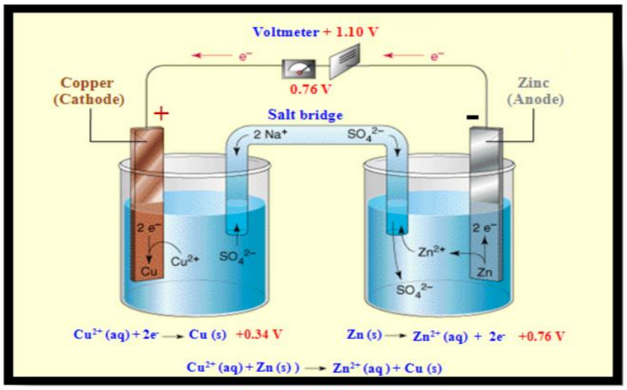
ELECTROCHEMISTRY

Electrochemistry is the study of production of electricity from energy released during spontaneous chemical reactions and the use of electrical energy to bring about non-spontaneous chemical transformations.
A galvanic cell is an electrochemical cell that converts the chemical energy of a spontaneous redox reaction into electrical energy. In this device the Gibbs energy of the spontaneous redox reaction is converted into electrical work which may be used for running a motor or other electrical gadget like heater, fan, geyser, etc.

Daniell cell: Daniell cell is the one such cell in which the following redox reaction occurs.



The Daniell Cell

Daniell cell having electrodes of zinc and copper dipping in the solutions of their respective salts.

(i) $Cu^{2+} + 2e^- \text{--->} Cu(s)$ (reduction half reaction)

(ii) $Zn(s) \text{--->} Zn^{2+} + 2e^-$ (oxidation half reaction)

$Zn(s) + Cu^{2+}(aq) \text{---->} Zn^{2+}(aq) + Cu(s)$

The reduction half reaction occurs on the copper electrode while the oxidation half reaction occurs on the zinc electrode. These two portions of the cell are also called **half-cells** or **redox couples**. The copper electrode may be called the reduction half-cell reaction and the zinc electrode, the oxidation half-cell reaction.

Electrode potential/Standard electrode potential:

A potential difference develops between the electrode and the electrolyte which is called **electrode potential**. When the concentrations of all the species involved in a half-cell is unity then the electrode potential is known as **standard electrode potential**. According to IUPAC convention, standard reduction potentials are now called standard electrode potentials. In a galvanic cell, the half-cell in which oxidation takes place is called **anode** and it has a negative potential with respect to the solution. The other half-cell in which reduction takes place is called **cathode** and it has a positive potential with respect to the solution. Thus, there exists a potential difference between the two electrodes and as soon as the switch is in the *on* position the electrons flow from negative electrode to positive electrode. The direction of current flow is opposite to that of electron flow.

The potential difference between the two electrodes of a galvanic cell is called the cell potential and is measured in volts. The cell potential is the difference between the electrode potentials (reduction potentials) of the cathode and anode. It is called the cell electromotive force (e.m.f) of the cell when no current is drawn through the cell.

EMF of a cell: The e.m.f of the cell is positive and is given by the potential of the half-cell on the right-hand side minus the potential of the half-cell on the left-hand side i.e.,

$\mathbf{E_{cell} = E_{right} - E_{left}}$

This is illustrated by the following example: Half-cell reactions:

Cathode (reduction): $2Ag^+$ (aq) + $2e^-$ --->2Ag(s)

Anode (oxidation): Cu(s) --->Cu^{2+} (aq) + 2e–

Overall reaction: Cu(s) + $2Ag^+$ (aq) ----> Cu^{2+} (aq) + 2 Ag(s)

Silver electrode acts as a cathode and copper electrode acts as an anode. The cell can be represented as: Cu(s)|Cu^{2+}(aq)||Ag^+(aq)|Ag(s)

$E_{cell} = E_{right} - E_{left} = E_{Ag^+/Ag} - E_{Cu^{2+}/Cu}$

In view of this convention, the half reaction for the Daniell cell in Fig. 3.1 can be written as:

Left electrode: Zn(s) → Zn^{2+} (aq, 1 M) + 2 e–

Right electrode: Cu^{2+} (aq, 1 M) + 2 e– → Cu(s)

The overall reaction of the cell is the sum of above two reactions and we obtain the equation:

Zn(s) + Cu^{2+} (aq) → Zn^{2+} (aq) + Cu(s)

e.m.f of the cell = E^0cell = $E^0_R - E^0_L$

= 0.34V – (– 0.76) V = 1.10 V

Nernst equation and its application to chemical cells:

For the electrode reaction:

M^{n+} (aq) + ne– ---> M(s)

The electrode potential at any concentration measured with respect to standard hydrogen electrode can be represented by:

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

but concentration of solid M is taken as unity and we have

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

R is gas constant (8.314 JK–1 mol^{-1}), F is Faraday constant (96487 C mol^{-1}), *T* is temperature in kelvin and [M^{n+}] is the concentration of the species, M^{n+}.

In Daniell cell, the electrode potential for any given concentration of Cu^{2+} and Zn^{2+} ions,

For Cathode:

$$E_{(Cu^{2+}/Cu)} = E^{\ominus}_{(Cu^{2+}/Cu)} - \frac{RT}{2F}\ln\frac{1}{[Cu^{2+}(aq)]}$$

For Anode:

$$E_{(Zn^{2+}/Zn)} = E^{\ominus}_{(Zn^{2+}/Zn)} - \frac{RT}{2F}\ln\frac{1}{[Zn^{2+}(aq)]}$$

The cell potential, $E_{(\text{cell})} = E_{(\text{Cu}^{2+}/\text{Cu})} - E_{(\text{Zn}^{2+}/\text{Zn})}$

$E_{cell} = E^0_{cell} - (RT/2F) \ln \{[Zn^{2+}] / [Cu^{2+}]\}$
E (cell) depends on the concentration of both Cu^{2+} and Zn^{2+} ions. It increases with increase in the concentration of Cu^{2+} ions and decrease in the concentration of Zn^{2+} ions.

We know that, lnX = 2.303logX, R is gas constant (8.314 JK–1 mol^{-1}), F is Faraday constant (96487 C mol^{-1}), *T* is temperature in kelvin, 298K. Then

$E_{cell} = E^0_{cell} - (0.059/2) \log \{[Zn^{2+}] / [Cu^{2+}]\}$

For a general electrochemical reaction of the type:

$$a\,A + bB \xrightarrow{ne} cC + dD$$

Nernst equation can be written as:

$$E_{(\text{cell})} = E^{\ominus}_{(\text{cell})} - \frac{RT}{nF} \ln Q$$

$$= E^{\ominus}_{(\text{cell})} - \frac{RT}{nF} \ln \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Equilibrium Constant from Nernst Equation:

If the circuit in Daniell cell (Fig. 3.1) is closed then we note that the reaction
$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$ takes place and as time passes, the concentration of Zn^{2+} keeps on increasing while the concentration of Cu^{2+} keeps on decreasing.
At the same time voltage of the cell as read on the voltmeter keeps on decreasing. After some time, we shall note that there is no change in the concentration of Cu^{2+} and Zn^{2+} ions and at the same time, voltmeter gives zero reading. This indicates that equilibrium has been attained. In this situation the Nernst equation may be written as:
$E_{cell} = 0 = E^0_{cell} - (RT/2F) \ln\{[Zn^{2+}] / [Cu^{2+}]\}$

$E^0_{cell} = (RT/2F) \ln\{[Zn^{2+}] / [Cu^{2+}]\}$
But at equilibrium,
$[Zn^{2+}] / [Cu^{2+}] = Kc$
at T = 298K the above equation can be written as
$E^0_{cell} = (0.059/2) \log Kc = 1.10\ V \quad (E^0_{cell} = 1.10\ V)$
$\log Kc = [(1.10V \times 2)]/0.059 = 37.288$
$Kc = 2 \times 10^{37}$ at 298K.
In general,
$E^0_{cell} = (2.303RT/nF) \ln Kc$

This gives a relationship between equilibrium constant of the reaction and standard potential of the cell in which that reaction takes place.

