SEMESTER–II (Period–VI)

C10CH7

7 TOPIC

Oxidation-Reduction Reaction

Learning Objectives

Upon completion of this topic, learners will be able to:

- Discuss the terms oxidation and reduction
- Discuss the difference between oxidizing and reducing agents
- Apply the concept of calculating oxidation numbers and
- Apply the rules for balancing redox reactions.

Introduction

In our daily life we come across processes like rusting of objects made of iron, fading of the colour of the clothes, burning of the combustible substances such as cooking gas, wood, coal, etc. All such processes fall in the category of specific type of chemical reactions called ***oxidation-reduction reactions*** or ***redox reactions***. A large number of industrial processes like, electroplating, extraction of metals like aluminium and sodium, bleaching of wood pulp, manufacture of caustic soda, etc., are also based upon the redox reactions. Redox reactions also form the basis of electrochemical and electrolytic cells. In order to have proper understanding of redox reactions let us define oxidation and reduction.

7.1. OXIDATION AND REDUCTION

7.1.1. Classical Concept of Oxidation and Reduction

According to classical concept following definitions were proposed to explain the process of oxidation and reduction.

Oxidation *is a process of chemical addition of oxygen or any electronegative radical or removal of hydrogen or any electropositive radical.*

***Reduction** is a process of chemical addition of hydrogen or any electropositive radical or removal of oxygen or any electronegative radical.*

Some examples of oxidation and reduction reactions are given below:

(i) Reaction of PbO and carbon

Oxidation

$$PbO + C \longrightarrow Pb + CO$$

Reduction

Here, oxygen is being removed from lead oxide (PbO) and is being added to carbon (C). Thus PbO is *reduced* while C is *oxidised*.

(ii) Reaction of H_2S and Cl_2

Oxidation

$$Cl_2 + H_2O \longrightarrow 2HCl + S$$

Reduction

Here, hydrogen is being removed hydrogen sulphide (H_2S) and is being added to chlorine (Cl_2). Thus H_2S is *oxidised* and Cl_2 is *reduced*.

ACTIVITY 7.1

Study of Oxidation of Copper Powder

- Take about 2 g of copper powder in a China dish and heat (Fig. 7.1)

  What do you observe?

  It is observed that the surface of copper powder becomes black.

  The surface of copper becomes black due to formation of copper (II) oxide by reaction between copper and oxygen present in the air

$$\underset{}{2Cu(s)} + O_2(g) \longrightarrow \underset{\substack{\text{Copper (II) oxide} \\ \text{(Black)}}}{2CuO(s)}$$

In this reaction copper is oxidised to copper (II) oxide.

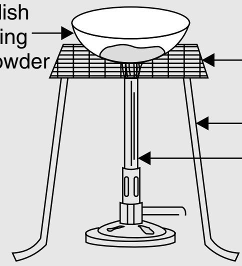


Fig. 7.1. Oxidation of copper to copper oxide

7.1.2. Electronic Concept of Oxidation and Reduction

According to electronic concept, the oxidation and reduction processes can be defined as follows oxidation. ***Oxidation*** *is a process in which an atom or a group of atoms taking part in chemical reaction loses one or more electrons*. The loss of electrons results in the increase of positive charge or decrease of negative charge of the species.

Some examples are as follows.

$$\underset{\text{Chloride ion}}{2Cl^-} \longrightarrow \underset{\text{Chlorine molecule}}{Cl_2 + e^-}$$

(*Decrease of negative charge*)

$$\underset{\text{Iron (II)}}{Fe^{2+}} \longrightarrow \underset{\text{Iron (III)}}{Fe^{3+} + e^-}$$

(*Increase of positive charge*)

$$\underset{\text{Copper}}{Cu} \longrightarrow \underset{\text{Copper (II)}}{Cu^{2+} + 2e^-}$$

(*Increase of positive charge*)

The species which undergo the loss of electrons during the reactions are called reducing agents or reductants. Cl^-, Fe^{2+} and Cu are reducing agents in the above examples.

