ELECTRO CHEMSITRY

CONCEPT OF ELECTROCHEMISTRY

Electrochemistry is the study of chemical application.

Electrochemistry deals with the interactions between electrical energy and chemical energy.

These interactions are of two types

i) Conversion of electrical energy into chemical energy

ii) Conversion of chemical energy into electrical energy

Electrical Conductors: Substances which allows electric current through it.

Ex: Metals, graphite,fused salts,aqueous solutions of acids, bases & salts.

Types of conductors
- 1)electronic conductors
- 2)electrolytic conductors

Non conductors or Insulators: Substances which does not allows electric current through it.

Ex: Rubber, paper ,dry wood ,etc

METALLIC CONDUCTORS:

- Metallic conductors conduct electricity due to the movement of electrons from one end to another end.

- In a solid, the electrical conduction involves the free movement of electrons in the metallic lattice, without any movement of the lattice atom; this type of conduction is called metallic conduction.

- In metallic conductors, the electricity is carried by the electrons, the atomic nuclei remaining stationary.

These conductors are further sub classified in to three types.

A. **Good conductor**
B. **Semi- conductor**
C. **Non- conductor or Insulator**

Good conductor:

It is a substance, which conducts electricity fully and freely.

EX: Metals like Copper, Aluminum, and Iron.

Semi- conductor:

It is a substance, which partially conducts electricity.

EX: Silicon, Germanium.

Electrolytic conductors

- Substances in their fused form or in aqueous form allow the passage of current undergoing a simultaneous chemical transformation are called electrolytes and the conduction as the electrolytic conductance

- Reciprocal of resistance is called as conductance

- C = 1/ R Units = mho

- Resistance (R) of a conductor is directly proportional to it's length (l)& inversely proportional to area of cross section (a) $R \alpha l/a$

Difference between metallic and electrolytic conductors

Metallic conductors	**Electrolytic conductors:**
1. Conductance is due to the flow of electrons.	1. Conductance is due to the movement of ions in a solution.
2. It does not result any chemical change.	2. Chemical reactions take place at the electrodes.
3. Metallic conduction decreases with increase in temperature.	3. Electrolytic conduction increases with increase in temperature.
4. It does not involve any transfer of matter	4. It involves transfer of matter.

- **Specific conductance:** Specific conductance is the conductance of all the ions that are present in 1 ml solution.

$$K = \frac{l}{s} \times \frac{1}{R}$$

Units; ohm^{-1}cm^{-1}

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- **Equivalent conductance:** Equivalent conductance is the conductance of total ions present in a solution containing 1 g equivalent of electrolyte.

$$\wedge_{v} = \frac{K \times 1000}{N} = \frac{s.p\ conductance \times 1000}{N}$$

Units:ohm^{-1}cm^{2}equiv^{-1}

- **Molar conductance:** Molar conductance is the conductance of all the ions of 1 mole of electrolyte present in a solution.

$$\mu = \frac{K \times 1000}{M} = \frac{s.p\ conductance \times 1000}{M}$$

- Units: $\frac{ohm^{-1}cm^{-1}cm^{3}}{mole}$ = $ohm^{-1}cm^{2}mole^{-1}$

➢EFFECT OF DILUTION:

- Generally conductance depends on three factors
  1.number of ions

  2.charge of ions

  3.mobilityof ions

- As the dilution increases more, the electrolyte ionises more &specific conductance decreases.

- Equivalent &Molar conductance increases with dilution

ELECTROMOTIVE FORCE

Electromotive Force is the difference of potential, which causes the current to flow from an electrode at higher potential to the one of lower potential.

$E_{cell} = E_{(right)} - E_{(left)}$

E_{cell} EMF of the cell.

E_{right} reduction potential of right hand side electrode.

E_{left} reduction potential of left hand side electrode.

Applications of EMF measurement:-

1.Potentiometric titrations can be carried out.

