

**Electrochemistry**

**UNIT-II**

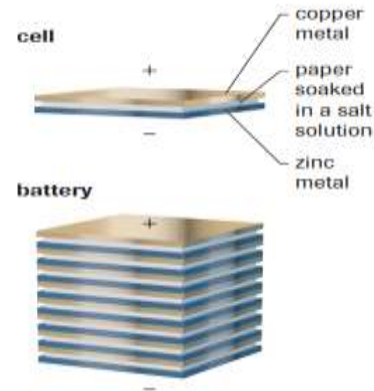
**Electrochemical  
Cells**

# Introduction to Electrochemistry

- **An *electric cell* converts chemical energy into electrical energy**
  - **Alessandro Volta** invented the first electric or electrolytic cell but got his inspiration from L. Galvani.
  - Galvani's crucial observation was that two different metals could make the muscles of a frog's legs twitch (Jerk).
  - Unfortunately, Galvani thought this was due to some mysterious "animal electricity". It was Volta who recognized this experiment's potential.
  - An electric cell produces very little electricity, so Volta came up with a better design:

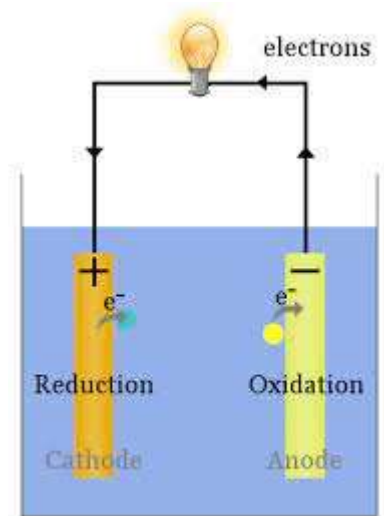
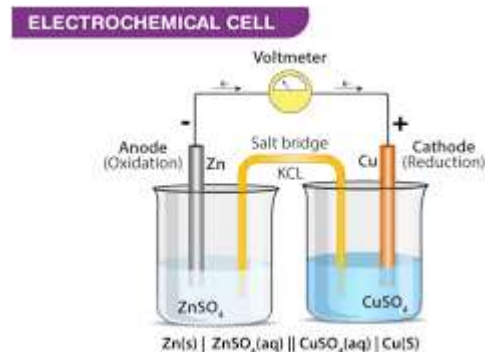
# Introduction to Electrochemistry

- Alessandro Volta's invention was an immediate technological success because it produced electric current more simply and reliable than methods that depended on static (fixed) electricity.
- It also produced a steady electric current –something no other device could do.



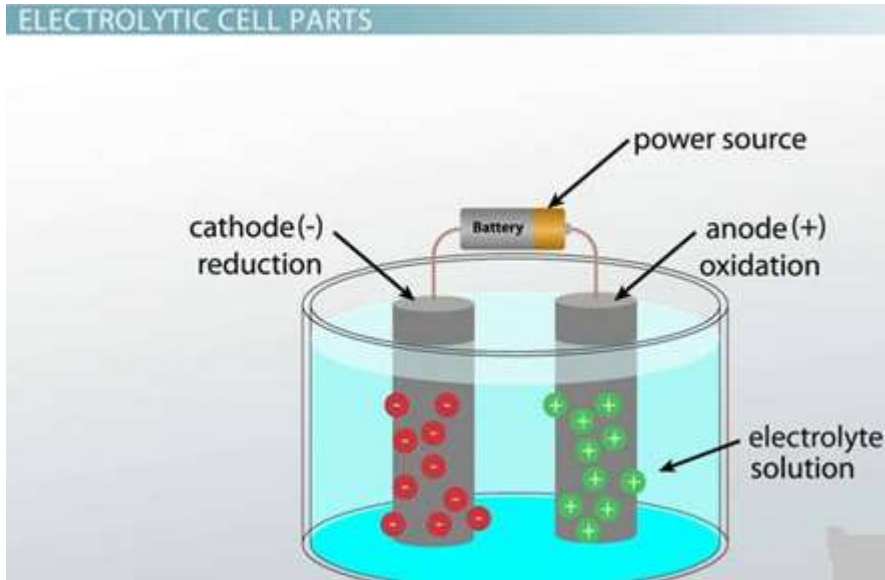
# ELECTROCHEMICAL CELLS

- An **electrochemical cell** is a device which converts chemical energy into electrical energy or electrical energy into chemical energy. Thus, there can be two types of electrochemical cells.



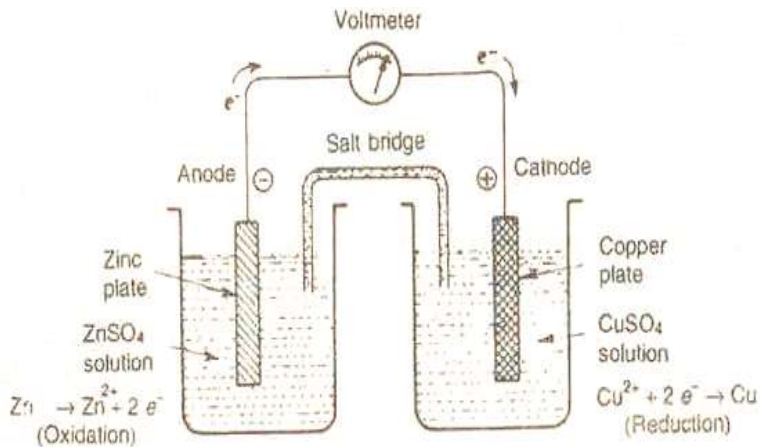
# Electrolytic cells

- **Electrolytic cells** are devices which convert electrical energy into chemical energy



# Galvanic cells (or voltaic cells)

- Galvanic cells (or voltaic cells) are devices which convert chemical energy into electrical energy.
- E.g. Daniel cell:



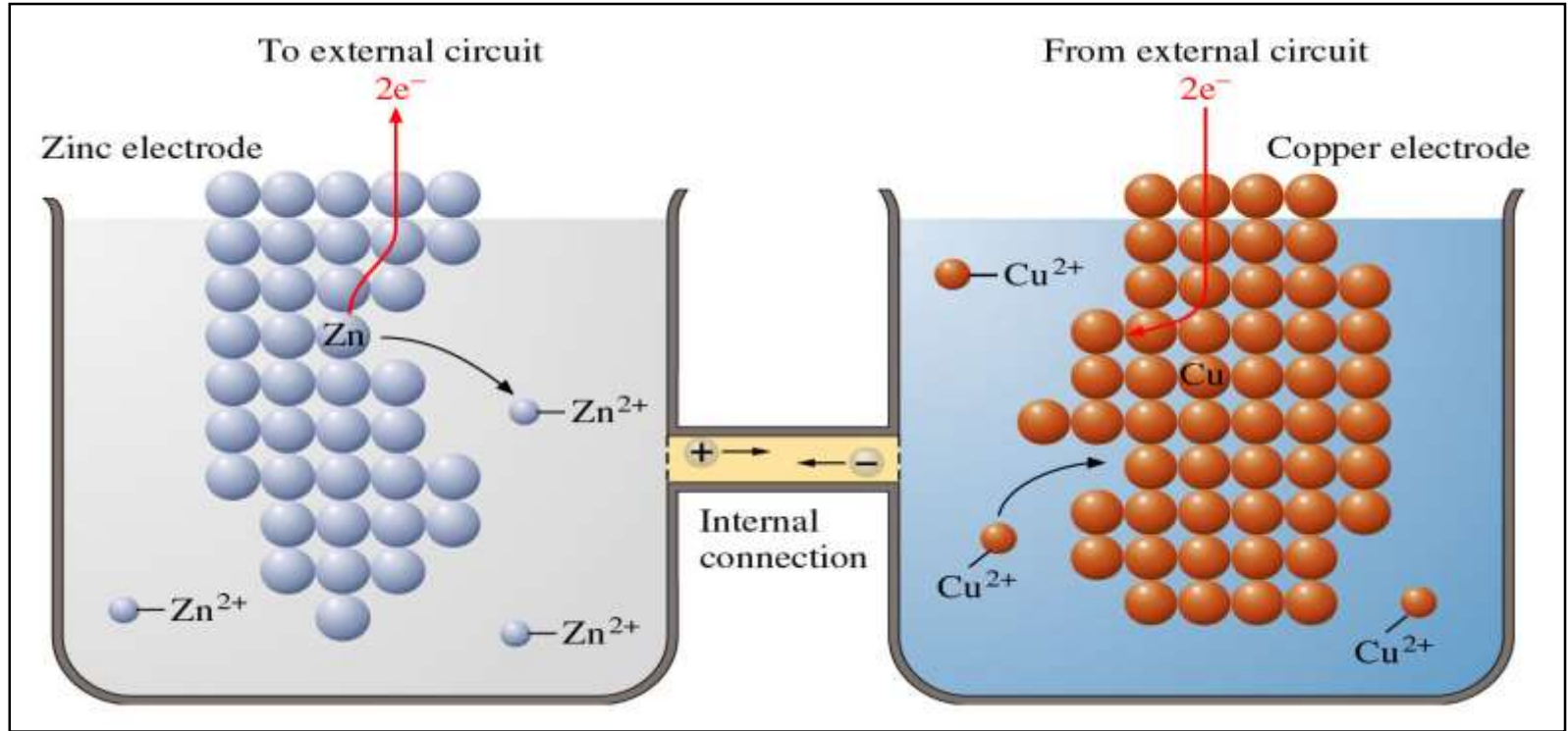
Anode (oxidation):  $\text{Zn} \rightarrow \text{Zn}^{2+} + 2e^-$

