Electrochemistry

- Electrochemistry is the branch of the chemistry which deals with the relationship in between chemical and electrical energy and how one can be converted into another.
- Chemical energy can be converted into electrical energy by batteries and fuel cells. Electrochemical reactions are energy efficient and ecofriendly.

Electrolysis

Electrolysis is the process in which, when current is passed through molten or aqueous state of an electrolyte then product are formed due to oxidation and reduction at anode and cathode respectively.

Electrochemical cells

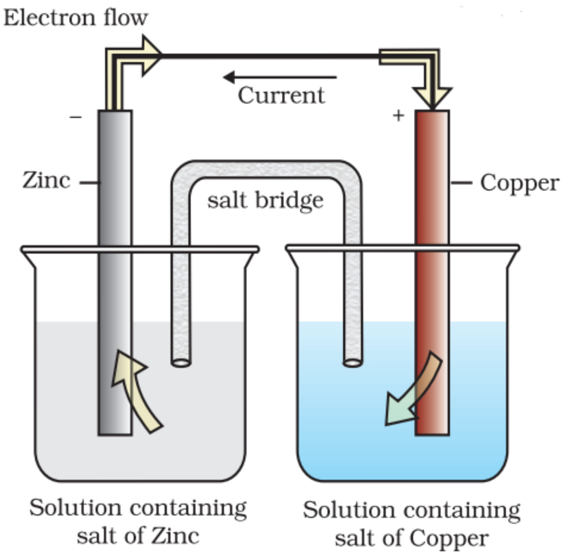

Figure: Daniell call

- The Daniell cell converts chemical energy (which is liberated during redox reaction) to electrical energy.

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

It has 1.1V electrical potential and concentration of Zn^{+2} and Cu^{+2} ions is 1mol dm^{-3}. Such a device is known as galvanic or a voltaic cell.

Galvanic cells

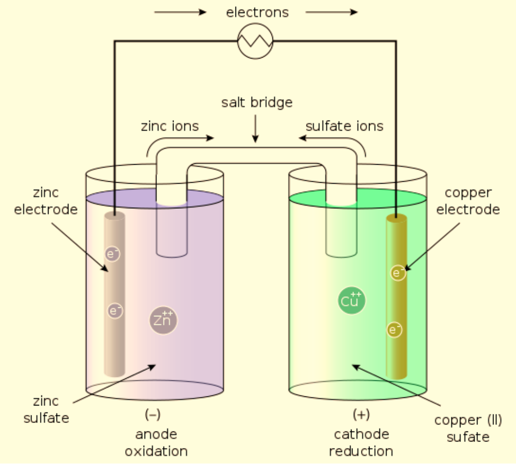

Figure: Galvanic cell

- An electrochemical cell which converts the chemical energy of a spontaneous redox reaction into electrical energy is known as galvanic cell.
- The Gibbs energy is converted into electrical energy which is used for running a motor or other electrical gadgets like fan, heater geyser, etc.
- Galvanic cell consists of two half cells and a salt bridge. There are two half reaction one is reduction and other one is oxidation. There is a potential difference between electrolyte and electrode which is known as electrode potential.
- If the concentration of all the species in a half cell is unity then electrode potential is named as standard electrode potential.
- The half-cell of galvanic cell in which oxidation takes place is known as anode. The other half cell at which reduction takes place is known as cathode. Anode has negative potential while cathode has positive potential with respect to solution.
- There is a potential difference between the two electrodes which is known as cell potential. Its unit is volt. Electrons flow from negative to positive electrode when switch is on.
- The direction of flow of current is opposite to the electron flow.
- A galvanic cell is represented by drawing a vertical line between two electrolytes connected by salt bridge.
- The emf of cell is as follows:

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

- Cell reaction-

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

- Half-cell reactions-

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

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

The cell can be represented as follows:

$Cu(s)\ \text{I}\ Cu^{+2}\ (aq)\ \text{II}\ Ag^{+}(aq)\ \text{I}\ Ag(s)$

$$E_{cell} = E_{right} - E_{left} = E_{Ag+\ I\ Ag} - E_{Cu+2\ I\ Cu}$$

Measurement of electrode potential-

- A half-cell is known as standard hydrogen electrode represented by –

  $Pt(s)\ \text{I}\ H_2(g)\ \text{I}\ H^{+}(aq)$

- It has zero potential at all temperatures corresponding to this reaction-

$$H^{+}\ (aq) + e- \rightarrow \frac{1}{2} H_2\ (g)$$

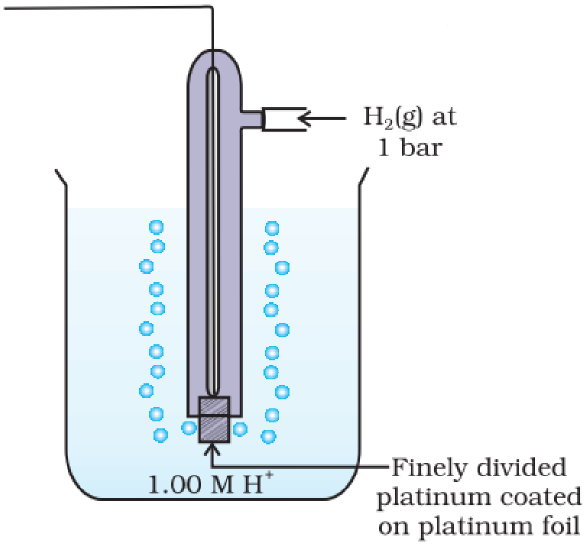

Figure: Standard Hydrogen Electrode

- The standard hydrogen electrode is made of platinum electrode which is coated with platinum black.
- The electrode is dipped in acidic solution and pure hydrogen gas is liberated in the form of bubbles.
- The pressure of hydrogen gas is one bar. The concentration of hydrogen ion in the solution is 1 molar.
- At 298K temperature the emf of cell-

$$E^\ominus = E^\ominus_R - E^\ominus_L$$

For standard hydrogen electrode $E^\ominus_L$ is zero.

- The measured emf of the cell is 0.34V.

Pt(s) l H2(g, 1 bar) l H^+ (aq, 1 M) ll Cu^{2+} (aq, 1 M) l Cu

The corresponding half-cell reaction-

Cu^{+2} (aq, 1M) + 2e- → Cu(s)

- The measured emf of the other cell is -0.76V.

Pt(s) l H2(g, 1 bar) l H^+ (aq, 1 M) ll Zn^{2+} (aq, 1 M) l Zn

The corresponding half-cell reaction-
Zn^{+2} (aq, 1M) + 2e- → Zn(s)

- The half reaction for the Daniell cell can be written as

At left electrode - Zn(s) + Cu^{2+} (aq) → Zn^{2+} (aq) + Cu(s)
At right electrode – Cu^{2+} (aq, 1M) + $2e^-$ → Cu(s)

- The overall reaction of cell:

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

emf of cell = $E^\ominus_{cell} = E^\ominus_R - E^\ominus_L$

= 0.34V – (- 0.76) V = 1.10V

- **In case of inert electrode –** platinum or gold is used as inert electrode. They do not participate in the reaction.

Example- Hydrogen electrode (platinum is used)

$Pt(s) \mid H_2(g) \mid H^+(aq)$

Half reaction: $H^+ (aq) + e^- \rightarrow \frac{1}{2} H_2 (g)$

Bromine electrode: $Pt(s) \mid Br_2(aq) \mid Br^- (aq)$

With half reaction: $\frac{1}{2} Br_2 (aq) + e^- \rightarrow Br^- (aq)$

Standard electrode potential

- Standard electrode potential helps to extract useful information about electrochemical reaction and electrode properties.
- **Case – I** if standard electrode potential > 0, this means the reduced form of electrode metal ion species is more stable compared to hydrogen gas.
- **Case – II** if standard electrode potential is negative, this means hydrogen gas is more stable than the reduced form of the species.
- The fluorine gas has the maximum tendency to get reduced to fluoride ions (F^-), thus fluorine gas is a strong oxidizing agent.
- Lithium has lowest electrode potential means it is a powerful reducing agent.
- **Standard electrode potential ∝ Oxidizing power ∝ 1/Reducing power**

Table: Standard Electrode Potential at 298K

Reaction (oxidized form + ne⁻ → Reduced form)		$E^\ominus/V$
$F_2(g) + 2e^-$	$\rightarrow 2F^-$	2.87
$Co^{3+} + 1e^-$	$\rightarrow Co^{2+}$	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
$Cr_2O_7^{2-} + 14H^+ + 6e^-$	$\rightarrow 2Cr^{3+} + 7H_2O$	1.33
$O_2(g) + 4H^+ + 4e^-$	$\rightarrow 2H_2O$	1.23

