UNIT

9

Redox Reactions

SYLLABUS

- Oxidation and reduction — electron transfer process.
- Redox reactions in aqueous solutions.
- Oxidation number.
- Balancing of chemical equations in redox reactions by oxidation number method and ion-electron method or half equation method.
- Simple idea of electrode potential, standard electrode potential.
- Stoichiometry of redox reactions in solutions.

9.1. Introduction

In the previous unit, we have studied *neutralization reactions* in which H^+ ions from an acid (HCl, H_2SO_4, CH_3COOH etc.) combine with OH^- ions of a base (NaOH, $Ca(OH)_2$, NH_4OH etc.) to form a salt and weakly ionized molecules of water. In this unit, we shall discuss another important class of reactions called *reduction-oxidation* or simply **redox reactions** (*red* from reduction and *ox* from oxidation). All these reactions are always accompanied by energy changes in form of heat, light or electricity.

A number of chemical and biological reactions fall in this category. Burning of different types of fuels such as wood, coal, kerosene, LPG (Liquefied Petroleum Gas) etc. for domestic purposes ; petrol, diesel, CNG (Compressed Natural Gas) etc. for transportion and industrial processes ; digestion of food in animals, photosynthesis by plants, corrosion of metals, electrochemical processes such as extraction of aluminium from purified alumina, and generation of electricity in dry and wet batteries are diverse examples of redox reactions. Before we discuss these redox reactions in detail, we must be familiar with the concepts of oxidation and reduction.

9.2. Oxidation-Reduction—Classical Concept

9.2.1. Oxidation. According to the classical concept.

Oxidation *may be defined as a process which involves the addition of oxygen or any other electronegative element, or as a process which involves the removal of hydrogen or any other electropositive element.*

For example,

(*i*) $\underline{2Mg}(s) + O_2(g) \longrightarrow 2MgO(s)$

(*Addition of oxygen*)

(*ii*) $\underline{Mg}(s) + Cl_2(g) \longrightarrow MgCl_2(s)$

(*Addition of electronegative element, chlorine*)

(*iii*) $\underline{2H_2S}(g) + O_2(g) \longrightarrow 2S(s) + 2H_2O(l)$

(*Removal of hydrogen*)

(*iv*) $\underline{2KI}(aq) + H_2O(l) + O_3(g) \longrightarrow 2KOH(aq) + I_2(s) + O_2(g)$

(*Removal of electropositive element, potassium*)

In all these reactions, the compound underlined has undergone oxidation.

9.2.2. Oxidising agent or oxidant. According to the classical concept,

An oxidising agent or oxidant** is a substance which supplies oxygen or any other electronegative element, or removes hydrogen or any other electropositive element. An oxidising agent after carrying out oxidation is itself **reduced in a chemical reaction.

For example, oxygen, chlorine and ozone in reactions (*i*) to (*iv*) listed above in **Sec. 9.2.1.** are oxidising agents. Some other important examples of oxidising agents are fluorine, manganese dioxide, hydrogen peroxide, potassium permanganate, potassium dichromate, nitric acid etc. These are illustrated by the following equations :

$$Mg\,(s) + F_2\,(g) \longrightarrow 2MgF_2\,(s)$$

$$4HCl(aq) + MnO_2(s) \longrightarrow MnCl_2(aq) + Cl_2(g) + 2H_2O(l)$$

$$H_2O_2(aq) + 2KI(aq) \longrightarrow 2KOH(aq) + I_2(s)$$

$$2KMnO_4(aq) + 10\,FeSO_4(aq) + 8H_2SO_4(aq) \longrightarrow 2MnSO_4(aq) + K_2SO_4(aq) + 5Fe_2(SO_4)_3(aq) + 8H_2O(l)$$

$$K_2Cr_2O_7(aq) + 3SO_2(g) + H_2SO_4(aq) \longrightarrow Cr_2(SO_4)_3(aq) + K_2SO_4(aq) + H_2O(l)$$

$$10HNO_3(aq) + I_2(s) \longrightarrow 10NO_2(g) + 2HIO_3(aq) + 4H_2O(l)$$

9.2.3. Reduction. According to the classical concept,

Reduction *may be defined as a process which involves the addition of hydrogen or any other electropositive element, or removal of oxygen or any other electronegative element.*

For example,

(*i*) $\underline{Br_2}(g) + H_2S(g) \longrightarrow 2HBr(g) + S(s)$

(Addition of hydrogen)

(*ii*) $\underline{2HgCl_2}\,(aq) + SnCl_2(aq) \longrightarrow Hg_2Cl_2(s) + SnCl_4(aq)$

(Addition of electropositive element, mercury)

(*iii*) $\underline{CuO}\,(s) + H_2(g) \longrightarrow Cu(s) + H_2O(l)$

(Removal of oxygen)

(*iv*) $\underline{2FeCl_3}\,(aq) + SO_2(g) + 2H_2O(l) \longrightarrow 2FeCl_2(aq) + H_2SO_4(aq) + 2HCl(aq)$

(Removal of electronegative element, chlorine)

In all these reactions, the compound underlined has undergone reduction.

9.2.4. Reducing agent or reductant. According to the classical concept,

A reducing agent or reductant ***may be defined as a substance which supplies hydrogen or any other electropositive element, or removes oxygen or any other electronegative element. A reducing agent after carrying out reduction is itself*** **oxidised** ***in a chemical reaction.***

For example, hydrogen sulphide, stannous chloride, hydrogen and sulphur dioxide respectively in reactions (*i*) to (*iv*) listed above in **Sec. 9.2.3.** are reducing agents. Some other important examples of reducing agents are carbon, carbon monoxide, aluminium, nitrous acid etc. These are illustrated by the following equations

$$CuO\,(s) + C(s) \longrightarrow CO(g) + Zn(s)$$

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

$$Fe_2O_3(s) + 2Al(s) \longrightarrow 2Fe(s) + Al_2O_3(s)$$

$$2KMnO_4(aq) + 3H_2SO_4(aq) + 5HNO_2(aq) \longrightarrow K_2SO_4(aq) + 2MnSO_4(aq) + 5HNO_3(aq) + 3H_2O(l)$$

9.2.5. Oxidation-reduction reactions are complementary.

Whenever any substance is oxidised, another substance is always reduced at the same time, and *vice-versa*. In other words, oxidation and reduction reactions are *complementary i.e., they always go hand in hand or side by side.* This is illustrated by the following examples :

(*i*) *Reaction between hydrogen sulphide and chlorine*

$$H_2S(g) + Cl_2(g) \longrightarrow 2HCl(g) + S\,(s)$$

Here, *H_2S is oxidised to S while Cl_2 is reduced to HCl.*

(*ii*) *Reaction between stannous chloride and mercuric chloride.*

$$SnCl_2(aq) + 2HgCl_2(aq) \longrightarrow SnCl_4(aq) + Hg_2Cl_2(s)$$

Here, $SnCl_2$ *is oxidised to* $SnCl_4$ *while* $HgCl_2$ *is reduced to* Hg_2Cl_2

(*iii*) *Reaction between manganese dioxide and hydrochloric acid.*

$$MnO_2(s) + 4HCl(aq) \longrightarrow MnCl_2(aq) + Cl_2(g) + 2H_2O(l)$$

Here, *HCl is oxidised to Cl_2 while MnO_2 is reduced to $MnCl_2$.*

9.3. Oxidation and Reduction—Electron Transfer Concept

It is a well known fact that the various chemical reactions occur through redistribution of electrons among the reacting substances. Any substance that loses electrons is said to be *oxidised* and the one which gains electrons is said to be *reduced*. Thus, according to the electronic concept, oxidation and reduction may be defined as follows :

Oxidation *may be defined as a process in which an atom or an ion loses one or more electrons. That is why oxidation is also called* **de-electronation.**

This loss of electrons either increases the positive charge or decreases the negative charge of the atom or the ion. For example,

(*i*) *Loss of electrons results in increase in positive charge* :

$$\mathrm{Na} \longrightarrow \mathrm{Na}^+ + e^-$$
$$\mathrm{Mg} \longrightarrow \mathrm{Mg}^{2+} + 2e^-$$
$$\mathrm{Fe}^{2+} \longrightarrow \mathrm{Fe}^{3+} + e^-$$
$$\mathrm{Sn}^{2+} \longrightarrow \mathrm{Sn}^{4+} + 2e^-$$

(*ii*) *Loss of electrons results in decrease in negative charge* :

$$\mathrm{MnO}_4^{2-} \longrightarrow \mathrm{MnO}_4^- + e^-$$
$$[\mathrm{Fe(CN)}_6]^{4-} \longrightarrow [\mathrm{Fe(CN)}_6]^{3-} + e^-$$
$$2\mathrm{Cl}^- \longrightarrow \mathrm{Cl}_2 + 2e^-$$
$$\mathrm{S}^{2-} \longrightarrow \mathrm{S} + 2e^-$$

Reduction *may be defined as a process in which an atom or an ion gains one or more electrons. That is why reduction is also called* **electronation.**

This gain of electrons either decreases the positive charge or increases the negative charge of the atom or the ion. For example,

(*i*) *Gain of electrons results in decrease in positive charge* :

$$\mathrm{Fe}^{3+} + e^- \longrightarrow \mathrm{Fe}^{2+}$$
$$2\mathrm{Hg}^{2+} + 2e^- \longrightarrow \mathrm{Hg}_2^{2+}$$
$$\mathrm{Sn}^{4+} + 2e^- \longrightarrow \mathrm{Sn}^{2+}$$
$$\mathrm{Sb}^{5+}\ 2e^- \longrightarrow \mathrm{Sb}^{3+}$$

(*ii*) *Gain of electrons results in increase in negative charge* :

$$\mathrm{Cl}_2 + 2e^- \longrightarrow 2\mathrm{Cl}^-$$
$$\mathrm{MnO}_4^- + e^- \longrightarrow \mathrm{MnO}_4^{2-}$$
$$\mathrm{S} + 2e^- \longrightarrow \mathrm{S}^{2-}$$
$$[\mathrm{Fe(CN)}_6]^{3-} + e^- \longrightarrow [\mathrm{Fe(CN)}_6]^{4-}$$

Oxidation-reduction as an electron-transfer process. We have discussed above that oxidation involves loss of electrons and reduction involves gain of electrons. Since there cannot be a net gain or loss of electrons in a chemical reaction, therefore, all chemical reactions involving loss or gain of electrons must occur simultaneously. In other words, in a chemical reaction, a substance can lose electrons only if there is present another substance which can gain electrons. Conversely, a substance can gain electrons only if another substance which can lose electrons is also present in the system. This implies that oxidation can take place only if reduction also occurs at the same time or *vice-versa*. In other words, oxidation-reduction reactions are complementary, *i.e., they always go side by side or hand in hand*. This may be illustrated by the following reactions :

$$2\mathrm{Mg}(s) + \mathrm{O}_2(g) \longrightarrow 2\mathrm{MgO}(s)$$
$$\mathrm{Mg}(s) + \mathrm{F}_2(g) \longrightarrow \mathrm{MgF}_2(s)$$
$$\mathrm{Mg}(s) + \mathrm{Cl}_2(g) \longrightarrow \mathrm{MgCl}_2(s)$$

In the formation of magnesium oxide, magnesium atom loses two electrons and thus gets *oxidised* to magnesium ion while the oxygen atom gains these two electrons and thus gets *reduced* to oxide ion.

$$\mathrm{Mg} \longrightarrow + \mathrm{Mg}^{2+} + 2e^- \quad (\textit{oxidation})$$
$$[\mathrm{O}] + 2e^- \longrightarrow [\mathrm{O}]^{2-} \quad (\textit{reduction})$$
$$\text{or} \quad \mathrm{O}_2 + 4e^- \longrightarrow 2[\mathrm{O}]^{2-}$$

The overall reaction may be written as follows:

$$2\,\mathrm{Mg}\!: + [\,\underset{\cdot\cdot}{\ddot{\mathrm{O}}}:]_2 \longrightarrow 2\,[\mathrm{Mg}^{2+}\!:\underset{\cdot\cdot}{\ddot{\mathrm{O}}}:^{2-}]$$

$$\text{or} \quad 2\mathrm{Mg}^{2+}\mathrm{O}^{2-}$$

Similarly in the formation of magnesium fluoride or chloride, magnesium loses two electrons and thus gets *oxidised* to magnesium ion while fluorine or chlorine molecule accepts these two electrons and thus gets *reduced* to two fluoride or chloride ions :

$$\mathrm{Mg}: + [\cdot\,\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}:]_2 \longrightarrow \mathrm{Mg}^{2+}\,[:\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}:^-]_2$$

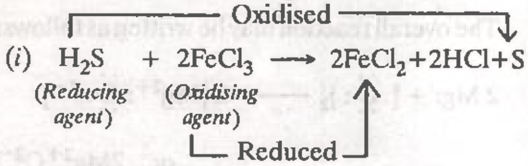
In all the reactions described above, electrons are transferred from one substance *i.e.* Mg to the other, *i.e.* O_2, F_2 or Cl_2. Thus *oxidation-reduction or redox reactions may be regarded as electron-transfer reactions in which the electrons are transferred from one reactant to the other.* The substance which loses electron is called a *reducing agent* while the other which accepts the electrons is called an *oxidising agent.* Thus

A substance (atom, ion or molecule) which can readily lose electrons to other substances is called a reducing agent or ***a reductant*** **while a** ***substance (atom, ion or molecule) which can readily accept electrons from other substances is called*** **an oxidising agent** ***or*** **an oxidant.**

Further since, reducing agents donate electrons to other substnaces while oxidising agents accept electrons from other substances, therefore, *reducing agents are* **electron donors** *while oxidising agents are* **electron acceptors.** In other words, reducing agents after reducing other substances themselves get oxidised while oxidising agents after oxidising other substances themselves get reduced in the process.

Let us now reconsider the two reactions (between Mg & O_2 and Cl_2) discussed above in the light of reducing and oxidising agents.

In the reaction of Mg with O_2, Mg gives electrons to oxygen which gets reduced to O^{2-} ion while Mg gets oxidised to Mg^{2+} ion. Conversely, O_2 accepts electrons from Mg and gets reduced to O^{2-} ion while Mg gets oxidised to Mg^{2+}. Therefore, *Mg is a reducing agent while O_2 is an oxidising agent. Similarly, in the reaction of Mg with F_2 or Cl_2, Mg acts as a reducing agent while F_2 or Cl_2 behaves as an oxidising agent.* For further illustration, consider the following reactions :

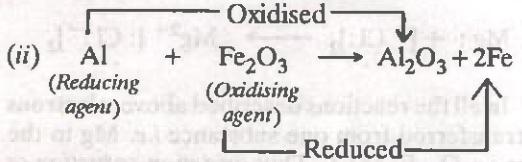


Oxidised

(*i*) $\underset{\text{(Reducing agent)}}{H_2S} + \underset{\text{(Oxidising agent)}}{2FeCl_3} \longrightarrow 2FeCl_2 + 2HCl + S$

Reduced

Here, H_2S reduces $FeCl_3$ to $FeCl_2$ while itself gets oxidised to S. Conversely, $FeCl_3$ oxidises H_2S to S while itself gets reduced to $FeCl_2$. Therefore, *H_2S acts as a reducing agent while $FeCl_3$ acts as an oxidising agent .*



Oxidised

(*ii*) $\underset{\text{(Reducing agent)}}{Al} + \underset{\text{(Oxidising agent)}}{Fe_2O_3} \longrightarrow Al_2O_3 + 2Fe$

Reduced

Here, Al reduces Fe_2O_3 to Fe while itself gets oxidised to Al_2O_3. Conversely, Fe_2O_3 oxidises Al to Al_2O_3 while itself gets reduced to Fe. Therefore, *Al acts as a reducing agent while Fe_2O_3 acts as an oxidising agent.*

From the above discussion, we conclude :-

> **Oxidation** *is a process in which one or more electrons are lost.*
>
> **Reduction** *is a process in which one or more electrons are gained.*
>
> **Oxidant** *is a substance which can accept one or more electrons.*
>
> **Reducant** *is a substance which can donate one or more electrons.*

In a **redox reaction,** *oxidant is reduced by accepting electrons and reductant is oxidised by losing electrons.*

EXAMPLE 9.1. *Using electron transfer, identify the oxidant and reductant in the following redox reaction.*

$$Zn(s) + 1/2\, O_2(g) \longrightarrow ZnO\ (s)$$

(N.C.E.R.T.)

Solution. Each atom of zinc loses two electrons to from Zn^{2+} while each atom of oxygen accepts these two electrons to form oxide ion (O^{2-}) as shown below :

$$Zn : + \frac{1}{2}\left[:\underset{..}{O}: \right]_2 \longrightarrow Zn^{2+}\left[:\ddot{\underset{..}{O}}:^{2-} \right]$$

Thus, Zn acts as reductant (or reducing agent) and oxygen acts as an oxidant (oxidising agent).

PROBLEMS FOR PRACTICE

Using electron-transfer concept, identify the oxidant and reductant in the following redox reactions.

(*a*) $Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$ *(N.C.E.R.T.)*

(*b*) $2[Fe(CN)_6]^{4-}(aq) + H_2O_2(aq) + 2H^+(aq) \longrightarrow 2[Fe(CN)_6]^{3-}(aq) + 2H_2O(aq)$

(*c*) $2[Fe(CN)_6]^{3-}(aq) + 2OH^-(aq) + H_2O_2(aq) \longrightarrow 2[Fe(CN)_6]^{4-}(aq) + 2H_2O(l)$

(*d*) $BrO_3^-(aq) + F_2(g) + 2OH^-(aq) \longrightarrow BrO_4^-(aq) + 2F^-(aq) + H_2O(l)$

(*e*) $2NaClO_3\,(aq) + I_2(aq) \longrightarrow 2NaIO_3(aq) + Cl_2(g)$

ANSWERS

Oxidants : (*a*) H^+ (*b*) H_2O_2 (*c*) $[Fe(CN)_6]^{3-}$ (*d*) F_2 (*e*) I_2

Reductants : (*a*) Zn (*b*) $[Fe(CN)_6]^{4-}$ (*c*) H_2O_2 (*d*) BrO_3^- (*e*) $NaClO_3$.

9.4. Classification of Redox Reactions

All the redox reactions may be divided into the following two types :

(*a*) **Direct redox reactions.** *Redox reactions in which oxidation and reduction take place in the same vessel are called* **direct redox reactions.** For example,

(*i*) Displacement of copper from $CuSO_4$ solution when a zinc rod is dipped in it.

(*ii*) Reduction of $HgCl_2$ to Hg_2Cl_2 by $SnCl_2$.

(*b*) **Indirect redox reactions.** *Redox reactions in which oxidation and reduction take place in different vessels are called* **indirect redox reactions.** These indirect redox reactions form the basis of electrochemical cells.

9.5. Direct Redox Reactions—Oxidation-Reduction Reactions in a Beaker

Take a zinc rod and clean it well with a sand paper. Now place it in a solution of copper sulphate in a beaker [Fig. 9.1(*a*)] for a few minutes. A spontaneous reaction occurs and the following changes would be observed.

(*i*) *Zinc rod gradually starts dissolving.*

(*ii*) *Copper metal either starts settling at the bottom of the beaker or depositing on the zinc rod.*

(*iii*) *The blue colour of the solution starts fading.*

(*iv*) *The reaction is exothermic and the solution becomes hot.*

(*v*) *The solution remains electrically neutral throughout.*

Let us try to explain these observations :

In aqueous solution, $CuSO_4$ dissociates to form $Cu^{2+}(aq)$ and $SO_4^{2-}(aq)$. When zinc rod is dipped in $CuSO_4$ solution, the following redox reaction occurs :

Oxidation (*loss of* $2e^-$)

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s) \quad ...(i)$$

Reduction (*gain of* $2e^-$)

In this reaction zinc acts a reducing agent and reduces Cu^{2+} to Cu metal by transferring two electrons.

Thus, during this redox reaction, zinc gets oxidised to Zn^{2+} ions while Cu^{2+} ions get reduced to copper metal. On the basis of this redox reaction, all the above observations can be easily explained :

(*i*) Since zinc is being oxidised to Zn^{2+} ions which go into solution, therefore, zinc rod starts dissolving.

(*ii*) Since each Cu^{2+} ion accepts two electrons lost by zinc, therefore, Cu^{2+} ions are reduced to copper metal which, in turn, settles down at the bottom of the beaker.

Mathematically,

$$\frac{\text{Loss in wt. of zinc rod}}{\text{Wt. of copper deposited}} = \frac{\text{Eq. wt. of zinc}}{\text{Eq. wt. of copper}} = \frac{32.5}{31.75}$$

(*iii*) Since the Cu^{2+} ions are reduced to copper metal, the blue colour of the solution which is due to Cu^{2+} ions slowly starts fading.

(*iv*) Since the above reaction occurs of its own, it is regarded as a *spontaneous change* and hence ΔG of the *reaction must be negative*. In other words, a certain amount of energy must be released in the reaction which appears as heat and hence the solution becomes hot.

(*v*) Since each Zn atom loses two electrons and each Cu^{2+} ion accepts two electrons, therefore, the number of electrons lost in the oxidation half reaction is equal to the number of electrons gained in the reduction half reaction. As a result, the solution remains electrically neutral throughout.

Similarly, when a copper rod is placed in a solution of silver nitrate in a beaker, we observe that the solution again *becomes hot and copper rod starts dissolving*. This is apparent from the fact that the solution which was originally colourless starts changing to blue due to the oxidation of Cu to Cu^{2+} ions. At the same time, Ag^+ ions get reduced to silver metal which in turn, settles down at the bottom of the beaker [Fig. 9.1 (*b*)]. The overall redox reaction may be written as follows :

Oxidation (*loss of* $2e^-$)

$$Cu(s) + 2Ag^+(aq) \longrightarrow Cu^{2+}(aq) + Ag(s) \quad ...(ii)$$

Reduction (*gain of* $2e^-$)

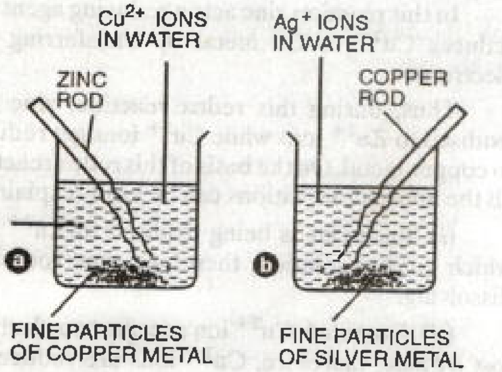


FIGURE 9.1. (a) Zinc dissolves to form Zn^{2+} ions while Cu^{2+} ions get reduced to copper metal which settles down in form of fine particles at the bottom of the beaker.
(b) Copper dissolves to form Cu^{2+} ions while $Ag+$ ions get reduced to silver metal which settles down in form of fine particles at the bottom of the beaker.

In this reaction, copper acts as a reduces agent and reduces Ag^+ to Ag metal by transferring two electrons.

In the first reaction, oxidation of zinc cannot occur unless Cu^{2+} ions accept electrons and reduction of Cu^{2+} ions cannot occur unless zinc donates electrons. Similarly, in the second reaction, oxidation of copper does not occur unless Ag^+ ions accept electrons and reduction of Ag^+ ions cannot occur unless copper metal donates electrons.

Thus, we conclude that *oxidation-reduction are complementary processes, i.e., one cannot occur unless the other occurs simultaneously. In oher words, one reactant is oxidised at the expense of the other which is reduced.*

It may be mentioned here that the role of a substance to act as an electron donor or an electron acceptor and hence as a reductant or an oxidant depends upon electron-accepting or donating ability of the other reactant. For example in Eq. (*i*), and Eq. (*ii*), the roles of Cu^{2+} and Cu are reversed. *In Eq. (i), Cu^{2+} acts as an oxidising agent and oxidises Zn to Zn^{2+} while in Eq. (ii), Cu acts as a reducing agent and reduces Ag^+ to Ag. The reason being that electron-donating ability of zinc is more than that of Cu while electron donating ability of Cu is more than that of Ag.*

9.6. Redox Reactions in Aqueous Solutions

A large number of redox reactions occur in aqueous solutions. Unlike acid-base and precipitation reactions which occur very quickly, most of the redox reactions proceed slowly in aqueous solutions. Each redox reaction can be considered as a sum of two **half reactions** – *one involving oxidation called* **oxidation half reaction** and the other *involving reduction usually called* **reduction half reaction.** To explain these half reactions, let us consider the oxidation of aqueous potassium iodide by hydrogen peroxide. This reaction can be divided into the following two half reactions :

$$2I^-(aq) \longrightarrow I_2(s) + 2e^- \qquad \textit{(oxidation)}$$

$$H_2O_2(aq) + 2e^- \longrightarrow 2OH^-(aq) \qquad \textit{(reduction)}$$

In order to get the overall equation for the redox reaction, the following two procedures are used. The underlying principle of both these procedures is that the *number of electrons lost during oxidation half reaction must be equal to the number of electrons gained during the reduction half reaction.*

(*i*) The two half reactions are simply added if the number of electrons lost during oxidation are equal to the *number of electrons* gained during reduction. For example,

$$2I^-(aq) \longrightarrow I_2(s) + 2e^- \qquad \textit{(oxidation)}$$

$$H_2O_2(aq) + 2e^- \longrightarrow 2OH^- \qquad \textit{(reduction)}$$

Overall redox reaction :

$$2I^-(aq) + H_2O_2(aq) \longrightarrow I_2(s) + 2OH^-(aq)$$

This represents the net **balanced ionic equation.**

Supplying the required number of **spectator ions**, the balanced redox equation is :

$$2KI(aq) + H_2O_2(aq) \longrightarrow I_2(s) + 2KOH(aq)$$

The ions which do not take part in any reaction but are simply added to balance the charge are called **spectator ions.** For example, in the above equation K^+ ions are the spectator ions.

(*ii*) If the number of electrons lost during oxidation half reaction are different from the number of electrons gained during reduction half reaction, the two half reactions are multiplied by suitable integers so that when the two equations are added, the electrons cancel out of the final redox equation. For example, consider the oxidation of aqueous ferrous sulphate to ferric sulphate by aqueous acidified $KMnO_4$ solution.

$$MnO_4^- (aq) + 8\,H^+ (aq) + 5\,e^- \longrightarrow Mn^{2+} (aq) + 4\,H_2O\,(l) \quad \textit{(reduction)}$$

$$Fe^{2+} (aq) \longrightarrow Fe^{3+} (aq) + e^-] \times 5 \quad \textit{(oxidation)}$$

Overall redox reaction:

$$MnO_4^- (aq) + 5\,Fe^{2+} (aq) + 8\,H^+ (aq) \longrightarrow Mn^{2+} (aq) + 5\,Fe^{3+} (aq) + 4\,H_2O\,(l)$$

Supplying the required spectator ions, the complete balanced redox equation is

$$KMnO_4\,(aq) + 5\,FeSO_4\,(aq) + 4\,H_2SO_4\,(aq) \longrightarrow MnSO_4\,(aq) + 5/2\,Fe_2(SO_4)_3\,(aq) + 4\,H_2SO_4\,(l)$$

To eliminate fractional numbers, multiply the entire equation by 2. We have,

$$2\,KMnO_4(aq) + 10\,FeSO_4(aq) + 8\,H_2SO_4(aq) \longrightarrow 2\,MnSO_4\,(aq) + 5\,Fe_2(SO_4)_3\,(aq) + 8\,H_2O\,(l)$$

For further illustration, consider the following equations :

(*iii*) *Oxidation of sodium thiosulphate to sodium tetrathionate by aqueous iodine*

$$2\,S_2O_3^{2-}\,(aq) \longrightarrow S_4O_6^{2-}\,(aq) + 2\,e^- \quad \textit{(oxidation)}$$

$$I_2\,(aq) + 2\,e^- \longrightarrow 2\,I^-\,(aq) \quad \textit{(reduction)}$$

Overall redox reaction :

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

Supplying the required number of spectator ions, the balanced redox equation is

$$2\,Na_2S_2O_3\,(aq) + I_2\,(aq) \longrightarrow Na_2S_4O_6\,(aq) + 2\,NaI\,(aq)$$

(*iv*) *Reduction of acidified potassium dichromate by sulphur dioxide.*

$$Cr_2O_7^{2-}\,(aq) + 14\,H^+\,(aq) + 6\,e^- \longrightarrow 2\,Cr^{3+}\,(aq) + 7\,H_2O\,(l) \quad \textit{(oxidation)}$$

$$SO_2\,(g) + 2\,H_2O\,(l) \longrightarrow SO_4^{2-}\,(aq) + 4\,H^+ + 2\,e^-] \times 3 \quad \textit{(reduction)}$$

Overall redox equation :

$$Cr_2O_7^{2-}\,(aq) + 3\,SO_2\,(g) + 2\,H^+\,(aq) \longrightarrow 2\,Cr^{3+}\,(aq) + 3\,SO_4^{2-}\,(aq) + H_2O\,(l)$$

Supplying the required spectator ions, we have

$$K_2Cr_2O_7\,(aq) + 3\,SO_2\,(g) + H_2SO_4\,(aq) \longrightarrow K_2SO_4\,(aq) + Cr_2(SO_4)_3\,(aq) + H_2O\,(l)$$

(*v*) *Reduction of mercuric chloride to mercurous chloride by stannous chloride.*

$$Sn^{2+}\,(aq) \longrightarrow Sn^{4+}\,(aq) + 2\,e^- \quad \textit{(oxidation)}$$

$$Hg^{2+}\,(aq) + e^- \longrightarrow Hg^+\,(aq)] \times 2 \quad \textit{(reduction)}$$

Overall redox reaction :

$$Sn^{2+}\,(aq) + 2\,Hg^{2+}\,(aq) \longrightarrow Sn^{4+}\,(aq) + 2\,Hg^+\,(aq)$$

Supplying the required spectator ions, we have

$$SnCl_2\,(aq) + 2\,HgCl_2\,(aq) \longrightarrow SnCl_4\,(aq) + Hg_2Cl_2\,(s)$$

(*vi*) *Self oxidation reduction of Cl_2 in presence of alkali*

$$Cl_2\,(g) + 2\,e^- \longrightarrow 2\,Cl^-\,(aq)] \times 5 \quad \textit{(reduction)}$$

$$Cl_2\,(g) + 12\,OH^-\,(aq) \longrightarrow 2\,ClO_3^-\,(aq) + 6\,H_2O\,(l) + 10\,e^- \quad \textit{(oxidation)}$$

Overall redox equation :

$$6\,Cl_2\,(aq) + 12\,OH^-\,(aq) \longrightarrow 10\,Cl^-\,(aq) + 2\,ClO_3^-\,(aq) + 6\,H_2O\,(l)$$

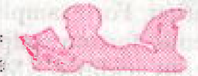
To remove the common factor, divide the entire equation by 2. We have,

$$3\,Cl_2\,(g) + 6\,OH^-\,(aq) \longrightarrow 5\,Cl^-\,(aq) + ClO_3^-\,(aq) + 3\,H_2O\,(l)$$

Supplying the required spectator ions, we have,

$$3\,Cl_2\,(g) + 6\,KOH\,(aq) \longrightarrow 5\,KCl\,(aq) + KClO_3^-\,(aq) + 3\,H_2O\,(l)$$

PROBLEMS FOR PRACTICE



1. Write the half reactions for the following redox reactions :

(a) $Fe^{2+}(aq) + 2I^-(aq) \longrightarrow 2Fe^{2+}(aq) + I_2(aq)$

(b) $Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$

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

(N.C.E.R.T.)

2. Split the following redox reactions in the oxidation and reduction half reactions.

(a) $2K(s) + Cl_2(g) \longrightarrow 2KCl(s)$

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

(N.C.E.R.T.)

ANSWERS

1. (a) $2I^-(aq) \longrightarrow I_2(aq) + 2e^-$ *...Oxidation*

$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$ [× 2 *...Reduction*

$2Fe^{3+}(aq) + 2I^-(aq) \longrightarrow 2Fe^{2+}(aq) + I_2(aq)$

...Overall redox reaction

(b) $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$ *...Oxidation*

$2H^+(aq) + 2e^- \longrightarrow H_2(g)$ *...Reduction*

$Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$

...Overall redox reaction

(c) $Al(s) \longrightarrow Al^{3+}(aq) + 3e^-$ *...Oxidation*

$Ag^+(aq) + e^- \longrightarrow Ag(s)$] × 3 *...Reduction*

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

...Overall redox reaction

2. $K(s) \longrightarrow K^+(g) + e^-$ [× 2 *...Oxidation*

$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(g)$ *...Reduction*

$K^+(g) + Cl^-(g) \longrightarrow KCl(s)$ [× 2

$2K(s) + Cl_2(g) \longrightarrow 2KCl(s)$

...Overall redox reaction

(b) $Al(s) \longrightarrow Al^{3+}(aq) + 3e^-$ [× 2 *...Oxidation*

$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$ [× 3 *...Reduction*

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

...Overall redox reaction

9.7. Oxidation Number

As already discussed, oxidation-reduction reactions involve the transfer of electrons from one atom or ion to the other. In case of ionic reactions, it is very easy to determine the total number of electrons transferred from one atom or ion to the other. However, in many redox reactions involving covalent compounds, it is not so easy to determine (*i*) direction of transfer of electrons and (*ii*) number of electrons transferred from one reactant to the other simply by looking at the chemical equations. For example, in the following redox reaction,

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$$

both the reactants and the products are covalent compounds. From our knowledge of chemical bonding, we know that during the formation of HCl molecule, an electron pair is shared between hydrogen and chlorine atoms and that electron is not completely transferred from hydrogen to chlorine atom. Yet in HCl molecule, Cl atom has higher electron density and thus there is a partial transfer of electronic charge from hydrogen to chlorine. In other words, we can easily say that hydrogen is a reductant and chlorine is an oxidant. Similarly, in the reaction,

$$CH_4(g) + 4F_2(g) \longrightarrow CF_4(g) + 4HF(g)$$

CH_4 acts as a reducing agent and F_2 acts as an oxidising agent. With a view to identify oxidant and reductant by keeping track of number of electrons transferred from one reactant to the other both in ionic and covalent compounds, and to help in balancing of equations, the concept of oxidation number was introduced. Thus,

Oxidation number of an element may be defined as the charge *which an atom of the element has in its ion or appears to have when present in the combined state with other atoms. Oxidation numbers are also called* oxidation states.

9.7.1. Rules for assigning Oxidation Numbers.

The following rules are applied to determine the oxidation number of an atom in an ion or a molecule.

1. *The oxidation number of all the atoms of different elements in their respective elementary states and allotropic forms is taken to be zero.* For example, in N_2, Cl_2, H_2, He, P_4, S_8, O_2, O_3, C (diamond or graphite), Br_2, Na, Fe, Ag etc., the oxidation number of each atom is zero.

2. *The oxidation number of a monoatomic ion is the same as the charge on it.* For example, oxidation numbers of Na^+, Mg^{2+} and Al^{3+} ions are +1, +2 and +3 respectively while those of Cl^-, S^{2-} and N^{3-} ions are −1, −2 and −3 respectively.

3. *The oxidation number of hydrogen is +1 when combined with non-metals and is −1 when combined with active metals called metal hydrides such as LiH, KH, MgH_2, CaH_2 etc.*

4. *The oxidation number of oxygen is −2 in most of its compounds, except in peroxides like H_2O_2, BaO_2 etc. where it is −1.* Another interesting exception is found in the compound OF_2 (*oxygen difluoride*) where the oxidation number of oxygen is +2. This is due to the fact that fluorine being the most electronegative element known has always an oxidation number of −1.

5. *In compounds formed by union of metals with non-metals, the metal atoms will have positive oxidation numbers and the non-metals will have negative oxidation numbers.* For example,

(*a*) *The oxidation number of alkali metals (Li, Na, K etc.) is always +1 and those of alkaline earth metals (Be, Mg, Ca etc) is +2.*

(*b*) *The oxidation number of halogens (F, Cl, Br, I) is always −1 in metal halides such as KF, $AlCl_3$, $MgBr_2$, CdI_2 etc.*

6. *In compounds formed by the union of different elements, the more electronegative atom will have negative oxidation number whereas the less electronegative atom will have positive oxidation number.* For example,

(*a*) N is given an oxidation number of −3 when it is bonded to less electronegative atom as in NH_3 and NI_3, but is given an oxidation number of +3 when it is bonded to more electronegative atoms as in NCl_3.

(*b*) Since fluorine is the most electronegative element known so its oxidation number is always −1 in its compounds i.e. oxides, interhalogen compounds etc.

(*c*) In interhalogen compounds of F, Cl, Br, and I; the more electronegative of the two halogens gets the oxidation number of −1. For example, in IF_7, the oxidation number of F is −1 while that of I is +7. Similarly, in $BrCl_3$, the oxidation number of Cl is −1 while that of Br is +3.

7. *In neutral compounds, the sum of the oxidation numbers of all the atoms is zero.*

8. *In complex ions, the sum of the oxidation numbers of all the atoms in the ion is equal to the charge on the ion.*

With the help of above rules, we can find out the oxidation number of any element in a molecule or an ion. Metals invariably have positive oxidation numbers while non-metals may have positive or negative oxidation numbers. Transition metals usually display several oxidation numbers. The highest positive oxidation number for *s*-block elements is equal to its group number but for *p*-block elements it is equal to group number *minus* 10 (except for noble gases). However, the highest negative oxidation number for *p*-block elements is equal to eight *minus* the number of electrons in the valence shell. In other words, the highest positive oxidation state increases across a period in the periodic table. For example, in the third period, the highest positive oxidation number increases from +1 to +7 as shown below :

Na^+ (+1), Mg^{2+} (+2), Al^{3+} (+3), Si (+4 as in $SiCl_4$, SiO_2 etc.), P (+5 as in PF_5, P_4O_{10} etc.), S (+6 as in SF_6, SO_3 etc.) and Cl (+7 as in Cl_2O_7 or ClO_4^- ion).

As stated above oxidation numbers are also called oxidation states. For example, in H_2O, the oxidation number and oxidation state of hydrogen is +1 while that of oxygen is −2.

We shall now illustrate the use of above rules in determining the oxidation numbers and also for identifying the reductants and oxidants in redox reactions.

EXAMPLE 9.2. *Calculate the oxidation number of (i) S in H_2S, (ii) C in CO_2, (iii) C in CH_2Cl_2, (iv) N in $(NH_4)_2SO_4$, (v) Pb in Pb_3O_4 and (vi) P in Na_3PO_4.*

−2 −2

Solution. (i) S in H_2S. Let the oxidation number of S in H_2S be x. Writing the oxidation number of each atom above its symbol,

$$\overset{+1}{H_2}\ \overset{x}{S}$$

($\because$ Oxidation number of H is +1)

Sum of oxidation numbers of various atoms in H_2S

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

But the sum of the oxidation numbers of various atoms in H_2S (*neutral*) is zero (**Rule 7**).