Electrochemical Cell and Gibbs Energy of the Reaction:

Electrical work done in one second is equal to electrical potential multiplied by total charge passed. If we want to obtain maximum work from a galvanic cell then charge has to be passed reversibly. The reversible work done by a galvanic cell is equal to decrease in its Gibbs energy and therefore, if the emf of the cell is E and nF is the amount of charge passed and $\Delta_r G$ is the Gibbs energy of the reaction, then $\Delta_r G = – nFE_{cell}$

Ecell is an intensive parameter but $\Delta_r G$ is an extensive thermodynamic property and the value depends on *n*.

Thus, if we write the reaction

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

$\Delta rG = – 2\ F\ E_{cell}$

If the concentration of all the reacting species is unity, then $E_{cell} = E^0_{cell}$

$\Delta_r G^0 = – n\ F\ E^0_{cell}$

We can calculate equilibrium constant by the equation:

$\Delta_r G^0 = –RT \ln K$.

Conductance of Electrolytic Solutions:

The electrical resistance is represented by the symbol *'R'* and it is measured in ohm (**Ω**).The electrical resistance of any object is directly proportional to its length, l, and inversely proportional to its area of cross section, *A*. That is,

$R \propto l /A$ or $R = \rho (l/A)$

The constant of proportionality, ρ (rho), is called **resistivity** (specific resistance). Its SI units are ohm metre (**Ω** m) or ohm centimetre (**Ω** cm).

The resistivity for a substance is its resistance when it is one metre long and its area of cross section is one m^2. It can be seen that:

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

The inverse of resistance, R, are called **conductance**, G, and we have the relation:

$G =1/R = A/\rho l = \kappa (A/l)$ $[\kappa = 1/ \rho]$

The SI unit of conductance is Siemens, represented by the symbol 'S' and is equal to $ohm^{–1}$ (also known as mho) or $\Omega^{–1}$.

The inverse of resistivity, called **conductivity** (specific conductance) is represented by the symbol, κ (Greek, kappa). The SI units of conductivity are $S\ m^{–1}$. Conductivity of a material in $S\ m^{–1}$ is its conductance when it is 1 m long and its area of cross section is 1 m^2. It may be noted that $1\ S\ cm^{–1} = 100\ S\ m^{–1}$.

Electrical conductance through metals is called metallic or electronic conductance and is due to the movement of electrons. The electronic conductance depends on:

(i) The nature and structure of the metal
(ii) The number of valence electrons per atom
(iii) Temperature (it decreases with increase of temperature).

When electrolytes are dissolved in water its conductivity increases. The conductance of electricity by ions present in the solutions is called electrolytic or ionic conductance. The conductivity of electrolytic (ionic) solutions depends on:

(i) The nature of the electrolyte added
(ii) Size of the ions produced and their solvation
(iii) The nature of the solvent and its viscosity
(iv) Concentration of the electrolyte
(v) Temperature (it increases with the increase of temperature)

Conductivity of Ionic Solutions: In the conductivity cell the solution confined between the electrodes is a column of length l and area of cross section A. The resistance of such a column of solution is given by the equation:

$R = \rho\, l/A = l/\kappa A$

The quantity l/A is called cell constant denoted by the symbol, G^*. It depends on the distance between the electrodes and their area of cross-section.

The cell constant, G^*, is then given by the equation:

$G^* = l/A = R\kappa$

K = cell constant/$R = G^*/R$

Molar conductivity: It is defined as the conducting power of all the ions produced by dissolving one mole of an electrolyte in solution**.** It is denoted by the symbol Λ_m (Λ = lambda). It is related to the conductivity of the solution by the equation:

Molar conductivity = $\Lambda_m = \kappa/c$

In the above equation, if κ is expressed in S m^{-1} and the concentration, c in mol m^{-3} then the units of Λ_m is in S m^2 mol^{-1}.