$MnO_2(s) + 4H^+ + 2e^-$	$\rightarrow Mn^{2+} + 2H_2O$	1.23
$Br_2 + 2e^-$	$\rightarrow 2Br^-$	1.09
$NO_3^- + 4H^+ + 3e^-$	$\rightarrow NO(g) + 2H_2O$	0.97
$2Hg^{2+} + 2e^-$	$\rightarrow Hg_2^{2+}$	0.92
$Ag^+ + 1e^-$	$\rightarrow Ag(s)$	0.80
$Fe^{3+} + 1e^-$	$\rightarrow Fe^{2+}$	0.77
$O_2(g) + 2H^+ + 2e^-$	$\rightarrow H_2O_2$	0.68
$I_2 + 2e^-$	$\rightarrow 2I^-$	0.54
$Cu^+ + 1e^-$	$\rightarrow Cu(s)$	0.52
$Cu^{2+} + 2e^-$	$\rightarrow Cu(s)$	0.34
$AgCl(s) + 1e^-$	$\rightarrow Ag(s) + Cl^-$	0.22
$AgBr(s) + 1e^-$	$\rightarrow Ag(s) + Br^-$	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
$Ni^{2+} + 2\ e^-$	$\rightarrow Ni(s)$	-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
$Na^+ + 1e^-$	$\rightarrow Na(s)$	-2.71
$Ca^{2+} + 2e^-$	$\rightarrow Ca(s)$	-2.87
$K^+ + 1e^-$	$\rightarrow K(s)$	-2.93
$L^+ + 1e^-$	$\rightarrow Li(s)$	-3.05

Ions are present as aqueous species and H_2O as liquid: gases and solids are shown by g and s.

Nernst Equation

- According to Nernst the electrode reaction is:

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

The electrode potential measured at any concentration wrt standard hydrogen electrode:

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

If concentration of Solid M =1

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

Here R = gas constant = 8.314 JK^{-1} mol^{-1}

F = Faraday constant = 96487 C mol^{-1}

T = temperature in kelvin

$[M^{n+}]$ = Concentration of species, M^{n+}

For a general electrochemical reaction:

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

The Nernst equation can be written as:

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

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

Example: The following reaction takes place in a cell:

$Mg(s) + 2Ag+ (0.0001M) \rightarrow Mg^{2+(}0.130M) + 2Ag(s)$

Calculate its $E_{(cell)}$ if $E^{\ominus}_{(cell)} = 3.17$ V

The cell can be written as Mg^{2+} I Mg^{2+}(0.130M) II Ag^{+}(0.0001M) I Ag

$$E_{(cell)} = E^{\ominus}_{(cell)} - \frac{RT}{2F} \ln \frac{[Mg^{2+}]}{[Ag^{+}]^2}$$

$$= 3.17\ V - \frac{0.059V}{2} \log \frac{0.130}{(0.0001)^2}$$

$$= 3.17\ V - 0.21V = 2.96\ V$$

Equilibrium constant from Nernst Equation

- In a Daniell cell if the circuit is closed then the reaction is:

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

The concentration of Zn^{2+} increases as the reaction time passes. The concentration of Cu^{2+} decreases.

- When the equilibrium attained, there is no change in concentration of Zn^{2+} and Cu^{2+}. The Nernst equation is:

$$E_{(cell)} = 0 \quad = E^{\theta}_{(cell)} - \frac{2.303RT}{2F} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

Or

$$E^{\theta}_{(cell)} - \frac{2.303RT}{2F} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

At equilibrium

$$\frac{[Zn^{2+}]}{[Cu^{2+}]} = K_c$$

At T= 298K the above reaction can be written as:

$$E^{\theta}_{(cell)} = \frac{0.059}{2} \log K_c = 1.1V$$

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

$$K_c = 2 \times 10^{37} \text{ at } 298K$$

In general

$$\mathbf{E^{\theta}_{(cell)} = \frac{2.303RT}{nF} \log K_c}$$

Example: Calculate the equilibrium constant of the reaction:

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

$E^\ominus_{(cell)} = 0.46\ V$

Solution: $E^\ominus_{(cell)} = \frac{0.059}{2} \log K_c = 0.46V$

$\log K_c = \frac{0.46V \times 2}{0.059V} = 15.6$

$K_c = 3.92 \times 10^{15}$

Electrochemical cell and Gibbs energy of the reaction:

- The electrical potential multiplied by total charge passed is equal to the electric work done in one second.
- If charge is passed reversibly then maximum work can be obtained from galvanic cell. The decrease in Gibbs energy is equal to reversible work done by the galvanic cell.

$$\Delta_r G = -nFE_{(cell)}$$

Here E = the emf of the cell
nF = the amount of charge passed
$\Delta_r G$ = the Gibbs energy of the reaction

- For the reaction

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

$$\Delta_r G = -2FE_{(cell)}$$

- When we write the reaction

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

$$\Delta_r G = -4FE_{(cell)}$$

- If the concentration of all the reacting species is unity, then

$$E_{(cell)} = E^\ominus_{(cell)}$$

$$\mathbf{\Delta_r G^\ominus = - nFE^\ominus_{(cell)}}$$

- We can calculate equilibrium constant

$$\mathbf{\Delta_r G^\ominus = - RT \ln K}$$

Example: The standard electrode potential for Daniell cell is 1.1V. Calculate the standard Gibbs energy for the following reaction –