$\therefore\ 2 + x = 0$ or $x = -2$

Thus the oxidation number of S in H_2S is −2.

(ii) C in CO_2. Let the oxidation number of C in CO_2 be x. Writing the oxidation number of each atom above its symbol,

$$\overset{x}{C}\ \overset{-2}{O_2}$$

($\because$ Oxidation number of O is −2)

$\therefore$ Sum of the oxidation numbers of various atoms in CO_2 $= x + 2(-2) = x - 4$

But the sum of oxidation numbers of various atoms in CO_2 (*neutral*) is zero (**Rule 7**).

$\therefore\ x - 4 = 0$ or $x = +4$

Thus the oxidation number of C in CO_2 is +4

(iii) C in CH_2Cl_2. Let the oxidation number of C in CH_2Cl_2 be x. Writing the oxidation number of each atom above its symbol,

$$\overset{x}{C}\ \overset{+1}{H_2}\ \overset{-1}{Cl_2}$$

($\because$ Oxidation number of H is +1 and that of Cl is −1)

$\therefore$ Sum of the oxidation numbers of various atoms in CH_2Cl_2 $= x + 2(+1) + 2(-1) = x$

But the sum of the oxidation numbers of various atoms in CH_2Cl_2 (*neutral*) is zero (**Rule 7**).

$\therefore\ x = 0$

Thus, the oxidation number of C in CH_2Cl_2 is **zero**

(iv) N in $(NH_4)_2SO_4$. Let the oxidation number of nitrogen in $(NH_4)_2SO_4$ be x. Writing the oxidation number of hydrogen above its symbol and that of SO_4^{2-} ion above its formula.

$$\left(\overset{x}{N}\ \overset{+1}{H_4}\right)_2\ \overset{-2}{SO_4}$$

($\because$ Oxidation number of SO_4^{2-} is −2)

$\therefore$ Sum of oxidation numbers of all the atoms in $(NH_4)_2SO_4$

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

But the sum of oxidation numbers of all the atoms in $(NH_4)_2SO_4$ (*neutral*) is zero (**Rule 7**).

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

Thus the oxidation number of nitrogen in $(NH_4)_2SO_4$ is −3

(v) Pb in Pb_3O_4. Let the oxidation number of Pb in Pb_3O_4 be x. Writing the oxidation number of each atom above its symbol

$$\overset{x}{Pb_3}\ \overset{-2}{O_4}$$

($\because$ Oxidation number of O is −2)

$\therefore$ Sum of the oxidation numbers of all the atoms in Pb_3O_4

$$= (3)x + 4(-2) = 3x - 8$$

But the sum of oxidation numbers of all the atoms in Pb_3O_4 (*neutral*) is zero (**Rule 7**).

$\therefore\ 3x - 8 = 0$ or $x = 8/3$

Thus the oxidation number of Pb in Pb_3O_4 = *8/3.*

(vi) P in Na_3PO_4. Let the oxidation number of P in Na_3PO_4 be x. Writing the oxidation number of each atom above its symbol,

$$\overset{+1}{Na_3}\ \overset{x}{P}\ \overset{-2}{O_4}$$

($\because$ Oxidation number of Na is +1 and that of O is −2)

Sum of the oxidation numbers of various atoms in Na_3PO_4

$$= 3(+1) + x + 4(-2) = x - 5$$

But the sum of oxidation numbers of all the atoms in Na_3PO_4 (*neutral*) in zero (**Rule 7**).

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

Thus the oxidation number of P in Na_3PO_4 *is* +5

EXAMPLE 9.3. *Calculate the oxidation number of (i) N in NO_3^- ; (ii) P in $H_3P_2O_7^-$ (iii) C in CO_3^{2-}, (iv) Cl in ClO_4^- and (v) Cr in $Cr_2O_7^{2-}$.*

Solution. (i) N in NO_3^-. Let the oxidation number of N in NO_3^- be x. Writing the oxidation number of each atom above its symbol.

$$\overset{x}{N}\ \overset{-2}{O_3}$$

$\therefore$ Sum of the oxidation number of all the atoms in NO_3^- ion $= x + 3(-2) = x - 6$

But the sum of oxidation numbers of all the atoms in NO_3^- ion is equal to the charge present on it, *i.e.* -1 **(Rule 8)**

$\therefore \quad x - 6 = -1$ or $x = +5$

Thus the oxidation number of N in NO_3^- is $+5$

(ii) P in $H_3P_2O_7^-$. Let the oxidation number of P in $H_3P_2O_7^-$ be x. Writing the oxidation number of each atom above its symbol.

$$\overset{+1}{H_3}\ \overset{x}{P_2}\ \overset{-2}{O_7}$$

($\because$ Oxidation number of H is $+1$ and that of O is -2)

Sum of the oxidation numbers of all the atoms in $H_3P_2O_7^-$

$= +1 \times 3 + 2(x) + 7(-2)$ or $2x - 11$

But the sum of oxidation numbers of all the atoms in $H_3P_2O_7^-$ is equal to the charge present on it *i.e.* -1 **(Rule 8)**

$\therefore \quad 2x - 11 = -1$ or $x = +5$

Thus the oxidation number of P in $H_3P_2O_7^-$ is $+5$

(iii) **C in CO_3^{2-}.** Let the oxidation number of C in CO_3^{2-} be x. Writing the oxidation number of each atom above its symbol,

$$\overset{x}{C}\ \overset{-2}{O_3}$$

$\therefore$ Sum of the oxidation numbers of all the atoms in CO_3^{2-} ion $= x + 3(-2) = x - 6$

$x + 3(-2)$

But the sum of oxidation numbers of all the atoms in CO_3^{2-} ion is -2 **(Rule 8)**

$\therefore \quad x - 6 = -2$

or $\quad x = +4$

Thus the oxidation state of C in CO_3^{2-} is $+4$

(iv) **Cl in ClO_4^-.** Let the oxidation number of Cl in ClO_4^- be x. Writing he oxidation numbers of each atom above its symbol,

$$\overset{x}{Cl}\ \overset{-2}{O_4}$$

$\therefore$ Sum of oxidation number of all the atoms in ClO_4^- ion $= x + 4(-2) = x - 8$

But the sum of oxidation numbers of all the atoms in ClO_4^- ion is equal to the charge present on it, *i.e.*, -1 **(Rule 8)**

$\therefore x - 8 = -1 \quad$ or $\quad x = +7$

Thus the oxidation number of Cl in ClO_4^- is $+7$

(v) Cr in $Cr_2O_7^{2-}$. Let the oxidation number of Cr in $Cr_2O_7^{2-}$ be x. Writing the oxidation number of each atom above its symbol.

$$\overset{x}{Cr_2}\ \overset{-2}{O_7}$$

$\therefore$ Sum of the oxidation numbers of all the atoms in $Cr_2O_7^{2-}$ ion $= 2(x) + 7(-2) = 2x - 14$

But the sum of oxidation numbers of all the atoms in $Cr_2O_7^{2-}$ is equal to the charge on it, *i.e.*, -2 **(Rule 8)**

$\therefore \quad 2x - 14 = 2$ or $x = 6$

Thus the oxidation number of Cr in $Cr_2O_7^{2-}$ ion is $+6$

EXAMPLE 9.4. *What is the the oxidation number of metals in (i) $[Fe(CN)_6]^{4-}$ and (ii) MnO_4^- ?*

Solution. (i) **Fe in $[Fe(CN)_6]^{4-}$.** Let the oxidation number of Fe in $[Fe(CN)_6]^{4-}$ be x. Writing the oxidation number of each atom above its symbol and that of cyanide ion above its formula, we get

$$\overset{x}{Fe}\ \overset{-1}{(CN)_6}$$

$x + 6(-1) = -4$
$x = 2$

$\therefore$ Sum of oxidation numbers of all the atoms in $[Fe(CN)_6]^{4-} = x + 6(-1) = x - 6$

But the sum of oxidation numbers of all the atoms in $Fe(CN)_6]^{4-}$ is equal to -4. **(Rule 8)**

$\therefore \quad x - 6 = -4 \quad$ or $\quad x = +2$

Thus the oxidation number of Fe in $[Fe(CN)_6]^{4-}$ is $+2$.

(ii) Mn in MnO_4^-. Let the oxidation number of Mn in MnO_4^- be x. Writing oxidation number of each atom above its symbol, we get

$$\overset{x}{Mn}\ \overset{-2}{O_4}$$

$\therefore$ Sum of the oxidation numbers of all the atoms in MnO_4^- $= x + 4(-2) = x - 8$

But the sum of oxidation numbers of all the atoms in MnO_4^- is -1 **(Rule 8)**

$\therefore \quad x - 8 = -1$

or $\quad x = +7$

Thus, the oxidation number of Mn in MnO_4^- *is* $+7$

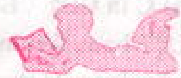
ADD TO YOUR KNOWLEDGE

1. The O.N. of C in its various compounds containing only H and O atoms can be easily calculated by the application of the following formula : $n_H(1) + n_O(-2) + n_c(\text{O.N. of C}) = 0$ or O.N. of C $= \dfrac{n_O(2) - n_H(1)}{n_C}$ where n_H, n_0 and n_C are the number of H, O and C atoms in the given compound. For example,

Compound	n_H	n_O	n_C	O.N. of C $= \dfrac{n_O(2) - n_H(1)}{n_C}$
CH_4	4	0	1	$0(2) - 4(1)/1 = -4$
C_2H_6	6	0	2	$0(2) - 6(1)/2 = -3$
C_2H_4	4	0	2	$0(2) - 4(1)/2 = -2$
CH_3OH	4	1	1	$1(2) - 4(1)/1 = -2$
C_2H_2	2	0	2	$0(2) - 2(1)/2 = -1$
CH_2O	2	1	1	$1(2) - 2(1)/1 = 0$
$HCOOH$	2	2	1	$2(2) - 2(1)/1 = +2$

2. If a compound contains two or more atoms of the same element, the O.N. determined by the application of the above rules is only an average of the O.N. of all the atoms present in the molecule. For example, O.N. of Fe in Fe_3O_4 (magnetic oxide of iron) is $3x + 4 \times -2 = 0$ or $x = +8/3$. Similarly, in ferriferrocyanide, $Fe_4[Fe(CN)_6]_3$ molecule the average O.N. of Fe is $7x + 18 \times -1 = 0$ or $x = 18/7$. The actual oxidation numbers of individual atoms can, however, be determined if the stoichiometry or the structure of the compound is known as discussed under *'Additional Useful Information for Competitive Examination.*

PROBLEMS FOR PRACTICE



1. Find the oxidation number of the element in bold in the following species :

(i) SiH_4, BH_3, BF_3, $S_2O_3^{2-}$ BrO_4^- and HPO_4^{2-} *(N.C.E.R.T.)*

(ii) $PbSO_4$, $U_2O_7^{4-}$, $B_4O_7^{2-}$, CrO_4^{2-}, K_2MnO_4.

2. Determine the oxidation number of C in the following :

C_2H_6, C_4H_{10}, CO, CO_2 and HCO_3^-. *(N.C.E.R.T.)*

3. Determine the oxidation number of O in the following :

OF_2, Na_2O_2 and CH_3COOH. *(N.C.E.R.T.)*

4. Find out the oxidation number of Cl in HCl, HClO, ClO_4^-, $CaOCl_2$ and ClO_2. *(N.C.E.R.T.)*

5. Find out the oxidation number of sulphur in the following species :

$(NH_4)_2SO_4$, H_2SO_4, $S_2O_4^{2-}$, $S_2O_7^{2-}$, HSO_3^- and HSO_4^-. *(N.C.E.R.T.)*

6. Determine the oxidation number of all the atoms in the following well known oxidants

$KMnO_4$, $K_2Cr_2O_7$ and $KClO_4$. *(N.C.E.R.T.)*

7. Determine the change in the oxidation number of S in H_2S and SO_2 in the following industrial reaction :

$$2H_2S\,(g) + SO_2\,(g) \longrightarrow 3S\,(s) + 2H_2O\,(g)$$

(N.C.E.R.T.)

ANSWERS

1. (*i*) Si = – 4 in SiH_4, B = – 3 in BH_3, B = + 3 in BF_3, S = + 2 in $S_2O_3^{2-}$, Br = + 7 in BrO_4^- and P = + 5 in HPO_4^{2-},
   (*ii*) S = + 6 in $PbSO_4$, U = + 5 in $U_2O_7^{4-}$, B = + 3 in $B_4O_7^{2-}$, Cr = + 6 in CrO_4^{2-} and Mn = + 6 in K_2MnO_4.
2. O.N. of C = – 3 in C_2H_6, – 2·5 in C_4H_{10}, + 2 in CO, + 4 in CO_2 and + 4 in HCO_3^-.
3. O.N. of O = + 2 in OF_2, – 1 in Na_2O_2 and – 2 in CH_3COOH.
4. O.N. of Cl = – 1 in HCl, + 1 in HClO + 7 in ClO_4^- in $CaOCl_2$ and + 4 in ClO_2.
5. O.N. of S = + 6 in $(NH_4)_2SO_4$, H_2SO_4 and HSO_4^- and $S_2O_7^{2-}$, + 4 in HSO_3^- and + 3 in $S_2O_4^{2-}$.
6. K = + 1, Mn = + 7, O = – 2 ; K = + 1, Cr = + 6, O = – 2 ; K = + 1, Cl = + 7, O = – 2.
7. O.N. of S changes from – 2 in H_2S and + 4 in SO_2 to zero in elemental sulphur.

9.8. Redox Reactions in Terms of Oxidation Number

9.8.1. Oxidation and Reduction in terms of Oxidation Number.

In terms of oxidation number,

Oxidation *may the defined as a chemical change in which there occurs an increase in the oxidation number of an atom or atoms while reduction may be defined as a chemical change in which there occurs a decrease in the oxidation number of an atom or atoms. A redox reaction may then be defined as a reaction in which the oxidation number of atoms undergoes a change.*

For example, consider the reaction between zinc and hydrochloric acid. Writing the oxidation number of all the atoms above their respective symbols, we have,

Oxidised

$$\overset{0}{Zn}(s) + 2\overset{+1}{H}\,\overset{-1}{Cl} \longrightarrow \overset{2+}{Zn}\,\overset{-1}{Cl_2} + \overset{0}{H_2}$$

Reduced

In this reaction, the oxidation number (O.N.) of zinc increases from 0 to +2, that of hydrogen decreases from +1 to 0 while that of chlorine remains unchanged. Thus, *zinc is oxidised while hydrogen is reduced.*

For further illustration, consider the following examples.

Oxidised

$$(i)\ 2\overset{+1}{H}\,\overset{-1}{I} + \overset{0}{Cl_2} \longrightarrow \overset{0}{I_2}(s) + 2\overset{+1}{H}\,\overset{-1}{Cl}$$

Reduced

Here, the oxidation number of iodine increases from –1 to 0, that of chlorine decreases from 0 to –1 while that of hydrogen remains unchanged. Therefore, *HI is oxidised to I_2* while Cl_2 is *reduced to Cl^- ions.*

Oxidised

$$(ii)\ 3\overset{+4}{Mn}\,\overset{-2}{O_2} + 4\overset{0}{Al} \longrightarrow 3\overset{0}{Mn} + 2\overset{+3}{Al_2}\,\overset{-2}{O_3}$$

Reduced

Here, the oxidation number of Mn decreases from +4 to 0, that of Al increases from 0 to +3 while that of oxygen remains unchanged. Thus, *MnO_2 is reduced to Mn while Al is oxidised to Al_2O_3.*

Reduced

$$(iii)\ 2\overset{+7}{Mn}\overset{-2}{O_4^-} + 10\overset{-1}{Cl^-} + 16\overset{+1}{H^+} \longrightarrow 2\overset{+2}{Mn^{2+}} + 5\overset{0}{Cl_2} + 8H_2\overset{-2}{O}$$

Oxidised

In this reaction, the oxidation number of manganese decreases from +7 in MnO_4^- to +2 in Mn^{2+} ions, that of chlorine increases from –1 in Cl^- ion to 0 in Cl_2 gas while that of oxygen and hydrogen remain unchanged. *Therefore, MnO_4^- is reduced while Cl^- is oxidised.*

9.8.2. Oxidising and Reducing agents in terms of Oxidation Number

Oxidising agents or Oxidants. Since oxidising agents are electron acceptors and acceptance of electrons causes a corresponding decrease in the oxidation number, therefore, in terms of oxidation number, An **oxidising agent** or an **oxidant** *may be defined as a substance the oxidation number of whose atom (or atoms) decreases.*

For instance, in the above examples, *i.e.*, (*i*) to (*iii*), the oxidation number of chlorine decreases from 0 in Cl_2 to -1 in Cl^- ion ; that of managanese decreases from $+4$ in MnO_2 to 0 in Mn ; that of manganese decreases from $+7$ in MnO_4^- to $+2$ in Mn^{2+} ion. Therefore, *all the three, i.e., Cl_2, MnO_2 and MnO_4^- are oxidising agents or oxidants.* Similarly, the oxidation number of N decreases from $+5$ in KNO_3 to $+3$ in KNO_2, therefore, KNO_3 is an oxidising agent.

O.N. decreases

$$2K\overset{+5}{N}O_3 \longrightarrow 2K\overset{+3}{N}O_2$$

Likewise, $KClO_3$ is an oxidising agent since the oxidation of Cl decreases from $+5$ in $KClO_3$ to -1 in Cl^- ion.

O.N. decreases

$$2K\overset{+5}{Cl}O_3 \longrightarrow 2K\overset{-1}{Cl} + 3O_2$$

Therefore, $KClO_3$ *also acts an oxidising agent*

Reducing agents or Reductants. Since reducing agents are electron donors and donation of electrons causes a corresponding increase in the oxidation number, therefore, according to the oxidation number concept,

A **reducing agent** or a **reluctant** *may be defined as a substance, the oxidation number of whose atom (or atoms) increases.*

For instance, in the examples (*i*) to (*iii*), the oxidation number of iodine increases from -1 in HI to 0 to I_2 ; that of aluminium increases from 0 in Al to $+3$ in Al_2O_3 and that of chlorine increases from -1 in Cl^- ion to 0 in Cl_2. Therefore, all the three, *i.e., HI, Al and Cl^- ion are reducing agents.* Further consider the following redox reaction between H_2S and HNO_3.

O.N. increases

$$H_2\overset{-2}{S} + H\overset{+5}{N}O_3 \longrightarrow \overset{+2}{N}O + \overset{0}{S} + H_2O$$

O.N. decreases

Here, the oxidation number of S increases from -2 in H_2S to 0 in elemental sulphur, while that of N decreases from $+5$ in HNO_3 to $+2$ in NO, therefore, *H_2S is a reducing agent while HNO_3 in an oxidising agent.*

• EXAMPLE 9.5. *Identify the oxidant and reductant in the following reactions :*

(a) $10H^+ (aq) + 4Zn (s) + NO_3^- (aq) \longrightarrow 4Zn^{2+} (aq) + NH_4^+ (aq) + 3H_2O (l)$

(b) $I_2 (g) + H_2S (g) \longrightarrow 2HI (g) + S (s).$

(N.C.E.R.T.)

Solution. (*a*) Writing the O.N. of all the atoms above their symbols, we have

$$10\overset{+1}{H^+} (aq) + 4\overset{0}{Zn} (s) + \overset{+5}{N}O_3^- (aq) \longrightarrow 4\overset{+2}{Zn^{2+}} (aq) + \overset{-3}{N}H_4^+ (aq) + 3\overset{+1}{H_2}\overset{-2}{O} (l)$$

Thus, there is no change in the O.N. of H and O-atoms. O.N. of Zn changes from zero in Zn to $+2$ in Zn^{2+} and, therefore, it is oxidised and hence *Zn acts as a reductant.*

The O.N. of N decreases from $+5$ in NO_3^- to -3 in NH_4^+ and, therefore, it is reduced and hence *NO_3^- acts as the oxidant.*

(*b*) Writing the O.N. of all the atoms above their symbols, we have,

$$\overset{0}{I_2} (g) + \overset{+1}{H_2}\overset{-2}{S} (g) \longrightarrow 2\overset{+1}{H}\overset{-1}{I} (g) + \overset{0}{S} (s)$$

Here O.N. of H does not change. The O.N. of I_2 decreases from zero in I_2 to -1 in HI, therefore, *I_2 is reduced and hence it acts as an oxidant.* The O.N. of S increases from -2 in H_2S to zero in S, therefore, *H_2S is oxidised and hence it acts as the reductant.*

9.9. Distinction between Valency and Oxidation Number

The term oxidation number and valency have different meanings as discussed below :

Valency	Oxidation Number
1. Valency is the combining capacity of an element. It is defined as the number of hydrogen atoms or double the number of oxygen atoms with which an atom of the element combines.	1. Oxidation number is the charge which an atom has or appears to have when present in the combined state.
2. Valency is only a number. As such it does not have plus or minus signs attached to it. For example, in H_2O, the valency of oxygen is two and that of hydrogen is one.	2. Since the oxidation number refers to the charge, it can be positive or negative. For example, in H_2O, the oxidation number of oxygen is —2 and that of hydrogen is +1.
3. Valency of an element cannnot be zero.	3. Oxidation number of an element can be zero. For example, the oxidation number of carbon in CH_2Cl_2 is zero.
4. Since atoms always combine in simple whole numbers, therefore, valency of an element is always a whole number.	4. Oxidation number may have fractional value. For example, the oxidation number of Fe in Fe_3O_4 is + 8/3 and that in $Na_2S_2O_3$ is + 2·5.
5. In some cases, the valency of an element is fixed in all its compounds. For example, the valency of C is 4 in all its compounds *viz.* CH_4, C_2H_6, CH_3Cl, C_2H_4 C_2H_2, CH_2Cl_2, $CHCl_4$ and CCl_4.	5. The oxidation number of an element may be different in different compounds. For example, the oxidation number of carbon is —4 in CH_4 — 3 in C_2H_6, —2 in CH_3Cl, – 1 in C_2H_2, zero in CH_2Cl_2, + 2 in $CHCl_3$ and + 4 in CCl_4.
6. The valency of an element may be variable but the variation is limited to only two values. For the valency of nitrogen is either 3 or 5 in all its compounds, *viz.*, N_2O, NO, N_2O_3, NO_2, N_2O_5, N_2, N_2H_4, N_3H_4 and NH_3.	6. The oxidation number of an element may also be variable but the variation is too large. For example oxidation number of N is +1 in N_2O, +2 in NO, +3 in N_2O_3, +4 in NO_2, +5 in N_2O_5, 0 in N_2, —1 in N_2H_2, —2 in N_2H_4 and —3 in NH_3.

9.10. Oxidation Number and Nomenclature

The compounds of metals which show more than one oxidation states are distinguished from one another by placing a Roman numeral such as I, II, III, IV, V, VI, VII etc. indicating the oxidation state of the metal within parenthesis after the symbol or name of the metal. For example, copper forms two oxides, *i.e.*, Cu_2O and CuO. In Cu_2O, the oxidation number of of copper is +1 while that in CuO, it is +2. Therefore, these two oxides are distinguished as $Cu_2(I)O$ and $Cu(II)O$ oxide respectively. This system of nomenclature was introduced by Stock and is commonly known as Stock notation after his name. As an illustration, consider the stock notations for the following compounds :

Formula and chemical name of the compound	Stock notation
Cu_2Cl_2, Cuprous chloride	$Cu_2(I)Cl_2$
$CuCl_2$, Cupric chloride	$Cu(II)Cl_2$
$FeSO_4$, Ferrous sulphate	$Fe(II)SO_4$
$Fe_2(SO_4)_3$, Ferric sulphate	$Fe_2(III)(SO_4)_3$
Cr_2O_3, Chromium trioxide	$Cr_2(III)O_3$
Na_2CrO_4, Sodium chromate	$Na_2Cr(VI)O_4$
V_2O_5 Vanadium pentoxide	$V_2(V)O_5$
$K_2Cr_2O_7$, Potassium dichromate	$K_2Cr(VII)O_7$
Mn_2O_7, Manganese heptoxide	$Mn(VII)O_7$

However, in case of compounds of non-metals which show variable oxidation states, stock notation is not generally used. For example, two halides of phosphorus such as PCl_3 and PCl_5 having phosphorous in oxidation state of +3 and +5 respectively are distinguished by names only, *i.e.*, phosphorus trichoride and phosphorus pentachloride respectively.

9.11. Balancing of Chemical Equations of Redox Reactions

According to the 'Law of Conversation of Mass', each chemical equation must be arithmetically balanced, *i.e.*, the number of atoms of each element on both sides of the chemical equation must be equal. Two methods which have been used to balance all types of chemical equations are

(*i*) *Hit and Trial Method*

(*ii*) *Partial Equation Method*

However, chemical equations which involve oxidation and reduction (*i.e.*, redox reactions can more easily be balanced with the help of the following two methods :

I. *Oxidation Number Method*

II. *Ion-Electron Method or Half Equation Method*

I. Oxidation Number Method

The various steps involved in the balancing of redox equations by oxidation number method are :

Step 1. *Write the skeletal equation of all the reactants and products of the reaction.*

Step 2. Indicate the oxidation number of each element above its symbol and identify the elements which undergo a change in the oxidation number (O.N.).

Step 3. *Calculate the increase or decrease in oxidation number per atom and identify the oxidising and reducing agents.* If more than one atom of the same element is involved, find out the total increase or decrease in O.N. by multiplying this increase or decrease in O.N. per atom by the number of atoms undergoing that change.

Step 4. *Multiply the formulae of the oxidising and the reducing agents by suitable integers so as to equalise the total increase or decrease in oxidation number as calculated* in step 3.

Step 5. *Balance all atoms other than H and O.*

Step 6. *Finally balance H and O atoms by adding H_2O molecules using hit and trial method.*

Step 7. In case of ionic reactions,

(*a*) **For acidic medium.** *First balance O atoms by adding H_2O molecules to whatever side deficient in O atoms and then balance H atoms by adding H^+ ions to whatever side deficient in H atoms.*

(*b*) **For basic medium.** *First balance O atoms by adding H_2O molecules to whatever side deficient in O atoms. The H atoms are then balanced by adding H_2O molecules equal in number to the deficiency of H atoms and an equal number of OH^- ions are added to the opposite side of the equation. Remove the duplication, if any.*

These rules are illustrated by the following examples.

EXAMPLE 9.6. *Balance the equation,*

$$Mg\,(aq) + HNO_3\,(aq) \longrightarrow Mg(NO_3)_2\,(aq) + N_2O\,(g) + H_2O\,(l)$$

Solution. Step 1. *Find out the elements which undergo a change in oxidation number (O.N.)*

O.N. increases by 2 per Mg atom

$$\overset{0}{Mg} + \overset{+1}{H}\overset{+5}{N}\overset{-2}{O_3} \longrightarrow \overset{+2}{Mg}(\overset{+5}{N}\overset{-2}{O_3})_2 + \overset{+1}{N_2}\overset{-2}{O} + \overset{+1}{H_2}\overset{-2}{O} \quad ...(i)$$

O.N. decreases by 4 per N atom

Here, O.N. of Mg increases from 0 in Mg metal to +2 in $Mg(NO_3)_2$ and that of N decreases from +5 in HNO_3 to +1 in N_2O.

Step 2. *Find out the total increase and decrease in O.N.*

Since there is only one Mg atom on either side of Eq. (*i*), therefore, *total increase in O.N. of Mg is 2. Further since there are two N atoms in N_2O on R.H.S. and only one in HNO_3 on L.H.S. of Eq.* (*i*), therefore, multiply HNO_3 on L.H.S. of Eq. (*i*) by 2 and thus the total decrease in O.N. of N is $2 \times 4 = 8$.

Step 3. *Balance increase/decrease in O.N.* Since the total increase in O.N. is 2 and decrease is 8, therefore, multiply Mg by 4. Combining steps 2 and 3, we have,

$$4\,Mg\,(s) + 2\,HNO_3\,(aq) \longrightarrow Mg(NO_3)_2\,(aq) + N_2O\,(g) + H_2O\,(l) \quad ...(ii)$$

Step 4. *Balance all atoms other than O and H.* To balance Mg on either side of Eq. (*ii*), multiply $Mg(NO_3)_2$ by 4, we have,

$$4\,Mg\,(s) + 2\,HNO_3\,(aq) \longrightarrow 4\,Mg(NO_3)_2\,(aq) + N_2O\,(g) + H_2O\,(l) \quad ...(iii)$$

Now, there are 10 nitrogen atoms on R.H.S. of Eq. (*iii*) and only 2 on L.H.S., therefore, to balance N-atoms, change the coefficient of HNO_3 from 2 to 10 HNO_3 by 10, on L.H.S. of Eq. (*iii*), we have,

$$4\,Mg\,(s) + 10\,HNO_3\,(aq) \longrightarrow 4\,Mg(NO_3)_2\,(aq) + N_2O\,(g) + H_2O\,(l) \quad ...(iv)$$

Step 5. *Balance O and H atoms by hit and trial method.*

Since there are 30 oxygen atoms on L.H.S. but only 26 oxygen atoms on R.H.S. of Eq. (*iv*), therefore, to balance O atoms, change the coefficient of H_2O from 1 to 5, we have,

$$4\,Mg\,(s) + 10\,HNO_3\,(aq) \longrightarrow 4\,Mg(NO_3)_2\,(aq) + N_2O\,(g) + 5\,H_2O\,(l) \quad ...(v)$$

The H atoms get automatically balanced. Thus, Eq. (*v*) represents the correct balanced equation.

- **EXAMPLE 9.7.** *Dichromate ion in aqueous acidic medium reacts with ferrous ion to give ferric and chromic ions. Write the balanced chemical equation corresponding to the reaction.* (N.C.E.R.T.)

Solution. Step 1. Write the skeletal equation of the given reaction,

$$Cr_2O_7^{2-}\,(aq) + Fe^{2+}\,(aq) \longrightarrow Cr^{3+}\,(aq) + Fe^{3+}\,(aq)$$

Step 2. *Identify the atoms which undergo a change in O.N.*

O.N. increases by 1 per Fe atom

$$[\overset{+6}{Cr_2}\,\overset{-2}{O_7}]^{2-}\,(aq) + \overset{+2}{Fe}\,(aq) \longrightarrow \overset{3+}{Cr}\,(aq) + \overset{3+}{Fe}\,(aq) \quad ...(i)$$

O.N. decreases by 3 per Cr atom

Total decrease = 2 × 3 = 6

Here O.N. of Fe increases from +2 in Fe^{2+} to +3 in Fe^{3+} while that of Cr decreases from +6 in $Cr_2O_7^{2-}$ to +3 in Cr^{3+}.

Step 3. *Calculate the total increase/decrease in O.N.* Since there is only one Fe atom on either side of Eq. (*i*), therefore, total increase in O.N. of Fe is 1. Further since there are two Cr atoms in $Cr_2O_7^{2-}$ on L.H.S. of Eq. (*i*) but only one in Cr^{3+}, therefore, multiply Cr^{3+} on R.H.S. of Eq. (*i*) by 2 and thus the total decrease in O.N. of Cr is 2 × 3 = 6

Step 4. *Balance increase/decrease in O.N.*

Since total increase in O.N. is 1 and decrease is 6, therefore, multiply Fe^{2+} by 6. Combining steps 2 and 3, we have,

$$Cr_2O_7^{2-}\,(aq) + 6\,Fe^{2+}\,(aq) \longrightarrow 2\,Cr^{3+}\,(aq) + Fe^{3+}\,(aq) \quad ...(ii)$$

Step 5. *Balance all atoms other than H and O.* To balance Fe on either side of Eq. (*ii*), multiply Fe^{3+} on R.H.S. of Eq. (*ii*) by 6, we have,

$$Cr_2O_7^{2-}\,(aq) + 6\,Fe^{2+}\,(aq) + H^+ \longrightarrow 2\,Cr^{3+}\,(aq) + 6\,Fe^{3}\,(aq) \quad ...(iii)$$

Step 6. *Balance O atoms by adding H_2O molecules.* Since there are 7 O atoms in $Cr_2O_7^{2-}$ but only one in H_2O, therefore, to balance O atoms, multiply H_2O by 7 on R.H.S. of Eq. (*iii*), we have,

$$Cr_2O_7^{2-}\,(aq) + 6\,Fe^{2+}\,(aq) + H^+\,(aq) \longrightarrow 2\,Cr^{3+}\,(aq) + 6\,Fe^{3+}\,(aq) + 7\,H_2O\,(l) \quad ...(iv)$$

Step 7. *Balance H atoms by adding H^+ ions since the reaction occurs in acidic medium.* Since there are 14 H atoms on R.H.S. and only one on L.H.S., therefore, multiply H^+ by 14 on L.H.S. of Eq. (*iv*), we have,

$$Cr_2O_7^{2-}\,(aq) + Fe^{2+}(aq) + 14\,H^+\,(aq) \longrightarrow 2\,Cr^{3+}\,(aq) + 6\,Fe^{3+}\,(aq) + 7\,H_2O\,(l) \quad ...(v)$$

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

- **EXAMPLE 9.8.** *Permanganate ion reacts with bromide ion in basic medium to give manganese dioxide and bromate ion. Write the balanced chemical equation for the reaction.* (N.C.E.R.T.)

Solution. Step 1. *Write the skeletal equation.* The skeletal equation for the given reaction is :

$$MnO_4^-\,(aq) + Br^-\,(aq) \longrightarrow MnO_2\,(s) + BrO_3^-\,(aq)$$

Step 2. *Find out the elements which undergo a change in oxidation number (O.N.)*

O.N. increases by 6 per Br atom

$$\overset{+7}{\mathrm{Mn}}O_4^- \,(aq) + \overset{-1}{\mathrm{Br}}{}^- \,(aq) \longrightarrow \overset{+4}{\mathrm{Mn}}O_2\,(s) + \overset{+5}{\mathrm{Br}}O_3^-\,(aq) \quad ...(i)$$

O.N. decreases by 3 per Mn atom

Here, O.N. of Br increases from − 1 in Br^- to + 5 in BrO_3^-, therefore, *Br^- acts as reductant.* Further, O.N. of Mn decreases from + 7 in MnO_4^- to + 4 in MnO_2, therefore, *MnO_4^- acts as oxidant.*

Step 3. *Find out total increase/decrease in O.N.*

Since there is only one Br atom on either side, therefore, *total increase in O.N. of Br is 6.* Further, since there is only one Mn atom on either side, therefore, *total decrease in O.N. of Mn is 3.*

Step 4. *Balance increase/decrease in O.N.* Since the total increase in O.N. is 6 and decrease in O.N. is 3, therefore, multiply MnO_4^- by 2. Combining steps 2 and 3, we have,

$$2MnO_4^-\,(aq) + Br^-\,(aq) \longrightarrow MnO_2\,(s) + BrO_3^-\,(aq) \quad ...(ii)$$

Step 5. *Balance all atoms other than O and H.* To balance Mn on either side of Eq. (*ii*), multiply MnO_2 by 2, we have,

$$2MnO_4^-\,(aq) + Br^-\,(aq) \longrightarrow 2MnO_2\,(s) + BrO_3^-\,(aq) \quad ....(iii)$$

Step 6. *Balance O atoms by adding H_2O molecules.* Since there are 8 oxygen atoms on L.H.S. of Eq. (*iii*) and only 7 on the R.H.S., therefore, add one H_2O to the R.H.S. of Eq. (*iii*), we have,

$$2MnO_4^-\,(aq) + Br^-\,(aq) \longrightarrow 2MnO_2\,(s) + BrO_3^-\,(aq) + H_2O\,(l) \quad ...(iv)$$

Step 7. *Balance H atoms by adding H_2O and OH^- since the reaction occurs in basic medium.* Since there are two H atoms on R.H.S. and none on L.H.S. of Eq. (*iv*), therefore, add $2H_2O$ to L.H.S. and $2OH^-$ to R.H.S. of Eq. (*iv*), we have,

$$2MnO_4^-\,(aq) + Br^-\,(aq) + 2H_2O\,(l) \longrightarrow 2MnO_2\,(s) + BrO_3^-\,(aq) + H_2O\,(l) + 2OH^-\,(aq)$$

or

$$MnO_4^-\,(aq) + Br^-\,(aq) + H_2O\,(l) \longrightarrow 2MnO_2\,(s) + BrO_3^-\,(aq) + 2OH^-\,(aq) \quad ...(v)$$

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

EXAMPLE 9.9. *Balance the oxidation reduction reaction,*

$$FeS_2 + O_2 \longrightarrow Fe_2O_3 + SO_2$$

Solution. This is an example of a reaction which occurs in absence of acids and bases and hence balancing of O atoms cannot be done by addition of H_2O molecules but has to be done on the basis of gain or loss of electrons. To balance such reactions, following steps are followed :

Step 1. *Identify atoms whose oxidation numbers undergo a change.* Writing the oxidation number of each atom above its symbol, we have,

$$\overset{+2}{\mathrm{Fe}}\,\overset{-1}{\mathrm{S}}_2 + \overset{0}{\mathrm{O}}_2 \longrightarrow \overset{+3}{\mathrm{Fe}}_2\,\overset{-2}{\mathrm{O}}_3 + \overset{+4}{\mathrm{S}}\,\overset{-2}{\mathrm{O}}_2$$

Here, the oxidation number of Fe has increased from + 2 to + 3 and that of S has increased from − 1 to + 4 while that of O has decreased from 0 to − 2. In other words, both Fe and S have been oxidised. *Since Fe and S must maintain their atomic ratio of 1 : 2, therefore, the change of oxidation number of these two atoms must be considered together.*

Step 2. *Determine the total increase and decrease in oxidation numbers.*

Indicating the increase and decrease in oxidation numbers in each case, we have,

$$\left.\begin{array}{lll} \overset{+2}{\mathrm{Fe}} \longrightarrow \overset{+3}{\mathrm{Fe}} & & 1\uparrow \\ \overset{-1}{\mathrm{S}_2} \longrightarrow 2\overset{+4}{\mathrm{S}} & & 10\uparrow \end{array}\right\} = 11\uparrow \quad ...(ii)$$

$$\text{and} \quad O_2 \longrightarrow 2\overset{2-}{\mathrm{O}} \qquad 4\downarrow \quad ...(iii)$$

Step 3. *Balance the total increase and decrease in oxidation numbers.*

To balance the total increase in oxidation number of Fe and S and decrease in oxidation number of O, multiply Eq. (*ii*) by 4 and Eq. (*iii*) by 11, and adding, we have,

$$4\,[\overset{+2}{\mathrm{Fe}} + \overset{-1}{\mathrm{S}_2}\,] + 11\,O_2 \longrightarrow 4\,\overset{+3}{\mathrm{Fe}} + 8\,\overset{+4}{\mathrm{S}} + 22\,\overset{-2}{\mathrm{O}} \quad ...(iv)$$

Since $\overset{2-}{\mathrm{O}}$ does not occur independently so the 22 $\overset{2-}{\mathrm{O}}$ must be factorized in such a manner that they become parts of Fe_2O_3 and SO_2. Rearranging, Eq. (*iv*), we have

$$4\,[\overset{+2}{Fe} + \overset{-1}{S_2}] + 11\,O_2 \longrightarrow [4\,\overset{+3}{Fe} + 6\,\overset{2-}{O}] + [8\,\overset{+4}{S} + 16\,\overset{2-}{O}]$$

$$\text{or } 4\,FeS_2 + 11\,O_2 \longrightarrow 2\,Fe_2O_3 + 8\,SO_2$$

This represents the required balanced equation.

