can be represented as:

$$4\overset{+3}{B}\overset{-1}{Cl}_{3(g)} + 3\overset{+1}{Li}\overset{+3}{Al}\overset{-1}{H}_{4(s)} \longrightarrow 2\overset{-3}{B}_2\overset{+1}{H}_{6(g)} + 3\overset{+1}{Li}\overset{-1}{Cl}_{(s)} + 3\overset{+3}{Al}\overset{-1}{Cl}_{3(s)}$$

In this reaction, the oxidation number of B decreases from +3 in BCl_3 to −3 in B_2H_6. i.e., BCl_3 is reduced to B_2H_6. Also, the oxidation number of H increases from −1 in $LiAlH_4$ to +1 in B_2H_6 i.e., $LiAlH_4$ is oxidized to B_2H_6. Hence, the given reaction is a redox reaction.

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

The oxidation number of each element in the given reaction can be represented as:

$$2\overset{0}{K}_{(s)} + \overset{0}{F}_{2(g)} \longrightarrow 2\overset{+1}{K^+}\overset{-1}{F^-}_{(s)}$$

In this reaction, the oxidation number of K increases from 0 in K to +1 in KF i.e., K is oxidized to KF. On the other hand, the oxidation number of F decreases from 0 in F_2 to –1 in KF i.e., F_2 is reduced to KF.

Hence, the above reaction is a redox reaction.

(e) $4NH_{3(g)} + 5O_{2(g)} \longrightarrow 4NO_{(g)} + 6H_2O_{(g)}$

The oxidation number of each element in the given reaction can be represented as:

$$4\overset{-3}{N}\overset{+1}{H}_{3(g)}+5\overset{0}{O}_{2(g)} \longrightarrow 4\overset{+2}{N}\overset{-2}{O}_{(g)}+6\overset{+1}{H}_2\overset{-2}{O}_{(g)}$$

Here, the oxidation number of N increases from −3 in NH_3 to +2 in NO. On the other hand, the oxidation number of O_2 decreases from 0 in O_2 to −2 in NO and H_2O i.e., O_2 is reduced. Hence, the given reaction is a redox reaction.

Question 8.4:

Fluorine reacts with ice and results in the change:

$H_2O(s) + F_2(g) \rightarrow HF(g) + HOF(g)$

Justify that this reaction is a redox reaction.

Answer

Let us write the oxidation number of each atom involved in the given reaction above its symbol as:

$$\overset{+1}{H}_2\overset{-2}{O}+\overset{0}{F}_2 \longrightarrow \overset{+1}{H}\overset{-1}{F}+\overset{+1}{H}\overset{-2}{O}\overset{+1}{F}$$

Here, we have observed that the oxidation number of F increases from 0 in F_2 to +1 in HOF. Also, the oxidation number decreases from 0 in F_2 to −1 in HF. Thus, in the above reaction, F is both oxidized and reduced. Hence, the given reaction is a redox reaction.

Question 8.5:

Calculate the oxidation number of sulphur, chromium and nitrogen in H_2SO_5,

$Cr_2O_7^{2-}$ and NO_3^- –. Suggest structure of these compounds. Count for the fallacy.

Answer

(i) $\overset{+1}{H}_2\overset{x}{S}\overset{-2}{O}_5$

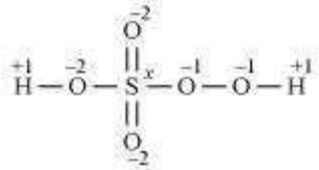
$$2(+1)+1(x)+5(-2)=0$$

$$\Rightarrow 2+x-10=0$$

$$\Rightarrow x=+8$$

However, the O.N. of S cannot be +8. S has six valence electrons. Therefore, the O.N. of S cannot be more than +6.

The structure of H_2SO_5 is shown as follows:



$$\text{Now, } 2(+1) + 1(x) + 3(-2) + 2(-1) = 0$$

$$\Rightarrow 2 + x - 6 - 2 = 0$$

$$\Rightarrow x = +6$$

Therefore, the O.N. of S is +6.

(ii) $\overset{x}{Cr_2}\overset{2-}{O_7^{2-}}$

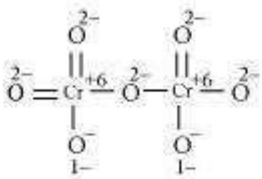
$$2(x) + 7(-2) = -2$$

$$\Rightarrow 2x - 14 = -2$$

$$\Rightarrow x = +6$$

Here, there is no fallacy about the O.N. of Cr in $Cr_2O_7^{2-}$.

The structure of $Cr_2O_7^{2-}$



is shown as follows:

Here, each of the two Cr atoms exhibits the O.N. of +6.

(iii) $\overset{x}{N}\overset{2-}{O_3^-}$

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

$$\Rightarrow x - 6 = -1$$

$$\Rightarrow x = +5$$

Here, there is no fallacy about the O.N. of N in NO_3^- .

The structure of NO_3^-

is shown as follows:

The N atom exhibits the O.N. of +5.

Question 8.6:

Write the formulae 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) Mercury (II) chloride:

$HgCl_2$

(b) Nickel (II) sulphate:

$NiSO_4$

(c) Tin (IV) oxide:

SnO_2

(d) Thallium (I) sulphate:

Tl_2SO_4

(e) Iron (III) sulphate:

$Fe_2(SO_4)_3$

(f) Chromium (III) oxide:

Cr_2O_3

Question 8.7:

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

Answer

The substances where carbon can exhibit oxidation states from –4 to +4 are listed in the following table.

Substance	O.N. of carbon
CH_2Cl_2	0
$ClC\equiv CCl$	+1
$HC\equiv CH$	−1
$CHCl_3$, CO	+2
CH_3Cl	−2
Cl_3C-CCl_3	+3
H_3C-CH_3	−3
CCl_4, CO_2	+4
CH_4	−4

The substances where nitrogen can exhibit oxidation states from −3 to +5 are listed in the following table.

Substance	O.N. of nitrogen
N_2	0
N_2O	+1
N_2H_2	−1
NO	+2
N_2H_4	−2
N_2O_3	+3
NH_3	−3
NO_2	+4
N_2O_5	+5

Question 8.8:

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

Answer

In sulphur dioxide (SO_2), the oxidation number (O.N.) of S is +4 and the range of the O.N. that S can have is from +6 to –2.

