Unit 4

REDOX REACTIONS

4.1 Introduction

In chemical reaction when there is oxidation reaction, there is always reduction reaction. Hence, study of redox reactions are essential. Many phenomena are included in chemistry. One of them is the change from one phenomenon to the other one, substance is converted to the other substance at the end of chemical reaction. One of them is redox reaction. Redox reactions are related to physical and biological phenomena. The wider use of this reaction is found in different fields like pharmaceutical science, biology, industrial metallurgy, agriculture etc. The redox reactions are included in obtaining household energy in the use of different types of fuels for commercial purpose, production of compounds like caustic soda. In recent time hydrogen as an economy energy source and also holes in ozone layer are notable redox reactions.

4.2.1 Oxidation and Reduction :

Basically the word oxidation is used to describe addition of oxygen to the substance. Many substances combine with oxygen because of its presence in atmosphere (nearly 20%). Because of this reason generally they are found in the form of oxides, the following reactions indicate oxidation :

$$2Mg_{(s)} + O_{2(g)} \rightarrow 2MgO_{(s)}$$

$$S_{(s)} + O_{2(g)} \rightarrow SO_{2(g)}$$

In the above reactions, by addition of oxygen to $Mg_{(s)}$ and $S_{(s)}$ oxidation reactions take place.

$$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}$$

$$2H_2S_{(g)} + O_{2(g)} \rightarrow 2S_{(s)} + 2H_2O_{(l)}$$

In the above reactions, with addition of oxygen, hydrogen is removed. Removal of hydrogen is called oxidation.

As mentioned in the following reactions Mg metal, reacts with difluorine, dichlorine and sulphur and experiences oxidation.

$$Mg_{(s)} + F_{2(g)} \rightarrow MgF_{2(s)}$$

$$Mg_{(s)} + Cl_{2(g)} \rightarrow MgCl_{2(s)}$$

$$Mg_{(s)} + S_{(s)} \rightarrow MgS_{(s)}$$

The reaction, in which oxygen is added or hydrogen is removed, is known as oxidation reaction but the reaction in which hydrogen is added or oxygen is removed is known as reduction. Hence, oxidation and reduction are reactions opposite to each other.

Oxidation: $H_2 \rightarrow H_2O$; Reduction: $O_2 \rightarrow H_2O$

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

Oxidation: $H_2 \rightarrow HCl$; Reduction: $Cl_2 \rightarrow HCl$

$$H_{2(g)} + Cl_{2(g)} \rightarrow 2HCl_{(g)}$$

Oxidation: $Al \rightarrow Al_2O_3$; Reduction: $Cr_2O_3 \rightarrow Cr$

$$2Al_{(s)} + Cr_2O_{3(s)} \rightarrow Al_2O_{3(s)} + 2Cr_{(s)}$$

Oxidation: $Al \rightarrow Al_2O_3$; Reduction: $Fe_3O_4 \rightarrow Fe$

$$8Al_{(s)} + 3Fe_3O_{4(s)} \rightarrow 4Al_2O_{3(g)} + 9Fe_{(s)}$$

The substance which loses oxygen or gains hydrogen is called oxidizing agent.

Oxidizing agent is reduced in the above reaction. Oxygen, chlorine, chromium trioxide, ferroso ferric oxide (Fe_3O_4) are oxidizing agents. The substance which loses hydrogen or gains oxygen is called reducing agent. In the above reactions hydrogen and aluminium are reducing agents. During the reaction, reducing agent is oxidized.

During the complete redox reaction oxidizing agent is reduced and the reducing agent is oxidized. Simultaneous oxidation reduction reactions are called redox reactions. Some methods are used to explain redox reactions, in which oxygen or hydrogen may not be taking part in the reaction.

4.2.2 Oxidation-Reduction and Electron Transfer Method :

(1) $2Na_{(s)} + Cl_{2(g)} \rightarrow 2NaCl_{(s)}$

(2) $4Na_{(s)} + O_{2(g)} \rightarrow 2Na_2O_{(s)}$

(3) $2Na_{(s)} + S_{(s)} \rightarrow Na_2S_{(s)}$

Above are redox reactions because sodium (Na) is converted into sodium chloride, sodium oxide and sodium sulphide. During this, the oxidation of sodium occurs with the addition of electronegative elements. Chlorine, oxygen and sulphur are reduced. All these elements are reacted with positively charged sodium ion. NaCl, Na_2O and Na_2S are ionic compounds, they can be written as $Na^+Cl^-_{(s)}$, $(Na^+)_2O^{2-}_{(s)}$ and $(Na^+)_2S^{2-}_{(s)}$, The above equations can be written in ionic forms as follows :

Loss of $2e^-$ ($Na \rightarrow Na^+$)

(1) $2Na_{(S)} + Cl_{2(g)} \rightarrow 2Na^+Cl^-_{(S)}$

Gain of $2e^-$ ($Cl_2 \rightarrow Cl^-$)

(2) $$2Na_{(s)} + O_{2(g)} \rightarrow (Na^+)_{2(l)}O^{2-}_{(s)}$$ (Loss of $2e^-$; Gain of $2e^-$)

(3) $$2Na_{(s)} + S_{(s)} \rightarrow (Na^+)_2S^{2-}_{(s)}$$ (Loss of $2e^-$; Gain of $2e^-$)

To make it simple, the above reactions can be divided into two independent steps. In the first step electron is lost and in the second step electron is gained. Electron exchange reactions can be written as.