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

Solution: F = 96487C mol^{-1}
$E^\ominus_{(cell)}$ = 1.1V
n = 2
$\mathbf{\Delta_r G^\ominus = - nFE^\ominus_{(cell)}}$
= 2 x 1.1 x 96487
= 21227 J mol^{-1}
$\Delta_r G^\ominus$ = - 212.27 kJ mol^{-1}

Conductance of electrolytic solutions

- The electrical resistance is represented by **R** and measured in ohms (**Ω**). In terms of SI unit **Ω** is equal to kg m^2. Electrical resistance can be measured by Wheatstone bridge.
- The electrical resistance is inversely proportional to its area of cross section and directly proportional to its length.

$$\mathbf{R \propto \frac{l}{A}}$$

$$\mathbf{R = \rho \frac{l}{A}}$$

- The proportionality constant = ρ = rho; it is known as resistivity or specific resistance.
- SI unit of resistivity is **Ω m.**
- 1 Ω m = 100 Ω cm ; 1 Ω cm = 0.01 Ω m
- The reciprocal of resistance is known as conductance. It is denoted by **G.**

$$\mathbf{G = 1/R}$$

$$\mathbf{G = A/ \rho l}$$

$$G = K\frac{A}{l}$$

- The unit of conductance is **siemens (S)**.

$$\textbf{Siemens} = S = ohm^{-1} = \Omega^{-1}$$

- The reciprocal of resistivity is known as conductivity; represented by **K** kappa. The SI unit of conductivity is S m^{-1}.

Table: The value of conductivity of some materials at 298K temperature

Material	Conductivity (S m^{-1})
Conductors	
Sodium	$2.1x10^3$
Copper	$5.9x10^3$
Silver	$6.2x10^3$
Gold	$4.5x10^3$
Iron	$1.0x10^3$
Graphite	1.2x10
Insulators	
Glass	$1.0x10^{-16}$
Teflon	$1.0x10^{-18}$
Aqueous Solutions	
Pure water	$3.5x10^{-5}$
0.1M HCl	3.91
0.01M KCl	0.14
0.01M NaCl	0.12
0.1M HAc	0.047
0.01M HAc	0.016
Semiconductors	
CuO	$1x10^{-7}$
Si	$1.5x10^{-2}$
Ge	2.0

- In metals the electric conductance is known as metallic or electronic conductance. The electronic conductance depends on following:
  1. The structure and nature of the metal
  2. The number of valence electrons present in an atom
  3. Temperature.

- The conductance of electricity by ions present in the solutions is known as ionic or electrolytic conductance. The conductivity of electrolytic solution depends on following:
  1. Nature of the electrolyte added
  2. Solvation and size of ions produced
  3. Electrolyte concentration
  4. Temperature

Molar conductivity

- The conductive power of all the ions produced by dissolving 1g mol of electrolyte in solution.

$$\Lambda_m = \frac{K}{C}$$

Here Λ_m = Molar conductivity (Unit = S m^2 mol^{-1})

C = the concentration in mol m^{-3}

1 mol m^{-3} = 1000(L/m^3) x molarity (mol/L)

$$\Lambda_m = \frac{K\ (S\ cm^{-1}) \times 1000}{\text{molarity}}$$

Example: the electric resistance of a column of 0.05mol L^{-1} NaOH solutions of diameter 1cm and length 50cm is 5.55 x10^3 ohm. Calculate the resistivity molar conductivity and conductivity.

Solution:

$A = \pi r^2 = 3.14 \times (0.5)^2 = 0.785 \times 10^{-4}\ m^2$

l = 50cm = 0.5 m

$$R = \frac{\rho\, l}{A}$$

$$\rho = \frac{R\, A}{l} = \frac{5.55 \times 10^3 \times 0.785}{50} = 87.135\ \Omega\ cm$$

Conductivity = K = 1/ρ = 1/87.135 = 0.01148 S cm^{-1}

$$\text{Molar conductivity} = \frac{K \times 1000}{c} = \frac{0.01148 \times 1000}{0.05} = 229.6 \text{ S cm}^2 \text{ mol}^{-1}$$

- Molar conductivity and conductivity change with the concentration of the electrolyte.

