Electrochemistry

- The amount of substance liberated or deposited at an electrode is directly proportional to the quantity of electricity passed through the solution.

$$W = Z * I * t$$

Where:
Z= electrochemical equivalent of the substance
I= current in amperes
t= time in seconds

- Conversion of electrical energy to chemical energy and vice versa is known as **electrochemistry**.
- Based on this there are two types of cells namely: **Electrolytic cell** and **Electrochemical cell**.
- A cell consists of two electrodes dipped in their respective electrolytes. Each electrode and its electrolyte acts as one **half cell**.
- In one half cell **oxidation** occur and is known as **Anode** whereas in the other half cell **reduction** occurs and is known as **Cathode**.

- The two electrolytes are connected by a **salt bridge** or a **porous pot**. This whole assembly is known as **Galvanic Cell or Voltaic cell**.
- A **battery** is the combination of two or more **galvanic cells** arranged in **series** or **parallel.**

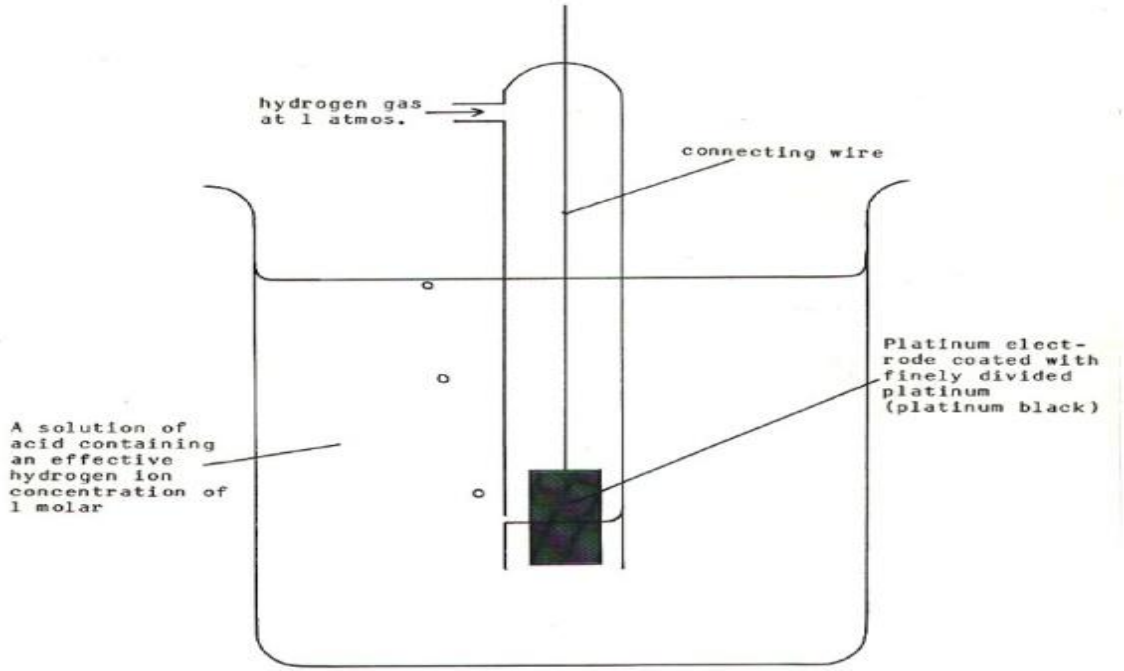
- **STANDARD ELECTRODE POTENTIAL** $[E^0]$is the ease with which an electrode can loose or gain electrons when it is in contact with its own ions of unit activity at 298K.
- **Positive value of emf means the reaction is spontaneous** i.e. the cell will operate spontaneously.
- If two different electrodes are connected to form a galvanic cell then one with higher positive reduction potential acts as **cathode** and the other as **anode**.
- Informations conveyed by reduction potential:
  1) Lower the reduction potential stronger will be the reducing agent.
  2) Higher the reduction potential stronger will be the oxidation agent.
  3) Element with lower value of reduction potential with replace the element with higher value from its salt solution.
  4) Element with negative reduction potential will displace di-hydrogen from acids.

NORMAL HYDROGEN ELECTRODE (NHE) or STANDARD HYDROGEN ELECTRODE:

It's a reference electrode having reduction potential 0.00V.