Reduction *is a process in which an atom or a group of atoms taking part in chemical reaction gains one or more electrons*. The gain of electrons results in the decrease of positive charge or increase of negative charge of the species. Some examples are as follows.

$$Ag^+ + e^- \longrightarrow Ag$$

(*Decrease of positive charge*)

$$\underset{\text{Iron (III)}}{Fe^{2+} + e^-} \longrightarrow \underset{\text{Iron (II)}}{Fe^{2+}}$$

(*Decrease of positive charge*)

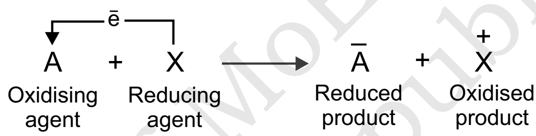
$$\underset{\text{Bromine molecule}}{Br_2 + 2e^-} \longrightarrow \underset{\text{Bromide ions}}{2Br^-}$$

(*Increase of negative charge*)

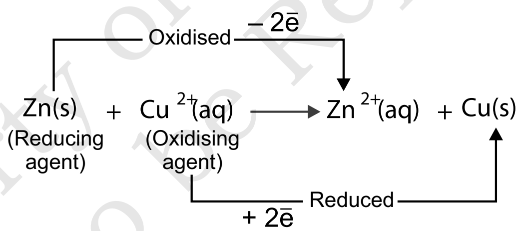
The species which undergo gain of electrons during the reactions are called **oxidising agents** or **oxidants**. In the above examples, Ag^{+}, Fe^{3+} ions, Br_2 molecule are oxidising agents.

7.1.3. Simultaneous Occurrence of Oxidation and Reduction

Since oxidation involves *loss* of electrons and reduction involves *gain* of electrons, it is evident that if one substance loses electrons, another substance at the same time must gain electrons because electrons cannot be the products in any chemical change. This means that in any process, oxidation can occur only if reduction is also taking place side by side and *vice versa*. Thus, neither oxidation, nor reduction can occur alone. Both the processes are complementary like *give* and *take* and proceed simultaneously. That is why chemical reactions involving reduction-oxidation are called **redox reactions**. In fact, during the redox reaction there is a ***transference of electrons from the reducing agent to the oxidising agent*** as shown below:



For example, consider a reaction between zinc and copper ions.



In this reaction, zinc atoms lose electrons and are oxidised to zinc ions (Zn^{2+}) whereas cupric ions (Cu^{2+}) gain electrons and are reduced to copper atoms. Thus, cupric ions act as *oxidising agent* and zinc atoms act as *reducing agent*. In fact, the oxidising agent gets reduced while reducing agent gets oxidised during the redox reactions.

7.1.4. Some Important Oxidising and Reducing Agents

Some important oxidising and reducing agents alongwith their corresponding reduction/oxidation half reactions are summarized below:

A. Oxidising Agents

1. **Potassium dichromate ($K_2Cr_2O_7$)**

   It is powerful oxidising agent. It acts as oxidising agent in acidic medium and gets reduced to Cr^{3+} ions

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

2. **Halogens.** Halogens are very good oxidising agents. They get reduced to halide ions.

$$X_2 + 2e^- \longrightarrow 2X^-$$

3. **Potassium iodate (KIO_3)**
It acts as oxidising agent in acidic medium and gets oxidised to I^- ions

$$IO_3^- + 6H^+ + 6e^- \longrightarrow I^- + 3H_2O$$

4. **Nitric acid (HNO_3)**
Both concentrated and dilute HNO_3 can act as oxidising agents. However, their reduction products are different.
Conc. HNO_3:

$$NO_3^- + 2H^+ + e^- \longrightarrow NO_2 + H_2O$$

Dil. HNO_3:

$$NO_3^- + 4H^+ + 3e^- \longrightarrow NO + 2H_2O$$

5. **Manganese dioxide (MnO_2)**
MnO_2 gets reduced to Mn^{2+} ions in acidic medium.

$$MnO_2 + 4H^+ + 2e^- \longrightarrow Mn^{2+} + 2H_2O$$

B. Reducing Agents

1. **Stannous chloride or Tin (II) chloride ($SnCl_2$)**
Sn increases its oxidation number from + 2 to + 4.

$$Sn^{2+} \longrightarrow Sn^{4+} + 2e^-$$

2. **Hydrogen sulphide (H_2S)**
H_2S gets oxidised to sulphur

$$S^{2-} \longrightarrow S + 2e^-$$

3. **Sulphur dioxide (SO_2)**
In aqueous solutions SO_2 exists as H_2SO_3, which gets oxidised to SO_4^{2-} ions.

$$SO_3^{2-} + H_2O \longrightarrow SO_4^{2-} + 2H^+ + 2e^-$$

4. **Oxalic acid ($H_2C_2O_4$)**
Oxalic acid gets oxidised to carbon dioxide. The oxidation number of carbon increases from + 3 to + 4.

$$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$$

5. **Metal atoms like Zn, Mg, etc.**
These are oxidised to their respective cations.

