Chapter – 8

India's First Colour Smart Book

REDOX REACTION

1 BASIC CONCEPT

In the previous chapter, 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 chapter, we shall discuss another important class of reactions called reduction–oxidation or simply redox reactions. All these reactions are always accompanied by energy changes in the form of heat, light or electricity.

A large number of chemical and biological reactions fall in this category. Burning of different types of fuels for obtaining energy for domestic, transport or industrial purpose, electrochemical processes like manufacturing of caustic soda, digestion of food in animals, photosynthesis by plants, corrosion of metals and operations of dry and wet batteries are diverse examples of redox reactions.

2 OXIDATION AND REDUCTION

In redox reactions one reactant called **reductant or reducing agent** is oxidised while the other reactant called **oxidant or oxidising agent** is reduced.

CLASSICAL CONCEPT OF OXIDATION AND REDUCTION

Originally, **oxidation** of a substance was defined as the addition of oxygen or any other electronegative element to it. Due to the presence of oxygen in the atmosphere, many elements combine with it. In fact the most common occurrence of elements on the earth is in the form of their oxides. **Later on, removal of hydrogen or any other electropositive element from a substance was also considered as oxidation.**

(i) $2Mg(s) + O_2(g) \longrightarrow 2MgO(s)$

Magnesium is oxidised by addition of oxygen to it.

(ii) $2H_2S(g) + O_2(g) \longrightarrow 2S(s) + 2H_2O(l)$

Hydrogen sulphide is oxidised by the removal of hydrogen from it.

(iii) $Mg(s) + F_2(g) \longrightarrow MgF_2(s)$

Magnesium is oxidised by the addition of fluorine to it.

(iv) $Mg(s) + S(s) \longrightarrow MgS(s)$

Magnesium is oxidised by the addition of sulphur to it.

Similarly reduction of a substance was initially introduced for the processes in which metal oxides were converted into metals by their reactions with hydrogen, carbon or other metals. Carbon monoxide is also used in the reduction of ferric oxide to iron.

(i) $CuO(s) + H_2(g) \longrightarrow Cu(s) + H_2O(l)$

(ii) $2CuO(s) + C(s) \longrightarrow 2Cu(s) + CO_2(g)$

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

Here, in all the three cases mentioned above metal oxide is reduced by hydrogen, carbon or carbon monoxide.

MODERN CONCEPT OF OXIDATION AND REDUCTION

The general definition of oxidation is ***loss of electrons***. In the above examples of oxidation magnesium is converted into Mg^{2+} ion and in the process it loses two electrons.

Similarly, reduction in general means ***acceptance of electrons***. When CuO reacts with hydrogen it gets converted into copper. In copper oxide, each Cu^{2+} ion accepts two electrons and gets reduced to copper.

COMPLIMENTARY NATURE OF OXIDATION AND REDUCTION REACTIONS

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 complimentary. This is illustrated by the following examples

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

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

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

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

The occurrence of electron transfer is more apparent in some redox reactions than others. When metallic zinc is added to a solution containing copper(II) sulphate, zinc reduces Cu^{2+} by donating two electrons to it.

$$Zn(s) + CuSO_4(aq) \longrightarrow ZnSO_4(aq) + Cu(s)$$

In the process, solution loses the blue colour that characterizes the presence of Cu^{2+} ions. The oxidation and reduction reactions are

$Zn \longrightarrow Zn^{2+} + 2e^-$ [Oxidation half reaction]

$Cu^{2+} + 2e^- \longrightarrow Cu$ [Reduction half reaction]

Similarly, metallic copper reduces silver ions in a solution of silver nitrate ($AgNO_3$)

$$Cu(s) + 2AgNO_3(aq) \longrightarrow Cu(NO_3)_2(aq) + 2Ag(s)$$

The oxidation and reduction reactions are

$Cu \longrightarrow Cu^{2+} + 2e^-$ [Oxidation half reaction]

$2Ag^+ + 2e^- \longrightarrow 2Ag$ [Reduction half reaction]

PRACTICE PROBLEM

PP1. Identify the oxidant and the reductant in the following reactions.

(a) $Zn(s) + \frac{1}{2}O_2(g) \longrightarrow ZnO(s)$

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

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

(d) $H_2S + 2FeCl_3 \longrightarrow 2FeCl_2 + 2HCl + S$

3 THE OXIDATION STATE OF AN ELEMENT

To describe the changes that occur in oxidation–reduction reactions and to write the correctly balanced equations for such reactions, it is helpful to know the concept of the oxidation state (or oxidation number) of an atom.

For monoatomic ions, **the oxidation state is simply the charge on the ion.** For example, oxidation states of Na^+, Mg^{2+}, Cl^- and N^{3-} are +1, +2, –1 and –3 respectively. For covalently bonded substances, the charge on an atom would be so small that it is impossible to calculate the exact charge on each atom in the molecule. Thus, oxidation state of an atom in a covalently bonded molecule is defined as **"the charge an atom would possess if all the bonds associated with that atom are broken heterolytically considering them to be completely ionic".** For example, in NH_3 there are three N–H bonds. If we consider all three N–H bonds to be ionic, then each H will possess a charge of +1 while N acquires a charge of –3 (because N is more electronegative than H). In H_2O_2, there are two O–H bonds and one O–O bond as evident from the structural formula H–O–O–H. Assuming each O–H bond to be ionic, each H atom would possess +1 charge while each O would possess –1 charge. The O–O bond is not ionic as the bond is between atoms of similar electronegativity. Thus oxidation state of each O-atom in H_2O_2 is –1.

It is not necessary to know the structure of a molecule in order to calculate the oxidation state of an atom in a molecule. The following set of rules are used to assign oxidation state to each atom in an ion or molecule.

1. Each pure element has an oxidation state of zero. This is true whether the element is a monoatomic gas, a metallic solid or a polyatomic molecule. Thus, Fe(s), N_2(g), P_4(s) and S_8(s) are all in the zero oxidation state.
2. In monoatomic ions, the oxidation state of the element is equal to the charge on the ion. Thus, oxidation state of all alkali metals is +1 and that of alkaline earth metals is +2 in all their compounds. In ionic solid K_2S, the oxidation states of potassium and sulfur are +1 and –2 respectively. In AgCl, the oxidation state of silver and chlorine are +1 and –1 respectively.
3. The oxidation state of hydrogen in any molecule in which it is combined with another element is +1, except in the metallic hydrides such as LiH or CaH_2, where the oxidation state of hydrogen is –1.
4. The oxidation state of oxygen in any molecule or ion in which it is combined with another element is –2, except in the peroxides, the superoxides and in OF_2. The peroxides (H_2O_2, Na_2O_2, BaO_2 etc.) are compounds in which there is an O–O covalent bond and the peroxide ion is O_2^{2-}. The oxidation state of oxygen in peroxides is –1. The superoxides (like KO_2, CsO_2 etc.) are ionic compounds involving the superoxide ion, O_2^-. The oxidation state of oxygen is –½ in superoxide ion. In OF_2, the oxidation state of oxygen is +2 since fluorine is more electronegative than oxygen.
5. The oxidation state of all the halogens is –1 in all their compounds except where they are combined with an element of higher electronegativity or in interhalogen compounds.. Oxidation state of fluorine is always –1, since it is the most electronegative element.
6. In covalent compounds not involving hydrogen or oxygen, the more electronegative element is assigned negative oxidation state while a less electronegative element is assigned a positive oxidation state.
7. The algebraic sum of the oxidation numbers of all the atoms combined in a molecule or complex ion must equal the net charge on the molecule or ion.