Therefore, SO_2 can act as an oxidising as well as a reducing agent.

In hydrogen peroxide (H_2O_2), the O.N. of O is –1 and the range of the O.N. that O can have is from 0 to –2. O can sometimes also attain the oxidation numbers +1 and +2. Hence, H_2O_2 can act as an oxidising as well as a reducing agent.

In ozone (O_3), the O.N. of O is zero and the range of the O.N. that O can have is from 0 to –2. Therefore, the O.N. of O can only decrease in this case. Hence, O_3 acts only as an oxidant.

In nitric acid (HNO_3), the O.N. of N is +5 and the range of the O.N. that N can have is from +5 to –3. Therefore, the O.N. of N can only decrease in this case. Hence, HNO_3 acts only as an oxidant.

Question 8.9:

Consider the reactions:

(a) $6\ CO_2(g) + 6H_2O(l) \rightarrow C_6\ H_{12}\ O_6(aq) + 6O_2(g)$

(b) $O_3(g) + H_2O_2(l) \rightarrow H_2O(l) + 2O_2(g)$

Why it is more appropriate to write these reactions as:

(a) $6CO_2(g) + 12H_2O(l) \rightarrow C_6\ H_{12}\ O_6(aq) + 6H_2O(l) + 6O_2(g)$

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

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

Answer

(a) The process of photosynthesis involves two steps.

Step 1:

H_2O decomposes to give H_2 and O_2.

$$2H_2O_{(l)} \longrightarrow 2H_{2(g)} + O_{2(g)}$$

Step 2:

The H_2 produced in **step 1** reduces CO_2, thereby producing glucose ($C_6H_{12}O_6$) and H_2O.

$$6\,CO_{2(g)} + 12\,H_{2(g)} \longrightarrow C_6H_{12}O_{6(s)} + 6\,H_2O_{(l)}$$

Now, the net reaction of the process is given as:

$$\left.2H_2O_{(l)} \longrightarrow 2H_{2(g)} + O_{2(g)}\right] \times 6$$

$$6CO_{2(g)} + 12H_{2(g)} \longrightarrow C_6H_{12}O_{6(g)} + 6H_2O_{(l)}$$

$$6CO_{2(g)} + 12H_2O_{(l)} \longrightarrow C_6H_{12}O_{6(g)} + 6H_2O_{(l)} + 6O_{2(g)}$$

It is more appropriate to write the reaction as given above because water molecules are also produced in the process of photosynthesis.

The path of this reaction can be investigated by using radioactive H_2O^{18} in place of H_2O.

(b) O_2 is produced from each of the two reactants O_3 and H_2O_2. For this reason, O_2 is written twice.

The given reaction involves two steps. First, O_3 decomposes to form O_2 and O. In the second step, H_2O_2 reacts with the O produced in the first step, thereby producing H_2O and O_2.

$$O_{3(g)} \longrightarrow O_{2(g)} + O_{(g)}$$

$$H_2O_{2(l)} + O_{(g)} \longrightarrow H_2O_{(l)} + O_{2(g)}$$

$$H_2O_{2(l)} + O_{3(g)} \longrightarrow H_2O_{(l)} + O_{2(g)} + O_{2(g)}$$

The path of this reaction can be investigated by using $H_2O_2^{18}$ or O_3^{18}.

Question 8.10:

The compound AgF_2 is an unstable compound. However, if formed, the compound acts as a very strong oxidizing agent. Why?

Answer

The oxidation state of Ag in AgF_2 is +2. But, +2 is an unstable oxidation state of Ag. Therefore, whenever AgF_2 is formed, silver readily accepts an electron to form Ag^+. This helps to bring the oxidation state of Ag down from +2 to a more stable state of +1. As a result, AgF_2 acts as a very strong oxidizing agent.

Question 8.11:

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 the oxidising agent is in excess. Justify this statement giving three illustrations.

Answer

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 the oxidising agent is in excess. This can be illustrated as follows:

(i) P_4 and F_2 are reducing and oxidising agents respectively.

If an excess of P_4 is treated with F_2, then PF_3 will be produced, wherein the oxidation number (O.N.) of P is +3.

$$P_4(\text{excess}) + F_2 \longrightarrow \overset{+3}{P}F_3$$

However, if P_4 is treated with an excess of F_2, then PF_5 will be produced, wherein the O.N. of P is +5.

$$P_4 + F_2(\text{excess}) \longrightarrow \overset{+5}{P}F_5$$

(ii) K acts as a reducing agent, whereas O_2 is an oxidising agent.

If an excess of K reacts with O_2, then K_2O will be formed, wherein the O.N. of O is −2.

$$4K(\text{excess}) + O_2 \longrightarrow 2K_2\overset{-2}{O}$$

However, if K reacts with an excess of O_2, then K_2O_2 will be formed, wherein the O.N. of O is −1.

$$2K + O_2(\text{excess}) \longrightarrow K_2\overset{-1}{O_2}$$

(iii) C is a reducing agent, while O_2 acts as an oxidising agent.

If an excess of C is burnt in the presence of insufficient amount of O_2, then CO will be produced, wherein the O.N. of C is +2.

$$C(\text{excess}) + O_2 \longrightarrow \overset{+2}{C}O$$

On the other hand, if C is burnt in an excess of O_2, then CO_2 will be produced, wherein the O.N. of C is +4.

$$C + O_2\,(\text{excess}) \longrightarrow \overset{+4}{C}O_2$$

Question 8.12:

How do you count 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?

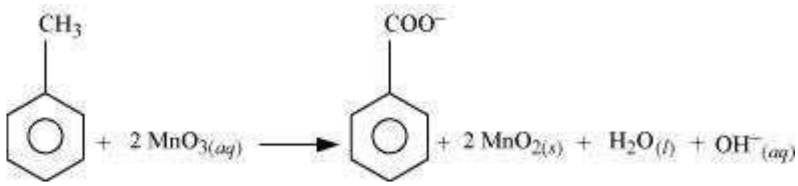
Answer

(a) In the manufacture of benzoic acid from toluene, alcoholic potassium permanganate is used as an oxidant because of the following reasons.