$$Zn \longrightarrow Zn^{2+} + 2e^-$$

7.1.5. Differences between Oxidising Agent and Reducing Agent

The following table illustrates some differences between oxidising and reducing agents:

Table 7.1. Differences between Oxidising Agent and Reducing Agent

	Oxidising Agent	Reducing Agent
Description	It is a process in which an atom or a group of atoms taking part in chemical reaction loses one or more electrons.	It is a process in which an atom or a group of atoms taking part in chemical reaction gains one or more electrons.
Nature	Acts as the electron acceptor	Acts as the electron donor
Examples	Concentrated H_2SO_4, $KMnO_4$, $K_2Cr_2O_7$, O_2, Cl_2, etc.	Concentrated HCl, pure metals, carbon, H_2, SO_2, H_2S, etc.

7.1.6. Testing for Oxidising and Reducing Agents

7.1.6.1. Testing for Presence of Oxidising Agents

ACTIVITY 7.2

Testing for Presence of Oxidising Agent

1. Add a reducing agent, e.g. aqueous potassium iodide (KI) to the oxidising agent.
2. Shake the mixture.
   What do you observe?
   A brown solution of iodine is produced.
3. To identify the presence of iodine, add starch solution to it.
   What do you observe?
   A dark blue coloration is obtained. It confirms the presence of Iodine (oxidising agent) because iodine reacts with starch.

The presence of oxidizing agent can also be detected using any of the following reagents.

(i) Sulphur (IV) oxides, SO_2 with acidified Barium trioxonitrate (V) solution
(ii) Iron (II) Chloride solution ($FeCl_2$)
(iii) Hydrogen sulphide gas (H_2S)

Table 7.2. Summary of Tests

S. No.	Test	Observation	Inference
1.	Oxidising Agent + $FeCl_2(aq)$	Green colour of Fe^{2+} solution turns to reddish-brown of Fe^{3+}	Oxidising agent is present
2.	Oxidising Agent + $H_2S(g)$	Formation of yellow deposits of sulphur	Oxidising agent is present
3.	Oxidising Agent + $SO_2(g)$ + dilute $HNO_3(aq)$ + $Ba(NO_3)_2(aq)$	White precipitate of insoluble $BaSO_4$ is formed	Oxidising agent is present

7.1.6.2. Testing for Presence of Reducing Agents

ACTIVITY 7.3

Testing for Presence of Reducing Agent

1. Add an oxidising agent, e.g. acidified potassium manganate (VII) to the reducing agent
2. Shake the mixture

   What do you observe?

   The acidified potassium manganate (VII) turns colourless on the addition of reducing agent. It confirms the presence of reducing agent.

The presence of reducing agents can also be detected using any of the following reagents.

(i) Acidified potassium dichromate(VI)

(ii) Chlorine (Cl_2)

Table 7.3. Summary of Tests

S. No.	Test	Observation	Inference
1.	Reducing Agent + acidified $K_2Cr_2O_7$	Orange solution of $K_2Cr_2O_7$ turns green on addition of reducing agent.	Reducing agent is present
2.	Reducing Agent + $Cl_2(g)$	Greenish-yellow coloured Cl_2 turns colourless on addition of reducing agent.	Reducing agent is present

Example 7.1: *Consider the combustion of magnesium in oxygen;*

$$2Mg + O_2 \longrightarrow 2MgO$$

Identify:

(i) *the substance undergoing oxidation*
(ii) *the substance undergoing reduction*
(iii) *the substance acting as oxidising agent*
(iv) *the substance acting as reducing agent.*

Solution:

(i) The given reaction may be written as:

$$2Mg + O_2 \longrightarrow 2Mg^{2+}\,O^{2-}$$

In this reaction Mg atom loses its two valence electrons and changes into Mg^{2+}.