Question: **Calculate the oxidation state of the underlined atoms in the given species.**

(a) $\underline{N}O_2^+$ **(b)** $\underline{N}O_3^-$

(c) $K\underline{Mn}O_4$ **(d)** $\underline{Cr}_2O_7^{2-}$

(e) $\underline{Fe}_2O_3$ **(f)** $\underline{Fe}_3O_4$

Solution:

(a) Let the oxidation state of N in NO_2^+ be 'x'.

$x + [2(-2)] = +1$

$x = +5$

Thus, oxidation state of N in NO_2^+ is **+5**.

(b) Let 'x' be the oxidation state of N in NO_3^-.

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

$x = +5$

Thus, oxidation state of N in NO_3^- is **+ 5**.

(c) Let the oxidation state of Mn in $KMnO_4$ be 'x'.

$[1(+1)] + x + [4(-2)] = 0$

$x = +7$

Thus, oxidation state of Mn in $KMnO_4$ is **+ 7**.

(d) Let the oxidation state of Cr in $Cr_2O_7^{2-}$ be 'x'.

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

$x = +6$

Thus, oxidation state of Cr in $Cr_2O_7^{2-}$ is **+6**.

(e) Let 'x' be the oxidation state of Fe in Fe_2O_3.

$2x + [3(-2)] = 0$

$x = +3$

Thus, oxidation state of Fe in Fe_2O_3 is **+3**.

(f) Let the oxidation state of Fe in Fe_3O_4 be 'x'.

$3x + [4(-2)] = 0$

$x = +8/3$

Thus, oxidation state of Fe in Fe_3O_4 is **+8/3**. This is the average oxidation state of Fe in Fe_3O_4. Actually, Fe_3O_4 is made up of equimolar quantity of FeO and Fe_2O_3.

4 TYPES OF REDOX REACTION

There are four general types of redox reactions, namely

1. Combination reactions.
2. Decomposition reactions.
3. Displacement reactions.
4. Disproportionation reactions.

COMBINATION REACTIONS

A combination reaction may be represented by

$$A + B \longrightarrow C$$

If either A or B is an element, then the reaction is usually redox in nature. ***Combination reactions*** are reactions in which two or more substances combine to form a single product.

For example,

0 0 +4 –2

$$S(s) + O_2(g) \longrightarrow SO_2(g)$$

$$3\overset{0}{Mg}(s) + \overset{0}{N_2}(g) \longrightarrow \overset{+2}{Mg_3}\overset{-3}{N_2}(s)$$

DECOMPOSITION REACTIONS

Decomposition reactions are the opposite of combination reactions. Specifically, a ***decomposition reaction*** is the breakdown of a compound into two or more components.

$$C \longrightarrow A + B$$

$$2\overset{+2}{Hg}\overset{-2}{O}(s) \longrightarrow 2\overset{0}{Hg}(l) + \overset{0}{O_2}(g)$$

$$2K\overset{+5}{Cl}\overset{-2}{O_3}(s) \longrightarrow 2K\overset{-1}{Cl}(s) + 3\overset{0}{O_2}(s)$$

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

Note that we show oxidation states only for the elements that are oxidized or reduced.

DISPLACEMENT REACTIONS

In a ***displacement reaction***, an ion (or atom) in a compound is replaced by an ion (or atom) of another element:

$$A + BC \longrightarrow AC + B$$

Most displacement reactions fit into one of three subcategories: hydrogen displacement, metal displacement or halogen displacement.

Hydrogen Displacement

All alkali metals and some alkaline earth metals (Ca, Sr and Ba), which are the most reactive of the metallic elements, will displace hydrogen from cold water.

$$2\overset{0}{Na}(s) + 2\overset{+1}{H_2}O(l) \longrightarrow 2\overset{+1}{Na}O\overset{+1}{H}(aq) + \overset{0}{H_2}(g)$$

$$\overset{0}{Ca}(s) + 2\overset{+1}{H_2}O(l) \longrightarrow \overset{+2}{Ca}(O\overset{+1}{H})_2(aq) + \overset{0}{H_2}(g)$$

Less reactive metals, such as aluminium and iron, react with steam to give hydrogen gas:

$$2\overset{0}{Al}(s) + 3\overset{+1}{H_2}O(g) \longrightarrow \overset{+3}{Al_2}O_3(s) + 3\overset{0}{H_2}(g)$$

$$2\overset{0}{Fe}(s) + 3\overset{+1}{H_2}O(g) \longrightarrow \overset{+3}{Fe_2}O_3(s) + 3\overset{0}{H_2}(g)$$

Many metals, including those that do not react with water, are capable of displacing hydrogen from acids. For example, zinc (Zn) and magnesium (Mg) do not react with water but do react with hydrochloric acid, as follows:

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

$$\overset{0}{Mg}(s) + 2\overset{+1}{H}Cl(aq) \longrightarrow \overset{+2}{Mg}Cl_2(aq) + \overset{0}{H_2}(g)$$

Metal Displacement

A metal in a compound can be displaced by another metal in the elemental state.

In addition to the two examples given in section 2.3 some more examples are given as follows

$$V_2O_5(s) + 5Ca(l) \longrightarrow 2V(l) + 5CaO(s)$$

$$TiCl_4(g) + 2Mg(l) \longrightarrow Ti(s) + 2MgCl_2(l)$$

Halogen Displacement

Another activity series summarizes the halogens behaviour in halogen displacement reactions:

$F_2 > Cl_2 > Br_2 > I_2$

The power of these elements as oxidizing agents decreases as we move down the group VII A from fluorine to iodine. So molecular fluorine can displace chloride, bromide and iodide ions in solution. In fact, molecular fluorine is so reactive that it also attacks water. Thus, these reactions cannot be carried out in aqueous solutions. On the other hand molecular chlorine can displace bromide and iodide ions in aqueous solution. The displacement equations are

$$\overset{0}{Cl_2}(g) + 2K\overset{-1}{Br}(aq) \longrightarrow 2K\overset{-1}{Cl}(aq) + \overset{0}{Br_2}(l)$$

$$\overset{0}{Cl_2}(g) + 2Na\overset{-1}{I}(aq) \longrightarrow 2Na\overset{-1}{Cl}(aq) + \overset{0}{I_2}(s)$$

DISPROPORTIONATION REACTIONS

A special type of redox reaction is the ***disproportionation reaction***. In this type of reactions, an element in one oxidation state is simultaneously oxidized and reduced. One reactant in a disproportionation reaction always contains an element that shows increase in its oxidation state in one product and decrease in its oxidation state in another product. The element itself is in an intermediate oxidation state, i.e., both higher and lower oxidation states of the element exist on the product side. The decomposition of hydrogen peroxide is an example of a disproportionation reaction

$$2H_2\overset{-1}{O_2}(aq) \longrightarrow 2H_2\overset{-2}{O}(l) + \overset{0}{O_2}(g)$$

Question: **Classify the following redox reactions and indicate changes in the oxidation states of the elements involved in each reaction.**

(a) $2N_2O(g) \longrightarrow 2N_2(g) + O_2(g)$

(b) $6Li(s) + N_2(g) \longrightarrow 2Li_3N(s)$

(c) $Ni(s) + Pb(NO_3)_2(aq) \longrightarrow Pb(s) + Ni(NO_3)_2(aq)$

(d) $2NO_2(g) + H_2O(l) \longrightarrow HNO_2(aq) + HNO_3(aq)$

Solution:

(a) This is a decomposition reaction because one reactant dissociates into two different products. The oxidation number of N changes from +1 to 0 while that of O changes from –2 to 0.

(b) This is a combination reaction because two reactants combine to form a single product. The oxidation number of Li changes from 0 to +1 while that of N changes from 0 to –3.

(c) This is a metal displacement reaction. The Ni metal displaces (reduces) the Pb^{2+} ion.
The oxidation number of Ni increases from 0 to +2 while that of Pb decreases from +2 to 0.