$2Na_{(s)} \rightarrow 2Na^+_{(g)} + 2e^-$ .... Oxidation half reaction

$Cl_{2(g)} + 2e^- \rightarrow 2Cl^-_{(g)}$ .... Reduction half reaction

$2Na_{(s)} + Cl_{2(g)} \rightarrow 2NaCl_{(s)}$ Redox reaction

Above reactions are called oxidation and reduction half reactions. Both the half reactions indicate the path of flow of electrons. The combination of these two reactions indicate the complete redox reaction. The reactions of magnesium with oxygen and chlorine can be explained by showing their outermost orbital electrons and the complete reaction can be written as.

$2Mg_{(s)} + O_{2(g)} \rightarrow 2Mg^{2+}O^{2-} \rightarrow 2MgO$

$Mg_{(s)} + Cl_{2(g)} \rightarrow Mg^{2+} 2Cl^- \rightarrow MgCl_2$

In the above reactions one atom of magnesium gives two electrons to one oxygen atom and two electrons to two chlorine atoms. As the number of electrons decreases in magnesium some positive charge is produced, and the number of electrons in oxygen atom and chlorine atom increases and so negative charge is produced on these atoms. Both these examples are the reduction-oxidation or redox reactions.

Redox reaction is such a reaction in which the exchange of electrons takes place from one reactant to the other reactant. Positively charged ion is obtained by loss of electron during oxidation reaction; while in reduction reaction there is decrease in positive charge and if the reactant is neutral, then it gives negative ion. The reactant which receives the electron and gets reduced is called oxidizing agent, Similarly, the reactant which loses electron and gets oxidized is called reducing agent. In the above reactions Mg loses the electrons and so it becomes reducing agent; while chlorine receives the electrons and so becomes oxidizing agent.

4.3 Competitive Electron Transfer Reaction

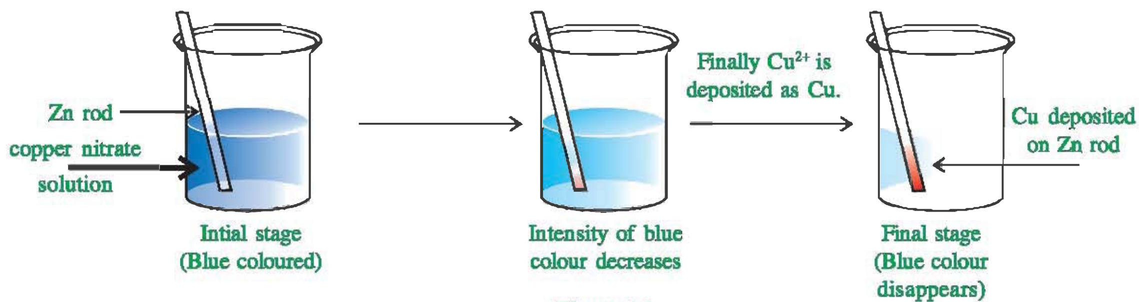


Figure 4.1

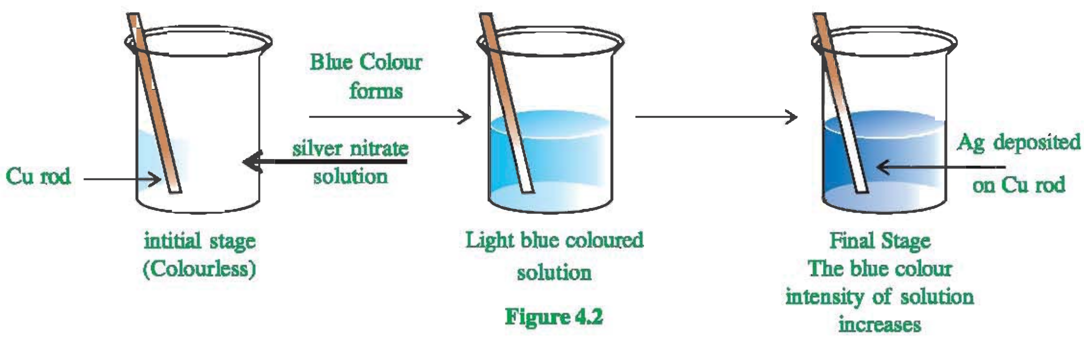


Figure 4.2

As shown in Fig. 4.1 when a rod of zinc (Zn) is placed in a solution of copper nitrate for some time, it is observed that the blue colour of copper nitrate solution disappears and reddish coloured copper (Cu) metal is deposited. As the Cu^{2+} ions are reduced in the solution, copper (Cu) is deposited on zinc (Zn) rod and the blue colour of solution disappears and a solution containing Zn^{2+} ions is formed which is colourless. The chemical reactions occur as follows :

$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$ ...... Oxidation half reaction

$Cu^{2+}_{(s)} + 2e^- \rightarrow Cu_{(s)}$ ...... Reduction half reaction

$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$ Complete Redox reaction

As shown in Fig. 4.2 when copper rod is placed in a solution of silver nitrate ($AgNO_3$) for some time, and observed, it is found that the Ag^+ ions in the solution are reduced and silver metal is deposited on copper rod. The copper rod is oxidized to Cu^{2+} ions so that the colour of solution becomes blue. The chemical reactions are as follows :