$$Mg - 2e^- \longrightarrow Mg^{2+}$$

Thus, *Mg undergoes oxidation.*

(ii) Oxygen atom accepts or gains two electrons and changes to O^{2-}

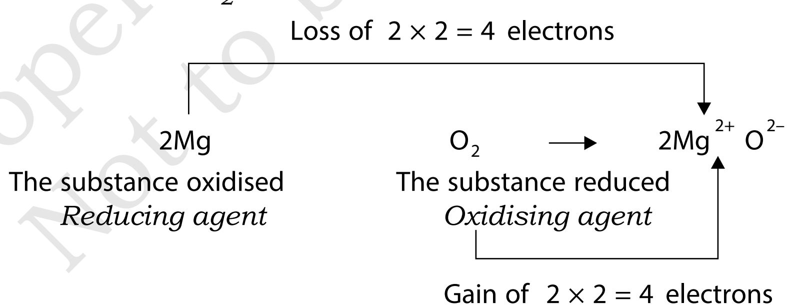
$$O + 2e^- \longrightarrow O^{2-}$$

$$\text{or} \quad O_2 + 4e^- \longrightarrow 2O^{2-}$$

Thus, *O_2 gains electrons and undergoes reduction.*

(iii) The electrons lost by Mg are gained by O_2 which undergoes reduction. Thus, *Mg is the reducing agent.*

(iv) Similarly, O_2 by accepting electrons brings about oxidation of Mg and hence *O_2 acts as oxidising agent.*



7.2. CALCULATING OXIDATION NUMBER

In many covalent reactions such as reaction between H_2 and Cl_2:

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

the loss and gain of electrons could not be easily explained. In order to explain transference of electrons in either of the species in a more convenient way, the concept of oxidation number has been introduced.

Oxidation number (O.N.): Oxidation number of the element in a compound is defined *as the residual charge which its atom has or appears to have when all other atoms from the molecule are assumed to be removed as ions by counting the shared electrons with more electronegative atom.*

For example, in hydrogen chloride molecule, chlorine is more electronegative than hydrogen. Therefore, the shared pair is counted towards chlorine atom as shown below:

$$\mathrm{H}\ {:}\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}{:}$$

As a result of this, chlorine gets one extra electron and acquires a unit negative charge. Hence, oxidation number of chlorine is –1. On the other hand, hydrogen atom without electron has a unit positive charge. Hence, oxidation number of hydrogen in hydrogen chloride is +1.

It may be noted that *electrons shared between two similar atoms are divided equally between the sharing atoms*. Hence in molecules like H_2, Cl_2, Br_2 the oxidation number of element is zero.

7.2.1. Rules for Assigning Oxidation Number to an Atom

The followings rules have been formulated on the basis of the assumption that electrons in a covalent bond belong entirely to the more electronegative atom.

1. *The oxidation number of the element in the free or elementary state is always zero irrespective of its allotropic form.* For example,
   Oxidation number of helium in $He = 0$
   Oxidation number of chlorine in $Cl_2 = 0$
   Oxidation number of sulphur in $S_8 = 0$
   Oxidation number of phosphorus in $P_4 = 0$.
2. *The oxidation number of the element in monoatomic ion is equal to the charge on the ion.* For example, in K^+Cl^-, the oxidation number of K is **+1** while that of Cl is **–1**. In the similar way, oxidation number of all the alkali metals is **+1** while those of alkaline earth metals is **+2** in their compounds.
3. *The oxidation number of fluorine is always **–1** in all its compounds.* Other halogens (Cl, Br and I) also have an oxidation number of **–1**, when they occur as halide ions in their compounds. However, in oxoacids and oxoanions they have positive oxidation numbers.
4. *Hydrogen is assigned oxidation number **+1** in all its compounds except in metal hydrides.* In metal hydrides like NaH, MgH_2, CaH_2, LiH, etc., the oxidation number of hydrogen is **–1**.

5. *Oxygen is assigned oxidation number* ***–2*** *in most of its compounds, however, in peroxides* (which contain O—O linkage) like H_2O_2, BaO_2, Na_2O_2, etc., its oxidation number is **–1**. Similarly, the exception also occurs in compounds of fluorine and oxygen like OF_2 (F—O—F) and O_2F_2 (F—O—O—F) in which the oxidation number of oxygen is **+2** and **+1** respectively.
6. *In accordance with principle of conservation of charge, the algebraic sum of the oxidation numbers of all the atoms in molecule is* ***zero****. But in case of polyatomic ion the sum of oxidation numbers of all its atoms is equal to the* **charge on the ion**.
7. *In binary compounds of metal and non-metal, the metal atom has positive oxidation number while the non-metal atom has negative oxidation number.* For example, O.N. of K in KI is +1 but O.N. of I is –1.
8. *In binary compounds of non-metals, the more electronegative atom has negative oxidation number, but less electronegative atom has positive oxidation number.* For example, O.N. of Cl in ClF_3 is positive (+3) while that in ICl is negative (–1).