(d) The oxidation number of N is +4 in NO_2, +3 in HNO_2 and +5 in HNO_3. Since oxidation state of N both increases and decreases, this is an example of a disproportionation reaction.

PRACTICE PROBLEM

PP2. What is the type of redox reactions given below?

(a) $Fe + H_2SO_4 \longrightarrow FeSO_4 + H_2$

(b) $S + 3F_2 \longrightarrow SF_6$

(c) $2CuCl \longrightarrow Cu + CuCl_2$

(d) $2Ag + PtCl_2 \longrightarrow 2AgCl + Pt$

5 BALNCING OF REDOX REACTION

Redox reactions involve both oxidation and reduction simultaneously. Oxidation means loss of electrons and reduction means gain of electrons. Thus redox reactions involve electron transfer and the number of electrons lost is same as the number of electrons gained during the reaction. This aspect of redox reaction can serve as the basis of a pattern for balancing redox reactions.

There are two common and useful methods to balance redox reactions. These are

(a) Oxidation state method and

(b) Ion–electron method.

BALANCING OF REDOX REACTIONS BY OXIDATION STATE METHOD

For balancing a redox reaction by oxidation state method, follow the order of steps as listed below. In balancing some reactions, all the steps may not be required.

(i) For each redox reaction, deduce the oxidation state of the elements that are undergoing oxidation and reduction.

(ii) Separate the reactants and products into two half–reactions involving the elements alone that show change in their oxidation states. Write the skeletal equations for each half–reaction.

(iii) For each half–reaction, first balance the number of atoms of the element undergoing change in oxidation state.

(iv) Now find the total change in oxidation state by determining the change per atom and multiplying it by the total number of atoms that undergo change in oxidation state. Also, decide whether electrons are lost or gained. An increase in oxidation state means loss of electrons and a decrease in oxidation state means gain of electrons.

(v) Add the electrons lost or gained to the half equation. Lost electrons are placed on the product side and gained electrons are kept on the reactant side.

(vi) Now add both the half reactions after multiplying by suitable integers to make the number of electrons lost and gained same.

(vii) Transfer the coefficients of each reactant and product to the main skeleton equation.

(viii) If the coefficients developed are not correct, then change them by inspection method. Such coefficient changes are required when an element from a compound goes in 2 different compounds, one with the same oxidation state and the other with different oxidation state.

(ix) Count the charges on both sides of the equation and balance the charges in the equation by adding requisite H^+ or OH^- to the required side. If the reaction occurs in acidic solution, use H^+ and if it occurs in basic solution, use OH^-. If the reaction occurs in neutral solution, use H^+ or OH^- on any of the side as needed i.e. in a neutral solution, if negative charges are needed for balancing, use OH^- and if positive charges are needed, use H^+.

(x) Balance the hydrogens and oxygens by adding the appropriate number of H_2O molecules on the required side.

Question: **Balance the following oxidation–reduction equation,**

$$KMnO_4 + KCl + H_2SO_4 \longrightarrow MnSO_4 + K_2SO_4 + H_2O + Cl_2$$

by oxidation state method.

Solution:

(i) Identify the oxidation and reduction half equations in ionic form.

Reduction half: $Mn^{7+} \longrightarrow Mn^{2+}$

Oxidation half: $Cl^- \longrightarrow Cl_2$

(ii) Balance the atoms that undergo change in oxidation state.

Reduction half: $Mn^{7+} \longrightarrow Mn^{2+}$

Oxidation half: $2Cl^- \longrightarrow Cl_2$

(iii) Add the electrons lost or gained to each half equation.

Reduction half: $5e^- + Mn^{7+} \longrightarrow Mn^{2+}$ ....A

Oxidation half: $2Cl^- \longrightarrow Cl_2 + 2e^-$ ....B

(iv) Multiply equation A with 2 and equation B with 5 and then add the two half reactions.

$$5e^- + Mn^{7+} \longrightarrow Mn^{2+}\ ] \times 2$$
$$2\,Cl^- \longrightarrow Cl_2 + 2e^-\ ] \times 5$$
$$2Mn^{7+} + 10\,Cl^- \longrightarrow 5Cl_2 + 2Mn^{2+}$$

(v) Transfer the coefficients to the main equation.

$2KMnO_4 + 10KCl + H_2SO_4 \longrightarrow 2MnSO_4 + K_2SO_4 + H_2O + 5Cl_2$

(vi) Balance H and O atoms

$2KMnO_4 + 10KCl + 8H_2SO_4 \longrightarrow 5Cl_2 + 2MnSO_4 + 8H_2O + 6K_2SO_4$

(vii) Finally balance by inspection method.

$2KMnO_4 + 10KCl + 8H_2SO_4 \longrightarrow 2MnSO_4 + 6K_2SO_4 + 8H_2O + 5Cl_2$

Question: **Balance the following redox equation,**

$$K_2Cr_2O_7 + HCl \longrightarrow KCl + CrCl_3 + Cl_2 + H_2O$$

using oxidation state method.

Solution:

(i) Identify the oxidation and reduction half equations in ionic form.

Reduction half: $Cr_2^{12+} \longrightarrow Cr^{3+}$

Oxidation half: $Cl^- \longrightarrow Cl_2$

(ii) Balance the atoms that undergo change in oxidation state.

Reduction half: $Cr_2^{12+} \longrightarrow 2Cr^{3+}$

Oxidation half: $2Cl^- \longrightarrow Cl_2$

(iii) Add the electrons lost or gained to each half equation.

Reduction half: $6e^- + Cr_2^{12+} \longrightarrow 2Cr^{3+}$ ....A

Oxidation half: $2Cl^- \longrightarrow Cl_2 + 2e^-$ ....B

(iv) Multiply equation B by 3 and add it to equation A.

$$6e^- + Cr_2^{12+} \longrightarrow 2Cr^{3+}$$
$$2Cl^- \longrightarrow Cl_2 + 2e^-\ ] \times 3$$
$$Cr_2^{12+} + 6Cl^- \longrightarrow 2Cr^{3+} + 3Cl_2$$

(v) Transfer the coefficients to the main equation.

$K_2Cr_2O_7 + 6HCl \longrightarrow KCl + 2CrCl_3 + 3Cl_2 + H_2O$

(vi) By inspection, it is seen that the coefficient of HCl developed is not correct, as the number of moles of Cl atoms on the product side are 13 while on the reactant side are only 6. So, the coefficient is changed appropriately, seeing that the net reaction is completely balanced.

$K_2Cr_2O_7 + 14HCl \longrightarrow 2KCl + 2CrCl_3 + 3Cl_2 + 7H_2O$

BALANCING REDOX REACTIONS BY ION–ELECTRON METHOD

This method of balancing redox reaction involves following steps.

(i) For each redox reaction, deduce the oxidation state of the elements that are undergoing oxidation and reduction.

(ii) Separate the reactants and products into two half–reactions involving the elements that show change in their oxidation states. Write the skeleton equations for each half–reaction.

(iii) Balance each half–reaction separately involving the given steps.

1. First balance the atoms of the element undergoing oxidation or reduction.
2. Then balance atoms of the elements other than hydrogen and oxygen.
3. For balancing oxygen atoms in acidic or neutral medium, add suitable number of H_2O molecules to the side deficient in O while in alkaline medium, add equal number of H_2O molecules as the excess of O on the side having excess of O atoms and add double the number of OH^- ions on the opposite side of the equation.
4. In order to balance the hydrogen atoms in acidic or neutral medium, add required number of H^+ to the side deficient in H while in alkaline medium, add equal number of OH^- ions as the excess number of H atoms on the side having excess H and add equal number of H_2O molecules on the opposite side of the equation.

(iv) Multiply each half–reaction by suitable integer to make the number of electrons lost and gained same and add both the half–equations to get a completely balanced reaction.