Conductivity ∝ Concentration of electrolyte

For strong electrolytes

$$\Lambda_m = \Lambda^\circ_m - A\, c^{1/2}$$

Here Λ°_m = limiting molar conductivity
A = constant for a given solvent and temperature depends on the type of electrolyte (charge on the cation and anion produced by dissociation of electrolyte)
c = concentration of electrolyte

According to 'Kohlrausch law of independent migration of ions' if an electrolyte dissociates into v_+ cations and v_- anions then its limiting molar conductivity is:

$$\Lambda^\circ_m = v_+ \lambda^\circ_+ + v_- \lambda^\circ_-$$

Here λ°_+ and λ°_- are limiting molar conductivities of cations and anions respectively.

Table: limiting Molar conductivities for some ions in water at 298 K

Ion	λ° (S cm^2 mol^{-1})
H^+	349.6
Na^+	50.1
K^+	73.5
Ca^{+2}	119.0
Mg^{+2}	106.0
OH^-	199.1
Cl^-	76.3
Br^-	78.1
CH_3COO^-	40.9
SO_4^{2-}	160.0

For weak electrolytes

$$\alpha = \frac{\Lambda_m}{\Lambda^\circ_m}$$

Here α = degree of dissociation
Λ°_m = limiting molar conductivity
Λ_m = molar conductivity

For a weak electrolytes like acetic acid -

$$K_a = \frac{c\alpha^2}{(1-\alpha)} = \frac{c\Lambda_m^2}{\Lambda_m^{\circ 2}\left(1-\frac{\Lambda_m}{\Lambda_m^\circ}\right)} = \frac{c\Lambda_m^2}{\Lambda_m^\circ\left(\Lambda_m^\circ - \Lambda_m\right)}$$

Example: Calculate Λ°_m for $CaCl_2$ and $MgSO_4$.
Solution: according to Kohlrausch law

$$\Lambda^\circ_{m(CaCl2)} = \lambda^\circ_{Ca2^+} + 2\,\lambda^\circ_{Cl^-}$$
$$=119.0 + 2(76.3)$$
$$= 271.6\ S\ cm^2\ mol^{-1}$$

$$\Lambda^\circ_{m(MgSO4)} = \lambda^\circ_{Mg^{2+}} + 2\,\lambda^\circ_{SO4^{-2}}$$
$$= 106.0 + 160.0$$
$$= 266\ S\ cm^2\ mol^{-1}$$

Electrolytic cells and Electrolysis

- The electrochemical reaction is initiated by external voltage.
- A simple electrolytic cell is made of two Cu strips dipped in an aqueous solution of copper sulphate. When DC voltage applied the Cu^{2+} discharge at cathode through following reaction:

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

  Copper metal is deposited on the cathode.
- At the anode, copper is converted into Cu^{2+} ions, through following reaction:

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

  Thus copper is deposited at the cathode and dissolved at anode.

- This is an industrial method to convert impure copper into pure copper.
- Many metals like sodium, magnesium and aluminum, etc. are purified at large scale by this method.

Quantitative aspects of electrolysis

- Quantitative aspects of electrolysis were first described by Michael Faraday.

Faraday's laws of electrolysis- Faraday investigated the electrolysis of various solutions and propounded two laws of electrolysis:

1. **First Law-** During electrolysis the amount of chemical reaction taking place at any electrode by a current is proportional to the quantity of electricity passed through the electrolyte.

2. **Second Law-** The amounts of different substances liberated by the same amount of electricity passed through the electrolytic solution are directly proportional to their chemical equivalent weights.

$$\mathbf{Q = It}$$

Here Q = the amount of electricity in coulombs
I = constant current in ampere
t = time in second

- The quantity of electricity needed to oxidize or reduce the metal species of the electrode depends upon the stoichiometry of the electrode reaction. For example:

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

Here for the reduction of one mole of silver ions one mole of the electron is required.

- The charge on one mole of electrons :

$$N_A \times \text{charge on one electron} = N_A \times 1.6021 \times 10^{-19}\ C$$
$$= 6.02 \times 10^{23}\ mol^{-1} \times 1.6021 \times 10^{-19}\ C$$
$$= 96487\ C\ mol^{-1}$$

The charge on one mole of electrons is called Faraday. It is represented by symbol 'F'.

$$1F \cong 96500 \text{ C mol}^{-1}$$

- The amount of substance deposited at electrodes is directly proportional to the current.

$$W \propto q$$
$$W \propto it$$
$$W = Zit$$

Here W = amount of substance deposited at the electrode
i = Electric current in ampere
t = time in sec
Z = the electrochemical equivalent (Atomic Mass of metal/number of electrons required to reduce the cation)

Example: A solution of copper sulphate is electrolyzed 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 seconds
Charge = ixt = 1.5 A x 600 sec = 900 C
The electrochemical reaction:

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

Here two faradays are required to deposit the 1 mol of copper i.e 63 g of copper.
The mass of copper deposited = 63 x 900 x 2 x 96487 = 0.2938 g.