REMEMBER

Oxidation Number of:

- Free elements = 0
- Flourine = –1
- Simple ions = Charge on them
- Oxygen = – 2 ; peroxides (–1); F_2O (+2); F_2O_2 (+1)
- Hydrogen = + 1 ; metal hydrides (–1)
- Sum of O.N. of atoms in molecules = 0
- Sum of O.N. of atoms in polyatomic ions = (Charge on them).

Example 7.2: *Determine oxidation number of carbon in CO_2 and CO_3^{2-}*

Solution:

(i) **C in CO_2:**

Let oxidation number of C be x

$$\text{O.N. of each O atom} = -2$$

$$\text{Sum of O.N. of all atoms} = x + 2(-2) = x - 4$$

As it is neutral molecule, the sum must be equal to zero.

$$\therefore \quad x - 4 = 0 \quad \text{or} \quad x = +4$$

(ii) **C in CO_3^{2-}**

Let O.N. of C be x

$$\begin{aligned} \text{O.N. of each O} &= -2 \\ \text{Sum of O.N. of all atoms} &= \text{Charge on ion} \\ \therefore \quad x + (-2) \times 3 &= -2 \\ \text{or} \quad x &= -2 + 6 = +4 \end{aligned}$$

Example 7.3: *Write the oxidation numbers of Cu, O and using these values calculate oxidation number of S in copper sulphate.*

Solution: In $CuSO_4$, O.N. of Cu = +2 as it exists as Cu^{2+} ion in the salt. O.N. of O is – 2.

Now, if O.N. of S is x, then sum of oxidation numbers of all the atoms = 0

$$\therefore \quad +2 + x + 4(-2) = 0 \text{ or } x = +6$$

Example 7.4: *Calculate the oxidation number of the underlined elements in the following species:*

$$\underline{Cr_2}O_7^{2-},\ \underline{Pb_3}O_4,\ H\,\underline{N}\,O_3$$

Solution:

(i) **Cr in $Cr_2O_7^{2-}$:**

$$\begin{aligned} \text{Let oxidation number of Cr} &= x \\ \text{O.N. of each O atom} &= -2 \\ \text{Sum of O.N. of all atoms} &= 2x + 7(-2) \\ &= 2x - 14 \end{aligned}$$

Sum of O.N. must be equal to the charge on the ion.

$$\begin{aligned} \text{Thus,} \quad 2x - 14 &= -2 \\ x &= -\frac{2+14}{2} = \mathbf{+6}. \end{aligned}$$

(ii) **Pb in Pb_3O_4:**

Let O.N. of Pb be x

$$\begin{aligned} \text{O.N. of each O atom} &= -2 \\ \text{Sum of O.N. of all atoms} &= 3x + 4(-2) \\ &= 3x - 8 \end{aligned}$$

The sum of O.N. must be equal to zero

$$\therefore \quad 3x - 8 = 0 \quad \text{or} \quad x = \frac{8}{3} = \mathbf{+2\frac{2}{3}}.$$

(iii) **N in HNO_3:**

Let O.N. of N be x

O.N. of each O atom = -2

O.N. of each H atom = $+1$

Sum of O.N. of various atoms

$$= x + 1 + 3(-2) = x + 1 - 6$$
$$= x - 5$$

In molecule, sum must be equal to zero

$\therefore$ $x - 5 = 0$ or $x = \mathbf{+5}$.

ACTIVITY 7.4

1. In small groups, discuss about, redox reactions and oxidation number.
2. Make presentations highlighting the following:
   - Oxidation number.
   - Oxidation and Reduction in terms of electrons as well as in terms of oxidation number.
   - Oxidising and Reducing agents with appropriate examples.

7.3. BALANCING SIMPLE REDOX EQUATIONS

We have learnt that redox reactions involve change in oxidation number of the elements due to the transference of electrons. *In such reactions the number of electrons lost during oxidation must be equal to the number of electrons gained during reduction*. This forms the **basic principle** for balancing the redox equations. We shall use the concept of half reactions here, to balance the redox equations which can appear both as **simple equations and ionic equations**.

7.3.1. Steps Involved in Balancing Redox Equations

The various steps involved in the balancing of redox equations ion-electron method are as follows:

1. Indicate the oxidation number of each atom involved in the reaction. Identify the elements which undergo a change in the oxidation number.
2. Divide the skeleton redox equation into two half reactions; oxidation half and reduction half. In each half reaction equalise the atoms which undergo the change in oxidation number.