Mostly, the medium in which a redox reaction is to be balanced is given in the problem but if the problem does not state the medium explicitly, then the medium is decided by looking at the reactants or products. If an acid or base is one of the reactants or products, then that reactant or product decides the medium. If ammonia is present, the solution would be basic, and if ammonium chloride is present, it would be acidic. If metals which form insoluble hydroxides are given in their ionic form in a redox reaction, the solution is acidic.

Although, both the oxidation state method and ion–electron method lead to the correct form of the balanced redox reaction but ion–electron method is considered to be superior to the oxidation state method due to following advantages:

(i) In ion–electron method, all reactants and products are completely balanced (i.e. coefficient is developed for each one of them) whether they participate in the redox change or not, while in oxidation state method, the balancing of coefficients is developed only for the species involved in the redox change.

(ii) The balancing coefficients developed in ion–electron method are always correct and need no amendment while such coefficients are to be changed sometimes in oxidation number method.

Question: **Balance the redox equation,**

$HNO_3 + H_2S \longrightarrow NO + S$

by ion–electron method (acidic medium).

Solution: (i) Identify the oxidation and reduction halves.

Reduction half: $HNO_3 \longrightarrow NO$

Oxidation half: $H_2S \longrightarrow S$

(ii) Atoms of the element undergoing oxidation and reduction are already balanced.

(iii) Balancing O atoms,

Reduction half: $HNO_3 \longrightarrow NO + 2H_2O$

Oxidation half: $H_2S \longrightarrow S$

(iv) Balancing H atoms,

Reduction half: $3H^+ + HNO_3 \longrightarrow NO + 2H_2O$

Oxidation half: $H_2S \longrightarrow S + 2H^+$

(v) Balancing charge,

Reduction half: $3e^- + 3H^+ + HNO_3 \longrightarrow NO + 2H_2O$……………….Ⓐ

Oxidation half: $H_2S \longrightarrow S + 2H^+ + 2e^-$ ……………….Ⓑ

(vi) Multiplying equation Ⓐ by 2 and equation Ⓑ by 3 and then adding them.

$3e^- + 3H^+ + HNO_3 \longrightarrow NO + 2H_2O\ ] \times 2$ ……………….Ⓐ

$H_2S \longrightarrow S + 2H^+ + 2e^-\ ] \times 3$ ……………….Ⓑ

$$\mathbf{2HNO_3 + 3H_2S \longrightarrow 3S + 2NO + 4H_2O}$$

Question: **Balance the following redox equation,**

$$AsO_3^{3-} + MnO_4^- \longrightarrow AsO_4^{3-} + MnO_2$$

using ion–electron method (alkaline medium).

Solution:

(i) Identify the oxidation and reduction halves.

Reduction half: $MnO_4^- \longrightarrow MnO_2$

Oxidation half: $AsO_3^{3-} \longrightarrow AsO_4^{3-}$

(ii) Atoms of the element undergoing oxidation and reduction are already balanced.

(iii) Balancing O atoms,

Reduction half: $2H_2O + MnO_4^- \longrightarrow MnO_2 + 4OH^-$

Oxidation half: $2OH^- + AsO_3^{3-} \longrightarrow AsO_4^{3-} + H_2O$

(iv) Balancing H atoms,

H atoms are already balanced in both the half–reactions.

(v) Balancing charge,

Reduction half: $3e^- + 2H_2O + MnO_4^- \longrightarrow MnO_2 + 4OH^-$………….Ⓐ

Oxidation half: $2OH^- + AsO_3^{3-} \longrightarrow AsO_4^{3-} + H_2O + 2e^-$………….Ⓑ

(vi) Multiply equation Ⓐ by 2 and equation Ⓑ by 3 and then add Ⓐ and Ⓑ.

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

$2OH^- + AsO_3^{3-} \longrightarrow AsO_4^{3-} + H_2O + 2e^-\ ] \times 3$

$$\mathbf{3\,AsO_3^{3-} + 2MnO_4^- + H_2O \longrightarrow 3\,AsO_4^{3-} + 2MnO_2 + 2OH^-}$$

6 ELECTROCHEMICAL CELLS

Let us take a zinc rod and immerse it in a solution of $CuSO_4$ taken in a beaker as shown in the figure 1. After some time, we see that the Zn rod starts dissolving and Cu starts depositing on its surface. This happens because Zn gets oxidised to Zn^{2+} ions, which passes into the solution and 2 electrons remain on the Zn rod for each Zn^{2+} ion going in solution. Then, Cu^{2+} ion from the solution takes up these 2 electrons to form Cu, which deposits on the Zn rod.

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

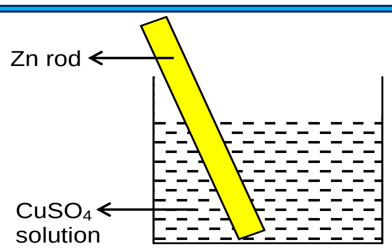

Figure 1

In this reaction, Zn acts as reducing agent, which is able to reduce Cu^{2+} to Cu by transferring 2 electrons and Cu^{2+} ion acts as an oxidising agent, which oxidises Zn to Zn^{2+} ions and itself gets reduced to Cu. In this case, there is a direct transfer of electrons from Zn rod to Cu^{2+} ion and some heat is also evolved.

The above experiment is slightly modified in a manner that for the same redox reaction, transfer of electrons takes place indirectly and the heat of the reaction is converted into electrical energy. This necessitates the separation of Zn rod from $CuSO_4$ solution. Such cells in which the oxidised and reduced species are separated and connected through electrical wires are called electrochemical cells.

Electrochemical cells are the cells in which chemical energy is transformed into electrical energy. This means that chemical reactions produce electric current.

An electrochemical cell consists of two half–cells or electrodes. The electrodes are metallic conductors dipped in an electrolyte, which is an ionic conductor dissolved in water. A conducting rod and a suitable electrolyte comprise an electrode or half–cell compartment. The two electrodes may share the same electrolyte or have different electrolytes.

In a given electrochemical cell, combination of any of the two electrodes can be used. The cell may even contain same type of electrodes with different concentration of electrolytes. When an 'inert metal' is part of the electrode, it acts as a source of electrons, but does not take part in the reaction. If the electrolytes are different, the two compartments may be joined by a salt bridge, which is a concentrated solution of KCl in agar–agar jelly that completes the electrical circuit and enables the cell to function. Thus, salt bridge provides an electrical contact between the two solutions without allowing them to mix with each other.

The simplest electrochemical cell to study is Daniel cell, which is shown in figure 2. This is prepared by dipping Zn rod in a solution of $ZnSO_4$ in one beaker and by dipping Cu strip in a solution of $CuSO_4$ in another beaker. It consists of two redox couples, Zn^{2+} | Zn at one end and Cu^{2+} | Cu at the other end. Since Zn has a higher oxidation potential than Cu, so it has a higher tendency to get oxidised than Cu and conversely Cu^{2+} has higher tendency to get reduced than Zn^{2+}. At this stage, no reaction takes place in either of the two beakers. Now, the two half–cells are connected by connecting wire through an ammeter. As soon as the connection is made, Zn rod starts dissolving i.e. Zn atom changes to Zn^{2+} by losing 2 electrons. The Zn^{2+} ion passes into the solution, thereby increasing its concentration and 2 electrons remain on the Zn rod. Thus, $ZnSO_4$ solution now has +2 unit extra charge and Zn rod has –2 unit extra charge. Thus, there is a charge separation of 4 units between the Zn rod and $ZnSO_4$ solution. This charge separation develops a potential referred to as oxidation potential; since oxidation takes place on this electrode. The potential is called standard oxidation potential, if the concentration of Zn^{2+} in the solution is 1 M. Similar potential is developed at Cu^{2+} | Cu half–cell also, when Cu^{2+} discharges and deposits on Cu rod. This potential is referred to as reduction potential; as reduction takes place on this electrode. The potential is called standard reduction potential, if the concentration of Cu^{2+} in the solution in 1 M.