$Cu_{(s)} \rightarrow Cu^{2+}_{(aq)} + 2e^-$ ...... Oxidation half reaction

$2Ag^+_{(aq)} + 2e^- \rightarrow 2Ag_{(s)}$ ...... Reduction half reaction

$Cu_{(s)} + 2Ag^+_{(aq)} \rightarrow Cu^{2+}_{(aq)} + 2Ag_{(s)}$ Complete Redox reaction

Redox reactions are shown by such type of two reactions. Hence the number of electrons lost and the electrons received in the complete reaction are equal. It is always necessary to balance the redox reactions.

Similarly, the redox reaction between cobalt metal and nickel sulphate solution occurs as follows :

$Co_{(s)} \rightarrow Co^{2+}_{(aq)} + 2e^-$ ... Oxidation half reaction

$Ni^{2+}_{(aq)} + 2e^- \rightarrow Ni_{(s)}$ ... Reduction half reaction

$Co_{(s)} + Ni^{2+}_{(aq)} \rightarrow Co^{2+}_{(aq)} + Ni_{(s)}$ Complete Redox reaction

4.4 Oxidation Number

Some redox reactions can be explained by electron exchange method but some of the reactions cannot be clearly explained by electron exchange method. In the study of this type of redox reactions the explanation of oxidation number is very important.

Any element or a compound is neutral while the element in certain compounds are not neutral but they possess positive or negative electrical charge. Hence, the oxidation number of element present in simple ionic compounds is equal to the electric charge on that element.

The oxidation number is expressed on the basis of number of electrons lost or gained by an element, molecule or ion. Thus oxidation state indicates the electrical charge of that atom.

4.4.1 Rules for Calculation of Oxidation Number :

(1) The oxidation number of each neutral atom molecule or compound is considered zero e.g Na, Mg, Ca, Ba, H_2, Cl_2, Br_2, P_4, S_8, NaCl, CaO, $BaCl_2$, $AlCl_3$

(2) The oxidation number of free ions which are of the same atom as well as in their ionic compounds is considered same as the electric charge on the ion e.g.

In $MgCl_2$ $Mg^{2+} = 2$ and $C1^- = -1$

In NaCl $Na^+ = +1$ and $Cl^- = -1$

In CaO $Ca^{2+} = +2$ and $O^{2-} = -2$

In $AlCl_3$ $Al^{3+} = +3$ and $Cl^- = -1$

In FeS $Fe^{2+} = +2$ and $S^{2-} = -2$

In Sb_2S_3 $Sb^{3+} = +3$ and $S^{2-} = -2$

(3) The oxidation number of negative ions is same as their electric charge and oxidation number of positive ion is equal to its electric charge e.g.

NH_4^+ has +1

PH_4^+ has +1

NO_2^{-1} has -1 CN^{-1} has -1

CH_3COO^{-1} has -1 CO_3^{2-} has -2

SO_4^{2-} has -2 PO_4^{3-} has -3

ClO_3^{-1} has -1 BO_3^{3-} has -3

(4) In compounds of hydrogen the oxidation number of hydrogen is +1 but as an exception in metallic hydride compounds it is considered as -1. The oxidation number of hydrogen is +1 e.g. H_2S, NH_3, PH_3, H_2O, H_3PO_4, H_2SO_4

Similarly in metallic hydride like BeH_2, LiH, NaH, AlH_3, CaH_2 the oxidation number of hydrogen is -1.

(5) In most of the compounds of oxygen the oxidation number of oxygen is –2

e.g. in H_2O oxidation number of O = –2

in H_2SO_4 oxidation number of O = –2

in $KMnO_4$ oxidation number of O = –2

Exception : In peroxide (O–O) compounds the oxidation number of oxygen is considerd as –1 e.g. in K_2O_2, Na_2O_2, BaO_2, H_2O_2, the oxidation number of oxygen is –1

Exception : In the compounds of super-oxide the oxidation number of oxygen is considered –0.5 (–1/2) e.g. KO_2, CsO_2

Exception : In the compounds of fluorine with oxygen, the oxidation number of oxygen should be considered positive because the electro-negativity of F is more than that of oxygen. Hence oxygen possesses positive (+ve) oxidation number.

In O_2F_2 oxidation number of O = +1

OF_2 oxidation number of O = +2

(6) In halide compounds, the oxidation number of halogen (F, Cl, Br, I) is considered –1 e.g.

In HF, F = –1, in $BaCl_2$, Cl = –1,

in NaBr, Br = –1, in KI, I = –1

Exception : In oxides and oxyacids of halogens (except F) the oxidation number of halogen is considered positive (+ve) e.g.

In Cl_2O_6 the oxidation number of Cl = +6

In $HClO_2$ the oxidation number of Cl = +3

In $HBrO_3$ the oxidation number of Br = +5

In HIO_4 the oxidation number of I = +7

(7) In organic compounds possessing covalent bonds, more electronegative atom is assigned negative oxidation number and other having less electronegativity is assigned positive oxidation number, e.g. in CCl_4 the oxidation number of more electronegative atom chlorine is –1 and oxidation number of less electronegative atom carbon is +4 and the oxidation number of carbon becomes (–4), in CH_4.

