# Unit

3

Electrochemistry

3.1 Introduction

We were studying inorganic and organic chemistry. The oldest branch is inorganic chemistry. The separate branch of organic chemistry was evolved by the research on urea by Wohler, similarly the third branch of chemistry was evolved as a separate branch of chemistry called physical chemistry from the study of electrochemistry. Later on, with the progress of the time, different branches like analytical chemistry, industrial chemistry etc. came into existence which are studied in the present time.

Chemical reactions are useful for the production of electrical energy. Electrical energy is useful to express chemical reactions which are not spontaneous. The study of electrochemistry is for the production of electricity which is free energy released during spontaneous chemical reactions and this electrical energy is used for transfer for chemical reactions which are not spontaneous. Theoretical and experimental proofs are inevitable for this subject. The production of many metals, sodium hydroxide, chlorine, fluorine and many more chemicals is carried out by electrochemical methods. Batteries and fuel cells transform chemical energy to electrical energy, and so it is used in larger proportion in different instruments and appliances. The electrochemical reactions are acceptable and less polluted. So the study of electrochemistry must be done as eco-friend for formation of new technologies.
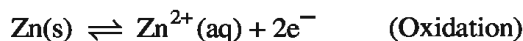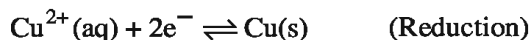
In the case of both the reactions-conduction of senses to the brain and opposite to that from brain-electrochemistry is involved. Hence, electrochemistry is a very widely developed interrelated subject. We will include the main structural points in this unit.

3.2 Electrochemical Cell

The reaction occurring in electrochemical cell is a redox reaction viz. If a thin plate of Zn metal is placed in an aqueous solution of $CuSO_4$, Cu metal is deposited on zinc plate and the original blue colour of solution appears to be light blue coloured; because in this reaction Cu^{2+} is reduced and Zn metal is oxidised. This total reaction occurs as follows :

$$Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$$
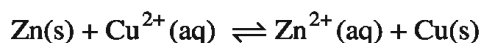
Really, this reaction is the sum of following two half reactions :

$$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s) \qquad \text{(Reduction)}$$

$$Zn(s) \rightleftharpoons Zn^{2+}(aq) + 2e^- \qquad \text{(Oxidation)}$$

A construction can be made where by the above reactions carried out without bringing Zn and Cu reactants in contact with each other.
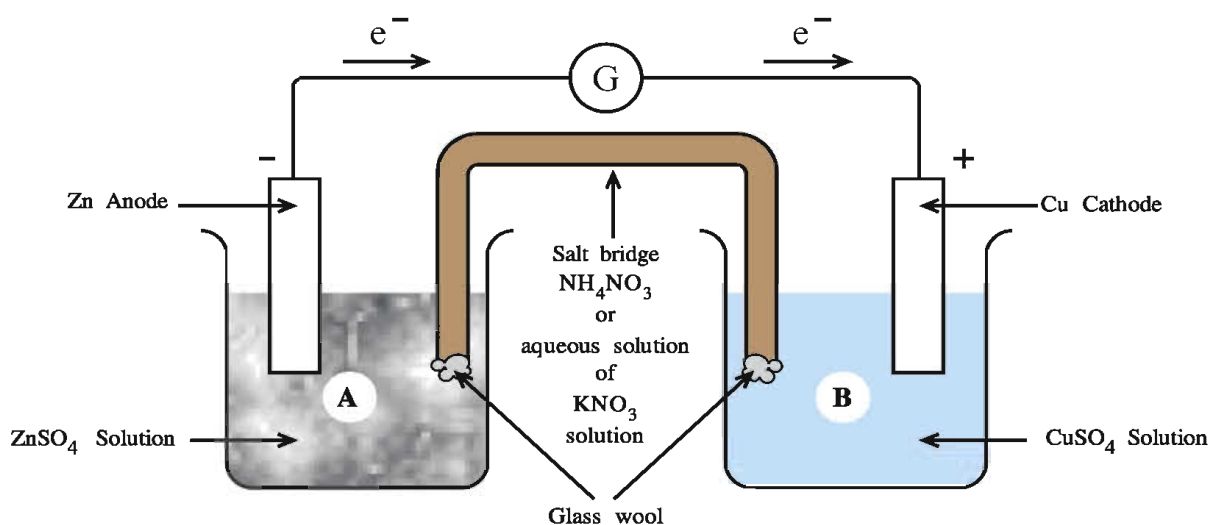

Fig. 3.1 Electrochemical cell (Zn-Cu Cell)

The contact between the reactants is to be kept only for the electron-exchange. Such a construction is called **electrochemical cell.** In the electrochemical cell, the energy produced in chemical reaction is transformed into electrical energy. The device which transforms the chemical energy into electrical energy is called **electrochemical cell.**

(i) Aqueous solution of $ZnSO_4$ is in beaker A. The weighed strip of zinc metal is placed in the solution so that part of it remains outside the solution. In this half cell the strip of Zn metal is in contact with 1M aqueous solution of Zn^{2+} ions which is expressed as $Zn(s) | Zn^{2+}(aq)$. Vertical line indicate contact between Zn metal strip and Zn^{2+} ions present in the solution.

(ii) Aqueous solution of $CuSO_4$ is in beaker B. The weighed strip of Cu metal is placed in the solution so that part of it remains outside the solution. In this half cell, the strip of Cu metal is in contact with 1M aqueous solution of $CuSO_4$, which is expressed by vertical line. $Cu(s) | Cu^{2+}(aq)$. Vertical line indicate contact between Cu metal strip and Cu^{2+} ions present in the solution.

(iii) Salt bridge is used to complete the electrical circuit and to connect the two solutions. The construction of saltbridge is like this. Aqueous solution of NH_4NO_3 is filled in U-shaped tube and its both the ends are closed by glass-wool. This tube is inverted and its one end is placed in beaker A and the other end in beaker B.

(iv) You know that the electrical current flowing through a circuit can be measured by joining ammeter and the direction of electrical current by joining galvanometer. Hence, Ameter or galvanometer can be selected, with the help of the ammeter the flowing electrical current and the direction of flow of electron are determined.

As shown in fig 3.1, if the strips of zinc metal and copper metal are connected through galvanometer or ammeter, it shows flow of electricity from the wire.

After sometime, if both the strips are taken out, washed carefully with distilled water dried and weighed, it will be found that the weight of zinc strip has decreased and the weight of copper strip has increased. This shows that the reaction $Zn(s) \rightleftharpoons Zn^{2+}(aq) + 2e^-$ must have occurred in beaker A containing solution of $ZnSO_4$ and the reaction $Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$ in the solution of $CuSO_4$ filled in beaker B.

The construction shown in fig. 3.1, is known as electrochemical cell or Galvanic cell or voltaic cell. The above special type of electrochemical cell is called Daniell cell. The strips dipped in solutions are called electrodes which is expressed as (e.g. $Zn(s) \mid Zn^{2+}(aq)$ and $Cu(s) \mid Cu^{2+}(aq)$). The electrode on which reduction reaction takes place is called cathode (+) and the electrode on which oxidation reaction takes places is called anode (−). If these two electrodes in electrochemical cell are connected by a copper wire in the external circuit, the current of electrons flow from anode to cathode. The U-tube filled in with solution of ammonium nitrate, used for the connection of two solutions is called salt bridge. The flow of current in solution occurs through the ions.

In the beaker (B) on the right hand side, copper is formed from Cu^{2+} by reduction and so, concentration of Cu^{2+} decreases due to which the solution of $CuSO_4$ becomes negatively charged because of SO_4^{2-} ions. The solution in the beaker (A) on left hand side Zn^{2+} ions are produced from Zn metal and so $ZnSO_4$ solution becomes positively charged. If it happens so, the chemical reaction of the cell will stop. Hence, both the solutions must be without any electric charge so that the reaction of cell takes place continuously. The salt bridge joining the two solutions in the beakers contains liquid medium of solution of proper salt. Hence, the salt bridge joins the two solutions and keeps the neutrality of electrical charge.

The cell in which the "concentrations of the ions associated with the reaction of the cell are 1 mole litre^{-1} and if any gas is associated with the reaction, then its pressure equal to 1 bar and if temperature is 298 K, is called standard cell.

3.3 Types of Electrodes

The metal strips dipped in the solution or rods of nonmetal like graphite and on whose surface reaction takes place is called an electrode. The electrodes used in electrochemical cells are mainly of three types.

(i) Active elecrodes of metal : The active electrodes of metal are metals like Zn, Ni, Cu, Ag etc. Atom of this kind of electrode undergo oxidation (anode) or cation in contact gets reduced on surface (cathode). The reactions taking place on such electrodes can be shown as below :

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

$$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$$
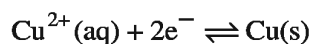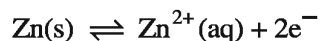
(ii) Inert electrode : Atoms of inert electrode do not experience either oxidation or reduction reaction but oxidation or reduction reaction takes place on the surface of this inert electrode. Graphite and platinum are inert electrodes. When the solutions containing Fe^{3+} and Fe^{2+} ions, are used in the

construction of the cell, platinum wire is used as the electrode. Fe^{3+} gets reduced to Fe^{2+} by receiving electron on strip of platinum or Fe^{2+} is oxidised to Fe^{3+} by giving electron to platinum wire. The reaction taking place on this type of electrode can be shown as below.

$$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$$
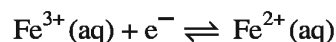
(iii) Gaseous electrode : Gaseous electrode mostly resembles the inert electrode. Here, gas is passed over the strip of platinum dipped in the solution. viz. If in hydrogen gas electrode containing $H^+(aq)$ in solution is passed over the strip of platinum kept in the solution, then $2H^+$ are reduced and the gas H_2 is formed or $2H^+$ are formed by oxidation of H_2 gas. Here, the strip of platinum provides the surface necessary for exchange of electrtons. The reaction taking place on such an electrode can be shown as below:

$$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$$
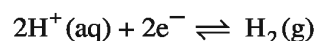
3.3.1 Half Cell : The metal which is kept in the aqueous soultion of its salt and a system formed is called electrode. **The electrode and the solution in which it is dipped is collectively known as half cell.** The representation of half cell is done by putting a vertical line between the formulas of electrode and the active ions.

$Zn(s) \mid Zn^{2+}(aq)$; $Cu(s) \mid Cu^{2+}(aq)$; $Fe(s) \mid Fe^{2+}(aq)$; $Ag(s) \mid Ag^+(aq)$
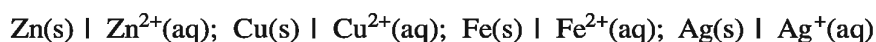
The representation of gaseous electrode is expressed by inert metal or formula of non metal, molecular formula of gas and the formula of active ions. e.g. **$Pt \mid H_2(g, 1\ bar) \mid H^+(aq)$.**

3.3.2 Symbolic representation of cell : In symbolic representation of electrochemical cell, the representation of both the half cells used in its construction are used. If a salt bridge is used to join solutions of both the half cells, then it is expressed by ‖ (two vertical lines). But if salt bridge is not used, then | (single vertical line) is used. Anode is always shown on the left hand side and the cathode on the right hand side in symbolic representation of the cell. The concentration of the salt used in the construction of the cell is expressed in molarity unit in bracket after the formula or symbol of the ion. If a gaseous electrode is used in the construction of cell, then its pressure is expressed in bar units after the formula of the gas.

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

(ii) $Pt \mid H_2(g, 1\ bar) \mid H^+(aq, 1M) \parallel Cu^{2+}(aq, 1M) \mid Cu(s)$

(iii) $Mg(s) \mid Mg^{2+}(aq, 1M) \parallel H^+(aq, 1M) \mid H_2(g, 1\ bar) \mid Pt$

(iv) $Ag(s) \mid Ag^+(aq, 1M) \parallel Cl^-(aq, 1M) \mid Cl_2(g, 1\ bar) \mid Pt$

If the concentration of solution is 1M in the half cell, or pressure of gas is 1 bar and temperature is 298 K, then such a half cell is called standard half cell. By connecting of two standard half cells, standard cell is formed.

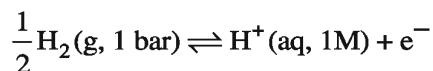**3.3.3 Standard Hydrogen Gas Electrode :** The comparison of different electrodes for the tendency to release the electron or to receive the electron can be carried out by using the standard hydrogen half cell because the hydrogen electrode works as a reference to other electrode. Hence, hydrogen electrode can be taken as reference electrode. The construction of standard hydrogen gas electrode is carried out as under :

As shown in fig 3.2 a solution of 1M H^+(aq) is taken in a beaker at 298 K. In this solution, the platinum strip which is electroplated with platinum black is dipped. This strip is connected with platinum wire in a tube closed at one end. Mercury is added on this wire to keep electrical contact and the other end of the wire is connected outside. Dihydrogen gas at 298 K temperature and 1 bar pressure is passed over the platinum.

Fig. 3.2 Standard hydrogen gas electrode

When this half cell is connected with other half cell and a complete cell is formed, it acts as cathode or anode. If it acts as cathode, the following reduction reaction takes place on the platinum strip.

$$H^+ (aq, 1M) + e^- \rightleftharpoons \frac{1}{2} H_2 (g, 1\ bar)$$
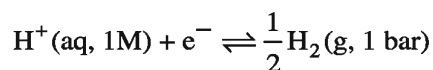
But if the standard hydrogen gas electrode acts as an anode the oxidation reaction takes place on the anode as shown below :

$$\frac{1}{2} H_2 (g, 1\ bar) \rightleftharpoons H^+ (aq, 1M) + e^-$$

Thus, standard hydrogen gas electrode possesses the tendency to receive the electron or to release the electron. The intensity of this tendency is accepted as zero volt at all temperatures. Hence, it is easy to obtain the relative values of intensity of the tendency of receiving the electron or the tendency of releasing the electron. **The relative intensity of tendency of receiving the electron is called reduction potential E_{red} or E^0_{red} and the relative intensity of electrodes for releasing electron is called oxidation potential E_{oxi} or E^0_{oxi}.**

Standard hydrogen electrode works as a reference electrode for other half cells. If the tendency of the other half cell to receive electron is more then standard hydrogen gas electrode acts as an anode and if standard hydrogen gas electrode has more tendency to receive the electron, it acts as a cathode.

Hence, the dependence of another half cell as anode or cathode remains with reference to standard hydrogen electrode, so it is called reference electrode. With reference to standard hydrogen gas electrode, standard Zn-half cell act as anode while standard Cu-half cell act as cathode.

3.4 Cell potential

The electrochemical cell is a device which can transform chemical energy into electrical energy. When two electrodes are joined, then the flow of electrons due to chemical reaction will be from anode to cathode in the external circuit under produced electromotive force. This electromotive force is called cell potential E_{Cell}. If the cell is in standard state, the standard potential is expressed as E^0_{Cell}. The voltage measured with voltmeter is really not the correct potential. **Potentiometer should be used to measure the correct potential.**

The cell potential is in fact the difference between the intensities of receiving electron of each electrode and possess the tendency to release the electron. The proof of this is obtained. From the following experimental results.

(i) $\overset{\ominus}{}$ $Zn(s) | Zn^{2+} (1\,M) || Cu^{2+} (1M) | Cu(s)$ $\overset{\oplus}{}$

When the above cell is in operation, the following reaction takes place:

$$Zn(s) + Cu^{2+} (aq, 1M) \rightleftharpoons Zn^{2+} (aq, 1M) + Cu(s)$$
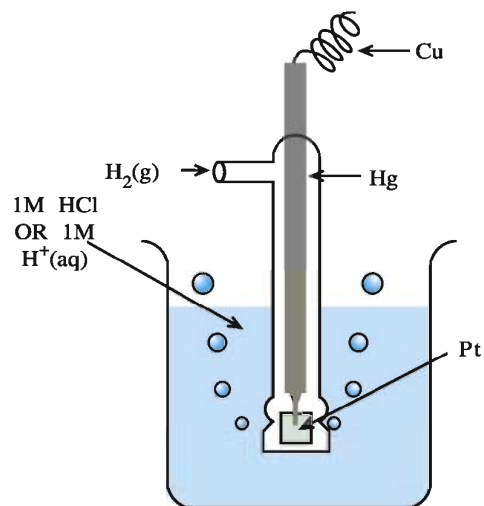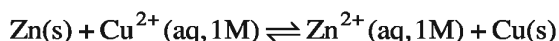
Here Zn releases the electron and Cu^{2+} receives the electron. The tendency of Cu^{2+} to receive the electron is more which can be said on the basis of the above reaction.

(ii) $^{\ominus}$ $Cu(s) | Cu^{2+}(1M) || Ag^+(1M) | Ag(s)$ $^{\oplus}$

When the above cell is in operation the following reaction takes place.

$$Cu(s) + 2Ag^+(aq, 1M) \rightleftharpoons Cu^{2+}(aq, 1M) + 2Ag(s)$$
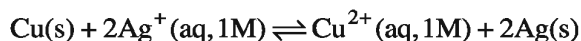
Here, Cu releases the electron and Ag^+ accepts the electron. The tendency of Ag^+ to receive electron is more than that of Cu, which can be said on the basis of the above reaction.

In the above reaction (i) the tendency of Cu, to receive electron is more than that of Zn; while in reaction (ii) the tendency of Cu to receive relectron is less than that of Ag. Hence, in reraction (i) Cu electrode acts as cathode and in reaction (ii) Cu electrode acts as anode. The potential is the difference of intensities of cathode and anode to receive electrons. The abosulte value of intensity of tendency to accept the electron cannot be measured because redox reaction is not completed by half cell. The value of E^0_{Cell} is the difference between the values of standard reduction potentials of two half cells. This relation is shown as below :

$$E^0_{Cell} = E^0_{red\,(RHS)} - E^0_{red\,(LHS)} \quad OR \quad E^0_{Cell} = E^0_{red\,(Cathode)} - E^0_{red\,(Anode)}$$

3.4.1 Method of determination of standard half cell potential :
To obtain the potential of any standard half cell, it is connected with the standard hydrogen half cell, through salt bridge. The cell potential E^0_{Cell} of the complete cell prepared like this is measured with the help of potentiometer.