(i) In a neutral medium, OH^- ions are produced in the reaction itself. As a result, the cost of adding an acid or a base can be reduced.

(ii) $KMnO_4$ and alcohol are homogeneous to each other since both are polar. Toluene and alcohol are also homogeneous to each other because both are organic compounds. Reactions can proceed at a faster rate in a homogeneous medium than in a heterogeneous medium. Hence, in alcohol, $KMnO_4$ and toluene can react at a faster rate.

The balanced redox equation for the reaction in a neutral medium is give as below:



(b) When conc. H_2SO_4 is added to an inorganic mixture containing bromide, initially HBr is produced. HBr, being a strong reducing agent reduces H_2SO_4 to SO_2 with the evolution of red vapour of bromine.

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

$$2HBr + H_2SO_4 \longrightarrow \underset{\text{(red vapour)}}{Br_2} + SO_2 + 2H_2O$$

But, when conc. H_2SO_4 is added to an inorganic mixture containing chloride, a pungent smelling gas (HCl) is evolved. HCl, being a weak reducing agent, cannot reduce H_2SO_4 to SO_2.

$$2NaCl + 2H_2SO_4 \longrightarrow 2NaHSO_4 + 2HCl$$

Question 8.13:

Identify the substance oxidised, reduced, oxidising agent and reducing agent for each of the following reactions:

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

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

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

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

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

Answer

(a) Oxidised substance → $C_6H_6O_2$

Reduced substance → AgBr

Oxidising agent → AgBr

Reducing agent → $C_6H_6O_2$

(b) Oxidised substance → HCHO

Reduced substance → $\left[Ag(NH_3)_2\right]^+$

Oxidising agent → $\left[Ag(NH_3)_2\right]^+$

Reducing agent → HCHO

(c) Oxidised substance → HCHO

Reduced substance → Cu^{2+}

Oxidising agent → Cu^{2+}

Reducing agent → HCHO

(d) Oxidised substance → N_2H_4

Reduced substance → H_2O_2

Oxidising agent → H_2O_2

Reducing agent → N_2H_4

(e) Oxidised substance → Pb

Reduced substance → PbO_2

Oxidising agent → PbO_2
Reducing agent → Pb

Question 8.14:

Consider the reactions:

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

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

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

Answer

The average oxidation number (O.N.) of S in $S_2O_3^{2-}$ is +2. Being a stronger oxidising agent than I_2, Br_2 oxidises $S_2O_3^{2-}$ to SO_4^{2-}, in which the O.N. of S is +6. However, I_2 is a weak oxidising agent. Therefore, it oxidises $S_2O_3^{2-}$ to $S_4O_6^{2-}$, in which the average O.N. of S is only +2.5. As a result, $S_2O_3^{2-}$ reacts differently with iodine and bromine.

Question 8.15:

Justify giving reactions that among halogens, fluorine is the best oxidant and among hydrohalic compounds, hydroiodic acid is the best reductant.

Answer

F_2 can oxidize Cl^- to Cl_2, Br^- to Br_2, and I^- to I_2 as:

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

On the other hand, Cl_2, Br_2, and I_2 cannot oxidize F^- to F_2. The oxidizing power of halogens increases in the order of $I_2 < Br_2 < Cl_2 < F_2$. Hence, fluorine is the best oxidant among halogens.

HI and HBr can reduce H_2SO_4 to SO_2, but HCl and HF cannot. Therefore, HI and HBr are stronger reductants than HCl and HF.

$$2HI + H_2SO_4 \longrightarrow I_2 + SO_2 + 2H_2O$$
$$2HBr + H_2SO_4 \longrightarrow Br_2 + SO_2 + 2H_2O$$

Again, I^- can reduce Cu^{2+} to Cu^+, but Br^- cannot.

$$4I^-_{(aq)} + 2Cu^{2+}_{(aq)} \longrightarrow Cu_2I_{2(s)} + I_{2(aq)}$$

Hence, hydroiodic acid is the best reductant among hydrohalic compounds.

Thus, the reducing power of hydrohalic acids increases in the order of HF < HCl < HBr < HI.

Question 8.16:

Why does the following reaction occur?

XeO_6^{4-} (aq) + $2F^-$ (aq) + $6H^+$(aq) → XeO_3(g) + 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

The given reaction occurs because XeO_6^{4-} oxidises F^- and F^-

$$\overset{+8}{X}eO_6^{4-}{}_{(aq)} + 2\overset{-1}{F^-}{}_{(aq)} + 6H^+_{(aq)} \longrightarrow \overset{+6}{X}eO_{3(g)} + \overset{0}{F}_{2(g)} + 3H_2O_{(l)}$$ reduces XeO_6^{4-}.

In this reaction, the oxidation number (O.N.) of Xe decreases from +8 in XeO_6^{4-} to +6 in XeO_3 and the O.N. of F increases from −1 in F^- to O in F_2.

Hence, we can conclude that Na_4XeO_6 is a stronger oxidising agent than F^-.

Question 8.17:

Consider the reactions:

(a) $H_3PO_2(aq) + 4\ AgNO_3(aq) + 2\ H_2O(l) \rightarrow H_3PO_4(aq) + 4Ag(s) + 4HNO_3(aq)$

(b) $H_3PO_2(aq) + 2CuSO_4(aq) + 2\ H_2O(l) \rightarrow H_3PO_4(aq) + 2Cu(s) + H_2SO_4(aq)$

(c) $C_6H_5CHO(l) + 2[Ag\ (NH_3)_2]^+(aq) + 3OH^-(aq) \rightarrow C_6H_5COO^-(aq) + 2Ag(s) + 4NH_3\ (aq) + 2\ H_2O(l)$

(d) $C_6H_5CHO(l) + 2Cu^{2+}(aq) + 5OH^-(aq) \rightarrow$ No change observed.

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

Answer

Ag^+ and Cu^{2+} act as oxidising agents in reactions **(a)** and **(b)** respectively.

In reaction **(c)**, Ag^+ oxidises C_6H_5CHO to $C_6H_5COO^-$, but in reaction **(d)**, Cu^{2+} cannot oxidise C_6H_5CHO.

Hence, we can say that Ag^+ is a stronger oxidising agent than Cu^{2+}.