(8) The algebraic sum of oxidation number of all elements in a polyatomic neutral molecules is zero which can be understood by examples given 1, 2, 3, 4, 5, 6... as mentioned in 4.4.2

(9) The algebraic sum of oxidation number of atoms present in polyatomic ion is equal to its electrical charge, which can be under-stood as mentioned in 4, 7 as in 4.4.2

(10) The oxidation number of alkali metals in its compounds is taken as +1 and the oxidation number of alkaline earth metal in its compounds is taken as +2. In fluoride compounds oxidation number of fluorine is always taken –1.

Thus, on the whole, the oxidation number of any neutral atom can be considered as zero, the oxidation number of any element in it can be calculated on the basis of above rules.

4.4.2 Calculation of Oxidation Number :

The oxidation number of molecule, ion or compound is calculated on the basis of the above rules.

(1) In $H_2\underline{S}$ molecule : Two atoms of hydrogen are present. The oxidation number of hydrogen is +1. As the oxidation number of H_2S is zero, the oxidation number of S will be –2 in H_2S

2 (oxidation number of H atom)

+ (oxidation number of S atom) = 0

$\therefore$ 2(1) + x = 0; $\therefore$ x = –2

Hence oxidation number of S = –2

(2) In $H_2\underline{S}O_4$ the oxidation number of S = x

$\therefore$ 2 (oxidation number of H atom) + (oxidation number of S atom) + 4 (oxidation number of O atom)

$\therefore$ 2(1) + x + 4 (–2) = 0

$\therefore$ 2 + x – 8 = 0 $\therefore$ x = +6

Hence oxidation number of S atom is + 6

(3) In $K_3\underline{P}O_4$ the oxidation number of P = x

3(oxidation number of K) + (oxidation number of P) + 4(oxidation number of O) = 0

$\therefore$ 3(1) + x + 4 (–2) = 0

$\therefore$ 3 + x – 8 = 0 $\therefore$ x = 5

Hence oxidation number of P is +5

(4) In $\underline{Cl}O_3^{-1}$ The oxidation number of Cl = x

(oxidation number of Cl) + 3(oxidation number of O) = –1

x + 3(–2) = –1

x – 6 = –1 $\therefore$ x = +5

Hence oxidation number of Cl is + 5

(5) In $\underline{C}H_2Cl_2$ molecule oxidation number of C = x

(oxidation number of C) + 2 (oxidation number of H) + 2 (oxidation number of Cl) = 0

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

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

Hence, oxidation number of C is 0.

(6) In $\underline{Si}O_2$ The oxidation number of Si = x

(oxidation number of Si) +2 (oxidation number of O) = 0

$x + 2(-2) = 0$

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

Hence, oxidation number of Si is +4

(7) In $\underline{Cr}O_4^{2-}$ oxidation number of Cr = x

(oxidation number of Cr) + 4(oxidation number of O) = -2

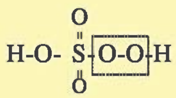
$x + 4(-2) = -2$

$x - 8 = -2 \quad \therefore x = +6$

Hence, oxidation number of Cr is +6

(8) Calculate some exceptional oxidation numbers of elements :

(1) $H_2\underline{S}O_5$ per mono sulphuric acid (Caro's acid). In per monosulpharic acid,



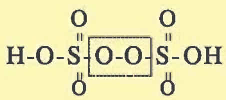
oxidation number of S = x

∴ 2 (oxidation number of H) + 2 (oxidation number of O atoms of peroxide) + (oxidation number of S) + 3 (oxidation number of oxygen) = 0

$\therefore 2(+1) + 2(-1) + x + 3(-2) = 0$

$\therefore x = +6$

(2) $H_2\underline{S}_2O_8$ perdisulphuric acid (Marshall's acid). In perdisulphuric acid



∴ oxidation number of S = x

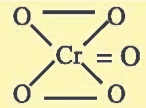
∴ 2 (oxidation number of H atom) + 2(oxidation number of O atoms of peroxide) + 2(oxidation number of S atom) + 6 (oxidation number of O atoms = 0

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

$\therefore 2x = +12$

$\therefore x = +6$

(3) $\underline{Cr}O_5$



In the given substance CrO_5 it possesses two peroxy rings, where oxidation number of O atom will be -1

suppose oxidation number of Cr = x in CrO_5

∴ x + 4 (oxidation number of 0 of peroxide) + 1(oxidation number of O atom) = 0

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

$\therefore x = +6$

4.4.3 Oxidation Number and Redox Reaction :

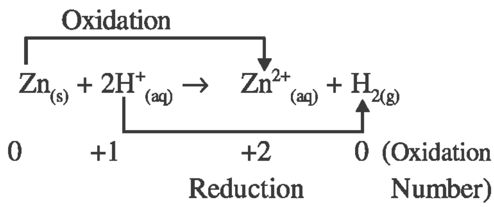
The reaction in which there is change in oxidation number of reactants is called redox reaction. The reaction in which, there is increase in oxidation number of reactant is called oxidation and the reaction in which there is decrease in oxidation number of reactant is called reduction reaction.