Batteries –

- We use battery or cell as a source of electrical energy.
- It is a galvanic cell where the chemical energy produced by redox reaction is converted into electrical energy.
- A battery should be compact, lightweight and its voltage should not fluctuate during use.

1. Primary Batteries –

- In this type of batteries, the chemical reaction occurs only once and after use over a period of time battery becomes dead and cannot be reused again.

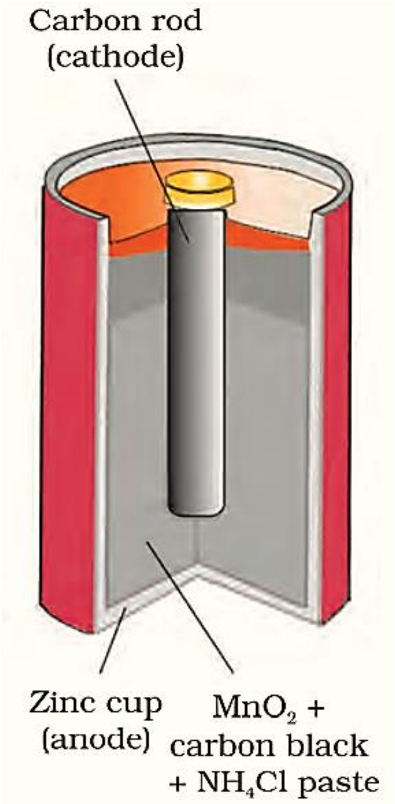

Figure: A commercial dry cell consists of a graphite/carbon cathode in a zinc container which is act as the anode

- The most familiar example of this type is the dry cell (known as Leclanche cell after its discoverer) which is used commonly in our transistors and clocks.
- The cell consists of a zinc container that also acts as anode and cathode is a carbon (graphite) rod surrounded by powdered manganese dioxide and carbon.
- The space between the electrodes is filled by a moist paste of ammonium chloride and zinc chloride.
- The electrode reaction is as follows:

Cathode: $MNO_2 + NH_4^+ + e^- \rightarrow MnO(OH) + NH_3$

Anode: $Zn(s) \rightarrow Zn^{2+} + 2e^-$

- Here in the reaction Mn is reduced to +3 from +4. Ammonia evolve in the reaction combine with Zn2+ to give $[Zn(NH_3)_4]^{2+}$.
- The cell has a potential $\sim 1.5V$.

Mercury Cell –

- Mercury cell is suitable for low current devices like watches, hearing aids, etc.
- It is consists of Zn-Hg amalgam as anode and a paste of mercuric oxide and carbon as cathode.
- A paste of KOH and ZnO is act as an electrolyte.
- The electrode reaction is as follows:

Anode: $Zn(Hg) + 2OH^- \rightarrow ZnO(s) + H_2O + 2e^-$

Cathode: $HgO + H_2O + 2e^- \rightarrow Hg(l) + 2OH^-$

- The overall reaction is as follows:

$$Zn(Hg) + HgO(s) \rightarrow ZnO(s) + Hg(l)$$

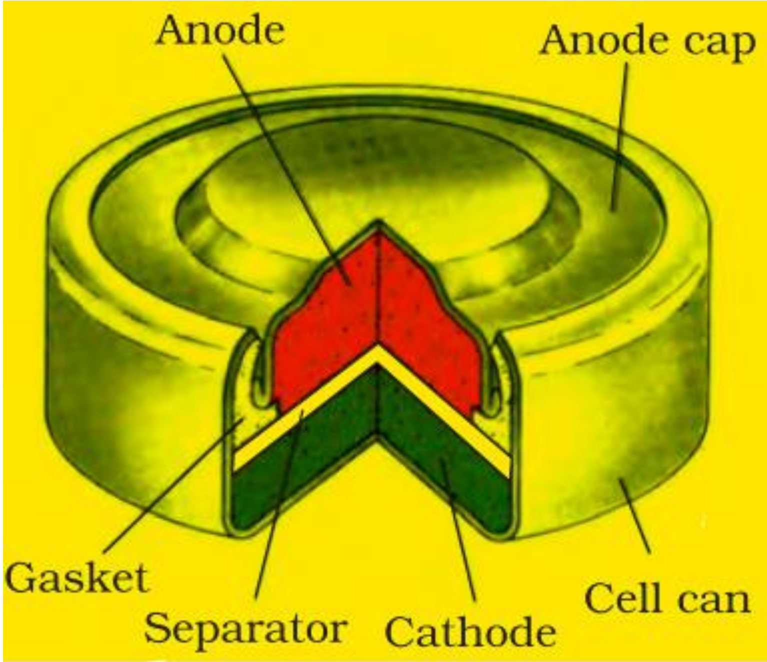

Figure: mercury cell

- The cell potential is ~1.35 V. It remains constant during its life as the overall reaction does not involve any ion in solution whose concentration can change during its life time.