2. Transport number of ions can be determined.

3. P^H can be measured.

4. Hydrolysis const. can be determined.

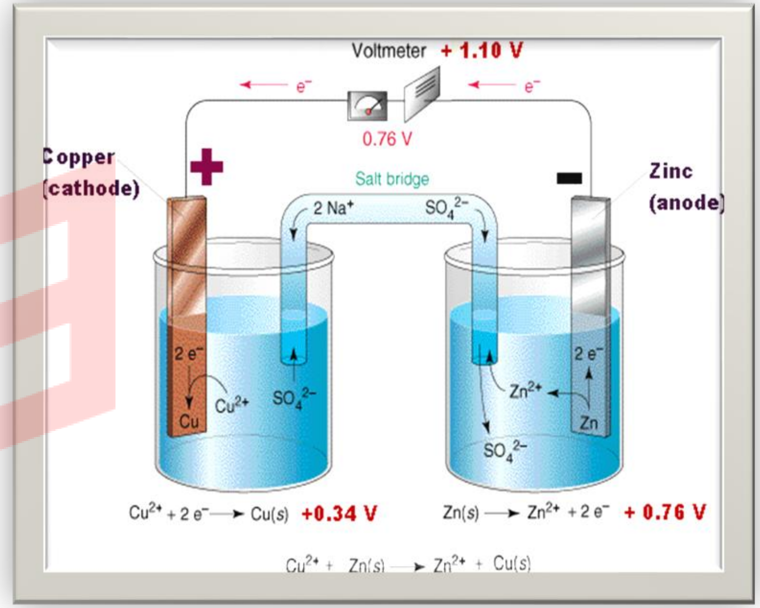
5. Solubility of sparingly soluble salts can be found.

GALVANIC CELL

It is a cell in which chemical energy is converted to electrical energy.
This cell consists of two half cells

1)Anodic half cell

2)Cathodic half cell



At anodic half cell, oxidation takes place
At cathodic half cell, reduction takes place

The following reactions take place in the cell.

At Anode:

$Zn \rightarrow Zn^{+2} + 2e^-$ (oxidation or de-elecronation)

At cathode:

$Cu^{+2} + 2e^- \rightarrow Cu$ (Reduction or electronatioin)

The movement of electrons from Zn to cu produces a current in the circuit.

The overall cell reaction is: $Zn + Cu^{+2} \rightarrow Zn^{+2} + Cu$

The galvanic cell can be represented by $Zn/znso_4//cuso_4/cu$

REFERENCE ELECTRODES

An electrode of known potential is called reference electrode.

Hydrogen electrode is the earliest primary reference electrode.

The secondary reference electrodes discussed here are

1)Calomel electrode

2)Quinhydrone electrode

Types of electrodes

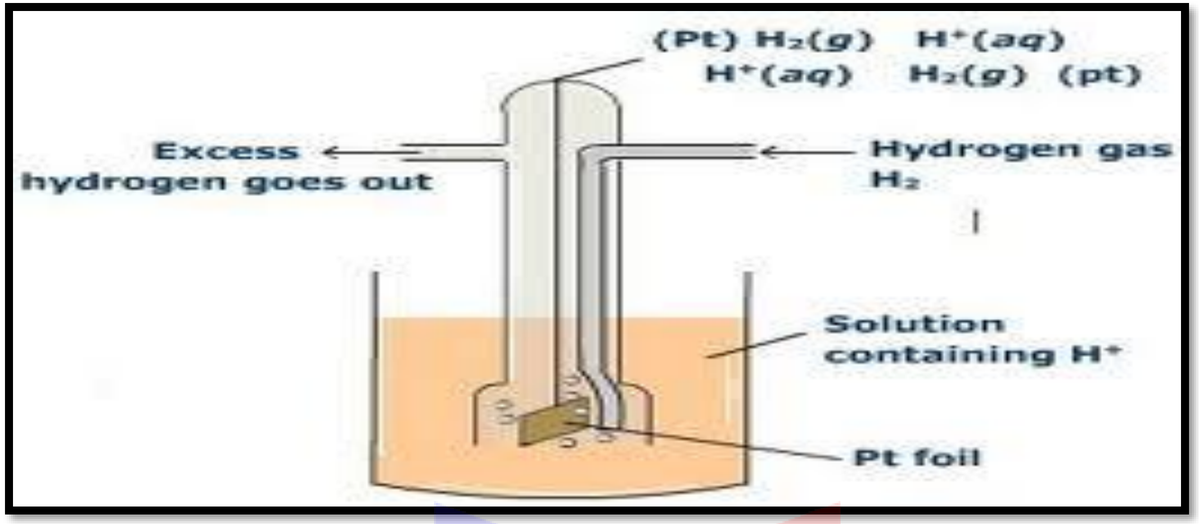
Primary & secondary reference electrodes :

- Standard hydrogen electrode(SHE):It is a primary reference electrode. The emf of such a cell is arbitrarily been fixed as zero.
- construction:

- It consists of a small platinum electrode coated with platinum black immersed in a 1M solution of H^+ ions maintained at 25^0c.