By the study of reaction between zinc and hydrochloric acid it is found that

$$Zn_{(s)} + 2HCl_{(aq)} \rightarrow ZnCl_{2(aq)} + H_{2(aq)}$$

OR

$$Zn_{(s)} + 2H^+_{(aq)} \rightarrow Zn^{2+}_{(aq)} + H_2$$



In this reaction zinc is converted to Zn^{2+} ion by loss of two electrons. So, it undergoes oxidation while H^+ ions are reduced by gain of electrons. Hence, zinc (Zn) is a reducing agent and H^+ ion is an oxidizing agent. Looking this reaction from oxidation number point of view the oxidation number zero (0) of Zn is increased to +2 and the oxidation number of H^+ ion is decreased from +1 to zero. Hence, it can be said that in oxidation reaction the oxidation number of one reactant increases and in reduction the oxidation number of other reactant decreases.

The following redox reaction can be explained by calculation of oxidation number :

(1) $2HI_{(aq)} + Br_{2(l)} \rightarrow I_{2(s)} + 2HBr_{(aq)}$

Change in oxidation number

I = 0 from -1(increase of 1 in oxidation number)

Br = -1 from 0(decrease of 1 in oxidation number)

H = +1 from +1(No change in oxidation number and so it is considered as spectator ion)

In the reaction iodide ion is oxidized and bromine is reduced

(2) $3MnO_{2(s)} + 4Fe \rightarrow 3Mn_{(s)} + 2Fe_2O_{3(s)}$

The change in oxidation number

Mn = 0 from +4(Decrease in oxidation number by 4)

Fe = +3 from 0 (Increase in oxidation number by 3)

O = -2 from -2 (No change in oxidation number-Spectator ion)

In this reaction oxidation of iron and reduction of manganese ion take place.

(3) $MnO_4^{-1}+5Fe^{2+}+8H^+ \rightarrow Mn^{2+}+5Fe^{3+}+ 4H_2O$

change in oxidation number

Mn = +2 from + 7 (Decrease in oxidation number by 5)

Fe = + 3 from + 2 (Increase in oxidation number by 1)

O = -2 from -2 (No change in oxidation number -spectator ion)

H = +1 from +1 (No change in oxidation number -spectator ion)

In this reaction oxidation of ferrous ion and reduction of manganese of $KMnO_4$ take place.

4.5 Oxidation Number and Nomenclature

Roman scientists used the oxidation state of element in the nomenclature of metal compounds. This nomeclature method is known as "Stock notation" in which the oxidation number of metal is expressed with Roman number in the bracket. The oxidation number of Cu in Cu_2O and CuO are +1 and +2 respectively. These two compounds are known as copper (I) oxide and copper (II) oxide. In the same way, oxides of iron FeO and Fe_2O_3 are known as iron (II) oxide and iron (III) oxide.

Stock notation method is used in type of metals which have more than one oxidation states e.g.

(1) $FeSO_4$ as iron (II) sulphate
(2) $Fe_2(SO_4)_3$ as iron (III) sulphate
(3) Na_2CrO_4 as sodium chromate (VI)
(4) K_2CrO_7 as Potassium dichromate (VI)
(5) Cr_2O_3 as Chromium (III) oxide
(6) Mn_2O_7 as Manganese (VII) oxide
(7) V_2O_5 as Vanadium (V) oxide

Generally Stock notation is used for metals but not for non metals.

4.6 Equation of Redox Reaction

Some general rules must be obeyed while showing redox reaction equation :

(1) The molecular formulas of reactants and products must be known.

(2) All the electrons released during oxidation half reaction, should be used in the reduction half rection that is to say, change of electron in the reaction, should be the same.

(3) The law of conservation of mass must be obeyed. The number of atoms or elements on both the sides of equation should be the same.

Redox reactions can occur in acidic, basic or neutral media. For reactions in acidic medium the requirement of oxygen is fulfilled by using H_2O and using H^+ for hydrogen. In basic medium the requirement of oxygen is fulfilled by H_2O and OH^- ions are used to fulfill requirement of hydrogen.

4.7 Balancing of Redox Reaction Equation

Two methods are used for the balancing of redox reaction equation.

(1) Oxidation number method (2) Oxidation number and half reaction equation method.

4.7.1 Balancing of Redox Reaction equation using Oxidation Number Method :

In balancing of redox reaction equation, the balance is carried by difference in oxidation number of reactants and products. It can be balanced in different media like acidic or basic. The balanced equation is obtained in redox equation equilibrium by using following points in sequence :

Points :

(1) Write oxidation number of all the elements in the redox equation.

(2) Balance the atoms of reactants and products in which oxidation numbers are changing. If one reactant is experiencing both oxidation and reduction reactions, it should be mentioned twice.

(3) Determine oxidation and reduction reactions on the basis of change of oxidation numbers and write the change in oxidation number.

(4) Multiply the oxidation and reduction reactions with proper coefficient for balancing the change in oxidation digit number.

(5) Obtain the balanced equation by adding H_2O to balance oxygen atoms by adding H^+ or OH^- on the basis of medium of reaction and the electric charge of reactants and products. Each spectator atom must also be balanced. If the medium is acidic, add

H^+ and H_2O and if the medium is basic, add OH^- and H_2O. The electric charges of reactants and products in the equation must be mentioned and that should be balanced.