Question 8.18:

Balance the following redox reactions by ion-electron method:

(a) MnO_4^- (aq) + I^- (aq) $\rightarrow MnO_2$ (s) + I_2(s) (in basic medium)

(b) MnO_4^- (aq) + SO_2 (g) $\rightarrow Mn^{2+}$ (aq) + HSO_4^- (aq) (in acidic solution)

(c) H_2O_2 (aq) + Fe^{2+} (aq) $\rightarrow Fe^{3+}$ (aq) + H_2O (l) (in acidic solution)

(d) $Cr_2O_7^{2-}$ + SO_2(g) $\rightarrow Cr^{3+}$ (aq) + SO_4^{2-} (aq) (in acidic solution)

Answer

(a) Step 1: The two half reactions involved in the given reaction are:

Oxidation half reaction: $\overset{-1}{I}_{(aq)} \longrightarrow \overset{0}{I}_{2(s)}$

$\overset{+7}{Mn}O^-_{4(aq)} \longrightarrow \overset{+4}{Mn}O_{2(aq)}$

Reduction half reaction:

Step 2:

Balancing I in the oxidation half reaction, we have:

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

Now, to balance the charge, we add 2 e^- to the RHS of the reaction.

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

Step 3:

In the reduction half reaction, the oxidation state of Mn has reduced from +7 to +4. Thus, 3 electrons are added to the LHS of the reaction.

$$MnO^-_{4(aq)} + 3e^- \longrightarrow MnO_{2(aq)}$$

Now, to balance the charge, we add 4 OH^- ions to the RHS of the reaction as the reaction is taking place in a basic medium.

$$MnO^-_{4(aq)} + 3e^- \longrightarrow MnO_{2(aq)} + 4OH^-$$

Step 4:

In this equation, there are 6 O atoms on the RHS and 4 O atoms on the LHS. Therefore, two water molecules are added to the LHS.

$$MnO^-_{4(aq)} + 2H_2O + 3e^- \longrightarrow MnO_{2(aq)} + 4OH^-$$

Step 5:

Equalising the number of electrons by multiplying the oxidation half reaction by 3 and the reduction half reaction by 2, we have:

$$6I^-_{(aq)} \longrightarrow 3I_{2(s)} + 6e^-$$

$$2MnO^-_{4(aq)} + 4H_2O + 6e^- \longrightarrow 2MnO_{2(s)} + 8OH^-_{(aq)}$$

Step 6:

Adding the two half reactions, we have the net balanced redox reaction as:

$$6I^-_{(aq)} + 2MnO^-_{4(aq)} + 4H_2O_{(l)} \longrightarrow 3I_{2(s)} + 2MnO_{2(s)} + 8OH^-_{(aq)}$$

(b) Following the steps as in part **(a)**, we have the oxidation half reaction as:

$$SO_{2(g)} + 2H_2O_{(l)} \longrightarrow HSO^-_{4(aq)} + 3H^+_{(aq)} + 2e^-_{(aq)}$$

And the reduction half reaction as:

$$MnO^-_{4(aq)} + 8H^+_{(aq)} + 5e^- \longrightarrow Mn^{2+}_{(aq)} + 4H_2O_{(l)}$$

Multiplying the oxidation half reaction by 5 and the reduction half reaction by 2, and then by adding them, we have the net balanced redox reaction as:

$$2MnO^-_{4(aq)} + 5SO_{2(g)} + 2H_2O_{(l)} + H^+_{(aq)} \longrightarrow 2Mn^{2+}_{(aq)} + 5\,HSO^-_{4(aq)}$$

(c) Following the steps as in part **(a)**, we have the oxidation half reaction as:

$$Fe^{2+}_{(aq)} \longrightarrow Fe^{3+}_{(aq)} + e^-$$

And the reduction half reaction as:

$$H_2O_{2(aq)} + 2H^+_{(aq)} + 2e^- \longrightarrow 2H_2O_{(l)}$$

Multiplying the oxidation half reaction by 2 and then adding it to the reduction half reaction, we have the net balanced redox reaction as:

$$H_2O_{2(aq)} + 2Fe^{2+}_{(aq)} + 2H^+_{(aq)} \longrightarrow 2Fe^{3+}_{(aq)} + 2H_2O_{(l)}$$

(d) Following the steps as in part **(a)**, we have the oxidation half reaction as:

$$SO_{2(g)} + 2H_2O_{(l)} \longrightarrow SO^{2-}_{4\,(aq)} + 4H^+_{(aq)} + 2e^-$$

And the reduction half reaction as:

$$Cr_2O^{2-}_{7\,(aq)} + 14H^+_{(aq)} + 6e^- \longrightarrow 2Cr^{3+}_{(aq)} + 7H_2O_{(l)}$$

Multiplying the oxidation half reaction by 3 and then adding it to the reduction half reaction, we have the net balanced redox reaction as:

$$Cr_2O^{2-}_{7\,(aq)} + 3SO_{2(g)} + 2H^+_{(aq)} \longrightarrow 2Cr^{3+}_{(aq)} + 3SO^{2-}_{4\,(aq)} + H_2O_{(l)}$$

Question 8.19:

Balance the following equations in basic medium by ion-electron method and oxidation number methods and identify the oxidising agent and the reducing agent.

$$\text{(a) } P_{4(s)} + OH^-_{(aq)} \longrightarrow PH_{3(g)} + HPO^-_{2\,(aq)}$$

$$\text{(b) } N_2H_{4(l)} + ClO^-_{3\,(aq)} \longrightarrow NO_{(g)} + Cl^-_{(g)}$$

$$\text{(c) } Cl_2O_{7\,(g)} + H_2O_{2(aq)} \longrightarrow ClO^-_{2(aq)} + O_{2(g)} + H^+_{(aq)}$$

Answer

(a) The O.N. (oxidation number) of P decreases from 0 in P_4 to – 3 in PH_3 and increases from 0 in P_4 to + 2 in HPO^-_2. Hence, P_4 acts both as an oxidizing agent and a reducing agent in this reaction.