II. Ion Electron Method or Half-Reaction Method

This method of balancing redox equations is based upon the principle that *electrons lost during oxidation half reaction of any redox reaction are equal to the electrons gained during reduction half reaction.* The various steps involved in this method are :

Step 1. *Write the skeletal equation and indicate the oxidation number (O.N.) of all the elements which appear in the skeletal equation above their respective symbols.*

Step 2. *Find out the species which are oxidised and which are reduced.*

Step 3. *Split the skeletal equation into two half reactions, i.e., oxidation half reaction and reduction half reaction .*

Step 4. *Balance the two half reaction equations separately by the rules described below :*

(*i*) *In each half reaction, first balance the atoms of the elements which have undergone a change in oxidation number.*

(*ii*) *Add electrons to whatever side is necessary to make up the difference in oxidation number in each half reaction.*

(*iii*) Balance charge by adding H^+ ions if the reaction occurs in the acidic medium and by adding OH^- ions if the reaction occurs in the basic medium.

(*iv*) *Balance oxygen atoms by adding required number of H_2O molecules to the side deficient in O atoms.*

(*v*) In the **acidic medium,** *H atoms are balanced by adding H^+ ions to the side deficient in H atoms. However, in the* **basic medium,** H atoms are *balanced by adding H_2O molecules equal in number to the deficiency of H atoms and an equal number OH^- ions are included in the opposite side of the equation. Remove the duplication, if any.*

Step 5. *The two half reactions are then multiplied by suitable integers so that the total number of electrons gained in one half reaction is equal to the number of electrons lost in the other half reaction. The two half reactions are then added up.* These rules are illustrated by the following examples.

- **EXAMPLE 9.10.** *Permanganate ion reacts with ferrous ion in acidic medium to give Fe^{3+} and Mn^{2+} ions. Write balanced chemical equation for the reaction.* **(N.C.E.R.T.)**

Solution. Step 1. *Write the skeletal equation for the given reaction*

$$MnO_4^-\,(aq) + Fe^{2+}\,(aq) \longrightarrow Mn^{2+}\,(aq) + Fe^{3+}\,(aq) \quad ...(i)$$

Step 2. *Write the O.N. of all the elements above their respective symbols.*

O.N. decreases by 5 per Mn atom

$$\overset{+7-2}{(MnO_4)^{-1}} + \overset{+2}{Fe} \longrightarrow \overset{2+}{Mn} + \overset{3+}{Fe}$$

O.N. increases by 1 per Fe atom

Step 3. *Find out the species which have been oxidised and reduced and split the given skeleton equation into two half reactions.*

Since the O.N. of Mn decreases from +7 in MnO_4^- to +2 in Mn^{2+} while that of Fe increases from +2 in Fe^{2+} to +3 in Fe^{3+}. Therefore, MnO_4^- gets reduced while Fe^{3+} gets oxidised. Thus, the above skeletal Eq. (*i*) can be divided into the following two half reaction equations :

Oxidation half equation :

$$Fe^{2+}\,(aq) \longrightarrow Fe^{3+}\,(aq) \quad ...(ii)$$

Reduction half equation :

$$MnO_4^-\,(aq) \longrightarrow Mn^{2+}\,(aq) \quad ...(iii)$$

Step 4. *To balance oxidation half equation (ii)*

(*a*) *Balance all atoms other than O and H not needed since Fe is already balanced.*

(*b*) *Balance the oxidation number by adding electrons.* The O.N. of Fe on L.H.S. of Eq. (*i*) in Fe^{2+} is +2 while on the R.H.S. in Fe^{3+} is +3. Therefore, add one e^- to R.H.S. of Eq. (*i*), we have,

$$Fe^{2+}\,(aq) \longrightarrow Fe^{3+}\,(aq) + e^- \quad ...(iv)$$

(*c*) *Balance charge by adding H^+ ions.* Not needed since the charge is already balanced. Thus, Eq. (*iv*) represents balanced oxidation half reaction.

Step 5. *To balance the reduction half equation (iii)* *(a) Balance all the atoms other than H and O.* Not needed since Mn is already balanced

$$MnO_4^- (aq) \longrightarrow Mn^{2+} (aq) \quad ...(iii)$$

(b) Balance the oxidation number by adding electrons. The oxidation number of Mn in MnO_4^- on L.H.S. of Eq. (*iii*) is +7 and +2 on the R.H.S. Therefore, add $5e^-$ to L.H.S. of Eq. (*iii*), we have,

$$MnO_4^- (aq) + 5e^- \longrightarrow Mn^{2+} (aq) \quad ...(v)$$

(c) Balance charge by adding H^+ ions since the reaction occurs in acidic medium. The total charge on the L.H.S. of Eq. (*v*) is −6 and on the R.H.S., it is +2. Therefore, add $8H^+$ to the L.H.S. We have,

$$MnO_4^- (aq) + 8H^+ (aq) + 5e^- \longrightarrow Mn^{2+} (aq) \quad ...(vi)$$

(d) Balance O atoms by adding H_2O molecules. Since there are four O-atoms on the L.H.S. of Eq. (*vi*) but no O-atom on the R.H.S., therefore, add $4 H_2O$ to the R.H.S. of Eq. (*vi*), we have,

$$MnO_4^- (aq) + 8H^+ (aq) + 5e^- \longrightarrow Mn^{2+} (aq) + 4H_2O (aq) \quad ...(vii)$$

The H-atoms get automatically balanced. Thus, Eq. (*vii*) represents the balanced reduction half equation.

Step 6. *To balance the electrons lost in Eq. (iv) and gained in Eq. (vii), multiply Eq. (iv) by 5 and add to Eq. (vii), we have,*

$$5Fe (aq) \longrightarrow 5Fe^{3+} (aq) + 5 e^-$$

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

$$MnO_4^- (aq) + 5Fe^{2+} (aq) + 8H^+ (aq) \longrightarrow Mn^{2+} (aq) + 5Fe^{3+} (aq) + 4H_2O (l)$$

This gives the final balanced redox equation.

EXAMPLE 9.11. *Balance the equation,*

$$As_2S_3 (s) + NO_3^- (aq) + H^+ (aq) \longrightarrow AsO_4^{3-} (aq) + S (s) + NO (g) + H_2O (l)$$

(N.C.E.R.T.)

Solution. Step 1. *To identify the atoms whose oxidation numbers have undergone a change.* Writing the oxidation number of each atom above its symbol, we have,

$$\overset{+3}{As_2}\,\overset{-2}{S_3} (s) + \overset{+5}{N}O_3^- (aq) + H^+ (aq) \longrightarrow \overset{+5}{As}O_4^{3-} (aq) + \overset{0}{S} (g) + \overset{+2}{N}O_2 (g) + H_2O (l)$$

Here, the oxidation number of As has increased from +3 to +5 and that of S has increased from −2 to 0 while that of N has decreased from +5 to +2. In other words, both As and S have been oxidised while NO_3^- has been reduced. *Since As and S must maintain their atomic ratio of 2 : 3 (as in As_2S_3) therefore, the change in oxidation numbers of these two atoms must be considered together.* Keeping in view these points, the above redox reaction can be split up into the following two half reactions :

Oxidation :

$$\overset{+3}{As_2}\,\overset{-2}{S_3} (s) \longrightarrow \overset{+5}{As}O_4^{3-} (aq) + \overset{0}{S} (s) \quad ...(i)$$

$$\textit{Reduction :} \quad \overset{+5}{N}O_3^- (aq) \longrightarrow \overset{+2}{N}O (g) \quad ...(ii)$$

Step 2. *To balance the oxidation half Eq. (i)*

(a) Balance all the atoms other than H and O. Multiply AsO_4^{3-} by 2 and S by 3 on R.H.S. of Eq. (*i*), we have,

$$\overset{+3}{As_2}\,\overset{-2}{S_3} (s) \longrightarrow 2\,\overset{+5}{As}O_4^{3-} (aq) + 3\,\overset{0}{S} (s) \quad ...(iv)$$

(b) Balance the oxidation number by adding electrons. Since each As atom loses two electrons and there are two As atoms, therefore, due to the oxidation of As alone add $4 e^-$ to R.H.S. of Eq. (*iii*). Further, since each S atom loses two electrons and there are three S atoms, therefore, due to the oxidation of S alone, add $6 e^-$ to R.H.S. of Eq. (*iii*). Combining those two oxidation steps together, add $10 e^-$ to R.H.S. of Eq. (*iii*). We have,

$$As_2S_3 (s) \longrightarrow 2 AsO_4^{3-} (aq) + 3 S (s) + 10 e^- \quad ...(iv)$$

(c) Balance charge by adding H^+ ions. The total charge on R.H.S. of Eq. (*iv*) is −16 and zero on the L.H.S., therefore, add $16 H^+$ to R.H.S. of Eq. (*iv*) we have,

$$As_2S_3 (s) \longrightarrow 2 AsO_4^{3-} (aq) + 3 S (s) + 16 H^+ (aq) + 10 e^- \quad ...(v)$$

(d) Balance O atoms by adding H_2O molecules. Since there are *eight* O-atoms on the R.H.S. of Eq. (*v*) but none on the L.H.S., therefore to balance O-atoms, add $8 H_2O$ to the L.H.S. of Eq. (*v*). We have,

$$As_2S_3\,(s) + 8\,H_2O\,(l) \longrightarrow 2\,AsO_4^{3-}\,(aq) + 3\,S\,(s)\ 16\,H^+ + 10\,e^- \quad ...(vi)$$

The H-atoms get automatically balanced. Thus Eq. (*vi*) represents the balanced oxidation half equation.

Step 3. *To balance the reduction half Eq. (ii)*

(*a*) *Balance oxidation number by adding electrons.* Oxidation of N is +5 on L.H.S. while it is +2 on R.H.S., therefore, add 3 e^- to L.H.S. of Eq. (*ii*). We have,

$$NO_3^-\,(aq) + 3\,e^- \longrightarrow NO\,(g) \quad ...(vii)$$

(*b*) *Balance charge by adding H^+ ions.* The total charge on L.H.S. is −4 while it is zero on R.H.S., therefore, add 4 H^+ to L.H.S. of Eq. (*vii*). We have,

$$NO_3^-\,(aq) + 4\,H^+\,(aq) + 3\,e^- \longrightarrow NO\,(g) \quad ...(viii)$$

(*c*) *Balance O atoms by adding H_2O molecules.* Since there are three O-atoms of the L.H.S. of Eq. (*viii*) but only one on the R.H.S., therefore, add 2 H_2O to the R.H.S. of Eq. (*viii*). We have,

$$NO_3^-\,(aq) + 4\,H^+\,(aq) + 3\,e^- \longrightarrow NO\,(g) + 2\,H_2O\,(l) \quad ...(ix)$$

The H-atoms are automatically balanced. Thus, Eq. (*ix*) represents the balanced reduction half equation.

Step 4. *To balance the electrons lost in Eq. (vi) and gained in Eq. (ix), multiply Eq. (ix) by 10 and Eq. (vi) by 3 and add.* We have,

$$3\,As_2S_3\,(s) + 24\,H_2O\,(l) \longrightarrow 6\,AsO_4^{3-}\,(aq) + 9\,S\,(s) + 48\,H^+\,(aq) + 30\,e^-$$

$$10\,NO_3^-\,(aq) + 40\,H^+\,(aq) + 30\,e^- \longrightarrow 10\,NO\,(g) + 20\,H_2O\,(l)$$

$$3\,As_2S_3\,(s) + 10\,NO_3^-\,(aq) + 4\,H_2O\,(l) \longrightarrow 6\,AsO_4^{3-}\,(aq) + 9\,S\,(s) + 10\,NO\,(g) + 8\,H^+\,(aq)$$

This gives the final balanced redox equation.

EXAMPLE 9.12. *In passing chlorine gas through a concentrated solution of alkali, we get chloride and chlorate ions. Obtain balanced chemical equation for this reaction.* (*N.C.E.R.T.*)

Solution. Step 1. *Write the skeletal equation for the given reaction*

$$Cl_2\,(g) + OH^-\,(aq) \longrightarrow Cl^-\,(aq) + ClO_3^-\,(aq) \quad ...(i)$$

Step 2. *Write the O.N. of all the elements above their respective symbols.*

O.N. of Cl increases by 5 per Cl atom

$$\overset{0}{Cl_2}\,(g) + OH^-\,(aq) \longrightarrow \overset{-1}{Cl^-}\,(aq) + \overset{+5}{ClO_3^-}\,(aq)$$

O.N. of Cl decreases by 1 per Cl atom

Total increase = 2 × 5 = 10

Total decrease = 2 × − 1 = − 2

Step 3. *Find out the oxidant and the reductant and split the skeletal Eq. (i) into two half reactions.*

Here, O.N. of Cl decreases from 0 in Cl_2 to −1 in Cl^-, therefore, *Cl_2 acts as an oxidant.* Further, the O.N. of Cl increases from 0 in Cl_2 to +5 in ClO_3^-, therefore, *Cl_2 acts as a reductant.* In other words, Cl_2 acts both as an oxidant as well as a reductant. Therefore, the two half reactions are :

Reduction half : $Cl_2\,(g) \longrightarrow Cl^-\,(aq)$ ...(*ii*)

Oxidation half : $Cl_2\,(g) \longrightarrow ClO_3^-\,(aq)$ ...(*iii*)

Step 4. *To balance the reduction half equation (ii).*

(*a*) *Balance all atoms other than O and H.* Since there are 2 Cl atoms. On L.H.S. of Eq. (*ii*) and only one on the R.H.S., therefore, multiply Cl^- ion by 2, we have,

$$Cl_2\,(aq) \longrightarrow 2Cl^-\,(aq) \quad ...(iv)$$

(*b*) *Balance oxidation number by adding electrons.* The O.N. of Cl in Cl_2 on L.H.S. of Eq. (*iv*) is 0 while on the R.H.S. it is −1. Thus each Cl accepts one electron. Since there are two Cl atoms on the R.H.S., therefore, add 2 e^- to L.H.S. of Eq. (*iv*), we have,

$$Cl_2\,(g) + 2\,e^- \longrightarrow 2Cl^-\,(aq) \quad ...(v)$$

(*c*) *Balance charge.* Not needed since charge on either side of Eq. (*v*) is balanced. Thus, Eq. (*v*) represents the balanced reduction half reaction.

Step 5. *To balance the oxidation half equation (iii)*

(*a*) *Balance all atoms other than O and H.*

Since there are 2 Cl atoms on L.H.S. of Eq. (*iii*) and only one on the R.H.S., therefore, multiply ClO_3^- ion by 2, we have,

$$Cl_2\,(g) \longrightarrow 2ClO_3^-\,(aq) \quad ...(vi)$$

(b) Balance oxidation number by adding electrons. The O.N. of Cl in Cl_2 on L.H.S. of eq. (*vi*) is zero while in the R.H.S. in ClO_3^-, it is + 5. Thus, each Cl atom loses five electrons. Since there are two Cl atoms on R.H.S., therefore, add $10\,e^-$ to R.H.S. of Eq. (*vi*), we have,

$$Cl_2\,(g) \longrightarrow 2ClO_3^-\,(aq) + 10\,e^- \quad ...(vii)$$

(c) Balance charge by adding OH^- ions since the reaction occurs in the basic medium. The total charge on the R.H.S. of Eq. (*vii*) is – 12 and zero on the R.H.S. Therefore, add 12 OH^- ions to the L.H.S., we have,

$$Cl_2\,(g) + 12OH^-\,(aq) \longrightarrow 2ClO_3^-\,(aq) + 10\,e^- \quad ...(viii)$$

(d) Balance O atoms. The R.H.S. of Eq. (*viii*) contains six O atoms but on the L.H.S., there are 12. Therefore, add $6H_2O$ to the R.H.S., we have,

$$Cl_2\,(g) + 12OH^-\,(aq) \longrightarrow 2ClO_3^-\,(aq) + 6H_2O\,(l) + 10\,e^- \quad ...(ix)$$

By doing so, H atoms are automatically balanced, therefore, Eq. (*ix*) represents the balanced oxidation half equation.

Step 6. *To balance the electrons gained in Eq. (v) and lost in Eq. (ix), multiply Eq. (v) by 5 and add to Eq. (ix), we have,*

$$5Cl_2\,(g) + 10\,e^- \longrightarrow 10Cl^-\,(aq)$$

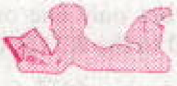
$$Cl_2\,(g) + 12OH^-\,(aq) \longrightarrow 2ClO_3^-\,(aq) + 6H_2O\,(l) + 10\,e^-$$

$$6Cl_2\,(g) + 12OH^-\,(aq) \longrightarrow 10Cl^-\,(aq) + 2ClO_3^-\,(aq) + 6H_2O\,(l)$$

or $$3Cl_2\,(g) + 6OH^-\,(aq) \longrightarrow 5Cl^-\,(aq) + ClO_3^-\,(aq) + 3H_2O\,(l)$$

This represents the final balanced redox equation.

PROBLEMS FOR PRACTICE



1. Balance the following equations in acidic medium by both oxidation number and ion electron methods and identify the oxidants and the reductants :

(*i*) $MnO_4^-\,(aq) + C_2H_2O_4\,(aq) \longrightarrow Mn^{2+}\,(aq) + CO_2\,(g) + H_2O\,(l)$ (*N.C.E.R.T.*)

(*ii*) $H_2S\,(aq) + Cl_2\,(g) \longrightarrow S\,(s) + Cl^-\,(aq)$ (*N.C.E.R.T.*)

(*iii*) $MnO_4^-\,(aq) + C_2H_5OH\,(aq) \longrightarrow Mn^{2+}\,(aq) + CH_3COOH\,(aq)$ (*N.C.E.R.T.*)

(*iv*) $Bi\,(s) + NO_3^-\,(aq) \longrightarrow Bi^{3+}\,(aq) + NO_2\,(g)$

(*v*) $Cr_2O_7^{2-}\,(aq) + C_2H_4O\,(aq) \longrightarrow Cr^{3+}\,(aq) + C_2H_4O_2\,(aq)$

(*vi*) $MnO_4^-\,(aq) + Br^-\,(aq) \longrightarrow Mn^{2+}\,(aq) + Br_2\,(aq)$

(*vii*) $Cu\,(aq) + NO_3^-\,(aq) \longrightarrow Cu^{2+}\,(aq) + NO_2\,(g)$ (*N.C.E.R.T.*)

(*viii*) $H_2S\,(g) + Fe^{3+}\,(aq) \longrightarrow Fe^{2+}\,(aq) + S\,(s) + H^+\,(aq)$

(*ix*) $I^-\,(aq) + IO_3^-\,(aq) + H^+\,(aq) \longrightarrow I_2\,(aq) + H_2O\,(l)$

(*x*) $Bi\,(s) + NO_3^-\,(aq) + H^+\,(aq) \longrightarrow Bi^{3+}\,(aq) + NO_2\,(g) + H_2O\,(l)$

(*xi*) $I^-\,(aq) + O_2\,(g) + H_2O\,(l) \longrightarrow I_2\,(aq) + OH^-(aq)$

(*xii*) $Cu + Au^+ \longrightarrow Au + Cu^{2+}$

(*xiii*) $Sn\,(s) + NO_3^-\,(aq) + H^+\,(aq) \longrightarrow Sn^{2+}\,(aq) + NH_4^+\,(aq) + H_2O\,(l)$

(*xiv*) $Cu\,(s) + NO_3^-\,(aq) + H^+\,(aq) \longrightarrow Cu^{2+}\,(aq) + NO\,(g) + H_2O\,(l)$

(*xv*) $Zn\,(s) + NO_3^-\,(aq) + H^+\,(aq) \longrightarrow Zn^{2+}\,(aq) + N_2O\,(g) + H_2O\,(l)$

(*xvi*) $Sn\,(aq) + NO_3^-\,(aq) + H^+\,(aq) \longrightarrow SnO_3^{2-}\,(aq) + NO_2\,(g) + H_2O\,(l)$

(*xvii*) $As\,(s) + NO_3^-\,(aq) + H^+(aq) \longrightarrow AsO_4^{3-}\,(aq) + NO_2\,(g) + H_2O\,(l)$

[Ans. (*i*) $2MnO_4^-\,(aq) + 6H^+\,(aq) + 5C_2H_2O_4\,(aq) \longrightarrow 2Mn^{2+}\,(aq) + 10CO_2\,(g) + 8H_2O\,(l)$

(*ii*) $H_2S\,(aq) + Cl_2\,(g) \longrightarrow S\,(s) + 2Cl^-\,(aq) + 2H^+\,(aq)$

(*iii*) $4MnO_4^-\,(aq) + 5C_2H_5OH\,(aq) + 12H^+\,(aq) \longrightarrow 4Mn^{2+} + 5CH_3COOH\,(aq) + 11H_2O\,(l)$

(*iv*) $Bi\,(s) + 3NO_3^-\,(aq) + 6H^+(aq) \longrightarrow Bi^{3+}(aq) + 3NO_2\,(g) + 3H_2O\,(l)$

(*v*) $Cr_2O_7^{2-}\,(aq) + 3C_2H_4O\,(aq) + 8H^+\,(aq) \longrightarrow 2Cr^{3+}\,(aq) + 3C_2H_4O_2\,(aq) + 4H_2O\,(l)$

(*vi*) $2MnO_4^-\,(aq) + 10Br^-\,(aq) + 16H^+\,(aq) \longrightarrow 2Mn^{2+}\,(aq) + 5Br_2\,(aq) + 8H_2O\,(l)$

(*vii*) $Cu\,(s) + 2NO_3^-\,(aq) + 4H^+\,(aq) \longrightarrow Cu^{2+}\,(aq) + 2NO_2\,(g) + 2H_2O\,(l)$

(*viii*) $H_2S\,(g) + 2Fe^{3+}\,(aq) \longrightarrow 2Fe^{2+}\,(aq) + S\,(s) + 2H^+\,(aq)$

(*ix*) $5I^-\,(aq) + IO_3^-\,(aq) + 6H^+\,(aq) \longrightarrow 3I_2\,(aq) + 3H_2O\,(l)$

(*x*) $Bi\,(s) + 3NO_3^-\,(aq) + 6H^+\,(aq) \longrightarrow Bi^{3+}\,(aq) + 3NO_2\,(g) + 3H_2O\,(l)$

(*xi*) $4I^-\,(aq) + O_2\,(g) + 2H_2O\,(l) \longrightarrow 2I_2\,(aq) + 4OH^-\,(aq)$

(*xii*) $Cu\,(s) + 2Au^+\,(aq) \longrightarrow 2Au\,(s) + Cu^{2+}\,(aq)$

(*xiii*) $4\,Sn\,(s) + NO_3^-\,(aq) + 10\,H^+\,(aq) \longrightarrow 4\,Sn^{2+}\,(aq) + NH_4^+\,(aq) + 3\,H_2O\,(l)$

(*xiv*) $3\,Cu\,(s) + 2\,NO_3^-\,(aq) + 8\,H^+\,(aq) \longrightarrow 3\,Cu^{2+}\,(aq) + 2\,NO\,(g) + 4\,H_2O\,(l)$

(*xv*) $4\,Zn\,(s) + 2\,NO_3^-\,(aq) + 10\,H^+\,(aq) \longrightarrow 4\,Zn^{2+}\,(aq) + N_2O\,(g) + 5\,H_2O\,(l)$

(*xvi*) $Sn\,(s) + 4\,NO_3^-\,(aq) + 2\,H^+\,(aq) \longrightarrow SnO_3^{2-}\,(aq) + 4\,NO_2\,(g) + H_2O\,(l)$

(*xvii*) $As\,(s) + 5\,NO_3^-\,(aq) + 2\,H^+\,(aq) \longrightarrow AsO_4^{3-}\,(aq) + 5\,NO_2\,(g) + H_2O\,(l)$]

2. Balance the following equations in basic medium by both oxidation number and ion electron methods and identify the reductants and the oxidants.

(*i*) $P\,(s) + OH^-\,(aq) \longrightarrow PH_3\,(g) + H_2PO_2^-\,(aq)$ (*N.C.E.R.T.*)

(*ii*) $N_2H_4\,(g) + ClO_3^-\,(aq) \longrightarrow NO\,(g) + Cl^-\,(aq)$ (*N.C.E.R.T.*)

(*iii*) $Cl_2O_7\,(g) + H_2O_2\,(aq) \longrightarrow ClO_2^-\,(aq) + O_2\,(g)$ (*N.C.E.R.T.*)

(*iv*) $Cr(OH)_4^-\,(aq) + H_2O_2\,(aq) \longrightarrow CrO_4^{2-}\,(aq) + H_2O\,(l)$

(*v*) $Zn\,(s) + NO_3^-\,(aq) \longrightarrow Zn^{2+}\,(aq) + NH_4^+\,(aq)$

(*vi*) $Al\,(s) + NO_3^-\,(aq) \longrightarrow Al(OH)_4^-\,(aq) + NH_3\,(g)$

(*vii*) $PbO_2\,(s) + Cl^-\,(aq) \longrightarrow Pb(OH)_3^-\,(aq) + ClO^-\,(aq)$

(*viii*) $Fe(OH)_2\,(aq) + H_2O_2\,(aq) \longrightarrow 2Fe(OH)_3\,(s)$

(*ix*) $Bi(OH)_3\,(s) + SnO_2^{2-}\,(aq) \longrightarrow Bi\,(s) + SnO_3^{2-}\,(aq)$

(*x*) $Cr\,(s) + ClO_4^-\,(aq) \longrightarrow Cr(OH)_3\,(s) + ClO_3^-\,(aq)$

[Ans. (*i*) $4P\,(s) + 3OH^-\,(aq) + 3H_2O\,(l) \longrightarrow PH_3\,(g) + 3H_2PO_2^-\,(aq)$

(*ii*) $3N_2H_4\,(g) + 4ClO_3^-\,(aq) \longrightarrow 6NO\,(g) + 4Cl^-\,(aq) + 6H_2O\,(l)$

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

(*iv*) $2Cr(OH)_4^-\,(aq) + 2OH^-\,(aq) + 3H_2O_2\,(aq) \longrightarrow 2CrO_4^{2-}\,(aq) + 8H_2O\,(l)$

(*v*) $4Zn\,(s) + NO_3^-\,(aq) + 7H_2O\,(l) \longrightarrow 4Zn^{2+}\,(aq) + NH_4^+\,(aq) + 10OH^-\,(aq)$

(*vi*) $8Al\,(s) + 3NO_3^-\,(aq) + 18H_2O\,(l) + 5OH^-\,(aq) \longrightarrow 8Al(OH)_4^-\,(aq) + 3NH_3\,(g)$

(*vii*) $PbO_2\,(s) + Cl^-\,(aq) + H_2O\,(l) + OH^-\,(aq) \longrightarrow Pb(OH)_3^-\,(aq) + ClO^-\,(aq)$

(*viii*) $2Fe(OH)_2\,(aq) + H_2O_2\,(aq) \longrightarrow 2Fe(OH)_3\,(s)$

(*ix*) $2\,Bi(OH)_3\,(s) + 3\,SnO_2^{2-}\,(aq) \longrightarrow 2\,Bi\,(s) + 3\,SnO_3^{2-}\,(aq) + 3\,H_2O\,(l)$

(*x*) $2\,Cr\,(s) + 3\,ClO_4^-\,(aq) + 3\,H_2O \longrightarrow 2\,Cr(OH)_3\,(s) + 3\,ClO_3^-\,(aq)$]

3. Balance the following redox reactions :

(*i*) $SnO_2 + C \longrightarrow Sn + CO$

(*ii*) $Fe_3O_4 + C \longrightarrow Fe + CO$

(*iii*) $I_2 + HNO_3 \longrightarrow HIO_3 + NO_2 + H_2O$

(*iv*) $FeSO_4 + HNO_3 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + NO + H_2O$

(*v*) $Fe + HNO_3 \longrightarrow Fe(NO_3)_2 + NH_4NO_3 + H_2O$

(*vi*) $Sb + HNO_3 \longrightarrow H_3SbO_4 + NO_2 + H_2O$

(*vii*) $Hg + HNO_3 \longrightarrow Hg_2(NO_3)_2 + NO + H_2O$

[Ans. (*i*) $SnO_2 + 2C \longrightarrow Sn + 2CO$

(*ii*) $Fe_3O_4 + 4C \longrightarrow 3Fe + 4CO$

(*iii*) $I_2 + 10\,HNO_3 \longrightarrow 2\,HIO_3 + 10\,NO_2 + 4\,H_2O$

(*iv*) $6\,FeSO_4 + 2\,HNO_3 + 3\,H_2SO_4 \longrightarrow 3\,Fe_2(SO_4)_3 + 2\,NO + 4\,H_2O$

(*v*) $4\,Fe + 10\,HNO_3 \longrightarrow 4\,Fe(NO_3)_2 + NH_4NO_3 + 3\,H_2O$

(*vi*) $Sb + 5\,HNO_3 \longrightarrow H_3SbO_4 + 5\,NO_2 + H_2O$

(*vii*) $6\,Hg + 8\,HNO_3 \longrightarrow 3\,Hg_2(NO_3)_2 + 2\,NO + 4\,H_2O$]

9.12. Stoichiometry of Redox Reactions in Solutions

Stoichiometry *of redox reactions means calculation of the quantities of the oxidising and reducing agents and their products in oxidation-reduction reactions.*

Stoichiometric calculations can be done either by using mole concept or by redox titrations using normality or molarity equation.

9.12.1. Determination of stoichiometry using mole concept. For carrying out stoichiometric calculations, we need a balanced redox equation for the reaction since the stoichiometric coefficients in the balanced equation tell us the ratio by moles in which the reactants combine and the products are formed. The following examples will illustrate the method.

- EXAMPLE 9.13. *How many grams of potassium dichromate are required to oxidise 15·2 g of $FeSO_4$ in acidic medium.*

Solution. Step 1. *To write balanced chemical equation of the redox reaction*

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

$$Fe^{2+} \longrightarrow Fe^{3+} + e^-\,] \times 6$$

$$Cr_2O_7^{2-} + 6\,Fe^{2+} + 14\,H^+ \longrightarrow 2\,Cr^{3+} + 6\,Fe^{3+}$$

Step 2. *To calculate the amount of $K_2Cr_2O_7$ required.*

It is evident from balanced equation that

1 mole of $Cr_2O_7^{2-} \equiv 6$ moles of Fe^{2+}

or 1 mole $K_2Cr_2O_7 \equiv 6$ moles $FeSO_4$

or $2 \times 39 + 2 \times 52 + 16 \times 7\,g \equiv 6 \times (56 + 32 + 16 \times 4)$

or $294\,g\ K_2Cr_2O_7 \equiv 6 \times 152\,g\ FeSO_4$

Now $6 \times 152\,g$ of $FeSO_4$ are oxidised by $K_2Cr_2O_7 = 294$ g

∴ 15·2 of $FeSO_4$ will require $K_2Cr_2O_7$

$$= \frac{294 \times 15{\cdot}2}{6 \times 152} = \mathbf{4{\cdot}9\ g}$$

EXAMPLE 9.14. *2·68 × 10^{-3} moles of a solution containing an ion A^{n+} require 1·61×10^{-3} moles MnO_4^- for the oxidation of A^{n+} to AO_3^- in acid medium. What is the value of n ?*

Solution. Step 1. *To write the reduction and oxidation half reactions.*

Reduction : $MnO_4^- + 8\,H^+ + 5\,e^- \longrightarrow Mn^{2+} + 4\,H_2O$ ...(*i*)

Oxidation : $A^{n+} + 3\,H_2O \longrightarrow \overset{+5}{AO_3^-} + 6\,H^+ + (5 - n)\,e^-$ ...(*ii*)

Step 2. *To find out the value of n.*

Since in a redox reaction, number of electrons lost = number of electrons gained, therefore, multiply oxidant of Eq. (*i*) *i.e.* MnO_4^- by (5–*n*) and reductant of Eq. (*ii*) *i.e.* A^{n+} by 5 and equate, we have,

$$(5-n)\,MnO_4^- = 5\,A^{n+}$$

i.e., (5–*n*) moles of MnO_4^- will oxidise A^{n+} = 5 moles

or $1\cdot61 \times 10^{-3}$ moles of MnO_4^- will oxidise A^{n+}

$$= \frac{5}{5-n} \times 1\cdot6 \times 10^{-3}\ \text{moles} \qquad ...(iii)$$

But the number of moles of A^{n+} actually oxidised

$$= 2\cdot68 \times 10^{-3}\ \text{moles} \qquad ...(iv)$$

Equating the values of Eq. (*iii*) and (*iv*), we have,

$$\frac{5}{5-n} \times 1\cdot61 \times 10^{-3} = 2\cdot68 \times 10^{-3}$$

$$\text{or} \quad 5 \times 1\cdot61 = (5-n) \times 2\cdot68$$

$$\text{or} \quad 2\cdot68\,n = 5\,(2\cdot68 - 1\cdot61)$$

$$= 5 \times 1\cdot07 = 5\cdot35$$

$$\text{or} \quad n = \frac{5\cdot35}{2\cdot68} = 2$$

9.12.2. Determination of stoichiometry using Redox titrations. These titrations involve the reaction between oxidising and reducing agents in acidic medium. Depending upon the nature of the oxidising agent, these are divided into the following categories :

1. Potassium permanganate titrations. In these titrations, reducing agents like $FeSO_4$, Mohr's salt $[(NH_4)_2SO_4 . FeSO_4 . 6\,H_2O]$, H_2O_2, As_2O_3, oxalic acid $(COOH)_2$ and oxalates $(COONa)_2$ etc. are directly titrated against $KMnO_4$ as the oxidising agent in acidic medium. For example,

(*i*) *Oxidation of ferrous salts.*

$$\underset{\text{Ferrous ion}}{5\,Fe^{2+}} + \underset{\text{Permaganate ion}}{MnO_4^-} + 8\,H^+ \longrightarrow 5\,\underset{\text{Ferric ion}}{Fe^{3+}} + Mn^{2+} + 4\,H_2O$$

(*ii*) *Oxidation of oxalates :*

$$5\,\underset{\text{Oxalate ion}}{\begin{array}{c}COO^-\\|\\COO^-\end{array}} + 2\,MnO_4^- + 16\,H^+ \longrightarrow 2\,Mn^{2+} + 10\,CO_2 + 8\,H_2O$$

2. Potassium dichromate titrations

In these titrations, the above listed reducing agents are directly titrated against $K_2Cr_2O_7$ as the oxidising agent in acidic medium. For example,

(*i*) *Oxidation of ferrous salts :*

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

(*ii*) *Oxidation of Mohr's salt :*

Mohr's salt is a double salt of $(NH_4)_2SO_4$ and $FeSO_4$ *i.e.* $(NH_4)_2SO_4.FeSO_4.6H_2O$. Out of these two salts, $Cr_2O_7^{2-}$ oxidises $FeSO_4$ to $Fe_2(SO_4)_3$ as per the equation shown under oxidation of ferrous salts.