In the complete cell constructed like this, the potential of one half cell - standard hydrogen half cell is zero as it is being accepted The potential of the other half cell will be the value equal to that of E^0_{Cell}. If the other half cell is functioning as anode the positive value of E^0_{Cell} indicating negative value of E^0_{red} of the electrode. But if it is functioning as cathode, then the value of potential E^0_{red} will be positive. If the electrochemical cell is formed by connecting zinc half cell with standard hydrogen electrode, the half cell of Zn acts as anode and hence the value of E^0_{Cell} will be equal to negative of reduction potential of Zn half cell. When the electrochemical cell is formed by connecting half cell of Cu with standard hydrogen electrode, it acts as the cathode half cell. Hence the positive value of Cu half cell will be equal to the positive value of reduction potential of half cell of Cu. The values of E^0_{red} and E^0_{oxi} of any electrode are same but the signs are opposite. The negative value of E^0_{red} shows positive value of E^0_{oxi}.

$$E^0_{red} = - E^0_{oxi}$$

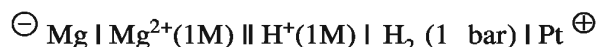$$E^0_{Mg^{2+} | Mg(red)} = -2.36 \ Volt$$

$$E^0_{Mg | Mg^{2+}(oxi)} = + 2.36 \ Volt$$

$$E^0_{Cu^{2+} | Cu} = +0.34 \ Volt$$

$$E^0_{Cu | Cu^{2+}} = -0.34 \ Volt$$

Example 1 : The potential of the following given cell is 2.36 volt at 298 K. Write the equation for reaction and calculate the reduction potential of magnesium half cell.

$$\ominus \text{Mg} \mid \text{Mg}^{2+}(1\text{M}) \parallel \text{H}^+(1\text{M}) \mid \text{H}_2 \ (1 \ \text{bar}) \mid \text{Pt} \oplus$$

Solution : Here, electrode of Mg is anode.

Cathode : $2\text{H}^+(\text{aq}) + 2e^- \rightleftharpoons \text{H}_2(\text{g})$ (Reduction)

Anode : $\text{Mg(s)} \rightleftharpoons \text{Mg}^{2+}(\text{aq}) + 2e^-$ (Oxidation)

Cell Reaction : $\text{Mg(s)} + 2\text{H}^+(\text{aq}) \rightleftharpoons \text{Mg}^{2+}(\text{aq}) + \text{H}_2(\text{g})$
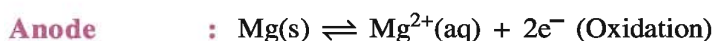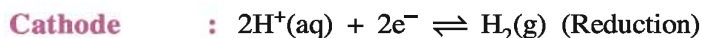
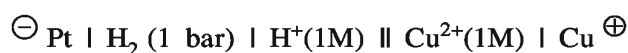$$E^0_{\text{Cell}} = E^0_{\text{red (Cathode)}} - E^0_{\text{red (Anode)}}$$

$$E^0_{\text{Cell}} = E^0_{\text{H}^+ \mid \frac{1}{2}\text{H}_2} - E^0_{\text{Mg}^{2+} \mid \text{Mg}}$$

$$\therefore \ 2.36 \ \text{volt} = 0.0 - E^0_{\text{Mg}^{2+} \mid \text{Mg}}$$

$$\therefore \ E^0_{\text{Mg}^{2+} \mid \text{Mg}} = -2.36 \ \text{volt}$$

The standard reduction potential of this half cell $E^0_{\text{Mg}^{2+} \mid \text{Mg}} = -2.36$ volt.

Example 2 : The potential of the given following cell is 0.34 volt at 298 K temperature calculate the standard reduction potential of copper half cell.

$$\ominus \text{Pt} \mid \text{H}_2 \ (1 \ \text{bar}) \mid \text{H}^+(1\text{M}) \parallel \text{Cu}^{2+}(1\text{M}) \mid \text{Cu} \oplus$$

Solution : Here, copper electrode is cathode

$$E^0_{\text{Cell}} = E^0_{\text{red (Cathode)}} - E^0_{\text{red (Anode)}}$$

$$\therefore \ E^0_{\text{Cell}} = E^0_{\text{Cu}^{2+} \mid \text{Cu}} - E^0_{\text{H}^+ \mid \text{H}_2}$$

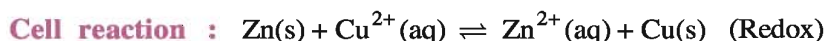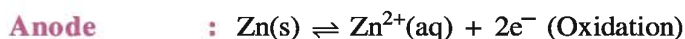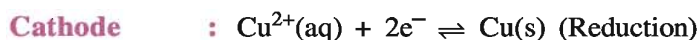$$\therefore \ 0.34 \ \text{Volt} = E^0_{\text{Cu}^{2+} \mid \text{Cu}} - 0.0$$

$$\therefore \ E^0_{\text{Cu}^{2+} \mid \text{Cu}} = 0.34 \ \text{volt}$$

The standard reduction potential of this half cell $E^0_{\text{Cu}^{2+} \mid \text{Cu}} = 0.34$ volt and the standard oxidation potential of this half cell will be $E^0_{\text{Cu} \mid \text{Cu}^{2+}} = -0.34$ volt.

It will be understood from the above two examples that reduction potentials of standard reduction half cells are positive. Their tendency to receive electron is more than that of hydrogen. Hence, if these half cell electrodes are connected with standard hydrogen gas electrode, they will act as cathode. As contrast to this, the potentials of standard half cells of standard electrodes are negative, their tendency to receive electron is less than that of hydrogen. Hence, if the half cells of this type are constructed, they act as anode.

If, instead of standard hydrogen gas electrode any other standard half cell is used for construction of cell, then, the half cell having more negative reduction potential will act as cathode. viz. $\text{Zn}^{2+}(1\text{M}) \mid \text{Zn(s)}$ and $\text{Cu}^{2+}(1\text{M}) \mid \text{Cu(s)}$ half cells are jonied and a complete cell is prepared then, the zinc electrode will

act as anode and copper electrode will act as cathode, because the value of $E^0_{Zn^{2+}|Zn} = -0.76$ volt which is less than the value of the $E^0_{Cu^{2+}|Cu} = 0.34$ volt. Thus the complete cell formed is $\ominus$ Zn(s) | Zn^{2+}(1M) ‖ Cu^{2+}(1M) | Cu(s) $\oplus$ and its standard potential can be calculated.

Cathode : $Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$ (Reduction)

Anode : $Zn(s) \rightleftharpoons Zn^{2+}(aq) + 2e^-$ (Oxidation)

Cell reaction : $Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$ (Redox)

$$E^0_{Cell} = E^0_{red\ (Cathode)} - E^0_{red\ (Anode)}$$

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

$$= 0.34 - (-0.76) = +0.34 + 0.76 = 1.1\ volt$$

3.5 emf series

When potential of a cell is measured with reference to standard hydrogen electrode, the potential of second electrode is known as **Electro Motive Force** which is known in brief as emf. If the values of the reduction potentials of standard electrodes of the half cells is arranged in the decreasing order, then the series of the electrodes, formed is called emf series. Earlier importance was given to oxidation potential. Now, according to SI units importance is given to reduction potentials. The series of standard reduction electrode potentials based on the values of E^0_{red} is given in table 3.1.

Table 3.1 Standard Electrode Potentials at 298 K
Ions are present as aqueous species and H_2O as liquid;
gases and solids are shown by g and s

Reaction (Oxidesed form + ne^-	$\rightarrow$	Reduced form)	E^0/V
$F_2(g) + 2e^-$	$\rightarrow$	$2F^-$	2.87
$Co^{3+} + e^-$	$\rightarrow$	Co^{2+}	1.81
$H_2O_2 + 2H^+ + 2e^-$	$\rightarrow$	$2H_2O$	1.78
$MnO_4^- + 8H^+ + 5e^-$	$\rightarrow$	$Mn^{2+} + 4H_2O$	1.51
$Au^{3+} + 3e^-$	$\rightarrow$	$Au(s)$	1.40
$Cl_2(g) + 2e^-$	$\rightarrow$	$2Cl^-$	1.36
$Cr_2O_7^{2-} + 14H^+ + 2e^-$	$\rightarrow$	$2Cr^{3+} + 7H_2O$	1.33
$O_2(g) + 4H^+ + 4e^-$	$\rightarrow$	$2H_2O$	1.23
$MnO_2(s) + 4H^+ + 4e^-$	$\rightarrow$	$Mn^{2+} + 2H_2O$	1.23

(Increasing strength of oxidising agent ↑) (Increasing strength of reducing agent ↓)

$Br_2 + 2e^-$	$\rightarrow$	$2Br^-$	1.09
$NO_3^- + 4H^+ + 3e^-$	$\rightarrow$	$NO(g) + 2H_2O$	0.97
$2Hg^{2+} + 2e^-$	$\rightarrow$	Hg_2^{2+}	0.92
$Ag^+ + e^-$	$\rightarrow$	$Ag(s)$	0.80
$Fe^{3+} + e^-$	$\rightarrow$	Fe^{2+}	0.77
$O_2(g) + 2H^+ + 2e^-$	$\rightarrow$	H_2O_2	0.68
$I_2 + 2e^-$	$\rightarrow$	$2I^-$	0.54
$Cu^+ + e^-$	$\rightarrow$	$Cu(s)$	0.52
$Cu^{2+} + 2e^-$	$\rightarrow$	$Cu(s)$	0.34
$AgCl(s) + e^-$	$\rightarrow$	$Ag(s) + Cl^-$	0.22
$AgBr(s) + e^-$	$\rightarrow$	$Ag(s) + Br^-$	0.10
$2H^+ + 2e^-$	$\rightarrow$	**$H_2(g)$**	**0.00**
$Pb^{2+} + 2e^-$	$\rightarrow$	$Pb(s)$	– 0.13
$Sn^{2+} + 2e^-$	$\rightarrow$	$Sn(s)$	– 0.14
$Ni^{2+} + 2e^-$	$\rightarrow$	$Ni(s)$	– 0.25
$Fe^{2+} + 2e^-$	$\rightarrow$	$Fe(s)$	– 0.44
$Cr^{3+} + 3e^-$	$\rightarrow$	$Cr(s)$	– 0.74
$Zn^{2+} + 2e^-$	$\rightarrow$	$Zn(s)$	– 0.76
$2H_2O + 2e^-$	$\rightarrow$	$H_2(g) + 2OH^-(aq)$	– 0.83
$Al^{3+} + 3e^-$	$\rightarrow$	$Al(s)$	– 1.66
$Mg^{2+} + 2e^-$	$\rightarrow$	$Mg(s)$	– 2.36
$Na^+ + e^-$	$\rightarrow$	$Na(s)$	– 2.71
$Ca^{2+} + 2e^-$	$\rightarrow$	$Ca(s)$	– 2.87
$K^+ + e^-$	$\rightarrow$	$K(s)$	– 2.93
$Li^+ + e^-$	$\rightarrow$	$Li(s)$	– 3.05

(Left vertical axis: Increasing strength of oxidising agent — arrow pointing up)

(Right vertical axis: Increasing strength of reducing agent — arrow pointing down)

(i) A negative E^0 means that the redox couple is a stronger reducing agent than the $H^+ | H_2$ couple.

(ii) A positive E^0 means that the redox couple is a weaker reducing agent than the $H^+ | H_2$ couple.

The following information can be obtained from the series given in table 3.1.

(1) In this series, the tendency to experience oxidation, tendency to release electron and the strength as reducing agent increases as we go from above to below.

(2) In this series, the tendency to experience reduction reaction, tendency to accept electron and strength as oxidising agents increase as we go from below to above.

(3) The standard potential of the complete cell formed by combination of two half cells and calculating their standard potentials. From this series, the information about which electrode will be anode and which will be cathode can also be obtained.

(4) If the rods of the metals in this series, which have lower positions are placed in the solutions of salts of metals having higher position in the series the ion will be replaced as metals by the metal rods. e.g. The position of Fe is below than the position of Cu in emf series, if Fe rod is placed in a solution of Cu^{2+} the rod of Fe will transfrom Fe to Fe^{2+} and Cu^{2+} to Cu(s).

Examples 3 : Write the symbolic representation of the cell formed by the use of following given standard half cells at 298 K. Write the cell reaction and calculate standard potential E^0_{Cell}.

(1) $E^0_{Zn^{2+}|Zn}$ = − 0.76 Volt   (2) $E^0_{Ag^+|Ag}$ = 0.80 Volt

Solution : The standard reduction potential of zinc being less, it will act as anode. Hence, it will be written on left hand side in symbolic representation.

Symbolic representation of cell : $\ominus$ Zn | Zn^{2+} (1M) || Ag^+(1M) | Ag $\oplus$

Cathode   : $2Ag^+(aq) + 2e^- \rightleftharpoons 2Ag(s)$ (Reduction)

Anode   : $Zn(s) \rightleftharpoons Zn^{2+}(aq) + 2e^-$ (Oxidation)

Cell reaction : $Zn(s) + 2Ag^+(aq) \rightleftharpoons Zn^{2+}(aq) + 2Ag(s)$ (Redox)

$$E^0_{Cell} = E^0_{red\ (Cathode)} - E^0_{red\ (Anode)}$$
$$= E^0_{Ag^+|Ag} - E^0_{Zn^{2+}|Zn}$$
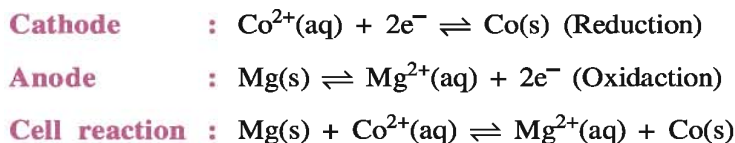$$= (0.80) - (-0.76)$$
$$= 1.56\ volt$$

In the equation the reaction at the cathode is multiplied by 2, even then the value of E^0_{red} is not multiplied by two because, for the balancing of equation the equation of the half cell is multiplied by two but the definition of standard cell for 1M concentration does not change.

Example 4 : Write the symbolic representation of cell formed by the given two following half cells at 298 K. Write the reaction of the cell and calculate its standard potential.

(1) $E^0_{Mg^{2+}|Mg}$ = − 2.37 volt   (2) $E^0_{Co^{2+}|Co}$ = − 0.28 volt

Solution : As the standard reduction potential of magnesium is less, it will act as anode. Hence, it can be written on left hand side in symbolic representation.

Symbolic representation of cell : $\ominus$ Mg(s) | Mg^{2+} (1M) || Co^{2+}(1M) | Co(s) $\oplus$

Cathode	: $Co^{2+}(aq) + 2e^- \rightleftharpoons Co(s)$ (Reduction)
Anode	: $Mg(s) \rightleftharpoons Mg^{2+}(aq) + 2e^-$ (Oxidaction)
Cell reaction	: $Mg(s) + Co^{2+}(aq) \rightleftharpoons Mg^{2+}(aq) + Co(s)$

$$E^0_{Cell} = E^0_{red\ (Cathode)} - E^0_{red\ (Anode)}$$
$$= E^0_{Co^{2+}|Co} - E^0_{Mg^{2+}|Mg}$$
$$= (-0.28) - (-2.37) = 2.09 \text{ volt}$$

3.6 Nernst Equation

It is not necessary always that the concentration of all the species involved in electrode reaction should be unity. The potential of the electrochemical cell depends on temperature, concentration of solutions associated with cell reaction and nature of electrode. Scientist Nernst first of all gave the equation showing relation between the potential of the electrochemical cell and the concentration of solutions associated with the reaction. He mentioned that this equation can be deduced on the basis of principles of thermodynamics.

According to Nernst, in the electrode reaction,

$M^{n+}(aq) + ne^- \rightleftharpoons M(s)$

The electrode potential at any concentration can be measured as the representative of the standard hydrogen electrode as follows :

$$E_{(M^{n+}|M)} = E^0_{(M^{n+}|M)} - \frac{RT}{nF} ln \frac{M}{[M^{n+}]}$$

But taking concentration of solid form M as constant,

$$E_{(M^{n+}|M)} = E^0_{(M^{n+}|M)} - \frac{RT}{nF} ln \frac{1}{[M^{n+}]}$$

$E^0_{(M^{n+}|M)}$ is already known. R = gas constant (8.314 J K^{-1} mol^{-1}) and F is Faraday constant (96500 coulomb mol^{-1}), T = Temperature in Kelvin and [M^{n+}] is the concentration of that form.

We can write the concentrations of Cu^{2+} and Zn^{2+} ions in Daniell cell, in the given electrode potential.