Λ_m (S cm^2 mol^{-1}) = [κ (S cm^{-1}) x 1000 (cm^3/L)] / Molarity (mol/L)

$$\boxed{\Lambda_m = [\kappa \text{ x } 1000] / \text{Molarity}}$$

1 S m^2 mol^{-1} = 10^4 S cm^2 mol^{-1} or

1 S $cm^2 mol^{-1}$ = 10^{-4} S m^2 mol^{-1}.

Variation of Conductivity and Molar Conductivity with Concentration:

Both conductivity and molar conductivity change with the concentration of the electrolyte. Conductivity always decreases with decrease in concentration both, for weak and strong electrolytes. This can be explained by the fact that the number of ions per unit volume that carry the current in a solution decrease on dilution. The conductivity of a solution at any given concentration is the conductance of one unit volume of solution kept between two platinum electrodes with unit area of cross section and at a distance of unit length.

This is clear from the equation: $G = \kappa A/l$ (both A and l is unity in their units in m or cm)

Molar conductivity of a solution at a given concentration is the conductance of the volume V of solution containing one mole of electrolyte kept between two electrodes with area of cross section A and distance of unit length. Therefore,

$\Lambda_m = \kappa A/l$

Since $l = 1$ and $A = V$ (volume containing 1 mole of electrolyte)

$\Lambda_m = \kappa V$

Molar conductivity increases with decrease in concentration. This is because the total volume, V, of solution containing one mole of electrolyte also increases. At a given concentration, Λ_m can be defined as the conductance of the electrolytic solution kept between the electrodes of a conductivity cell at unit distance but having area of cross section large enough to accommodate sufficient volume of solution that contains one mole of the electrolyte. When concentration approaches zero, the molar conductivity is known as **limiting molar conductivity** and is represented by the symbol Λ_m^0. The variation in Λ_m with concentration is different for strong and weak electrolytes.

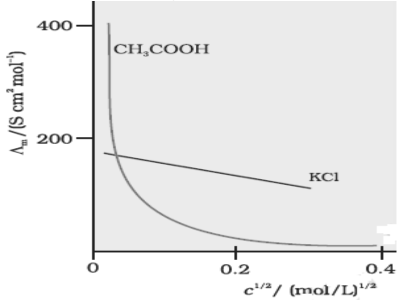


Fig. 3.6: Molar conductivity Λ_m versus c½ for acetic acid (weak electrolyte) and potassium chloride (strong electrolyte) in aqueous solutions.

Strong Electrolytes

For strong electrolytes, Λ_m increases slowly with dilution and can be represented by the equation:
$\Lambda_m = \Lambda_m^0 - A\, c^{½}$
If we plot Λ_m against $c^{1/2}$, we obtain a straight line with intercept equal Λ_m^0 and slope equal to '*A*'. The value of the constant '*A*' for a given solvent and temperature depends on the type of electrolyte i.e., the charges on the cation and anion produced on the dissociation of the electrolyte in the solution. Thus, NaCl, $CaCl_2$, $MgSO_4$ are known as 1-1, 2-1 and 2-2 electrolytes respectively. All electrolytes of a particular type have the same value for '*A*'.

Kohlrausch's law of independent migration of ions. The law states that limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte.
If $\lambda°_{Na+}$ and $\lambda°_{Cl-}$ are limiting molar conductivity of the sodium and chloride ions respectively, then the limiting molar conductivity for sodium chloride is given by the equation:
$\Lambda_m^0 = \lambda°_{Na+} + \lambda°_{Cl-}\ {}^{\nu}$
In general, if an electrolyte on dissociation gives ν_+ cations and ν_- anions then its limiting molar conductivity is given by: $\Lambda_m^0 = \nu_+\lambda°_+ + \nu_-\lambda°_-$
$\lambda°_+ + \lambda°_-$ are the limiting molar conductivities of the cation and anion respectively.

Weak Electrolytes

Weak electrolytes like acetic acid have lower degree of dissociation at higher concentrations, for such electrolytes, the change in Λ_m with dilution is due to increase in the degree of dissociation. At any concentration *c*, if α is the degree of dissociation, then
$\alpha = \Lambda_m / \Lambda_m^0$

ELECTROLYSIS: It is a process of decomposition of an electrolyte by the passage of electricity through its aqueous solution or molten (fused) state of electric current.