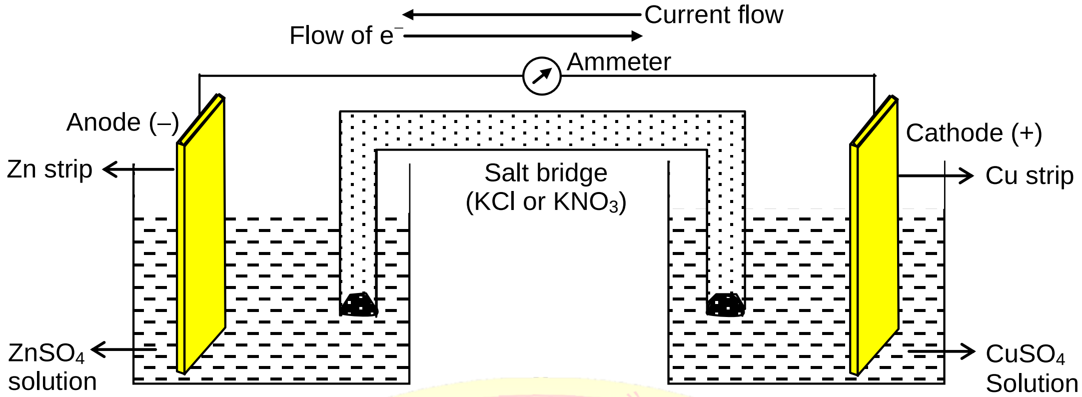

Figure 2. Setup of a Daniel cell

The zinc rod which has the electrons left by the zinc (that got oxidized) becomes negatively charged while the Cu rod which lost electrons to Cu^{2+} becomes positively charged. Thus, electric current flows through the connected wire, which is indicated by a deflection in ammeter showing that a chemical reaction is occurring in the cell. During the course of reaction, zinc rod gets dissolved and copper gets deposited on the copper rod. Thus, the concentration of the anode solution increases while that of cathode solution decreases. The flow of electrons occurs from the zinc rod to copper rod in the external circuit and indirectly from cathode to anode in the internal circuit.

The current flow is in the direction opposite to electron flow. The reactions occurring at the two electrodes are

At anode: $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$

At cathode: $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$

This current flow stops after some time. Think, why it happens? As zinc rod dissolves, let one mole of Zn atoms dissolve to form Zn^{2+} ions, which pass into the solution and 2 mole of electrons remain on the rod. Thus, rod becomes negatively charged and the solution becomes positively charged. With the passage of time, the solution becomes so much positively charged that any Zn atom getting oxidised and trying to get into the solution, would be repelled by the solution and thus the oxidation of Zn stops. Same phenomenon occurs at cathode and the reduction of Cu^{2+} at cathode ceases. As the flow of electrons stop, so does the flow of current. This problem can be removed with the use of salt bridge. The salt bridge contains a highly soluble electrolyte (like KCl, NH_4NO_3, NH_4Cl, KNO_3 etc) in which ionic mobilities of cation and anion are of comparable order.

Now, let us examine the function of salt bridge. Since zinc ions are produced as electrons leave the zinc electrode, this tends to produce a net positive charge in the left compartment. The salt bridge then throws ions having equivalent opposite charge into the solution to maintain electrical neutrality. Thus, the salt bridge keeps the solution neutral by passing appropriate amounts of cations or anions to the two half–cells (compartments). Thus, the purpose of the salt bridge is to prevent any net charge accumulation in either of the compartments. Salt bridge does not participate chemically in the cell reaction but it is essential for the cell to operate. With the use of salt bridge, the flow of electrons becomes continuous and cell continues to operate. But after some more time, cell ceases to operate. Can you guess why it stops operating now?

CELL NOTATION OF AN ELECTROCHEMICAL CELL

(i) Anode is written on the left side and cathode is written on the right side.
(ii) Phase boundaries are indicated by vertical bar or slash.
(iii) Concentration of the electrolytes in the anode and cathode must be written in parenthesis.
(iv) In case of a gas, the partial pressure is to be mentioned in atm or mm Hg.
(v) A comma is used to separate two chemical species present in the same solution.
(vi) A double vertical line i.e. || denotes that a salt bridge is present.
(vii) EMF of the cell is written on the extreme right of the representation.

For example,

(i) $Zn(s) \mid ZnSO_4(c_1\ M) \parallel CuSO_4(c_2\ M) \mid Cu(s)$; E_{cell}
(ii) $Pt \mid H_2(P_1\ atm) \mid HCl\ (c\ M) \mid AgCl(s) \mid Ag$; E'_{cell}
(iii) $Pt \mid Fe^{2+}\ (c_1\ M), Fe^{3+}(c_2\ M) \parallel Ag^+\ (c\ M) \mid Ag$; E''_{cell}

Note: In some cell representations (as in (ii) above), the salt bridge is not indicated which implies that the electrolyte is common to both anode and cathode compartments.

7 STANDARD REDUCTION

When the concentrations of the Cu^{2+} and Zn^{2+} ions are both 1.0 M, we find that the voltage or emf of the Daniell cell is 1.10 V at 25°C. This voltage must be related directly to the redox reaction, but how? just as the overall cell reaction can be thought of as the sum of two half−cell reactions, the measured emf of the cell can be treated as the sum of the electrical potentials at the Zn and Cu electrodes. Knowing one of these electrode potentials, we could obtain the other by subtraction. It is impossible to measure the potential of just a single electrode, but if we arbitrarily set the potential value of a particular electrode at zero, we can use it to determine the relative potentials of other electrodes. The hydrogen electrode, serves as the reference for this purpose. Hydrogen gas is bubbled into a hydrochloric acid solution at 25°C. The platinum electrode has two functions. First, it provides a surface on which the dissociation of hydrogen molecules can take place

$$H_2 \longrightarrow 2H^+ + 2e^-$$

Second, it serves as an electrical conductor to the external circuit. Under standard state conditions (when the pressure of H_2 is 1 atm and the concentration of the HCl solution is 1 M), the potential for the reduction of H^+ at 25°C is taken to be exactly zero:

$$2H^+\ (1\ M) + 2e^- \longrightarrow H_2(1\ atm) \quad ; \quad E° = 0\ V$$

The superscript "o" denotes standard–state conditions and E° is ***standard reduction potential***, or the voltage associated with a reduction reaction at an electrode when all solutes are 1 M and all gases are at 1 atm. Thus, the standard reduction potential of the hydrogen electrode is defined as zero. The hydrogen electrode is called the standard hydrogen electrode (SHE).

We can use the SHE to measure the potentials of other kinds of electrodes. For example, consider an electrochemical cell with a zinc electrode and a SHE. In this case the zinc electrode is anode and the SHE is the cathode. We deduce this fact from the decrease in mass of the zinc electrode during the operation of the cell, which is consistent with the loss of zinc to the solution caused by the oxidation reaction:

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

The cell diagram is

$$Zn(s) \mid Zn^{2+}\ (1\ M) \parallel H^+\ (1\ M) \mid H_2\ (1\ atm) \mid Pt(s)$$

As mentioned earlier, the Pt electrode provides the surface on which the reduction takes place. When all the reactants are in their standard states (that is, H_2 at 1 atm, H^+ and Zn^{2+} ions at 1 M each, the emf of the cell is 0.76 V at 25°C.