For cathode : $E_{(Cu^{2+}|Cu)} = E^0_{(Cu^{2+}|Cu)} - \frac{RT}{2F} ln \frac{1}{[Cu^{2+}]}$ (1)

For anode : $E_{(Zn^{2+}|Zn)} = E^0_{(Zn^{2+}|Zn)} - \frac{RT}{2F} ln \frac{1}{[Zn^{2+}]}$ (2)

Cell potential : $E_{Cell} = E_{(Cu^{2+}|Cu)} - E_{(Zn^{2+}|Zn)}$

$$= E^0_{(Cu^{2+}|Cu)} - \frac{RT}{2F} ln \frac{1}{[Cu^{2+}]} - E^0_{(Zn^{2+}|Zn)} + \frac{RT}{2F} ln \frac{1}{[Zn^{2+}]}$$

$$= E^0_{(Cu^{2+}|Cu)} - E^0_{(Zn^{2+}|Zn)} - \frac{RT}{2F} ln \frac{1}{[Cu^{2+}]} + \frac{RT}{2F} ln \frac{1}{[Zn^{2+}]}$$

$$\therefore E_{Cell} = E^0_{Cell} - \frac{RT}{2F} ln \frac{[Zn^{2+}]}{[Cu^{2+}]} \tag{3}$$

It can be said from this that E_{Cell} depends on the concentration of Cu^{2+} and Zn^{2+} ions. Its value increases with increase in concentration of Cu^{2+} and decreases with increase in concentration of Zn^{2+}.
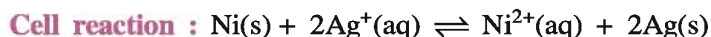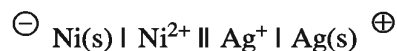
Putting the values of R, F and T and converting natural logarithm to the base-10 then, the equation (3) will be like this.

$$\frac{2.303 \, RT}{F} = 0.059$$

Thus, $E_{Cell} = E^0_{Cell} - \dfrac{0.059}{2} \log \dfrac{[Zn^{2+}]}{[Cu^{2+}]}$ $\qquad$ (4)

As same number of electrons(n) are taken for both the electrodes, cell can be shown as above.

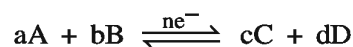In the same way, if we have different electrons for the two electrodes, the cell can be shown as below :

$$\overset{\ominus}{} \, Ni(s) \, | \, Ni^{2+} \, \| \, Ag^+ \, | \, Ag(s) \, \overset{\oplus}{}$$

Cell reaction : $Ni(s) + 2Ag^+(aq) \rightleftharpoons Ni^{2+}(aq) + 2Ag(s)$

It can be written according to Nernst equation as follows :

$$E_{Cell} = E^0_{Cell} - \frac{0.059}{n} \log \frac{[Ni^{2+}]}{[Ag^+]^2}$$

The general equation of electrochemical equation will be like this

$$aA + bB \xrightarrow{ne^-} cC + dD$$

According to Nernst equation,

$$E_{Cell} = E^0_{Cell} - \frac{RT}{nF} \mathmit{ln}K \quad \text{Where K = equilibrium constant}$$

$$= E^0_{Cell} - \frac{RT}{nF} \mathmit{ln} \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

The potential of non-standard half cells can be calculated by Nernst equation. If we write $Co^{2+} \, | \, Co$ half cell reaction as reduction reaction then it will be, $Co^{2+}(aq) + 2e^- \rightleftharpoons Co(s)$.

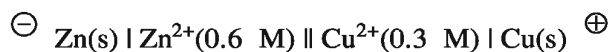$$E_{(Co^{2+} \, | \, Co)} = E^0_{(Co^{2+} \, | \, Co)} - \frac{0.059}{2} \log \frac{1}{[Co^{2+}]}$$

But if we write $Co \, | \, Co^{2+}$ half cell reaction as oxidation reaction, then, it will be $Co(s) \rightleftharpoons Co^{2+}(aq) + 2e^-$

$$E_{(Co \, | \, Co^{2+})} = E^0_{(Co \, | \, Co^{2+})} - \frac{0.059}{2} \log [Co^{2+}]$$

in which the potential expressed is oxidation potential.

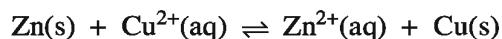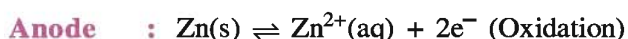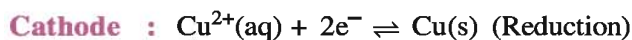**Example 5 :** Calculate the cell potential of the following cell as 298 K.

$\ominus$ Zn(s) | Zn^{2+}(0.6 M) || Cu^{2+}(0.3 M) | Cu(s) $\oplus$

$E^0_{(Zn^{2+}|Zn)} = -0.76$ volt, $\qquad E^0_{(Cu^{2+}|Cu)} = 0.34$ volt,

Solution : Here zinc electrode is anode and copper electrode is cathode. Its standard electrode potential values are given. On the basis of which E^0_{Cell} can be calculated.

$$E^0_{Cell} = E^0_{(Cu^{2+}|Cu)} - E^0_{(Zn^{2+}|Zn)}$$

$$= 0.34 \text{ volt} - (-0.76 \text{ volt})$$

$$= 0.34 + 0.76$$

$$= 1.10 \text{ volt}$$

Cell reaction :

Cathode : Cu^{2+}(aq) + 2e$^-$ $\rightleftharpoons$ Cu(s) (Reduction)

Anode : Zn(s) $\rightleftharpoons$ Zn^{2+}(aq) + 2e$^-$ (Oxidation)
_____

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

Here n equal to 2.

$$E_{Cell} = E^0_{Cell} - \frac{0.059}{2} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$= 1.10 - \frac{0.059}{2} \log \frac{[0.6]}{[0.3]}$$

$$= 1.10 - 0.0295 \log 2.0$$

$$= 1.10 - (0.0295)(0.3010)$$

$$= 1.10 - 0.0089 = 1.0911 \text{ volt}$$

Example 6 : The following reaction occurs in the cell

Mg(s) + 2Ag$^+$(0.0001M) $\rightleftharpoons$ Mg^{2+}(0.130M) + 2Ag(s) Calculate E$_{Cell}$. E^0_{Cell} = 3.17 volt
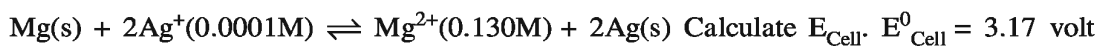
Solution : The cell can be written like this

$\ominus$ Mg(s) | Mg^{2+}(0.130M) || Ag$^+$(0.0001M) | Ag(s) $\oplus$

Cell reaction :

Cathode   : 2Ag$^+$(aq) + 2e$^-$ $\rightleftharpoons$ 2Ag(s)

Anode   : Mg(s) $\rightleftharpoons$ Mg^{2+}(aq) + 2e$^-$
_____

Mg(s) + 2Ag$^+$(aq) $\rightleftharpoons$ Mg^{2+}(aq) + Ag(s)
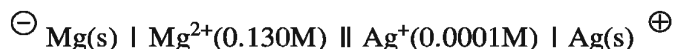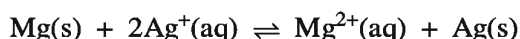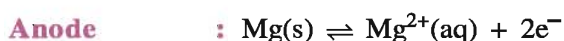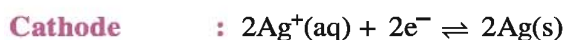
Hence n equal to 2

$$E_{Cell} = E^0_{Cell} - \frac{RT}{2F} ln \frac{[Mg^{2+}]}{[Ag^+]^2}$$

$$E_{Cell} = 3.17 - \frac{0.059}{2} log \frac{[Mg^{2+}]}{[Ag^+]^2}$$

$$E_{Cell} = 3.17 - \frac{0.059}{2} log \frac{[0.130]}{(0.0001)^2}$$

$$= 3.17 - 0.21 = 2.96 \text{ volt}$$

3.6.1 Concentration Cell :

If the two electrodes of the electrochemical cell are same but the concentrations of the solutions of the electrolyte are different, then it is called concentration cell. viz

$$Cu(s) \mid Cu^{2+} (C_1) \parallel Cu^{2+} (C_2) \mid Cu(s)$$

The concentrations of ions change in cell reaction of concentration cell as shown below; which is the result of redox reaction. The ions of concentrated solution move towards dilute solution and so this type of cell is called concentration cell.

In this cell for the reaction $^\ominus Cu(s) \mid Cu^{2+}(C_1) \parallel Cu^{2+}(C_2) \mid Cu(s)^\oplus$, $E^0_{Cell} = 0.0$ volt
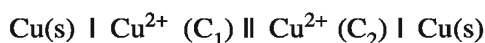
Cathode : $Cu^{2+}(C_2) + 2e^- \rightleftharpoons Cu(s)$

Anode : $Cu(s) \rightleftharpoons Cu^{2+}(C_1) + 2e^-$

Cell reaction : $Cu^{2+}(C_2) \rightleftharpoons Cu^{2+}(C_1)$

Generally reduction occurs in concentrated solution and so it will be written on right hand side and will act as cathode. The cell potential of concentration cell is calculated by the following formula.

$$E_{Cell} = E^0_{Cell} - \frac{0.059}{n} log \frac{[C_1]}{[C_2]}$$

Here, $E^0_{Cell} = 0.0$ volt because both the electrodes are same and the values of their standard oxidation and reduction potentials are same but the sign is positive or negative and so its sum will be zero. In both the half cells, concentrations of Cu^{2+} are different, but positive ion is same in the solution. The values of electrode potentials of anode half cell and cathode half cell are same but of opposite signs. Hence, $E^0_{Cell} = 0.0$ volt.

$$E_{Cell} = 0.0 - \frac{0.059}{n} log \frac{[C_1]}{[C_2]}$$

Example 7 : The standard reduction potential of $Ag^+ \mid Ag$ half cell is 0.80 volt. Calculate the potential of the following given cell at 298 K.

$$^\ominus Ag(s) \mid Ag^+(0.25M) \parallel Ag^+(0.75M) \mid Ag(s)^\oplus$$
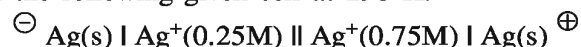
Solution :

Cathode : $Ag^+ (0.75M) + e^- \rightleftharpoons Ag(s)$ (Reduction)

Anode : $Ag(s) \rightleftharpoons Ag^+(0.25M) + e^-$ (Oxidation)

Cell reaction : $Ag^+(0.75M) \rightleftharpoons Ag^+ (0.25M)$

It appears from the above equation that when cell is in operation the ions of concentratred solution move towards the dilute solution. For this cell, $E^0_{Cell} = 0.0$ volt

$$E_{Cell} = E^0_{Cell} - \frac{0.059}{n} \log \frac{[C_1]}{[C_2]}$$

$$= 0.00 - \frac{0.059}{1} \log \frac{0.25}{0.75} \quad \text{(Here taking } n = 1)$$

$$= -0.059 \times \left(\log \frac{1}{3} \right) = -0.0592 \times (\log 1 - \log 3)$$

$$= -0.059 \times (-0.4771) = +0.0282 \text{ volt}$$

Example 8 : The reduction potential of half cell $Cu^{2+} \mid Cu$ is 0.34 volt. Calculate the potential of the given following cell.

$$^{\ominus} Cu(s) \mid Cu^{2+}(0.1M) \parallel Cu^{2+}(1M) \mid Cu(s) \, ^{\oplus}$$

Solutoin :

Cathode : $Cu^{2+}(1M) + 2e^- \rightleftharpoons Cu(s)$ (Reduction)

Anode : $Cu(s) \rightleftharpoons Cu^{2+}(0.1M) + 2e^-$ (Oxidation)

Cell reaction : $Cu^{2+}(1M) \rightleftharpoons Cu^{2+}(0.1M)$

$\qquad\qquad\qquad\quad (C_2) \qquad\qquad (C_1)$

In concentration cell, the ions of the solution travel towards dilute solution and in concentration cell $E^0_{Cell} = 0.00$.

$$E_{Cell} = E^0_{Cell} - \frac{0.059}{n} \log \frac{[C_1]}{[C_2]}$$

$$= 0.00 - \frac{0.059}{2} \log \frac{(0.1)}{(1.0)} \quad \text{(Here taking } n = 2)$$

$$= -0.0295 \times \log \frac{0.1}{1} = -0.0295 \times \log \frac{1}{10}$$

$$= -0.0295 \times (-1) = 0.0295 \text{ volt}$$

The potential of concentration cell is comparatively less. As the ions from the concentration solution travel towards dilute soultion, there is an effort for equalisation of same concentration of both the half cells.

If the value of the potential of the cell obtained is negative it is believed that the electrode which was assumed to be anode is in fact cathode and the electrode which was assumed to be cathode is in fact anode.

3.7 Some Applications of Cell Potentials

(1) On the basis of the values of cell potential the equilibrium constant of the reaction taking place in the cell can be calculated.

(2) By construction of proper cell and on the basis of its potential value the pH of acidic solutions and ionic product of water can be calculated.

(3) Some titrations can be carried out using cell potentials.

Calculation of Equilibrium constant : Daniell cell (fig.3.1) possesses closed circuit and we have, noted the following reaction.

$$Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$$
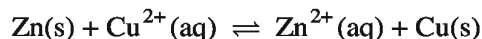
In the cell indicating this reaction, the concentration of Zn^{2+} increases and the concentration of Cu^{2+} decrease with the lapse of time. At this time, the potential of the cell can be read on the voltmeter or potentiometer in which the decrease in volt will appear. After some time, we can record that there is no change in concentrations of Cu^{2+} and Zn^{2+} ions at that time. This situation is the indication of equilibrium. In this case, Nernst equation can be written as follows :

$$E_{Cell} = E^0_{Cell} - \frac{2.303\,RT}{2F} \log \frac{[Zn^{2+}]}{[Cu^{2+}]} \quad \text{or}$$

$$E_{Cell} = E^0_{Cell} - \frac{0.059}{2} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

But at equilibrium $\dfrac{[Zn^{2+}]}{[Cu^{2+}]} = K_C$ Hence, the above equation can be written for this reaction (reaction equation) and T = 298 K.

$$\therefore\ E^0_{Cell} = \frac{2.303\,RT}{nF} \log K_C \tag{5}$$

$$E^0_{Cell} = \frac{0.059}{2} \log K_C = 1.1\,\text{volt} \quad (\because E^0_{Cell} = 1.1\ \text{volt})$$

$$\log K_C = \frac{(1.1 \times 2)}{(0.059)} = 37.288$$

At 298 temperature $K_C = 1.941 \times 10^{37}$

Thus, equation (5) shows the relation between standard electrode potential and the equilibrium constant for the reaction taking place. Thus, it is difficult to measure equilibrium constant; but the calculation related to E^0 can be carried out.

Example 9 : Calculate the equilibrium constant of the reaction.

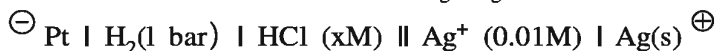$$Cu(s) + 2Ag^+(aq) \rightleftharpoons Cu^{2+}(aq) + 2Ag(s); \quad E^0_{Cell} = 0.46\ \text{volt}$$
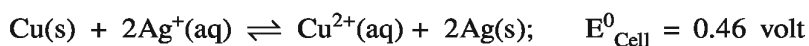
Solution :

$$E^0_{Cell} = \frac{0.059}{2} \log K_C = 0.46\ \text{volt} \quad \text{or}$$

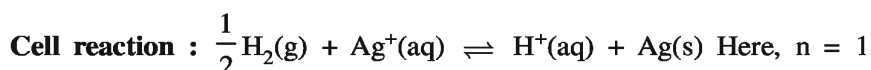$$\log K_C = \frac{0.46 \times 2}{0.059} = 15.593$$

$$\therefore\ K_C = 3.92 \times 10^{15}$$

Example 10 : The potential of the following given cell is 1.02 volt at 298 K temperature. Calculate the pH of HCl solution. ($E^0_{Ag^+ | Ag}$ = 0.80 volt).

$$\overset{\ominus}{} Pt \mid H_2(1 \text{ bar}) \mid HCl \text{ (xM)} \parallel Ag^+ \text{ (0.01M)} \mid Ag(s) \overset{\oplus}{}$$

Solution : $E^0_{Cell} = E^0_{red \text{ (Cathode)}} - E^0_{red \text{ (Anode)}}$

$$= E^0_{(Ag^+ | Ag)} - E^0_{(H^+ | \frac{1}{2} H_2)}$$

$$= 0.80 - 0.0$$

$$E^0_{Cell} = 0.80 \text{ volt}$$

Cell reaction : $\frac{1}{2} H_2(g) + Ag^+(aq) \rightleftharpoons H^+(aq) + Ag(s)$ Here, n = 1

$$E_{Cell} = E^0_{Cell} - \frac{0.059}{n} \log \frac{[H^+]}{[Ag^+]}$$

$$1.02 = 0.80 - 0.059 \ \log \frac{[H^+]}{[0.01]}$$

$$\frac{0.22}{0.059} = -\log [H^+] + (-2.0)$$

$$3.729 = pH - 2.0$$

$$\therefore \ pH = 5.729$$

Example 11 : The potential of the given following cell is 0.096 volt at 298 K temperature. Calculate pH of HCl solution ($E^0_{(Sn^{2+} | Sn)}$ = − 0.14 volt)

$$\overset{\ominus}{} Sn \mid Sn^{2+}(0.05M) \parallel H^+(xM) \mid H_2 \ (1 \ bar) \mid Pt \overset{\oplus}{}$$
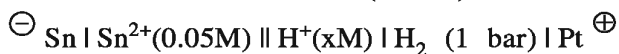
Solution : $E^0_{Cell} = E^0_{(H^+ | \frac{1}{2} H_2)} - E^0_{(Sn^{2+} | Sn)}$

$$E^0_{Cell} = 0.0 - (- 0.14) = 0.14 \text{ volt}$$

Cell reaction : $Sn(s) + 2H^+(aq) \rightleftharpoons Sn^{2+}(aq) + H_2(g)$; (Here, n = 2).
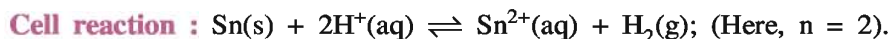
$$E_{Cell} = E^0_{Cell} - \frac{0.059}{n} \log \frac{[Sn^{2+}]}{[H^+]^2}$$

$$\therefore \ 0.096 = 0.14 - 0.0295 \ \log \frac{(0.05)}{[H^+]^2}$$

$$\therefore \ \frac{-0.096 - 0.14}{0.0295} = -\log \frac{(0.05)}{[H^+]^2}$$

$$\therefore \ \frac{-0.044}{0.0295} = -\log (0.05) + 2\log [H^+]$$

$$\therefore \frac{-0.044}{0.0295} = 1.3010 + 2\log[H^+]$$

$$\therefore -1.491 = -1.3010 + 2\log[H^+]$$

$$\therefore 1.491 + 1.3010 = -2\log[H^+]$$

$$\therefore 1.491 + 1.3010 = 2 \times pH$$

$$\therefore \frac{2.792}{2} = pH$$

$$\therefore pH = 1.396$$

Example 12 : The potential of the given following cell is 0.53 volt. Calculate the ionic product (K_W) of water.

$$^\ominus Pt \mid H_2(1 \text{ bar}) \mid KOH(0.002M) \parallel HCl(0.005M) \mid H_2(1 \text{ bar}) \mid Pt^\oplus$$

Solution :

Cathode   : $H^+(0.005M) + e^- \rightleftharpoons \frac{1}{2} H_2(1 \text{ bar})$ (reduction)

Anode   : $\frac{1}{2} H_2(1 \text{ bar}) \rightleftharpoons H^+ (xM) + e^-$ (oxidation)

Cell reaction : $H^+(0.005 \text{ M}) \rightleftharpoons H^+(xM)$
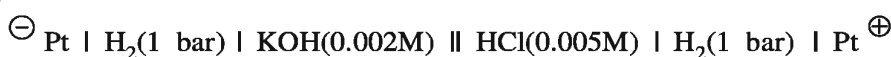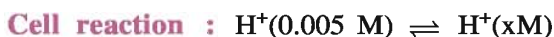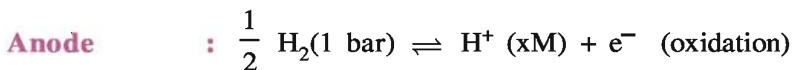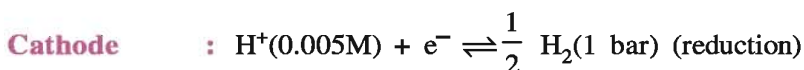
The change is only in concentrations of H^+

$\therefore E^0_{Cell} = 0.00$ volt in this cell.