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

Cell reaction:  $\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}$

- Zinc starts to dissolve.
- Copper gets deposited on copper rod.
- The ammeter indicates the flow of electrons from zinc to copper rod.
- The zinc sulphate solution becomes richer with  $\text{Zn}^{2+}$  ions.
- The copper sulphate solution becomes more dilute with respect to  $\text{Cu}^{2+}$  ions.

# Atomic view of voltaic cell.



# Parts of the voltaic or galvanic cell...

**Anode → the electrode where oxidation occurs**

After a period of time, the anode may appear to become smaller as it falls into solution.

**Cathode → the anode where reduction occurs**

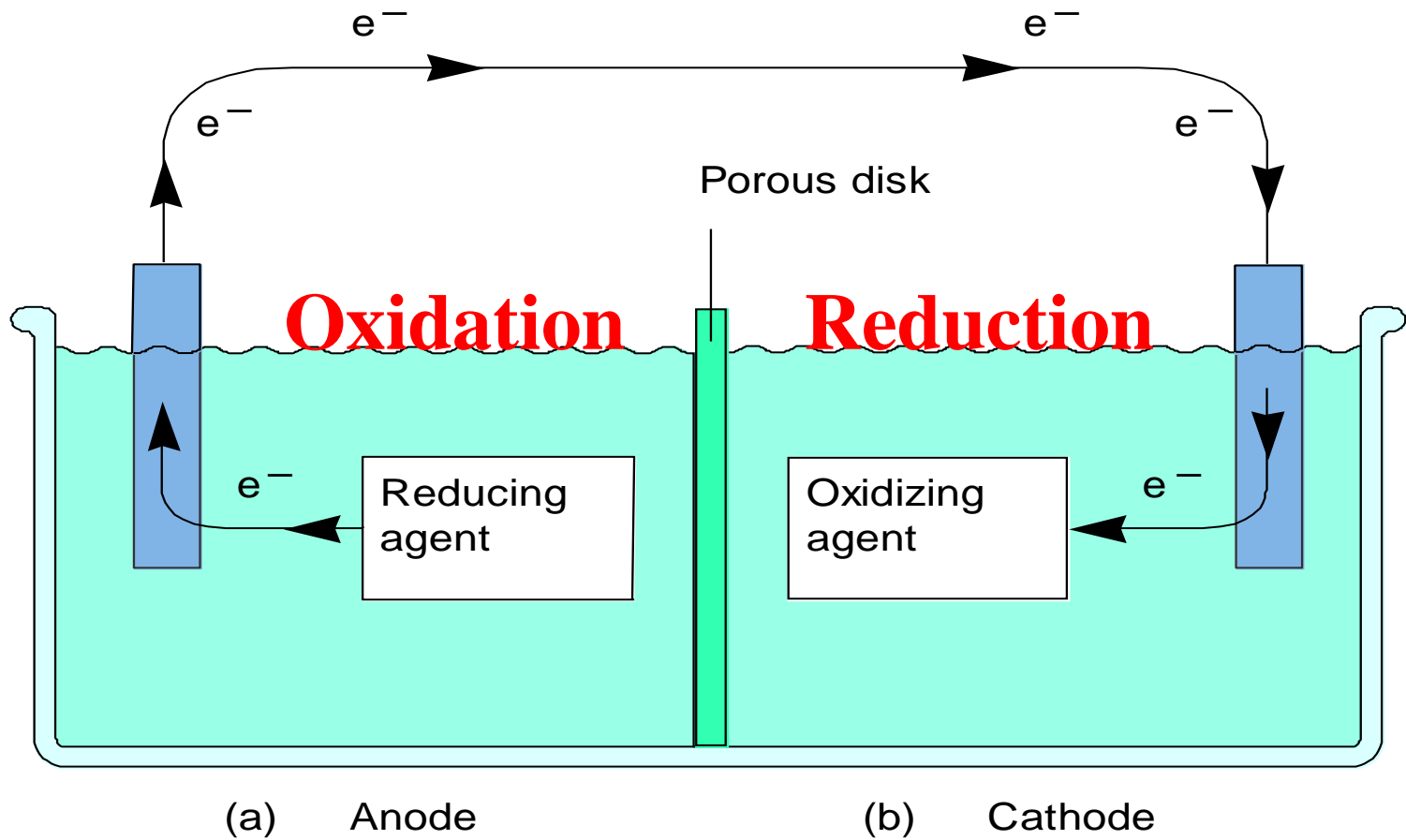
After a period of time it may appear larger, due to ions from solution plating onto it.