Example 4.1 : Balance the following reaction by oxidation number method :

$MnO^{-1}_4 + H_2S + H^+ \rightarrow Mn^{2+} + S$ (Acidic Medium)

(1) Write oxidation number of elements

$MnO_4^{-1} \;+\; H_2S \;\rightarrow\; Mn^{2+} + S$

(+7)(–2) (+1)(–2) +2 0

(2) Balance the number of atoms of the elements in which oxidation number changes

$MnO_4^{-1} \;+\; H_2S \;\rightarrow\; Mn^{2+} + S$

(+7) (-2) (+2) 0

(3) Decide the oxidation and reduction reaction on the basis of difference of oxidation number.

Increase in oxidation number by 2(Oxidation)

$MnO_4^{-1} + H_2S \rightarrow Mn^{2+} + S$

Decrease in oxidation number by 5(Reduction)

(4) On multiplying oxidation reaction by 5 and reduction reaction by 2 to balance the change in oxidation number.

$2MnO_4^{-1} + 5H_2S \rightarrow 2Mn^{2+} + 5S$

(5) Balance the electric charge and atoms which do not change in oxidation number (spectator ion).

$2MnO_4^{-1} + 5H_2S + 6H^+ \rightarrow 2Mn^{2+} + 5S + 8H_2O$

$2(-1) + 5(0) + 6(+1) = 2(+2) + 5(0) + 8(0)$

$-2 + 6 = +4$

$+4 = +4$

In the above reaction the reactants and products are balanced in terms of electric charge and mass equivalence.

Example 4.2 : Balance the following redox reaction by oxidation number method.

$P_4 + OH^- \rightarrow PH_3 + H_2PO_2^{1-}$

(Basic indium)

(1) Write oxidation numbers of elements

$P_4 + OH^- \rightarrow PH_3 + H_2PO_2^{1-}$

0 -2+1 -3+1 + 1+1-2

(2) Balance the atom of elements and write the change in oxidation number.

$P_4 + P_4 \rightarrow 4PH_3 + 4H_2PO_2^{1-}$

0 0 4(–3) 4(1)

–12 +4

(3) Decide the oxidation and reduction reaction on the basis of change in oxidation number.

Increase in oxidation number by 4(+1) = +4 (oxidation)

$P_4 + P_4 \rightarrow 4PH_3 + 4H_2PO_3^{-1}$

Decrease in oxidation number by 4(–3) = –12 (Reduction)

(4) To balance the change in oxidation number multiply oxidation reaction by 3

$P_4 + 3P_4 \rightarrow 4PH_3 + 12H_2PO_2^{1-}$

$\therefore 4P_4 \rightarrow 4PH_3 + 12H_2PO_2^{1-}$

Dividing by common factor 4

$P_4 \rightarrow PH_3 + 3H_2PO_2^{1-}$

(5) To balance the electric charge and atoms which do not change in oxidation number (Spectators)

$P_4 + 3OH^- + 3H_2O \rightarrow PH_3 + 3H_2PO_2^{1-}$

4(0)+3(-1)+3(0) 0 + 3(–1)

–3 = –3

The above reaction is balanced in terms of electric charge and mass equivalence.

4.7.2 Balancing of Redox Reaction equation using Half Reaction equation Method : The balanced equation is obtained by using following points in sequence.

Points :

(1) Find the elements whose oxidation numbers change and write half reactions.

(2) Separate both the half reactions in which oxidation numbers change and balance their atoms.

(3) Put number of electrons equivalent to the oxidation numbers in both half reactions.

(4) On the basis of total electric charge in both the half reactions and the medium of the reaction, add H^+, OH and H_2O and balance the equation.

(5) Obtain the balanced equation by equalizing both the half reactions by number of electrons and then add up.

Example 4.3 : Balance the following redox reaction by half reaction equation :

$MnO_4^{1-} + H_2S \rightarrow Mn^{1+} + S$ (Acidic Medium)

(1) Write the Oxidation number of elements and half reaction

$MnO_4^- + H_2S \rightarrow Mn^{2+} + S$

(+7) (−2) (+1)(−2) +2 0

$MnO_4^{-1} \rightarrow Mn^{2+}$	$H_2S \rightarrow S$
(+7) (+2)	(−2) (0)
Decrease in oxidation number	Increase in oxidation number
∴Reduction half reaction	∴Oxidation half reaction

(2) Balance the atoms of elements in both half reactions

$MnO_4^- \rightarrow Mn^{2+}$	$H_2S \rightarrow S$
(+7) +2	(−2) 0

(3) Add electrons on the basis of change in oxidition number in both half reaction

$MnO_4^{-1} + 5e^- \rightarrow Mn^{2+}$ | $H_2S \rightarrow S + 2e^-$

(4) Add H^+ and H_2O on the basis of acidic medium to balance electric charge in both half reactions.

$MnO_4^- + 5e^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O$ | $H_2S \rightarrow S + 2e^- + 2H^+$

(5) To equalize the number of electrons in both half reactions, oxidation half reaction is multiplied by 5 and reduction half reaction by 2 and then adding up both the half reactions.