3. Ceric sulphate titrations. In these titrations, the reducing agents such as Fe^{2+} salts, Cu^+ salts, nitrites, arsenites, oxalates etc. are directly titrated against ceric sulphate, $Ce(SO_4)_2$ as the oxidising agent. For example,

(*i*) *Oxidation of ferrour salts :*

$$\underset{\text{Ferrous ion}}{Fe^{2+}} + \underset{\text{Ceric ion}}{Ce^{4+}} \longrightarrow \underset{\text{Ferric ion}}{Fe^{3+}} + \underset{\text{Cerous ion}}{Ce^{3+}}$$

(*ii*) Oxidation of aresinites (AsO_3^{3-}) to arsenates (AsO_3^{4-}).

$$\underset{\text{Arsenite ion}}{AsO_3^{3-}} + \underset{\text{Ceric ion}}{2\,Ce^{4+}} + H_2O \longrightarrow \underset{\text{Arsenate ion}}{AsO_4^{3-}} + \underset{\text{Cerous ion}}{Ce^{3+}} + 2\,H^+$$

(*iii*) *Oxidation of oxalic acid :*

$$\underset{\text{Oxalic acid}}{(COOH)_2} + 2\,Ce^{4+} \longrightarrow 2\,CO_2 + 2\,Cr^{3+} + 2\,H^+$$

4. Iodimetric titrations. These titrations involve the direct use of *iodine as the oxidising agent* (in neutral or slightly acidic medium) using starch as an indicator. The various reducing agents used in these titrations are *thiosulphates, sulphites, arsenites and antimonites.*

$$I_2 + \underset{\text{Thiosulphate ion}}{S_2O_3^{2-}} \longrightarrow 2\,I^- + \underset{\text{Tetrathionate ion}}{S_4O_6^{2-}}$$

$$I_2 + \underset{\text{Sulphite ion}}{SO_3^{2-}} + H_2O \longrightarrow 2\,I^- + SO_4^{2-} + 2\,H^+$$

$$I_2 + \underset{\text{Arsenite ion}}{AsO_3^{3-}} + H_2O \longrightarrow 2\,I^- + \underset{\text{Arsenate ion}}{AsO_4^{3-}} + 2\,H^+$$

$$I_2 + \underset{\text{Antimonite ion}}{SbO_3^{3-}} + H_2O \longrightarrow 2\,I^- + \underset{\text{Antimonate ion}}{SbO_4^{3-}} + 2\,H^+$$

5. Iodometric titrations. These titrations are carried out in two steps. In the first step, oxidising agents such as $KMnO_4$, $K_2Cr_2O_7$, $CuSO_4$, peroxides etc. are treated with an excess of KI when

I_2 is liberated quickly and quantitatively. For example,

$$2\,MnO_4^- + 16\,H^+ + 10\,I^- \longrightarrow 2\,Mn^{2+} + 5\,I_2 + 8\,H_2O$$

$$Cr_2O_7^{2-} + 14\,H^+ + 6\,I^- \longrightarrow 2\,Cr^{3+} + 3\,I_2 + 7\,H_2O$$

$$2\,Cu^{2+} + 4\,I^- \longrightarrow Cu_2I_2 + I_2$$

In the second step, the liberated iodine is titrated against a standard solution of sodium thiosulphate using starch as an indicator. *All such titrations in which iodine liberated from potassium iodide with the help of an oxidising agent is titrated against a standard solution of sodium thiosulphate are called* **iodometric titrations.**

Before we solve problems on stoichiometry of redox reactions we must be familiar with the following three concepts :

(*i*) *Equivalent weights of oxidising and reducing agents.*

(*ii*) *Normality equation.*

(*iii*) *Molarity equation.*

(*i*) Equivalent weights of oxidising and reducing agents. The equivalent weights of oxidising and reducing agents can be calculated by the number of electrons gained or lost. Thus, *the equivalent weight of an oxidising agent is equal to the molecular weight of the substance divided by the number of electrons gained as represented in the balanced chemical equation.*

Further, we know that the total number of electrons gained or lost in any balanced oxidation/reduction half reaction is equal to the total change in the O.N. of a particular atom of the oxidising/reducing agent. Therefore, *equivalent weights can also be determined simply by diving the molecular weight of the substance/species by the total change in the O.N. of a particular atom.* For example,

(*i*) Equivalent weight of $KMnO_4$

(*a*) In acidic medium,

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

No. of electrons gained = 5

Total change in O.N. of Mn = 7 − 2 = 5

$$\therefore \text{ Eq. wt. of } MnO_4^- = \frac{\text{Mol. wt. of } MnO_4^-}{5}$$

$$= \frac{55 + 64}{5} = 23\cdot 8$$

$$\text{or Eq. wt. of } KMnO_4 = \frac{\text{Mol. wt. of } KMnO_4}{5}$$

$$= \frac{39 + 55 + 64}{5} = 31\cdot 6$$

(*b*) In neutral or alkaline medium

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

Total number of electrons gained = 3

Total change in O.N. of Mn = 7 − 4 = 3

$$\therefore \text{ Eq. wt. of } MnO_4^- = \frac{\text{Mol. wt.}}{3} = \frac{55 + 64}{3}$$

$$= 39\cdot 66$$

$$\text{Eq. wt. of } KMnO_4 = \frac{39 + 55 + 64}{3} = 52\cdot 66$$

(*ii*) Equivalent weight of $K_2Cr_2O_7$

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

Total number of electrons gained = 6

Total change in O.N. of Cr

$$= 2 \times 6 - 2 \times 3 = 6$$

$$\therefore \text{ Eq. wt. of } Cr_2O_7^{2-} = \frac{\text{Mol. wt. of } Cr_2O_7^{2-}}{6}$$

$$= \frac{2 \times 52 + 7 \times 16}{6} = 36$$

$$\text{or Eq. wt. of } K_2Cr_2O_7 = \frac{\text{Mol. wt. of } K_2Cr_2O_7}{6}$$

$$= \frac{2 \times 39 + 2 \times 52 + 7 \times 16}{6} = 49$$

Likewise, the equivalent weight of a reducing agent is equal to its molecular weight divided by the number of electrons lost as represented in the balanced chemical equation. For example,

(*i*) Equivalent weight of H_2O_2 :

$$H_2O_2 \longrightarrow 2\,H^+ + O_2 + 2\,e^-$$

(acidic medium)

$$H_2O_2 + 2\,OH^- \longrightarrow 2\,H_2O + O_2 + 2\,e^-$$

(basic medium)

Total number of electrons lost = 2

Total change in O.N. of O = 0 − (− 2) = 2

$$\text{Eq. wt. of } H_2O_2 = \frac{\text{Mol. wt. of } H_2O_2}{2}$$

$$= \frac{2 + 32}{2} = 17$$

(*ii*) Equivalent weight of $(COOH)_2$:

$$\underset{\text{Oxalic acid}}{C_2H_2O_4} \longrightarrow 2\,CO_2 + 2\,H^+ + 2\,e^-$$

Total no. of electrons lost = 2

Total change in O.N. of C = 2 × 4 − 2 × 3 = 2

∴ Eq. wt. of oxalic acid

$$= \frac{\text{Mol. wt. of } C_2H_2O_4}{2}$$

$$= \frac{24 + 2 + 64}{2} = 45$$

(*iii*) Equivalent weight of $FeSO_4$:

$$FeSO_4 + \frac{1}{2}H_2SO_4 \longrightarrow \frac{1}{2}Fe_2(SO_4)_3 + e^-$$

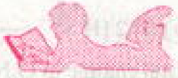
Total number of electrons lost = 1

Total change in O.N. of Fe = 3 − 2 = 1

$$\therefore \text{ Eq. wt. of } FeSO_4 = \frac{\text{Mol. wt. of } FeSO_4}{1}$$

$$= \frac{56 + 32 + 4 \times 16}{1} = 152$$

PROBLEMS FOR PRACTICE



1. Find out the equivalent weight of the underlined species in terms of its molecular weight M in each of the following redox reactions.

(*i*) $\underline{2\,CuSO_4} + 4\,KI \longrightarrow Cu_2I_2 + I_2 + 2\,K_2SO_4$

(*ii*) $\underline{2\,Na_2S_2O_3} + I_2 \longrightarrow Na_2S_4O_6 + 2\,Na$

(*iii*) $\underline{KHC_2O_4} + MnO_4^- \longrightarrow MnO_2 + 2\,CO_2$

(*iv*) $\underline{FeS_2} + O_2 \longrightarrow Fe_2O_3 + SO_2$

(*v*) $\underline{As_2S_3} + H^+ + NO_3^- \longrightarrow NO + H_2O + AsO_4^{3-} + SO_4^{2-}$

[Ans. (*i*) M (*ii*) M (*iii*) M/2 (*iv*) M/14 (*v*) M/28]

2. Determine the equivalent weight of the underlined species/compounds in the following equations :

(*a*) $\underline{S_2O_3^{2-}} + 5\,H_2O + 4\,Cl_2 \longrightarrow 2\,SO_4^{2-} + 8\,Cl^- + 10\,H^+$

(*b*) $\underline{2\,HS^-} + \underline{4\,HSO_3^-} \longrightarrow 3\,S_2O_3^{2-} + 3\,H_2O$

(*c*) $\underline{3\,MnO_2} + 6\,KOH + \underline{KClO_3} \longrightarrow 3\,K_2MnO_4 + KCl + 3\,H_2O$

(*d*) $3\,Cl_2 + 6\,NaOH \longrightarrow 5\,NaCl + \underline{NaClO_3} + 3\,H_2O$

(*e*) $4\,Fe^{2+} + \underline{2\,NH_2OH} \longrightarrow 4\,Fe^{2+} + N_2O + 4\,H^+$

(*f*) $\underline{IO_3^-} + \underline{3\,HSO_3^-} \longrightarrow I^- + 3\,H^+ + 3\,SO_4^{2-}$

(*g*) $\underline{MnO_2} + 4\,HCl \longrightarrow MnCl_2 + Cl_2 + 4\,H_2O$

(*h*) $\underline{Sn} + \underline{4\,HNO_3}\,(conc.) \longrightarrow H_2SnO_3 + 4\,NO_2 + 2\,H_2O$

(*i*) $3\,Ag + \underline{4\,HNO_3}\,(dil) \longrightarrow 3\,AgNO_3 + NO + 2\,H_2O$

(*j*) $4\,Zn + \underline{10\,HNO_3}\,(dil) \longrightarrow 4\,Zn\,(NO_3)_2 + NH_4NO_3 + 3\,H_2O$

[Ans. (*a*) 14 ; (*b*) HS^- = 8·25, HSO_3^- = 40·5 ; (*c*) MnO_2 = 43·5, $KClO_3$ = 20·4 ; (*d*) 21·3 (*e*) 16·5 (*f*) IO_3^- = 87·5, HSO_3^- = 40·5 ; (*g*) 43·5 (*h*) Sn = 29·7, HNO_3 = 63 ; (*i*) 21 ; (*j*) 7·88]

HINTS FOR DIFFICULT PROBLEMS

1. (*iv*) Calculate the total change in O.N. of one molecule of FeS_2

$$FeS_2 = Fe^{2+} + 2\,S^{2-}$$

$$\overset{2+}{2\,Fe} \xrightarrow[\text{by } 2 \times 1 = 2]{\text{O.N. increases}} \overset{+3}{Fe_2O_3}$$

$$\overset{2-}{2\,S} \xrightarrow[\text{by } 2 \times 6 = 12]{\text{O.N. increases}} \overset{+4}{2\,SO_2}$$

Total increase in O.N. = 2 + 12 = 14

Hence, Eq. wt. = M/14

(*v*) Calculate the total change in O.N. of one molecule of As_2S_3

$$As_2S_3 = 2\,As^{3+} + 3\,S^{2-}$$

$$2\,As^{3+} \xrightarrow[\text{by } 2 \times 2 = 4]{\text{O.N. increases}} \overset{+5}{2\,AsO_4^{3-}}$$

PRACTICE PROBLEMS CONTD.

$$3\overset{2-}{S} \xrightarrow[\text{by } 3 \times 8 = 24]{\text{O.N. increases}} 3\,(\overset{+6}{S}O_4)^{2-}$$

Total increase in O.N. = 4 + 24 = 28

Hence, Eq. wt. = M/28.

2. (*a*) $\overset{+2}{S_2}\overset{2-}{O_3} \longrightarrow 2\overset{+6}{S}\overset{2-}{O_4}$

Total change in O.N. of S = 2 × 6 − 2 × 2 = 8

$\therefore$ Eq. wt. of $S_2O_3^{2-}$ = Mol. wt./8

= 112/8 = **14**

(*b*) (*i*) $2\,[H\overset{-2}{S}]^- \longrightarrow \overset{+2}{S_2}\overset{2-}{O_3}$

Total change in O.N. of S

= 2 × (+ 2) − (2 × − 2) = 8

$\therefore$ Eq. wt. of $HS^- = \dfrac{2 \times \text{Mol. wt.}}{8}$

$= \dfrac{2 \times 33}{8} = \mathbf{8 \cdot 25}$

(*ii*) $2\,H\overset{+4}{S}O_3^- \longrightarrow \overset{+2}{S_2}O_3^{2-}$

Total change in O.N. of S = 2 × 4 − 2 × 2 = 4

$\therefore$ Eq. wt. of $HSO_3^- = \dfrac{2 \times \text{Mol .wt.}}{4}$

$= \dfrac{2 \times 81}{4} = \mathbf{40 \cdot 5}$

(*c*) (*i*) $\overset{+4}{Mn}O_2 \longrightarrow K_2\overset{+6}{Mn}O_4$

Total change in O.N. of Mn = 6 − 4 = 2

$\therefore$ Eq. wt. of $MnO_2 = \dfrac{\text{Mol. wt.}}{2} = \dfrac{55 + 32}{2} = \mathbf{43 \cdot 5}$

(*ii*) $K\overset{+5}{Cl}O_3 \longrightarrow K\overset{-1}{Cl}$

Total change in O.N. of Cl = 5 − (− 1) = 6

$\therefore$ Eq. wt. of $KClO_3 = \dfrac{\text{Mol.wt.}}{6} = \dfrac{122 \cdot 5}{6} = \mathbf{20 \cdot 4}$

(*d*) $\overset{0}{Cl_2} \longrightarrow 2\,Na\overset{+5}{Cl}O_3$

Total change in O.N. of Cl = 2 × 5 − 0 = 10

$\therefore$ Eq. wt. of $NaClO_3 = \dfrac{2 \times \text{Mol. wt.}}{10}$

$= \dfrac{2\,(23 + 35 \cdot 5 + 48)}{10} = \mathbf{21 \cdot 3}$

(*e*) $2\,\overset{-1}{N}H_2OH \longrightarrow \overset{+1}{N_2}O$

Total change in O.N. = 2 × 1 − 2 (− 1) = 4

$\therefore$ Eq. wt. of $NH_2OH = \dfrac{2 \times \text{Mol. wt.}}{4}$

$= \dfrac{2 \times 33}{4} = \mathbf{16 \cdot 5}$

(*f*) (*i*) $IO_3^- \longrightarrow I^-$

Total change in O.N. of I = + 5 − (− 1) = 6

$\therefore$ Eq. wt. of $IO_3^- = \dfrac{\text{Mol. wt.}}{6} = \dfrac{127 + 48}{2} = \mathbf{87 \cdot 5}$

(*ii*) $H\overset{+4}{S}O_3^- \longrightarrow \overset{+6}{S}O_4^{2-}$

Total change in O.N. of HSO_3 = + 6 − 4 = 2

$\therefore$ Eq. wt. of $HSO_3^- = \dfrac{\text{Mol. wt.}}{2} = \dfrac{81}{2} = \mathbf{40 \cdot 5}$

(*g*) $\overset{+4}{Mn}O_2 \longrightarrow \overset{+2}{Mn}Cl_2$

Eq. wt. of $MnO_2 = \dfrac{\text{Mol. wt.}}{2} = \dfrac{87}{2} = \mathbf{43 \cdot 5}$

(*h*) (*i*) $Sn \longrightarrow H_2\overset{+4}{Sn}O_3$

$\therefore$ Eq. wt. of $Sn = \dfrac{\text{At. wt.}}{4} = \dfrac{118 \cdot 7}{4} = \mathbf{29 \cdot 7}$

(*ii*) $H\overset{+5}{N}O_3 \longrightarrow \overset{+4}{N}O_2$

Eq. wt. = Mol. wt. = 1 + 14 + 48 = **63**

(*i*) $H\overset{+5}{N}O_3 \longrightarrow \overset{+2}{N}O$

Eq. wt. = Mol. wt./3 = 63/3 = **21**

(*j*) $H\overset{+5}{N}O_3 \longrightarrow [\overset{-3}{N}H_4]^+$

Total change in O.N. of N = 5 − (− 3) = 8

$\therefore$ Eq. wt. = Mol. wt./8 = 63/8 = **7·88**

(*i*) **Normality* equation.** This equation is based upon the *law of chemical equivalents* which states that substances react in the ratio of their equivalent weights. To derive this equation, let us consider the volumetric titration between acidified $KMnO_4$ and $FeSO_4$ solutions. Let N_1 and N_2 be the normalities of $KMnO_4$ and $FeSO_4$ solutions respectively. Suppose V_1 cm³ of N_1 $KMnO_4$ solution react completely with V_2 cm³ of $FeSO_4$ solution.

$\therefore$ V_1 cm³ of N_1 $KMnO_4$ contains $KMnO_4$

$$= \frac{N_1}{1000} \times V_1 \text{ gram equivalents}$$

and V_2 cm³ of N_2FeSO_4 contain $FeSO_4$

$$= \frac{N_2}{1000} \times V_2 \text{ gram equivalents}$$

Since substances react in ratio of their gram equivalent weights, therefore,

---

*Normality is defined as the number of gram equivalent weights of a substance dissolved per litre of the solution.

$$N_1V_1/1000 = N_2V_2/1000$$

or $$\boxed{N_1 \times V_1 = N_2 \times V_2}$$

This is called **normality equation.** With the help of this equation, we can easily determine the normality (N_1) of any unknown solution if we know the volume (V_1) of this solution which reacts completely with another solution of normality (N_2) and volume (V_2). Having determined be normality of the desired solution, its strength can then be calculated by the relation,

$$\boxed{\text{Strength} = \text{Normality of the solution} \times \text{Eq. wt. of the solute}}$$

The above method of determining the stoichiometry of redox reactions requires the knowledge of equivalent weights which are not easy to determine as discussed above. Furthermore, like atomic weight and molecular weight, equivalent weight is not a fixed quantity ; it varies from reaction to reaction. In view of these difficulties, it is easier to express the concentration of a solution in terms of molarity (*i.e.*, number of moles/litre) rather than normality. Therefore, these days, morality equation is more commonly used.

(*ii*) **Molarity equation.** In order to derive molarity equation, we must know what are **stoichiometric coefficients.** For this purpose, consider the following general balanced chemical equation for a redox reaction,

$$a\,A + b\,B \longrightarrow c\,C + d\,D$$

Here A and B are the reactants while C and D are the products. The coefficients *a, b, c* and *d* are called **stoichiometric coefficients.** These coefficients indicate the number of moles of the reactants used and the products obtained in the reaction. In the previous section, we have discussed how to balance redox reactions and determine the value of these coefficients. With the help of these coefficients, we can derive the molarity equation. Consider for example, the volumetric titration between $KMnO_4$ and $FeSO_4$ solutions. The balanced chemical equation for this reaction is

$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 5Fe(SO_4)_3 + 8H_2O \quad ...(i)$$

Suppose V_1 cm³ of M_1 $KMnO_4$ solution react completely with V_2 cm³ of M_2 $FeSO_4$ solution.

$\therefore$ V_1 cm³ of M_1 $KMnO_4$ contains $KMnO_4$

$$= \frac{M_1}{1000} \times V_1 \text{ moles}$$

and V_2 cm³ of M_2 $FeSO_4$ contain $FeSO_4$

$$= \frac{M_2}{1000} \times V_2 \text{ moles}$$

But according to balanced redox Eq. (*i*), the molar ratio in which $KMnO_4$ and $FeSO_4$ react completely is 2 : 10. Therefore,

$$\frac{M_1\,V_1/1000}{M_2\,V_2/1000} = \frac{2}{10} \text{ or } \frac{M_1V_1}{2} = \frac{M_2V_2}{10} \quad ...(ii)$$

where 2 and 10 are the stoichiometric coefficients in the balanced chemical equation (*i*). If we now represent these stoichiometric coefficients by n_1 and n_2 respectively, therefore, Eq. (*ii*) can be rewritten as

$$\frac{M_1V_1}{n_1} = \frac{M_2V_2}{n_2}$$

This is called **morality equation** and can be used to determine any unknown quantity if the other three quantities are known.

In general, for any volumetric titration involving reaction between A and B, the molarity equation is

$$\frac{\text{Molarity of sol. A} \times \text{Vol. of sol. A}}{\text{No. of moles of A in balanced Eq.}} = \frac{\text{Molarity of sol. B} \times \text{Vol. of sol. B}}{\text{No. of moles of B in balanced Eq.}}$$

ADD TO YOUR KNOWLEDGE

In all types of titrations, $N_1V_1 = N_2V_2$ but $M_1V_1 \neq M_2V_2$

However, in **acid-base titrations** when the basicity of the acid or acidity of the base are equal or in **redox titrations,** the number of moles of the reducing agent and the oxidising agent taking part in the balanced redox equation are equal (*i.e.*, the number of electrons lost by the reducing agent per mole is equal to the number of electrons gained by the oxidising agent per mole), the molarity equation, $M_1V_1 = M_2V_2$ is always applicable.

PROBLEMS ON REDOX TITRATIONS

EXAMPLE 9.15. *A particular acid rain water contains sulphite (SO_3^{2-}) ions. If a 25·0 cm³ sample of this water requires 35·0 cm³ of 0·02 M $KMnO_4$ solution for titration, what is the amount of SO_3^{2-} ions per litre in rain water ?*

Solution. **Step 1.** *To write the balanced equation for the redox reaction.*

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

$$SO_3^{2-} + H_2O \longrightarrow SO_4^{2-} + 2\,H^+ + 2\,e^-] \times 5$$

$$2\,MnO_4^- + 5\,SO_3^{2-} + 6\,H^+ \longrightarrow 2\,Mn^{2+} + 5\,SO_4^{2-} + 3\,H_2O$$

Step 2. *To determine the molarity of SO_3^{2-} ion solution.*

Let M_1 be the molarity of SO_3^{2-} ions in acid rain water. Applying molarity equation,

$$\frac{M_1V_1}{n_1}(SO_3^{2-}) = \frac{M_2V_2}{n_2}(MnO_4^-)$$

we have,

$$\text{or} \quad \frac{M_1 \times 25}{5} = \frac{35 \times 0{\cdot}02}{2}$$

$$\text{or} \quad M_1 = \frac{35 \times 0{\cdot}02 \times 5}{2 \times 25} = 0{\cdot}07$$

Thus, the molarity of SO_3^{2-} ions in acid rain water = 0·07 M.

Mol. wt. of SO_3^{2-} ions = 32 + 48 = 80

∴ Amount of SO_3^{2-} ions in rain water $= 0{\cdot}07 \times 8 = 0{\cdot}56\ g\ l^{-1}$.

EXAMPLE 9.16. *1·44 g of pure FeC_2O_4 was dissolved in dil. H_2SO_4 and the solution diluted to 100 cm³. Calculate the volume of 0·01 M $KMnO_4$ required to oxidise FeC_2O_4 solution completely.*

Solution. **Step 1.** *To write the balanced equation for the redox reaction.*

Both the cationic and anionic components of FeC_2O_4 (ferrous oxalate), *i.e.*, Fe^{2+} and $C_2O_4^{2-}$ are oxidised by $KMnO_4$ to Fe^{3+} and CO_2 respectively. the complete balanced redox equation is

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

$$5\,C_2O_4^{2-} + 2\,MnO_4^- + 16\,H^+ \longrightarrow 10\,CO_2 + 2\,Mn^{2+} + 8\,H_2O$$

$$5\,FeC_2O_4 + 3\,MnO_4^- + 24\,H^+ \longrightarrow 5\,Fe^{3+} + 10\,CO_2 + 3\,Mn^{2+} + 12\,H_2O$$

Step 2. *To determine the molarity of FeC_2O_4 solution*

Mol. wt. of FeC_2O_4 $= 56 + 2 \times 12 + 4 \times 16 = 144\,g$

Wt. of FeC_2O_4 dissolved = 1·44 g

Volume = 100 cm³

$$\therefore \text{Molarity} = \frac{\text{Weight}}{\text{Mol. wt.}} \times \frac{1000}{\text{Volume}} = \frac{1{\cdot}44}{144} \times \frac{1000}{100} = 0{\cdot}1\,M$$

Step 3. *To calculate the volume of 0·01 M $KMnO_4$ solution*

Applying molarity equation to balanced redox equation,

$$\frac{M_1V_1}{n_1}(FeC_2O_4) = \frac{M_1V_2}{n_2}(KMnO_4)$$

$$\text{or} \quad \frac{0{\cdot}1 \times 100}{5} = \frac{0{\cdot}01 \times V_2}{3}$$

$$\text{or} \quad V_2 = \frac{3 \times 0{\cdot}1 \times 100}{5 \times 0{\cdot}01} = 600\ cm^3$$

Thus, volume of 0·01 M $KMnO_4$ solution required = **600 cm³**.

EXAMPLE 9.17. *25·0 cm³ of a solution containing 15·0 g of a partially oxidisied sample of green vitriol ($FeSO_4 . 7\,H_2O$) per litre required 20·0 cm³ ml of 0·01 M potassium dichromate solution for oxidation in acidic medium. Find out the percentage purity of the given sample of green vitriol.*

Solution. **Step 1.** *To write balanced equation for the redox reaction*

$$K_2Cr_2O_7 + 4\,H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4\,H_2O + 3\,O$$

$$2\,FeSO_4 + H_2SO_4 + O \longrightarrow Fe_2(SO_4)_3 + H_2O\ [\times 3$$

$$K_2Cr_2O_7 + 6\,FeSO_4 + 7\,H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 3\,Fe_2(SO_4)_3 + 7\,H_2O$$

From the above equation

1 mole of $K_2Cr_2O_7$ = 6 moles of $FeSO_4$

Step 2. *To find percentage purity of green vitriol.*

Let M_1 be the molarity of the oxidised sample of green vitriol. Applying molarity equation, we have,

$$\frac{M_1 \times 25}{6}(FeSO_4) = \frac{20 \times 0\cdot01}{1}(K_2Cr_2O_7)$$

$$\text{or } M_1 = \frac{20 \times 0\cdot01 \times 6}{25} = 0\cdot048 \text{ M}$$

Mol. wt. of $FeSO_4.7\,H_2O$

$= 56 + 32 + 4 \times 16 + 7 \times 18 = 278$

Wt. of pure $FeSO_4.7\,H_2O$

$= 278 \times 0\cdot048 = 13\cdot344\, g\, L^{-1}$

% purity of green vitriol

$$= \frac{13\cdot444}{15} \times 100 = 88\cdot96$$

EXAMPLE 9.18 *25·0 cm³ of an aqueous solution of H_2O_2 was treated with excess of KI solution in acidic medium and the liberated iodine required 10·0 cm³ of 0·1 M thiosulphate solution. Find out the concentration of H_2O_2 in grams per litre ?*

Solution. Step 1. *To write the balanced chemical equation of the redox reaction.*

$$2\,KI + H_2SO_4 + H_2O_2 \longrightarrow K_2SO_4 + I_2 + H_2O$$

$$2\,Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2\,NaI$$

$$2\,KI + H_2SO_4 + 2\,Na_2S_2O_3 + H_2O_2 \longrightarrow K_2SO_4 + Na_2S_4O_6 + 2\,NaI + 2\,H_2O$$

From the above equation,

1 mole of H_2O_2 = 1 mole of I_2

= 2 moles of $Na_2S_2O_3$

Step 2. *To find out the concentration of H_2O_2.*

Let the molarity of H_2O_2 solution = M_1

Applying molarity equation,

$$\frac{M_1V_1}{n_1}(H_2O_2) = \frac{M_2V_2}{n_2}(Na_2S_2O_3)$$

$$\text{or } \frac{M_1 \times 25}{1} = \frac{10 \times 0\cdot1}{2}$$

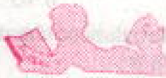
$$\text{or } M_1 = \frac{10 \times 0\cdot1}{2 \times 25} = 0\cdot02 \text{ M}$$

Mol. wt. of $H_2O_2 = 2 \times 1 + 2 \times 16 = 34$

∴ Concentration of H_2O_2

$= 0\cdot02 \times 34 = \mathbf{0\cdot68\, g\, L^{-1}}$.

PROBLEMS FOR PRACTICE



1. Calculate the volume of 0·05 M $KMnO_4$ solution required to oxidise completely 2·70 *g* of oxalic acid ($H_2C_2O_4$) in acidic medium. **[Ans. 240 cm³]**
2. How many grams of $K_2Cr_2O_7$ are required to oxidise Fe^{2+} present in 15·2 *g* of $FeSO_4$ to Fe^{3+} if the reaction is carried out in an acidic medium. **[Ans. 4·9 *g*]**
3. 15·0 cm³ of 0·12 M $KMnO_4$ solution are required to oxidise 20·0 ml of $FeSO_4$ solution in acidic medium. What is the concentration of $FeSO_4$ solution. **[Ans. 0·45 M]**
4. Calculate the percentage of oxalate ions in a given sample of oxalate salt, 3·0 *g* of which has been dissolved per litre of the solution. 10 ml of the oxalate salt solution required 8 ml of 0·01 M $KMnO_4$ solution for complete oxidation. **[Ans. 58·67%]**
5. A solution of ferrous oxalate has been prepared by dissolving 3·6 *g* L^{-1}. Calculate the volume of 0·01 M $KMnO_4$ solution required for complete neutralization of ferrous oxalate solution in acidic medium. **[Ans. 150 ml]**
6. Metallic tin in presence of HCl is oxidised by $K_2Cr_2O_7$ to stannic chloride. What volume of decinormal dichromate solution will be reduced by 1 *g* of tin ? At. wt. of Sn = 118·7) **[Ans. 336·9 cm³]**
7. How many millimoles of potassium dichromate is required to oxidise 24 cm³ of 0·5 M Mohr's salt solution in acidic medium ? **[Ans 2 milimoles]**
8. 2·48 *g* of $Na_2S_2O_3 . x\, H_2O$ was dissolved per litre of the solution. 20 cm³ of this solution required 10 cm³ of 0·01 M iodine solution. Find out the value of *x* **[Ans 5]**

PRACTICE PROBLEMS CONTD.

9. 0·2 g of a sample of H_2O_2 reduced 20 ml of 0·1 M $KMnO_4$ solution in acidic medium. What is the percentage purity of the sample of H_2O_2 ? [Ans. 85%]

10. 16·6 g of pure potassium iodide was dissolved in water and the solution was made upto one litre. V cm^3 of this solution was acidified with 20 cm^3 of 2 M HCl. The resulting solution required 10 cm^3 of decimolar KIO_3 for complete oxidation of I^- ions to ICl. Find out the value of V. [Ans. 20 cm^3]

11. Both $Cr_2O_7^{2-}$ (aq) and MnO_4^- (aq) can be used to titrate Fe^{2+} (aq). If in a given titration, 24·50 cm^3 of 0·1 M $Cr_2O_7^{2-}$ were used, then what volume of 0·1 M MnO_4^- solution would have been used for the same titration ? [Ans. 29·4 cm^3]

HINTS FOR DIFFICULT PROBLEMS

1. Balanced equation for the redox reaction is :

$$2\,KMnO_4 + 5\,(COOH)_2 + 3\,H_2SO_4 \longrightarrow K_2SO_4 + 2\,MnSO_4 + 10\,CO_2 + 8\,H_2O$$

No. of moles of oxalic acid = 2·70/90 = 0·03 mole

From the balanced equation,

5 moles of $(COOH)_2$ = 2 moles of $KMnO_4$

$\therefore$ 0·03 mole of $(COOH)_2 = 2/5 \times 0{\cdot}03$

$= 0{\cdot}012$ mole of $KMnO_4$

Now 0·05 mole of $KMnO_4$ is present in solution

$= 1000\ cm^3$

$\therefore$ 0·012 mole of $KMnO_4$ is present in solution

$$= \frac{1000 \times 0{\cdot}012}{0{\cdot}05} = \mathbf{240\ cm^3}$$

2. The balanced chemical equation for the redox reaction is :

$$K_2Cr_2O_7 + 6\,FeSO_4 + 7\,H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + Cr_2(SO_4)_3 + 7\,H_2O$$

From the balanced equation, it is clear that

6 moles of $FeSO_4$ = 1 mole of $K_2Cr_2O_7$

or 6 × 152 g of $FeSO_4$ are oxidised by

$K_2Cr_2O_7 = 294\ g$

or 15·2 g of $FeSO_4$ are oxidised by $K_2Cr_2O_7$

$$= \frac{294}{6 \times 152} \times 15{\cdot}2$$

$$= \mathbf{4{\cdot}9\ g}$$

3. The balanced chemical equation for the redox reaction is :

$$2\,KMnO_4 + 10\,FeSO_4 + 8\,H_2SO_4 \longrightarrow K_2SO_4 + 2\,MnSO_4 + 5\,Fe_2(SO_4)_3 + 8\,H_2O$$

Applying molarity equation to the above redox reaction,

$$\frac{15 \times 0{\cdot}12}{2}\,(KMnO_4) = \frac{20 \times M_1}{10}\,(FeSO_4)$$

$$\text{or} \quad M_1 = \frac{15 \times 0{\cdot}12 \times 10}{2 \times 20} = \mathbf{0{\cdot}45\ M}$$

4. Balanced chemical equation for the redox reaction is :

$$2\,MnO_4^- + 16\,H^+ + 5\,C_2O_4^{2-} \longrightarrow 2\,Mn^{2+} + 10\,CO_2 + 8\,H_2O$$

Applying molarity equation,

$$\frac{M_1 \times 10}{5}\,(C_2O_4^{2-}) = \frac{0{\cdot}01 \times 8}{2}\,(MnO_4^-)$$

$$\text{or} \quad M_1 = 0{\cdot}02\ M$$

Mol. wt. of $C_2O_4^{2-}$ = 88

Conc. of $C_2O_4^{2-}$ in g L^{-1} = 88 × 0·02 = 1·76 g

$$\%\ C_2O_4^{2-} = \frac{1{\cdot}76 \times 100}{3} = \mathbf{58{\cdot}67.}$$

5. Molarity of FeC_2O_4 solution

$$= \frac{\text{Wt. in g } L^{-1}}{\text{Mol. wt.}}$$

$$= \frac{3{\cdot}6}{144} = 0{\cdot}025\ M$$

The balanced chemical equation for the redox reaction is :

$$5\,FeC_2O_4 + 3\,MnO_4^- + 24\,H^+ \longrightarrow 5\,Fe^{3+} + 3\,Mn^{2+} + 10\,CO_2 + 12\,H_2O$$

Applying molarity equation, we have,

$$\frac{0{\cdot}01 \times V}{3}\,(MnO_4^-) = \frac{0{\cdot}025 \times 100}{5}\,(FeC_2O_4)$$

$$\text{or} \quad V = \frac{0{\cdot}025 \times 100 \times 3}{5 \times 0{\cdot}01}$$

$$= \mathbf{150\ cm^3}$$

HINTS CONTD.

6. Balanced chemical equation is :

$$\underset{\substack{2(2\times 39+2\times 52+7\times 16)\\ =2\times 294\\ =588\text{ g}}}{2\,K_2Cr_2O_7} + \underset{\substack{3\times 118\cdot 7\\ =356\cdot 1\text{ g}}}{3\,Sn} + 28\,HCl \longrightarrow$$

$$4\,KCl + 4\,CrCl_3 + 3\,SnCl_4 + 14\,H_2O$$

Now 356·1 *g* Sn react with $K_2Cr_2O_7 = 588\,g$

$\therefore$ 1 *g* Sn will react with $K_2Cr_2O_7 = \frac{588}{356\cdot 1}\,g$

$= 1\cdot 651\,g$

Eq. wt. of $K_2Cr_2O_7 = \frac{\text{Mol. wt.}}{6} = \frac{294}{6} = 49.$

Decinormal $K_2Cr_2O_7$ solution means 1000 cm^3 solution contains 4·9 *g* $K_2Cr_2O_7$, *i.e.* 4·9 *g* $K_2Cr_2O_7$ are present in 1000 cm^3 solution

$\therefore$ 1·651 *g* $K_2Cr_2O_7$ will be present in

$$\frac{1000}{4\cdot 9} \times 1\cdot 651\ cm^3 = 336\cdot 9\ cm^3$$

7. No. of millimoles of $K_2Cr_2O_7$ present in 24 cm^3 of 0·5 M solution = 24 × 0·5 = 12

The balanced chemical equation for the redox reaction is :

$$K_2Cr_2O_7 + 6\,(NH_4)_2SO_4\,.\,FeSO_4\,.\,6\,H_2O + 7\,H_2SO_4 \longrightarrow K_2SO_4 + 6\,(NH_4)_2SO_4 + 3\,Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + 43\,H_2O$$

From the balanced equation,

6 moles Mohr's salt are oxidised by $K_2Cr_2O_7$

= 1 mole

$\therefore$ 12 millimoles of Mohr's salt will be oxidised by

$K_2Cr_2O_7 = \frac{1}{6} \times 12$

= 2 millimoles

8. The balanced equation for the redox reaction is :

$$2\,Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2\,NaI$$

Let the molarity of $Na_2S_2O_3\,.x\,H_2O$ solution = M_1

Applying molarity equation to the above redox reaction, we have,

$$\frac{M_1 \times 20}{2}(Na_2S_2O_3) = \frac{10 \times \cdot 01}{1}(I_2)$$

$\therefore$ $M_1 = 0\cdot 01$ M

Mol. wt. of $Na_2S_2O_3\,.xH_2O$

$= 2 \times 23 + 2 \times 32 + 3 \times 16 + x \times 18$

$= 158 + 18\,x$

$\therefore$ Amount of $Na_2S_2O_3\,.xH_2O$ present per litre

$= (158 + 18\,x) \times 0\cdot 01\,g$

But the actual amount dissolved = 2·48 *g*

Equating these values, we have,

$(158 + 18\,x) \times 0\cdot 01 = 2\cdot 48$ or $x = 5$

9. No. of moles of $KMnO_4$ present in 20 ml of 0·1 M $KMnO_4$ solution $= \frac{20}{1000} \times 0\cdot 1 = 2 \times 10^{-3}$

The balanced equation for the redox reaction is :

$$2\,KMnO_4 + 5\,H_2O_2 + 3\,H_2SO_4 \longrightarrow K_2SO_4 + 2\,MnSO_4 + 8\,H_2O + 5\,O_2$$

From the equation,

2 moles of $KMnO_4 \equiv 5$ moles of H_2O_2

$\therefore$ 2×10^{-3} moles of $KMnO_4$ will react with

$H_2O_2 = \frac{5}{2} \times 2 \times 10^{-3} = 5 \times 10^{-3}$ moles

Mol. wt. of $H_2O_2 = 34$

$\therefore$ Amount of H_2O_2 actually present

$= 34 \times 5 \times 10^{-3} = 0\cdot 17\,g$

$\therefore$ %age purity of $H_2O_2 = \frac{0\cdot 17}{0\cdot 20} \times 100 = 85$

10. The chemical equation for the redox reaction is :

$$IO_3^- + 2\,I^- + 6\,HCl \longrightarrow 3\,ICl + 3\,Cl^- + 3\,H_2O$$

Molarity of KI solution $= \frac{16\cdot 6}{166} = 0\cdot 1$ M

Applying molarity equation,

$$\frac{0\cdot 1 \times V}{2}(KI) = \frac{10 \times 0\cdot 1}{1}(KIO_3)$$

or $\quad$ **V = 20 cm^3**

11. Suppose V_2 cm^3 of M_2 Fe^{2+} is titrated against 24·50 cm^3 0·1 M $Cr_2O_7^{2-}$ and V_1 cm^3 of 0·1 M MnO_4^- solutions, then,

$$\frac{24\cdot 5 \times 0\cdot 1}{1}(Cr_2O_7^{2-}) = \frac{M_2V_2}{6}(Fe^{2+}) \qquad ...(i)$$

and $$\frac{V_1 \times 0\cdot 1}{1}(MnO_4^-) = \frac{M_2V_2}{5}(Fe^{2+}) \qquad ...(ii)$$

Equating (*i*) and (*ii*), **V_1 = 29·4 cm^3**

9.13. Indirect Redox Reactions—Electrochemical Cells

We have discussed in **Sec. 9.5** that when a zinc rod is placed in $CuSO_4$ solution, a redox reaction occurs. During this reaction, Zn is oxidised to Cu^{2+} ions while Cu^{2+} ions are reduced to Cu by direct transfer of electrons from Zn to Cu^{2+} ions. Since here transfer of electrons occurs directly over short-distances (generally within molecular diameters) no useful electrical work can be obtained. Instead, the chemical energy of the reaction appears as heat. If, now the same redox reaction is carried out in such a manner that the transfer of electrons is allowed to take place only indirectly over large distances through metallic wires so that chemical energy is converted into electrical energy. This is possible only if zinc rod is separated from $CuSO_4$ solution. Such a device for carrying out an indirect redox reaction is called an electrochemical cell. Thus,

An **electrochemical cell or simply a chemical cell may be defined as a** ***device to convert chemical energy produced in an indirect redox reaction into electrical energy.*** **Electrochemical cells are also called galvanic cells or voltaic cells after the names of the scientists, Luigi Galvani (1780) and Alessandro Volta (1800) who were the first to perform experiments on the conversion of chemical energy into electrical energy.**

9.13.1. Construction of an Electrochemical Cell

In order to carry out the above redox reaction indirectly, place zinc rod in 1M $ZnSO_4$ solution in the **left beaker** and a copper rod in a 1M$CuSO_4$ solution in the **right beaker.** No reaction takes place in either of the two beakers, and at the interface of the metal and its salt solution in each beaker both the reduced and oxidized forms of the same species are present. Each beaker constitutes a **half cell.** It is also called as an **electrode** or a **redox couple.**

A redox couple ***may be defined as combination of the oxidised and reduced forms of the same substance taking part in an oxidation or reduction half reactions.***

A redox couple is usually represented by separating the oxidised form and the reduced form by a vertical line or a slash which represents the interface (solid/solution). For example, in the above experiment, two redox couples are represented as Zn^{2+}/Zn and Cu^{2+}/Cu. In both cases, oxidised form is put before the reduced form.