Ion–electron method:

The oxidation half equation is:

$$P_{4(s)} \longrightarrow HPO^{-}_{2(aq)}$$

The P atom is balanced as:

$$\overset{0}{P}_{4(s)} \longrightarrow 4H\overset{2+}{P}O^{-}_{2(aq)}$$

The O.N. is balanced by adding 8 electrons as:

$$P_{4(s)} \longrightarrow 4HPO^{-}_{2(aq)} + 8e^{-}$$

The charge is balanced by adding 12OH⁻ as:

$$P_{4(s)} + 12OH^{-}_{(aq)} \longrightarrow 4HPO^{-}_{2(aq)} + 8e^{-}$$

The H and O atoms are balanced by adding $4H_2O$ as:

$$P_{4(s)} + 12OH^{-}_{(aq)} \longrightarrow 4HPO^{-}_{2(aq)} + 4H_2O_{(l)} + 8e^{-} \text{ ....(i)}$$

The reduction half equation is:

$$P_{4(s)} \longrightarrow PH_{3(g)}$$

The P atom is balanced as

$$\overset{0}{P}_{4(s)} \longrightarrow 4\overset{-3}{P}H_{3(g)}$$

The O.N. is balanced by adding 12 electrons as:

$$P_{4(s)} + 12e^{-} \longrightarrow 4PH_{3(g)}$$

The charge is balanced by adding 12OH⁻ as:

$$P_{4(s)} + 12e^{-} \longrightarrow 4PH_{3(g)} + 12OH^{-}_{(aq)}$$

The O and H atoms are balanced by adding $12H_2O$ as:

$$P_{4(s)} + 12H_2O_{(l)} + 12e^{-} \longrightarrow 4PH_{3(g)} + 12HO^{-}_{(aq)} \qquad \text{(ii)}$$

By multiplying equation (i) with 3 and (ii) with 2 and then adding them, the balanced chemical equation can be obtained as:

$$5P_{4(s)} + 12H_2O_{(l)} + 12HO^{-}_{(aq)} \longrightarrow 8PH_{3(g)} + 12HPO^{-}_{2(aq)}$$

(b)

O.N. of N increases by 4 per atom

$$\overset{-2}{N_2H_4}{}_{(l)} + \overset{+5}{ClO_3^{-}}{}_{(aq)} \longrightarrow \overset{+2}{NO}_{(g)} + \overset{-1}{Cl}_{(aq)}$$

O.N. of Cl decreases by 6 per atom

The oxidation number of N increases from – 2 in N_2H_4 to + 2 in NO and the oxidation number of Cl decreases from + 5 in ClO_3^- to – 1 in Cl^-. Hence, in this reaction, N_2H_4 is the reducing agent and ClO_3^- is the oxidizing agent.

Ion–electron method:

The oxidation half equation is:

$$\overset{-2}{N_2}H_{4(l)} \longrightarrow \overset{+2}{N}O_{(g)}$$

The N atoms are balanced as:

$$N_2H_{4(l)} \longrightarrow 2NO_{(g)}$$

The oxidation number is balanced by adding 8 electrons as:

$$N_2H_{4(l)} \longrightarrow 2NO_{(g)} + 8e^-$$

The charge is balanced by adding 8 OH^-ions as:

$$N_2H_{4(l)} + 8OH^-_{(aq)} \longrightarrow 2NO_{(g)} + 8e^-$$

The O atoms are balanced by adding $6H_2O$ as:

$$N_2H_{4(l)} + 8OH^-_{(aq)} \longrightarrow 2NO_{(g)} + 6H_2O_{(l)} + 8e^- \text{ ....(i)}$$

The reduction half equation is:

$$\overset{+5}{Cl}O^-_{3(aq)} \longrightarrow \overset{-1}{Cl}{}^-_{(aq)}$$

The oxidation number is balanced by adding 6 electrons as:

$$ClO^-_{3(aq)} + 6e^- \longrightarrow Cl^-_{(aq)}$$

The charge is balanced by adding $6OH^-$ ions as:

$$ClO^-_{3(aq)} + 6e^- \longrightarrow Cl^-_{(aq)} + 6OH^-_{(aq)}$$

The O atoms are balanced by adding $3H_2O$ as:

$$ClO^-_{3(aq)} + 3H_2O_{(l)} + 6e^- \longrightarrow Cl^-_{(aq)} + 6OH^-_{(aq)} \text{ ....(ii)}$$

The balanced equation can be obtained by multiplying equation (i) with 3 and equation (ii) with 4 and then adding them as:

$$3N_2H_{4(l)} + 4ClO^-_{3(aq)} \longrightarrow 6NO_{(g)} + 4Cl^-_{(aq)} + 6H_2O_{(l)}$$

Oxidation number method:

Total decrease in oxidation number of N = 2 × 4 = 8

Total increase in oxidation number of Cl = 1 × 6 = 6

On multiplying N_2H_4 with 3 and ClO_3^- with 4 to balance the increase and decrease in O.N., we get:

$$3N_2H_{4(l)} + 4ClO^-_{3(aq)} \longrightarrow NO_{(g)} + Cl^-_{(aq)}$$

The N and Cl atoms are balanced as:

$$3N_2H_{4(l)} + 4ClO^-_{3(aq)} \longrightarrow 6NO_{(g)} + 4Cl^-_{(aq)}$$

The O atoms are balanced by adding $6H_2O$ as:

$$3N_2H_{4(l)} + 4ClO^-_{3(aq)} \longrightarrow 6NO_{(g)} + 4Cl^-_{(aq)} + 6H_2O_{(l)}$$

This is the required balanced equation.

(c)

O.N. of Cl decreases by 4 per atom

$$\overset{+7}{Cl_2O_{7(g)}} + \overset{-1}{H_2O_{2\,(aq)}} \longrightarrow \overset{+3}{ClO_2^-}_{(g)} + \overset{0}{O_{2\,(g)}} + H^+$$

O.N. of O increases by 1 per atom

The oxidation number of Cl decreases from + 7 in Cl_2O_7 to + 3 in ClO_2^- and the oxidation number of O increases from – 1 in H_2O_2 to zero in O_2. Hence, in this reaction, Cl_2O_7 is the oxidizing agent and H_2O_2 is the reducing agent.