- Hydrogen gas at one atmosphere pressure enters the glass hood and bubbles over the platinum electrode.

- The H_2 gas at the platinum electrode passes into the solution forming H^+ ions & electrons. $H_2 \rightarrow 2H^+ + 2e^-$



- By convention the standard electrode potential of hydrogen electrode when the hydrogen gas passed at one atmosphere pressure is bubbled through a solution of hydrogen ions of unit concentration is orbitarily fixed as zero.

- Nernst equation:

At latm

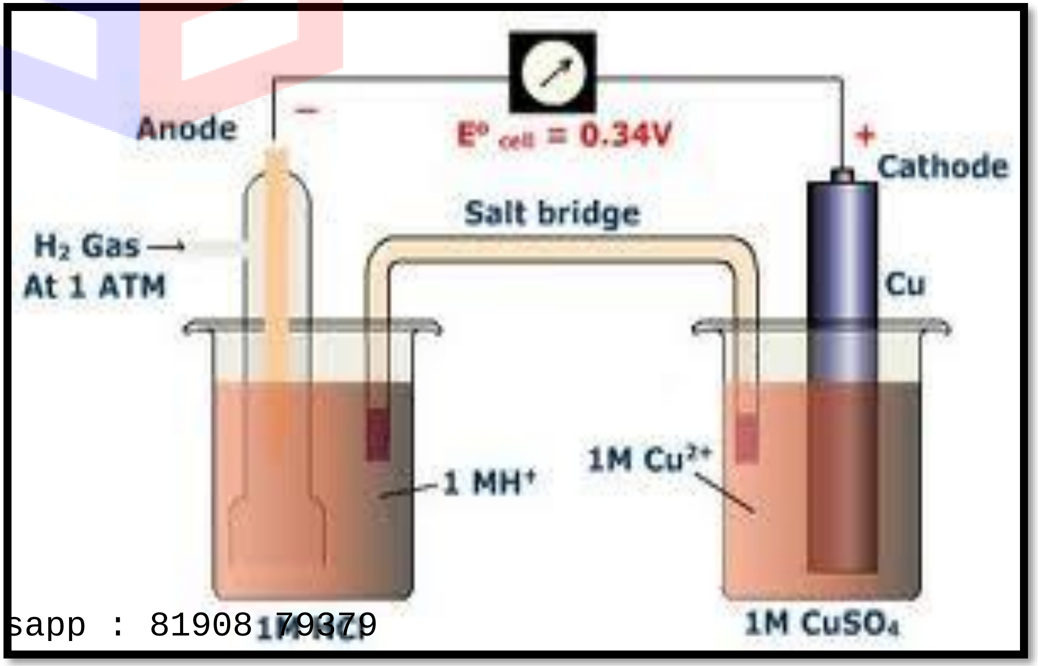
$$E_{pt,}H_{2/}H^{+} = E^{0}_{pt,}H_{2/H+} - \quad 0.059 \ \log \ a_{H+}$$

$$= E^{0}_{pt,} H_{2}/H^{+} \quad + 0.059 \ p^{H}$$

- Depending on a half cell to which it is attached hydrogen electrode can act as a cathode or an anode.

- But in the given figure hydrogen electrode is connected to copper electrode & it act as anode ,when it is acting as anode ,oxidation takes place.

- $1/2H_2(g)(1atm) \rightarrow H^+ (1M)+e$



Calomel electrode

The calomel electrode consists of a glass tube having two side tubes. A small quantity of pure mercury is placed at the bottom of the vessel and is covered with a paste of Hg and Hg_2Cl_2.

- KCl solution of known concentration is filled through side tube, Shown on the right side of the vessel.

- The KCl sol. is filled in the left side tube which helps to make a connection through a salt bridge with the other electrode, which potential has to be determined.

- A ‘pt’ wire is sealed into a glass tube as shown in the fig which is in contact with Hg.

- When the cell is set up it is immersed in the given solution.