3. In order to make up for the difference in oxidation numbers, add electrons to left hand side to right hand side of the arrow in each half reaction.
4. Balance **oxygen** atoms by adding the proper number of H_2O molecules to the side which is falling short of O atoms in each half reactions.
5. This step is meant only for **equations in ionic form ionic equations**. It involves the balancing of **H atoms** in each half reaction as follows:
   (i) *For acidic medium.* Add proper number of H^+ ions to the side falling short of H atoms.
   (ii) *For basic medium.* Add proper number of H_2O molecules to the side falling short of H atoms and equal number of OH^- ions to the other side.
6. Equalise the number of electrons lost and gained by multiplying the half reactions with suitable integer. Finally add the two half reactions to get the final equation.

The application of various steps described above has been illustrated as follows by balancing the redox equation representing the reaction between iodine and nitric acid.

$$HNO_3 + I_2 \longrightarrow HIO_3 + NO_2 + H_2O$$

Step 1: Indication of oxidation numbers of each atom.

$$\overset{+1+5-2}{NHO_3} + \overset{0}{I_2} \longrightarrow \overset{+1+5-2}{HIO_3} + \overset{+4\ -2}{NO_2} + \overset{+1\ -2}{H_2O}$$

Thus, only nitrogen and iodine undergo change in oxidation number.

Step 2: Division into two half reactions and balancing the atoms undergoing change in O.N.

$$\overset{0}{I_2} \longrightarrow \overset{+5}{2NHO_3} \qquad (\textit{Oxidation half reaction})$$

$$\overset{+5}{HNO_3} \longrightarrow \overset{+4}{NO_2} \qquad (\textit{Reduction half reaction})$$

Step 3: Addition of electrons to make up the difference in O.N.

$$\overset{0}{I_2} \longrightarrow \overset{+5}{2HIO_3} + 10e^-$$

(Each I atom loses $5e^-$ therefore, two iodine atoms would lose $10e^-$)

$$\overset{+5}{HNO_3} \longrightarrow \overset{+4}{NO_2}$$

(Each N atom gains 1 electron).

$$\overset{+5}{HNO_3} + e^- \longrightarrow \overset{+4}{NO_2}$$

(Each N atom gains 1 electron).

Step 4: Balancing of O atoms by adding proper number of H_2O molecule to the side falling short of O atoms.

$$I_2 + 6H_2O \longrightarrow 2HIO_3 + 10e^-$$
$$HNO_3 + e^- \longrightarrow NO_2 + H_2O.$$

Step 5: Not required because the equation is not ionic.

Step 6: To equalise the electrons lost and gained, multiply reduction half reaction by 10 and add the two half reactions.

$$I_2 + 6H_2O \longrightarrow 2HIO_3 + 10e^-$$
$$[HNO_3 + e^- \longrightarrow NO_2 + H_2O] \times 10$$
$$\overline{I_2 + 10HNO_3 \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O}$$

Let us now understand the balancing of ionic equations in acidic and basic mediums by balancing the following skeleton equations.

(i) $Cr_2O_7^{2-} + Fe^{2+} \longrightarrow Cr^{3+} + Fe^{3+} + H_2O$ (in acidic medium)

(ii) $Cr(OH)_3 + IO_3^- \longrightarrow I^- + CrO_4^{2-}$ (in basic medium)

(i) $(Cr_2O_7)^{2-} + Fe^{2+} \longrightarrow Cr^{3+} + Fe^{3+} + H_2O$

Step 1: Indication of O.N. of each atom.

$$\overset{+6}{Cr_2}\overset{-2}{O_7})^{2-} + Fe^{2+} \longrightarrow Cr^{3+} + Fe^{3+} + \overset{+1}{H_2}\overset{-2}{O}$$

Thus, Cr in $Cr_2O_7^{2-}$ and Fe change their oxidation numbers.

Step 2: Writing the oxidation and reduction half reactions and equalising the atoms changing their oxidation numbers.

$$\overset{+6}{Cr_2}\overset{-2}{O_7})^{2-} \longrightarrow 2Cr^{3+} \quad (\textit{Reduction half})$$

$$Fe^{+2} \longrightarrow Fe^{3+} \quad (\textit{Oxidation half})$$

Step 3: Addition of e– to make up the difference in O.N.

$$\overset{+6}{Cr_2}O_7)^{2-} + 6e^- \longrightarrow 2Cr^{3+}$$

(Each Cr atom gains $3e^-$. Thus, 2Cr atom will gain $6e^-$)

$$Fe^{2+} \longrightarrow Fe^{3+} + e^-$$

Step 4: Balance 'O' atoms by adding equal number of H_2O molecules to the side which is deficient in O atoms.