It consists of a platinum electrode coated with platinum black dipped in 1 molar acidic solution. Hydrogen gas under the pressure of 1atm is passed in the solution at 298K.

FIG. 11.12. A diagram of a standard hydrogen electrode



DEPENDANCE OF ELECTRODE POTENTIAL ON CONCENTRATION OF ELECTROLYTE AND TEMPERATURE.
This is also called NERNST EQUATION.

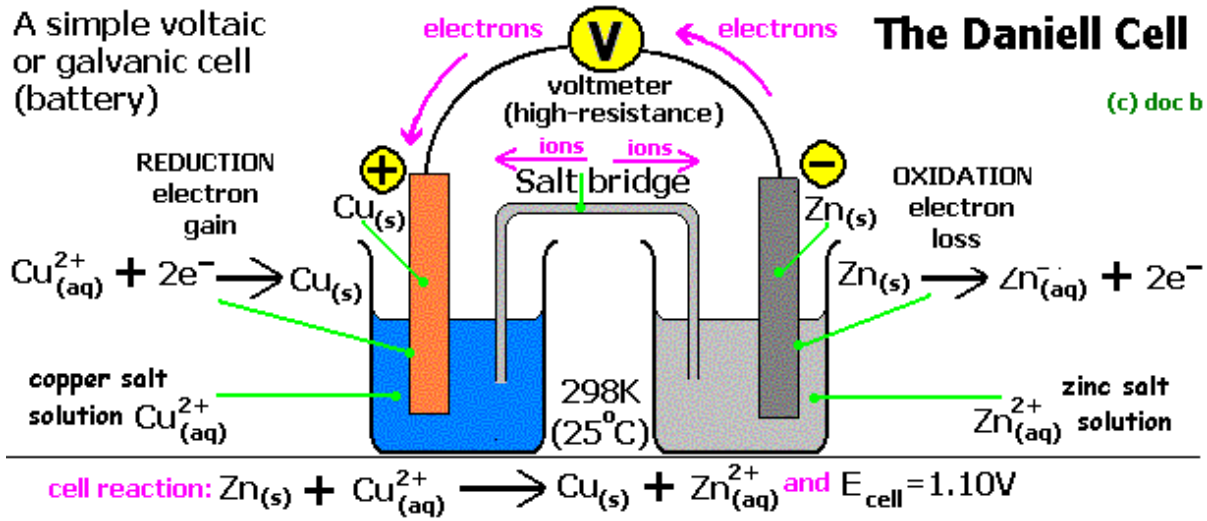
$$E = E^0 - (\left(\frac{2.303RT}{n}\right)\log\left(\frac{1}{[\mathrm{M^{n+}}]}\right))$$

At 298K the equation is modified as:

$$E = E^0 - (\left(\frac{0.0591RT}{n}\right)\log\left(\frac{1}{[\mathrm{M^{n+}}]}\right))$$

Where:
E= electrode potential under given conditions
E^0= standard electrode potential
R= gas constant
T=temperature in Kelvin
F=1 Faraday (96500 C)
N=number of electrons involved in the reaction

Electrochemical cells or Galvanic cell or Voltaic cell:
It's a chemical device in which redox reactions take place indirectly and chemical energy is converted into electrical energy which appears in the form of electric current.
Eg: Daniel cell



Reaction in right beaker: (reduction half cell reaction)

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

Reaction in left beaker: (oxidation half cell reaction)

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

Cell reaction:

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

- Nature and function of SALT BRIDGE:
  1) Salt in salt bridge should be a strong electrolyte
  2) It should be inert towards 2 solutions. KCl and NaCl cant be used of the solution contains Ag+
  3) It maintains the neutrality of the 2 solutions

4) Completes the inner circuit
5) The 2 ions should have the same mobility ie ionic size.
6) The transport number of the 2 ions by the solution should be same. Transport number is the fraction of the total current carried by an ion.