Quantitative Aspects of Electrolysis

Faraday's Laws of Electrolysis:

(i) **Faraday** first law of electrolysis: The amount of chemical reaction which occurs at any electrode during electrolysis by a current is proportional to the quantity of electricity passed through the electrolyte (solution or melt).

$w \propto Q$ or $w = ZQ$, Where Z is called electrochemical equivalent. If a current of I amperes is passed for t seconds, then $Q = It$ so that, $w = ZIt$

(ii) **Faraday** first law of electrolysis: The amounts of different substances liberated by the same quantity of electricity passing through the electrolytic solution are proportional to their chemical equivalent weights (Atomic Mass of Metal ÷ Number of electrons required to reduce the cation). For example, when same current is passed through two electrolytic solutions, containing copper sulphate and silver nitrate connected in series, the weight of copper and silver deposited are:

(Weight of Cu deposited) / (Weight of Cu deposited) = (Eq. wt. of Cu) / (Eq. wt. of Ag)

The amount of electricity (or charge) required for oxidation or reduction depends on the stoichiometry of the electrode reaction. For example, in the reaction:
$Ag^+ (aq) + e^- \rightarrow Ag(s)$
One mole of the electron is required for the reduction of one mole of silver ions.
The charge on one electron is equal to 1.6021×10^{-19} C.
Therefore, the charge on one mole of electrons is equal to:
$N_A \times 1.6021 \times 10^{-19}\ C = 6.02 \times 10^{23}\ mol^{-1} \times 1.6021 \times 10^{-19}\ C = 96487\ C\ mol^{-1}$
This quantity of electricity is called **Faraday** and is represented by the symbol **F**.
For approximate calculations we use $1F \simeq 96500\ C\ mol^{-1}$.

$Mg^{2+} + 2e^- \rightarrow Mg$
$Al^{3+} + 3e^- \rightarrow Al$
For the above electrode reactions, one mole of Mg^{2+} and Al^{3+} require 2 mol of electrons (2F) and 3 mol of electrons (3F) respectively.

Products of Electrolysis:

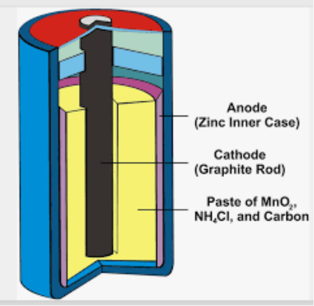
The products of electrolysis depend on the different oxidising and reducing species present in the electrolytic cell and their standard electrode potentials. Moreover, some of the electrochemical processes although feasible, are so slow kinetically that at lower voltages these do not seem to occur. For the occurrence of such reactions some extra potential (called *over potential*) is required.
(i)Electrolysis of molten sodium chloride: During the electrolysis of molten NaCl, the products of electrolysis are sodium metal and Cl_2 gas. The reactions may be expressed as:
At cathode: $2Na^+ + 2e– \rightarrow 2Na$ (reduction)
At anode: $2Cl^- \rightarrow Cl_2 + 2e–$ (oxidation)
The overall reaction: $2NaCl \dashrightarrow 2Na + Cl_2$

(ii) Electrolysis of aqueous sodium chloride: During the electrolysis of aqueous sodium chloride solution, the products are NaOH, Cl_2 and H_2.
At the cathode: $Na+ (aq) + e– \rightarrow Na (s)$ $E^0cell = – 2.71$ V
$H^+ (aq) + e– \rightarrow ½ H_2 (g)$ $E^0cell = 0.00$ V
The reaction with higher value of E^0 is preferred and therefore, the reaction at the cathode during electrolysis is:
$H+ (aq) + e– \rightarrow ½ H_2 (g)$