2. Secondary batteries –

- A secondary cell after use can be recharged by passing current in the opposite direction through it so that it can be reused.
- A good secondary cell can undergo a large number of discharging and charging cycles. The most important secondary cell is the lead storage battery.

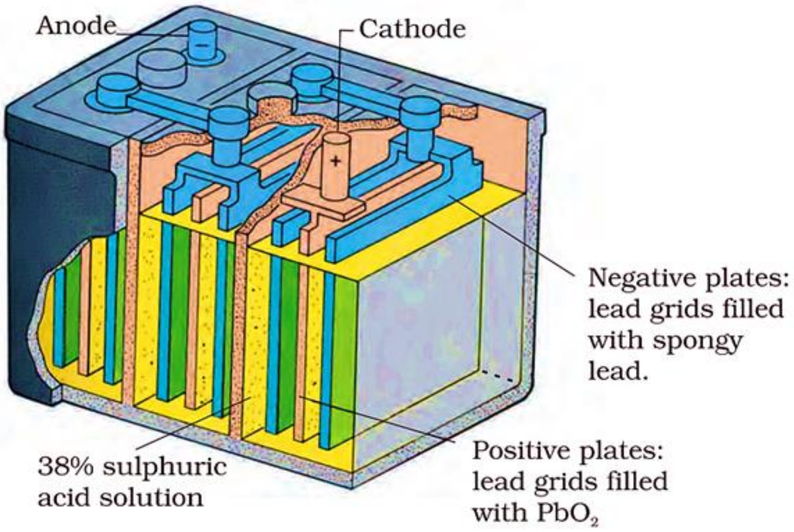

Figure: the lead storage battery

- It is used in automobiles and invertors.
- It consists of a lead anode and a grid of lead packed with lead dioxide as cathode. A 38% solution of H_2SO_4 is used as an electrolyte.
- The cell reactions when the battery is in use are given below:

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

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

- The cell reaction consisting of cathode and anode reactions is:

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

- On charging the battery the reaction is reversed and lead sulphate on anode and cathode is converted into Pb and PbO2, respectively.

Nickel-cadmium cell

- It has longer life than the lead storage cell but it is more expensive to manufacture.
- It is rechargeable cell in a jelly roll arrangement and separated by a layer soaked in moist sodium or potassium hydroxide.
- The overall electrode reaction during discharge is:

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

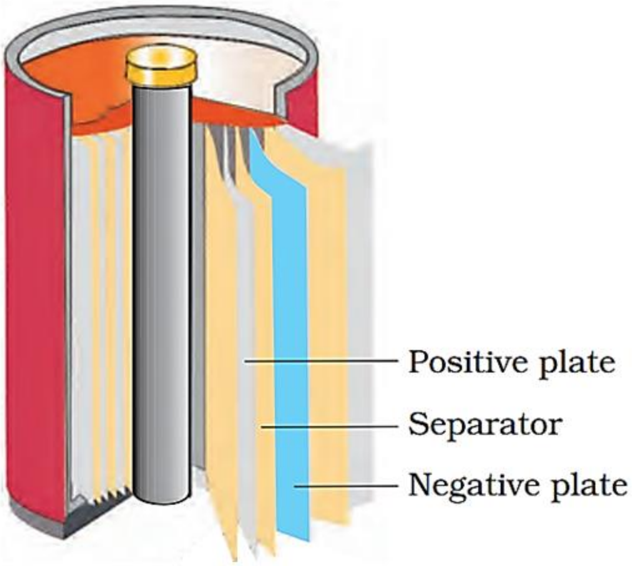

Figure: Ni-Cd cell

Fuel Cell –

- The chemical energy (i.e. heat of combustion) of fossil fuels like coal, gas or oil; is first used for converting water into high pressure steam. Then it is used to run a turbine to produce electricity in plants.
- A galvanic cell directly converts chemical energy into electricity and it is highly efficient.
- It is now possible to make such cells in which reactants are fed continuously to the electrodes and products are removed continuously from the electrolyte compartment.
- Galvanic cells that are designed to convert the energy of combustion of fuels like H_2, CH_4, CH_3OH etc. directly into electrical energy are called fuel cells.
- One of the most successful fuel cells uses the reaction of hydrogen with oxygen to form water.
- This cell was used for providing electrical power in the Apollo space Programme. The water vapors produced during the reaction were condensed and added to the drinking water supply for the astronauts.
- In the cell, hydrogen and oxygen are bubbled through porous carbon electrodes into concentrated aqueous NaOH solution.
- Catalysts like finely divided Pt or Pd metal are incorporated into the electrodes for increasing the rate of electrode reactions.