**Salt Bridge → a device used to maintain electrical neutrality in a galvanic cell**

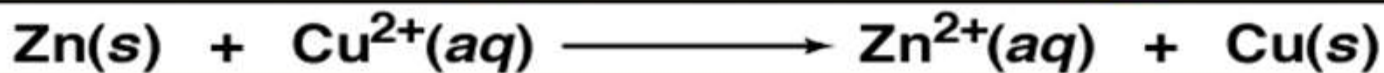
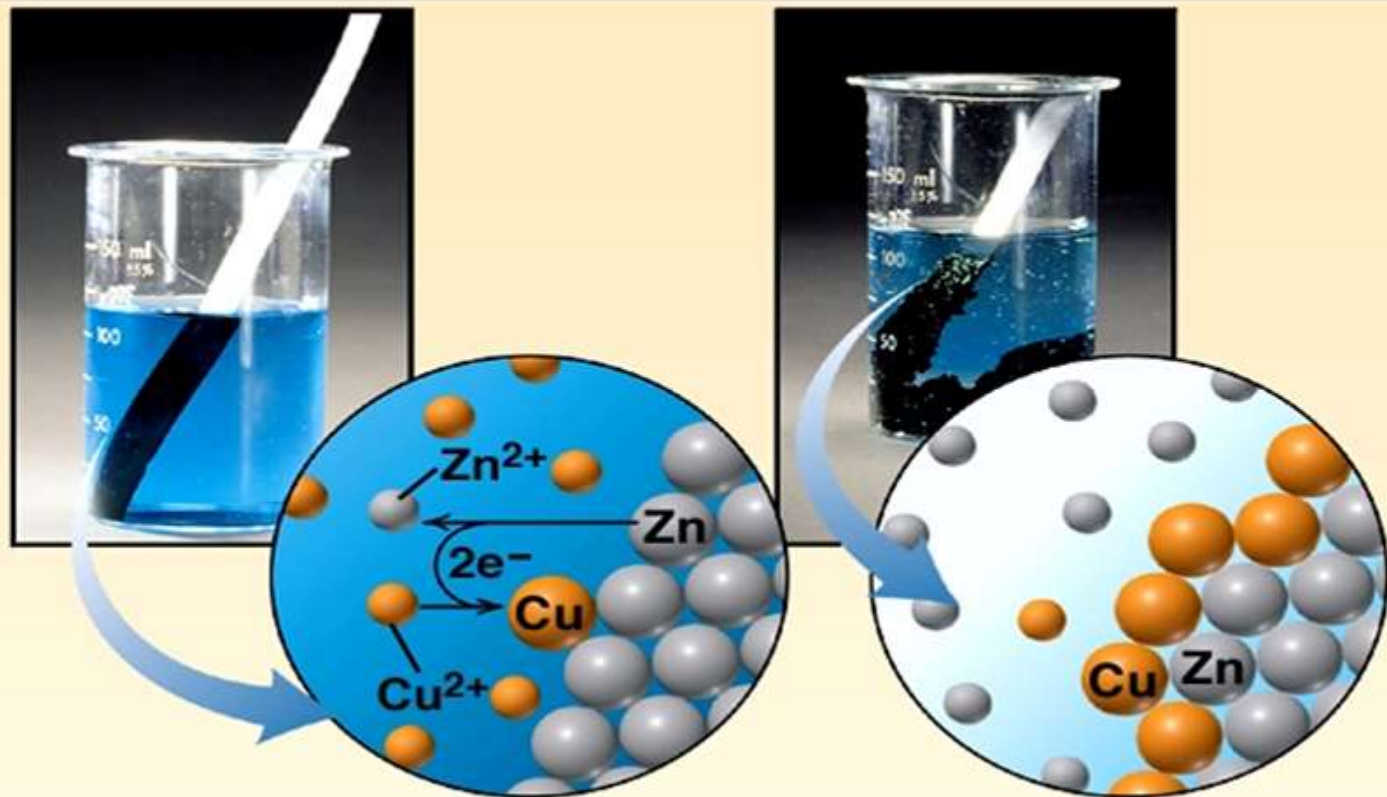
This may be filled with agar which contains a neutral salt or it may be replaced with a porous cup.

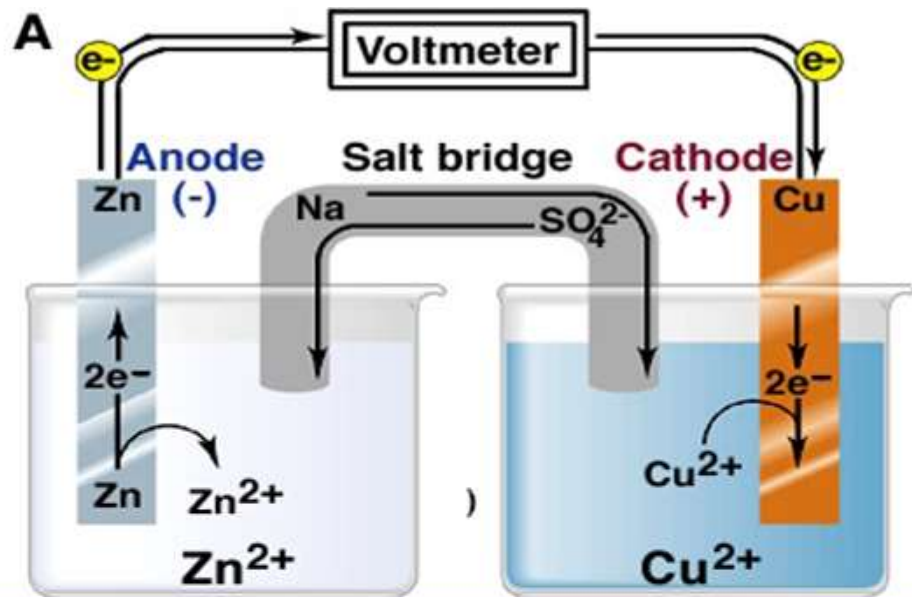
**Electron Flow → always from anode to cathode (through the wire)**





# Spontaneous Reaction between Zn and $\text{Cu}^{2+}$





**Zinc-Copper  
Reaction  
Voltaic Cell**

# Naming the Electrodes

CATIONS migrate towards the CATHODE

ANIONS migrate towards the ANODE

Reduction occurs at the cathode

Oxidation occurs at the anode

$\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$  occurs at the anode

$\text{Cu}^{+2} + 2\text{e}^- \rightarrow \text{Cu}$  occurs at the cathode

## Cell notation and convention:

- **By convention**, the electrode at which oxidation occurs is **anode** and the electrode where reduction occurs is **cathode**.
- Thus in the Daniel cell zinc electrode acts as anode. Copper electrode acts as cathode.
- In a galvanic cell anode is **negative** and cathode is **positive**.
- The reason, to this is that oxidation is accompanied by the liberation of electrons which are given up to that electrode, which thereby acquires a negative charge.
- Reduction, on the other hand, is accompanied by the absorption of electrons by the reactant in the solution from the electrode, which thereby acquires a positive charge.

The present conventions, a galvanic cell is represented by keeping view the following points:

- **Anode is written on the left-hand side; while cathode is written on the right-hand side.**
- **The electrode on the left (i.e., anode) is written by writing the metal (or solid phase) first and then the electrolyte.** Two are separated by a vertical line or a semicolon. The electrolyte may be represented by the formula of the whole compound or by ionic species.

Eg.,  $\text{Zn} \mid \text{Zn}^{2+}$  or  $\text{Zn} ; \text{Zn}^{2+}$  or  $\text{Zn} \mid \text{ZnSO}_4(1\text{M})$   
 $\text{Pt}, \text{H}_2 (1 \text{ atm.}) \mid \text{H}^+(1\text{M}).$

•The cathode of the cell (at which reduction takes place) is written on the right-hand side.

The electrolyte is represented first and the metal (or solid phase) thereafter.

E.g.,  $\text{Cu}^{2+} | \text{Cu}$  or  $\text{Cu}^{2+}; \text{Cu}$  or  $\text{Cu}^{2+} (1\text{M}) | \text{Cu}$  or  $\text{Cu}^{2+} (1\text{M}); \text{Cu}$

•A salt bridge is indicated by two vertical lines, separating the two half cells.

•Thus applying above considerations to Daniel cell, we may represent as:

$\text{Zn} | \text{Zn}^{2+} (1\text{M}) || \text{Cu}^{2+}(1\text{M}) | \text{Cu}$

# Electromotive force of the cell (EMF)

**Electromotive force of the cell (EMF):** The difference in potential, which causes a current to flow from an electrode of higher potential to that of lower potential is called the electromotive force.

**The cell potential is represented as  $E_{\text{cell}}$**

$$E_{\text{cell}} = E_{\text{RHS}} - E_{\text{LHS}}$$

$$\text{or } E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$



# Standard EMF of the cell

**Standard emf of the cell** is defined as the emf of the galvanic cell when the reactants and products of the cell reaction are at unit concentration or unit activity, at 298K and 1 atmosphere pressure.

**The standard electrode potential is represented as  $E^0_{\text{cell}}$**

$$E^0_{\text{cell}} = E^0_{\text{RHS}} - E^0_{\text{LHS}}$$

# Salt bridge

A salt bridge or ion bridge, is a device used to connect the oxidation and reduction half-cells of a galvanic cell (voltaic cell).