Now connect the zinc and the copper rods by a copper wire through a voltmeter or ammeter and an on-off switch (Fig. 9.2). Also connect the solutions in the two beakers by a salt bridge which provides electric contact between the two solutions without allowing them to mix with each other. A salt bridge consists of a U-tube containing a semi-solid paste obtained by adding agar- agar or gelatine in the solution of a strong but inert* electrolyte such as KCl, KNO_3, K_2SO_4, NH_4NO_3 etc. which does not change chemically during the process. In the present case, a solution of K_2SO_4 is used in the salt bridge.

When the switch is in the off position, no reaction takes place in either of the beakers and no

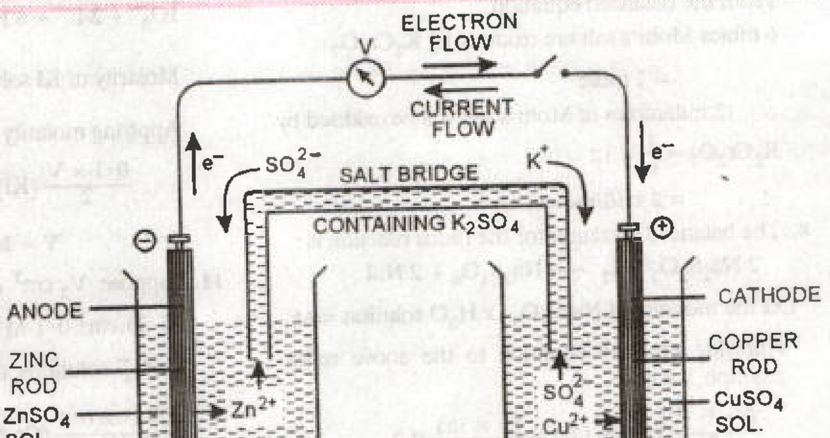


FIGURE 9.2. An electrochemical or galvanic cell.

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*An inert electrolyte is one whose ions do not take part in the redox reaction and also do not react with the solutions of the electrolytes taken in the beakers. For example, KCl cannot be used if one of the electrodes is silver electrode containing $AgNO_3$ solution because KCl reacts with $AgNO_3$ solution to form white ppt. of AgCl.

current flows through the metallic wire. As soon as the switch is in the on position, the voltmeter shows a deflection thereby indicating the flow of current through the circuit.

Let us investigate as to why this current flows. This current is due to chemical reaction taking place in two beakers.

Left beaker. Zinc rod starts dissolving and zinc sulphate solution becomes more concentrated, *i.e.*, each zinc atom loses two electrons to form Zn^{2+} *(aq)* ion. The zinc ions then migrate away from the rod into solution while the electrons move through the wire, via voltmeter and ultimately reach the copper rod. The change taking place may be represented as :

$$Zn\,(s) \longrightarrow Zn^{2+}\,(aq) + 2\,e^- \quad ...(i)$$

Right beaker. Copper sulphate solution starts getting more diluted and metallic copper starts depositing, *i.e.* the electrons released by zinc atoms in the left beaker on reaching the copper rod combine with Cu^{2+} *(aq)* ions present in the solution to form neutral copper atoms which, in turn, get deposited on the copper rod. The change taking place may be represented as :

$$Cu^{2+}\,(aq) + 2\,e^- \longrightarrow Cu\,(s) \quad ...(ii)$$

The overall reaction taking place in two beakers is

$$Zn\,(s) + Cu^{2+}\,(aq) \longrightarrow Zn^{2+}\,(aq) + Cu\,(s)$$

It may be noted here that this is the same reaction which takes place when zinc rod is placed in copper sulphate solution. The only difference is that by this arrangement we have separated the two half reactions, *i.e.*, oxidation of zinc occurs in one beaker and reduction of Cu^{2+} ions takes place in another beaker. Further, the transfer of electrons now does not take place directly from Zn to Cu^{2+} but through the metallic wire connecting the two rods as shown by the deflection in the voltmeter which shows the flow of current.

The cell based on the above reaction is commonly called **Daniell cell.** A popular form of this cell is shown in Fig. 9.3. Here, salt bridge is replaced by a porous pot through which SO_4^{2-} ions migrate from $CuSO_4$ solution to the $ZnSO_4$ solution.

9.13.2. Salt bridge and its functions. The two main functions of the salt bridge are as follows :

(*i*) It allows the movement of ions from one solution to the other without mixing of the two solutions. Thus, whereas electrons flow in the outer circuit in the wire, the inner circuit is completed by the flow of ions from one solution to the other and hence the current flows.

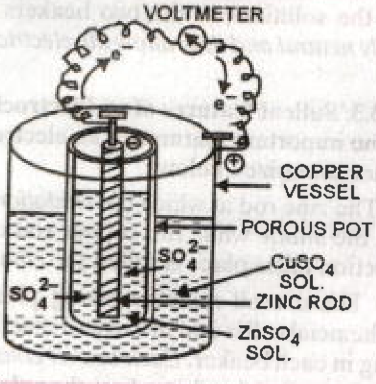


FIGURE 9.3. A popular form of Daniell cell.

(*ii*) It helps to maintain the electrical neutrality of the solutions in the two half cells due to flow of ions (e.g. SO_4^{2-} ions may shift and combine with the Zn^{2+} ions in the first half cell).

If the salt bridge is not employed, the flow of electric current will not occur as explained below :

The moment the two rods are connected by a copper wire, the flow of electrons from zinc to copper rod occurs for a short while. As a result of this transference of electrons, a net positive charge is developed near the zinc rod. On the other hand, Cu^{2+}*(aq)* ions accept the electrons released by zinc rod and get deposited on the copper rod as Cu(*s*). This leads to an excess of SO_4^{2-} ions in the solution and hence a net negative charge is developed around copper rod. The positive charge accumulated around zinc rod will prevent electrons to flow from zinc rod towards copper rod while the negative charge developed around copper rod will not allow Cu^{2+}*(aq)* ions to accept the electrons released by zinc rod. Consequently, the reaction will stop and no current will flow. The use of salt bridge, on the other hand, avoids this situation as explained below :

As Zn^{2+} ions are produced near the zinc rod, an equal number of SO_4^{2-} ions will move from the salt bridge towards zinc rod thereby neutralizing the positive charge around zinc rod. Similarly, K^+ ions will move from the salt bridge towards copper rod thereby neutralizing the negative charge (due to an excess of SO_4^{2-} ions around copper rod). As a result, the solutions in the two beakers remain *electrically neutral and thus allow the electric current to flow.*

9.13.3. Salient features of an Electrochemical cell. Some important features of an electrochemical cell are sumarized below :

(*i*) The zinc rod at which the *oxidation* occurs is called the *anode* while the copper rod at which the reduction takes place is called the *cathode*.

(*ii*) The overall reaction taking place in an electrochemcial cell is due to two half reaction ; one occurring in each beaker. *Each beaker constitutes a half cell also called the electrode or the redox couple. Thus, a half cell or an electrode consists of a metal rod dipped in the solution of its own ions.*

(*iii*) *The reaction taking place in a half cell is called a* **half cell reaction.** *Thus, equations (i) and* (*ii*) represent two half cell reactions.

(*iv*) The half-cell reaction occurring at anode is called *oxidation half cell reaction* while that occurring at the cathode is called *reduction half cell reaction*. For example, equation (*i*) represents oxidation half cell reaction whereas equation (*ii*) represents reduction half cell reaction. The overall redox reaction is then obtained by adding the two half cell reactions.

(*v*) The two half reactions always take place simultaneously, *i.e., half cell reactions cannot take place independently.*

(*vi*) Sine electrons are produced at the zinc electrode, this electrode is *rich* in electrons and pushes these electrons into the external circuit and hence acts as the **negative pole or electrode.** The copper electrode, on the other hand, is *deficient* in electrons (since it needs electrons to reduce $Cu^{2+}(aq)$ ions into Cu) and thus *pulls* the electrons from the external circuit. As a result, it acts as *a* **positive pole or electrode.**

(*vii*) The electrons flow from the negative pole to the positive pole in the external circuit. However, conventionally, *the current is said to flow in the opposite direction*.

(*viii*) As copper from copper sulphate solution is deposited on the copper electrode and sulphate ions migrate to the other side, the concentration of copper sulphate solution decreases as the cell operates. Consequently, the current falls with the passage of time.

(*ix*) As a result of redox reaction, the weight of copper rod increases while that of zinc rod decreases. This gain and loss in weights of the metal rods is in the ratio of their equivalent weights. For example,

$$\frac{\text{Loss in weight of zinc rod}}{\text{Gain in weight of copper rod}} = \frac{\text{Eq. wt. of Zn}}{\text{Eq. wt. of Cu}} = \frac{32 \cdot 50}{31 \cdot 75}$$

Some imporatnt generalizations about an electrochemical cell may be summed up as follows :

Oxidation *occurs at the anode while* **reduction** *occurs at the cathode*

Anode acts as a **negative pole** *while cathode acts as the* **positive pole**

Electrons flow from anode to cathode **in the external circuit** *while current flows from cathode to anode.*

Chemical energy of the redox reaction occurring in the galvanic cell is converted into **electrical energy.**

The two main functions of the salt bridge are as follows :-

(*i*) It allows the ions to flow through it from one solution to the other without mixing the two solutions. This helps to complete the inner circuit (whereas electrons flow in the outer circuit in the wire).

ADD TO YOUR KNOWLEDGE

1. *Only those electrolytes for which cations and anions have nearly the same ionic mobilities (i.e. distance travelled by an ion per second under a potential gradient of one volt/metre) are used as electrolytes in the salt bridge.* Thus KCl, KNO_3, K_2SO_4 and NH_4NO_3 are preferred over $NaCl$, $NaNO_3$ and Na_2SO_4.

2. *Among cations, H^+ ion has the highest ionic mobility and among anions, OH^- has the highest ionic mobility.* The ionic mobility of some common cations and anions follows the order :

Cations : $H^+ > NH_4^+ = K^+ > Ag^+ > Ca^{2+} < Mg^{2+}, Na^+ > Li^+$

ADD TO YOUR KNOWLEDGE CONTD.

Anions : $OH^- > SO_4^{2-} > Cl^- > NO_3^- > CO_3^{2-} > F^- > CH_3COO^-$.

3. **Agar-agar** *is a seaweed colloid. It is a mixture of two polysaccharides, i.e. agarose (main) and agaropectin.* It dissolves in hot water and sets, on cooling, to a jelly at concentration as low as 0·5%. Its chief uses are as a solid medium for cultivating micro-organisms, as a thickner, as an emulsion stabilizer in food industry and as a laxative.

9.13.4. Representation of an Electrochemical Cell

An electrochemical cell is represented in a manner as illustrated below for the Daniell cell :

$$Zn \mid Zn^{2+}(c_1) \| Cu^{2+}(c_2) \mid Cu$$

By convention, the electrode on which oxidation occurs is written on the left hand side and the electrode on which reduction occurs is written on the right hand side. The electrode on the left hand side is written by writing the symbol of the metal (or the gas) first followed by the symbol of the ion with its concentration in brackets. The electrode on the right hand side is written by first writing the ion along with its concentration in brackets followed by the symbol of the metal (or the gas). Single vertical lines represent the interface between the two phases (*e.g.* solid/liquid or liquid/gas) and the double line represents the salt bridge ; c_1 and c_2 represent the concentration of Zn^{2+} (aq) ions and $Cu^{2+}(aq)$ ions respectively.

In a similar manner $Cu - AgNO_3$ cell may be represented as $Cu \mid Cu^{2+}(c_1) \| Ag^+(c_2) \mid Ag$

Instead of writing single vertical lines, sometimes *semicolons* are used. Thus, the above cells may be represented as

$$Zn \,;\, Zn^{2+}(c_1) \| Cu^{2+}(c_2) \,;\, Cu$$

$$Cu \,;\, Cu^{2+}(c_1) \| Ag^+(c_2) \,;\, Ag$$

Further, when the ions are in direct contact *e.g.* for Daniell cell using a porous pot, a single vertical line instead of a double vertical line is used. Thus, in such a case, we have :

$$Zn \,;\, Zn^{2+}(c_1) \mid Cu^{2+}(c_2) \,;\, Cu$$

9.14. Electrode Potential

9.14.1. Definition.

It has been discused above that each electrochemical cell consists of two electrodes or half cells. Each electrode, in turn, consists of a metal dipped in the solution of its own ions. At one of these electrodes, oxidation occurs while at the other, reduction takes place. In other words, one electrode has a tendency to lose electrons while the other has a tendency to gain electrons.

The tendency of an electrode to lose or gain electrons is called* electrode potential.** ***Since each electrode represents a half cell, therefore, electrode potential is also called potential for half cell.

Further, the electrode potential is termed as **oxidation potential** if the electrode loses electrons and is called the **reduction potential** if the electrode gains electrons. Oxidation and reduction potentials are just reverse of each other. For example, if the oxidation potential of an electrode is *x volts* then its reduction potential is *– x volts.*

9.14.2. Effect of Concentration (or metal ions) and Temperature on the Electrode Potential – Standard Electrode Potential.

When an electrode say zinc rod is dipped in the solution of its own ions, the following two opposing tendencies may occur :

(*i*) The zinc atoms of the rod may lose electrons to form Zn^{2+} ions which pass into the solution and the electrons thus released accumulate on the rod (Fig. 9.4 *a*).

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

(*ii*) These accumulated electrons may attract the Zn^{2+} ions from the solution to form atoms of zinc metal which get deposited on the zinc rod.

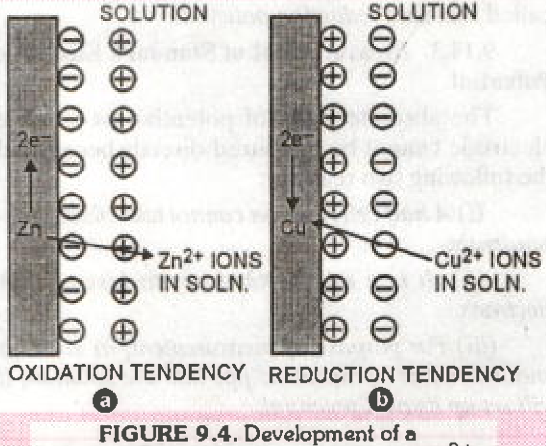


FIGURE 9.4. Development of a potential difference between (a) Zn and Zn^{2+} ions and (b) Cu and Cu^{2+} ions.

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

These two opposing tendencies will continue and eventually the following equilibrium is reached.

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

Now if the metal has a higher tendency to get oxidised, then at equilibrium the metal rod will acquire a net negative charge *w.r.t.* the solution. If, however, the metal ions have a higher tendency to get reduced (Fig. 9.4 *b*), a net positive charge will develop on the rod *w.r.t.* the solution. This separation of charges, in turn, creates a potential difference between the metal rod and the solution. *This potential difference which is set up between the metal and its own ions in the solution is called the* **electrode potential.** The magnitude of this potential difference, however depends upon the following factors.

(i) the nature of the metal and its ions

(ii) the concentration of the ions in solution

(iii) temperature

Thus, we conclude that electrode potentials depend upon the concentration of the metal ions in solution and the temperature. Therefore, electrode potentials are generally measured under standard conditions *i.e.* 1 molar *concentration of metal ions (1 mol* L^{-1}*) and a temperature of 298 K and are called* **standard electrode potentials** and are denoted by E°.

Thus, to define a standard electrode potential for a half cell or an electrode, we write

$$Cu^{2+}(1 \text{ mol } L^{-1}, aq) + 2e^- \longrightarrow Cu(s)$$

The equation for the half cell is written as a reduction reaction and the electrode potential is called *standard reduction potential.*

9.14.3. Measurement of Standard Electrode Potential.

The absolute value of potential for a single electrode cannot be measured directly because of the following two reasons :

(i) A half cell reaction cannot take place independently.

(ii) It is a relative tendency to lose or gain electrons.

(iii) For purpose of measurement, as soon as another metal conductor is put into the solution, it will set up its own potential.

In view of these difficulties, the electrode potential has to be measured against some **reference electrode.** The reference electrode used is the **standard or normal hydrogen electrode (NHE).**

It consists of a platinized platinum electrode (platinum electrode having a coating of black platinum) dipped in 1 M* (more precisely unit activity) solution of H^+ ions (1 M HCl) at 298 K and pure hydrogen gas maintained at a pressure of 1 bar* is bubbled through the solution containing platinized platinum electrode (Fig. 9.5).

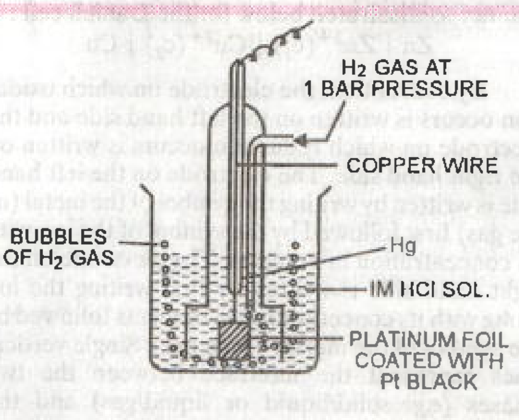


FIGURE 9.5. Standard Hydrogen Electrode.

The finely divided black platinum coated over platinum absorbs H_2 and thus helps to establish a rapid equilibrium between H_2 and H^+ ions :

When in a cell, this electrode acts as the *anode i.e. oxidation* takes place, the following reaction occurs, *i.e.*, some hydrogen gas changes into H^+ ions which go into the solution.

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

When this electrode acts as the *cathode, i.e. reduction* takes place, the following reaction occurs :

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

i.e. some H^+ ions from the solution change into H_2 gas. Thus, *the electrode is reversible with respect to* H^+ *ions.* This electrode is usually represented as : Pt , H_2(g, 1 bar), H^+ (aq, conc = c)

The electrode potential of the standard hydrogen electrode is taken as **zero.**

---

*The activities of pure solids and liquids are taken as unity and in dilute aqueous solutions, the activity of a given solution is nearly equal to its molarity. For gaseous species, the activity is nearly equal to its partial pressure expressed in bar. Thus at 1 bar pressure, the activity of the gaseous species is nearly one.

To determine the electrode potential of any electrode, a cell is set up using this electrode as one of the electrodes and the second electrode is the standard hydrogen electrode. The EMF of the cell is measured. As the EMF of the cell is the difference in the electrode potentials of the two half cells and since the electrode potential of the standard hydrogen electrode is taken to be zero, therefore the EMF of such a cell will directly give the electrode potential of the cell under investigation.

The direction of flow of current further indicates whether oxidation or reduction takes place at the electrode under investigation with respect to the hydrogen electrode. According to IUPAC convention, the electrode potential is given a positive sign if reduction occurs and a negative sign if oxidation occurs at the electrode under investigation with respect to the hydrogen electrode.

The determination of electrode potential may be further illustrated with the help of the following two simple examples :

***(i)* Determination of standard electrode potential of Zn^{2+}/Zn electrode.** A cell comprising of zinc electrode, *i.e.*, Zn rod immersed in 1 M $ZnSO_4$ solution is on the left and the standard hydrogen electrode on the right is set up as shown in Fig. 9.6.

Here, the reading of the voltmeter is 0.76 volts and the direction of flow of electrons is from zinc electrode to the hydrogen electrode. Since oxidation occurs at the zinc electrode, therefore, the standard electrode potential for Zn^{2+}/Zn half cell is -0.76 volt.

The two half reactions taking place in this cell are :

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^- \quad (oxidation)$$
$$2H^+(aq) + 2e^- \longrightarrow H_2(g) \quad (reduction)$$

***(ii)* Determination of the standard electrode potential of Cu^{2+}/Cu electrode.** A cell comprising of standard hydrogen electrode on the left and copper electrode, *i.e.*, Cu rod immersed in 1M $CuSO_4$ solution on the right is set up as shown in Fig. 9.7.

Here, the EMF of the cell comes out to be 0.34 volt and the direction of flow of electrons is from the hydrogen electrode to the copper electrode *i.e.* reduction occurs at the copper electrode. Since reduction occurs at the copper electrode, therefore, the standard electrode potential for Cu^{2+}/Cu half cell is $+\ 0.34$.

The two half reactions taking place in this cell are :

$$H_2(s) \longrightarrow 2H^+(aq) + 2e^- \quad (oxidation)$$
$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s) \quad (reduction)$$

Similarly, we can determine the electrode potential for non- metals which give negative ions

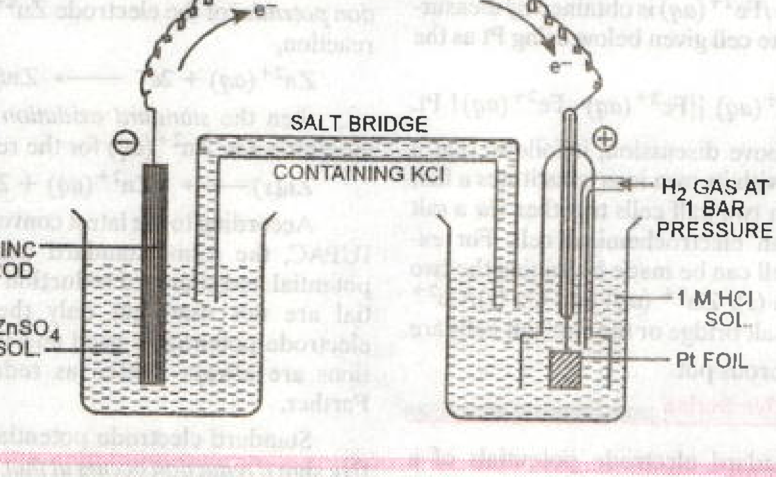


FIGURE 9.6. Measurement of standard electrode potential of Zn^{2+}/Zn electrode using standard hydrogen as the reference electrode.

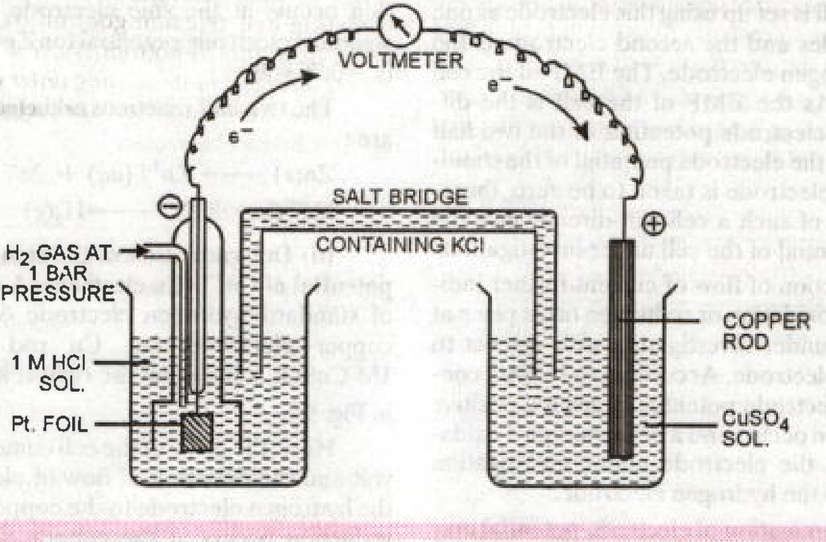


FIGURE 9.7. Measurement of standard electrode potential of Cu^{2+}/Cu electrode using standard hydrogen as the reference electrode.

in aqueous solution. For example, the standard electrode potential of chlorine can be determined by using an electrode consisting of Cl_2 gas at one bar pressure in equilibrium with 1 molar concentration of chloride ions. The half reaction for such an electrode is

$$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$$

Further, by using standard hydrogen electrode, we can determine the electrode potential for metal ions involving variable oxidation states. For example, the electrode potential for the system, $Fe^{3+}(aq)/Fe^{2+}(aq)$ is obtained by measuring the EMF of the cell given below using Pt as the inert electrodes,

$$Pt\,|\,H_2(g)\,|\,H_3O^+(aq)\,||\,Fe^{3+}(aq)\,;\,Fe^{2+}(aq)\,|\,Pt.$$

From the above discussion, it follows that a metal in contact with its own ions constitutes a half cell and if we join two half cells together *via* a salt bridge, we get an electrochemical cell. For example, Daniell cell can be made by joining the two half cells *i.e.*, Zn (s)/ Zn^{2+} (aq) and Cu (s)/Cu^{2+} (aq) by a K_2SO_4 salt bridge or the two half cells are separated by a porous pot.

9.15. Electromotive Series

The standard electrode potentials of a large number of electrodes have been determined using standard hydrogen electrode as the reference electrode, for which the electrode potential has been arbitrarily taken as zero. By convention, *standard electrode potentials refer to reduction reactions. It is because of this reason that earlier they were referred to as standard reduction electrode potentials.* If, however, reactions are written in the opposite way *i.e.* as an oxidation reaction, the electrode potentials are referred to as *standard oxidation electrode potentials.* Since reduction half reaction is just the reverse of oxidation half reaction, the oxidation potential of any electrode is obtained from the reduction potential just by changing the sign. For example, the *standard reduction potential* of the electrode $Zn^{2+}/Zn(aq)$ for the reaction,

$$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s) \text{ is } -0.76 \text{ V},$$

then the *standard oxidation potential* of the electrode $Zn/Zn^{2+}(aq)$ for the reaction,

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^- \text{ is } +0.76 \text{ V}.$$

According to the latest convention adopted by IUPAC, the terms standard oxidation electrode potential and standard reduction electrode potential are not used but only the term standard electrode potential is used and the half cell reactions are always written as reduction reactions. Further,

Standard electrode potential is given a **positive sign** *if reduction occurs at that electrode w.r.t. the standard hydrogen electrode and is given a* **negative sign** if oxidation *occurs at the electrode w.r.t. the* *standard hydrogen electrode. Futher, the magnitude of the standard electrode potential is a measure of the tendency of the half reaction to occur in the forward direction i.e., in the direction of reduction.*

The standard electrode potentials of a number of electrodes at 1 M concentration of the dissolved ions at 298 K are given in Table 9.1. In this table, the reducing agents are written in decreasing order of their strength *i.e.*, the tendency of the oxidation half reaction goes on decreasing as we move from top to bottom. *Such a list of reducing agents arranged in decreasing order of their strength is called the* **activity** *or* **electromotive** or **electrochemical series.**

TABLE 9.1. Standard electrode potentials at 298 K

Electrode Reaction	Standard electrode potential E°_{298} (in volts)
$Li^+(aq) + e^- \longrightarrow Li(s)$	—3·05
$K^+(aq) + e^- \longrightarrow K(s)$	—2·93
$Ba^{2+}(aq) + 2e^- \longrightarrow Ba(s)$	—2·90
$Ca^{2+}(aq) + 2e^- \longrightarrow Ca(s)$	—2·87
$Na^+(aq) + e^- \longrightarrow Na(s)$	—2·71
$Mg^{2+}(aq) + 2e^- \longrightarrow Mg(s)$	—2·37
$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$	—1·66
$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$	—0·83
$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$	—0·76
$Cr^{3+}(aq) + 3e^- \longrightarrow Cr(s)$	— 0·74
$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$	—0·40
$Cd^{2+}(aq) + 2e^- \longrightarrow Cd(s)$	—0·40
$PbSO_4(s) + 2e^- \longrightarrow Pb(s) + SO_4^{2-}(aq)$	—0·31
$Co^{2+}(aq) + 2e^- \longrightarrow Co(s)$	—0·28
$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$	—0·25
$Sn^{2+}(aq) + 2e^- \longrightarrow Sn(s)$	—0·14
$Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$	—0·13
$Fe^{3+}(aq) + 3e^- \longrightarrow Fe(s)$	—0·036
$2H^+(aq) + 2e^- \longrightarrow H_2(g)$ (Standard electrode)	0·00
$AgBr(s) + e^- \longrightarrow Ag(g) + Br^-$	+ 0·10
$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-$	+ 0·22
$Cu^{2+}(aq) + e^- \longrightarrow Cu^+(aq)$	+ 0·18
$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$	+ 0·34
$Cu^+(aq) + e^- \longrightarrow Cu(s)$	+ 0·52
$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$	+ 0·54
$O_2(g) + 2H^+ + 2e^- \longrightarrow H_2O_2(l)$	+ 0·68
$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	+ 0·77
$Hg_2^{2+}(aq) + 2e^- \longrightarrow 2\,Hg(l)$	+ 0·79

TABLE 9.1. Contd......

$Ag^+(aq) + e^-$	$\longrightarrow$	$Ag(s)$	$+ 0{\cdot}80$
$Hg^{2+}(aq) + 2e^-$	$\longrightarrow$	$Hg(l)$	$+ 0{\cdot}85$
$NO_3^-(aq) + 4H^+ + 3e^-$	$\longrightarrow$	$NO(g) + 2H_2O(l)$	$+ 0{\cdot}97$
$Br_2(g) + 2e^-$	$\longrightarrow$	$2Br^-(aq)$	$+ 1{\cdot}08$
$\frac{1}{2}O_2(g) + 2H_3O^+(aq) + 2e^-$	$\longrightarrow$	$3H_2O(l)$	$+ 1{\cdot}23$
$Cr_2O_7^{2-}(aq) + 4H^+ + 6e^-$	$\longrightarrow$	$2Cr^{3+}(aq) + 7H_2O(s)$	$+ 1{\cdot}33$
$Cl_2(g) + 2e^-$	$\longrightarrow$	$2Cl^-(aq)$	$+ 1{\cdot}36$
$MnO_4^-(aq) + 8H_3O^+(aq) + 5e^-$	$\longrightarrow$	$Mn^{2+}(aq) + 12H_2O(l)$	$+ 1{\cdot}49$
$Au^{3+}(aq) + 3e^-$	$\longrightarrow$	$Au(s)$	$+ 1{\cdot}50$
$H_2O_2(aq) + 2H^+ + 2e^-$	$\longrightarrow$	$2H_2O(l)$	$+ 1{\cdot}78$
$Co^{3+}(aq) + e^-$	$\longrightarrow$	$Co^{2+}(aq)$	$+ 1{\cdot}81$
$F_2(g) + 2e^-$	$\longrightarrow$	$2F^-(aq)$	$+ 2{\cdot}87$

9.15.1. Applications of the Electromotive Series

Some of the important applications are given below :

1. To compare the reducing and oxidising capability of elements. *If the standard electrode potential is greater than zero, then reduced form is more stable than hydrogen gas. Similarly, if the standard electrode potential is negative, then hydrogen gas is more stable than the reduced form of species. In other words, a negative E° means that the redox couple is a stronger reducing agent than the H^+/H_2 couple and a positive E° means that the redox couple is a weaker reducing agent than the H^+/H_2 couple.* The standard electrode potential of fluorine is the maximum in the Table 9.1, therefore, F_2 is the strongest oxidising agent and F^- ion is a very poor reducing agent. Since the standard electrode potentials of halogens decreases in the order $F_2 > Cl_2 > Br_2 > I_2$, therefore, their oxidising power decreases in the same order, *i.e.*, $F_2 > Cl_2 > Br_2 > I_2$. Conversely, the standard electrode potentials for halide ions decreases in the order : I^- (– 0·53 V) > Br^- (– 1·08 V) Cl^- (– 1·36 V) > F^- (– 2·87 V), therefore, reducing powers of the halides decreases in the same order, *i.e.*, $I^- > Br^- > Cl^- > F^-$

Among alkali metals, Li (– 3·05 V) has the lowest while Li^+ (+ 3·05 V) has the highest electrode potential, therefore, Li metal is the strongest reducing agent while Li^+ is the weakest oxidising agent. Since the electrode potentials increase in the order Li < K < Na therefore, their reducing power decreases in the opposite, *i.e.*, Li > K > Na.

Besides the above applications, electrochemical cells are extensively used for determining the activity coefficient of electrolytes, pH of solutions, solubility product and for potentiometric titrations. Electrode potentials can also be used to determine the stability of inorganic and organic species.

From the above discussion, it follows that a metal which lies higher up in the series is a better reducing agent in the aqueous solution than the one which lies below it. Thus, whereas zinc can displace tin, lead, copper and other metals lying below it from the aqueous solutions of their salts but copper cannot displace lead, tin, zinc and other metals lying above it from the aqueous solutions of their salts. Similary, copper can displace silver from its salts but the reverse does not happen.

2. To predict whether a metal will liberate hydrogen from the aqueous solutions of acids or not. All metals with negative electrode potentials are stronger reducing agents than hydrogen and hence would liberate hydrogen from the aqueous solutions of acids. Conversely, all metals with positive values of electrode potentials are weaker reducing agents than hydrogen and hence will not liberate hydrogen from the the aqueous solutions of acids. Thus, metals like Mg, Al, Zn, Fe, Sn etc. will liberate hydrogen but metals like Cu, Hg, Ag etc. do not liberate hydrogen from the aqueous solutions of acids.

PROBLEMS ON ELECTROMOTIVE SERIES

EXAMPLE 9.19. *The standard electrode potential corresponding to the reaction $Au^{3+}(aq) + 3e^- \longrightarrow Au(s)$ is 1·50 V. Predict if gold can be dissolved in 1M HCl solution and on passing hydrogen gas through gold salt solution, metallic gold will be precipitated or not.* (N.C.E.R.T.)

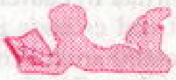
Solution. Consider the half reactions,

$$2H^+(aq) + 2e^- \longrightarrow H_2(g) \;;\; E° = 0{\cdot}0\ V$$

$$Au^{3+}(aq) + 3e^- \longrightarrow Au(s) \;;\; E° = 1{\cdot}50\ V$$

Since E° (1·50 V) for Au^{3+}/Au is higher than that $H^+/\frac{1}{2}H_2$ (0·0 V), therefore, Au^{3+} can be more easily reduced than H^+ ions. This implies that Au^{3+} ions can be reduced to metallic gold by H_2 gas but H^+ ions cannot oxidise metallic gold to Au^{3+} ions. In other words, *metallic gold does not dissolve in 1 M HCl. Instead H_2 gas can reduce gold* salt to metallic gold.

PROBLEMS FOR PRACTICE



1. With the help of table 9.1 select the oxidant which can oxidise oxidise

(*a*) $Cl^-(aq)$ to $Cl_2(g)$

(*b*) Fe (*s*) to $Fe^{2+}(aq)$ and

(*c*) $I^-(aq)$ to $I_2(aq)$ *(N.C.E.R.T.)*

2. With the help of table 9.1 select the reducing agent which can reduce the following ions to their metallic state (*a*) $Ag^+(aq)$, (*b*) $Al^{3+}(aq)$ and

(*c*) $Ni^{2+}(aq)$. *(N.C.E.R.T.)*

3. Identify the strongest and weakest reducing agents from the following metals : Zn, Cu, Ag, Na, Sn. *(N.C.E.R.T.)*

ANSWERS

1. (*a*) All species having E° higher than Cl^-/Cl_2 electrode, *i.e.,* F_2, MnO_4^-, Au^{3+}, acidified H_2O_2, Co^{3+} etc.

(*b*) All species having E° higher than Fe^{2+}/Fe electrode, *i.e.,* Ni^{2+}, Sn^{2+}, Cu^{2+}, I_2, O_2, Ag^+, Hg^{2+}, NO_3^-, Br_2, $Cr_2O_7^{2-}$ and all other oxidants listed under Ans. 1 (a).

(*c*) All species having E° higher than I^-/I_2 electrode, *i.e.* Br_2, $Cr_2O_7^{2-}$, Cl_2 and other oxidants listed under Ans. 1 (a).

2. (*a*) All metals having E° lower than Ag^+/Ag electrode, *i.e.,* Mg, Al, Zn, Fe, Ni, Sn etc.

(*b*) All metals having E° lower than Al^{3+}/Al electrode, *i.e.,* Li, K, Ca, Na, Mg etc.

(*c*) All metals having E° lower than Ni^{2+}/Ni electrode, *i.e.,* Fe, Cr, Zn, Al, Mg, Na, Ca, K, Li etc.

3. Among the elements listed, Na has the most negative E° and hence it is the strongest reducing agent while Ag has the highest E° and hence it is the weakest reducing agent.

9.16. EMF of an Electrochemical Cell

It is a well known fact that whenever a current flows through two points, a potential difference is said to exist between them. The potential difference generated by a cell when the circuit draws no current (under conditions of zero electron flow) is called **electromotive force (EMF)** or **the cell potential.**

We know that an electrochemical cell consists of two half cells, *i.e.,* electrodes. One of these electrodes must have a higher electrode potential (higher tendency to lose electrons) than the other electrode. As a result of this potential difference, the electrons flow from the electrode at a higher potential to the electrode at a lower potential, *i.e.,* from negative electrode to less negative or positive electrode or from less positive electrode to more positive electrode. However, current flow is in a direction opposite to the electron flow. Thus,

EMF of a cell may be defined as the difference in the electrode potentials of the two half cells when the cell is not sending current through the circuit.

The standard EMF of the cell (E°_{cell}) may be obtained by subtracting the standard electrode potential of the anode from that of the cathode, *i.e.*,

$$E^\circ_{cell} = \begin{bmatrix}\text{Standard electrode} \\ \text{potential of cathode}\end{bmatrix} - \begin{bmatrix}\text{Standard electrode} \\ \text{potential of anode}\end{bmatrix} \quad ...(i)$$

$$\text{or} \quad E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} \quad ...(ii)$$

Further by convention, the anode is placed on the left and cathode is placed on the right while representing an electrochemical cell, therefore, the EMF of the cell is given by the expression

$$E^\circ_{cell} = E^\circ_R - E^\circ_L \quad ...(iii)$$

where E°_R and E°_L refer to the standard electrode potentials of the cathode and anode respectively.