Ion–electron method:

The oxidation half equation is:

$$H_2\overset{-1}{O}_{2(aq)} \longrightarrow \overset{0}{O}_{2(g)}$$

The oxidation number is balanced by adding 2 electrons as:

$$H_2O_{2(aq)} \longrightarrow O_{2(g)} + 2e^-$$

The charge is balanced by adding $2OH^-$ions as:

$$H_2O_{2(aq)} + 2OH^-_{(aq)} \longrightarrow O_{2(g)} + 2e^-$$

The oxygen atoms are balanced by adding $2H_2O$ as:

$$H_2O_{2(aq)} + 2OH^-_{(aq)} \longrightarrow O_{2(g)} + 2H_2O_{(l)} + 2e^- \qquad \text{(i)}$$

The reduction half equation is:

$$\overset{+7}{Cl_2}O_{7(g)} \longrightarrow \overset{+3}{Cl}O^-_{2(aq)}$$

The Cl atoms are balanced as:

$$Cl_2O_{7(g)} \longrightarrow 2ClO^-_{2(aq)}$$

The oxidation number is balanced by adding 8 electrons as:

$$Cl_2O_{7(g)} + 8e^- \longrightarrow 2ClO^-_{2(aq)}$$

The charge is balanced by adding $6OH^-$ as:

$$Cl_2O_{7(g)} + 8e^- \longrightarrow 2ClO^-_{2(aq)} + 6OH^-_{(aq)}$$

The oxygen atoms are balanced by adding $3H_2O$ as:

$$Cl_2O_{7(g)} + 3H_2O_{(l)} 8e^- \longrightarrow 2ClO^-_{2(aq)} + 6OH^-_{(aq)} \qquad \text{(ii)}$$

The balanced equation can be obtained by multiplying equation (i) with 4 and adding equation (ii) to it as: $Cl_2O_{7(g)} + 4H_2O_{2(aq)} + 2OH^-_{(aq)} \longrightarrow 2ClO^-_{2(aq)} + 4O_{2(g)} + 5H_2O_{(l)}$

Oxidation number method:

Total decrease in oxidation number of Cl_2O_7 = 4 × 2 = 8

Total increase in oxidation number of H_2O_2 = 2 × 1 = 2

By multiplying H_2O_2 and O_2 with 4 to balance the increase and decrease in the oxidation number, we get:

$$Cl_2O_{7(g)} + 4H_2O_{2(aq)} \longrightarrow ClO^-_{2(aq)} + 4O_{2(g)}$$

The Cl atoms are balanced as:

$$Cl_2O_{7(g)} + 4H_2O_{2(aq)} \longrightarrow 2ClO^-_{2(aq)} + 4O_{2(g)}$$

The O atoms are balanced by adding $3H_2O$ as:

$$Cl_2O_{7(g)} + 4H_2O_{2(aq)} \longrightarrow 2ClO^-_{2(aq)} + 4O_{2(g)} + 3H_2O_{(l)}$$

The H atoms are balanced by adding $2OH^-$ and $2H_2O$ as:

$$Cl_2O_{7(g)} + 4H_2O_{2(aq)} + 2OH^-_{(aq)} \longrightarrow 2ClO^-_{2(aq)} + 4O_{2(g)} + 5H_2O_{(l)}$$

This is the required balanced equation.

Question 8.20:

What sorts of informations can you draw from the following reaction ?

$$(CN)_{2(g)} + 2OH^-_{(aq)} \longrightarrow CN^-_{(aq)} + CNO^-_{(aq)} + H_2O_{(l)}$$

Answer

The oxidation numbers of carbon in $(CN)^2$, CN^- and CNO^- are +3, +2 and +4 respectively.

These are obtained as shown below:

Let the oxidation number of C be x.

$(CN)_2$

$2(x - 3) = 0$

$\therefore x = 3$

CN^- $x - 3 = -1$

$\therefore x = 2$

CNO^-

$x - 3 - 2 = -1$

$\therefore x = 4$

The oxidation number of carbon in the various species is:

$$\left(\overset{+3}{C}N\right)_{2(g)} + 2OH^-_{(aq)} \longrightarrow \overset{+2}{C}N^-_{(aq)} + \overset{+4}{C}NO^-_{(aq)} + H_2O_{(l)}$$

It can be easily observed that the same compound is being reduced and oxidised simultaneously in the given equation. Reactions in which the same compound is reduced and oxidised is known as disproportionation reactions. Thus, it can be said that the alkaline decomposition of cyanogen is an example of disproportionation reaction.

Question 8.21:

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 given reaction can be represented as:

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

The oxidation half equation is:

$$\overset{+3}{M}n^{3+}_{(aq)} \longrightarrow \overset{+4}{M}nO_{2(s)}$$

The oxidation number is balanced by adding one electron as:

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

The charge is balanced by adding 4H⁺ ions as:

$$Mn^{3+}_{(aq)} \longrightarrow MnO_{2(s)} + 4H^+_{(aq)} + e^-$$

The O atoms and H^+ ions are balanced by adding $2H_2O$ molecules as:

$$Mn^{3+}_{(aq)} + 2H_2O_{(l)} \longrightarrow MnO_{2(s)} + 4H^+_{(aq)} + e^- \text{ ....(i)}$$

The reduction half equation is:

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

The oxidation number is balanced by adding one electron as:

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

The balanced chemical equation can be obtained by adding equation (i) and (ii) as:

$$2Mn^{3+}_{(aq)} + 2H_2O_{(l)} \longrightarrow MnO_{2(s)} + 2Mn^{2+}_{(aq)} + 4H^+_{(aq)}$$

Question 8.22:

Consider the elements:

Cs, Ne, I and F

(a) Identify the element that exhibits only negative oxidation state.

(b) Identify the element that exhibits only postive oxidation state.

(c) Identify the element that exhibits both positive and negative oxidation states. (d) Identify the element which exhibits neither the negative nor does the positive oxidation state.

Answer

(a) F exhibits only negative oxidation state of −1.

(b) Cs exhibits positive oxidation state of +1.

(c) I exhibits both positive and negative oxidation states. It exhibits oxidation states of – 1, + 1, + 3, + 5, and + 7.

(d) The oxidation state of Ne is zero. It exhibits neither negative nor positive oxidation states.