EMF or the Electro Motive Force of a cell is the potential difference between 2 electrodes of the cell, when no current is drawn from the circuit i.e, circuit is open.

$$E^0_{cell} = E^0_{cathode} - E^0_{anode}$$

Its essential that E^0_{cell} is positive, only then the redox reaction will take place.
EMF of the cell can also be represented as:

$$E^0_{cell} = \left(\frac{2.303RT}{nF}\right) logKc$$

At 298K:

$$E^0_{cell} = \left(\frac{0.0591}{n}\right) logKc$$

Gibbs energy of the reaction:

$$\Delta G^0 = -nFE^0_{cell}$$

Where: $\Delta G^0 = 2.303RT * logKc$
CONDUCTANCE OF ELECTROLYTIC SOLUTIONS:

$$R \propto \left(\frac{l}{A}\right)$$

$$R = \left(\frac{\rho l}{A}\right)$$

Conductance (G) is the reciprocal of resistance (R)
Hence;

$$G = \left(\frac{1}{R}\right) = \left(\frac{A}{\rho l}\right) = \kappa\left(\frac{A}{l}\right)$$

Where: κ is the specific conductance or conductivity

Cell Constant: $\left(\frac{l}{A}\right) = \left(\frac{\kappa}{G}\right) = \kappa * R$

Molar conductance at a given dilution:

Its the total conductance offered by all the ions given by 1 mole of an electrolyte dissolved in given volume of solution.

$$\Lambda_m = \Lambda_m^0 - b\sqrt{c}$$

c=concentration of electrolyte

b=constant depending on the nature of solvent, electrolyte and temperature.

The above equation is valid for strong electrolytes.

Kohlrausch law of independent migration of ions:

"Each ion makes a definite contribution towards the total conductance irrespective of the nature of the other ion associated with it."

$$\Lambda_m^0 AB = \lambda^0 A^+ + \lambda^0 B^-$$

This is used for:

1) The molar conductance of a weak electrolyte at infinite direction.
2) Calculation of degree of dissociation of a weak electrolyte & dissociation constant.
3) Calculation of solubility of a sparingly soluble salt.
4) Calculation of ionic product of water.

Electrolytic cell and electrolysis:

Faradays law:

1) The amount of a substance deposited at an electrode is directly proportional to quantity of charge passed.

$$w \propto Q$$

w=amount of substance deposited on an electrode

Q=quantity of charge in Coulombs

Q=I*t;

I=current in amperes

t=time in seconds

2) When same quantity of charge is passed through the solution of different electrolytes the amounts of substances liberated at different electrodes are in the ratio of their equivalent weight.

$$\left(\frac{weight\ of\ A}{weight\ of\ B}\right) = \left(\frac{E * weight\ of\ A}{E * weight\ of\ B}\right)$$

Corrosion is also an electrochemical reaction.

All batteries are based on the electrochemical processes.

Sample Examples

- Find the charge in coulomb on 1 g-ion of N^{3-}

Solution: Charge on one ion of N^{3-}

$= 3 \times 1.6 \times 10^{-19}$ coulomb

Thus, charge on one g-ion of N^{3-}

$= 3 \times 1.6\ 10^{-19} \times 6.02 \times 10^{23}$

$= 2.89 \times 10^{5}$ coulomb

- How much charge is required to reduce (a) 1 mole of Al^{3+} to Al and (b)1 mole of to Mn^{2+}?

Solution: (a) The reduction reaction is

$Al^{3+} + 3e^{-} \rightarrow Al$

1 mole 3 mole

Thus, 3 mole of electrons are needed to reduce 1 mole of Al^{3+}.

Q = 3 × F

= 3 × 96500 = 289500 coulomb

(b) The reduction is

Mn_4^- + 8H+ $5e^-$ --> MN^{2+} + $4H_2O$

1 mole 5 mole

Q = 5 × F

= 5 × 96500 = 48500 coulomb

- How much electric charge is required to oxidise (a) 1 mole of H_2O to O_2 and (b)1 mole of FeO to Fe_2O_3?

Solution: (a) The oxidation reaction is

H_2O --> 1/2 O_2 + $2H^+$ + $2e^-$

1 mole 2 mole

$Q = 2 \times F$

$= 2 \times 96500 = 193000$ coulomb

(b) The oxidation reaction is

$$FeO + 1/2\ H_2O \rightarrow 1/2\ Fe_2O_3 + H^+ + e^-$$

$Q = F = 96500$ coulomb