In order to determine the reaction taking place in the cell, the following steps are followed.

(*i*) *Write reduction equations for both the electrodes along with their electrode potentials, one after the other.*

(*ii*) *Balance the electrical charges and the number of atoms of each element on either side of each of the above two reduction equations.*

(*iii*) *Multiply each reduction equation by a suitable integer so that the number of electrons involved in both the half reactions are equal.*

It may be noted that while multiplying half reactions with suitable integers, their E° values are not multiplied by any such integers because these values simply convey the tendency for reduction.

(*iv*) *Subtract the equation with lower electrode (reduction) potential from the one having higher electrode potential. This difference gives the EMF of the cell.*

The electrode with higher reduction potential has a strong tendency to gain electrons and hence acts as the **cathode** *while the electrode with lower reduction has a strong tendency to get oxidised potential acts as the* **anode.**

EXAMPLE 9.20. *A cell is prepared by dipping a chromium rod in 1 M $Cr_2(SO_4)_3$ solution and an iron rod in 1 M $FeSO_4$ solution. The standard reduction potentials of chromium and iron electrodes are −0·75 V and −0·45 V respectively.*

(a) What will be the cell reaction ?

(b) What will be the standard EMF of the cell ?

(c) Which electrode will act as anode ?

(d) Which electrode will act as cathode ?

Solution. The two half cell reduction equations are :

$$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s); \quad E^\circ = -0{\cdot}45\text{ V} \quad ...(i)$$

$$Cr^{3+}(aq) + 3e^- \longrightarrow Cr(s); \quad E^\circ = -0{\cdot}75\text{ V} \quad ...(ii)$$

Since Cr^{3+}/Cr electrode has lower reduction potential, therefore, it acts as the *anode* while Fe^{2+}/Fe electrode with higher electrode potential acts as the *cathode.*

To equalise the number of electrons, multiply Eq. (*i*) by 3 and Eq. (*ii*) by 2. But do not multiply their E° values. Thus,

$$3\,Fe^{2+}(aq) + 6e^- \longrightarrow 3\,Fe(s); \quad E^\circ = -0{\cdot}45\text{ V} \quad ...(iii)$$

$$2\,Cr^{3+}(aq) + 6e^- \longrightarrow 2\,Cr(s); \quad E^\circ = -0{\cdot}75\text{ V} \quad ...(iv)$$

To obtain equation for the cell reaction, subtract Eq. (*iv*) from Eq. (*iii*), we have,

$$2\,Cr(s) + 3\,Fe^{2+}(aq) \longrightarrow 2\,Cr^{3+}(aq) + 3\,Fe(s);$$

$$E^\circ_{cell} = -0{\cdot}45 - (-0{\cdot}75\text{ V}) = +0{\cdot}30\text{ V}$$

Thus, the EMF of the cell = **+ 0·30 V**

EXAMPLE 9.21. *The half cell reactions with their oxidation potentials are*

$$Pb(s) \longrightarrow Pb^{2+}(aq) + 2e^-; \quad E^\circ_{oxi} = +0{\cdot}13\text{ V}$$

$$Ag(s) \longrightarrow Ag(aq) + e^-; \quad E^\circ_{oxi} = -0{\cdot}80\text{ V}$$

Write the cell reaction and calculate its EMF.

Solution. Rewrite the two equations in the reduction form. Thus,

$$Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s); \quad E^\circ = -0{\cdot}13\text{ V} \quad ...(i)$$

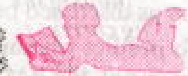
$$Ag^+(aq) + e^- \longrightarrow Ag(s); \quad E^\circ = +0{\cdot}80\text{ V} \quad ...(ii)$$

To obtain the equation for the cell reaction, multiply Eq. (*ii*) with 2 and subtract from Eq. (*i*), from Eq. (*ii*), we have,

$$Pb\,(s) + 2\,Ag^+\,(aq) \longrightarrow Pb^{2+}\,(aq) + 2\,Ag\,(s)\,;$$

$$E^\circ_{cell} = +\,0{\cdot}80 - (-\,0{\cdot}13) = \mathbf{+\,0{\cdot}93\ V}$$

PROBLEMS FOR PRACTICE



1. Calculate the standard e.m.f. of the cells formed by different combinations of the following half cells :

$Zn\,(s) \mid Zn^{2+}\,(aq)$, $Cu\,(s) \mid Cu^{2+}\,(aq)$,
$Ni\,(s)/Ni^{2+}\,(aq)$, and $Ag\,(s) \mid Ag^+\,(aq)$

(N.C.E.R.T.)

(*i*) $Zn\,(s) \mid Zn^{2+}(aq) \mid\mid Cu^{2+}\,(aq) \mid Cu\,(s)\,;$
$E^\circ_{cell} = +\,0{\cdot}34 - (-\,0{\cdot}76) = \mathbf{+\,1{\cdot}1\ V}$

(*ii*) $Zn\,(s) \mid Zn^{2+}\,(aq) \mid\mid Ni\,(aq) \mid Ni\,(s)\,;$
$E^\circ_{cell} = -\,0{\cdot}44 - (-\,0{\cdot}76) = \mathbf{+\,0{\cdot}22\ V}$

(*iii*) $Zn\,(s) \mid Zn^{2+}\,(aq) \mid\mid Ag^+\,(aq) \mid Ag\,(s)\,;$
$E^\circ_{cell} = +\,0{\cdot}80 - (-\,0{\cdot}76) = \mathbf{+\,1{\cdot}56\ V}$

(*iv*) $Ni\,(s) \mid Ni^{2+}\,(aq) \mid\mid Cu^{2+}\,(aq) \mid Cu\,(s)\,;$
$E^\circ_{cell} = +\,0{\cdot}340 - (-\,0{\cdot}44) = \mathbf{+\,0{\cdot}78\ V}$

(*v*) $Ni\,(s) \mid Ni^{2+}\,(aq) \mid\mid Ag^+\,(aq) \mid Ag\,(s)\,;$
$E^\circ_{cell} = +\,0{\cdot}80 - (-\,0{\cdot}44) = \mathbf{+\,1{\cdot}24\ V}$

(*vi*) $Cu\,(s) \mid Cu^{2+}\,(aq) \mid\mid Ag^+\,(aq) \mid Ag\,(s)\,;$
$E^\circ_{cell} = +\,0{\cdot}80 - (-\,0{\cdot}34) = \mathbf{+\,0{\cdot}46\ V}.$

2. A cell is prepared by dipping copper rod in 1M copper sulphate solution and zinc rod in 1M $ZnSO_4$ solution. The standard reduction potentials of copper and zinc are 0·34 and – ·76 V respectively.

(*i*) What is the cell reaction ?

(*ii*) What will be the standard electromotive force (EMF) of the cell ?

(*iii*) Which electrode will be positive ?

(*iv*) How will the cell be represented ?

[Ans. (*i*) $Zn\,(s) + CuSO_4\,(aq) \longrightarrow ZnSO_4\,(aq) + Cu\,(s)$ (*ii*) $E^\circ_{cell} = 1{\cdot}1$ V (*iii*) Cu electrode (*iv*) $Zn \mid ZnSO_4\,(1\,M) \mid\mid CuSO_4\,(1\,M) \mid Cu$]

3. Following cell is st up between copper and silver electrodes : $Cu \mid Cu^{2+}\,(aq) \mid\mid Ag^+\,(aq) \mid Ag$

If its two half cells work under standard conditions, calculate the e.m.f. of the cell

[Given $E^\circ_{Cu^{2+}/Cu}\,(E^\circ_{red}) = +\,0{\cdot}34$ volt
$E^\circ_{Ag^+/Ag}\,(E^\circ_{red}) = +\,0{\cdot}80$ volt]

(A.I.S.B. 1986, P.S.B. 1988, 1989) **[Ans. 0·46 volt]**

4. Write the cell reaction and calculate the standard E° of the cell :

$Zn \mid Zn^{2+}\,(1\,M) \mid\mid Cd^{2+}\,(1\,M) \mid Cd$

Given $E^\circ_{Zn,\ Zn^{2+}} = 0{\cdot}763$ volt
$E^\circ_{Cd,\ Cd^{2+}} = 0{\cdot}403$ volt

[Ans. 0·360 volt, $Zn + Cd^{2+} \longrightarrow Zn^{2+} + Cd$]

5. The standard EMF of the cell

$Ni \mid Ni^{2+} \mid\mid Cu^{2+} + Cu$

is 0·59 volt. The standard electrode potential (reduction potential) of copper electrode is 0·34 volt. Calculate the standard electrode potential of nickel electrode. **[Ans. $E^\circ_{Ni^{2+},\ Ni} = -0{\cdot}25$ volt]**

6. The e.m.f. (E°) of the following cells are

$Ag \mid Ag^+\,(1\,M) \mid\mid Cu^{2+}\,(1\,M)\,Cu\,;$
$E^\circ = -0{\cdot}46$ V

$Zn \mid Zn^{2+}\,(1\,M) \mid\mid Cu^{2+}\,(1\,M) \mid Cu\,;$
$E^\circ = +\,1{\cdot}10$ V

Calculate the e.m.f. of the cell

$Zn \mid Zn^{2+}\,(1\,M) \mid\mid Ag^+\,(1\,M) \mid Ag$

(A.I.S.B. 1989) **[Ans. 1·56 V]**

7. Two half cells are

$Al^{3+}\,(aq)/Al$ and $Mg^{2+}\,(aq)/Mg$

The reduction potentials of these half cells are —1·66 V and —2·36 V respectively. Calculate the cell potential. Write the cell reaction also.

(P.S.B. 1997) **[Ans. 0·70 V, $3\,Mg + 2\,Al^{3+} \longrightarrow 3\,Mg^{2+} + 2\,Al$]**

8. Calculate E° for the cell

$Al \mid Al^{3+}\,(1\,M) \mid\mid Cu^{2+}\,(1\,M) \mid Cu.$

Given : $E^\circ_{Al^{3+}/Al}$ and $E^\circ_{Cu^{2+}/Cu}$ as —1·66 v and 0·34 V respectively. *(H.P.S.B. 1997)* **[Ans. 2·0 V]**

9.16.1. To predict the Spontaneity of a Redox Reaction

The EMF of a cell is an important property. It can be used to predict the spontaneity of a redox reaction as discussed below.

To predict whether a given redox reaction is feasible or not, the EMF of the cell based upon the given redox reaction is calculated. *If the EMF comes out to be positive, the reaction takes place.* If, however, the EMF comes out to be negative, the forward reaction as shown by the redox equation does not occur ; instead, the reverse reaction occurs. The following examples will illustrate this point :

PROBLEMS ON PREDICTING SPONTANEITY OF A REACTION

EXAMPLE 9.22. *Predict whether zinc and silver react with 1 M sulphuric acid to give out hydrogen or not. Given that the standard potentials of zinc and silver are – 0.76 volt and + 0.80 volt respectively.*

Solution. (*a*) *To predict reaction of zinc with sulphuric acid :*

If Zn reacts, the following reaction should take place

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$

i.e., $$Zn + 2H^+ \longrightarrow Zn^{2+} + H_2$$

By convention, the cell will be represented as

$$Zn \mid Zn^{2+} \parallel H^+ \mid H_2$$

Standard EMF of the cell

$$E^\circ_{cell} = (E^\circ_{right}) - E^\circ_{left}$$

$$= 0 - (-0.76) = +0.76 \text{ volt}$$

Thus the EMF of the cell comes out to be positive. Hence the reaction takes place.

(*b*) *To predict the reaction of silver with sulphuric acid .*

If Ag reacts, the following reaction should take place :

$$2Ag + H_2SO_4 \longrightarrow Ag_2SO_4 + H_2$$

i.e. $$2Ag + 2H^+ \longrightarrow 2Ag^+ + H_2$$

By convention, the cell may be represented as

$$Ag \mid Ag^+ \parallel H^+ \mid H_2$$

$$\therefore \quad E^\circ_{cell} = E^\circ_{H^+,H_2} - E^\circ_{Ag^+,Ag}$$

$$= 0 - 0.80$$

$$= -0.80 \text{ volt}$$

Thus the EMF of the supposed cell comes out to be negative. Hence this reaction does not take place.

EXAMPLE 9.23. *Can a solution of 1 M copper sulphate be stored in a vessel made of nickel metal ? Given that $E^\circ_{Ni,Ni^{2+}} = +0.25$ volt, $E^\circ_{Cu,Cu^{2+}} = -0.34$ volt.*

or Is it possible to store copper sulphate solution in a nickel vessel ? **(N.C.E.R.T.)**

Solution. In this problem, we want to see whether the following reaction takes place or not

$$Ni + CuSO_4 \longrightarrow NiSO_4 + Cu$$

i.e. $$Ni + Cu^{2+} \longrightarrow Ni^{2+} + Cu$$

By convention, the cell may be represented as

$$Ni \mid Ni^{2+} \parallel Cu^{2+} \mid Cu$$

We are given that the oxidation potentials as

$$E^\circ_{Ni,Ni^{2+}} = +0.25 \text{ volt}$$

and $$E^\circ_{Cu,Cu^{2+}} = -0.34 \text{ volt}$$

Hence the reduction potentials will be

$$E^\circ_{Ni^{2+},Ni} = -E^\circ_{Ni,Ni^{2+}}$$

$$= -0.25 \text{ volt}$$

and $$E^\circ_{Cu^{2+},Cu} = -E^\circ_{Cu,Cu^{2+}}$$

$$= +0.34 \text{ volt}$$

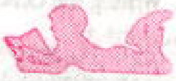
Now $$E^\circ_{cell} = E^\circ_{right} - E^\circ_{left}$$

$$= +0.34 - (-0.25)$$

$$= +0{\cdot}59 \text{ volt}$$

Thus EMF comes out to be positive. This implies that $CuSO_4$ reacts with nickel. Hence *$CuSO_4$ solution cannot be stored in a nickel vessel.*

PROBLEMS FOR PRACTICE



1. Predict reaction of 1N sulphuric acid with the following metals :

   (*i*) copper (*ii*) lead (*iii*) iron

   Given $E^\circ_{Cu^{2+}, Cu} = 0.34$ volt ; $E^\circ_{Pb^{2+}, Pb} = -0.13$ volt ; and $E^\circ_{Fe^{2+}, Fe} = -0.44$ volt

   [Ans. (*i*) No (*ii*) Yes (*iii*) Yes]

2. Can a solution of 1 M $ZnSO_4$ be stored in a vessel made of copper ? Given that $E^\circ_{Zn, Zn^{2+}} = +0.76$ volt, and $E^\circ_{Cu^{2+}, Cu} = 0.34$ volt

   [Ans. Yes]

3. Is it safe to stir 1 M $AgNO_3$ solution with a copper spoon ? Given $E^\circ_{Ag^+, Ag} = 0.80$ volt $E^\circ_{Cu, Cu^{2+}} = -0.34$ volt. Explain

   [Ans. No]

4. Can we use a copper vessel to store 1 M $AgNO_3$ solution ? Given that $E^\circ_{Cu^{2+}/Cu} = +0.34$ V and $E^\circ_{Ag^+/Ag} = +0.80$ V.

   [Ans. No]

5. Why blue colour of copper sulphate solution gets discharged when zinc rod is dipped in it ?

   (Given $E^\circ_{Cu^{2+}/Cu} = 0.34$ V and $E^\circ_{Zn/Zn^{2+}} = 0.76$ V)

Conceptual Questions

Q. 1. What are the maximum and minimum oxidation numbes of N, S and Cl ?

Ans. (*i*) The highest oxidation number (O.N.) of N is +5 since it has five electrons in the valence shell ($2s^2\,2p^3$) and its minimum O.N. is –3 since it can accept three more electrons to acquire the nearest inert gas (Ne) configation.

(*ii*) Similarly, the highest O.N. of S is +6 since it has six electrons in the valence shell ($3s^2\,3p^4$) and its minimum O.N. is –2 since it needs two more electrons to acquire the nearest inert gas (Ar) configuration.

(*iii*) Likewise the maximum O.N. of Cl is +7 since it has seven electrons in the valence shell ($3s^2\,3p^5$) and its minimum O.N. is –1 since it needs only one more electron to acquire the nearest (Ar) gas configuration.

Q. 2. Nitric acid acts only as an oxidising agent while nitrous acid acts both as an oxidising as well as a reducing agent. Why ?

Ans. (*i*) HNO_3 : Oxidation number of N is $HNO_3 = +5$

Maximum oxidation number of N = + 5

Minimum oxidation number of N = –3

Since the oxidation number of N is HNO_3 is maximum (+5), therefore, it can only decrease. Hence HNO_3 acts only as an oxidising agent.

(*ii*) HNO_2 : Oxidation number of N in $HNO_2 = +3$

Maximum oxidation number of N = + 5

Minimum oxidation number of N = – 3

Thus, the oxidation number of N can increase by losing electrons or can decrease by accepting electrons. Therefore, HNO_2 acts both as an oxidising as well as a reducing agent.

Q. 3. Can the reaction, $Cr_2O_7^{2-} + H_2O \rightleftharpoons 2\,CrO_4^{2-} + 2\,H^+$ be regartded as a redox reaction ?

Ans. Oxidation number of Cr in $Cr_2O_7^{2-} = +6$

Oxidation number of Cr in $CrO_4^{2-} = +6$

Since during this reaction, the oxidation number of Cr has neither decreased nor increased, therefore, the above reaction cannot be regarded as a redox reaction.

Q. 4. Identify the oxidants and reductants in the following reactions :

(*a*) $CH_4(g) + 4Cl_2(g) \longrightarrow CCl_4(g) + 4HCl(g)$

(*b*) $C_2H_2O_4(aq) + 2H^+(aq) + MnO_2(s) \longrightarrow Mn^{2+}(aq) + 2CO_2(g) + 2H_2O(l)$

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

(*d*) $Cl_2(g) + 2Br^-(aq) \longrightarrow 2Cl^-(aq) + Br_2(aq)$.

(*N.C.E.R.T.*)

Ans. Writing the O.N. of all the atoms above their symbols, we have,

$$(a)\ \overset{-4}{C}\,\overset{+1}{H_4}\,(g) + 4\,\overset{0}{Cl_2}\,(g) \longrightarrow \overset{+4}{C}\,\overset{-1}{Cl_4}\,(g) + 4\,H\,\overset{-1}{Cl}\,(g)$$

O.N. of C increases from – 4 in CH_4 to +4 in CCl_4 and that of Cl decreases from 0 in Cl_2 to – 1 in CCl_4 or HCl, therefore, *Cl_2 acts as the oxidant and CH_4 acts as the reductant.*

$$(b)\ \overset{-3}{C_2}\,\overset{+1}{H_2}\,\overset{-2}{O_4}\,(aq) + 2\,H^+\,(aq) + \overset{+4}{Mn}\,O_2\,(s) \longrightarrow \overset{+2}{Mn}\,(aq) + 2\,\overset{+4}{C}O_2\,(g) + 2\,H_2O\,(l)$$

O.N. of C increases from – 3 in $C_2H_2O_4$ to +4 in CO_2 and that of Mn decreases from +4 in MnO_2 to +2 in Mn^{2+}, therefore, *MnO_2 acts as the oxidant while $C_2H_2O_4$ acts as the reductant.*

$$(c)\ \overset{0}{I_2}\,(aq) + 2\,\overset{+2}{S_2}\,\overset{2-}{O_3}\,(aq) \longrightarrow 2\,I^-\,(aq) + \overset{+2\cdot5}{S_4}\,\overset{2-}{O_6}\,(aq)$$

Here, O.N. of I decreases from 0 in I_2 to – 1 in I^- and that of S increases from +2 in $S_2O_3^{2-}$ to +2·5 in $S_4O_6^{2-}$, therefore, I_2 *acts as the oxidant while $S_2O_3^{2-}$ acts as the reductant.*

$$(d)\ \overset{0}{Cl_2}\,(g) + 2\,\overset{-1}{Br^-}\,(aq) \longrightarrow 2\,\overset{-1}{Cl^-}\,(aq) + \overset{0}{Br_2}\,(aq)$$

Here O.N. of Cl_2 decreases from 0 in Cl_2 to –1 in Cl^- ion while that of Br increases from –1 in Br^- ion to 0 in Br_2, therefore, *Cl_2 acts as the oxidant while Br^- ion acts as the reductant.*

Q. 5. The electrode potential of four metallic elements (A, B, C and D) are + 0·80, –0·76, +0·12 and +0·34 V respectively. Arrange them in order of decreasing electropositive character.

Ans. Higher the electrode potential (E°) lower is the tendency of the metal to lose electrons and hence lower is the electropositive character of the metal. Since the electrode potentials increase in the order: —0·76 (B), +0·12 (C), + 0·34 (C) and +0·80 (D), therefore, *electropositive character decreases in the same order : B, C, D, A.*

Q. 6. I_2 and Br_2 are added to a solution containing Br^- and I^- ions. What reaction will occur if,

$$I_2 + 2\,e^- \longrightarrow 2\,I^-\ ;\ E° = +0{\cdot}54\ V \text{ and } Br_2 + 2\,e^- \longrightarrow 2Br^-\ ;\ E° = +\,1{\cdot}09\ V\ ?$$

Ans. Since E° of Br_2 is higher than that of I_2, therefore, Br_2 has a higher tendency to accept electrons that I_2. Conversely, I^- ion has a higher tendency to lose electrons than Br^- ion. Therefore, the following reaction will occur :

$$\begin{array}{c} 2\,I^- \longrightarrow I_2 + 2\,e^- \\ Br_2 + 2\,e^- \longrightarrow 2\,Br^- \\ \hline 2\,I^- + Br_2 \longrightarrow I_2 + 2\,Br^- \end{array}$$

In other words I^- ion will be oxidised to I_2 while Br_2 will be reduced to Br^- ions.

Q. 7. Is it possible to store :

(i) Copper sulphate solution in a zinc vessel ? **(ii) Copper sulphate solution in a nickel vessel ?**
(iii) Copper sulphate solution in a silver vessel ? **(iv) Copper sulphate solution in a gold vessel ?**

(N.C.E.R.T.)

Ans. (*i*) We cannot place $CuSO_4$ solution in a zinc vessel, if the following redox reaction occurs :

$$Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu \quad \text{or} \quad Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$$

By convention, the cell may be represented as $Zn \mid Zn^{2+} \parallel Cu^{2+} \mid Cu$

$$\therefore E°_{cell} = E°_{Cu^{2+},\ Cu} - E°_{Zn^{2+},\ Zn} = 0{\cdot}34 - (-\,0{\cdot}76) = +\,1{\cdot}10\ V$$

Since EMF comes out be positive, therefore, $CuSO_4$ reacts with zinc. In other words, *$CuSO_4$ solution cannot be stored in a zinc vessel.*

(*b*) Same as solved in example 9.23 on page 9/46.

(*c*) We cannot store $CuSO_4$ solution in a silver vessel if the following redox reaction occurs :

$$2\,Ag + Cu^{2+} \longrightarrow 2\,Ag^+ + Cu$$

By convention, the cell of the above redox reaction may be represented as

$$Ag \mid Ag^+ \mid\mid Cu^{2+} \mid Cu \quad \text{and} \quad E^\circ_{cell} = E^\circ_{Cu^{2+},\,Cu} - E^\circ_{Ag^+,\,Ag} = 0{\cdot}34 - 0{\cdot}80 = -0{\cdot}56\ V$$

Since the EMF of the cell is –ve, therefore, $CuSO_4$ does not react with silver. In other words, *$CuSO_4$ solution cannot be stored in a silver vessel.*

(*d*) We cannot store, $CuSO_4$ solution in a gold vessel if the following redox reaction occurs :

$$2\,Au + 3\,Cu^{2+} \longrightarrow 2\,Au^{3+} + 3\,Cu$$

The cell corresponding to the above redox reaction may be represented as

$$Au \mid Au^{3+} \mid\mid Cu^{2+} \mid Cu \quad \text{and} \quad E^\circ_{cell} = E^\circ_{Cu^{2+},\,Cu} - E^\circ_{Au^{3+},\,Au} = 0{\cdot}34 - 1{\cdot}50 = -1{\cdot}26\ V$$

Since the EMF of the above reaction is –ve, therefore, $CuSO_4$ solution does not react with gold. In other words, *$CuSO_4$ solution can be stored in a gold vessel.*

Very Short Answer Questions CARRYING 1 MARK

Q. 1. Define oxidation and reduction in terms of electrons.

Ans. Oxidation involves loss and reduction involves gain of electrons.

Q. 2. What is a redox reaction. Give one example.

Ans. Oxidation—reduction reactions are called redox reactions, $Mg + F_2 \longrightarrow Mg^{2+}(F^-)_2$.

Q. 3. Define oxidising and reducing agents in terms of electrons.

Ans. Oxidising agents are electron acceptors while reducing agents are electron donors.

Q. 4. What is a standard hydrogen electrode ?

Ans. Refer to the text on page 9/38.

Q. 5. The standard electrode potentials of a few metals are given below :

Al (–1·66V), Cu (+ 0·34V), Li (– 3·05V), Ag (+ 0·80V) and Zn (–0·76V).

Which of these will behave as the strongest oxidising agent and which as the strongest reducing agent ?

Ans. Li is the strongest reducing agent while Ag^+ is the strongest oxidising agent.

Q. 6. In the reaction, $MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$ which species is oxisied ?

(B.I.T. Ranchi 1990)

Ans. HCl is oxidised to Cl_2.

Q. 7. What is the oxidation number of

(*i*) C in CH_2O *(M.L.N.R. Allahabad 1990)*

(*ii*) Pt in $[Pt(C_2H_4)Cl_3]^-$ *(M.L.N.R. Allahabad 1993)*

Ans. (*i*) zero (*ii*) 2.

Q. 8. What is the oxidation state of Ni in $Ni(CO)_4$? *(A.I.S.B. 1995)*

Ans. Zero.

Q. 9. Why is it not possible to measure the voltage of an isolated reduction half reaction ? *(H.S.B. 1995)*

Ans. Consult sec. 9.14.3 on page 9/38.

Q. 10. What is a redox couple ? *(N.C.E.R.T.)*

Ans. A redox couple consists of oxidised and reduced form of the same substance taking part in an oxidation or reduction half reaction. For example, Zn^{2+} *(aq)*/Zn, Cl_2 *(g)*/Cl^- *(aq)* etc.

Q. 11. On the basis of stoichiometry, determine the oxidation number of

(*i*) Fe in Fe_3O_4 and $Fe_4[Fe(CN)_6]$ (*ii*) Cl in $CaOCl_2$. *(N.C.E.R.T.)*

Ans. (*i*) The composition of Fe_3O_4 is $FeO.Fe_2O_3$.

∴ The O.N. of Fe in FeO is + 2 while in Fe_2O_3, it is + 3.

In $Fe_4[Fe(CN)_6]$, the O.N. of Fe inside the coordination sphere is + 2 while that of Fe outside the coordination sphere is + 3.

(*ii*) The composition of $CaOCl_2$ is Ca(OCl)Cl. Hence, O.N. of Cl in OCl^- is + 1 while in Cl^- ion, it is – 1.

Short Answer Questions CARRYING 2 or 3 MARKS

Sec. 9.1. to 9.3.

1. Explain the terms : oxidation and reduction in terms of electrons. Give one example in each case.
2. Define the terms : oxidising agent and reducing agents according to the electronic concept. Give one example in each case.
3. Comment upon the statement : oxidation and reduction reactions go side by side.

Sec. 9.4. to 9.6.

4. What do you understnad by the terms : direct redox reaction and indirect redox reaction ? Give one example in each case.
5. Explain oxidation-reduction reactions occurring in a beaker. Give two examples to illustrate your answer.
6. Explain what happens when a zinc rod is dipped in $CuSO_4$ solution ?
7. What are half cells and half cell reactions ? Explain with examples.
8. Write the following redox reactions using half equations.

(*i*) $Zn(s) + PbCl_2(aq) \longrightarrow Pb(s) + ZnCl_2(aq)$ (*ii*) $2Fe^{3+}(aq) + 2I^-(aq) \longrightarrow I_2(s) + 2Fe^{2+}(aq)$

(*iii*) $2Na(s) + Cl_2(g) \longrightarrow 2\,NaCl(s)$ (*iv*) $Mg(s) + Cl_2(g) \longrightarrow MgCl_2(s)$

(*v*) $Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$

In each of the reactions given above, mention

(*i*) which reactant is oxidized ? To what ? (*ii*) which reactant is the oxidiser ?

(*iii*) which reactant is reduced ? To what ? (*iv*) which reactant is the reducer ?

[**Ans.** (*i*) $Zn(s) \longrightarrow Zn^{2+} + 2e^-$ (*oxidation*), $Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$ (*reduction*)

Zn is oxidised to Zn^{2+}, Pb^{2+} is reduced to Pb ; Pb^{2+} is the oxidiser and Zn is the reducer.

(*ii*) $2Fe^{3+} + 2e^- \longrightarrow 2Fe^{2+}$ (*reduction*), $2I^- \longrightarrow I_2 + 2e^-$ (*oxidation*)

Fe^{3+} is reduced to Fe^{2+}, I^- is oxidised to I_2 ; I^- is the reducer and Fe^{3+} is the oxidiser.

(*iii*) $2Na \longrightarrow 2Na^+ + 2e^-$ (*oxidation*), $Cl_2 + 2e^- \longrightarrow 2\,Cl^-$ (*reduction*)

Na is oxidised to Na^+ and Cl_2 is reduced to Cl^- ; Na is the reducer and Cl_2 is the oxidiser.

(*iv*) $Mg \longrightarrow Mg^{2+} + 2e^-$ (*oxidation*), $Cl_2 + 2e^- \longrightarrow 2\,Cl^-$ (*reduction*)

Mg is oxidised to Mg^{2+} while Cl_2 is reduced to Cl^-; Mg is the reducer and Cl_2 is the oxidiser.

(*v*) $Zn \longrightarrow Zn^{2+} + 2e^-$ (*oxidation*), $2H^+ + 2e^- \longrightarrow H_2$ (*reduction*)

Zn is oxidised to Zn^{2+} while H^+ is reduced to H_2 ; Zn is the reducer and H^+ is the oxidiser.]

Sec. 9.7. to 9.10.

9. Define oxidation and reduction in terms of oxidation number. Give examples in each case to illustrate your answer.
10. Define oxidising and reducing agents in terms of oxidation number. Cite two examples in each case to support your answer.
11. H_2S acts only as a reductant whereas SO_2 acts oxidant and reductant both. Why.
12. H_2O_2 acts as reductant as well as oxidant. Explain.
13. Explain the difference between valency and oxidation number.
14. State and explain the 'Stock notation' used to name inorganic compounds involving different oxidation states.

Sec. 9.11.

15. Starting with the correctly balanced half reactions, write the overall net ionic reaction in the following changes :

(*i*) Chloride ion is oxidised to Cl_2 by $\underline{Mn}O_4^-$ (in acid solution)

(*ii*) Nitrous acid ($H\underline{N}O_2$) reduces MnO_4^- (in acid solution)

(*iii*) Nitrous acid ($H\underline{N}O_2$) oxidises I^- to I_2 (in acid solution) (*iv*) Chlorate ion ($\underline{Cl}O_3^-$) oxidises Mn^{2+} to MnO_2 (*s*) (in acid solution)

(*v*) Chromite ion ($\underline{Cr}O_3^-$) is oxidised by H_2O_2 (in strongly basic medium)

Also find out the change in the oxidation number of the underlined atoms.

[Ans. (*i*) $2MnO_4^- + 16H^+ + 10Cl^- \longrightarrow 5Cl_2 + 2Mn^{2+} + 8H_2O$

Oxidation number of Mn changes from +7 in MnO_4^- to +2 in Mn^{2+}

(*ii*) $2MnO_4^- + 6H^+ + 5NO_2^- \longrightarrow 5NO_3^- + 3H_2O + 2Mn^{2+}$

Oxidation number of N changes from +3 in NO_2^- ion to +5 in NO_3^- ion

(*iii*) $2I^- + 4H^+ + 2NO_2^- \longrightarrow I_2 + 2NO + 2H_2O$

Oxidation number of N changes from +3 is NO_2^- to +2 in NO

(*iv*) $3Mn^{2+} + ClO_3^- + 6H^+ \longrightarrow 3Mn^{4+} + Cl^- + 3H_2O$

Oxidation number of Cl changes from + 5 in ClO_3^- to −1 in Cl^-

(*v*) $2CrO_3^- + H_2O_2 + 2OH^- \longrightarrow 2CrO_4^{2-} + 2H_2O$

Oxidation number of Cr changes from +5 in CrO_3^- to +6 in CrO_4^{2-}]

Sec. 9.12. 16. What do you mean by iodometric and iodimetric titrations. Give one example of each type.

Sec. 9.13. to 9.16. 17. Draw a labelled diagram for the Daniel cell. Discuss its working.

18. Discuss briefly the function of the salt bridge in an electrochemical cell.

19. Give the construction of S.H.E. What is its standard reduction potential ? How does it help to determine the standard electrode potentials of other elements ?

20. Write a note an standard hydrogen electrode.

21. What is an electrochemical series ? How can this be used to explain the oxidising and reducing abilities of elements ?

22. Why does the blue colour of copper sulphate solution get discharged when an iron rod is dipped into it ? Given : $E^\circ_{Cu^{2+}/Cu} = 0{\cdot}34$ V and $E^\circ_{Fe^{2+}/Fe} = -0{\cdot}44$ V

23. Arrange the following metals in increasing order of reactivity. Which one will be the strongest reducing agent and which is the weakest ? Mg, Na, Ag, Cu, Fe, Zn

Long Answer Questions CARRYING 5 or more MARKS

Sec. 9.1. to 9.6. 1. Explain the terms : (*i*) oxidation, (*ii*) reduction, (*iii*) oxidising agent and (*iv*) reducing agent in terms of electrons. Give two examples in ech case to justify you answer.

2. Briefly discuss some redox reactions occurring in aqueous solutions.

Sec. 9.7. to 9.10. 3. Define oxidation number. How does it differ from valency ? Write the general rules of assigning oxidation numbers to various atoms in ions and molecules.

4. Explain the terms : (*i*) oxidation, (*ii*) reduction, (*iii*) oxidising agent and (*iv*) reducing agent in terms of oxidation number. Give two examples in each case to illustrate you answer.

5. Giving one example in each case discuss (*i*) oxidation number method and (*ii*) ion-electron method for balancing redox reactions.

Sec. 9.12. 6. Discuss briefly stoichiometry of redox reactions in aqueous solutions.

Sec 9.13. to 9.16. 7. What is an electrochemical cell ? Briefly discuss its construction and working. How is it represented ?

8. What is a standard hydrogen electrode ? How can it be used to determine standard electrode potential of an electrode.

9. What is electrochemical series ? How does it help us (*i*) comparing the oxidising and reducing power of different elements and (*ii*) predicting whether a metal will react with a mineral acid to give hydrogen gas or not ?

COMPETITION FOCUS

ADDITIONAL USEFUL INFORMATION

Exceptional Cases on the Determination of Oxidation Number

Although the rules discussed in **Sec. 9.7** can generally be used to determine the oxidation number (O.N.) of a particular atom in simple molecules, but these rules often fail in the following cases. In all such cases the *determination of oxidation number should be made by using the original concept of chemical bonding.*

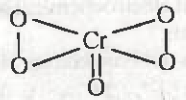
Case I. *When the given compound contains peroxide linkages besides other element-oxygen bonds.* For example,

(a) Oxidation number of Cr in CrO_5

(i) By conventional method : $\overset{x}{Cr}\,\overset{-2}{O_5}$ or $x + 5 \times (-2) = 0$ or $x = +10$ (*wrong*)

But this is wrong because the maximum O.N. of Cr cannot be more than +6 since it has 5 electrons in $3d$-orbitals and one electron in $4s$-orbital. This problem has arisen because four of the five oxygen atoms in it are present as two peroxide bonds :

(ii) By chemical bonding method : The structure of CrO_5 is



$\therefore$ O.N. of Cr in CrO_5 can be calculated as follows:

$$\underset{(\text{for Cr})}{x} + \underset{(\text{one}=\text{O})}{1 \times (-2)} + \underset{(\text{for O}-\text{O})}{4 \times (-1)} = 0 \quad \text{or} \quad x - 2 - 4 = 0 \quad \text{or} \quad x = +6$$

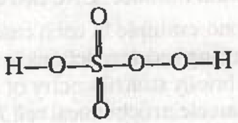
Thus, the O.N. of Cr in CrO_5 = +6

(b) Oxidation number of S in H_2SO_5 (Caro's acid or permonosulphuric acid)

(i) By conventional method : $\overset{+1}{H_2}\,\overset{x}{S}\,\overset{-2}{O_5}$ or $2 \times (+1) + x + 5 \times (-2) = 0$ or $x = +8$ (*wrong*)

But this is wrong because the maximum oxidation number of S cannot be more than +6 since it has only six electrons in its valence shell. This unusual value of O.N. for S is due to the reason that the two of the oxygen atoms in H_2SO_5 are joined by a peroxide linkage.

(ii) By chemical bonding method. The structure of H_2SO_5 is



$$\text{H—O—}\overset{\overset{\text{O}}{\|}}{\underset{\underset{\text{O}}{\|}}{\text{S}}}\text{—O—O—H}$$

$\therefore$ The O.N of S can be calculated as follows :

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

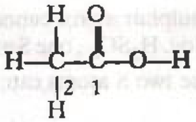
Thus, the O.N. of S in H_2SO_5 is = +6

ADDITIONAL USEFUL INFORMATION contd.

Case II. *When the compound contains covalent and coordinate covalent bonds.* To calculate the oxidation number of atoms in such molecules, the following rules are generally used.