We can write the half–cell reactions as follows:

Anode (oxidation):	$Zn(s) \longrightarrow Zn^{2+}(1\ M) + 2e^-$
Cathode (reduction):	$2H^+(1\ M) + 2e^- \longrightarrow H_2(1\ atm)$
Overall:	$Zn(s) + 2H^+(1\ M) \longrightarrow Zn^{2+}(1\ M) + H_2(1\ atm)$

By convention, the ***standard emf*** of the cell, E^o_{cell}, which is composed of a contribution from the anode and a contribution from the cathode, is given by

$$E^o_{cell} = E^o_{cathode} - E^o_{anode}$$

where $E^o_{cathode}$ and E^o_{anode} are the standard reduction potential of the cathode and anode respectively. For the Zn–SHE cell, we write

$$E^o_{cell} = E^o_{H^+|H_2} - E^o_{Zn^{2+}|Zn}$$

$$0.76\ V = 0 - E^o_{Zn^{2+}|Zn}$$

where the subscript $H^+ | H_2$ means $2H^+ + 2e^- \longrightarrow H_2$ and the subscript $Zn^{2+} | Zn$ means $Zn^{2+} + 2e^- \longrightarrow Zn$. Thus the standard reduction potential of zinc, $E^o_{Zn^{2+}|Zn}$, is –0.76 V.

The standard electrode potential of copper can be obtained in a similar fashion, by using a cell with a copper electrode and a SHE. In this case, the copper electrode is the cathode because its mass increases during the operation of the cell, as is consistent with the reduction reaction:

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

The cell diagram is

$$Pt(s) \mid H_2(1\ atm) \mid H^+(1\ M) \parallel Cu^{2+}(1\ M) \mid Cu(s)$$

and the half–cell reactions are

Anode (oxidation):	$H_2(1\ atm) \longrightarrow 2H^+(1\ M) + 2e^-$
Cathode (reduction):	$Cu^{2+}(1\ M) + 2e^- \longrightarrow Cu(s)$
Overall:	$H_2(1\ atm) + Cu^{2+}(1\ M) \longrightarrow 2H^+(1\ M) + Cu(s)$

Under standard–state conditions and at 25°C, the emf of the cell is 0.34 V, so we write

$$E^o_{cell} = E^o_{cathode} - E^o_{anode}$$

$$0.34\ V = E^o_{Cu^{2+}|Cu} - E^o_{H^+|H_2}$$

$$= E^o_{Cu^{2+}|Cu} - 0$$

In this case the standard reduction potential of copper, $E^o_{Cu^{2+}|Cu}$, is 0.34 V, where the subscript $Cu^{2+} | Cu$ means $Cu^{2+} + 2e^- \longrightarrow Cu$.

Having known the values of standard reduction potential of copper electrode $E^o_{Cu^{2+}|Cu}$ and that of zinc electrode $E^o_{Zn^{2+}|Zn}$ it is possible to find out the standard EMF (E^o_{cell}) of the following electrochemical cell

$$Zn(s) \mid Zn^{2+}(1M) \parallel Cu^{2+}(1M) \mid Cu(s)$$

Anode (oxidation):	$Zn(s) \longrightarrow Zn^{2+}(1\ M) + 2e^-$
Cathode (reduction):	$Cu^{2+}(1\ M) + 2e^- \longrightarrow Cu(s)$
Overall:	$Zn(s) + Cu^{2+}(1\ M) \longrightarrow Zn^{2+}(1\ M) + Cu(s)$

The standard EMF of the cell is given by

$$E^o_{cell} = E^o_{cathode} - E^o_{anode}$$
$$= E^o_{Cu^{2+}|Cu} - E^o_{Zn^{2+}|Zn}$$
$$= 0.34\ V - (-0.76\ V)$$
$$= 1.10\ V.$$

ELECTROCHEMICAL SERIES

S. No.	Reduction half cell reaction	E° in volts at 25°C
1.	$F_2 + 2e^- \longrightarrow 2F^-$	+ 2.65
2.	$S_2O_8^{2-} + 2e^- \longrightarrow 2SO_4^{2-}$	+ 2.01
3.	$Co^{3+} + e^- \longrightarrow Co^{2+}$	+ 1.82
4.	$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \longrightarrow PbSO_4 + 2H_2O$	+ 1.65
5.	$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$	+ 1.52
6.	$Au^{3+} + 3e^- \longrightarrow Au$	+ 1.50
7.	$Cl_2 + 2e^- \longrightarrow 2Cl^-$	+ 1.36
8.	$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$	+ 1.33
9.	$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$	+ 1.229
10.	$Br_2 + 2e^- \longrightarrow 2Br^-$	+ 1.07
11.	$NO_3^- + 4H^+ + 3e \longrightarrow NO + 2H_2O$	+ 0.96
12.	$2Hg^{2+} + 2e^- \longrightarrow Hg_2^{2+}$	+ 0.92
13.	$Cu^{2+} + I^- + e^- \longrightarrow CuI$	+ 0.86
14.	$Ag^+ + e^- \longrightarrow Ag$	+ 0.799
15.	$Hg_2^{2+} + 2e^- \longrightarrow 2\ Hg$	+ 0.79
16.	$Fe^{3+} + e^- \longrightarrow Fe^{2+}$	+ 0.77
17.	$I_2 + 2e^- \longrightarrow 2I^-$	+ 0.535
18.	$Cu^+ + e^- \longrightarrow Cu$	+ 0.53
19.	$Cu^{2+} + 2e^- \longrightarrow Cu$	+ 0.34
20.	$Hg_2Cl_2 + 2e^- \longrightarrow 2Hg + 2Cl^-$	+ 0.27
21.	$AgCl + e^- \longrightarrow Ag + Cl^-$	+ 0.222
22.	$Cu^{2+} + e^- \longrightarrow Cu^+$	+ 0.15
23.	$Sn^{4+} + 2e^- \longrightarrow Sn^{2+}$	+ 0.13
24.	$2H^+ + 2e^- \longrightarrow H_2$	0.00
25.	$Fe^{3+} + 3e^- \longrightarrow Fe$	– 0.036
26.	$Pb^{2+} + 2e^- \longrightarrow Pb$	– 0.126
27.	$Sn^{2+} + 2e^- \longrightarrow Sn$	– 0.14
28.	$AgI + e^- \longrightarrow Ag + I^-$	– 0.151
29.	$Ni^{2+} + 2e^- \longrightarrow Ni$	– 0.25
30.	$Co^{2+} + 2e^- \longrightarrow Co$	– 0.28
31.	$Cd^{2+} + 2e^- \longrightarrow Cd$	– 0.403
32.	$Cr^{3+} + e^- \longrightarrow Cr^{2+}$	– 0.41
33.	$Fe^{2+} + 2e^- \longrightarrow Fe$	– 0.44
34.	$Cr^{3+} + 3e^- \longrightarrow Cr$	– 0.74

35.	$Zn^{2+} + 2e^- \longrightarrow Zn$	– 0.762
36.	$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$	– 0.828
37.	$Mn^{2+} + 2e^- \longrightarrow Mn$	– 1.18
38.	$Al^{3+} + 3e^- \longrightarrow Al$	– 1.66
39.	$H_2 + 2e^- \longrightarrow 2H^-$	– 2.25
40.	$Mg^{2+} + 2e^- \longrightarrow Mg$	– 2.37
41.	$Na^+ + e^- \longrightarrow Na$	– 2.71
42.	$Ca^{2+} + 2e^- \longrightarrow Ca$	– 2.87
43.	$Ba^{2+} + 2e^- \longrightarrow Ba$	– 2.90
44.	$Cs^+ + e^- \longrightarrow Cs$	– 2.92
45.	$K^+ + e^- \longrightarrow K$	– 2.93
46.	$Li^+ + e^- \longrightarrow Li$	– 3.05

The above table lists standard reduction potentials for a number of half–cell reactions. By definition, the SHE has an E° value of 0.00 V. Below the SHE the negative standard reduction potentials increase and above it the positive standard reduction potentials increase. It is important to know the following points about the table in calculations:

1. The E° values apply to the half–cell reactions as read in the forward (left to right) direction.
2. The more positive E° is, the greater the tendency for the substance to be reduced. For example, the half–cell reaction

   $$F_2\,(1\text{ atm}) + 2e^- \longrightarrow 2F^-\,(1\text{ M}) \quad ; \quad E° = 2.87\text{ V}$$

   has the highest positive E° value among all the half–cell reactions. Thus, F_2 is the strongest oxidizing agent because it has the greatest tendency to be reduced. At the other extreme is the reaction

   $$Li^+\,(1\text{ M}) + e^- \longrightarrow Li\,(s) \quad ; \quad E° = -3.05\text{ V}$$

   which has the most negative E° value. Thus Li^+ is the weakest oxidizing agent because it is the most difficult species to reduce. Conversely, we say that F^- is the weakest reducing agent and Li metal is the strongest reducing agent. Under standard–state conditions, the oxidizing agents (the species on the left–hand side of the half–reactions in the given table) increase in strength from bottom to top and the reducing agents (the species on the right–hand side of the half–reactions) increase in strength from top to bottom.
3. The half–cell reactions are reversible. Depending on the conditions, any electrode can act either as an anode or as a cathode. Earlier we saw that the SHE is the cathode (H^+ is reduced to H_2) when coupled with zinc in a cell and that it becomes the anode (H_2 is oxidized to H^+) when used in a cell with copper.
4. Under standard–state conditions, any species on the left of a given half–cell reaction will react spontaneously with a species that appears on the right of any half–cell reaction located below it in the given table. This principle is sometimes called the diagonal rule. In the case of the Daniel cell

   $$Cu^{2+}\,(1\text{ M}) + 2e^- \longrightarrow Cu(s) \quad ; \quad E° = 0.34\text{ V}$$
   $$Zn^{2+}\,(1\text{ M}) + 2e^- \longrightarrow Zn(s) \quad ; \quad E° = -0.76\text{ V}$$

   We see that the substance on the left of the first half–cell reaction is Cu^{2+} and the substance on the right in the second half–cell reaction is Zn. Therefore, as we saw earlier, Zn spontaneously reduces Cu^{2+} to form Zn^{2+} and Cu.
5. Changing the stoichiometric coefficients of a half–cell reaction does not affect the value of E° because electrode potentials are intensive properties. This means that the value of E° is

unaffected by the size of the electrodes or the amount of solutions present.
For example,

$$I_2(g) + 2e^- \longrightarrow 2I^- (1\ M) \quad ; \quad E° = 0.53\ V$$

but E° does not change if we multiply the half–reaction by 2 :

$$2I_2(s) + 4e^- \longrightarrow 4I^- (1\ M) \quad ; \quad E° = 0.53\ V$$

Question: **Predict what will happen if molecular bromine (Br_2) is added to a solution containing NaCl and NaI at 25°C. Assume all species are in their standard states. [Use $E^o_{Cl_2|Cl^-} = 1.36V$, $E^o_{Br_2|Br^-} = 1.07V$ and $E^o_{I_2|I^-} = 0.53V$]**

Solution:

To predict what redox reaction(s) will take place, we need to compare the standard reduction potentials for the following half–reactions.

$$Cl_2\ (1\ atm) + 2e^- \longrightarrow 2Cl^-\ (1\ M) \quad ; \quad E° = 1.36\ V$$
$$Br_2(l) + 2e^- \longrightarrow 2Br^-\ (1\ M) \quad ; \quad E° = 1.07\ V$$
$$I_2(s) + 2e^- \longrightarrow 2I^-\ (1\ M) \quad ; \quad E° = 0.53\ V$$

Applying the diagonal rule, we see that Br_2 will oxidize I^- but will not oxidize Cl^-. Therefore, the only redox reaction that will occur appreciably under standard state conditions is

Oxidation: $2I^-\ (1\ M) \longrightarrow I_2(s) + 2e^-$

Reduction: $Br_2(l) + 2e^- \longrightarrow 2Br^-\ (1\ M)$

Overall: $2I^-\ (1\ M) + Br_2(l) \longrightarrow I_2(s) + 2Br^-\ (1\ M)$

PRACTICE PROBLEMS

PP3. Can Sn reduce $Zn^{2+}(aq)$ under standard state conditions?

PP4. What is the standard emf of an electrochemical cell made of a Cd–electrode in a 1.0 M $Cd(NO_3)_2$ solution and a Cr electrode in a 1.0 M $Cr(NO_3)_3$ solution? ($E^o_{Cd^{2+}|Cd} = -0.403\ V$; $E^o_{Cr^{+3}|Cr} = -0.74\ V$)

8 REDOX REACTIONS AS THE BASIS FOR TITRATION

In acid-base systems we come across with a titration method for finding out the strength of one solution against the other using a pH sensitive indicator. Similarly, in redox systems, the titration method can be adopted to determine the strength of a reductant/ oxidant using a redox sensitive indicator. The usage of indicators in redox titration is illustrated below:

(i) In one situation, the reagent itself is intensely coloured, e.g. permanganate ion, MnO_4^-. Here MnO_4^- acts as the self indicator. The visible end point in this case is achieved after the last of the reductant (Fe^{+2} or $C_2O_4^{2-}$) is oxidised and the first lasting tinge of pink colour appears at MnO_4^-, concentration as low as 10^{-6} mol dm^{-3}. This ensures a minimal 'overshoot' in colour beyond the equivalence point, the point where the reductant and the oxidant are equal to terms of their mole stoichiometry.

(ii) If there is no dramatic auto-colour change (as with the MnO_4^- titration), there are indicators which are oxidised immediately after the last bit of the reactant is consumed, producing a dramatic colour change. Example: $Cr_2O_7^{2-}$ is not a self-indicator, but oxidises the indicator substance diphenylamine just after the equivalence point to produce an intense blue colour, thus signaling the end point.

(iii) There is yet another method which is interesting and quite common. Its use is restricted to those reagents which are able to oxidise I^- ions, say, for example, Cu(II):

$$2Cu^{+2}(aq) + 4I^-(aq) \rightarrow Cu_2I_2(s) + I_2(aq)$$

This method relies on the facts that iodine itself gives an intense blue colour with starch and has a very specific reaction with thiosulphate ions $\left(S_2O_3^{2-}\right)$, which too is a redox reaction:

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

I_2, though insoluble in water, remains in solution containing KI as KI_3.

On addition of starch after the liberation of iodine from the reaction of Cu^{+2} ions on iodide ions, an intense blue colour appears. This colour disappears as soon as the iodine is consumed by the thiosulphate ions. Thus, the end-point can easily be tracked and the rest is the stoichiometric calculation only.

EXERCISE

CBSE PROBLEMS

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

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

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

(c) $CH_4(g) + 4Cl_2(g) \longrightarrow CCl_4(g) + 4HCl(g)$

(d) $2[Fe(CN)_6]^{3-}(aq) + 2OH^-(aq) + H_2O_2(aq) \longrightarrow 2[Fe(CN)_6]^{4-}(aq) + 2H_2O(l) + O_2(g)$

2. Determine the oxidation state of the element underlined in the following species.

$\underline{Si}H_4$, $\underline{B}F_3$, $\underline{O}F_2$, $H\underline{I}O_4$, $K\underline{Mn}O_4$, $K_2\underline{Cr_2}O_7$

3. Find out the oxidation state of Cl in HCl, HClO, ClO_4^-, ClO_2.

4. Can the reaction,

$$Cr_2O_7^{2-} + H_2O \rightleftharpoons 2CrO_4^{2-} + 2H^+$$

be considered a redox reaction?