The electrode potentials of calomel electrode of different concentrations at 25^0c are

0.1 M KCl/ Hg_2cl_2 (s) / Hg,pt → 0.33v

1M KCl / H g_2cl_2 (s) / Hg,pt → 0.28v

Saturated kcl /Hg_2 cl_2 (s) /Hg, pt → 0.24v

The corresponding electrode reaction is

$Hg_2\ Cl_2 + 2e^- \rightarrow 2Hg + 2cl^-$

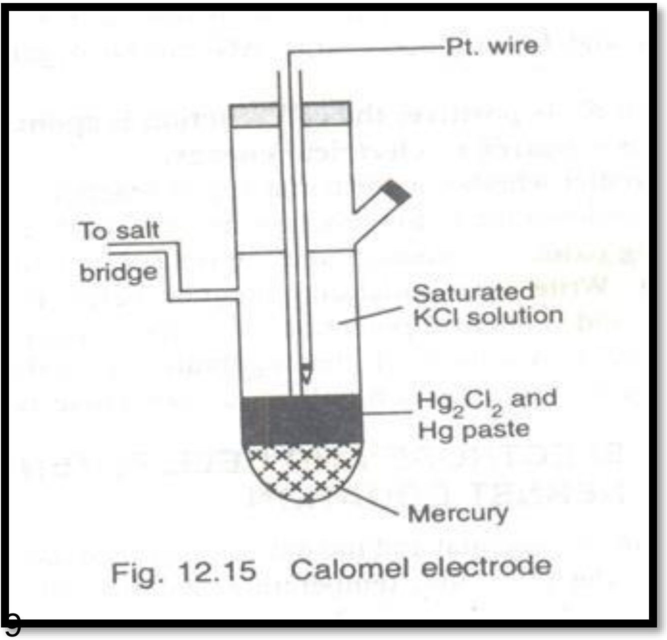


Fig. 12.15 Calomel electrode

Glass electrode

- Glass electrode is one of the type of ion selective electrode. (ISE). It is is made up of glass tube ended with small glass bulb sensitive to protons.

Glass electrode

- The tube has strong and thick walls and the bulb is made as thin as possible.

- Inside of the electrode is usually filled with buffered solution of chlorides in which silver wire is covered with AgCl is immersed. The pH of internal solution can be varies.

- In this electrode, active part of electrode is the glass bulb. The surface of the glass is protonated by both internal and external solution till equilibrium is achieved.

- Both sides of the glass are changed by the absorbed protons. And this charge is responsible for potential difference.

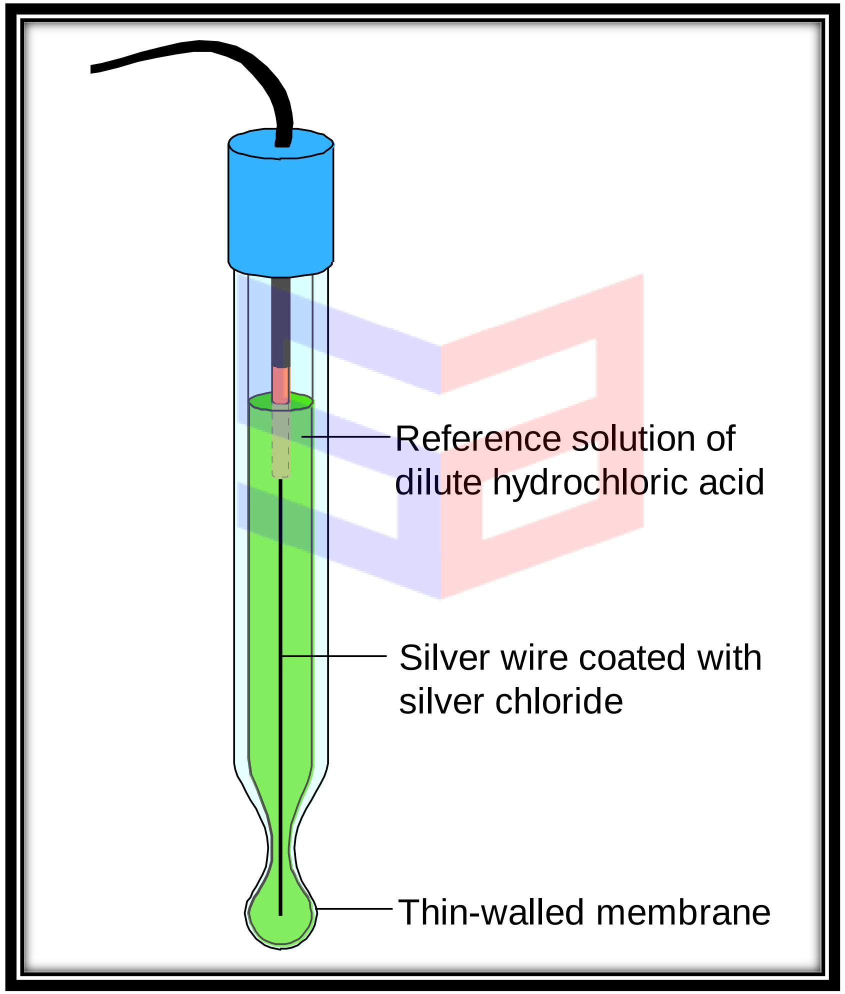
- This potential is directly proportional to the pH difference between the solutions on both sides of the glass.