But H+ (aq) is produced by the dissociation of H_2O, i.e., $H_2O\ (l) \rightarrow H^+\ (aq) + OH^-\ (aq)$
Therefore, the net reaction at the cathode: $H_2O\ (l) + e^- \rightarrow \frac{1}{2}H_2\ (g) + OH^-\ (aq)$
At the anode: $Cl– (aq) \rightarrow \frac{1}{2}\ Cl_2\ (g) + e^-\ E^0cell = +1.36\ V$
$2H2O\ (l\ ) \rightarrow O_2\ (g) + 4H^+(aq) + 4e^-\ E^0cell = +1.23\ V$
The reaction at anode with lower value of E^0 is preferred and therefore, water should get oxidised in preference to Cl^- (aq). However, on account of over potential of oxygen, the reaction $Cl^-\ (aq) \rightarrow \frac{1}{2}\ Cl_2\ (g)$ is preferred. Thus, the net reactions may be summarized as:
$NaCl\ (aq) \xrightarrow{H2O} Na^+\ (aq) + Cl^-\ (aq)$
At cathode: $H_2O\ (l\ ) + e^- \rightarrow \frac{1}{2}\ H_2(g) + OH^-\ (aq)$
At anode: $Cl^-\ (aq) \rightarrow \frac{1}{2}Cl_2\ (g) + e^-$
Net reaction: $NaCl\ (aq) + H_2O\ (l) \rightarrow Na^+(aq) + OH^-(aq) + \frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g)$
$NaCl\ (aq) + H_2O\ (l) \rightarrow NaOH\ (aq) + \frac{1}{2}H_2\ (g) + \frac{1}{2}Cl_2(g)$

Dry Cell:

A dry cell consists of a metal container in which a low moisture electrolyte paste covers the graphite rod or a metal electrode. Generally, the metal container will be zinc whose base acts as a negative electrode (anode) and a carbon road acts as a positive electrode (cathode).
It is surrounded by manganese dioxide and low moisture electrolyte like ammonium chloride paste, which will produce a maximum of 1.5V of voltage, and they are not reversible.

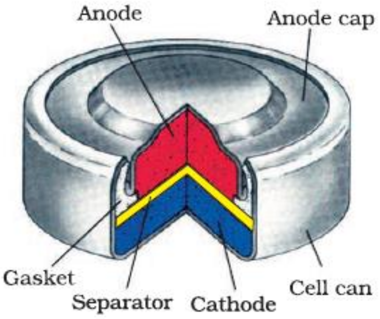


Anode: $Zn(s) \rightarrow Zn^{2+} + 2e^-$
Cathode: $2MnO_2 + 2NH_4^+ + 2e^- \rightarrow 2MnO\ (OH) + 2NH_3$

$$\underline{Zn(s) + 2MnO_2 + 2NH_4^+ \rightarrow Zn^{2+} + 2MnO\ (OH) + 2NH_3}$$

Mercury cell: It consists of zinc – mercury Amalgam as anode and a paste of HgO and carbon as the cathode. The electrolyte is a paste of KOH and ZnO.
The electrode reactions for the cell are given below:
Anode: $Zn\ (Hg) + 2OH^- \longrightarrow ZnO(s) + H_2O + 2e^-$
Cathode: $HgO + H_2O + 2e^- \rightarrow Hg\ (l) + 2OH^-$

$$\underline{Zn(Hg) + HgO(s) \longrightarrow ZnO(s) + Hg(l)}$$



The cell potential is approximately 1.35 V.
It is suitable for low current devices like hearing aids, watches, etc.

A secondary cell (lead storage battery) commonly used in automobiles and invertors. It consists of a lead anode and a grid of lead packed with lead dioxide (PbO_2) as cathode. A 38% solution of Sulphuric acid is used as an electrolyte.
The cell reactions when the battery is in use are given below:

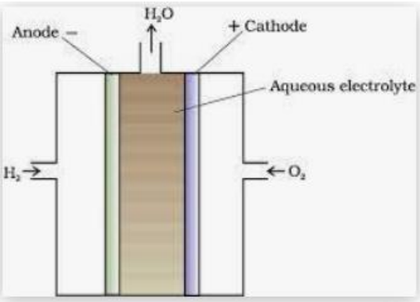
Anode: $Pb(s) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s) + 2e^-$
Cathode: $PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O(l)$

$$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \longrightarrow 2PbSO_4(s) + 2H_2O(l)$$

On charging the battery the reaction is reversed and $PbSO_4(s)$ on anode and cathode is converted into Pb and PbO_2, respectively.