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

Step 5: Balance H atoms by adding H^+ ions to the side which is deficient in H atoms.

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

Step 6: Multiply oxidation half reaction by 6 to equalise the electrons lost and gained and add the two half reactions.

$$Cr_2O_7^{2-} + 6e^- + 14H^+ \longrightarrow 2Cr^{3+} + 7H_2O$$
$$[Fe^{2+} \longrightarrow Fe^{3+} + e^-] \times 6$$

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

It may be remembered that in balanced equation the number of atoms and also the electrical charges must be equal on both the sides of arrow.

(ii) $Cr(OH)_3 + IO_3^- \longrightarrow I^- + CrO_4^{2-}$ (*in basic medium*)

Step 1: Indication of oxidation number of each element.

$$\overset{+3}{Cr}(\overset{-2}{O}\overset{+1}{H})_3 + (\overset{+5}{I}\overset{-2}{O}_3)^- \longrightarrow I- + (\overset{+6}{Cr}\overset{-2}{O}_4)^{2-}$$

Thus, we find that Cr in $Cr(OH)_3$ and iodine in IO_3^- undergo change in oxidation number.

Step 2: Writing oxidation and reduction half reactions.

$$\overset{+3}{Cr}(OH)_3 \longrightarrow (\overset{+6}{Cr}O_4)^{2-} \quad \text{(Oxidation half)}$$
$$(\overset{+5}{I}O_3)^- \longrightarrow I^- \quad \text{(Reduction half)}$$

Step 3: Addition of e^- to make up the difference in O.N.

$$\overset{+3}{Cr}(OH)_3 \longrightarrow (\overset{+6}{Cr}O_4)^{2-} + 3e^-$$
$$d(\overset{+5}{I}O_3)^- + 6e^- \longrightarrow I^-$$

Step 4: Balance O atoms by adding H_2O molecules to the side deficient in 'O' atoms.

$$Cr(OH)_3 + H_2O \longrightarrow CrO_4^{2-} + 3e^-$$
$$IO_3^- + 6e^- \longrightarrow I- + 3H_2O$$

Step 5: Balance H atoms. Since the medium is basic, therefore add proper number of H_2O molecules to the side falling short of H atoms and equal number of OH^- ions to the other side.

$$Cr(OH)_3 + H_2O + 5OH^- \longrightarrow CrO_4^{2-} + 3e^- + 5H_2O$$

$$IO_3^- + 6e^- + 6H_2O \longrightarrow I^- + 3H_2O + 6OH^-$$

Step 6: Equalise the electrons lost and gained by multiplying the oxidation half reaction with 2.

$$[Cr(OH)_3 + H_2O + 5OH^- \longrightarrow CrO_4^{2-} + 3e^- + 5H_2O] \times 2$$

$$IO_3^- + 6e^- + 6H_2O \longrightarrow I^- + 3H_2O + 6OH^-$$

$$2Cr(OH)_3 + 4OH^- + IO_3^- \longrightarrow 2CrO_4^{2-} + 5H_2O + I^-$$

Example 7.5: *Write skeleton equation for the following process and balance it by half reaction method. permanganate ion oxidises oxalate ion in acidic medium to form carbon dioxide, water and dipositive manganese ion as product.*

Solution: The skeleton equation for the process is:

$$MnO_4^- + C_2O_4^{2-} + H^+ \longrightarrow Mn^{2+} + CO_2 + H_2O$$

Step 1: Indication of oxidation number

$$(\overset{+7}{Mn}\overset{-2}{O_4})^{2-} + (\overset{+3}{C_2}\overset{-2}{O_4})^{2-} \longrightarrow Mn^{2+} + \overset{+4}{C}\overset{-2}{O_2} + \overset{+1}{H_2}\overset{-2}{O}$$

Step 2: Writing oxidation and reduction half reactions

$$(\overset{+3}{C_2}O_4)^{2-} \longrightarrow 2\overset{+4}{C}O_2 \quad (\textit{Oxidation half reaction})$$

$$(\overset{+7}{Mn}O_4)^- \longrightarrow Mn^{2+} \quad (\textit{Reduction half reaction})$$

Step 3: Adding electrons to make up the difference in O.N.

$$(\overset{+3}{C_2}O_4)^{2-} \longrightarrow 2\overset{+4}{C}O_2 + 2e^-$$

(Each carbon atom loses one electron)

$$(\overset{+7}{Mn}O_4)^- + 5e^- \longrightarrow Mn^{2+}$$

(Each Mn atom gains $5e^-$)