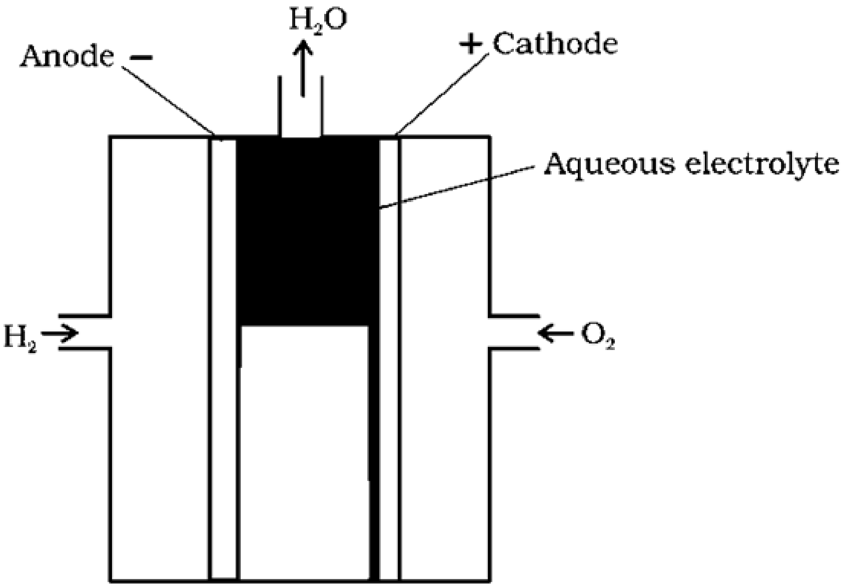

Figure: Fuel cell

- The electrode reactions are given below:
  Cathode: O_2 (g) + $2H_2O$(l) + $4e^-$ → $4OH^-$ (aq)

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

  Overall reaction being:

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

- The cell runs continuously as long as the reactants are supplied.
- Fuel cells produce electricity with an efficiency of approximately 70 % compared to thermal plants whose efficiency is approximately 40%.
- Fuel cells are pollution free.

Corrosion –

- Corrosion slowly coats the surfaces of metallic objects with oxides or other salts of the metal.
- The rusting of Fe, tarnishing of Ag, development of green coating on Cu and bronze are some of the examples of corrosion.
- It causes enormous damage to buildings, bridges, ships and to all objects made of metals especially that of iron.
- In corrosion, a metal is oxidized by loss of electrons to oxygen and formation of oxides. Corrosion of iron (i.e. rusting) occurs in presence of water and air.

- It is an electrochemical phenomenon. At a particular spot of an object made of iron, oxidation takes place and that spot behaves as anode.
- The reaction is as follows:

  Anode: $2Fe\ (s) \rightarrow 2\ Fe^{2+} + 4\ e^{-}$ **$E^{\ominus}$**$_{(Fe2+/Fe)} = -0.44$ V

- Electrons released at anodic spot move through the metal and go to another spot on the metal and reduce oxygen in the presence of H^+ (which is believed to be available from H_2CO_3 formed due to dissolution of CO_2 from air into water. H^+ in water may also be available due to dissolution of other acidic oxides from the atmosphere). This spot behaves as cathode with the reaction following reaction:

  Cathode: $O_2(g) + 4\ H^+\ (aq) + 4\ e^{-} \rightarrow 2\ H_2O\ (l)$ **$E^{\ominus}$** $_{H+I\ O2\ I\ H2O} = 1.23$ V

  The overall reaction is:

  $2Fe(s) + O_2\ (g) + 4H^+\ (aq) \rightarrow 2Fe^{2+}(aq) + 2\ H_2O\ (l)$ **$E^{\ominus}$** (cell) = 1.67 V

- The ferrous ions are further oxidized 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 hydrogen ions.
- Prevention of corrosion is of prime importance. It not only saves money but also helps in preventing accidents such as a bridge collapse or failure of a key component due to corrosion.
- One of the simplest methods of corrosion prevention is to prevent the surface of the metallic object to come in direct contact with atmosphere. This can be done by covering the surface with paint or by some chemicals like bisphenol.
- Another simple method is to cover the surface by other metals (Sn, Zn, etc.) that are inert or react to save the object.
- An electrochemical method is to provide a sacrificial electrode of another metal like Mg, Zn, etc.; which corrodes itself but saves the object.