Another important secondary cell is the nickel-cadmium cell which has longer life than the lead storage cell but more expensive to manufacture.
The overall reaction during discharge is:
$Cd(s) + 2Ni(OH)_3(s) \longrightarrow CdO(s) + 2Ni(OH)_2(s) + H_2O(l)$

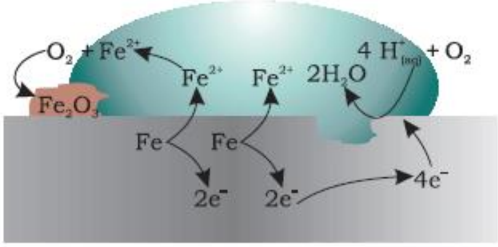
Fuel cells: To convert the energy of combustion of fuels like hydrogen, methane, methanol, etc. directly into electrical energy are called **fuel cells**.
Fuel cells use the reaction of hydrogen with oxygen to form water. The cell was used for providing electrical power in the Apollo space Programme. Fuel cells are pollution free.



Fuel cell using H_2 and O_2 produces electricity.

The electrode reactions are given below:
Cathode: $O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$
Anode: $2H_2(g) + 4OH^-(aq) \longrightarrow 4H_2O(l) + 4e^-$
Overall reaction being:
$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$

Corrosion:
In corrosion, a metal is oxidised by loss of electrons to oxygen and formation of oxides. Corrosion of iron (commonly known as rusting) occurs in presence of water and air. The chemistry of corrosion is an electrochemical phenomenon.



Corrosion of iron in atmosphere

We can write the reaction
Anode: $2Fe(s) \longrightarrow 2Fe^{2+} + 4e^-$ $\qquad E^0_{(Fe2+/Fe)} = -0.44$ V

Cathode: O_2 (g) + 4 H^+ (aq) + 4 e^- →2 H_2O (l) $E^0_{(H+/O2/H2O)}$ = 1.23 V
The overall reaction being:
2Fe(s) + O_2 (g) + $4H^+$ (aq) →$2Fe^{2+}$ (aq) + 2 H_2O (l) E^0_{cell} =1.67 V
The ferrous ions are oxidised by atmospheric oxygen to ferric ions which come out as rust in the form of hydrated ferric oxide ($Fe_2O_3.\ x\ H_2O$) and with further production of hydrogen ions.
Prevention of corrosion can be done by covering the surface with paint or by some chemicals (e.g. bisphenol).

ASSIGNMENT:
Q1. Λ_m^0 for NaCl, HCl and CH_3COONa are 126.4, 425.9 and 91.0 S cm^2 mol^{-1} respectively. Calculate Λ_m^0 for CH_3COOH.
Solution: Λ_m^0 (HCl) + Λ_m^0 (CH_3COONa) - Λ_m^0 (NaCl)
425.9 + 91.0 - 126.4 = 390.5 S cm^2 mol^{-1}

Q2. Calculate E_{cell} for the reaction given below, if E^0_{cell} = 3.17V
Mg (s) + $2Ag^+$ (0.0001M) →Mg^{2+} (0.130M) + 2Ag (s)
Solution:
$E_{cell} = E^0_{cell} – (0.059/2) \log \{[Mg^{2+}] / [Ag^+]^2 \}$

$= 3.17 – 0.0295 \log [(0.130)/(0.0001)^2]$
= 3.17 V – 0.21V = 2.96 V

Q3. A solution of $CuSO_4$ is electrolysed for 10 minutes with a current of 1.5 amperes. What is the mass of copper deposited at the cathode?
Solution: t = 10 x 60 = 600 s
Q = I X t = 1.5 A × 600 s = 900 C
According to the reaction:
Cu^{2+} (aq) + $2e^-$ = Cu(s)
We require 2F or 2 × 96500 C to deposit 1 mol or 63 g of Cu.
For 900 C, the mass of Cu deposited
= (63 g mol^{-1} × 900 C)/ (2 × 96500 C mol^{-1})
= 567 / 1930 g
= 0.2938 g.