(a) **For each covalent bond** *between two dissimilar atoms, assign an oxidation number of +1 to the less electronegative atom and —1 to the more electronegative element.*

For example, O.N. of the two carbon atoms in CH_3COOH may be calculated as follows :



$$\mathrm{H-\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}_2-\overset{O}{\overset{\|}{C}}_1-O-H}$$

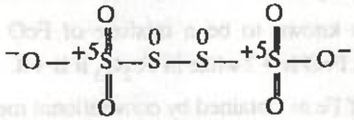
C_2 is attached to three H-atoms (less electronegative than carbon) and one —COOH group (more electronegative than carbon), therefore, O.N. of C_2 is $3 \times (+1) + x + 1 \times (-1) = 0$ or $x = -2$

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 is $+1 + x \times (-2) + 1 \times (-1) = 0$ or $x = +2$

If, however, the covalent bond is between two similar atoms or between two similar atoms which are further attached to similar species, each atom is given an O.N. of zero. For example, the central C atom in carbon suboxide (C_3O_2) has an O.N. of zero while each terminal carbon has an oxidation state of +2.

$$O = \overset{+2}{C} = \overset{0}{C} = \overset{+2}{C} = O$$

Similarly in tetrathionate ion ($S_4O_6^{2-}$), O.N. of each of the S-atoms linked with each other in the middle is zero while that of each of the reamining two S-atoms is +5.



$$^{-}O-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{\overset{+5}{S}}}}}-\overset{0}{S}-\overset{0}{S}-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{\overset{+5}{S}}}}}-O^{-}$$

(b) **In case of coordinate covalent bonds,** *two cases arise* :

(i) If a coordinate bond is formed between same atoms or dissimilar atoms but the donor atom is less electronegative than the acceptor atom, assign an oxidation number of +2 to the donor atom and —2 to the acceptor atom.

(ii) Conversely, if the donor atom is more electronegative than the acceptor atom, neglect the contribution of the coordinate bond.

The following examples will illustrate the above rules :

(c) **Oxidation number of C in $H-C \equiv N$ and $H-N \overset{\rightarrow}{\equiv} C$**

(i) By conventional method. Since there are no standard rules for determining the oxidation numbers of C and N, therefore, conventional method cannot used to calculate the O.N. of C in HCN or HNC.

(ii) By chemical bonding method. Since N is more electronegative than C, therefore, each covalent bond gives an O.N. of —1 to N. Now since there are three covalent bonds, therefore, the O.N. of N is HCN is —3.

Now, $\overset{+1}{H}\ \overset{x}{C}\ \overset{-3}{N}\quad \therefore\quad +1 + x - 3 = 0\ \text{ or }\ x = +2$

Thus, the oxidation number of C in HCN = + 2.

Oxidation number of C in $H-N \overset{\rightarrow}{\equiv} C$. Here the contribution of coordinate bond is neglected because the donor atom, *i.e.* N is more electronegative than the acceptor atom, *i.e.*, C. Thus, the O.N. of N in $H-N \overset{\rightarrow}{\equiv} C$ remains to be —3 since it has three covalent bonds. Thus,

$$\underset{\text{(for H)}}{1 \times (+1)} + \underset{\text{(for N)}}{1 \times (-3)} + \underset{\text{(for C)}}{x} = 0 \quad \text{or} \quad +1 - 3 + x = 0 \quad \text{or} \quad x = +2$$

Thus, the oxidation number of C in HNC = + 2.

ADDITIONAL USEFUL INFORMATION contd.

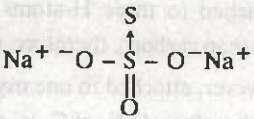
Case III. *When the compound contains two or more atoms of the same element in different oxidation states.* For example

(a) Oxidation numbers of S atoms in $Na_2S_2O_3$

(*i*) By conventional method : $\overset{+1}{Na_2}\ \overset{x}{S_2}\ \overset{-2}{O_3}$ or $2 \times (+1) + 2x + 3 \times (-2) = 0$ or $x = +2$ (*wrong*)

But this is wrong because both the sulphur atoms cannot be in the same oxidation state as is evident from the fact that when $Na_2S_2O_3$ is treated with dil. H_2SO_4, one S atom gets precipitated while the other gets converted into SO_2. The oxidation numbers of these two S atoms can, however, be determined by the chemical bonding method.

(*ii*) *By chemical bonding method.* The structure of $Na_2S_2O_3$ is



$$Na^+\ {}^-O - \overset{\overset{\displaystyle S}{\uparrow}}{\underset{\underset{\displaystyle O}{||}}{S}} - O^-Na^+$$

Since there is a coordinate bond between the two S atoms, therefore, the acceptor S atom has an O.N. of —2. The O.N. of the other S atom can be calculated as follows :

$$\underset{\text{(for Na)}}{2 \times (+1)} + \underset{\text{(for O atoms)}}{3 \times (-2)} + x + \underset{\text{(for coordinate S)}}{1 \times (-2)} = 0 \quad \text{or} \quad +2-6+x-2 = 0 \quad \text{or} \quad x = +6$$

Thus, the two S atoms in $Na_2S_2O_3$ have oxidation numbers of —2 and +6.

(b) Oxidation number of iron atoms in magnetic oxide (Fe_3O_4).

(*i*) *By conventional method.* $\overset{x}{Fe_3}\ \overset{-2}{O_4}$ or $3x - 2 \times 4 = 0$ or $x = +8/3$.

(*ii*) *By stoichiometry.* Fe_3O_4 is known to be a mixture of FeO and Fe_2O_3 having the composition : $FeO.Fe_2O_3$. Therefore, O.N. of Fe in FeO is +2 while in Fe_2O_3 it is +3.

The value of 8/3 for the O.N. of Fe as obtained by conventional method is infact the average of the actual O.N. of all the Fe atoms in the formula, *e.g.*, $(1 \times 2 + 2 \times 3)/3 = 8/3$.

(c) Oxidation number of iron in $Fe_4[Fe(CN)_6]_3$

(*i*) *By conventional method.* $\overset{x}{Fe_4}\,[\overset{x}{Fe}\,(\overset{-1}{CN})_6]_3$ or $4x + 3 \times [x + 6 \times -1] = 0$ or $x = 18/7$

(*ii*) *By stoichiometry.* From our knowledge of coordinate compounds, we know that Fe_4 is the +ve part while the complex ion, *i.e.* $[Fe(CN)_6]_3$ is –ve part. Therefore, total +ve charge on 4 Fe atoms outside the coordination sphere is balanced by total –ve charge on the complex ion. Since Fe has two oxidation states, *i.e.* +2 and +3, therefore, Fe in the complex ion has an O.N. of +2 while the Fe atoms outside the coordination sphere have an O.N. of +3 and the average value of O.N. of the Fe atoms in the molecule = $(4 \times 3 + 3 \times 2)/7 = 18/7$.

(*d*) Oxidation number of chlorine in bleaching powder, $CaOCl_2$

Average O.N. of Cl in $CaOCl_2$ is $\overset{2+}{Ca}\ \overset{-2}{O}\ \overset{x}{Cl_2}$ or $2x + 2 - 2 = 0$ or $x = 0$

(*ii*) *By stoichiometry.* The composition of bleaching powder is $Ca^{2+}(OCl^-)Cl^-$. Here O.N. of Cl in OCl^{-1} is +1 while that in Cl^- is —1 and the average of two oxidation numbers = $1 \times +1 + 1 \times -1 = 0$.

C.B.S.E.-P.M.T. (MAINS) SPECIAL

A. SUBJECTIVE QUESTIONS (Common with I.I.T.)

Q. 1. Copper dissolves in dilute nitric acid but not in dilute HCl. Explain.

Ans. Since E° of Cu^{2+}/Cu electrode (+ 0·34 V) is higher than that of H^+/H_2 electrode (0·0 V), therefore, H^+ ions cannot oxidise Cu to Cu^{2+} ions and hence Cu does not dissolve in dil. HCl. In contrast, the electrode potential of NO_3^- ion, *i.e.*, NO_3^-/NO, electrode (+ 0·97 V) is higher than that of copper electrode and hence it can oxidise Cu to Cu^{2+} ions and hence Cu dissolves in dil. HNO_3. *Thus, Cu dissolves in dil. HNO_3 due to oxidation of Cu by NO_3^- ions and not by H^+ ions.*

Q. 2. Arrange A, B, C, D, E and H in order of increasing electrode potential in the electrochemical series if

$$A + H_2SO_4 \longrightarrow ASO_4 + H_2$$
$$ACl_2 + C \longrightarrow CCl_2 + A$$
$$ECl_2 + C \longrightarrow \text{No reaction}$$
$$2\,BCl + D \longrightarrow DCl_2 + 2\,B$$
$$H_2SO_4 + D \longrightarrow \text{No reaction}$$

Ans. (*i*) Since A reacts with H_2SO_4 to liberate H_2 but D does not, therefore, *A lies above and D lies below H in the electrochemical series.*

(*ii*) Further since D displaces B from BCl, therefore, E° of D is lower than that of B, *i.e.*, D lies above B in the electrochemical series.

From (*i*) and (*ii*), the order of increasing E° of the four elements *i.e.*, A, H, D, B.

(*iii*) Since C displaces A from ACl_2 but not E from ECl_2, therefore, E° of C is lower than that of A and that of E is lower than that of C.

From (*i*), (*ii*) and (*iii*), it is evident that the *overall order of increasing electrode potentials of these five elements is : E, C, A, H, D, B.*

Q. 3. What is the difference in the definition of an equivalent in an acid-base reaction and an equivalent in an oxidation-reduction reaction ?

(B.I.T. Ranchi 1990)

Ans. *Equivalent weight in acid-base reaction* is the weight in grams which supplies or accepts one mole of H^+ ions.

Equivalent weight in oxidation-reduction reaction is the weight of the substance which gains or loses one mole of electrons.

Q. 4. Find out the ratio of equivalent weight of $H_2C_2O_4 . 2\,H_2O$ as an acid and its equivalent weight as a reductant.

(West Bengal J.E.E. 2004)

Ans. (*i*) Mol. wt. of $H_2C_2O_4 . 2\,H_2O$ (oxalic acid) = 126

$$\therefore \text{ Eq. wt. of acid} = \frac{\text{Mol. wt. of acid}}{\text{Basicity}}$$

$$= \frac{126}{2} = 63$$

(*ii*) Oxidation of oxalic acid involves $2\,e^-$ change, *i.e.*,

$$\begin{matrix} COO^- \\ | \\ COO^- \end{matrix} \longrightarrow 2\,CO_2 + 2\,e^-$$

Thus, Eq. wt. of $H_2C_2O_4 . 2\,H_2O$

$$= \frac{\text{Mol. wt.}}{\text{No. of electrons lost}}$$

$$= \frac{126}{2} = 63{\cdot}0$$

∴ Ratio of Eq. wt. of oxalic acid as an acid to its Eq. wt. as a reductant is 63/63 = 1.

Q. 5. How does Cu_2O act as both oxidant and reductant ? Explain with proper reactions showing the change of oxidation numbers in each example. ***(West Bengal J.E.E. 2004)***

Ans. Cu_2O undergoes disproportionation to form Cu^{2+} and Cu.

$$2\,Cu^+\,(aq) \rightleftharpoons Cu^{2+}\,(aq) + Cu\,(s)$$

Thus, Cu^+ or Cu_2O acts both as an oxidant as well as a reductant

(*i*) When heated in air, Cu_2O is oxidised to CuO

$$\overset{+1}{CuO} + 1/2\,O_2 \longrightarrow 2\,\overset{+2}{CuO}$$

and Cu_2O acts as a reductant and reduces O_2 to O^{2-}.

(*ii*) When heated with Cu_2S, *it oxidises S^{2-} to SO_2 and hence Cu_2O acts as an oxidant*

$$2\,\overset{+1}{Cu_2O} + \overset{+1}{Cu_2S} \longrightarrow 6\,\overset{0}{Cu} + SO_2$$

Q. 6. **Balance the following equations by oxidation number method :**

(i) $S + HNO_3 \longrightarrow SO_2 + NO_2 + H_2O$

(ii) $P_4 + NaOH + H_2O \longrightarrow PH_3 + NaH_2PO_2$.

(West Bengal J.E.E. 2004)

Ans. (*i*) $S + 4\,HNO_3 \longrightarrow SO_2 + 4\,NO_2 + 2\,H_2O$

(*ii*) $P_4 + 3NaOH + 3H_2O \longrightarrow PH_3 + 3\,NaH_2PO_2$

B. PROBLEMS

Problem 1. **6·70 *g* of an alkali metal oxalate was dissolved per litre of the solution. 10 cm³ of this solution required 20 cm³ of 0·01 M potassium permanganate solution in acidic medium. What is the atomic weight of the alkali metal.**

Solution. The balanced chemical equation for the redox reaction is

$$2\,KMnO_4 + 5\,(COOM)_2 + 8\,H_2SO_4 \longrightarrow K_2SO_4 + 2\,MnSO_4 + 5\,M_2SO_4 + 10\,CO_2 + 8\,H_2O$$

where M is the alkali metal

Let M_1 be the molarity of the alkali metal oxalate solution. Applying molarity equation, we have,

$$\frac{M_1 \times 10}{5} = \frac{20 \times 0\cdot01}{2} \text{ or } M_1 = 0\cdot05\text{ M}$$

Let A be the atomic weight of the alkali metal.

∴ Mol. wt. of $(COOM)_2 = 2\,A + 88$

Thus, amount of metal oxalate present per litre of the solution $= (2\,A + 88) \times 0\cdot05\ g$

But the amount of alkali metal oxalate solution

$= 6\cdot7\ g\ L^{-1}$ (*given*)

∴ $(2\,A + 88) \times 0\cdot05 = 6\cdot7$ or $A = 23$

Problem 2. **1·5 *g* of pyrolusite ore were treated with 10 g of Mohr's salt and dilute H_2SO_4. After the reaction, the solution was diluted to 250 cm³. 50 cm³ of diluted solution required 10 cm³ of 0·1 N $K_2Cr_2O_7$ solution. Find out percentage of pure MnO_2 in pyrolusite.**

Solution. Pure MnO_2 present in pyrolusite oxidises Fe^{2+} of Mohr's salt $((NH_4)_2SO_4 \cdot FeSO_4 \cdot 6\,H_2O)$ to Fe^{3+}. Unreacted Fe^{2+} of Mohr's salt is determined by $K_2Cr_2O_7$.

Chemical equations are :

$$MnO_2 + 2\,Fe^{2+} + 4\,H^+ \longrightarrow Mn^{2+} + 2\,Fe^{3+} + 2\,H_2O$$

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

Step 1. To determine unreacted Mohr's salt.

50 cm³ of diluted Mohr's salt

$\equiv 10\text{ cm}^3$ of $0\cdot1$ N $K_2Cr_2O_7$

∴ Normality of diluted solution $= 0\cdot02$ N

Mol. wt. of Mohr's salt = 392

∴ Amount of unreacted Mohr's salt present in 250 cm³ solution

$$= \frac{0\cdot02 \times 392}{4} = 1\cdot96\ g$$

Amount of Mohr's salt used $= 10 - 1\cdot96 = 8\cdot04\ g$

From balanced equation,

2 Moles of Mohr's salt (*i.e.* $2 \times 392\ g$) react with one mole of $MnO_2 = 87\ g$

∴ $8\cdot04\ g$ of Mohr's salt will react with MnO_2

$$= \frac{87}{2 \times 392} \times 8\cdot04\ g = 0\cdot892\ g$$

Now $0\cdot892\ g$ of pure MnO_2 are present in $1\cdot5\ g$ of pyrolusite

∴ %age of MnO_2 in pyrolusite $= \dfrac{0\cdot0892}{1\cdot5} \times 100$

$= 59\cdot48\%$

Problem 3. **25 cm³ of a solution containing ferrous sulphate and ferric sulphate acidified with H_2SO_4 is reduced by metallic zinc. The solution required 34·25 cm³ of 0·1 N $K_2Cr_2O_7$ solution for oxidation. However, before reduction with zinc, 25 cm³ of the same solution required 22·45 cm³ of the same $K_2Cr_2O_7$ solution. Calculate the amount of ferrous sulphate and ferric sulphate present per litre of the solution.**

Solution. Titration before reduction gives only $FeSO_4$. After reduction, $Fe_2(SO_4)_3$ is also reduced to $FeSO_4$ and titration gives total concentration of $FeSO_4$ and $Fe_2(SO_4)_3$.

Milliequivalents of $K_2Cr_2O_7$ used after reduction

$=$ volume × normality $= 34\cdot25 \times 0\cdot1$

$= 3\cdot425$

Milliequivalents of $K_2Cr_2O_7$ used before reduction

$= 22\cdot45 \times 0\cdot1 = 2\cdot245$

∴ Milliequivalents of $FeSO_4$ in 25 cm³ $= 2\cdot245$

and milliequivalents of $Fe_2(SO_4)_3$ in 25 cm³

$= 3\cdot425 — 2\cdot245 = 1\cdot180$

Now Eq. wt. of $FeSO_4 = 152/1 = 152$

Eq. wt. of $Fe_2(SO_4)_3$ = 400/2 = 200

Hence $FeSO_4\ (g\ L^{-1}) = \dfrac{2\cdot245}{1000} \times 152 \times \dfrac{1000}{25}$

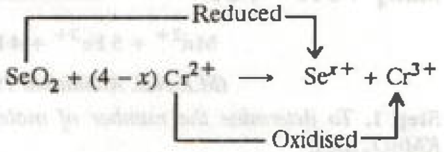
$= 13\cdot65$

$Fe_2(SO_4)_3\ (g\ L^{-1}) = \dfrac{1\cdot180}{1000} \times 200 \times \dfrac{1000}{25}$

$= 9\cdot44.$

Problem 4. **12·53 cm³ of 0·051 M SeO_2 reacts exactly with 25·5 cm³ of 0·1 M $CrSO_4$ which is oxidised to $Cr_2(SO_4)_3$. To what oxidation state is the selenium converted during the reaction ?**

Solution. Let O.N. of Se in the new compound = x



Now 12·53 cm³ of 0·051 M SeO_2

$= 12\cdot53 \times 0\cdot051$

$= 0\cdot64$ millimoles of SeO_2

and 25·5 cm³ of 0·1 M $CrSO_4 = 25\cdot5 \times 0\cdot1$

$= 2\cdot55$ millimoles of $CrSO_4$

But according to balanced redox equation, $(4-x)$ moles of $CrSO_4$ reduce 1 mole of SeO_2

$\therefore$ 2·55 millimoles of $CrSO_4$ will reduce SeO_2

$= \dfrac{2\cdot55}{(4-x)}$ millimoles

But SeO_2 actually reduced = 0·64 millimoles

Equating these two values, we have,

$\dfrac{2\cdot55}{4-x} = 0\cdot64$ or $\boldsymbol{x = 0}$

Problem 5. **1·1 g of a sample of copper ore is dissolved and Cu^{2+} *(aq)* is treated with KI. The iodine thus liberated required 12·12 cm³ of 0·1 M $Na_2S_2O_3$ solution for titration. What is the percentage of copper in the ore ?**

Solution. The complete balanced equation for the redox reactions is

$$2\,Cu^{2+} + 4\,I^- + 2\,S_2O_3^{2-} \longrightarrow Cu_2I_2 + S_4O_6^{2-} + 2\,I^-$$

No. of moles of $S_2O_3^{2-}$ used $= \dfrac{12\cdot12}{1000} \times 0\cdot1$

$= 1\cdot212 \times 10^{-3}$ moles

From the balanced equation,

2 moles of $S_2O_3^{2-}$ reduce Cu^{2+} = 2 moles

$\therefore$ $1\cdot212 \times 10^{-3}$ moles of $S_2O_3^{2-}$ will reduce

$Cu^{2+} = 1\cdot212 \times 10^{-3}$ moles

$\therefore$ Wt. of pure Cu present in the ore

$= 1\cdot212 \times 10^{-3} \times 63\cdot5 = 0\cdot077\ g$

Thus, %age of Cu in the ore $= \dfrac{0\cdot077}{1\cdot1} \times 100$

$= 7\%$

I.I.T. (MAINS) SPECIAL

Q. 1. **5·0 g of a sample of brass were dissolved in 1 litre dil. H_2SO_4. 20 cm³ of this solution were mixed with KI and liberated iodine required 20 cm³ of 0·0327 M hypo solution for titration. Calculate the percentage of copper in the alloy.**

Ans. Brass is an alloy of Cu and Zn. When brass is treated with dil. H_2SO_4 in presence of air, $CuSO_4$ and $ZnSO_4$ are obtained according to the following equations :

$$2\,Cu + 2\,H_2SO_4 + O_2 \longrightarrow 2\,CuSO_4 + 2\,H_2O$$
$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$

Out of $CuSO_4$ and $ZnSO_4$, only $CuSO_4$ reacts with KI to form I_2 which can be titrated against hypo solution. The complete balanced equation for the redox reactions is

$$2\,CuSO_4 + 4\,KI \longrightarrow 2\,K_2SO_4 + 2\,CuI_2$$
$$2\,CuI_2 \longrightarrow Cu_2I_2 + I_2$$
$$I_2 + 2\,Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2\,NaI$$
$$2\,CuSO_4 + 4\,KI + 2\,Na_2S_2O_3 \longrightarrow Cu_2I_2 + K_2SO_4 + Na_2S_4O_6 + 2\,NaI$$

Step 1. ***To find out the molarity of $CuSO_4$ solution***

Let the molarity of $CuSO_4$ soln. = M_1

Applying molarity equation,

$$\frac{M_1V_1}{2}\ (CuSO_4) = \frac{M_2V_2}{2}\ (Na_2S_2O_3)$$

or $M_1 \times 20 = 0{\cdot}0327 \times 20$ or $M_1 = 0{\cdot}0327$

Step 2. *To find out the percentage of copper in the alloy*

Volume of alloy solution = 1000 cm^3

Molarity of alloy solution *w.r.t.* Cu^{2+}

$= 0{\cdot}0327$ M

But At. wt. of Cu = 63·5

∴ Amount of Cu^{2+} formed

$= 0{\cdot}0327 \times 63{\cdot}5 = 2{\cdot}076\ g$

But the amount of Cu^{2+} ions in solution is equal to the amount of Cu in the alloy.

∴ Amount of copper in the alloy = 2·076 *g*

But the amount of alloy (brass) taken = 5·0 *g*

∴ % of copper in the alloy

$$= \frac{2{\cdot}076}{5} \times 100 = 41{\cdot}52\%$$

Thus, the percentage of copper in the alloy

= 41·52%

Q. 2. **In an ore, the only oxidisable material is Sn^{2+}. This ore is titrated with a dichromate solution containing 2·5 *g* of $K_2Cr_2O_7$ in 0·50 litre. The 0·40 *g* sample of the ore required 10·0 cm^3 of titrant to reach equivalent point. Calculate the percentage of tin in the ore. (K = 39·1, Cr = 52, Sn = 118·7)** ***(Roorkee 1993)***

Ans. Wt. of $K_2Cr_2O_7$ present in 500 cm^3 = 2·5 *g*

∴ Wt. of $K_2Cr_2O_7$ present in 10 cm^3

$$= \frac{2{\cdot}5}{500} \times 10\ g$$

Mol. wt. of $K_2Cr_2O_7$ = 294

∴ No. of moles of $K_2Cr_2O_7$ present in 10 cm^3

solution $= \dfrac{2{\cdot}5 \times 10}{500 \times 294} = 0{\cdot}00017$

The balanced chemical equation for the redox reaction is :

$$Cr_2O_7^{2-} + 14\,H^+ + 3\,Sn^{2+} \longrightarrow 2\,Cr^{3+} + 3\,Sn^{4+} + 7\,H_2O$$

From the above balanced equation,

$$Cr_2O_7^{2-} \equiv K_2Cr_2O_7 \equiv 3\,Sn^{2+}$$

i.e., 1 mole $K_2Cr_2O_7^{2-}$ oxidises Sn^{2+} = 3 moles

∴ 0·00017 mole $K_2Cr_2O_7$ will oxidise Sn^{2+}

$= 3 \times 0{\cdot}00017 = 0{\cdot}00051$ mole

∴ Amount of Sn^{2+} oxidised $= 118{\cdot}7 \times 0{\cdot}00051$

$= 0{\cdot}06\ g$

∴ %age of Sn in the ore $= \dfrac{0{\cdot}06}{0{\cdot}40} \times 100 = 15$

Q. 3. **A sample of hydrazine sulphate ($N_2H_6SO_4$) was dissolved in 250 ml of water. 10 ml of this solution was reacted with excess of ferric chloride solution and warmed to complete the reaction. Ferrous ion formed was estimated and it required 10 ml of M/25 potassium permanganate solution. Estimate the amount of hydrazine sulphate dissolved in 250 ml of this solution**

$$4\,Fe^{3+} + N_2H_4 \longrightarrow N_2 + 4\,Fe^{2+} + 4\,H^+$$

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

(M.L.N.R. Allahabad 1993)

Ans. Step 1. *To determine the number of moles of $KMnO_4$ used.*

We are given 10 ml of $N_2H_6SO_4$ sol.

≡ 10 ml of M/25 $KMnO_4$ sol.

∴ 250 ml of $N_2H_6SO_4$ sol

≡ 250 ml of M/25 $KMnO_4$

$$= \frac{1}{25} \times \frac{1}{1000} \times 250 \text{ moles of } KMnO_4$$

= 0·01 mole of $KMnO_4$

Step 2. *To find out the amount of $N_2H_6SO_4$*

Multiplying first Eq. given in the question with 5 and second Eq. with 4 to cancel Fe^{2+} and then on adding, we get,

$$4\,MnO_4^- + 5\,N_2H_4 + 12\,H^+ \longrightarrow \text{Products}$$

Thus 4 moles of $KMnO_4$ react with 5 moles of $N_2H_6SO_4$

∴ 0·01 mole $KMnO_4$ will react with $N_2H_6SO_4$

$= \dfrac{5}{4} \times 0{\cdot}01$ mole $= 0{\cdot}0125$ mole

$= 0{\cdot}0125 \times 130\ g$ (Mol. wt. of $N_2H_6SO_4$ = 130)

= 1·625 *g*

Q. 4. **0·5 g sample containing MnO_2 is treated with HCl liberating Cl_2. The chlorine is passed into a solution of KI and 30·0 cm^3 of 0·01 M $Na_2S_2O_3$ are required to titrate the liberated iodine. Calculate the percentage of MnO_2 in the sample (At. wt. of Mn = 55).** ***(Roorkee 1994)***

Ans. **Step 1.** *To write the complete equation for the redox reactions*

$$MnO_2 + 4\,HCl \longrightarrow MnCl_2 + Cl_2 + 2\,H_2O$$

$$2\,KI + Cl_2 \longrightarrow 2\,KCl + I_2$$

$$I_2 + 2\,Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2\,NaI$$

$$MnO_2 + 4\,HCl + 2\,KI + 2\,Na_2S_2O_3 \longrightarrow MnCl_2 + 2\,KCl + Na_2S_4O_6 + 2\,NaI + 2\,H_2O$$

Step 2. *To calculate the percentage of MnO_2 in the sample*

No. of moles of $Na_2S_2O_3$ present in 30 cm³ of 0·1 M $Na_2S_2O_3$ solution

$$= \frac{30}{1000} \times 0\cdot1 = 0\cdot003 \text{ mole}$$

From the balanced equation, it is evident that,

2 moles of $Na_2S_2O_3$ = 1 mole of MnO_2

$\therefore$ 0·003 mole of $Na_2S_2O_3$

$$= \frac{1}{2} \times 0\cdot003 = 0\cdot0015 \text{ mole } MnO_2$$

Now Mol. wt. of $MnO_2 = 55 + 2 \times 16 = 87$

$\therefore$ Wt. of MnO_2 reacted = Moles × Mol. wt.

$$= 0\cdot0015 \times 87 = 0\cdot1305 \text{ g}$$

%age of MnO_2 in the sample

$$= \frac{0\cdot1305}{0\cdot5} \times 100 = 26\cdot1\%.$$

Q.5. **0·5 g mixture of $K_2Cr_2O_7$ and $KMnO_4$ was treated with excess KI in acidic medium. Iodine liberated required 100 cm³ of 0·15 N sodium thiosulphate solution for titration. Find the percent amount of each in the mixture (At. wts. K = 39, Cr = 52, Mn = 55, Na = 23 S = 32)** *(Roorkee 1995)*

Ans. The reactions involved are :

$$\underset{294\text{ g}}{K_2Cr_2O_7} + 7\,H_2SO_4 + 6\,KI \longrightarrow 4\,K_2SO_4 + Cr_2(SO_4)_3 + 7\,H_2O + \underset{\substack{3\times254\\=762\text{ g}}}{3\,I_2} \qquad ...(i)$$

$$\underset{\substack{2\times158\\=316\text{ g}}}{2\,KMnO_4} + 3\,H_2SO_4 + 10\,KI \longrightarrow K_2SO_4 + 2\,MnSO_4 + 8\,H_2O + \underset{\substack{5\times254\\=1270\text{ g}}}{5\,I_2} \qquad ...(ii)$$

$$2\,Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2\,NaI$$

Suppose weight of $K_2Cr_2O_7$ in the mixture = x g

Then weight of $KMnO_4$ in the mixture

$$= (0\cdot5 - x)\,g$$

Iodine produced from x g $K_2Cr_2O_7 = \frac{762}{294} \times x\,g$

Iodine produced from $(0\cdot5 - x)$ g $KMnO_4$

$$= \frac{1270}{316} \times (0\cdot5 - x)\,g$$

Total iodine produced

$$= \frac{762\,x}{294} + \frac{1270\,(0\cdot5 - x)}{316}\,g$$

100 cc of 0·15 N $Na_2S_2O_3$

$$= 100 \text{ cc of } 0\cdot15 \text{ N } I_2 \text{ solution}$$

$$= \frac{127 \times 0\cdot15}{1000} \times 100\,g = 1\cdot905\,g$$

Hence $\frac{762x}{294} + \frac{1270\,(0\cdot5 - x)}{316} = 1\cdot905$

which on solving gives $x = 0\cdot073\,g$

$\therefore$ % age of $K_2Cr_2O_7$ in the mixture

$$= \frac{0\cdot073}{0\cdot5} \times 100 = \mathbf{14\cdot6\%}$$

and % age of $KMnO_4$ in the mixture

$$= 100 - 14\cdot6 = \mathbf{85\cdot4\%}$$

Q. 6. **A 3·0 g sample containing Fe_3O_4, Fe_2O_3 and an inert impure substance, is treated with excess of KI solution in presence of dilute H_2SO_4. The entire iron is converted into Fe^{2+} alongwith liberation of iodine. The resulting solution is diluted to 100 ml. A 20 ml of the diluted solution requires 11·0 ml of 0·5 M $Na_2S_2O_3$ solution to reduce the iodine present. A 50 ml of the diluted solution after complete extraction of the iodine requires 12·80 ml of 0·25 M $KMnO_4$ solution in dilute H_2SO_4 medium for the oxidation of Fe^{2+}. Calculate the percentages of Fe_2O_3 and Fe_3O_4 in the original sample.** *(I.I.T. 1996)*

Ans. Fe_3O_4 is an equimolar mixture of FeO and Fe_2O_3

The reactions involved are :

(*i*) $FeO + H_2SO_4 \longrightarrow FeSO_4 + H_2O$

(*ii*) $Fe_2O_3 + 2\,H_2SO_4 \longrightarrow 2\,FeSO_4 + 2\,H_2O + (O)$

$$2\,KI + H_2SO_4 \longrightarrow K_2SO_4 + 2\,HI$$

$$2\,HI + (O) \longrightarrow H_2O + I_2$$

$$Fe_2O_3 + 3\,H_2SO_4 + 2\,KI \longrightarrow 2\,FeSO_4 + K_2SO_4 + 3\,H_2O + I_2$$

(*iii*) $2\,Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2\,NaI$

(*iv*) $2\,KMnO_4 + 3\,H_2SO_4 \longrightarrow$

$$K_2SO_4 + 2\,MnSO_4 + 3\,H_2O + 5\,(O)$$

$2\,FeSO_4 + H_2SO_4 + (O) \longrightarrow$

$$Fe_2(SO_4)_3 + H_2O] \times 5$$

$2\,KMnO_4 + 8\,H_2SO_4 + 10\,FeSO_4 \longrightarrow$

$$K_2SO_4 + 2\,MnSO_4 + Fe_2(SO_4)_3 + 8\,H_2O$$

Resulting solution containing $I_2 + Fe^{2+}$ after dilution = 100 ml

20 ml of diluted solution = 11·0 ml of 0·5 M $Na_2S_2O_3$

∴ 100 ml of diluted solution

$= 55{\cdot}0$ ml of 0·5 M $Na_2S_2O_3$

$= \frac{0{\cdot}5}{1000} \times 55 = 0{\cdot}0275$ mole $Na_2S_2O_3$

$= \frac{0{\cdot}0275}{2} = 0{\cdot}01375$ moles I_2

$= 0{\cdot}01375$ mole Fe_2O_3

Again, 50 ml of diluted solution

$= 12{\cdot}80$ ml of 0·25 M $KMnO_4$

∴ 100 ml of diluted solution

$= \frac{0{\cdot}25}{1000} \times 25{\cdot}60 = 0{\cdot}0064$ mole $KMnO_4$

$= 5 \times 0{\cdot}0064 = 0{\cdot}032$ mole $FeSO_4$

Thus 0·032 mole $FeSO_4$ has been obtained from 0·01375 mole Fe_2O_3 and the remaining from FeO.

As 1 mole Fe_2O_3 = 2 moles $FeSO_4$

∴ 0·01375 mole $Fe_2O_3 = 2 \times 0{\cdot}01375$ moles $FeSO_4 = 0{\cdot}0275$ mole $FeSO_4$

∴ $FeSO_4$ formed from

FeO $= 0{\cdot}032 - 0{\cdot}0275$

$= 0{\cdot}0045$ mole

But 1 mole $FeSO_4$ = 1 mole FeO

∴ 0·0045 mole $FeSO_4$ = 0·0045 mole FeO

As Fe_3O_4 contains equal moles of FeO and Fe_2O_3

∴ Fe_2O_3 present in Fe_3O_4 = 0·0045 mole

∴ Free Fe_2O_3 present in the mixture

$= 0{\cdot}01375 - 0{\cdot}0045$ mole

$= 0{\cdot}00925$ mole

Thus in the mixture

$Fe_3O_4 = 0{\cdot}0045$ mole $232 \times 0{\cdot}0045 = 1{\cdot}044\,g$

$Fe_2O_3 = 0{\cdot}00925$ mole $160 \times 0{\cdot}00925 = 1{\cdot}48\,g$

∴ % age of Fe_3O_4 in the mixture

$= \frac{1{\cdot}044}{3} \times 100 = 34{\cdot}8\%$

% age of Fe_2O_3 in the mixture

$= \frac{1{\cdot}48}{3} \times 100 = 49{\cdot}33\%$

Q. 7. **One litre of a mixture of O_2 and O_3 at NTP was allowed to react with an excess of acidified solution of KI. The iodine liberated required 40 ml of M/10 sodium thiosulphate solution for titration. What is the weight percent of ozone in the mixture ? Ultraviolet radiations of wavelength 300 nm can decompose ozone. Assuming that one photon can decompose one ozone molecule, how many photons would have been required for the complete decomposition of ozone in the original mixture ?** *(I.I.T. 1997)*

Ans. $O_3 \longrightarrow O_2 + O$

$2\,KI + H_2SO_4 + (O) \longrightarrow K_2SO_4 + H_2O + I_2$

$2\,Na_2SO_3 + I_2 \longrightarrow Na_2S_4O_6 + 2\,NaI$

$2\,Na_2S_2O_3 + 2\,KI + O_3 + H_2SO_4 \longrightarrow$

$$O_2 + K_2SO_4 + H_2O + Na_2S_4O_6 + 2\,NaI$$

2 moles of $Na_2S_2O_3$ react with one mole of O_3

No. of moles of $Na_2S_2O_3$ in 40 ml of $\frac{M}{10}$ $Na_2S_2O_3$

$= \frac{1}{10} \times \frac{1}{1000} \times 40 = 4 \times 10^{-3}$ mole

∴ O_3 reacted (present) $= 2 \times 10^{-3}$ mole

(∵ 2 mole $Na_2S_2O_3 \equiv 1$ mole O_3)

Volume of $O_3 = 2 \times 10^{-3} \times 22{\cdot}4$ L

$= 0{\cdot}0448$ L

∴ Volume of $O_2 = 1 - 0{\cdot}0448 = 0{\cdot}9552$ L

Weight of $O_3 = 2 \times 10^{-3} \times 48 = 0{\cdot}096$ g

Weight of $O_2 = \frac{0{\cdot}9552}{22{\cdot}4} \times 32 = 1{\cdot}3646$ g

∴ Weight of mixture

$= 0{\cdot}096 + 1{\cdot}3646 = 1{\cdot}4606$ g

$\therefore$ % of O_3 by weight

$$= \frac{0 \cdot 096}{1 \cdot 4606} \times 100 = 6 \cdot 573\%$$

No. of molecules in 2×10^{-3} mole of O_3

$$= 2 \times 10^{-3} \times 6 \cdot 022 \times 10^{23}$$

$$= 1 \cdot 2044 \times 10^{21}$$

$\therefore$ No. of photons required $= 1 \cdot 2044 \times 10^{21}$

Q. 8. An aqueous solution of 0·10 g KIO_3 (formula weight = 214·0) was treated with an excess of KI solution. The solution was acidified with HCl. The liberated I_2 consumed 45·0 ml of thiosulphate solution to decolourise the blue starch iodine complex. Calculate the molarity of sodium thiosulphate solution. *(I.I.T. 1998)*

Ans. The reactions involved are :

$$2IO_3^- + 12H^+ + 10e^- \longrightarrow 6\,H_2O + I_2$$

$$10\,I^- \longrightarrow 5\,I_2 + 10\,e^-$$

$$2\,IO_3^- + 12\,H^+ + 10\,I^- \longrightarrow 6\,I_2 + 6\,H_2O$$

$$2\,S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2\,I^-] \times 6$$

$$2\,IO_3^- + 12\,H^+ + 12\,S_2O_3^{2-} \longrightarrow 6\,S_4O_6^{2-} + 2\,I^- + 6\,H_2O$$

No. of moles of $KIO_3 = \frac{0 \cdot 1}{214}$

No. of moles of $Na_2S_2O_3$ reacted $= \frac{0 \cdot 1}{214} \times 6$, which are present in 45·0 ml.

Hence molarity of $Na_2S_2O_3$ sol.

$$= \frac{0 \cdot 1 \times 6}{214} \times \frac{1000}{45}$$

$$= 0 \cdot 0623\ \text{M}.$$

MULTIPLE CHOICE QUESTIONS

For CBSE– PMT (Preliminary), IIT Screening, AIEEE, AIIMS, AFMC, DPMT, CPMT, BHU and All Other Competitive Examinations

1. Oxidation number of sodium in sodium amalgam is

(*a*) +1 (*b*) 0

(*c*) –1 (*d*) + 2.

2. For the reaction,

$$M^{x+} + MnO_4^- \longrightarrow MO_3^- + Mn^{2+} + 1/2\,O_2$$

if one mole of MnO_4^- oxidises 1·67 moles of M^{x+} to MO_3^-, then the value of x in the reaction is

(*a*) 5 (*b*) 3

(*c*) 2 (*d*) 1.