The concentration of OH^- in 0.002 M KOH is 0.002 M. In any aqueous solution, existence of H^+ and OH^- is there and the product of their concentration is K_w. Hence, for KOH solution.

$[H^+][OH^-] = K_w$, but $[OH^-] = 0.002$ M

$$\therefore [H^+] \text{ in KOH solution } = \frac{K_W}{(0.002)}$$

$$E_{Cell} = E^0_{Cell} - \frac{0.059}{1} \log \frac{(\text{Concentration } H^+ \text{ in KOH solution})}{(\text{Concentration } H^+ \text{ in HCl solution})}$$

$$0.53 = 0.00 - \frac{0.059}{1} \log \frac{K_w/0.002}{0.005}$$

$$\frac{0.53}{0.059} = -\log\left(\frac{K_w}{0.002 \times 0.005}\right) = -\log K_w + \log(10^{-5})$$

$$8.983 = -\log K_w - 5.0$$

$$\log K_w = -8.983 - 5.0 = -13.983$$

$$\therefore K_w = \text{antilog } \overline{14}.017 = 1.04 \times 10^{-14}$$

3.8 Electrolysis

Electrolysis is redox reaction. In electrolysis, electrical energy is transformed to chemical energy. The apparatus used for this is called electrolytic cell. When electric current is passed through an aqueous solution of electrolyte or molten electrolyte, by dipping proper electrodes in the solution, this type of redox reaction resulting from oxidation and reduction reactions at the electrodes, of products are obtained. The result of this type of redox reaction is known as electrolysis. viz. If few drops or sulphuric acid are added to distilled water and it is electrolysed with inert electrodes of platinum, dihydrogen gas is produced at the cathode and dioxygen gas at the anode.
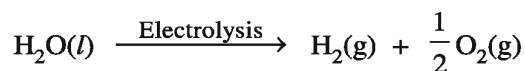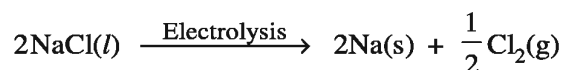
$$H_2O(l) \xrightarrow{\text{Electrolysis}} H_2(g) \ + \ \frac{1}{2}O_2(g)$$

Similarly, by electrolysis of molten sodium chloride, sodium metal is obtained at the cathode and dichlorine gas at the anode.

$$2NaCl(l) \xrightarrow{\text{Electrolysis}} 2Na(s) \ + \ \frac{1}{2}Cl_2(g)$$

Faraday's laws of Electrolysis : Scientist Michael Faraday, in 1834, established the following relations, regarding the amounts of the products obtained by the reaction and the quantity of the electricity used for it. They are called Faraday's laws of electrolysis.

(i) First law : The amount of products produced at the electrodes by electrolysis are directly proportional to the quantity of the electricity passed through the electrolytic cell. If W is the mass of the product produced and Q is value of the quantity of electricity passed, then $W \propto Q$.

(ii) Second law : If the different electrolytic cells, containing different electrolytes are joined in series and same quantity of electricity is passed through them, then the amounts of products obtained at the electrodes are directly proportional to their equivalent weights.

$W \propto Eq$, where, W = Mass of product obtained and Eq = Equivalent weight of product.

After the establishment of above Faraday's laws, in the starting years of the twentieth century, the knowledge about the electronic configuration of the atom was developed and hence the basic information about redox reaction could be obtained. During this, the concept of mole was also accepted. Hence, the **modern presentation** of Faraday's law was made as follows:

"The products, obtained at the electrodes by oxidation and reduction half-reactions have the relation with the moles of the products and stoichiometry of the reaction and the quantity of electricity." The explanation of this law can be understood in detail by the following illustrations.

$$Na^+(l) \ + \ e^- \rightarrow Na(s) \ \text{ or } \ Na^+(l) \ + \ e^- \rightarrow Na(s)$$

$$Mg^{2+}(l) \ + \ 2e^- \rightarrow Mg(s) \ \text{ or } \ \frac{1}{2}Mg^{2+}(l) \ + \ e^- \rightarrow \frac{1}{2}Mg(s)$$

$$Al^{3+}(l) \ + \ 3e^- \rightarrow Al(s) \ \text{ or } \ \frac{1}{3}Al^{3+}(l) \ + \ e^- \rightarrow \frac{1}{3}Al(s)$$
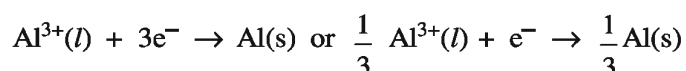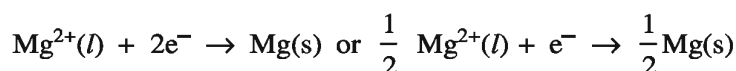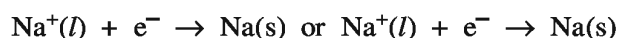
This reduction half cells indicate that if 1 mole electrons electric current is passed, 1 mole sodium, $\frac{1}{2}$ mole magnesium and $\frac{1}{3}$ mole aluminium masses will be respectively obtained.

The quantity of electricity passed by 1 mole electrons is called one Faraday. It is expressed as F.

The electric quantity on one electron is 1.602×10^{-19} coulomb

Hence, the electric quantity of one mole of electron is

1 Faraday (F) $= 1.602 \times 10^{-19} \times 6.022 \times 10^{23}$ electron mole^{-1}

$= 96487 \quad (\cong 96500)$ Coulomb mole^{-1} (electron)

In Coulomb unit, 1 Faraday = 96487 coulombs

But generally **96500** coulombs is accepted for calculations.

If I ampere current is passed through electrolytic cell for t seconds, the quantity of electricity Q in coulomb units can be calculated by the following equation.

$Q = I \times t$ (I = electric current in amperes, t = time in seconds)

The amounts of substances liberated at the electrodes depend upon the quantity of electricity passed. If quantity of electricity equal to 1 Faraday is passed then $\frac{1}{n}$ mole substance will be liberated at the electrode; where n is the number of moles of electrons associated with the reaction at the cathode.

Table 3.2 Electricity Quantity and Electrolysis

Sr	Reaction occurring at the electrode	Number of moles of electron	Quantity of electricity (F)	$\dfrac{\text{Moles}}{\text{F}}$
1.	$Ag^+(aq) + e^- \rightarrow Ag(s)$	1	1	1
2.	$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	2	2	$\dfrac{1}{2}$
3.	$Al^{3+}(l) + 3e^- \rightarrow Al(s)$	3	3	$\dfrac{1}{3}$
4.	$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$	2	2	$\dfrac{1}{2}$
5.	$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$	4	4	$\dfrac{1}{4}$

The efficiency of the electrolytic cell is not always 100 percent. Hence, the efficiency of the cell can be calculated by the following formula.

Efficiency of cell (%) $= \dfrac{\text{Experimental value of product}}{\text{Theoretical value of product}} \times 100$

Example 13 : In the electrolysis of aqueous solution of $CuCl_2$ copper is deposited on the negative electrode and chlorine gas liberated on the positive electrode at 800 K temperature and 1 bar pressure. How much copper and chlorine gas will be liberated if 2.0 ampere current is passed for 1 hour ? (F = 96500 Coulomb) (Cu = 63.5u, Cl = 35.5 u) (R = 0.08314 bar Litre mol^{-1} K^{-1}).

Solution : We will calculate the total quantity of electricity passed according to the definition $Q = I \times t$

Quantity of electricity = $2 \times 60 \times 60$ = 7200 coulomb

$$= \frac{7200}{96500} = 0.075 \text{ F}$$

Reaction occurring at cathode : $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

$$\text{(2 mole)} \quad \text{(63.5 gram mole}^{-1}\text{)}$$

In the above reaction, 2F are associated with 1 mole Cu. Hence, the Cu associated with 0.075 F.

$$\text{mole of Cu} = \frac{0.075}{2} = 0.0375 \text{ mole}$$

$$= 0.0375 \times 63.5$$

$$= 2.38 \text{ gram Cu will be obtained.}$$

Similarly,

At the anode $2Cl^-(aq) \rightarrow Cl_2 (g) + 2e^-$

i.e. 1 mole Cl_2 gas is associated with 2F quantity of electricity.

Cl_2 gas associated with 0.075 F quantity of electricity = $\dfrac{1 \times 0.075}{2}$ = 0.0375 mole

According to simple gas equation. PV = nRT

The volume of Cl_2 gas at 300 K temperature and 1 bar pressure

$$= \frac{0.0375 \times 0.08314 \times 300}{1}$$

$$= 0.9353 \text{ litre}$$

Example 14 : How much O_2 gas will be collected at the anode at 300 K temperature and 1 bar pressure if 2.5 ampere electric current is passed for one hour in electrolysis of aqueous soultion of Na_2SO_4. (F = 96500 coulomb) [1 mole gas volume is 22.4 litre at STP].

Solution : $2H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^-$

$$\text{1 mole} \quad \text{4F} \quad \text{(22.4 litre at STP)}$$

The volume of liberated O_2 at 300 K temperature and 1 bar pressure

$$= \frac{2.5 \times 60 \times 60}{96500} \times \frac{1}{4} \times \frac{22400}{1} \times \frac{300}{273} \times \frac{1}{1}$$

$$= 573.93 \text{ ml}$$

Example 15 : 2.68 ampere electric curent is passed for 1 hour from the solutions of $Hg_2(ClO_4)_2$, $Hg(ClO_4)_2$, $CuSO_4$ and $AgNO_3$. How many moles of each metal will be deposited on cathode ?

Solution :
$$\frac{1}{2} Hg_2^{2+}(aq) + e^- \longrightarrow Hg(l)$$

$$\frac{1}{2} Hg^{2+}(aq) + e^- \longrightarrow \frac{1}{2} Hg(l)$$

$$\frac{1}{2} Cu^{2+}(aq) + e^- \longrightarrow Cu(s)$$

$$Ag^+(aq) + e \longrightarrow Ag(s)$$
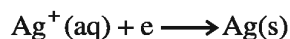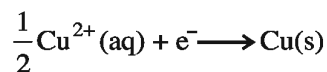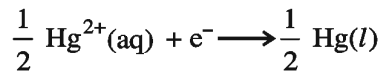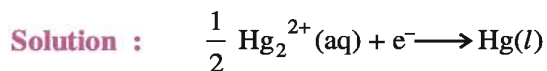
As the electrolytes are arranged in the series and same quantity of electricity will pass through them.

Quantity of electricity $= 2.68 \times 3600 = 9648$

$$= \frac{9648}{96500} = 0.09998 \, F = 0.1 \, F$$

Thus, 0.1F quantity of electricity will pass through each electrolyte. Hence, as shown earlier 0.1 mole Hg_2^{2+}, 0.05 mole Hg^{2+}, 0.05 mole Cu^{2+} and 0.01 mole Ag^+ will be reduced to metal getting deposited on the cathode.

Example 16 : How many grams of Cu and what volume of O_2 gas will be obtained at 300 K temperature and 1 bar pressure by passing 10 ampere curent for 193 minutes from an aqueous solution of $CuSO_4$? The efficiency of the electrolytic cell is 80% (Cu = 63.5 u).

Solution : The quantity of electricity passed $= I \times t$

$$= 10 \times 193 \times 60 \text{ coulomb}$$

$$= \frac{10 \times 193 \times 60}{96500} = 1.2 \, F$$

Chemical reactions :

Cathode : $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

$\qquad\qquad$ (2F) $\quad$ (1 mole)

Anode : $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

$\qquad\qquad$ (1 mole) $\qquad\qquad$ (4F)
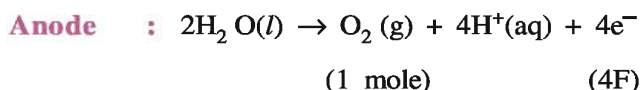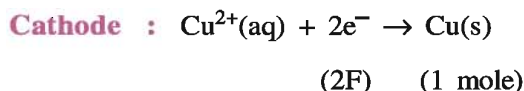
Acording to the reaction; by passing 2 Faraday electric current 1 mole Cu and by passing 4 Faraday electric current 1 mole O_2 gas are produced.

For Cu : when 2 Faraday electric current is passed 1 mole Cu will be obtained

When 1.2 Faraday electric current is passed $\dfrac{1.2}{2} = 0.6$ mole Cu will be obtained.

Weight of copper = 0.6 × 63.5 = 38.1 gram

As the efficiency of the cell is 80 % so, $\dfrac{38.1 \times 80}{100}$ = 30.48 gram Cu will be obtained.

For O_2 gas, when 4 Faraday, electric current is passed 1 mole O_2 gas is produced.

When 1.2 Faraday electric current is passed $= \dfrac{1.2}{4}$ = 0.3 mole O_2 gas will be obtained.

According to simple gas equation, PV = nRT

$$V = \dfrac{nRT}{P} = \dfrac{0.3 \times 0.08314 \times 300}{1} = 7.4826 \text{ litre.}$$

As the efficiency of the cell is 80 % so, $\dfrac{7.4826 \times 80}{100}$ = 5.986 litre

Example 17 : 0.972 gram Ag is obtained by passing 5 ampere electric cureent for 193 seconds through an aqueous solution of silver nitrate ($AgNO_3$) between graphite electrodes, calculate the efficiency of the eletrolytic cell.

Solution : The quantity of electricity passed = I × t

= 5 × 193 = 965 coulomb

$= \dfrac{5 \times 193}{96500} = 0.01$ Faraday

Cathode : $Ag^+ (aq) + e^- \rightarrow Ag(s)$

According to the reaction when 1 Faraday of electric current is passed 1 mole Ag is obtained. So, 0.01 Faraday electric current is passed, 0.01 mole Ag will be obtained.

∴ Weight of Ag = mole of Ag × atomic weight of Ag

= 0.01 mole × 108 g mol^{-1} = 1.08 gram Ag will be obtained

This is the value obtained by calculation and so it is considered as theoretical value. 0.972 gram Ag is released in the electrolytic cell during electrolysis. it becomes experimental value.

Efficiency of the cell $= \dfrac{\text{Experimental value}}{\text{Theoretical value}} \times 100$
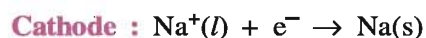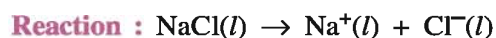
$= \dfrac{0.972 \times 100}{1.08} = 90\%$

The efficiency of the cell is 90%.
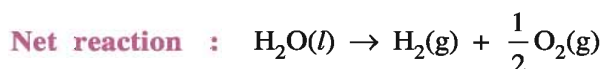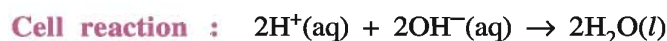
3.9 Products Obtained by Electrolysis

Which products will be obtained by electrolysis of aqueous solutions of salts depend upon the nature of the electrodes used for it, concentration of solutions and the electromotive force. Some of the illustrations strenghtening this statement are given below :

3.9.1 Electrolysis of NaCl :

(a) **Electrolysis of molten NaCl :** Na metal and Cl_2 gas are obtained on the cathode and anode respectively when molten NaCl is electrolysed using cathode of steel and anode of graphite.