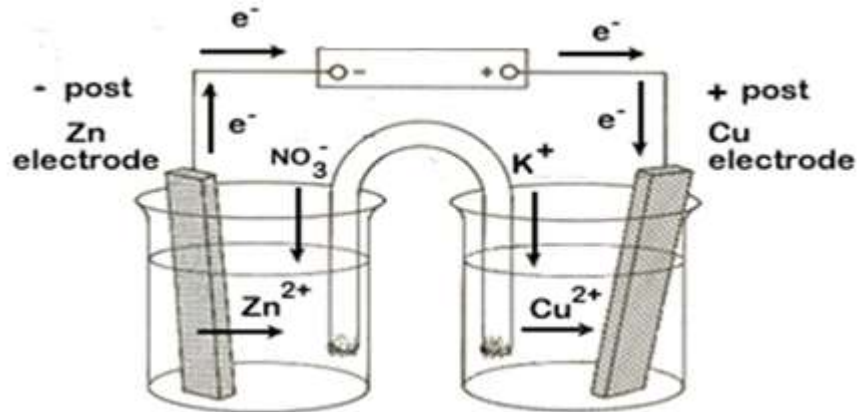
- To avoids the liquid junction potential and provides the contact between the two solutions.



- It consists of saturated solution of a salt, such as  $\text{KCl}$  or  $\text{NH}_4\text{NO}_3$ , whose ions have almost same migration velocities.
- The positive and negative ions of the salt in the salt bridge migrate with equal speed into cathode and anode compartments respectively.
- During the cell reaction, either  $\text{Cl}^-$  diffuse from the salt bridge into the zinc half-cell or  $\text{Zn}^{2+}$  ions diffuse into the salt bridge to keep the zinc-half cell electrically neutral.



- At the same time, the copper half-cell is kept electrically neutral by the diffusion of either the positive ( $\text{K}^+$ ) ions from the salt bridge to the copper cell or diffusion of  $\text{NO}_3^-$  ions from the copper cell into the salt bridge.
- Without the salt bridge no electrical current would be produced by the galvanic cell since electrolytic contact must be maintained for the cell to function



### FUNCTIONS OF SALT BRIDGE

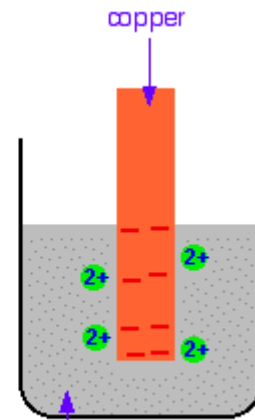
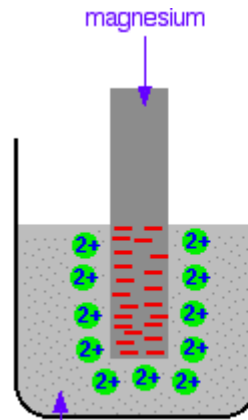
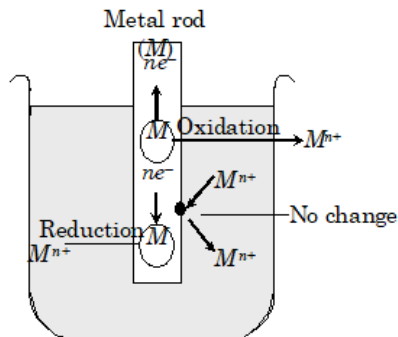
1. Permits the passage of electric current internally,
2. Maintains the electrical neutrality of the solution,
3. Prevents intermixing of the solutions,
4. It does not take part in cell reaction.



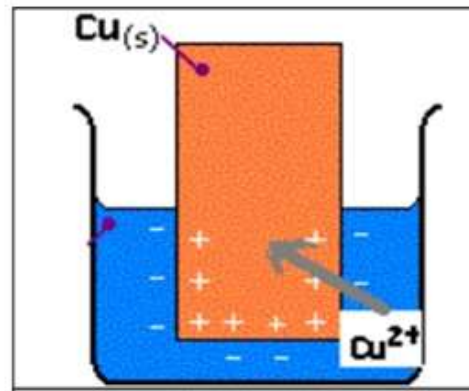
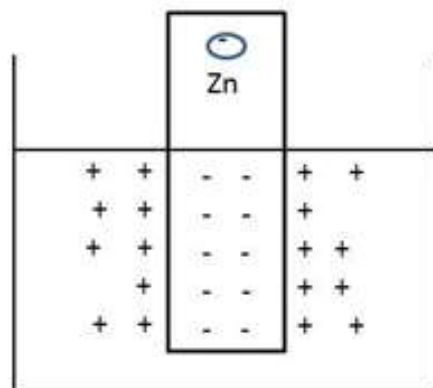
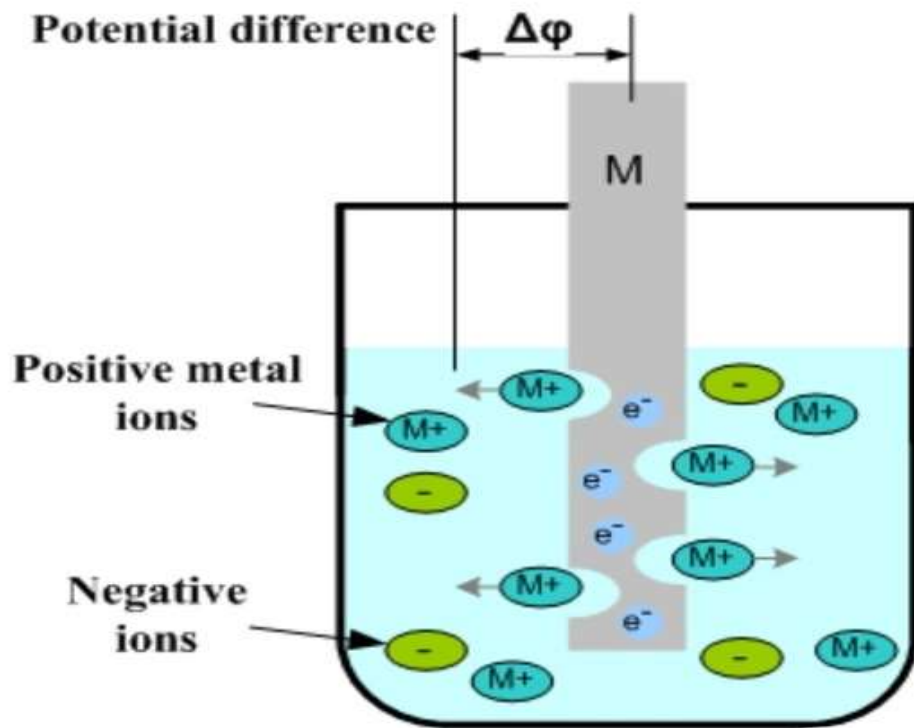
# Single electrode potential

**Electrode potential or single electrode potential** is defined as the potential developed on the electrode at the interface when it is in contact with a solution of its own ions.

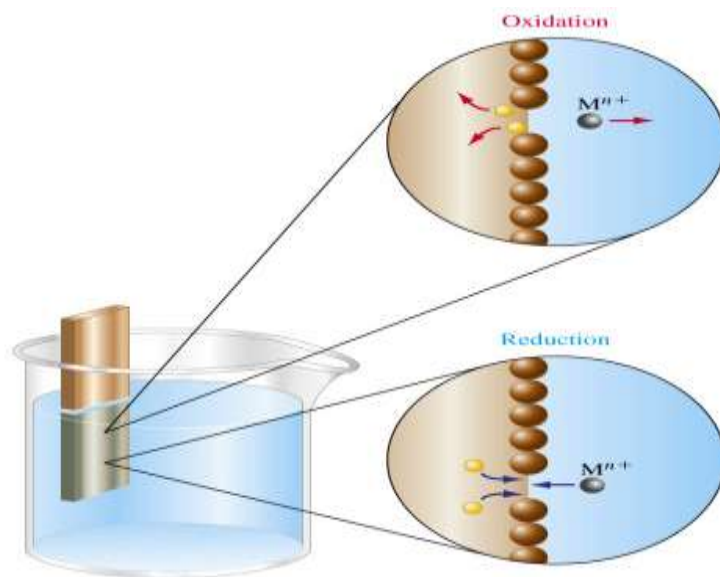
It is denoted by  $E$ . All single electrode potentials represent reduction potentials which is the measure of the tendency of an electrode to undergo reduction.