$2MnO_4^- + 10e^- + 16H^+ \rightarrow 2Mn^{2+} + 8H_2O$

$5H_2S \rightarrow 5S + 10e^- + 10H^+$

$2MnO_4^- + 5H_2S + 6H^+ \rightarrow 2Mn^{2+} + 8H_2O + 5S$

2(-1) + 5(0) 6(+1) 2(+2) 8(0) + 5(0)

−2 + (0) + 6 (+1) = +4

+4 = +4

The above reaction is balanced in terms of electric charge and mass equivalence.

Example 4.4 : Balance the following redox reaction by half reaction method :

$P_4 + OH^{1-} \rightarrow PH_3 + H_2PO_2^{1-}$ (Basic Medium)

(1) Write oxidation number of elements and half reaction

$P_4 + OH^{1-} \rightarrow PH_3 + H_2PO_2^{1-}$

0 −2 +1 −3(+1) +1 +1 −2

$P_4 \rightarrow H_2PO_2^{1-}$	$P_4 \rightarrow PH_3$
Increase in oxidation number.	Decrease in oxidation number
∴Oxidation half reaction	∴ Reduction half reaction

(2) Balance the atoms of elements in both half reactions.

$P_4 \rightarrow 4H_2PO_2^{1-}$	$P_4 \rightarrow 4PH_3$
4(0) 4(1)	0 4(−3)
0 +4	−12

(3) Add electrons on the basis of change in oxidation number in both half reactions.

$P_4 \rightarrow 4H_2PO_2^{1-} + 4e^-$ | $P_4 + 12e^- \rightarrow 4PH_3$

(4) Add OH^- and H_2O on the basis of basic medium to balance the electric charge in both half reactions.

$P_4 + 8OH^- \rightarrow 4H_2PO_2^{1-} + 4e^-$ | $P_4 + 12e^- + 12H_2O \rightarrow 4PH_3 + 12OH^-$

(5) To equalize the number of electrons in both half reactions, multiply oxidation reaction by 3 and adding up both half reactions.

$3P_4 + 24OH^- \rightarrow 12H_2PO_2^{1-} + 12e^-$

$P_4 + 12e^- + 12H_2O \rightarrow 4PH_3 + 12OH^-$

$4P_4 + 12H_2O + 12OH^- \rightarrow 12H_2PO_2^{1-} + 4PH_3$

dividing by common factor 4

$P_4 + 3H_2O + 3OH^- \rightarrow 3H_2PO_2^{1-} + PH_3$

(0) + (0) 3(−1) 3(−1)+ 0

−3 = −3

The above redox reaction is balanced in terms of electric charge and mass equivalence.

SUMMARY

The form of redox reaction is such an important reaction in which oxidation and reduction reactions occur simultaneously. The points involved in are electron transfer, oxidation number etc. An attempt is made to give a deep explanation of these points. The concepts of oxidation, reduction, oxidizing agents, reducing agent are given in sequence. To find out oxidation number rules are also given in sequence which may be followed and oxidation number can be calculated.

The nomenclature, in compounds of metals, Stock notation can be used. To balance the reaction equation, two methods (i) Oxidation Number Method (ii) Half Rection Equation Method can be used which are explained in both acidic and basic medium with illustration.

EXERCISE

1. Select the proper choice from the given multiple choices :

(1) What is the reaction called in which hydrogen is added during the reaction ?

(A) Oxidation (B) Reduction

(C) Redox (D) All the given

(2) In the reaction $H_{2(g)} + Br_{2(g)} \rightarrow 2HBr_{(g)}$ which substance undergoes oxidation ?

(A) H_2 (B) Br_2

(C) HBr (D) H_2 and Br_2

(3) Which of the following statement is correct ?

(A) Reducing agent is reduced.

(B) Oxidising agent is oxidized.

(C) Reducing agent is oxidized.

(D) Oxidation or reduction does not occur in the reaction.

(4) Which substance is the oxidizing agent in redox reaction ?

R-CHO + 2CuO $\rightarrow$ Cu_2O + R-COOH

(A) CuO (B) R-CHO

(C) Cu_2O (D) R-COOH

(5) Which of the following reactions is a redox reaction ?

(A) $NaOH_{(aq)} + HCl_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$

(B) $CH_3COOH + CH_3OH \rightarrow CH_3COOCH_3 + H_2O$

(C) $K_2SO_{4(aq)} + BaCl_{2(aq)} \rightarrow 2KCl_{(aq)} + BaSO_{4(s)}$

(D) $H_2S_{(aq)} + 3H_2SO_{4(aq)} \rightarrow 4SO_{2(g)} + 4H_2O_{(l)}$

(6) In which order is oxidation number of underlined elements in <u>Ba</u>O_2 and <u>Si</u>O_2 ?

(A) +2,+4 (B) +2, +2

(C) +4, +2 (D) +4, +4

(7) Which substance is the reducing agent in the reaction ?

$CH_3CHO_{(s)} + Ag_2O_{(s)} \rightarrow CH_3COOH + 2Ag$

(A) CH_3CHO (B) Ag_2O

(C) CH_3COOH (D) Ag

(8) What is the oxidation number of N in N_3H ?