Reaction : $NaCl(l) \rightarrow Na^+(l) + Cl^-(l)$

Cathode : $Na^+(l) + e^- \rightarrow Na(s)$

Anode (Graphite) : $Cl^-(l) \rightarrow \dfrac{1}{2} Cl_2(g) + e^-$

(b) **Electrolysis of dilute aqueous solution of NaCl :** When dilute aqueous solution of NaCl is electrolysed using graphite electrodes, dihydrogen gas at cathode and dioxygen gas at anode are obtained by net reaction of only electrolysis of water. In dilute solution as concentration of Cl^- ion is less, Hence, dioxygen O_2 is obtained instead of Cl_2. Similarly reduction $Na^+(aq)$ on cathode being difficult it is difficult to have its reduction on cathode. Instead of Na, H_2 gas is obtained by reduction of H_2O and $OH^-(aq)$ are formed.

Cathode : $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

Anode : $H_2O(l) \rightarrow \dfrac{1}{2}O_2(g) + 2H^+(aq) + 2e^-$

Cell reaction : $2H^+(aq) + 2OH^-(aq) \rightarrow 2H_2O(l)$

Net reaction : $H_2O(l) \rightarrow H_2(g) + \dfrac{1}{2}O_2(g)$
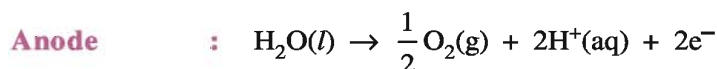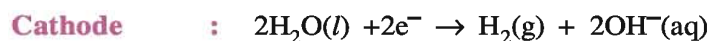
Thus, the electrolysis of dilute aqueous solution of NaCl, in fact is the electrolysis of water.

(c) **Electrolysis of Concentrated Aqueous Solution of NaCl :** During the electrolysis of concentrated aqueous soultion of NaCl between graphite electrodes, takes place by following reaction. As concentration of Cl^- is more in concentrated solution of NaCl, Cl^- ions are oxidised at the anode instead of H_2O and so Cl_2 gas is obtained.

Cathode : $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

Anode : $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$
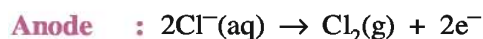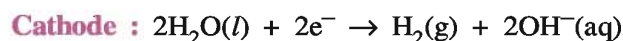
$Na^+(aq)$ ions of the solution does not undergo reduction reaction because reduction of H_2O is easier, H_2 gas is obtained at the cathode. Thus, by electrolysis of concentrated aqueous solution of NaCl, Cl_2 gas is obtained at the cathode and Na^+ ions of the solution combine with OH^- near the cathode and gives NaOH.

It is observed from all the above three illustrations, that different products are obtained by electrolysis of a substance in its different concentrations and also in its molten state.

3.10 Electrolysis of aqueous solution of Na_2SO_4

In the electrolysis of dilute aqueous solution of Na_2SO_4 between graphite electrodes, O_2 gas is obtained at the anode and H_2 gas is obtained at the cathode in the net reaction of electrolysis of water. Reduction at Na^+ ion and oxidation of SO_4^{2-} ions being difficult, these ions do not experience the reaction.

Cathode : $2H_2O\ (l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

Anode : $H_2O(l) \rightarrow \frac{1}{2}O_2(g) + 2H^+(aq) + 2e^-$

Cell reation : $2H^+(aq) + 2OH^-(aq) \rightarrow 2H_2O(l)$

Net reaction : $H_2O(l) \rightarrow H_2(g) + \frac{1}{2}O_2(g)$
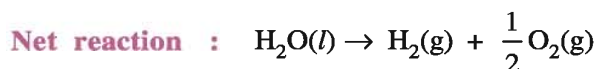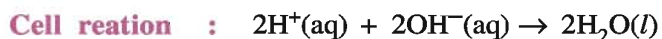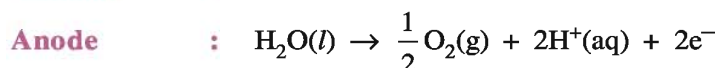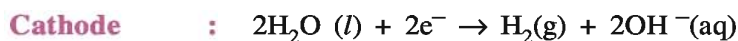
3.11 Electrolysis of aqueous solution of $CuSO_4$

(a) If the electrolysis of aqueous solution of $CuSO_4$ between copper electrodes, is carried out, the copper of anode deposits on the cathode as the net reaction. The copper electrode (anode) being active, it experiences oxidation reaction during electrolysis.

Cathode (Copper) : $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Anode (Copper) : $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$

Net reaction : $Cu(s)$ (anode) $\rightarrow Cu(s)$ (cathode)
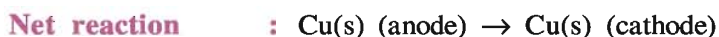
As the reaction proceeds (cathode) further, the weight of copper anode decreases because the anode of copper being active produces Cu^{2+} by experiencing oxidation reaction.

Copper metal $Cu(s)$ is deposited at the cathode by experiencing reduction reaction and so weight of cathode increases. If electrolysis is carried out using impure copper as anode at proper electrical potential the impuries which do not experience oxidation, remain in the solution. In the metallurgy of copper, the inert metals like Au, Pt which do not experience oxidation, are released from the anode and deposited at the bottom of the cell. It is called anode mud.

(b) If electrolysis of aqueous solution of $CuSO_4$ between inert electrodes like graphite or platinum is carried out, the reactions take place as follows:

Cathode : $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Anode : $H_2O(l) \rightarrow 2H^+(aq) + \frac{1}{2}O_2(g) + 2e^-$
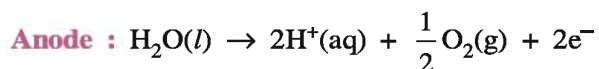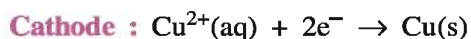
The oxidation of SO_4^{2-} in the solution is difficult in comparison to oxidation of H_2O. H_2O gets oxidised and $H^+(aq)$ and O_2 gas are produced. The reduction take place of $Cu^{2+}(aq)$ ion and they are removed from the solution. In this electrolysis, copper is deposited on cathode and O_2 gas is produced anode and H_2SO_4 is produced in solution.

Electrolysis being very important reaction, production of metals like Na, Ag, Al and production of NaOH, KOH and refining (purification) of metals like Cu, Ag, Au are carried out by electrolysis. Electrolysis-reaction is also used in electroplating of metals.

3.12 Gibbs' Free Energy and Cell Potential

You have necessary information about Gibbs' free energy in thermodynamics. You have studied in detail that for spontaneous reactions the free energy of the system decreases that means the change in free energy becomes negative. For the electrochemical cells, when electrodes are connected the chemical reactions occur spontaneously and so the value of ΔG is negative. If the potential of the cell is E_{Cell} and if n Faraday electricity is obtained from the cell then, $\Delta G = -nFE_{Cell}$

where F is Faraday constant. The above equation for a standard cell can be written like this $\Delta G^0 = -nFE^0_{Cell}$

If the evolved electrical energy is completely transformed into electrical work then, $\Delta G = W_{electrical} = -nFE_{Cell}$

Thus, change in free energy is equivalent to electrical work.

Example 18 : The electric current is produced in an electrochemical cell by the given following reaction.

$$Fe(s) + Cu^{2+}(aq) \rightarrow Fe^{2+}(aq) + Cu(s)$$
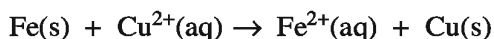
If 0.85 Faraday electricity is obtained from standard cell, then what maximum work can be done ? The value of potential of this standard cell is 0.78 volt.

Solution : Maximum electrical work $\Delta G^0 = W_{electrical} = -nFE^0_{Cell}$

$$= -0.85 \times 96500 \times 0.78$$

$$= -63979.50 \text{ volt coulmbous}$$

$$= -6.398 \times 10^4 \text{ joules (1 volt coulmbous = 1 joule)}$$

The equilibrium constant of a cell reaction can be calculated on the basis of value of cell potential. For this we will see the following example.

Example 19 : Calculate the equilibrium constant and free energy change of given following reaction for Daniell cell at 298 K temperature.

$$Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$$
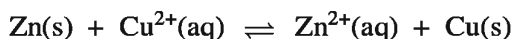
Cell potential = 1.1 volt (F = 96500 coulomb)

Solution : For this reaction n = 2,

$$\Delta G^0 = -nFE^0_{Cell} = -RT\ln K = -2.303RT\log K$$

$$\log K = \frac{nFE^0_{Cell}}{2.303RT}$$

$$= \frac{2 \times 96500 \times 1.1}{2.303 \times 8.314 \times 298}$$

$$\log K = 37.2074$$

$$K = 1.61 \times 10^{37}$$

$$\Delta G^0 = -nFE^0_{Cell} = -2 \times 96500 \times 1.1 \text{ volt coulomb}$$

$$= -212300.0 \text{ joule} = -2.123 \times 10^5 \text{ joule}$$

3.13 Difference between Electrochemical Cell and Electrolytic Cell

The difference between electrochemical cell and electrolytic cell can be understood by the following points :

Electrochemical cell	Electrolytic cell
(1) Chemical energy is transformed to electrical energy in this cell.	(1) Electrical energy is transformed to chemical energy in this cell.
(2) Electrical energy is produced by spontaneous redox reaction	(2) Redox reaction takes place by supplying electrical energy does not take place on its own.
(3) Two electrodes are generally in two different vessels containing solutions.	(3) Both the electrodes are dipped in the same vessel containing solution of electrolytes or molten salts.
(4) The electrode on which reduction occurs is called cathode and the electrode on which oxidation occurs is called anode.	(4) The electrode which is connected to the positive electrode of battery is called anode and oxidation takes place there and similarly the electrode connected to the negative electrode of the battery is called cathode and reduction takes place there.
(5) Salt bridge is required in construction of this cell.	(5) Salt bridge is not required in the construction of this cell.
(6) e.g. Daniell cell, Galvanic cell, storage cell	(6) e. g. Electroplating, Electrorefining

3.14 Electrolysis for Industrial Products

As shown in the table 3.3, important chemicals are obtained at the cathode and anode

Table 3.3

Sr.	Electrolyte	Cathode	Anode
1.	NaCl (Molten)	Na	Cl_2
2.	NaCl (concentrated solution)	H_2, NaOH in solution	Cl_2
3.	NaCl (dilute solution)	H_2	O_2
4.	Al_2O_3	Al	O_2, CO_2
5.	KHF_2 in anhydrous HF	H_2	F_2

3.15 Electrical Conduction

Substances are of two types-solid or liquid from electrical conduction point of view.

Solid or liquid substances which conduct electric current are called conducting substances and from which the electric current does not conduct are called insulators.

Generally, two types of conducting substances are available (1) Metallic conductors and (2) Conduction of electricity through solutions of electrolytes.

(1) Metallic conductors : Metals and alloys are electric conductors. The conduction of electricity through them is due to the delocalised electrons in the outer orbit of the atoms of metals. There is no chemical change in the substance during electrical conduction but in physical change, the temperature increases.

(2) Conduction of electricity through solution of electrolytes : The substances which release ions in water by ionisation are called electrolyte substances and such solutions are called electrolytic solutions. If electric current is passed through aqueous solutions of acid, base as well as salts, the electrcial conduction takes place through ions. It is necessary to know the concept of electrical resistance to understand the electrical conduction in electrolytic substances.

Less proportion of conduction of electricity occurs due the resistance of the ions present in the solutions of electrolytes. If more is the resistance by ions, less will be the conduction of electricity and lesser the resistance by ions, more will be the conduction of electricity. The electrical resistance is expressed by R and is measured by Wheatstone bridge.

The resistance of a uniform conductor is directly proportional to its length (l) and inversely proportions to its area of cross section (A)

$$R \, \alpha \, \frac{l}{A}$$

$$R = \rho \frac{l}{A}$$ where, R = Resitance, A = Area of cross section, l = length, ρ = proportionality constant.

The proportionality constant (ρ) is called resistivity or specific resistance. The SI unit of resistivity is ohm meter (Ω m) but mostly ohm cm (Ω cm) unit is used.

3.16 Resistivity (Specific Resistance)

The resistance of a conductor having one meter length and one square meter of unit cross sectional area is called its resitance (specific resistance).

1 Ω meter = 100 Ω cm or 1 Ω cm = 0.01 Ω m

Conductivity : The inverse of resistance R is called conductivity G.

$$G = \frac{1}{R} = \frac{A}{\rho.l} = K \frac{A}{l} \quad \text{where} \quad K = \frac{1}{\rho} \qquad K = G \cdot \frac{l}{A}$$

The SI unit of conductivity is Siemens which is expressed as S. It is expressed as ohm^{-1} or Ω^{-1} or mho or $\mho$.

Specific conductivity : The inverse of resistivity is called specific conductivity. It is accepted by IUPAC that specific conductivity be accepted as conductivity. Hence, the word conductivity is used instead of specific conductivity. The value of $\frac{l}{A}$ in the formula of conductivity is the cell constant of the apparatus used to measure conductivity. Its value can be determined from $\frac{l}{A}$ or in chemistry, by using a solution of KCl of known concentration. Its value is determined at the experimental temperature by measuring its conductivity and obtaining its value from literature. The obtained conductivity G is multiplied by cell constant and so specific conductivity is obtained which is expressed as K from the Greek word kappa.

Specific conductivity K = observed conductivity G × cell constant

The SI unit of specific conductivity is S m^{-1} or S cm^{-1}. The conductivity of the conductor having unit length of 1 meter and unit area of cross section 1 square meter is S m^{-1}. 1 S cm^{-1} = 0.01 S m^{-1}.

Material	Conductivity S m^{-1}	Material	Conductivity S m^{-1}
Conductors		**Aqueous-solutions**	
Sodium	2.1×10^3	Pure water	3.5×10^{-5}
Copper	5.9×10^3	0.1 M HCl	3.91
Silver	6.2×10^3	0.1 M KCl	0.14
Gold	4.5×10^3	0.1 M NaCl	0.12
Iron	1.0×10^3	0.1 M CH_3COOH	0.047
Graphite	1.2×10	0.01 M CH_3COOH	0.016
Insulator		**Semiconductors**	
Glass	1.0×10^{-16}	CuO	1×10^{-7}
Teflon	1.0×10^{-18}	Si	1.5×10^{-2}
		Ge	2.0

It is clear from the above table, that the values of conductivities of different substances have very large difference. This depends on the characteristics of substance; temperature, pressure are also the factors affecting the measurement of conductivity.

The classification of conducting substances is carried out on the basis of the magnitude of their conductivity values, as follows :

(1) Good conductors : As the conductivities of metals and alloys are more, they are called good conductors. Some non metallic substances like graphite, organic polymets are also good conductors.

(2) Insulators : The conductivity of glass and ceramic substances is in very less proportion and so they are called insulators.

(3) Semiconductors : The values of conductivities of the substances, which are in between the values of good conductors and insulators are known as semiconductors. Silicon, germanium, gallium arsenide etc. are semiconductors.

The resistivities of some substances are zero and their conductivities are extremely high. They are called superconductors. Earlier metals and alloys were considered superconductors at low temperature (0 to 15 K) but many ceramic susbtances and mixed oxides are known as superconductors at higher temperature (150 K).

The conduction of electricity through metals is called metallic or electronic conduction. It occurs due to migration of electrons. The electronic conductivity depends on the following factors :

(1) Structure of metal and its characteristics.

(2) The number of electrons in the valence shell of atoms of metal.

(3) The electrical conductivity of metal decreases with increase in temperature.

There is no change in the structure of the metal during electrical conduction.

3.17 Ionic Mobility

The proportion of hydrogen and hydroxyl ions in water is very less, 10^{-7} M. Because of this, water is known as bad conductor of electricity (conducitivity = 3.5×10^{-5} S m^{-1}).

When electrolyte is dissolved in water, the conductivity of solution increases due to ionisation of the electrolyte in water. The conductivity of the solution is mostly due to the ions present in the solution. This type of conductivity is called ionic conductivity. The dependence of ions conductivity is on the following factors :

- Nature of the added electrolyte
- The size of the ions produced and their hydration.
- The nature of the solvent and its viscosity
- Concentration of electrolyte
- Temperature

In the ionic solutions, when electric current is passed, electrochemical reactions take place and the structure of solution changes.

Molar conductivity : The solutions of different electrolytes in the same solvent have different conductivities at the same temperature. The reason for this is the size of ions produced and the electrical charge on the ions. The migration of ions under the effect of concentration of electrolyte and electrical pressure are responsible for different conductivities. So it is more meaningful to express the conductivities of these solutions as molar conductivities.

Molar conductivity is expressed as $\wedge_m$ (Greek alphabet lambda).

Molar conductivity $\wedge_m = \dfrac{K \times 1000}{C}$

where, K = (Kappa) specific conductivity, C = Concentration if solution in unit of molarity.

The unit of molar conductivity is mho cm^2 mol^{-1}. If the concentration of solution is taken in normality or gram equivalent weight, then the unit will be mho cm^2 gm eq^{-1}.

The changes in conductivity of the solution with changes in its concentration : If there is change in concentration of electrolyte dissolved in solution then its conductivity as well as molar conductivity changes. In both weak and strong electrolytes the conductivity increase with decreases in concentration of solution. With the decrease in concentration of solution, the number of ions in unit volume carrying electric charge increases. It is clear from this fact that the conductivity of solution increases.

The electrical conduction by the solution of electrolyte a given concentration having unit volume, between two platinum electrodes possessing unit cross section and at a distance of unit length is called conductivity of solution.

The above fact will be clear from the following formula.

$G = \dfrac{KA}{l} = K$, Taking the units A and l in the unit meter or cm.