- Glass electrode work in the pH range of 1-12 the glass electrode may be represented as

Ag, AgCl/ Hcl (0.1N) / glass / H^+ (unknown)

Here Ag/AgCl acts as internal reference electrode.

Glass electrode diagram



Nernst equation

- Nernst studied the theoretical relationship between electrode reaction and the corresponding cell e.m.f. This relationship generally Known as Nernst equation.

- Consider a galvanic cell aA + bB → cC + dD.

- Where a,b,c,d represents no. of moles respectively at equilibrium.

- The Nernst eq’ for the cell is written as

$$E_{cell} = E^0 - \frac{RT}{nF} \ln \frac{C^c}{A^a}\frac{D^d}{B^b}$$

$$E_{cell} = E^0 - 2.303\frac{\mathrm{RT}}{\mathrm{nF}}\log\frac{\mathrm{C^c}}{\mathrm{A^a}}\frac{D^d}{B^b}$$

In the above eq' R= 8.314 J/K. T=298K, F=96, 500 columbs.
By substituting the values in the eq'

$$E_{cell} = E^0 - 0.0591 \log\frac{\mathrm{C^c}}{\mathrm{A^a}}\frac{D^d}{B^b}$$

Applications:

1.It can be used to study the effect of electrolyte concentration on electrode potential.

2.the ph of the solution can be calculated from the measurement of emf and Nernst equation.

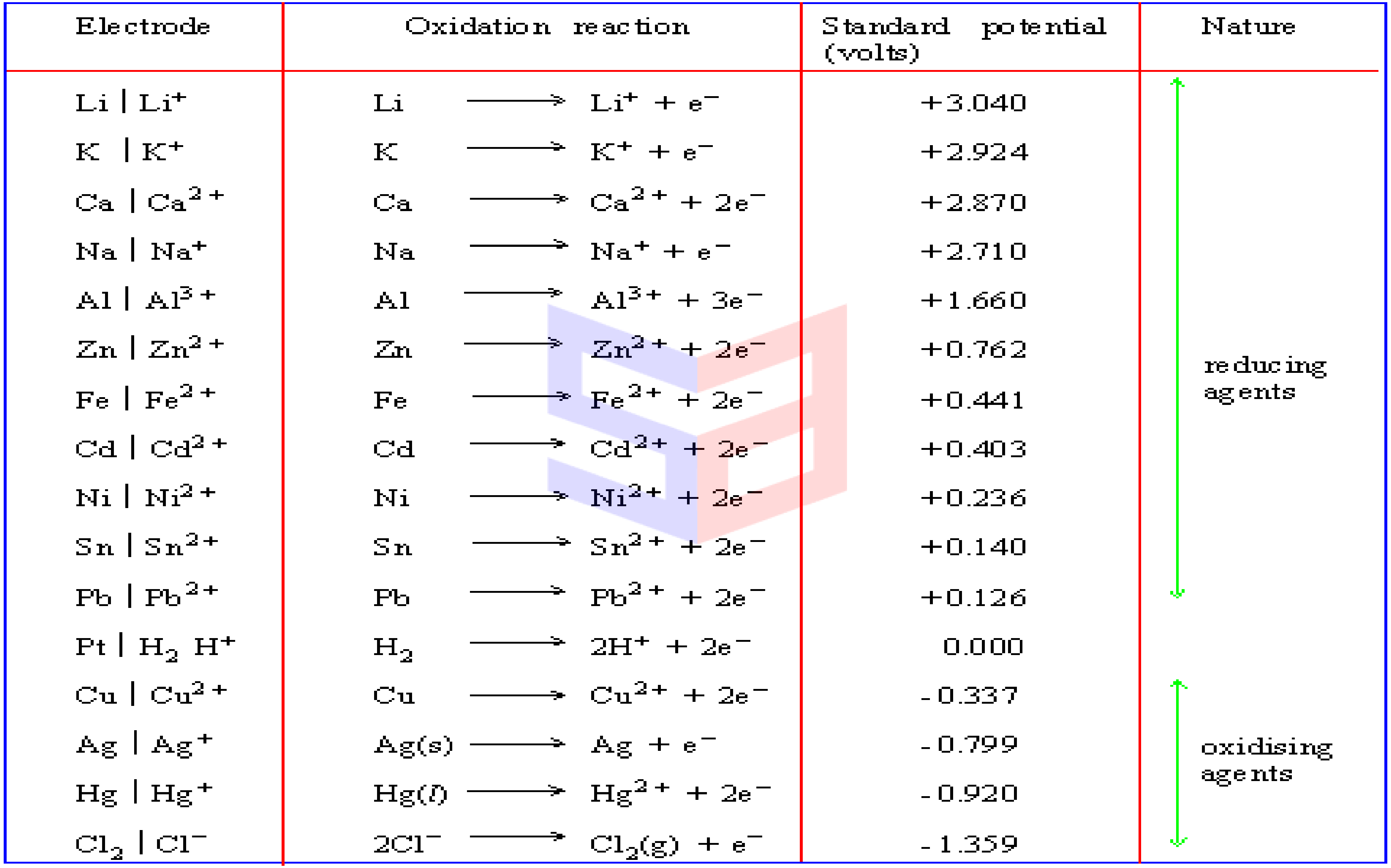
3.Nernst equation can also be used for finding the valency of an ions or the number of electrons involved in the electrode reaction