## Single electrode cell (half-cell)

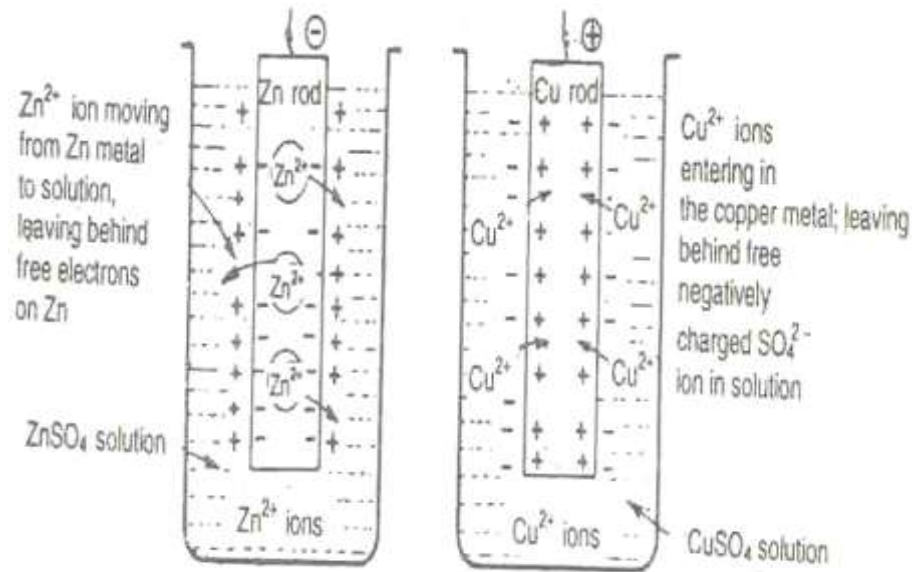


# An Electrochemical Half Cell





# Origin of electrode potential



Helmholtz Electrical Double Layer (HDL)

# NERNST EQUATION

**Standard electrode potential** is the potential developed when the electrode (metal) is in contact with solution of unit concentration (1M) at 298K.

Nernst equation is a thermodynamic equation which relates the change in free energy and cell potential with concentration,  $M^{n+}$ . The decrease in free energy ( $-\Delta G$ ) represents maximum amount of work that can be obtained from a chemical reaction.

$$-\Delta G = W_{\max} \dots\dots\dots (1)$$

The work performed by an electrochemical cell depends on (i) number of coulombs that flow and (ii) the energy available per coulomb.

$$\text{Work} = \text{number of coulombs} \times \text{energy available/ coulomb}$$

The number of coulombs that flow is equal to the product of number of moles of electrons that are involved in the cell reaction and faraday (F).

$$\text{Number of coulombs} = nF$$

Energy available per coulomb is the emf of the cell (E), since volt is equal to energy per coulomb. When the emf is maximum, work derived from the cell is also maximum.

The maximum is the cell potential  $E_{\text{cell}}$ . Thus  $W_{\text{max}}$  for an electrochemical cell (expressed in joule) is given by the equation.

$$W_{\text{max}} = n \times F \times E \dots\dots\dots(2).$$

$$\text{(mole of } e^-) \quad (\text{C mol}^{-1}) \quad (\text{JC}^{-1})$$

Equating (1) and (2),

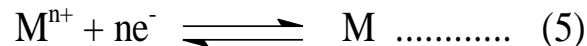
$$\Delta G = - nFE \dots\dots\dots (3).$$

Under standard conditions, i.e., when the concentrations of all species is unity, the standard free energy  $\Delta G^0$  is given by the equation,

$$\Delta G^0 = - nFE^0 \dots\dots\dots (4).$$

Where  $E^0$  is a constant called the standard reduction (electrode) potential.

For a reaction,



**The equilibrium constant  $K_c$  is related to change in free energy by the thermodynamic equation,**

$$\Delta G = \Delta G^0 + RT \ln K_c \dots\dots\dots (6)$$

$$\text{Since } K_c = [M] / [M^{n+}]$$

$$\Delta G = \Delta G^0 + RT \ln [M] / [M^{n+}] \dots\dots\dots (7)$$

**Substituting from equations (3) and (4) for  $\Delta G$  and  $\Delta G^0$**

$$- nFE = - nFE^0 + RT \ln [M] / [M^{n+}]$$

**Dividing throughout by  $- nF$**

$$- \quad nFE / - nF = - nFE^0 / - nF + (RT / - nF) \ln [M] / [M^{n+}]$$

$$E = E^0 - (RT/nF) \ln [M] / [M^{n+}]$$

$$E = E^0 - RT/nF \ln 1/[M^{n+}]$$

$$E = E^0 + 2.303RT/nF \log [M^{+n}]$$

$$E = E^0 + \frac{0.0591}{n} \log [M^{n+}]$$

- It may be seen from equation (8) that  $E = E^0$  where  $[M^{n+}]$  is unity.
- If concentration of solution  $[M^{n+}]$  is increased, the electrode potential increases and vice versa.
- If temperature is increased, the electrode potential increases and vice versa.

## Nernst equation for emf of cells:

Nernst equation may also be used to calculate the emf of chemical cells

$$E_{\text{cell}} = E_{\text{cell}}^0 - (0.0591/n) \log [\text{products}] / [\text{reactants}]$$

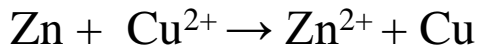
or,

$$E_{\text{cell}} = E_{\text{cell}}^0 + (0.0591/n) \log [\text{reactants}] / [\text{products}]$$

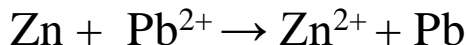
or,

$$= E_{\text{cell}}^0 + (0.0591/n) \log [\text{species at cathode}] / [\text{species at anode}]$$

In Daniel cell,



$$E_{\text{Daniel cell}} = E_{\text{Daniel cell}}^0 + (0.0591/n) \log [\text{Cu}^{2+}] / [\text{Zn}^{2+}]$$





1. A cell is constructed by coupling Fe-rod dipped in 0.5M FeSO<sub>4</sub> and Ni rod dipped in 0.05M NiSO<sub>4</sub>. Write the cell representation, cell reaction. Calculate EMF of the cell, given that standard reduction potentials Fe and Ni as -0.44 and -0.25 volt respectively.



$$\text{Emf of the cell } E = E^0 + \frac{0.0591}{n} \log [\text{Ni}^{+2}] / [\text{Fe}^{+2}]$$

$$= (-0.25 - (-0.44)) + 0.0591/2 \log [0.05]/[0.5]$$

$$\text{In calculator} \quad = 0.19 + (((0.0591/2) \log ((0.05)/(0.5)))$$

$$= \underline{0.1604\text{V}}$$

2. A cell is constructed by coupling Zn-rod dipped in 0.5M ZnSO<sub>4</sub> and Ni-rod dipped in 0.05M NiSO<sub>4</sub>. Write the cell representation, cell reaction. Calculate EMF of the cell, given that standard reduction potentials Zn and Ni as -0.76 and -0.25 volt respectively

$$E = E^0 + \frac{0.0591}{n} \log [M^{n+}]$$

Cell representation    Zn / Zn<sup>2+</sup>(0.5M) // Ni<sup>2+</sup> (0.05M) / Ni