3. The oxidation number of phosphorus in $Ba(H_2PO_2)_2$ is

(*a*) + 3 (*b*) + 2

(*c*) + 1 (*d*) – 1. *(I.I.T. 1990)*

4. For the redox reaction,

$$MnO_4^- + C_2O_4^{2-} + H^+ \longrightarrow Mn^{2+} + CO_2 + H_2O$$

the correct coefficients of the reactants for the balanced reaction are :

	MnO_4^-	$C_2O_4^{2-}$	H^+
(*a*)	2	5	16
(*b*)	16	5	2
(*c*)	5	16	2
(*d*)	2	16	5

(I.I.T. 1992)

5. If a half cell reaction, $A + e^- \longrightarrow A^-$ has a large negative reduction potential, it follows that

(*a*) A is easily reduced

(*b*) A is readily oxidised

(*c*) A^- is readily reduced

(*d*) A^- is readily oxidised. *(M.L.N.R. Allahabad 1992)*

6. The oxidation state of chromium in $Cr(CO)_6$ is

(*a*) 0 (*b*) +2

(*c*) –2 (*d*) +6. *(A.I.I.M.S. 1993)*

7. Which of the following *is not* a redox reaction ?

(*a*) $CaCO_3 \rightarrow CaO + CO_2$

(*b*) $O_2 + 2H_2 \rightarrow 2H_2O$

(*c*) $Na + H_2O \rightarrow NaOH + 1/2\,H_2$

(*d*) $MnCl_3 \rightarrow MnCl_2 + 1/2\,Cl_2$ *(A.I.I.M.S. 1993)*

ANSWERS

1. *b* 2. *c* 3. *c* 4. *a* 5. *d* 6. *a* 7. *a*

8. A mole of N_2H_4 loses ten moles of electrons to form a new compound Y. Assuming that all the nitrogen appears in the new compound, what is the oxidation state of nitrogen in Y ? (there is no change in the oxidation number of hydrogen)

(*a*) –1 (*b*) –3
(*c*) +3 (*d*) +5. *(B.H.U. 1994)*

9. When copper is treated with a certain concentration of nitric acid, nitric oxide and nitrogen dioxide are liberated in equal volumes according to the equation,

$x\,Cu + y\,HNO_3 \longrightarrow Cu(NO_3)_2 + NO + NO_2 + H_2O.$

The coefficients of *x* and *y* are

(*a*) 2 and 3 [✓ (*b*) 2 and 6]
(*c*) 1 and 3 (*d*) 3 and 8. *(C.B.S.E. P.M.T. 1994)*

10. In which of the following pairs, there is greatest difference in the oxidation number of the underlined elements ?

(*a*) $\underline{N}O_2$ and $\underline{N}_2O_4$ (*b*) $\underline{P}_2O_5$ and $\underline{P}_4O_{10}$
(*c*) $\underline{N}_2O$ and $\underline{N}O$ [✓ (*d*) $\underline{S}O_2$ and $\underline{S}O_3$.] *(D.C.E. 1994)*

11. In the reaction,

$2FeCl_3 + H_2S \longrightarrow 2FeCl_2 + 2HCl + S$

[✓ (*a*) $FeCl_3$ acts as an oxidizing agent]
(*b*) Both H_2S and $FeCl_3$ are oxidized.
(*c*) $FeCl_3$ is oxidised while H_2S is reduced
(*d*) H_2S acts as an oxidizing agent. *(U.P. S.E.A.T. 1996)*

12. Number of moles of $KMnO_4$ required to oxidise one mole of $Fe(C_2O_4)$ in acidic medium is

(*a*) 0·6 (*b*) 1·67
(*c*) 0·2 (*d*) 0·4 *(Haryana C.E.E.T. 1996)*

13. In the reaction,

$3Br_2 + 6CO_3^{2-} + 3H_2O \longrightarrow 5Br^- + BrO_3^- + 6HCO_3^-$

(*a*) Bromine is oxidised and carbonate is reduced
(*b*) Bromine is reduced and water is oxidised
(*c*) Bromine is neither reduced nor oxidised
[✓ (*d*) Bromine is both reduced and oxidised.] *(I.I.T. 1996)*

14. A standard hydrogen electrode has zero electrode potential because

(*a*) hydrogen is easiest to oxidize
[✓ (*b*) this electrode potential is assumed to be zero]
(*c*) hydrogen atom has only one electron
(*d*) hydrogen is the lighest element. *(I.I.T. 1997)*

15. Which of the following is a redox reaction ?

(*a*) H_2SO_4 with NaOH
(*b*) In atmosphere, O_3 from O_2 by lightning
[✓ (*c*) Nitrogen oxides from nitrogen and oxygen by lightning]
(*d*) Evaporation of H_2O. *(C.B.S.E. P.M.T. 1997)*

16. The oxidation potentials of A and B are +2·37 V and +1·66 V respectively. In a chemical reaction,

(*a*) A will be replaced by B
[✓ (*b*) A will replace B]
(*c*) A will not replace B
(*d*) A and B will not replace each other. *(U.P.S.E.A.T. 1996 ; Pb.C.E.T. 1997)*

17. Which among the following is the strongest reducing agent ?

Given, $Fe^{2+} + 2e^- \longrightarrow Fe\ (-0{\cdot}44\,V)$;
$Ni^{2+} + 2e^- \longrightarrow Ni\ (-0{\cdot}25\,V)$;
$Sn^{2} + 2e^- \longrightarrow Sn\ (-0{\cdot}14\,V)$ and
$Fe^{3+} + e^- \longrightarrow Fe^{2+}\ (-0{\cdot}77\,V)$

(*a*) Fe [✓ (*b*) Fe^{2+}]
(*c*) Ni (*d*) Sn *(B.H.U. 1998)*

18. Without losing its concentration, $ZnCl_2$ solution cannot be kept in contact with

(*a*) Au [✓ (*b*) Al]
(*c*) Pb (*d*) Ag. *(C.B.S.E. P.M.T. 1998)*

19. The standard reduction potential values of three metallic cations, X, Y, Z are 0·52, –3·03 and –1·18 V respecively. The order of reducing power of the corresponding metal is

[✓ (*a*) Y > Z > X] (*b*) X > Y > Z
(*c*) Z > Y > X (*d*) Z > X > Y. *(I.I.T. 1998)*

20. The oxidation number of sulphur in S_8, S_2F_2, H_2S respectively, are

[✓ (*a*) 0, + 1 and –2] (*b*) + 2, +1 and –2
(*c*) 0, +1 and + 2 (*d*) –2, + 1 and –2. *(I.I.T. 1999)*

ANSWERS

8. *c*	9. *b*	10. *d*	11. *a*	12. *a*	13. *d*	14. *b*	15. *c*	16. *b*	17. *b*
18. *b*	19. *a*	20. *a*							

21. A gas at 1 atm is bubbled through a solution containing a mixture of 1 M Y^- and 1 M Z^- at 25°C. If the reduction potential of Z > Y > X, then

(*a*) Y will oxidize X and not Z
(*b*) Y will oxidize Z and not X
(*c*) Y will oxidize both X and Z
(*d*) Y will reduce both X and Z. *(I.I.T. 1999)*

22. A metal ion M^{3+} loses 3 electrons, its oxidation number will be

(*a*) +3 (*b*) + 6
(*c*) 0 (*d*) –3 *(C.P.M.T. 1999)*

23. To an acid solution of an anion, a few drops of $KMnO_4$ solution are added. Which of the following, if present, will not decolourise the $KMnO_4$ solution ?

(*a*) CO_3^{2-} (*b*) NO_2^-
(*c*) S^{2-} (*d*) Cl^- *(D.C.E. 1999)*

24. The partial ionic equation,

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

suggests that the equivalent weight of $Cr_2O_7^{2-}$ will be equal to its formula weight divided by

(*a*) 3 (*b*) 6
(*c*) 1 (*d*) 14. *(D.C.E. 1999)*

25. Oxidation state of osmium (Os) in OsO_4 is

(*a*) + 7 (*b*) + 6
(*c*) + 4 (*d*) + 8. *(A.I.I.M.S. 1999)*

26. Fluorine is the best oxidising agent because it has

(*a*) highest electron affinity
(*b*) highest $E°_{reduction}$
(*c*) highest $E°_{oxidation}$
(*d*) lowest electron affinity. *(Haryana C.E.E.T. 1999)*

27. A compound contains atoms of three elements — A, B and C. If the oxidation number of A is + 2, B is + 5 and that of C is – 2, the possible formula of the compound is

(*a*) $A_3(BC_4)_2$ (*b*) $A_3(B_4C)_2$
(*c*) ABC_2 (*d*) $A_3(BC_3)_2$. *(C.B.S.E. P.M.T. 2000)*

28. In the given reaction,

$$K_2Cr_2O_7 + XH_2SO_4 + YSO_2 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + ZH_2O$$

X, Y, Z are

(*a*) 1, 3, 1 (*b*) 4, 1, 4
(*c*) 3, 2, 3 (*d*) 2, 1, 2. *(B.H.U. 1994, 2000)*

29. The oxidation number of iron is Fe_3O_4 is

(*a*) + 2 (*b*) + 3
(*c*) 8/3 (*d*) 2/3. *(C.B.S.E. P.M.T. 1999 ; Haryana C.E.E.T. 2000)*

30. Which will be the proper alternative in place of A in the following equation.

$$2\,Fe^{3+}(aq) + Sn^{2+}(aq) \longrightarrow 2\,Fe^{2+}(aq) + A$$

(*a*) Sn^{4+} (*b*) Sn^{3+}
(*c*) Sn^{2+} (*d*) Sn. *(M.P.C.E.E. 2000)*

31. Number of moles of $K_2Cr_2O_7$ reduced by 1 mole of Sn^{2+} is

(*a*) 1/6 (*b*) 1/3
(*c*) 2/3 (*d*) 1. *(Haryana C.E.E.T. 1996, 2000)*

32. Which of the following is not a reducing agent ?

(*a*) SO_2 (*b*) H_2O_2
(*c*) CO_2 (*d*) NO_2. *(D.C.E. 2000)*

33. Equivalent mass of oxidising agent in the reaction, $SO_2 + 2\,H_2S \longrightarrow 3\,S + 2\,H_2O$ is

(*a*) 32 (*b*) 64
(*c*) 16 (*d*) 8. *(D.C.E. 2000)*

34. The oxidation state of chromium in $[Cr(PPh_3)_3(CO)_3]$ is

(*a*) + 3 (*b*) + 8
(*c*) zero (*d*) + 5. *(D.C.E. 2000)*

35. The values of *x* and *y* in the following redox reaction,

$$x\,Cl_2 + 6\,OH^- \longrightarrow ClO_3^- + y\,Cl^- + 3\,H_2O \text{ are}$$

(*a*) $x = 2, y = 4$ (*b*) $x = 5, y = 3$
(*c*) $x = 3, y = 5$ (*d*) $x = 4, y = 2$. *(C.P.M.T. 2000)*

36. Amongst the following, identify the species with an atom in +6 oxidation state

ANSWERS

21. *a* **22.** *b* **23.** *a* **24.** *b* **25.** *d* **26.** *b* **27.** *a* **28.** *a* **29.** *c* **30.** *a*
31. *b* **32.** *c* **33.** *c* **34.** *c* **35.** *c*

(*a*) MnO_4^- (*b*) $Cr(CN)_6^{3-}$

(*c*) NiF_6^{2-} (*d*) CrO_2Cl_2

(I.I.T. 2000)

37. For the electrochemical cell, $M \mid M^+ \parallel X^- \mid X$, $E^\circ_{M^+/M} = 0{\cdot}44$ V and $E^\circ_{X/X^-} = 0{\cdot}33$ V. From these data one can deduce that

(*a*) $M + X \longrightarrow M^+ + X^-$ is the spontaneous reaction

(*b*) $M^+ + X^- \longrightarrow M + X$ is the spontaneous reaction

(*c*) $E_{cell} = 0{\cdot}77$ V

(*d*) $E_{cell} = -0{\cdot}77$ V *(I.I.T. 2000)*

38. In the standardization of $Na_2S_2O_3$ using $K_2Cr_2O_7$ by iodometry, the equivalent weight of $K_2Cr_2O_7$ is

(*a*) (molecular weight)/2

(*b*) (molecular weight)/6

(*c*) (molecular weight)/3

(*d*) same as molecular weight. *(I.I.T. 2001)*

39. The reaction, $3\,ClO^-\,(aq) \longrightarrow ClO_3^-\,(aq) + 2\,Cl^-\,(aq)$ is an example of

(*a*) Oxidation reaction

(*b*) Reduction reaction

(*c*) Disproportionation reaction

(*d*) Decomposition reaction. *(I.I.T. 2001)*

40. Standard electrode potentials are

Fe^{2+}/Fe $E^\circ = -0{\cdot}44$ V, Fe^{+3}/Fe^{+2} $E^\circ = 0{\cdot}77$ V

Fe^{+2}, Fe^{+3} and Fe blocks are kept together, then

(*a*) Fe^{+3} increases

(*b*) Fe^{+3} decreases

(*c*) Fe^{+2}/Fe^{+3} remains unchanged

(*d*) Fe^{+2} decreases

(C.B.S.E. P.M.T. 2001)

41. The reduction potentials of Zn, Cu, Fe and Ag are in the order :

(*a*) Ag, Cu, Fe, Zn (*b*) Cu, Ag, Fe, Zn

(*c*) Zn, Cu, Fe, Ag (*d*) Fe, Zn, Cu, Ag

(N.S.E. 2001)

42. Standard electrode potential data are useful for understanding the suitability of an oxidant in a redox titration. Some half cell reactions and their standard potentials are given below :

$$MnO_4^-\,(aq) + 8H^+\,(aq) + 6\,e^- \longrightarrow Mn^{2+}\,(aq) + 4H_2O\,(l)\ E^\circ = 1{\cdot}51\text{ V}$$

$$Cr_2O_7^{2-}\,(aq) + 14H^+\,(aq) + 6\,e^- \longrightarrow 2Cr^{3+}\,(aq) + 7H_2O\,(l)\,;\ E^\circ = 1{\cdot}38\text{ V}$$

$$Fe^{3+}\,(aq) + e^- \longrightarrow Fe^{2+}\,(aq)\,;\ E^\circ = 0{\cdot}77\text{ V}$$

$$Cl_2\,(g) + 2\,e^- \longrightarrow 2Cl^-\,(aq)\,;\ E^\circ = 1{\cdot}40\text{ V}$$

Identify the only incorrect statement regarding the quantitative estimatiion of aqueous $Fe(NO_3)_2$

(*a*) MnO_4^- can be used in aqueous HCl

(*b*) $Cr_2O_7^{2-}$ can be used in aqueous HCl

(*c*) MnO_4^- can be used in aqueous H_2SO_4

(*d*) $Cr_2O_7^{2-}$ can be used in aqueous H_2SO_4

(I.I.T. 2002)

43. When $KMnO_4$ acts as an oxidising agent and ultimately forms MnO_4^{-2}, MnO_2, Mn_2O_3 and Mn^{+2}, then the number of electrons transferred in each case respectively is

(*a*) 4, 3, 1, 5 (*b*) 1, 5, 3, 7

(*c*) 1, 3, 4, 5 (*d*) 3, 5, 7, 1

(A.I.E.E.E. 2002)

44. Which of the following is a redox reaction ?

(*a*) $NaCl + KNO_3 \longrightarrow NaNO_3 + KCl$

(*b*) $CaC_2O_4 + 2HCl \longrightarrow CaCl_2 + H_2C_2O_4$

(*c*) $Mg(OH)_2 + 2NH_4Cl \longrightarrow MgCl_2 + 2NH_4OH$

(*d*) $Zn + 2AgCN \longrightarrow 2Ag + Zn(CN)_2$

(A.I.E.E.E. 2002)

45. A smuggler could not carry gold by depositing iron on the gold surface since

(*a*) Gold is denser

(*b*) Iron rusts

(*c*) Gold has higher electrode potential than iron

(*d*) Gold has lower electrode potential than iron

(Karnataka C.E.T. 2002)

46. The oxidation states of sulphur in the anions SO_3^{2-}, $S_2O_4^{2-}$ and $S_2O_6^{2-}$ follow the order :

(*a*) $S_2O_4^{2-} < SO_3^{2-} < S_2O_6^{2-}$

(*b*) $SO_3^{2-} < S_2O_4^{2-} < S_2O_6^{2-}$

ANSWERS

36. *d* **37.** *b* **38.** *b* **39.** *c* **40.** *b* 41. *a* 42. *a* 43. *c* 44. *d* 45. *c* (*c*) $S_2O_4^{2-} < S_2O_6^{2-} < SO_3^{2-}$

(*d*) $S_2O_6^{2-} < S_2O_4^{2-} < SO_3^{2-}$

(C.B.S.E. P.M.T. 2003)

47. Which of the following is actually possible if oxidation potentials of Zn = + 0·76 V and Ag = – 0·80 V ?

(*a*) $Zn + 2\,Ag^+ \longrightarrow Zn^{2+} + 2\,Ag$

(*b*) $Zn^{2+} + 2\,Ag \longrightarrow Zn + 2\,Ag^+$

(*c*) $2\,Zn + 2\,Ag \longrightarrow Zn^{2+} + 2\,Ag^+$

(*d*) $Zn^{2+} + Ag^+ \longrightarrow Zn + Ag$

(Wardha M.G.I.M.S. 2003)

48. For decolourization of 1 mole of $KMnO_4$, the moles of H_2O_2 required is

(*a*) 1/2 (*b*) 3/2

(*c*) 5/2 (*d*) 7/2

(A.I.I.M.S. 2004)

49. The pair of compounds having metals in their highest oxidation state is

(*a*) MnO_2, $FeCl_3$

+4 +3

(*b*) MnO_4^-, CrO_2Cl_2

+7 +6

(*c*) $[Fe(CN)_6]^{3-}$, $[Co(CN)_3]$

–3 0

(*d*) $[NiCl_4]^{2-}$, $[CoCl_4]^-$ *(I.I.T. 2004)*

+2

50. Consider the following E° values

$E°_{Fe^{3+}/Fe^{2+}} = 0{\cdot}77$ V, $E°_{Sn^{2+}/Sn} = -\,0{\cdot}14$ V

Under standard conditions, the potential for the reaction,

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

is

(*a*) 0·63 V (*b*) 1·40 V

(*c*) 0·91 V (*d*) 1·68 V

(A.I.E.E.E. 2004)

51. The $E°_{M^{3+}/M^{2+}}$ values for Cr, Mn, Fe and Co are –0·41, + 1·57, + 0·77 and + 1·97 V respectively. For which one of these metals, the change in oxidation state from + 2 to + 3 is easiest ?

(*a*) Co (*b*) Mn

(*c*) Fe (*d*) Cr *(A.I.E.E.E. 2004)*

52. Excess of KI reacts with $CuSO_4$ solution and $Na_2S_2O_3$ solution is added to it. Which of the statements is *incorrect* for the reaction ?

(*a*) Evolved I_2 is reduced

(*b*) CuI_2 is formed

(*c*) $Na_2S_2O_3$ is oxidised

(*d*) Cu_2F_2 is formed *(A.I.E.E.E. 2004)*

53. The oxidation number of carbon in CH_2Cl_2 is

(*a*) 0 (*b*) 2

(*c*) 3 (*d*) 5 *(A.F.M.C. 2004)*

54. What is the equivalent mass of IO_4^- when it converted into I_2 in acid medium ?

(*a*) M/6 (*b*) M/7

(*c*) M/5 (*d*) M/4

(*e*) none of these *(Kerala M.E.E. 2004)*

55. $a\,K_2Cr_2O_7 + b\,KCl + c\,H_2SO_4 \longrightarrow x\,CrO_2Cl_2 + y\,KHSO_4 + z\,H_2O$

The above equation balances when

(*a*) $a = 2, b = 4, c = 6$ and $x = 2, y = 6, z = 3$

(*b*) $a = 4, b = 2, c = 6$ and $x = 6, y = 2, z = 3$

(*c*) $a = 6, b = 4, c = 2$ and $x = 6, y = 3, z = 2$

(*d*) $a = 1, b = 4, c = 6$ and $x = 2, y = 6, z = 3$

(*e*) $a = 1, b = 6, c = 4$ and $x = 6, y = 2, z = 3$

(Kerala E.E.E. 2004)

56. Aluminium displaces hydrogen from dilute HCl whereas silver does not. The E.M.F. of the cell prepared by combining Al/Al^{3+} and Ag/Ag^+ is 2·46 V. The reduction potential of silver electrode is + 0·80 V. The reduction potential of aluminium electrode is

(*a*) + 1·66 V (*b*) – 3·26 V

(*c*) 3·26 V (*d*) – 1·66 V

(Karnataka C.E.T. 2004)

57. Which of the following statements is true for the electrochemical Daniel cell ?

(*a*) Electrons flow from copper electrode to zinc electrode

(*b*) Current flows from zinc electrode to copper electrode

(*c*) Cations move towards copper electrode

(*d*) Cations move towards zinc electrode

(A.I.I.M.S. 2004)

58. Which is the best description of the behaviour of bromine in the reaction given below ?

$$H_2O + Br_2 \longrightarrow HOBr + HBr$$

ANSWERS

46. *a* 47. *a* 48. *c* 49. *b* 50. *c* 51. *d* 52. *b* 53. *a* 54. *b* 55. *d*
56. *d* 57. *c*

(a) Proton acceptor only
(b) Both oxidised and reduced
(c) Oxidised only
(d) Reduced only *(C.B.S.E. P.M.T. 2004)*

59. In a galvanic cell, the electrons flow from
(a) anode to cathode through the solution
(b) cathode to anode through the solution
(c) anode to cathode through the external circuit
(d) cathode to anode through the external circuit *(Karnataka C.E.T. 2004)*

60. An aqueous solution containing one mole per litre of each $Cu(NO_3)_2$, $AgNO_3$, $Hg_2(NO_3)_2$, $Mg(NO_3)_2$ is being electrolysed using inert electrodes. The values of standard electrode potential (reduction potential) are $Ag^+/Ag = +0{\cdot}80$ $Hg^+/Hg = +0{\cdot}79$, $Cu^{2+}/Cu = +0{\cdot}34$ V, $Mg^{2+}/Mg = -2{\cdot}37$.
With increasing voltage, the sequence of deposition of metals on cathode will be
(a) Ag, Hg, Cu, Mg (b) Mg, Cu, Hg, Ag
(c) Ag, Hg, Cu (d) Cu, Hg, Ag
(e) Cu, Hg, Ag, Mg *(I.I.T. 1984 ; Kerala M.E.E. 2004)*

61. $Cr_2O_7^{2-} + X \xrightarrow{H^+} Cr^{3+} + H_2O$ + oxidised product of X. X in the above reaction cannot be
(a) $C_2O_4^{2-}$ (b) Fe^{2+}
(c) SO_4^{2-} (d) S^{2-} *(C.P.M.T. 2004)*

HINTS/EXPLANATIONS to Multiple Choice Questions

1. Sodium amalgam is a homogenous mixture of Na and Hg and as such Na exists in the elemental state and hence its O.N. is zero.

2. $\overset{+7}{MnO_4^-} + 5\,e^- \longrightarrow Mn^{2+}$

Since 1 mole of MnO_4^- accepts 5 moles of electrons, therefore, 5 moles of electrons are lost by 1·67 moles of M^{x+}

∴ 1 mole of M^{x+} will lose electrons = 5/1·67 = 3 moles (*approx.*)

Since M^{x+} changes to MO_3^- (where O.N. of M = + 5) by accepting 3 electrons

∴ Oxidation state of M, *i.e.*,

$$x = +5 - 3 = +2$$

4. The balanced redox equation is

$$2\,MnO_4^- + 5\,C_2O_4^{2-} + 16\,H^+ \longrightarrow 2\,Mn^{2+} + 10\,CO_2 + 8\,H_2O$$

Thus, the coefficients of MnO_4^-, $C_2O_4^{2-}$ and H^+ respectively are 2, 5 and 16.

5. Large negative potential for the reaction, $A + e^- \longrightarrow A^-$ implies that the reverse reaction occurs, *i.e.*, A^- is readily oxidised.

7. The O.N. of Ca, C and O remain the same

8. Total O.N. of 2 nitrogen atoms in N_2H_4 is —4. Since it loses 10 moles of electrons, therefore, the total O.N. of two N atoms in Y increases by 10, *i.e.* the total O.N. of two N atoms in

$$Y = -4 + 10 = +6.$$

∴ O.N. of each N is Y = + 6/2 = + 3.

9. Balanced equations for producing NO and NO_2 respectively are :

$$3\,Cu + 8\,HNO_3 \longrightarrow 3\,Cu(NO_3)_2 + 2\,NO + 4\,H_2O \quad ...(i)$$

$$Cu + 4\,HNO_3 \longrightarrow Cu(NO_3)_2 + 2\,NO_2 + 2\,H_2O \quad ...(ii)$$

Adding Eqns. (i) and (ii), we have

$$4\,Cu + 12\,HNO_3 \longrightarrow 4\,Cu(NO_3)_2 + 2\,NO_2 + 2\,NO + 6\,H_2O$$

or $$2\,Cu + 6\,HNO_3 \longrightarrow 2\,Cu\,(NO_3)_2 + NO_2 + NO + 3\,H_2O$$

Thus coefficients x and y of Cu and HNO_3 respectively are 2 and 6.

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

$FeC_2O_4 \longrightarrow Fe^{2+} + C_2O_4^{2-}$

$Fe^{2+} \longrightarrow Fe^{3+} + e^-$

$C_2O_4^{2-} \longrightarrow 2\,CO_2 + 2\,e^-$

Since one mole of FeC_2O_4 loses 3 moles of electrons while one mole of $KMnO_4$ accepts five

ANSWERS

58. *b* **59.** *c* **60.** *c* **61.** *c* moles of electrons, therefore, number of $KMnO_4$ required to oxidise one mole of FeC_2O_4 = 3/5 = 0·6 mole.

16. A metal with higher O.P. (*i.e.* A) replaces a metal with lower O.P. (*i.e.* B) from its aqueous solution.

17. The species with the lowest electrode potential is the strongest reducing agent *i.e.* Fe^{2+}.

18. Only Al ($E^\circ = -1 \cdot 66$ V) has lower electrode potential than Zn ($E^\circ = -0 \cdot 76$ V) and hence it will reduce Zn^{2+} to Zn while all others have higher electrode potentials than Zn.

19. Lower the reduction potential, stronger the reducing agent. Y (− 3·03 V) > Z (− 1·66 V) > X (+ 0·52 V)

21. Since the reduction potential of Y is greater than that of X but lower than that of Z, therefore, Y will oxidize X but not Z.

22. $M^{3+} \longrightarrow M^{6+} + 3e^-$.

23. In CO_3^{2-}, C has highest oxidation state of + 4, therefore, it cannot act as a reducing agent while all others act as reducing agents and hence will not decolourise $KMnO_4$ solution.

24. Six electron change,

∴ Eq. wt. = mol. wt./6.

27. $3 \times (+2) + 2 \times (+5 + 4 \times -2)$

$$= +6 + 2(-3) = 0.$$

28. The balanced equation is

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O.$$

Therefore, X, Y and Z, the coefficients of H_2SO_4, SO_2 and H_2O respectively are 1, 3, 1.

30. The balanced equation is :

$$2Fe^{3+}(aq) + Sn^{2+}(aq) \longrightarrow 2Fe^{2+}(aq) + Sn^{4+}(aq)$$

Thus A is Sn^{4+}.

31.

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

$$Sn^{2+} \longrightarrow Sn^{4+} + 2e^-] \times 3$$

$$Cr_2O_7^{2-} + 14H^+ + 3Sn^{2+} \longrightarrow 3Sn^{4+} + 2Cr^{3+} + 7H_2O$$

From the above Eqn., it is evident that 3 moles of Sn^{2+} reduce 1 mole of $Cr_2O_7^{2-}$

∴ 1 mole of Sn^{2+} will reduce 1/3 mole of $Cr_2O_7^{2-}$.

32. C in CO_2 has the maximum O.N. of + 4 and hence it cannot act as a reducing agent.

33. In this reaction SO_2 oxidises H_2S to S, therefore, SO_2 acts as the oxidising agent. During oxidation, four electrons are lost, *i.e.*,

$$SO_2 + 4e^- \longrightarrow S + 2O^{2-}$$

Thus, Eq. wt. of SO_2 = Mol. wt./4

= 64/4 = 16.

34. Since both the ligands, *i.e.*, PPh_3 (triphenylphosphine) and CO are neutral and the complex does not carry any charge, therefore, O.N. of Cr is zero.

35. The balanced chemical equation is :

$$3Cl_2 + 6OH^- \longrightarrow ClO_3^- + 5Cl^- + 3H_2O$$

37.

$$M^+ + e^- \longrightarrow M \; ; \quad E^\circ = +0 \cdot 44 \text{ V} \quad ...(i)$$

$$X + e^- \longrightarrow X^- \; ; \quad E^\circ = +0 \cdot 33 \text{ V} \quad ...(ii)$$

Subtracing Eqn. (*ii*) from Eqn. (*i*), we have

$$M^+ - X \longrightarrow M - X^- ; \quad E^\circ = +0 \cdot 11 \text{ V}$$

or $$M^+ + X^- \longrightarrow M + X \; ; \quad E^\circ = +0 \cdot 11 \text{ V}$$

i.e., $M^+ + X^- \longrightarrow M + X$

is the spontaneous reaction.

38. Since $K_2Cr_2O_7$ accepts 6 electrons for its reduction to Cr^{3+} ions. ∴ Eq. wt. = Mol. wt./6.

40. Since $E^\circ_{Fe^{2+}/Fe}$ is —ve, therefore, Fe has a high tendency to pass into Fe^{2+} ions. As a result, $[Fe^{2+}]$ increases and hence that of $[Fe^{3+}]$ decreases. Alternatively, Since Fe^{3+}/Fe^{2+} is +ve, therefore, Fe^{3+} has a strong tendency to pass into Fe^{2+} and hence $[Fe^{2+}]$ increases and that of $[Fe^{3+}]$ decreases.

41. E° values decrease in the order :

Ag (+ 0·80 V), Cu (+ 0·34 V), Fe (—0·44 V), Zn (—0·76 V).

42. MnO_4^- will oxidise Cl^- ion according to the equation,

$$2KMnO_4^- + 16H^+ + 10Cl^- \longrightarrow 2Mn^{2+} + 8H_2O + 5Cl_2$$

The cell corresponding to this reaction is

$$Pt, Cl_2 (1bar) \mid Cl^- \parallel MnO_4^-, Mn^{2+}, H^+ \mid Pt$$

$$E^\circ_{cell} = 1 \cdot 51 - 1 \cdot 40 = 0 \cdot 11 \text{ V}$$

As E°_{cell} is +ve, the above reaction is feasible and MnO_4^- will oxidise not only Fe^{2+} ion but Cl^- ion also.

43. $\overset{+7}{KMnO_4} + e^- \longrightarrow \overset{+6}{(MnO_4)^{-2}}$,

$\overset{+7}{KMnO_4} + 3e^- \longrightarrow \overset{+4}{MnO_2}$

$\overset{+7}{KMnO_4} + 4e^- \longrightarrow 1/2\,\overset{+3}{Mn_2O_3}$

$\overset{+7}{KMnO_4} + 5e^- \longrightarrow \overset{+2}{Mn}$

44. $Zn \xrightarrow{Oxd} Zn^{2+} + 2e^-$; $Ag^+ + e^- \xrightarrow{Red} Ag$

45. Gold has higher E° (+ 1·50 V) than Fe (− 0·44 V) and hence can oxidise Fe to Fe^{2+}.

46. $S_2O_4^{2-}$ (+ 3) < SO_3^{2-} (+ 4) < $S_2O_6^{2-}$ (+ 5).

47. For the reaction, $Zn + 2\,Ag \longrightarrow Zn^{2+} + 2\,Ag$, the corresponding cell is $Zn \mid Zn^{2+} \mid\mid Ag^+ \mid Ag$ Since the E.M.F. of this cell is +ve, *i.e.*

$0{\cdot}80 - (-0{\cdot}76) = +1{\cdot}56$ V,

therefore, this reaction will occur.

50. $Sn \mid Sn^{2+} \mid\mid Fe^{3+} \mid Fe^{2+}$

$E^\circ_{cell} = 0{\cdot}77 - (0{\cdot}14) = +0{\cdot}91$ V

51. $Cr^{3+} + e^- \longrightarrow Cr^{2+}\ E^\circ = -0{\cdot}41$ V

Since the E° for this half reaction is –ve, therefore, the reaction occurs in the backward direction, *i.e.*, Cr^{2+} gets oxidised to Cr^{3+}. For all other half reactions, E° are +ve and hence reactions occur in the forward direction, *i.e.* + 3 oxidation state is reduced to + 2.

52. (*i*) $2\,CuSO_4 + 4\,KI \longrightarrow Cu_2I_2 + I_2 + 2\,K_2SO_4$

(*ii*) $2\,Na_2S_2O_3 + I_2 \longrightarrow Na_2S_2O_6 + 2\,NaI$

CuI_2 is only incorrect statement.

54. $2\,IO_4^- + 16\,H^+ + 14\,e^- \longrightarrow I_2 + 8\,H_2O$

Eq. wt. of $IO_4^- = \frac{2 \times \text{Mol. wt.}}{14} = M/7$

55. $K_2Cr_2O_7 + 2\,H_2SO_4 \longrightarrow 2\,KHSO_4 + 2\,CrO_3 + H_2O$

$2\,KCl + H_2SO_4 \longrightarrow 2\,KHSO_4 + 2\,HCl \times 2$

$CrO_3 + 2\,HCl \longrightarrow CrO_2Cl_2 + H_2O \times 2$

$K_2Cr_2O_7 + 4\,KCl + 6\,H_2SO_4 \longrightarrow 2\,CrO_2Cl_2 + 6\,KHSO_4 + 3\,H_2O$

56. $Al \mid Al^{3+} \mid\mid Ag^+ \mid Ag$

$E^\circ_{cell} = E^\circ_{Ag^+/Ag} - E^\circ_{Ag^{3+}/Al}$

or $2{\cdot}46 = 0{\cdot}80 - E^\circ_{Al^{3+}/Al}$

or $E^\circ_{Al^{3+}/Al} = -1{\cdot}66$ V

60. Higher the reduction potential more easily it is reduced. Since the reduction potential (—2·37 V) of Mg^{2+} is much lower than that of water (—0·83 V), therefore, H_2O gets reduced in preference to Mg^{2+} ions. In other words, Mg cannot be obtained by electrolytic reduction of Mg^{2+} ions in aqueous solution. Thus, the actual sequence of deposition is Ag, Hg, Cu.

61. SO_4^{2-} is not a reducing agent and hence does not reduce $Cr_2O_7^{2-}$.

ADDITIONAL QUESTIONS

For All Competitive Examinations

Assertion-Reason Type Questions

The questions given below consist of an 'Assertion' in column 1 and the 'Reason' in column 2. Use the following key to choose the appropriate answer.

(a) If both assertion and reason are CORRECT and reason is the CORRECT explanation of the assertion.

(b) If both assertion and reason are CORRECT but reason is not the CORRECT explanation of the assertion.

(c) If assertion is CORRECT but the reason is INCORRECT.

(d) If both assertion and reason are INCORRECT.

	Assertion (Column 1)	Reason (Column 2)
1.	Blue colour of $CuSO_4$ solution fades away when iron plate is placed in it.	Cu^{2+} ion is oxidised by Fe.
2.	Copper liberates hydrogen from a dilute solution of hydrochloric acid.	Hydrogen is below copper in the electrochemical series. *(A.I.I.M.S. 1995)*
3.	Zinc displaces copper from copper sulphate solution.	E° of Zn is — 0·76 V and that of Cu is + 0·34 V. *(A.I.I.M.S. 1999)*

True/False Statements

Which of the following statements are true and which are false ? Rewrite the false statements correctly.

1. Oxidation is a process which involves loss of electrons.
2. Reducing agents are electron acceptors.
3. Copper metal can be oxidised by Zn^{2+} ions.
4. Cl_2 can oxidise Br^- iosn to Br_2.
5. Copper sulphate solution can be placed in a vessel made of zinc.
6. Stock notation is used to name compounds of metals which involve variable oxidation states.
7. The oxidation number of N in NF_3 is +3.
8. Metals whose electrode potentials are lower than that of standard hydrogen electrode react with aqueous mineral acids to evolve H_2 gas.
9. $HgCl_2$ and $SnCl_2$ cannot exist as such if present together in an aqueous solution.

Fill In The Blanks

1. Oxidising agents are .... while reducing agents are ....
2. In oxidation, the oxidation number of an element .... while in reduction, it ....
3. A substance which increases the oxidation number of some other substance in a chemical reaction is called an ....
4. The oxidation number of N in NI_3 is ....
5. The tendency of an electrode to gain or lose electrons is called ....
6. Standard electrode potentials are measured under .... concentration of metal ions and a temperature of ....
7. The standard electrode potentials of single electrodes are measured with reference to ....
8. In the electrochemical series, the elements are arranged in order of their increasing ....
9. The compound $YbBa_2Cu_3O_7$ which shows superconductivity, has copper in oxidation state .... Assume that the rare earth element ytterbium is in the usual +3 oxidation state.

(I.I.T. 1994)

Matching Type Questions

Match the appropriate entries in columns X and Y

X	Y
1. Fluorine	(*a*) Liberates Cl_2 from Cl^- ions
2. Zinc, magnesium, iron etc. react with dil. H_2SO_4 to evolve	(*b*) Reduces $HgCl_2$ to Hg_2Cl_2
3. Stannous chloride	(*c*) Hydrogen gas

ANSWERS

ASSERTION-REASON TYPE QUESTIONS

1. (*c*) **2.** (*d*) **3.** (*a*).

TRUE/FALSE STATEMENTS

True : 1, 4, 6, 7, 8, 9

False : 2, 3, 5

FILL IN THE BLANKS

1. Electron acceptors, electron donors **2.** increases, decreases **3.** oxidising agent **4.** –3, **5.** electrode potential **6.** 1.0 molar, 298 K **7.** standard hydrogen electrode **8.** electrode potentials **9.** 7/3.

MATCHING TYPE QUESTIONS

1. (*a*) **2.** (*c*) **3.** (*b*)

HINTS/EXPLANATIONS to Assertion-Reason Type Questions

1. **Correct reason :** Cu^{2+} is reduced by Fe.
2. **Correct assertion :** Copper does not liberate hydrogen from a dilute solution of hydrochloric acid.

   Correct reason : Copper lies below hydrogen in the electrochemical series.