Step 4: Balancing of O atom by adding H_2O molecules

$$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$$

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

Step 5: Balancing of H atoms by adding H^+ ions

$$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$$
$$MnO_4^- + 5e^- + 8H^+ \longrightarrow Mn^{2+} + 4H_2O$$

Step 6: Multiply the oxidation half reactions by 2 and reduction half reaction by 5 to equalise the electrons lost and gained and add the two half reactions.

$$[C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-] \times 5$$
$$[MnO_4^- + 5e^- + 8H^+ \longrightarrow Mn^{+2} + 4H_2O] \times 2$$

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$$

GLOSSARY

- **Oxidation Number:** A residual charge which an atom of the element appears to have when other atoms from the molecule are removed as ions by counting the electrons with more electronegative element.
- **Oxidation:** A process involving increase in oxidation number by the loss of electrons.
- **Oxidising Agent:** A substance which involves decrease in oxidation number of one or more of its elements.
- **Reducing Agent:** A substance which involves increase in oxidation number of one or more of its elements.
- **Reduction:** A process involving decrease in oxidation number by gain of electrons.

SUMMARY

- According to classical concept:
  - (i) Oxidation is a process of chemical addition of oxygen or any electronegative radical or removal of hydrogen or any electropositive radical.
  - (ii) Reduction is a process of chemical addition of hydrogen or any electropositive radical or removal of oxygen or any electronegative radical.
- According to electronic concept:
  - (i) Oxidation is a process in which an atom or a group of atoms taking part in chemical reaction loses one or more electrons.

(ii) Reduction is a process in which an atom or a group of atoms taking part in chemical reaction gains one or more electrons.

- Chemical reactions involving reduction-oxidation are called redox reactions.
- The species which undergo gain of electrons during the reactions are called oxidising agents or oxidants. Examples: halogens, potassium permanganate, potassium dichromate, nitic acid, manganese dioxide, etc.
- The species which undergo the loss of electrons during the reactions are called reducing agents or reductants. Examples: hydrogen sulphide, sulphur dioxide, oxalic acid, metals like Zn, Mg, etc.
- Oxidation number of the element in a compound is defined as the residual charge which its atom has or appears to have when all other atoms from the molecule are assumed to be removed as ions by counting the shared electrons with more electronegative atom.
- In a redox reactions the number of electrons lost during oxidation must be equal to the number of electrons gained during reduction.

EVALUATION

I. Multiple Choice Questions

1. The process of oxidation involves

(a) addition of oxygen (b) addition of hydrogen
(c) removal of oxygen (d) None of these

2. The process of reduction involves

(a) addition of oxygen (b) addition of hydrogen
(c) removal of hydrogen (d) None of these

3. This species undergoes the loss of electron during chemical reaction.

(a) oxidising agent (b) reducing agent
(c) both (a) & (b) (d) none of these

4. Which of the following is an oxidising agent?

(a) Nitric acid (HNO_3) (b) Sulphur dioxide (SO_2)
(c) Hydrogen sulphide (H_2S) (d) Oxalic acid ($H_2C_2O_4$)

5. In which of the following species oxidation number of C is –3?

(a) C_2H_2 (b) CO_2
(c) HCO_3^- (d) None of these

6. Oxidation number of free electrons is

(a) Zero (b) +1

(c) –1 (d) –2

II. State True or False

1. Oxidising reagents undergo the gain of electron during chemical reaction.
2. Chemical reactions involving oxidation-reduction are called redox reactions.
3. Manganese dioxide is a reducing agent.
4. In redox reactions, the number of electrons lost during oxidation must be equal to the number of electrons gained during reduction.
5. Oxidising agent acts as electron donor.
6. Concentrated nitric acid is an oxidising agent.

III. Answer the Following Questions

1. Explain the terms: oxidation, reduction in terms of electrons. Give suitable examples.
2. In the formation of a compound AB, atoms of element A lost two electrons each while atoms of B gained two electrons each. Which of the elements A and B isoxidised in the formation of AB?
3. An element Y forms a chloride YCl. In terms of gain and loss of electrons, find out which atom is oxidised and which atom is reduced.
4. Explain the terms oxidising and reducing agents. Give some examples.
5. What are the differences between oxidising and reducing agents?
6. Explain the term oxidation number giving examples.
7. Write the rules for assigning oxidation number to an atom.
8. Assign oxidation number to the underlined elements in each of the following species:

(a) $NaH\underline{S}O_4$ (b) $H_4\underline{P}_2O_7$

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