Question 8.23:

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

Answer

The given redox reaction can be represented as:

$$Cl_{2(s)} + SO_{2(aq)} + H_2O_{(l)} \longrightarrow Cl^-_{(aq)} + SO_4^{2-}{}_{(aq)}$$

The oxidation half reaction is:

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

The oxidation number is balanced by adding two electrons as:

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

The charge is balanced by adding $4H^+$ ions as:

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

The O atoms and H^+ ions are balanced by adding $2H_2O$ molecules as:

$$SO_{2(aq)} + 2H_2O_{(l)} \longrightarrow SO_4^{2-}{}_{(aq)} + 4H^+_{(aq)} + 2e^- \text{ ....(i)}$$

The reduction half reaction is:

$$Cl_{2(s)} \longrightarrow Cl^-_{(aq)}$$

The chlorine atoms are balanced as:

$$\overset{0}{C}l_{2(s)} \longrightarrow \overset{-1}{C}l^-_{(aq)}$$

The oxidation number is balanced by adding electrons

$$Cl_{2(s)} + 2e^- \longrightarrow 2Cl^-_{(aq)} \text{ ....(ii)}$$

The balanced chemical equation can be obtained by adding equation (i) and (ii) as:

$$Cl_{2(s)} + SO_{2(aq)} + 2H_2O_{(l)} \longrightarrow 2Cl^-_{(aq)} + SO_4^{2-}{}_{(aq)} + 4H^+_{(aq)}$$

Question 8.24:

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 can show disproportionation reaction.

Answer

In disproportionation reactions, one of the reacting substances always contains an element that can exist in at least three oxidation states.

(a) P, Cl, and S can show disproportionation reactions as these elements can exist in three or more oxidation states.

(b) Mn, Cu, and Ga can show disproportionation reactions as these elements can exist in three or more oxidation states.

Question 8.25:

In Ostwald's process for the manufacture of nitric acid, the first step involves the oxidation of ammonia gas by oxygen gas to give nitric oxide gas and steam. What is the maximum weight of nitric oxide that can be obtained starting only with 10.00 g. of ammonia and 20.00 g of oxygen?

Answer

The balanced chemical equation for the given reaction is given as:

$$\begin{array}{llll} 4NH_{3(g)} + & 5O_{2(g)} \longrightarrow & 4NO_{(g)} & + 6H_2O_{(g)} \\ 4\times 17g & 5\times 32g & 4\times 30g & 6\times 18g \\ =68g & =160g & =120g & =108g \end{array}$$

Thus, 68 g of NH_3 reacts with 160 g of O_2.

Therefore, 10g of NH_3 reacts with $\frac{160\times 10}{68}$ g of O_2, or 23.53 g of O_2.

But the available amount of O_2 is 20 g.

Therefore, O_2 is the limiting reagent (we have considered the amount of O_2 to calculate the weight of nitric oxide obtained in the reaction).

Now, 160 g of O_2 gives 120g of NO.

Therefore, 20 g of O_2 gives $\frac{120\times 20}{160}$ g of N, or 15 g of NO.

Hence, a maximum of 15 g of nitric oxide can be obtained.

Question 8.26:

Using the standard electrode potentials given in the 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^{2+}(aq) Answer

(a) The possible reaction between $Fe^{3+}_{(aq)} + I^-_{(aq)}$ is given by,

$$2Fe^{3+}_{(aq)} + 2I^-_{(aq)} \longrightarrow 2Fe^{2+}_{(aq)} + I_{2(s)}$$

$$\begin{array}{lll} \text{Oxidation half equation :} & 2I^-_{(aq)} \longrightarrow I_{2(s)} + 2e^- ; & E^\circ = -0.54V \\ \text{Reduction half equation :} & [Fe^{3+}_{(aq)} + e^- \longrightarrow Fe^{2+}_{(aq)}]\times 2; & E^\circ = +0.77V \\ \hline & 2Fe^{3+}_{(aq)} + 2I^-_{(aq)} \longrightarrow 2Fe^{2+}_{(aq)} + I_{2(s)}\ ; & E^\circ = +0.23V \end{array}$$

E° for the overall reaction is positive. Thus, the reaction between $Fe^{3+}_{(aq)}$ and $I^-_{(aq)}$ is feasible.

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

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

$$\begin{array}{lll} \text{Oxidation half equation :} & Cu_{(s)} \longrightarrow Cu^{2+}_{(aq)} + 2e^- & ; E^\circ = -0.34V \\ \text{Reduction half equation :} & [Ag^+_{(aq)} + e^- \longrightarrow Ag_{(s)}]\times 2 & ; E^\circ = +0.80V \\ \hline & 2Ag^+_{(aq)} + Cu_{(s)} \longrightarrow 2Ag_{(s)} + Cu^{2+} & ; E^\circ = +0.46V \end{array}$$

E° positive for the overall reaction is positive. Hence, the reaction between $Ag^+_{(aq)}$ and $Cu_{(s)}$ is feasible.

(c) The possible reaction between $Fe^{3+}_{(aq)}$ and $Cu_{(s)}$ is given by,

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

$$\text{Oxidation half equation: } Cu_{(s)} \longrightarrow Cu^{2+}_{(aq)} + 2e^- \quad ; E^\circ = -0.34V$$

$$\text{Reduction half equation: } [Fe^{3+}_{(aq)} + e^- \longrightarrow Fe^{2+}_{(s)}] \times 2 \quad ; E^\circ = +0.77V$$

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

E° positive for the overall reaction is positive. Hence, the reaction between $Fe^{3+}_{(aq)}$ and $Cu_{(s)}$ is feasible.

(d) The possible reaction between $Ag_{(s)}$ and $Fe^{3+}_{(aq)}$ is given by,

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

$$\text{Oxidation half equation: } Ag_{(s)} \longrightarrow Ag^{+}_{(aq)} + e^- \quad ; E^\circ = -0.80V$$

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

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

Here, E° for the overall reaction is negative. Hence, the reaction between $Ag_{(s)}$ and $Fe^{3+}_{(aq)}$ is not feasible.

(e) The possible reaction between $Br_{2(aq)}$ and $Fe^{2+}_{(aq)}$ is given by,

$$Br_{2(s)} + 2Fe^{2+}_{(aq)} \longrightarrow 2Br^{-}_{(aq)} + 2Fe^{3+}_{(aq)}$$

$$\text{Oxidation half equation: } Fe^{2+}_{(aq)} \longrightarrow Fe^{3+}_{(aq)} + e^-] \times 2 \quad ; E^\circ = -0.77V$$

$$\text{Reduction half equation: } Br_{2(aq)} + 2e^- \longrightarrow 2Br^{-}_{(aq)} \quad ; E^\circ = +1.09V$$

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

Here, E° for the overall reaction is positive. Hence, the reaction between $Br_{2(aq)}$ and $Fe^{2+}_{(aq)}$ is feasible.