(A) 2 (B) 1

(C) $-\frac{1}{3}$ (D) 0

(9) $K_2Cr_2O_7$ + (a)SO_2 + (b)H_2SO_4 $\rightarrow$ K_2SO_4 + $Cr_2(SO_4)_3$ + (c)H_2O In the reaction what will be the respective number of coefficients (a), (b), and (c).

(A) 1,1,3 (B) 3,1,1

(C) 1,3,1 (D) 3,1,3

(10) Which of the following atoms can have positive and negative oxidation number in their compounds ?

(A) F (B) Na

(C) Ar (D) Cl

(11) Mention the values of a, b, c and d respectively for the balanced chemical rection

BrO^{3-} + (a)Br^- + (b) H^+ $\rightarrow$ (c) Br_2 + (d) H_2O

(A) 5,6,3,3 (B) 5,4,3,4

(C) 3,5,6,3 (D) 3,3,6,5

(12) In which reaction, H_2SO_4 acts as an oxidizing agent ?

(A) $2KOH + H_2SO_4 \rightarrow K_2SO_4 + 2H_2O$

(B) $2HCl + H_2SO_4 \rightarrow Cl_2 + SO_2 + 2H_2O$

(C) $Ba(OH)_2 + H_2SO_4 \rightarrow BaSO_4 + 2H_2O$

(D) $NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$

2. Write the answers of the following questions in short :

(1) What is oxidation reaction ?

(2) What is reduction reaction ?

(3) Give an example of oxidation reaction.

(4) Give an example of reduction reaction.

(5) What is an oxidizing agent ?

(6) What is a reducing agent ?

(7) What is an oxidation number ?

(8) What is Stock notation method ? To what it is applied ?

(9) Calculate oxidation number of S in $H_2\underline{S}O_5$.

(10) Write the chemical reaction when Cu rod is placed in solution of silver nitrate.

(11) Write chemical reaction when Zn rod is placed in solution of H_2SO_4.

(12) Write the name of $K_2Cr_2O_7$ according to Stock notation.

3. Write the answers of the following questions :

(1) Explain oxidation reduction (Redox) reaction.

(2) Find oxidation number of carbon in following compounds :

CH_4, CO, H_2CO_3, K_2CO_3

(3) Find oxidation number of nitrogen in following compounds.

$(NH_4)_2CO_3$, N_2H_4, $NaNO_3$, $Ba(NO_3)_2$

(4) Explain Stock notation method with example.

(5) Are the following reactions-redox or not ? Explain :

(1) $H_2S_{(aq)} + Cl_{2(g)} \rightarrow S_{(g)} + Cl^{-}_{(aq)}$

(2) $2Na_{(g)} + Cl_{2(g)} \rightarrow 2NaCl_{(s)}$

(3) $FeSO_{4(aq)} + Mg_{(s)} \rightarrow MgSO_{4(aq)} + Fe_{(s)}$

(4) $Cu_{(s)} + 4HNO_{3(aq)} \rightarrow Cu(NO_3)_{2(aq)} + 2NO_{2(g)} + 2H_2O_{(l)}$

(6) $Cr^{3+}_{(aq)} + ClO^{1-}_{3(aq)} \rightarrow Cr_2O^{2-}_{7(aq)} + ClO^{1-}_{2(aq)}$

Give the following informations :

(1) Which reactant is oxidized ?

(2) Which reactant is reduced ?

(3) Which reactant is an oxidizing agent ?

(4) Which reactant is a reducing agent ?

4. Write the answers of the following questions in detail :

(1) Explain any three oxidation-reduction (redox) reactions on the basis of electron exchange.

(2) Balance the following reactions by both (oxidation number and half reaction equation) methods.

(1) $MnO_4^{1-} + As_2O_3 \rightarrow Mn^{2+} + AsO_4^{3-}$ (pH <7)

(2) $Br_2 + OH^- \rightarrow BrO_3^- + Br^-$ (Basic medium)

(3) $S + HNO_3 \rightarrow H_2SO_4 + NO$ (Acidic medium)

(4) $P_4 + NO_3^- \rightarrow PO_4^{3-} + NO_2$ (Acidic medium)

(5) $FeS + H_2O_2 \rightarrow FeO + SO_2$ (Acidic medium)

(6) $Cr(OH)_3^{1-} + HO_2^{1-} \rightarrow Cr_2O_7^{2-} + OH^-$ (Basic medium)

(7) $As_2O_3 + CrO_4^{2-} \rightarrow H_3AsO_3 + Cr_2O_3$ (Acidic medium)

(8) $S_2O_3^{2-} + Br_2 \rightarrow S_4O_6^{2-} + Br^-$

(9) $Cu_2S + SO_4^{2-} \rightarrow CuO + SO_2$ (Acidic medium)

(10) $P_4 + NaOH \rightarrow PH_3 + NaH_2PO_2$ (Basic medium)

(11) $V + H_2O \rightarrow H_4V_6O_{17} + H_2$ (Basic medium)

(12) $Ag_2S + CN^{1-} + O_2 \rightarrow Ag(CN)_2^- + S$ (Basic medium)

(13) $Cl_2 + NaOH \rightarrow ClO_3^- + NaCl$ (Basic medium)

(14) $CuS + SO_4^{2-} \rightarrow CuO + SO_2$ (Acidic medium)

(15) $FeS_2 + O_2 \rightarrow Fe_2O_3 + SO_2$