Anode:                      Zn → Zn<sup>2+</sup> + 2e<sup>-</sup>

Cathode:                  Ni<sup>2+</sup> + 2e<sup>-</sup> → Ni

Net cell reaction: Ni<sup>2+</sup> + Zn → Ni + Zn<sup>2+</sup>

$$\text{Emf of the cell } E = E^0 + \frac{0.0591}{n} \log [Ni^{2+}]/[Zn^{2+}]$$

$$\begin{aligned} & (-0.25 + 0.76) + 0.0591/2 \log [0.05/0.5] \\ & (0.51) + ((0.0591) \log((0.05) / (0.5))) \\ & \mathbf{0.48045V} \end{aligned}$$

3. Calculate the potential of Ag-Zn cell at 298K if the concentration of  $\text{Ag}^+$  and  $\text{Zn}^{2+}$  are  $5.2 \times 10^{-6}$  M and  $1.3 \times 10^{-3}$  M respectively.  $E^0$  of the cell at 298K is 1.5V. Calculate the change in free energy  $\Delta G$  for the reduction of 1mole of  $\text{Ag}^+$ . 1 faraday =  $96.5 \text{ KJ V}^{-1} \text{ mole}^{-1}$

Cell representation     $\text{Zn} / \text{Zn}^{2+}(1.3 \times 10^{-3} \text{ M}) // \text{Ag}^+(5.2 \times 10^{-6} \text{ M}) / \text{Ag}$

Anode:                     $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$

Cathode:                 $2\text{Ag}^+ + 2\text{e}^- \rightarrow 2\text{Ag}$

Standard electrode potential of Zn-Ag cell ( $E^0$ ) = 1.5V

$$E = E^0 + \frac{0.0591}{n} \log [\text{Ag}^+]^2 / [\text{Zn}^{2+}]$$

$$= 1.5 + \frac{0.0591}{n} \log [5.2 \times 10^{-6}]^2 / [1.3 \times 10^{-3}]$$

$$= 1.5 + (((0.0591/2) \log ((5.2 \times 10^{-6})^2 / (1.3 \times 10^{-3})))$$

$$= 1.272 \text{ V}$$

$$\Delta G = - nFE$$

$$-1 \text{ mole} \times 96.5 \text{ KJ/mole/V} \times 1.27 \text{ V}$$

$$-122.555 \text{ KJ/mol}$$

**Electrochemical series:** When elements are arranged in increasing order of (downwards) of their standard electrode potential, a series called electrochemical series (or emf series).

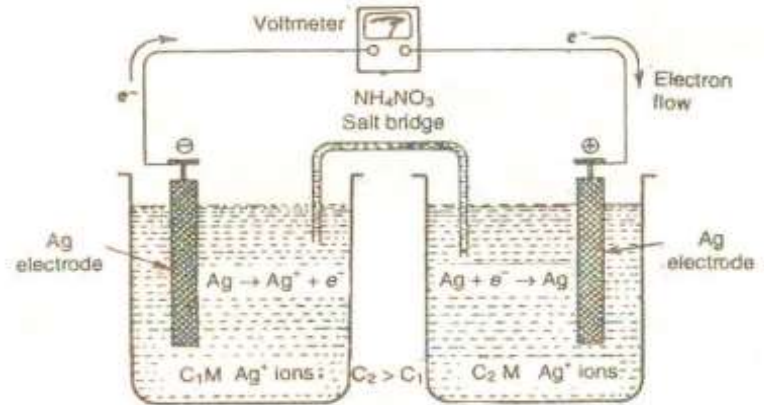
$M^{n+}/M$	$E^0(V)$ at 298K
$Li^+/Li$	-3.05 (Anode)
$K^+/K$	-2.93
$Ba^{2+}/Ba$	-2.90
$Ca^{2+}/Ca$	-2.87
$Na^+/Na$	-2.71
$Mg^{2+}/Mg$	-2.37
$Al^{3+}/Al$	-1.66
$Zn^{2+}/Zn$	-0.76
$Cr^{3+}/Cr$	-0.74
$Fe^{2+}/Fe$	-0.44
$Cd^{2+}/Cd$	-0.40
$Ni^{2+}/Ni$	-0.23
$Sn^{2+}/Sn$	-0.14
$Pb^{2+}/Pb$	-0.13
$H^+/H_2$	0.00 (Reference)
$Cu^{2+}/Cu$	0.34
$Ag^+/Ag$	0.80
$Hg^{2+}/Hg$	0.85
$Pt^{2+}/Pt$	1.20
$Au^{3+}/Au$	1.38 (Cathodic)

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

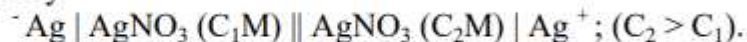
# Concentration cell

A **concentration cell** is an electrochemical cell made of two half cells having identical electrodes, identical electrolyte, except that concentrations of the electrolyte solutions are different.

A **concentration cell** produces a small voltage as it attempts to reach equilibrium.



The cell is represented by



The Ag electrode which is in contact with lower concentration ( $C_1$ ) of the electrolyte acts as anode where oxidation occurs and enters into the solution. The Ag electrode which is in contact with higher concentration ( $C_2$ ) of the electrolyte acts as cathode where reduction occurs and deposition of Ag occurs.

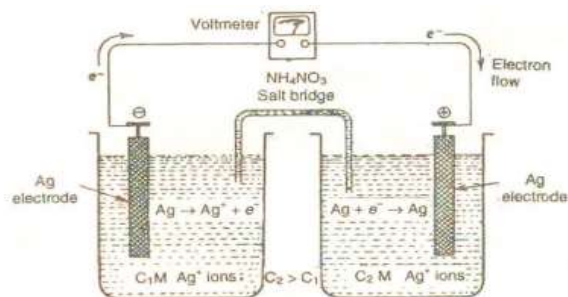
*Electrode reactions:* Anode :  $\text{Ag (s)} \rightarrow \text{Ag}^+(\text{C}_1\text{M}) + \text{e}^-$

Cathode:  $\text{Ag}^+(\text{C}_2\text{M}) + \text{e}^- \rightarrow \text{Ag (s)}$

Cell reaction:  $\text{Ag}^+(\text{C}_2\text{M}) \rightarrow \text{Ag}^+(\text{C}_1\text{M})$

There is no net chemical reaction but only concentration change takes place. Evidently, the emf so developed is due to the mere transference of metal ions from the solution of higher concentration ( $C_2$ ) to the solution of lower concentration ( $C_1$ ).

$$\text{Emf of the cell (E}_{\text{cell}}) = E_{\text{cathode}} - E_{\text{anode}}$$



$$E_{\text{cell}} = \left[ E^0 + \frac{RT}{nF} \ln C_2 \right] - \left[ E^0 + \frac{RT}{nF} \ln C_1 \right]$$

$$E_{\text{cell}} = \frac{RT}{nF} \ln [C_2] / [C_1] \text{ -----(1)}$$

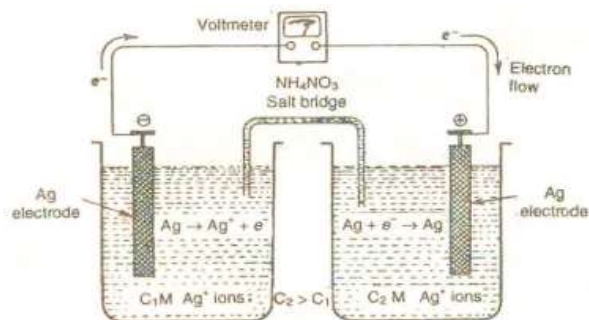
At 298K,

$$E_{\text{cell}} = \frac{0.0591}{n} \log [C_2] / [C_1] \text{ -----(2)}$$

Note: (i) When  $C_1 = C_2$  (concentrations are equal),  $\log [C_2 / C_1] = 0$  and hence no electricity flows (since  $\text{emf} = 0$ ).