Thus, the conductivity of V volume having 1 mole electrolyte solution between two electrodes possessing unit cross section and at a distance of unit length is called molar conductivity.

$$\Lambda_m = \frac{KA}{l} = K \qquad l = 1 \text{ and } A = V \text{ (volume of solution of electrolyte)}$$

$$\therefore \ \Lambda_m = K \cdot V$$

If the total volume V of a solution of 1 mole electrolyte is increased, the concentration of the solution decreases and so the molar conductivity increases. When the value of concentration becomes about zero i.e. at infinite dilution the molar conductivity is called limiting molar conductivity or molar conductivity at infinite dilution. Limiting molar conductivity is expressed as $\overset{0}{\wedge}m$ and gives different proportions of ions which may be more or less. Hence, one which gives more ionis will show more conductivity. It is called strong electrolyte viz. Aqueous solutons of NaCl, KCl, $MgCl_2$, KNO_3. If an electrolyte ionises less in aqueous solution and gives less number of ions and therefore shows less conductivity is called weak electrolyte e.g. Aqueous solutions of CH_3COOH, NH_4OH, HCN.

Conductivity of strong electrolytes : There is increase in the value of $\wedge_m$ of a strong electrolyte on dilution of its solution.

$$\wedge_m = \overset{0}{\wedge}m - AC^{\frac{1}{2}}$$

If a graph of values of $\wedge_m$ against $C^{\frac{1}{2}}$ is plotted, a straight line is obtained. The intercept of this graph will be the value of $\overset{0}{\wedge}m$ and the value of the slope will be A. The value of A depends on the type electrolyte (its dissociation into positive ion and negative ion), given solvent and temperature. NaCl, KCl, $CaCl_2$ and $MgCl_2$ are strong electrolyes having 1:1, 1:1, 2:1, and 2:1 type valencies. The values A are same for all the same type of electrolytes.
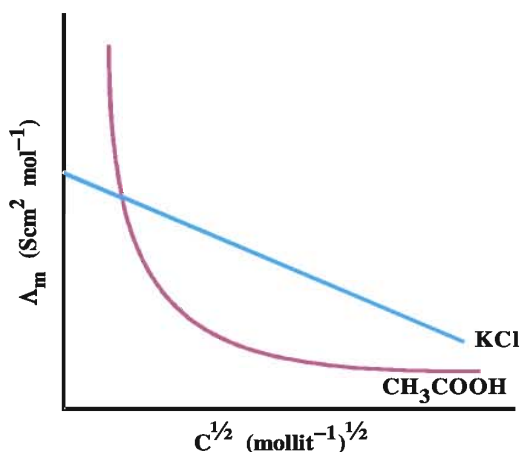
Conductivity of weak electrolytes : The study of changes in conductivity with dilution was carried out by scientist Ostwald. It was found that the conductivity of weak electrolyte increases more with dilution. This type of study is known as **Ostwald's law** of dilution.

The degree of dissociation is very less for such weak electrolyte like acetic acid having more concentration. When a solution of such electrolytes having 1 mole electrolyte is diluted, and with that volume increases and with that the degree of dissociation increases. As a result the number of ions increases and **molar conductivity ($\wedge_m$)** also increaes. It is clear from the graph that the molar conductivity at infinite dilution increases in the form of a curve when the graph of $\overset{0}{\wedge}m$ for such solutions is extrapolated towards X-axis, The value of **limiting molar conductivity** at infinite dilution (almost zero concentration) is not obtained.

The values of limiting molar conductivity at such electrolytes can be obtained by Kohlrausch's law of independent migration.

The value of degree of dissociation for such an electrolyte at the given concentratin will be as below :

Degree of dissociation $(\alpha) = \dfrac{\text{Molar conductivity of the solution of a given concentration } \wedge_m}{\text{Molar conductivity of the solution at infinite dilution } \wedge_m^0}$

We know that, $K = \dfrac{C\alpha^2}{(1-\alpha)}$ where, K = Dissociation constant of weak electrolyte, C = concentration of solution, α = degree of dissociation of weak electrolyte

$$= \dfrac{C \wedge_m^2}{\overset{0}{\wedge}_m{}^2 \left(1 - \dfrac{\wedge_m}{\overset{0}{\wedge}_m}\right)} = \dfrac{C \wedge_m^2}{\overset{0}{\wedge}_m \left(\overset{0}{\wedge}_m - \wedge_m\right)}$$

Example 20 : The conductivity of 0.001028 mole litre^{-1} acetic acid is 4.95×10^{-5} S cm^{-1}. If the limiting molar conductivity of acetic acid is 390.5 S cm^2 mol^{-1} calculate dissociation constant.

Solution : $\wedge_m = \dfrac{K}{C} = \dfrac{4.95 \times 10^{-5}\text{S cm}^{-1}}{0.001028\ \text{mol L}^{-1}} \times \dfrac{1000\ \text{cm}^3}{L} = 48.15$ S cm^2 mol^{-1}

$\alpha = \dfrac{\wedge_m}{\overset{0}{\wedge}_m} = \dfrac{48.15\ \text{S cm}^2\ \text{mol}^{-1}}{390.5\ \text{S cm}^2\ \text{mol}^{-1}} = 0.1233$

$K_a = \dfrac{C\alpha^2}{1-\alpha} = \dfrac{0.001028\ \text{mol L}^{-1} \times (0.1233)^2}{1 - 0.1233}$

$K_a = 1.78 \times 10^{-5}$ mol L^{-1}

3.18 Kohlrausch's law of Independent migration of Ions

The value of molar conductivity $(\wedge_m)$ for different electrolytes can be obtained. In addition, the values of molar conductance $(\wedge_m)$ will also change with change in concentration. It is found from the study that a straight line graph is obtainead for the molar conductivity $(\wedge_m)$ at different concentrations of the strong electrolyte like KCl. In this graph, the value of limiting, molar conductivity extended to zero concentration (infinite dilution), the intercept is obtained or molar conductivity $(\overset{0}{\wedge}_m)$ at infinite dilution will be obtained. But for weak electrolyte like CH_3COOH the graph of molar conductivity at different dilutions of weak electrolyte does not give straight line but a curve. So their intercepts obtained are not correct and the true values of molar conductivity at infinite dilution cannot be obtained.

Scientist Kohlrausch studied the $\overset{0}{\wedge}_m$ values of some strong electrolytes. He observed some characteristics viz. The difference between the value of $\overset{0}{\wedge}_m$ of two strong electrolyte like NaX and KX (X = Cl, Br, I) was found to be same. e.g.,

$$\overset{0}{\wedge}_m KCl - \overset{0}{\wedge}_m NaCl = \overset{0}{\wedge}_m KBr - \overset{0}{\wedge}_m NaBr = \overset{0}{\wedge}_m KI - \overset{0}{\wedge}_m NaI = 23.4 \ \text{mho cm}^2 \ \text{mol}^{-1}$$

Similarly, $\overset{0}{\wedge}_m NaBr - \overset{0}{\wedge}_m NaCl = \overset{0}{\wedge}_m KBr - \overset{0}{\wedge}_m KCl = 1.8 \ \text{mho cm}^2 \ \text{mol}^{-1}$.

It can be concluded from this study, that the molar conductivity of a strong ionic electrolyte is equal to the sum of the molar ionic conductivity of the positive ion and the molar ionic conductivity of negative ion. $\overset{0}{\wedge}_m NaCl = \overset{0}{\lambda}_m Na^+ + \overset{0}{\lambda}_m Cl^-$

If the electrolyte gives v_+ and v_- ions due to dissociation, then their molar conductances, can be written as $\overset{0}{\wedge}_m = v_+ \overset{0}{\lambda}_{m^+} + v_- \overset{0}{\lambda}_{m^-}$ (where, $\overset{0}{\lambda}_{m^+}$ and $\overset{0}{\lambda}_{m^-}$ respectively are ionic molar conductivity of positive and negative ion.)

From this, Kohlrausch's law can be written as follows. **"The molar conductivity of an electrolyte at infinite dilution $\overset{0}{\wedge}_m$ is the sum of the values of the molar conductivities of positive ion and negative ion present in them $\overset{0}{\lambda}_{m^+}$ and $\overset{0}{\lambda}_{m^-}$ "**.

In the use of Kohlrausch's law, the molar conductivity at infinite dilution for a weak. electrolyte can be obtained by adding of subtracting the values of molar conductivities at infinite dilution of the solutions of proper strong electrolytes. This will be clear from the following example.

Suppose the molar conductivity of weak electrolyte CH_3COOH is to be determined, then it can be obtained by determining molar conductivities of strong electrolytes like CH_3COONa, HCl and NaCl; then computing.

$$\overset{0}{\wedge}_m CH_3COOH = \overset{0}{\wedge}_m CH_3COONa + \overset{0}{\wedge}_m HCl - \overset{0}{\wedge}_m NaCl$$

According to Kohlrausch law,

$$\overset{0}{\wedge}_m CH_3COOH = \overset{0}{\lambda}_m CH_3COO^- + \overset{0}{\lambda}_m Na^+ + \overset{0}{\lambda}_m H^+ + \overset{0}{\lambda}_m Cl^- - (\overset{0}{\lambda}_m Na^+ + \overset{0}{\lambda}_m Cl^-)$$

$$= \overset{0}{\lambda}_m CH_3COO^- + \overset{0}{\lambda}_m Na^+ + \overset{0}{\lambda}_m H^+ + \overset{0}{\lambda}_m Cl^- - \overset{0}{\lambda}_m Na^+ - \overset{0}{\lambda}_m Cl^-$$

$$\overset{0}{\wedge}_m CH_3COOH = \overset{0}{\lambda}_m CH_3COO^- + \overset{0}{\lambda}_m H^+$$

Table 3.5 Limiting molar conductivity for some ions in water at 298 K

ion	$\overset{0}{\lambda}$ (S cm^{2}mol^{-1})	ion	$\overset{0}{\lambda}$ (S cm^{2}mol^{-1})
H^+	349.6	OH^-	199.1
Na^+	50.1	Cl^-	76.3
Ca^{2+}	119.0	CH_3COO^-	40.9
		Br^-	78.1
Mg^{2+}	106.0	SO_4^{2-}	160.0

Example 21 : Calculate the limiting molar conductivities of $CaCl_2$ and $MgSO_4$

Ion	Limiting molar conductivity $S\ cm^2\ mol^{-1}$
Ca^{2+}	119.0
Mg^{2+}	106.0
SO_4^{2-}	160.0
Cl^-	76.3

Solution : According to Kohlrausch's law,

(i) $\overset{0}{\wedge}_m CaCl_2 = \overset{0}{\lambda} Ca^{2+} + 2\overset{0}{\lambda} Cl^-$

$= 119 + 2\ (76.3)$

$= 271.6\ S\ cm^2\ mol^{-1}$

(ii) $\overset{0}{\wedge}_m MgSO_4 = \overset{0}{\lambda} Mg^{2+} + \overset{0}{\lambda} SO_4^{2-}$

$= 106.0 + 160.0$

$= 266.0\ S\ cm^2\ mol^{-1}$

Example 22 : If the values of limiting molar conductivities of NaCl, HCl, and CH_3COONa are 126.4, 425.9 and 91.0 $S\ cm^2\ mol^{-1}$ respectively, then calculate the limiting molar conductivity of acetic acid.

Solution : $\overset{0}{\wedge}_m CH_3COOH = \overset{0}{\lambda} H^+ + \overset{0}{\lambda} CH_3COO^-$

$= \overset{0}{\lambda} H^+ + \overset{0}{\lambda} Cl^- + \overset{0}{\lambda} CH_3COO^- + \overset{0}{\lambda} Na^+ - \overset{0}{\lambda} Cl^- - \overset{0}{\lambda} Na^+$

$= \overset{0}{\wedge}_m HCl + \overset{0}{\wedge}_m CH_3COONa - \overset{0}{\wedge}_m NaCl$

$= (425.9 + 91.0 - 126.4) = 390.5\ S\ cm^2\ mol^{-1}$

3.19 Batteries

Commercial cells and Fuel cells :

Any battery is a source for obtaining electric current. In a cell (battery) the chemical energy obtained by chemical reaction in it, is transformed to electrical energy.

Dry cell, Ni-Cd storage cell, lead storage cell, fuel cell etc. are included in the cells for industrial use. It can be divided into two types. (1) Primary cell and (ii) Secondary cell.

(1) Primary cell : The cell which is dead after a long use and which cannot be regenerated i.e. which cannot be reproduced, is called **primary cell.** e.g. Dry cell.

(2) Secondary cell : The cell which can be regenerataed or reproduced is called secondary cell. e.g. lead storage cell and Ni-Cd storage cell.

3.19.1 Dry cell : This type of dry cell or primary cell was first of all prepared by French Scientist Lechlanche in 1867. Hence, it is also called Leclanche cell.

In this cell, there is a thin porous layer of paper on inner side of a cylinder of zinc metal, closed at the bottom. In this cyliner, graphite rod is placed in the centre so that it does not touch the bottom and small amount of mixture of MnO_2 and carbon is filled, the remaining part is filled with a paste of the mixture of NH_4Cl and $ZnCl_2$ and the mouth

Fig. 3.3 Dry cell

of the cyliner is sealed with a special type of wax in a such a way that graphite rod is slightly outside. The insulating layer of thick paper is applied on the outer part of the cylinder (Fig. 3.3)
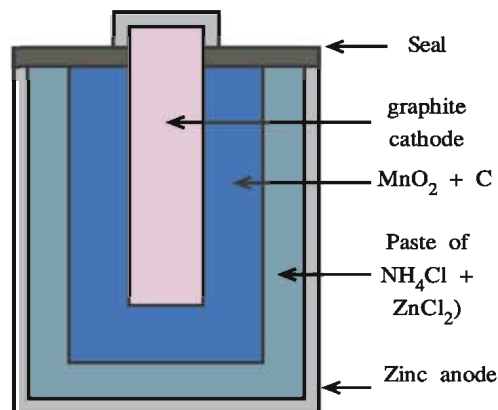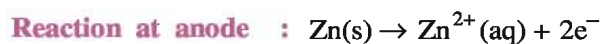
When the cylinder of zinc and the rod of graphite are connected by a conducting wire, zinc acts as anode and the rod of graphite in the contact of MnO_2 acts as a cathode. The reactions occurring at these electrodes are as follows :

Reaction at cathode : $2MnO_2 + 2NH_4^+ + 2e^- \rightarrow Mn_2O_3 + 2NH_3 + H_2O$

Reaction at anode : $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

In fact, the product-containing manganese-obtained depends on the time of continuous use and the interval between times of the two uses. The potential of this cell is about 1.5 volt. Here oxidation of Mn (III) to Mn (IV) can not be possible by reversing the direction of the current and so, once this cell is dead means has become useless, it cannot be regenerated or reproduced. Hence this cell is known as primary cell. Dry cell is not really dry becaue wet paste of NH_4Cl and $ZnCl_2$ is filled in it. If this cell is completely dry, then the electric current cannot pass throught it. To obtain more voltage, two or more cells are joined in series and more voltage can be obtained; so dry cell is used in torch, transistor, radio and other big or small electronic devices.

Fig. 3.4

Mercury cell : Mercury cell is a systematic device to produce low electric current. It is used mostly in hearing aids, watches etc. In this cell layer of zinc-mercury (Zn-Hg) is in the form of anode and paste of mercuric oxide and carbon is as cathode. In it, electrical paste filled is prepared from KOH and ZnO. The reactions occurring at the electrode in this cell are as under :

Fig. 3.5 Mercury cell
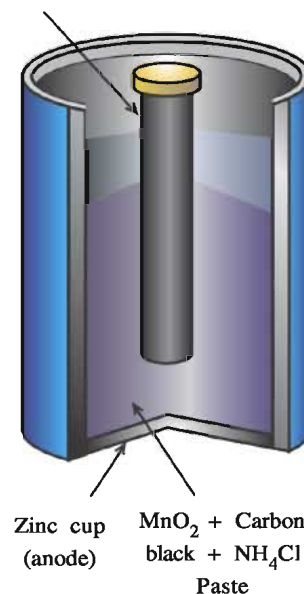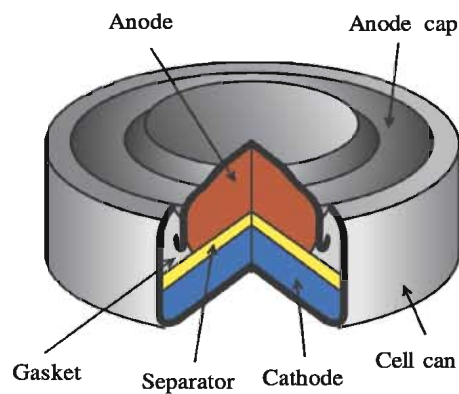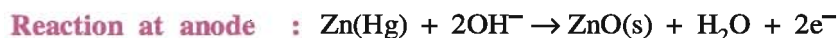
Reaction at cathode : $HgO + H_2O + 2e^- \rightarrow Hg(l) + 2OH^-$

Reaction at anode : $Zn(Hg) + 2OH^- \rightarrow ZnO(s) + H_2O + 2e^-$
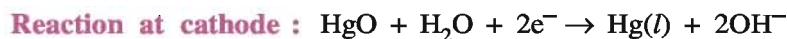
The complete equation of these reactions is as follows :

$Zn(Hg) + HgO \rightarrow ZnO(s) + Hg(l)$
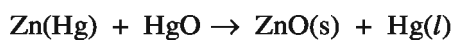
The cell potential of this cell is about 1.35 volt and during the whole life of this cell, no ions are produced in the complete reaction.

3.19.2 Secondary cells : The cells which can be regenerated or reproduced are called secondary cells. Lead storage cell and Ni-Cd storage cells are secondary cells.

Lead storage cell : When two or more cells are joined in series to obtain more voltage which can be recharged are called storage cells.