Question 8.27:

Predict the products of electrolysis in each of the following:

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

(ii) An aqueous solution $AgNO_3$ 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) $AgNO_3$ ionizes in aqueous solutions to form Ag^+ and NO_3^- ions.

On electrolysis, either Ag^+ ions or H_2O molecules can be reduced at the cathode. But the reduction potential of Ag^+ ions is higher than that of H_2O.

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

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

Hence, Ag^+ ions are reduced at the cathode. Similarly, Ag metal or H_2O molecules can be oxidized at the anode. But the oxidation potential of Ag is higher than that of H_2O molecules.

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

$$2H_2O_{(l)} \longrightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^-;\ E^\circ = -1.23V$$

Therefore, Ag metal gets oxidized at the anode.

(ii) Pt cannot be oxidized easily. Hence, at the anode, oxidation of water occurs to liberate O_2. At the cathode, Ag^+ ions are reduced and get deposited.

(iii) H_2SO_4 ionizes in aqueous solutions to give H^+ and SO_4^{2-} ions.

$$H_2SO_{4(aq)} \longrightarrow 2H^+_{(aq)} + SO_4^{2-}{}_{(aq)}$$

On electrolysis, either of H^+ ions or H_2O molecules can get reduced at the cathode. But the reduction potential of H^+ ions is higher than that of H_2O molecules.

$$2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)}\ ;\ E^\circ = 0.0V$$

$$2H_2O_{(aq)} + 2e^- \longrightarrow H_{2(g)} + 2OH^-_{(aq)}\ ;\ E^\circ = -0.83V$$

Hence, at the cathode, H^+ ions are reduced to liberate H_2 gas.

On the other hand, at the anode, either of SO_4^{2-} ions or H_2O molecules can get oxidized. But the oxidation of SO_4^{2-} involves breaking of more bonds than that of H_2O molecules. Hence, SO_4^{2-} ions have a lower oxidation potential than H_2O. Thus, H_2O is oxidized at the anode to liberate O_2 molecules.

(iv) In aqueous solutions, $CuCl_2$ ionizes to give Cu^{2+} and Cl^- ions as:

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

On electrolysis, either of Cu^{2+} ions or H_2O molecules can get reduced at the cathode. But the reduction potential of Cu^{2+} is more than that of H_2O molecules.

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

Hence, Cu^{2+} ions are reduced at the cathode and get deposited.

Similarly, at the anode, either of Cl^- or H_2O is oxidized. The oxidation potential of H_2O is higher than that of Cl^-.

$$2Cl^-_{(aq)} \longrightarrow Cl_{2(g)} + 2e^- \quad ; E^\circ = -1.36V$$
$$2H_2O_{(l)} \longrightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^-\ ; E^\circ = -1.23V$$

But oxidation of H_2O molecules occurs at a lower electrode potential than that of Cl^- ions because of over-voltage (extra voltage required to liberate gas). As a result, Cl^- ions are oxidized at the anode to liberate Cl_2 gas.

Question 8.28:

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

A metal of stronger reducing power displaces another metal of weaker reducing power from its solution of salt.

The order of the increasing reducing power of the given metals is Cu < Fe < Zn < Al < Mg.

Hence, we can say that Mg can displace Al from its salt solution, but Al cannot displace Mg.

Thus, the order in which the given metals displace each other from the solution of their salts is given below:

Mg>Al> Zn> Fe,>Cu

Question 8.29:

Given the standard electrode potentials,

$K^+/K = -2.93V$, $Ag^+/Ag = 0.80V$, Hg^{2+}/Hg

$= 0.79V$

$Mg^{2+}/Mg = -2.37V$. $Cr^{3+}/Cr = -0.74V$

Arrange these metals in their increasing order of reducing power.

Answer

The lower the electrode potential, the stronger is the reducing agent. Therefore, the increasing order of the reducing power of the given metals is Ag < Hg < Cr < Mg < K.

Question 8.30:

Depict the galvanic cell in which the reaction $Zn(s) + 2Ag^+(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s)$ takes place, further show:

(i) which of the electrode is negatively charged,

(ii) the carriers of the current in the cell, and (iii) individual reaction at each electrode.

Answer

The galvanic cell corresponding to the given redox reaction can be represented as:

$$Zn \mid Zn^{2+}_{(aq)} \parallel Ag^{+}_{(aq)} \mid Ag$$

(i) Zn electrode is negatively charged because at this electrode, Zn oxidizes to Zn^{2+} and the leaving electrons accumulate on this electrode.

(ii) Ions are the carriers of current in the cell.

(iii) The reaction taking place at Zn electrode can be represented as:

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

And the reaction taking place at Ag electrode can be represented as:

$$Ag^+_{(aq)} + e^- \longrightarrow Ag_{(s)}$$.

(iv) In aqueous solutions, $CuCl_2$ ionizes to give Cu^{2+} and Cl^- ions as:

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

On electrolysis, either of Cu^{2+} ions or H_2O molecules can get reduced at the cathode. But the reduction potential of Cu^{2+} is more than that of H_2O molecules.

$$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(aq)} ; E° = +0.34V$$

$$H_2O_{(l)} + 2e^- \longrightarrow H_{2(g)} + 2OH^- ; E° = -0.83V$$

Hence, Cu^{2+} ions are reduced at the cathode and get deposited.

Similarly, at the anode, either of Cl^- or H_2O is oxidized. The oxidation potential of H_2O is higher than that of Cl^-.

$$2Cl^-_{(aq)} \longrightarrow Cl_{2(g)} + 2e^- \quad ; E° = -1.36V$$

$$2H_2O_{(l)} \longrightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^- ; E° = -1.23V$$

But oxidation of H_2O molecules occurs at a lower electrode potential than that of Cl^- ions because of over-voltage (extra voltage required to liberate gas). As a result, Cl^- ions are oxidized at the anode to liberate Cl_2 gas.