(ii) When  $[C_2 / C_1] > 1$  (i.e.,  $C_2 > C_1$ ),  $\log [C_2 / C_1]$  is positive. Thus the direction of spontaneous reaction is from the more concentrated solution ( $C_2$ ) to less concentrated solution ( $C_1$ ).

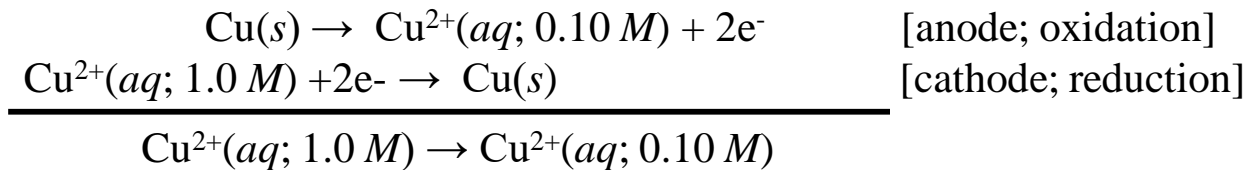
(iii) Higher the ratio  $C_2/C_1$ , higher is the value of cell potential. For eg. if the ratio  $C_2/C_1$  increases from 0.001 to 0.1 (i.e., 100 times) the voltage increases three fold.



## Concentration Cells

A *concentration cell* exploits the effect of concentration changes on cell potential.

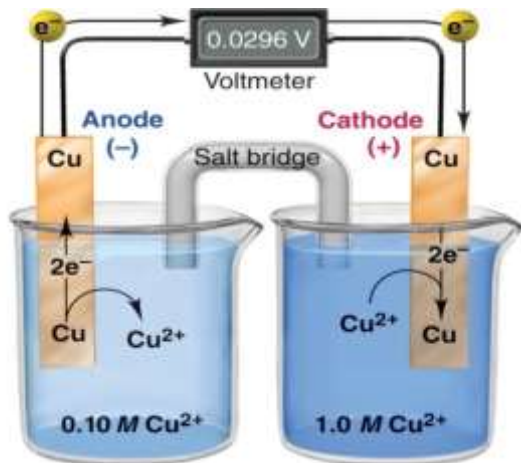
The cell has the same half-reaction in both cell compartments, but with different concentrations of electrolyte:



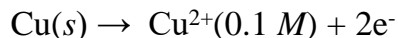
As long as the concentrations of the solutions are different, the cell potential is  $> 0$  and the cell can do work.



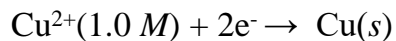
A concentration cell based on the  $\text{Cu}/\text{Cu}^{2+}$  half-reaction.



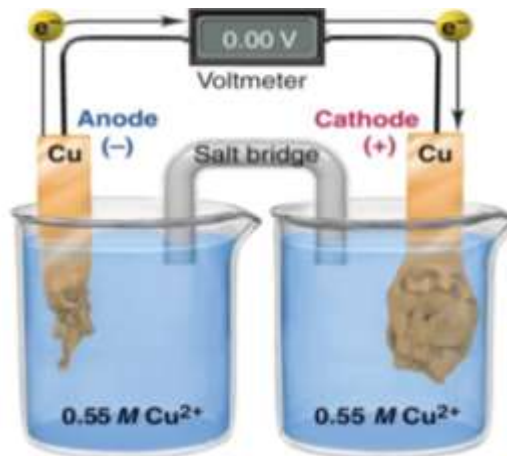
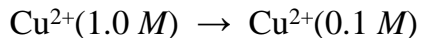
Oxidation half-reaction



Reduction half-reaction



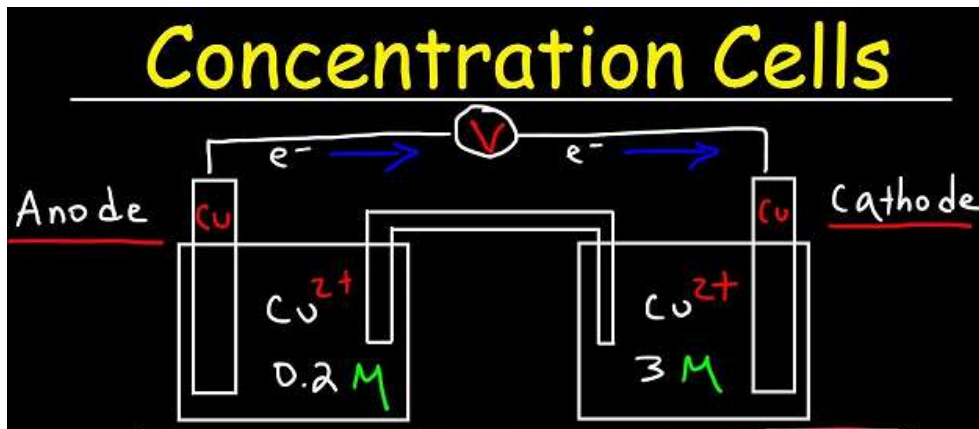
Overall (cell) reaction



$E_{\text{cell}} > 0$  as long as the half-cell concentrations are different.

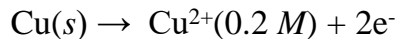
The cell is no longer able to do work once the concentrations are equal.

1. A concentration cell consists of two  $\text{Cu}/\text{Cu}^{2+}$  half-cells. In half-cell A, the electrolyte is  $0.2\text{ M CuSO}_4$ ; in another half cell, the concentration of  $\text{CuSO}_4$  is  $3\text{ M}$ . Write the cell representation, cell reaction and calculate the emf of concentration cell ?

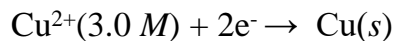


$$E_{\text{cell}} = \frac{0.0591}{n} \log \frac{[C_2]}{[C_1]}$$

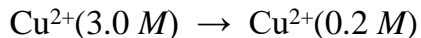
Oxidation half-reaction



Reduction half-reaction



Overall (cell) reaction



Where  $C_2 = 3\text{M}$  and  $C_1 = 0.2\text{M}$

$$= \left( \frac{0.0591}{2} \log \left( \frac{3}{0.2} \right) \right)$$

$$= 0.03475\text{V}$$

## Concentration cell

2. Calculate the emf of the following cell at 298K



$$E_{\text{cell}} = \frac{0.0591}{n} \log [C_2] / [C_1]$$

$$\begin{aligned} E_{\text{conc. cell}} &= 0.0591/1 \log ((0.1) / (0.01)) \\ &= 0.0591\text{V} \end{aligned}$$

### Concentration cell

3. The spontaneous galvanic cell  $\text{Tin} \mid \text{tin ion (0.024M)} \parallel \text{tin ion (0.064M)} \mid \text{Tin}$ , develops an EMF of 0.0126V at  $25^\circ\text{C}$ . Calculate the valency of tin?

$$E_{\text{cell}} = \frac{0.0591}{n} \log [C_2] / [C_1]$$



$$E_{\text{conc. cell}} = 0.0591/n \log ((0.064) / (0.024))$$

$$0.0126 n = 0.0591 \log ((0.064)/ (0.024))$$

$$0.0126n = 0.0252$$

$$\text{Therefore } n = 0.0252/0.0126$$

$$n=2$$

### Concentration cell

4. The emf of the cell  $\text{Cd}/\text{CdSO}_4(0.093\text{M})//\text{CdSO}_4(x\text{ M})$  is  $0.086\text{V}$  at  $25^\circ\text{C}$ . Find the value of  $x$ .

$$E_{\text{cell}} = \frac{0.0591}{n} \log [C_2] / [C_1]$$

$$E_{\text{conc. cell}} = 0.0591/2 \log ((x\text{M})/ (0.093\text{M}))$$

$$0.086 \times 2 = 0.0591 \log x/0.093$$

$$0.086 \times 2/0.0591 = \log x/0.093$$

$$2.9103 = \log x/0.093$$

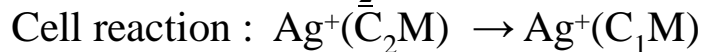
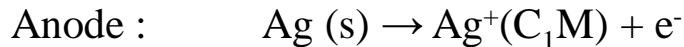
$$\text{Antilog } (2.9103) = x/0.093$$

$$813.39 = x/0.093$$

$$X = 75.64\text{M}$$

## Concentration cell

PROBLEM 5: A concentration cell consists of two Ag/Ag<sup>+</sup> half-cells. In half-cell, the electrolyte is 0.0100 *M* AgNO<sub>3</sub>; in half-cell, it is 4.0x10<sup>-4</sup> *M* AgNO<sub>3</sub>. What is the cell potential?