Electrochemical series

- When the metals are arranged in the order of increasing reduction potentials or decreasing oxidation potentials which are determined with respect to one molar solutions of their ions and measured on the hydrogen scale, along series or list, resulted is called electrochemical or galvanic series.

- The higher a metal is in the series, the greater is its tendency to be oxidized.
- Applications :
  1. relative corrosion tendencies of the metals& alloys.
  2.relative ease of oxidation or reduction of metals.
  3.replacement tendency of metals.

STANDARD REDUCTION POTENTIAL



Electrode	Oxidation reaction	Standard potential (volts)	Nature
$Li \mid Li^+$	$Li \longrightarrow Li^+ + e^-$	+3.040	↕ reducing agents
$K \mid K^+$	$K \longrightarrow K^+ + e^-$	+2.924	
$Ca \mid Ca^{2+}$	$Ca \longrightarrow Ca^{2+} + 2e^-$	+2.870	
$Na \mid Na^+$	$Na \longrightarrow Na^+ + e^-$	+2.710	
$Al \mid Al^{3+}$	$Al \longrightarrow Al^{3+} + 3e^-$	+1.660	
$Zn \mid Zn^{2+}$	$Zn \longrightarrow Zn^{2+} + 2e^-$	+0.762	
$Fe \mid Fe^{2+}$	$Fe \longrightarrow Fe^{2+} + 2e^-$	+0.441	
$Cd \mid Cd^{2+}$	$Cd \longrightarrow Cd^{2+} + 2e^-$	+0.403	
$Ni \mid Ni^{2+}$	$Ni \longrightarrow Ni^{2+} + 2e^-$	+0.236	
$Sn \mid Sn^{2+}$	$Sn \longrightarrow Sn^{2+} + 2e^-$	+0.140	
$Pb \mid Pb^{2+}$	$Pb \longrightarrow Pb^{2+} + 2e^-$	+0.126	
$Pt \mid H_2\ H^+$	$H_2 \longrightarrow 2H^+ + 2e^-$	0.000	
$Cu \mid Cu^{2+}$	$Cu \longrightarrow Cu^{2+} + 2e^-$	-0.337	↕ oxidising agents
$Ag \mid Ag^+$	$Ag(s) \longrightarrow Ag + e^-$	-0.799	
$Hg \mid Hg^+$	$Hg(l) \longrightarrow Hg^{2+} + 2e^-$	-0.920	
$Cl_2 \mid Cl^-$	$2Cl^- \longrightarrow Cl_2(g) + e^-$	-1.359	