5. Nitric acid acts as an oxidising agent while nitrous acid acts both as an oxidising as well as a reducing agent. Why?

6. Write a balanced ionic equation to represent the oxidation of iodide ion (I^-) by permanganate ion (MnO_4^-) in basic solution to yield molecular iodine (I_2) and manganese (IV) dioxide (MnO_2).

7. What is the function of salt bridge? What kind of electrolytes should be used in a salt bridge?

8. What is a cell diagram? Write the cell diagram for an electrochemical cell consisting of an aluminium electrode placed in a 1 M $Al(NO_3)_3$ solution and a silver electrode placed in 1 M $AgNO_3$ solution. Determine standard emf of the cell if $E^o_{Al^{+3}|Al} = -1.66V, E^o_{Ag^+|Ag} = 0.799V.$

9. Determine the oxidation state of bold lettered atoms in the following reactions:

(a) $3K\mathbf{Cl}O_3 + 24\,H\mathbf{Cl} \rightarrow 8\,K\mathbf{Cl} + 12H_2O + 9\mathbf{Cl_2} + 6\mathbf{Cl}O_2$

(b) $3\mathbf{I}_2 + 6NaOH \rightarrow Na\mathbf{I}O_3 + 5Na\mathbf{I} + 3H_2O$

10. Identify the reactants getting oxidised or reduced in each of the following reactions.

(a) $CuSO_4 + KI \rightarrow 2CuI + I_2 + 2K_2SO_4$

(b) $2NaBr + Cl_2 \rightarrow 2NaCl + Br_2$

11. State which of the following changes are oxidation, reduction, both or none?

(a) $Na \rightarrow NaOH$

(b) $Cl_2 \rightarrow Cl^- + ClO_3^-$

12. Six mole of Cl_2 undergoes a loss and gain of 10 mole of electrons to form two oxidation states of Cl (viz. Cl^{+5}, Cl^{-1}). Write down the complete reaction involved.

13. Arrange the following compounds in the order of

(a) increasing oxidation state of Mn: $MnCl_2$, MnO_2, $KMnO_4$.

(b) increasing oxidation state of N: NH_3, N_3H, N_2O, NO, N_2O_5.

(c) decreasing oxidation state of X: HXO, HXO_3, HXO_2, HXO_4.

14. Name one compound each in which oxidation number of

(a) Oxygen is +2 (b) Oxygen is –1 (c) Hydrogen is –1

(d) Nitrogen is +1 (e) Cl is +4 (f) Oxygen is –2

15. Balance the following redox reactions by ion electron method

(a) $H_2O_2 + Fe^{2+} \longrightarrow Fe^{3+} + H_2O$ (in acidic medium)

(b) $Br_2 \longrightarrow BrO_3^- + Br^-$ (in basic medium)

(c) $S_2O_3^{2-} + I_2 \longrightarrow I^- + S_4O_6^{2-}$ (in acidic medium)

16. State true or false

(a) A redox change involves oxidation and reduction both occurring simultaneously.

(b) Oxidation number of Ni in $Ni(CO)_4$ is +2.

17. Predict the reductant in the reaction $C_2O_4^{2-} + MnO_4^- + H^+ \rightarrow Mn^{+2} + CO_2$,

18. Calculate the number of electrons lost when 2g of Cl^- ion is oxidised to Cl_2.

$$2Cl^- \rightarrow Cl_2 + 2e^-$$

19. What may be the possible values of x in the reaction?

$$2ICl_x + (2x)K \rightarrow (2x)KCl + I_2$$

20. In the conversion of $Br_2 \rightarrow BrO_3^-$, the oxidation state of bromine changes from __to __.

ANSWERS TO PRACTICE PROBLEMS

PP1. Oxidant (reduces itself) | **Reductant (oxidizes itself)**

(a) $O_2(g)$ — $Zn(s)$

(b) $H^+(aq)$ — $Zn(s)$

(c) Fe_2O_3 — Al

(d) $FeCl_3$ — H_2S

PP2. (a) Hydrogen displacement reaction

(b) Combination reaction

(c) Disproportionation reaction

(d) Metal displacement reaction

PP3. No $\left(E^o_{Sn^{2+}|Sn} > E^o_{Zn^{2+}|Zn}\right)$

PP4. $E^o_{cell} = E^o_{Cd^{2+}|Cd} - E^o_{Cr^{3+}|Cr} = -0.403 - (-0.74) = 0.337$ V.

ANSWERS TO EXERCISE

CBSE PROBLEMS

1. Oxidant (reduces itself) | Reductant (oxidizes itself)

(a) H^+ — Zn

(b) I_2 — $Na_2S_2O_3$

(c) Cl_2 — CH_4

(d) $[Fe(CN)_6]^{3-}$ — H_2O_2

2. Si = –4 ; B = +3, O = +2, I = +7, Mn = +7, Cr = +6.

3. Oxidation state of Cl in HCl, HClO, ClO_4^-, ClO_2 are –1, +1, +7 and +4 respectively.

4. Oxidation state of Cr in $Cr_2O_7^{2-}$ = +6.

Oxidation state of Cr in CrO_4^{2-} = +6.

So, the above reaction cannot be regarded as a redox reaction.

5. In HNO_3, the oxidation state of N is maximum +5; while in HNO_2, the oxidation state of N is +3 and hence, HNO_2 can act both as an oxidising as well as a reducing agent.

6. $6I^- + 2MnO_4^- + 4H_2O \longrightarrow 3I_2 + 2MnO_2 + 8OH^-$

7. The function of salt bridge is to maintain the solution neutral by passing appropriate amount of cations or anions to the two half cells. Any one of the four electrolytes, namely. KCl, NH_4Cl, NH_4NO_3 or KNO_3 can be used in a salt bridge.

8. Al | Al^{+3} (1M) || Ag^+ (1M) | Ag ; $E^o_{cell} = E^o_{Ag^+|Ag} - E^o_{Al^{3+}|Al} = 0.799 - (-1.66) = 2.459$ V.

9. (a) Oxidation state of Cl in $KClO_3$, HCl, KCl, Cl_2 and ClO_2 is +5, –1, –1, 0, and +4 respectively.

(b) Oxidation state of I in I_2, $NaIO_3$ and NaI is 0, +5, and –1

10. (a) Oxidised: KI ; Reduced: $CuSO_4$

(b) Oxidised: NaBr ; Reduced: Cl_2

11. (a) Oxidation (b) Both oxidation and reduction.

12. $6Cl_2 \rightarrow 2Cl^{+5} + 10\,Cl^-$

13. (a) $\overset{+2}{Mn}Cl_2$, $\overset{+4}{Mn}O_2$, $K\overset{++}{Mn}O_4$

(b) $\overset{-3}{N}H_3$, $\overset{-\frac{1}{3}}{N_3}H$, $\overset{+1}{N_2}O$, $\overset{+2}{N}O$, $\overset{+5}{N_2}O_5$

(c) $H\overset{+7}{X}O_4$, $H\overset{+5}{X}O_3$, $H\overset{+3}{X}O_2$, $H\overset{+1}{X}O$

14. (a) OF_2 (b) Na_2O_2 (c) NaH (d) N_2O (e) ClO_2 (f) H_2O

15. (a) $H_2O_2 + 2Fe^{2+} + 2H^+ \longrightarrow 2Fe^{3+} + 2H_2O$

(b) $3Br_2 + 6OH^- \longrightarrow BrO_3^- + 5Br^- + 3H_2O$

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

16. (a) True (b) False. It is zero.

17. $C_2O_4^{2-}$

18. Number of moles of the Cl^- ions oxidised = $\frac{2}{35.5}$

Number of moles of electrons lost $= \frac{2}{35.5}$

Number of electrons lost $= \frac{2}{35.5} \times 6.023 \times 10^{23} = 3.39 \times 10^{22}$

19. The possible values of x may 1, 3 or 5

20. zero to +5