In the construction of this cell, sponge like lead plate and thin plate of lead on which layer of PbO_2 is applied are dipped in 38 % (W/W) concentration sulphuric acid containg vessel. When these two plates are connected by conducting wire the following discharging reactions take place and electric current is produced.
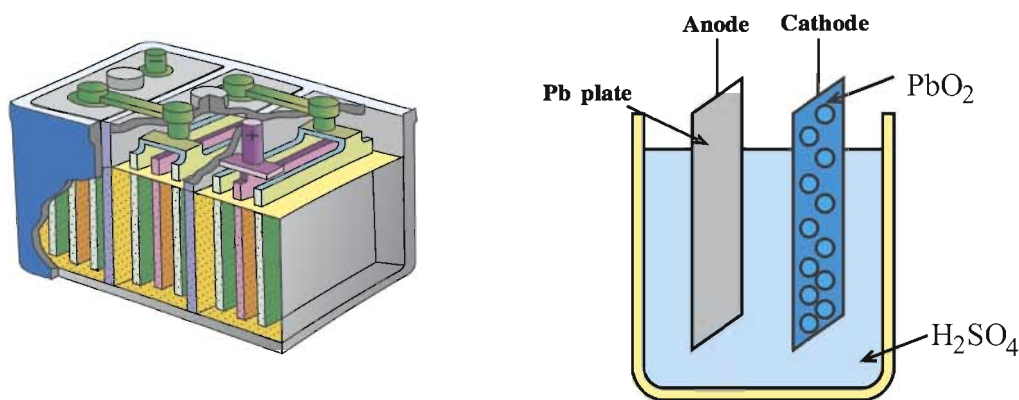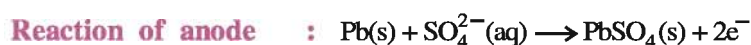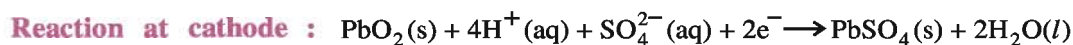
Reaction at cathode : $PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O(l)$

Reaction of anode : $Pb(s) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s) + 2e^-$

Fig. 3.6 Lead storage battery

$PbSO_4$ produced here remains stuck to the surface of the electrodes. The cell potential of this cell is about 2 volt. When the cell is in operation the density of sulphuric acid solution in reaction decreases. In the beginning the density of the solution is 1.25-1.30 gm ml^{-1} but when cell stops producing electric current, the density of the solution decreases and becomes 1.10-1.15 gm ml^{-1}. If the cell is joined to a high electrical voltage containing any cell and passing the electric curent in opposite direction, the reverse reactions take place on the electrodes and the cell becomes capable to produce electric current again. Even then, the efficiency of the method to regenerate is not 100 %. Hence, at intervals, solution of H_2SO_4 containing 38% (W/W) concentration is to be added. After a long time use, this cell becomes useless. The charging reactions taking place in lead storage cell are as follows :

Cathode : $PbSO_4(s) + 2e^- \rightarrow Pb(s) + SO_4^{2-}(aq)$

Anode : $PbSO_4(s) + 2H_2O(l) \rightarrow PbO_2(s) + 4H^+(aq) + SO_4^2 \ (aq) + 2e^-$
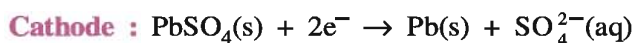
If in one vessel of lead storage cell more than one anodes and cathodes are dipped in the vessel containing solution and joining them in series, more than 2.0 volt potential can be obtained. In the car battery, six cells are joined and 12 volts can be obtained. 22 to 24 volt electric current can be obtained by combining 11 to 12 cells in series.

Ni-Cd storage cell : Nickel-cadmium cell is important as a secondary cell like the lead storage cell. Its life is more than that of lead storage cell but its production is very costly. There are charging and discharging reactions in the method of working of this cell. The complete reaction of discharging is as follows.

$Cd(s) + 2Ni(OH)_3(s) \rightarrow CdO(s) + 2Ni(OH)_2(s) + H_2O(l)$

3.19.3 Fuel cell : The cell which can transform the energy obtained by combustion of fuels like H_2, CO or methane, into electrical energy in only one step is called fuel cell. When hydrogen is oxidised large amount of energy is produced in the form of heat.

$H_2(g) + O_2(g) \rightarrow 2H_2O(l) + 571.70 \ kJ$

We know that when fuel is combusted, heat is produced. In the thermal power stations like Sabarmati, Gandahinagar, Dhuvaran, Vanakbori, etc. mainly mineral coal is used as the fuel and water is transformed into steam by this produced heat. Electricity is produced by using this steam using turbine.

Fig. 3.7 Ni-Cd Storage battery

Maximum 35% of this combustion energy is converted to electrical energy that is, its working efficiency is much less. But, if the energy produced by combustion reaction is directly obtained in the form of electrical energy, then the wastage of energy can be decreased. This purpose is achieved in fuel cell. Different types of fuels can be used in fuel cell. First of all, the fuel cell was presented by scientist Bacon.

Hydrogen Fuel cell : The simple understanding of a fuel cell using hydrogen as fuel is given in fig 3.8. In a vessel, two porous carbon membranes are arranged and concentrated aqueous solution of NaOH is filled between them. This membranes work as inert electrodes. Platinum is used for electrode acting as anode and mixed powder of paltinum and silver oxide is used as a catalyst in the electrode which acts as cathode. On passing hydrogen gas from anode and oxygen gas from cathode, the reactions take place at the electrodes and electric current is produced.
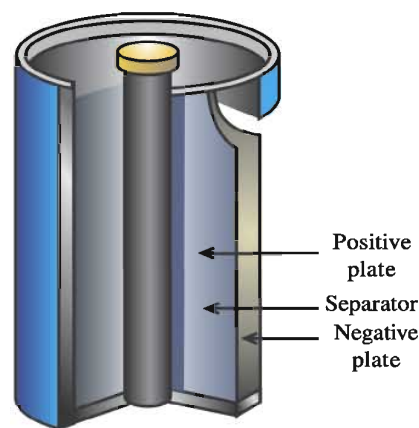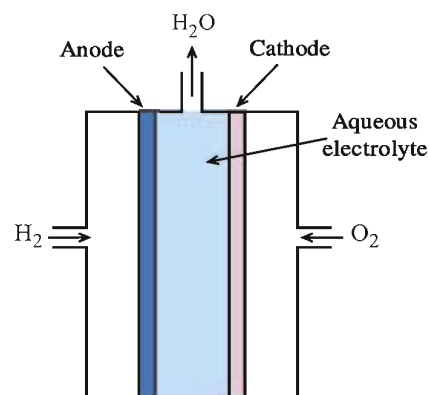

Fig. 3.8 Fuel cell

Cathode : $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$

Anode : $2H_2(g) + 4OH^-(aq) \rightarrow 4H_2O(l) + 4e^-$

Cell reaction : $2H_2(g) + O_2(g) \rightarrow 2H_2O(l) + 571.7 \text{ kJ}$
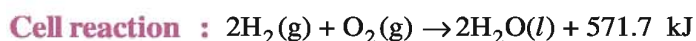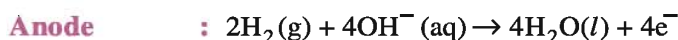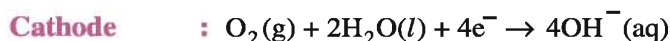
Theoretically the efficiency for the production of electricity by this type of cell can be expected to be 100% but, really, the efficiency obtained is about 70 - 75%. The potential of this cell is about 1.23 volt.

Advantages : There are number of advantages of fuel cell in comparison to other cells. Air is not polluted by fuel cell. Also, it does not create sound and possesses very high efficiency in comparison to electricity produced by thermal power stations. This type of cell was used in space shuttle programme Appolo carried out by American scientist. In addition, the vapour of water obtained during cell reaction was cooled and was used for drinking purpose. In foreign countries, the use of such fuel cells is increasing.

3.20 Corrosion

Some metals are slowly corroded in contact with air or the rust forms on iron. Green coloured salt produced on the vessels of copper and brass. The lustre of silver also fades. The reason for this is the chemical reaction between the surface of the metals and oxygen. The real reactions are mostly complicated. Even then, here we shall study the reaction with iron by the following illustration :
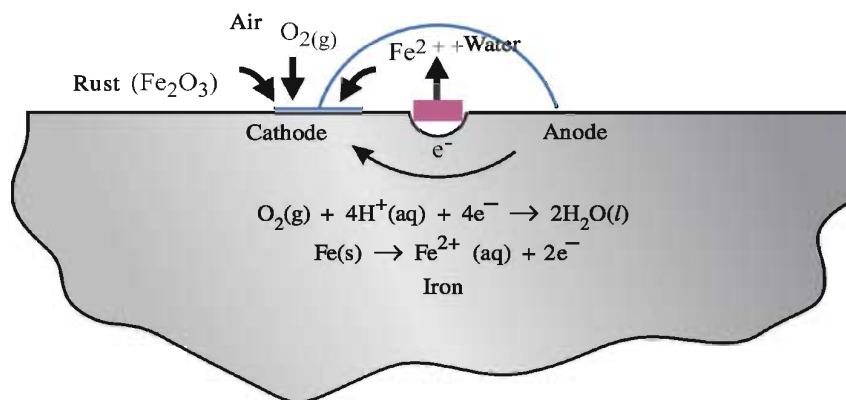

Air $O_{2(g)}$ Fe^{2++} Water

Rust (Fe_2O_3)

Cathode e^- Anode

$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$

$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$

Iron

Fig. 3.9 Reaction of corrosion of iron

The arrangement of atoms can never be systemetic in the rod or vessel of iron viz. In the rod, where there is a bent, its structures in a trace proportions will not be systematic. In addition, its crystal lattice is also defective. Also, there are impurities of other metals like copper is present in iron in trace proportions.

This microscopic surface being active, the atoms on the surface lose electrons easily and get transformed into positive ions. Hence, the atoms of iron near the bent on the surface of iron oxidation reaction occurs.

$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$
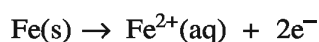
The molecules of water required for this reaction to occur, are available from moisture of air. Hence, the surface near the bent acts as anode. The flow of the electrons produced takes place through the rod of iron and will reach to that point on the surface where oxygen of the air will carry out reduction reaction in presence of H^+. This point acts as cathode because following reaction takes place.

$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$ (reduction)
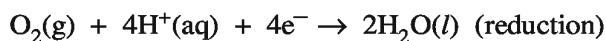
H^+ required for this reaction can also be available from dissociatoin of H_2CO_3 produced by dissolution of carbon dioxide in water on the surface of the iron rod. Thus, one type of electorochemical cell is formed on the surface of the iron rod and it acts as anode. The formation of rust starts from this point. Fe^{2+} ions produced by oxidation are oxidised to Fe^{3+} ions by the oxygen of the air which diffuses towards the cathode and finally Fe_2O_3. xH_2O is formed. If H^+ are not available then oxygen dissolved in moisture get reduce by electrons.

$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$
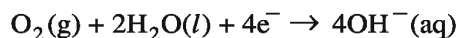
Methods of prevention of Corrosion : Iron is an important metal industrially and in different transportation devices. A huge loss occurs in the world due to corrosion. Hence, one of the methods to prevent is that the moisture should not be allowed to have contact with the surface. This purpose is achieved by applying layer of zinc on iron. This iron is called galvanised iron. In case, if the layer of zinc from the surface of the galvanised iron is removed. even then iron does not get rusted; because the value of $E^0_{Fe|Fe^{2+}}$ is more than that of $E^0_{Zn|Zn^{2+}}$. Hence, the atoms of zinc diffuses on the open surface of iron.

In the other method of prevention of corrosion, it is the combination of metals like Mg or Zn having higher values of E^0_{oxi} with the sheets of iron and buried under the soil. To prevent the iron plates of steamers. being corroded; they are connected with iron plates and then allowed to come in contact with sea water. By doing so, the plate of iron acts as cathode, and blocks of Mg or Zn as anode. These blocks are continuously corroded and so are to be replaced at intervals. Such blocks of Mg or Zn act as anode. These block are continuously corroded and so are sacrificial anodes.

In addition, to apply wax, to paint and use some chemical substances called inhibitors are used. By using them there is no direct contact of gases present in air with the surface of the metal. As a result chemical reaction does not occur and so corrosion is prevented.

SUMMARY

- The reaction taking place in electrochemical cell is a redox reaction.

- In electrochemical cell, chemical energy is transformed to electrical energy and produce electrical energy.

- Electrochemical cell is known as voltaic or galvanic cell.

- The salt bridge functions to connect the two solutions and to maintain electrical neutrality of solutions.

- The symbolic representation of chemical reaction $Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$ is expressed as follows $^\ominus$ Zn(s) | Zn^{2+}(1M) || Cu^{2+}(1M) | Cu(s) $^\oplus$ where one vertical line | indicates the electrode and two vertical lines || indicate the salt bridge.

- The types of electrodes are (i) Active electrodes of metal (ii) Inert electrodes (iii) Gaseous electrodes. The combined system consisting of electrode and the solution in which it is dipped is jointly known as half cell. The representation of half cell is made by putting a vertical line between the electrode and the formula of the active ions. e.g. $Zn(s) | Zn^{2+}(aq)$; $Fe(s) | Fe^{2+}(aq)$.

- The representation of gaseous electrode is made by inert metal, formula of gas and the formula of active ions e.g. $Pt | H_2(g)$ (1 bar) $| H^+(aq)$.

- Standard hydrogen electrode acts as a reference half cell. Its standard potential is accepted as 0.0 volt. The values of standard potential of unknown electrodes are determined with the help of H-electrode.

- Electrochemical cell is a device to convert chemical energy to electrical energy.

- The flow of electrons, when two electrodes are combined, obtained on the basis of chemical reaction under the evolved electromotive force is from anode to cathode in the external circuit. This electromotive force is called cell potential E_{Cell}.

- If the cell is standard one, than the cell potential is expressed as E^0_{Cell}. Potentiometer is used to determine the correct potential of the cell.

- Cell potential E_{Cell} = Reduction potential of $E_{Cathode}$ – Reduction potential of E_{Anode}

  E^0_{Cell} = Standard potential of $E_{Cathode}$ – Standard potential of E_{Anode}

- When the potential of the electrical cell is determined with reference to hydrogen electrode, then it is known as electromotive force (emf).

- Nernst equation $E_{Cell} = E^0_{Cell} - \dfrac{0.059}{n} \log \dfrac{[C_1]}{[C_2]}$ where the value 0.059 is the value of

  $\dfrac{2.303RT}{F}$ at 298 K temperature. (R = 8.314 J K^{-1} mol^{-1}) and F = 96500 coulomb.

- With the help of the Nernst equation, K_C equilibrium constant, pH, K_W (ionic product of water) can be determined.

- Even if the anode and cathode may be of same electrode, but if the concentrations of the solutions of their salts are different, electrochemical cell is formed which is called concentration cell. e.g. $\ominus$ $Fe(s) | Fe^{2+}$ (0.6M) $\| Fe^{2+}$ (0.8M) $| Fe(s)$ $\oplus$ is a concentration cell.

- Electrolytic cell is the cell of opposite type of electrochemical cell. In the electrolytic cell the electrical energy is transformed to chemical energy. During electrolysis of acidic water, hydrogen gas is obtained at the cathode and oxygen gas is obtained at the anode.

- The modern law as proposed after the first and second law of electrolysis by Michael Faraday. "The number of moles of products obtained at the electrodes by oxidation and reduction half reacations, is related with the electrical quantity passing through cell according to their stoichiometry."

- The quantity of electricity flowing by one mole electrons is called one Faraday which is expressed by the symbol F. 1 Faraday (F) = 96487 ≈ 96500 coulomb.

  For electric charge (Q) = electric current (I) × time (t)

  $$F = \frac{I \times t}{96500}$$

  The products obtained by electrolysis,

- Viz. Na metal and Cl_2 gas are obtained by electrolysis of molten NaCl.

- In electrolysis of concentrated NaCl between graphite electrodes, Cl_2 gas is obtained and NaOH can be obtained in solution which is industrial production of NaOH.

- Impure metal is taken as anode and the electrolysis is carried out in the solution of salt of that metal, the metal can be refined and pure metal can be obtained on the cathode. The noble metals remain as anode mud.

- The electrolysis of aqueous solution of Na_2SO_4, is in fact electrolysis of water.

- The relation between Gibbs' free energy (G) and the potential of the electrochemical cell in which sponteneous reaction, can be be shown by the formula. $\Delta G^0 = -nFE^0_{Cell}$

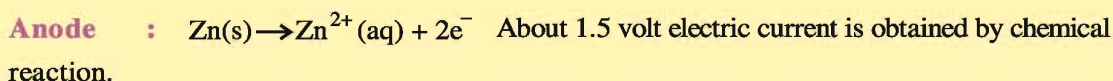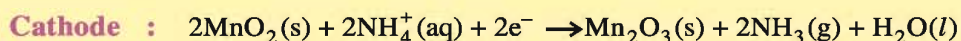 To obtain equilibrium constant from $\Delta G^0 = -nFE^0_{Cell} = -RTlnK_C$

  $$\log K_C = \frac{nFE^0_{Cell}}{2.303RT}$$

- The solid or liquid substances are of two types according to their electrical conduction : The substances which conduct electric current are called conductors and which do not conduct electric current are called non-conductors (insulators).

- The two types of conducting substances are (i) metallic conductors (ii) conduction of electrical current by electrolytic solutions. It is necessary to have the idea about electrical resistance in electrical conduction by electrolytic solutions, so that electrical conductivity can be understood.

- The resistance of any uniform conductor is directly proportional to its length (l) and inversely proportional to its area of cross section (A). $R \propto \frac{l}{A}$ $R = \rho \frac{l}{A}$, ρ is the proportionality constant which is called resistivity. It is also called specific resistance.