Q4. The electrical resistance of a column of 0.05 mol L^{-1} NaOH solutions of diameter 1 cm and length 50 cm is 5.55×10^3 ohm. Calculate its resistivity, conductivity and molar conductivity.
Solution:
A = π r2 = 3.14 × 0.52 cm^2 = 0.785 cm^2 = 0.785×10^{-4} m^2
l = 50 cm = 0.5 m
R = ρ l/ A
ρ (resistivity) = RA/l = [5.55×10^3 ohm x 0.785 cm^2] / 50 cm = 87.135 ohm cm
Conductivity (κ) = 1/ ρ = [1 / 87.135] S cm^{-1} = 0.01148 S cm^{-1}

Molar conductivity, Λ_m = [κ (S cm^{-1}) x 1000 (cm^3/L)] / Molarity (mol/L)
= [0.01148 ×1000]/ 0.05
= 229.6 S cm^2 mol^{-1}

Q5. Conductivity of 0.00241 M acetic acid is 7.896×10^{-5} S cm^{-1}. Calculate its molar conductivity. If Λ^0_m for acetic acid is 390.5 S cm^2 mol^{-1}. What is the dissociation constant?
Answer: Molar conductivity, $\Lambda_m = 32.76$ S cm^2 mol^{-1}
$\alpha = 32.76/390.5 = 8.39 \times 10^{-2}$
Dissociation constant = 1.86 x 10-5

Q6. Explain the following:

1. How much charge is required for 1 mol of MnO_4^- to Mn^{2+}
2. How much electricity is required in coulomb for the oxidation of 1 mol of H_2O to O_2
3. How much electricity in terms of Faraday is required to produce 40g of Al from molten Al_2O_3

Answer: 1. 5 x 96500 C, 2. 2 x 96500 C, 3. 4.4 F

Q7. The standard electrode potential for Daniell cell is 1.1V. Calculate the standard Gibbs energy for the reaction: $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$
Solution: $\Delta_r G^0 = - n F E^0_{cell}$
The value of n in the above equation is 2, F = 96500 C mol–1 and E^0cell = 1.1 V
Therefore, $\Delta r G^0 = - 2 \times 1.1 V \times 96500$ C mol^{-1}
$= - 212300$ J mol^{-1}
$= - 212.3$ kJ mol^{-1}

Q8. Calculate the equilibrium constant of the reaction:
$Cu(s) + 2Ag^+(aq) \longrightarrow Cu^{2+}(aq) + 2Ag(s)$
E^0cell =0.46 V
Ans. $K_c = 3.92 \times 10^{15}$

Q9. The standard electrode potential for Daniell cell is 1.1V. Calculate the standard Gibbs energy for the reaction: $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$
Solution: $\Delta_r G^0 = - n F E^0_{cell}$
The value of n in the above equation is 2, F = 96500 C mol–1 and E^0cell = 1.1 V
Therefore, $\Delta r G^0 = - 2 \times 1.1 V \times 96500$ C mol^{-1}
$= - 212300$ J mol^{-1}
$= - 212.3$ kJ mol^{-1}

Q10. Predict the products of electrolysis in each of the following:
(i) An aqueous solution of $AgNO_3$ with silver electrodes.
(ii) An aqueous solution of $AgNO_3$ with platinum electrodes.
(iii) A dilute solution of H_2SO_4 with platinum electrodes.
(iv) An aqueous solution of $CuCl_2$ with platinum electrodes.
Answer: (i) At cathode- Ag^+ ions ($AgNO_3$), At anode- Ag electrode
(ii) At cathode- Ag^+ ions ($AgNO_3$), At anode- Ag is not attacked. OH^- gives O_2
(iii) At cathode- H^+ ions (H_2SO_4), At anode- OH^- gives O_2
(iii) At cathode- Cu^{2+} ions ($CuCl_2$), At anode- Cl^-, Cl_2 is liberated.