- The SI unit of resistivity is Ohmmeter (Ω m). The reciprocal or resistance R is called conductance G.

  $$G = \frac{1}{R} = \frac{A}{\rho l} = K\frac{A}{l} \quad \text{where,} \quad K = \frac{1}{\rho}$$

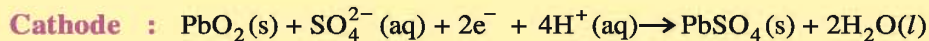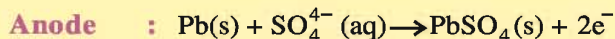- The SI unit of conductance is Siemens expressed as S. It is expresed as ohm^{-1}, (ohm^{-1} or Ω^{-1}) Mho (mho or $\mho$). Specific conductance which is expressed by Greek letter K (Kappa) is obtained by multiplying specific resistivity by cell constant.

- Specific conductance (K) = observed conductance × cell constant. The SI unit of specific conductance is $S\ m^{-1}$ or $S\ cm^{-1}$.

- The classification of conducting substance is carried out on the basis of the magnitudes of the values of their conductance. (i) Good conductor (ii) Semiconductor (iii) Bad conductor (insulator). The substances whose resistivity is zero and whose conductivity is very high are called superconductors. The metals and non-metals are superconductors at 0 to 15 K temperature. The ceramic substances and mixed oxides are superconductors at 150 K temperature.

- Ionic mobility and molar conductivity $\wedge_m = \dfrac{K \times 1000}{C}$ where, K (Kappa) = Conductivity C = molar concentration of solution. The unit of molar conductivity is $mho\ cm^2\ mol^{-1}$. If the concentration of solution is in normality or gram equivalent weight then, the unit of equivalent conductivity is $mho\ cm^2\ gmequ.^{-1}$.

- "The conduction of electricity by a solution at a given concentration of solution between two platinum electrodes at a distance of unit length having unit area of cross section is called the conductivity of solution."

- Hence, $G = \dfrac{KA}{l} = K$ (A and l are in unit measure)

- Molar conductivity $\wedge_m = \dfrac{KA}{l} = K$ where, $l = 1$ and A = V (volume of solution of 1 mole electrolyte)

  $\therefore \Lambda_m = K \cdot V$

- The molar conductivity at infinite dilution is expresed as limiting molar conductivity $\overset{0}{\wedge}_m$. The law of Kohlrausch regarding independent mobility of ions," The value of molar conductivity at infinite dilution ($\overset{0}{\wedge}_m$) of an electrolyte is equal to the sum of molar conductivities at infinite dilution of positive ion and negative ion ($\overset{0}{\lambda}_m{}^+ + \overset{0}{\lambda}_m{}^-$).

- In the utility of Kohlrausch's law, the molar conductivity of weak electrolyte can be obtained by addition or subtraction of molar conductivities of suitable strong electrolytes.

- Any battery is a source of obtaining electric current. The cells for industrial use are of two types (i) primary which can not be regenerated or reproduced after a long use. (ii) Secondary cell which can be regenerated or reproduced when it has become dead after a long use. Dry cell is a primary cell and storage cell is a secondary cell. Dry cell is also called Leclanche cell. The reaction taking place in dry cell are.

  Cathode : $2MnO_2(s) + 2NH_4^+(aq) + 2e^- \longrightarrow Mn_2O_3(s) + 2NH_3(g) + H_2O(l)$

  Anode : $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$ About 1.5 volt electric current is obtained by chemical reaction.

- Mercury cell is also a primary cell whose cell potential is about 1.35 volt,

  Storage cell : Lead storage cell is a secondary cell. The chemical reactions are :

  Anode : $Pb(s) + SO_4^{4-}(aq) \longrightarrow PbSO_4(s) + 2e^-$

  Cathode : $PbO_2(s) + SO_4^{2-}(aq) + 2e^- + 4H^+(aq) \longrightarrow PbSO_4(s) + 2H_2O(l)$

  In this cell, about 2.0 volt electric current is produced during chemical reaction. Nickel-cadmium storage cell can be used for a long time because it possesses long life.

  $Cd(s) + 2Ni(OH)_3(s) \longrightarrow CdO(s) + 2Ni(OH)_2 + H_2O$
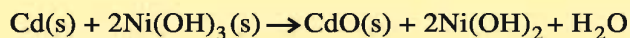
- Electrical energy is produced only in one step from the heat of combustion produced by the combustion of gaseous fuels. Such a cell is called fuel cell. Nowadays fuel cells are used because of less efficiency in production of electricity by thermal power station and to prevent pollution due to it.

- A loss of billions of rupees occur due to metallic corrosion. Metallic corrosion is a redox reaction in which the chemical reactions of electrochemical cell are taking place at anode and cathode. Its prevention can be carried out by inhibitors or electroplating.

EXERCISE

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

   (1) Which reaction takes place in electrochemical cell ?

   (A) Oxidation   (B) Reduction   (C) Redox   (D) All the given

   (2) Which of the following reactions is for Daniell cell ?

   (A) $Cu^{2+}(aq) + Fe(s) \rightleftharpoons Fe^{2+}(aq) + Cu(s)$

   (B) $Zn^{2+}(aq) + Mg(s) \rightleftharpoons Zn(s) + Mg^{2+}(aq)$

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

   (D) All the given reactions.

   (3) Which cell differs from principle point of view?

   (A) Storage cell   (B) Electrolytic cell   (C) Fuel Cell   (D) Leclanche cell.

   (4) Which phenomenon does not occur in Daniell cell ?

   (A) Increase in weight of plate of Cu.

   (B) The conduction of electricity takes place by salt bridge.

   (C) Increase in weight of plate of Zn.

   (D) There is no change in colour of $ZnSO_4$ solution.

(5) The electrochemical cell stops working after sometime. Why ?

(A) Increase of temperature

(B) The difference of cell potentials of both electrodes become zero.

(C) By reversing the direction of reaction taking place in the cell.

(D) Due to change in concentration

(6) What is used for the measurement of accurate potential of electrochemical cell ?

(A) Galvanometer   (B) Ammeter   (C) Voltmeter   (D) Potentiometer

(7) If M, N, O, P and Q are in the increasing order of their standard potentials in standard conditions of their standard half cells, then by combination of which two half cells maximum cell potential will be obtained ?

(A) M and N   (B) M and Q   (C) M and P   (D) M and O

(8) E^0_{red} =

(A) E^0_{oxi} (B) $-E^0_{red}$ (C) $-E^0_{oxi}$ (D) E^0_{redox}

(9) What will be the symbolic representation of the cell for the given following reaction :

$Fe(s) + Cd^{2+}(aq) \rightleftharpoons Fe^{2+}(aq) + Cd(s)$

(A) $\ominus$ Fe(s) I Fe^{2+}(1M) II Cd(s) I Cd^{2+}(1M) $\oplus$

(B) $\ominus$ Cd(s) I Cd^{2+}(1M) II Fe^{2+}(1M) I Fe(s) $\oplus$

(C) $\ominus$ Cd(s) I Cd^{2+}(1M) II Fe(s) I Fe^{2+}(1M) $\oplus$

(D) $\ominus$ Fe(s) I Fe^{2+}(1M) II Cd^{2+}(1M) I Cd(s) $\oplus$

(10) The solution of silver nitrate becomes coloured when pieces of nickel are added to solution of silver nitrate because

(A) Nickel is oxidised   (B) Silver is oxidised

(C) Nickel is reduced   (D) Silver is precipitated

(11) The values of standard reduction potential of X, Y and Z metals are 0.34 V, 0.80 V and –0.45 V. Mention their order of strength as reducing agent

(A) Z > Y > X   (B) Z > X > Y   (C) X > Y > Z   (D) Y > Z > X

(12) If one mole electrons are passed through solutions of $MgSO_4$, $AgNO_3$ and $AlCl_3$, in what mole ration the metals Mg, Ag and Al will be deposited at the electrodes ?

(A) 1 : 1 : 1   (B) 1 : 2 : 3   (C) 2 : 1 : 3   (D) 3 : 6 : 2

(13) What will be obtained at cathode and anode obtained respectively when electrolysis of aqueous solution of concentrated NaCl, out between graphite electrodes ?

(A) Cl_2 and Na metal   (B) H_2 and O_2

(C) Cl_2 and H_2 (D) H_2 and Cl_2

(14) The resistance of any uniform conductor is

(A) in inverse proportion to its length

(B) in direct proportion to its length

(C) in the inverse proportion of the square of its area of cross section

(D) in direct proporiton of the area of its cross section.

(15) Which is more corroded when the iron plates of steamers are connected with block of Zn metal and kept in contact of sea water ?

(A) Iron   (B) Zinc   (C) Both   (D) Neither of the metals

(16) Which is the device used for measurement of electrical resistance ?

(A) Voltmeter   (B) Wheatstone bridge

(C) Galvanometer   (D) Ammeter

(17) At which temperatures ceramic materials are known as superconductor ?

(A) 0 K   (B) 200 K   (C) 150 K   (D) 15 K

(18) l = length, R = resistance, A = area of cross section, then.

(A) $R \propto \dfrac{l}{A}$ (B) $R \propto \dfrac{A}{l}$ (C) $R \propto \dfrac{1}{Al}$ (D) $R \propto lA$

2. **Answers the following question in brief :**

(1) What is an electrochemical cell ?

(2) Write the function of salt bridge ?

(3) Write the names of the solution used for filling in salt bridge.

(4) What is a gas electrode ? Describe any one of them.

(5) Write definition of cell potential.

(6) By which two instruments cell potential is determined ?

(7) Write Nernst equation and on the basis of which rules it can be derived.

(8) From which the value 0.059 is obtained in Nernst equation.

(9) What is concentration cell ?

(10) In which parameters the values of E_{Cell} and E^0_{Cell} become 0.0 volt.

(11) Write usefulness of cell potential.

(12) Write Faraday's modern law of electrolysis.

(13) What will be the value of cell potential under the circumstances of concentration of anode in concentration cell is more than concentration in cathode ? What it will indicate ?

(14) On which factors do the products obtained during electrolysis of aqueous solution of salt depend ?

(15) What is meant by primary and secondary cells ?

(16) Write usefulness of electrolysis.

(17) Write the names of the chemicals used in dry cell.

(18) Write names of catalysts used in hydrogen fuel cell.

(19) Dry cell cannot be regenerated ? Why ?

(20) What fault is produced in the lead storage cell so that the production of electric current is stopped ? Why ?

(21) Write the principle of fuel cell.

(22) Mention advantages of fuel cell.

(23) The ring of silver has fallen into the solution of an acid ? Will there be reason to worry ? Why ?

(24) Can the solution of copper sulphate be filled in the bucket of aluminium ? Why ?

(25) What is emf series ?

(26) What will you observe with naked eye when the Daniell cell is operative ?

(27) If 1.93 ampere current is passed from an electrical conductor. How many electrons will pass through that point in one second ?

(28) How electrical resistance is expressed and write a law pertaining to it ?

(29) What is meant by specific conductivity ?

(30) Write Kohlrausch's law.

(31) Classify the conducting substances on the basis of their values of conductivity

(32) What is indicated by $\overset{0}{\Lambda_m} = v_+ \overset{0}{\lambda_m}{}^+ + v_- \overset{0}{\lambda_m}{}^-$?

(33) What are called superconducting substances ? Write the effect of temperature on it.

(34) Write reduction reaction of moisture containing oxygen gas for corrosion of metal.

(35) Explain the terms : 'Sacrificial anode' and 'Inhibitors'.

3. **Write answers of following questions :**

(1) What is electrochemical cell ? Write equation of Daniell cell and mention anode and cathode ?

(2) Write the construction of salt bridge and explain its function.

(3)   What is electrode ? Write its types and give one example of each.

(4)   What is emf series ? Write the information available from it.

(5)   Write the reaction of the electrochemical cell formed with the help of $E^0_{Ni^{2+}|Ni} = -0.23$ V, $E^0_{Ag^+|Ag} = 0.80$ and give symbolic representation.

(6) H_2 gas is liberated by reaction of Fe with HCl, but H_2 gas is not liberated when Cu reacts with HCl. Explain.

(7)   Write usefulness of cell potential.

(8)   Write Nernst equation and explain the terms involved in it.

(9)   Write laws of Faraday for electrolysis.

(10) Explain the electrolysis of dilute aqueous solution of NaCl between graphite electrodes.

(11) If 1.08 gram Ag is deposited on the cathode when 7.5 ampere current passed through aqueous solution of $AgNO_3$ for 200 seconds, then calculate efficiency. (Ag = 108 u, N = 14 u 0 = 16 u)

(12) The electrolysis of aqueous solution of sodium sulphate is in fact the electrolysis of water. Explain.

(13) Explain Gibbs' free energy and cell potential.

(14) Find the change in free energy and equilibrium constant of an electrochemical cell having standard potentials, cell having

$E^0_{Cu^{2+}|Cu} = 0.34$ V and $E^0_{Fe^{2+}|Fe} = -0.45$ V.

(15) Explain resistivity and specific conductance.

(16) Write the classification of cells which are industrially useful and give example.

(17) Explain Lec Lanche cell.

(18) Write methods of preventing corrosion.

(19) Write reactions of corrosion of iron.

(20) Find the value of E_{Cell} of electrochemical cell.

Zn(s) | Zn^{2+}(0.6M) ‖ Cd^{2+}(0.85M) | Cd(s).

$(E^0_{Zn^{2+}|Zn} = -0.76$ V, $E^0_{Cd^{2+}|Cd} = -0.40$ V)
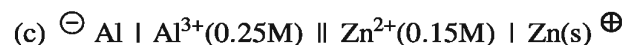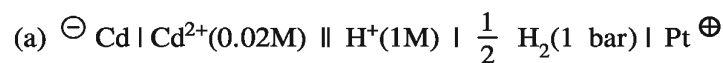
4. **Write the answers of the following questions in detail :**

(1) Draw the labelled diagram of electrochemical cell based on the reaction

$Zn(s) + Ag^+(aq) \rightleftharpoons Zn^{2+}(aq) + Ag(s)$ and answer the following questions.

(i) Show the anode and the cathode and write the reactions on them

(ii) Show the direction of flow of electrons

(iii) Carry out symbolic representation

(2) What is electrolysis : Explain the electrolysis of aqueous solution of $CuSO_4$ between graphite electrodes.

(3) Explain the electrolysis of aqueous solution of $CuSO_4$ by active electrode of Cu and write its usefulness.

(4) Write the Kohlrausch's law of independent migration of ions and explain.

(5) What is storage cell ? Explain lead storage cell.

(6) What is fuel cell ? Explain hydrogen fuel cell.

(7) Explain metallic corroison.

(8) Explain ionic mobility: Explain the factors on which it depends.

(9) Explain in detail "Standard hydrogen gas electrode."

(10) Explain electrical conduction.

(11) Explain molar conductivity and also explain the effect of changes in concentration on conductivity.

(12) Explain mercury and Ni-Cd cells

(13) Calculate the following examples :

(1) By using the standard electrode potentials given below, construct the cell having maximum and minimum potentials, write cell reactions and calculate equilibrium constant.

$E^0_{Fe^{2+}|Fe} = -0.45$ V, $E^0_{Ag^+|Ag} = 0.80$ V, $E^0_{Mg^{2+}|Mg} = -2.37$ V.

(2) Find the value of cell potential of the following cells at 298 K temperature

(a) $^\ominus Cd \,|\, Cd^{2+}(0.02M) \,\|\, H^+(1M) \,|\, \frac{1}{2} \, H_2(1 \text{ bar}) \,|\, Pt \,^\oplus$

(b) $^\ominus Mg \,|\, Mg^{2+}(0.18M) \,\|\, Ag^+(0.01M) \,|\, Ag(s) \,^\oplus$

(c) $^\ominus Al \,|\, Al^{3+}(0.25M) \,\|\, Zn^{2+}(0.15M) \,|\, Zn(s) \,^\oplus$

(3)   The values of standard potentials of the half cells, $Sn^{2+}\,|\,Sn$ and $Ni^{2+}\,|\,Ni$ are -0.14 V and -0.23 V respectively. Calculate the equilibrium constant at 298 K temperature.

(4)   The cell potential of the given following cell is 0.52 V at 298 K temperature, calculate the pH of HCl solution $(E^0_{Cu^{2+}|Cu} = 0.34$ V$)$

$^\ominus$ Pt | H_2(1bar) | HCl (xM) ‖ Cu^{2+}(0.02M) | Cu(s) $^\oplus$.

(5)   The potential of the given following cell is 0.586 V at 298K temperature, calculate the ionic product (K_w) of water.

$^\ominus$ Pt | H_2(1 bar) | NaOH (0.01M) ‖ HCl (0.01M) | H_2 (1 bar) | Pt $^\oplus$

(6)   How many grams of Cu and what volume of O_2 gas will be obtained if 18.4 ampere electric current is passed through the electrolytic cell of $CuSO_4$ for 1 hour and 42 minutes between graphite electrodes at 298 K temperature and 1 bar pressure ? (Cu = 63.5u O = 16u)

(7)   How many amperes of current should be passed when aqueous solutoin of Na_2SO_4 is electrolysed between graphite electrodes at 300 K temperature so, that 250 ml min^{-1} O_2 gas is obtained under 1.0 bar pressure.

(8)   How many spoons can be electroplated by silver when 5 ampere current is passed through electrolytic cell of $AgNO_3$ for 2.7 hours ? 0.01 gram Ag layer is deposited on each spoon (Ag = 108 u).

(9)   For how much time 48 ampere current should be passed through 400 ml 0.04M $AgNO_3$ solution during electrolysis so that Ag is completely deposited?

(10) How many grams of Cu will be obtained by passing 4.5 ampere current through 1 litre 0.6M $CuCl_2$ aqueous solution by dipping inert electrodes ? What will be the change in concentration ?

$\bullet$