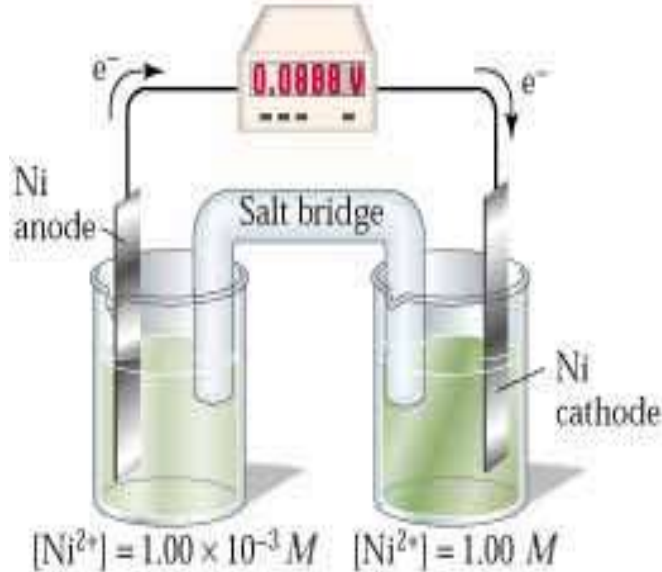
$$E_{\text{cell}} = \frac{0.0591 \log [\text{C}_2] / [\text{C}_1]}{n}$$

$$= 0.0591/1 \log((0.01)/ (0.0004))$$

$$= 0.0422\text{V}$$

# Concentration cell

6. A concentration cell consists of two half-cells. In one half-cell, the electrolyte is  $1 \times 10^{-3} \text{ M}$   $\text{NiSO}_4$ ; and in another half cell, the concentration of  $\text{NiSO}_4$  is  $1 \text{ M}$ . Write the cell representation, cell reaction and calculate the emf of the concentration cell ?



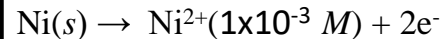
$$E_{\text{cell}} = \frac{0.0591}{n} \log \frac{[C_2]}{[C_1]}$$

Where  $C_2 = 1 \text{ M}$  and  $C_1 = 1 \times 10^{-3} \text{ M}$

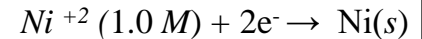
$$= 0.0591/2 \log ((1)/(1 \times 10^{-3}))$$

$$= 0.08865 \text{ V}$$

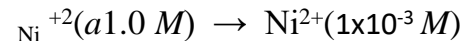
Oxidation half-reaction



Reduction half-reaction



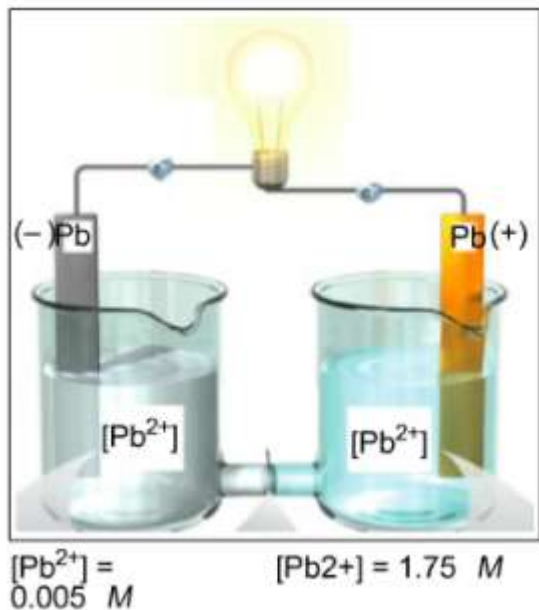
Overall (cell) reaction



**Concentration cell of Nickel system**

## Concentration cell

7. A concentration cell consists of two Pb/Pb<sup>2+</sup> half-cells. In One half-cell the electrolyte concentration is 0.005 M PbNO<sub>3</sub>; and in other half-cell, its concentration is 1.75 M PbNO<sub>3</sub>. What is the cell potential?

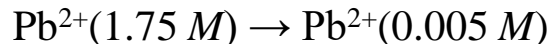
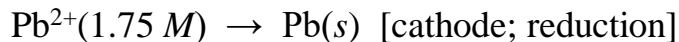
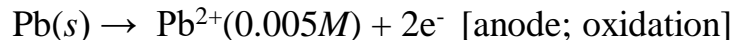


$$E_{\text{cell}} = \frac{0.0591}{n} \log \frac{[C_2]}{[C_1]}$$

Where  $C_2 = 1.75\text{M}$  and  $C_1 = 0.005\text{M}$

$$= (0.0591/2) \log((1.75)/(0.005))$$

$$= \mathbf{0.07517V}$$

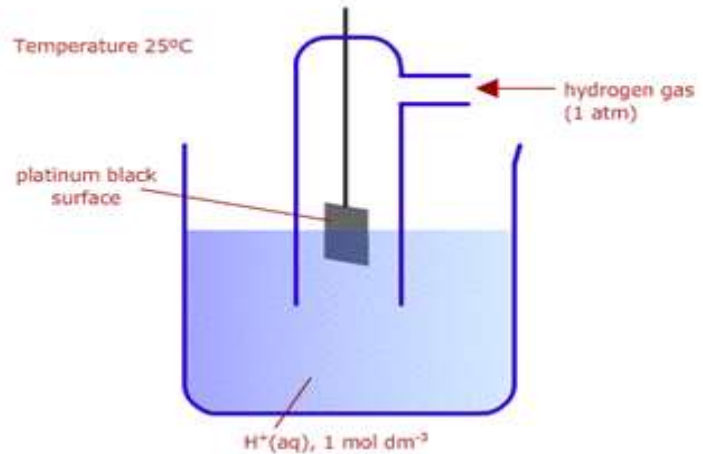




# Reference electrode

Any electrode of constant and reproducible potential, used to determine the potential of other electrode.

E.g., Standard hydrogen electrode



# Measurement of single electrode potential

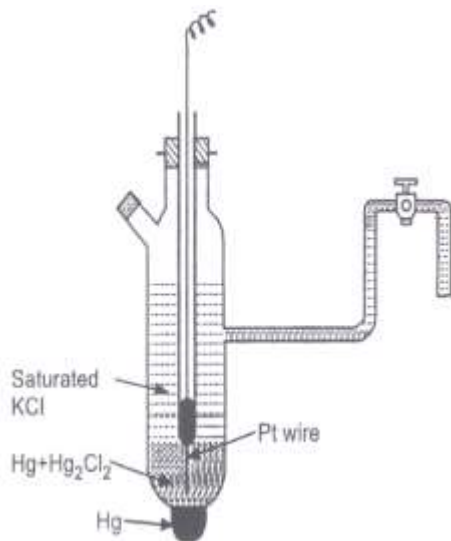
The potential of a given electrode is measured using standard hydrogen electrode (SHE) whose potential is arbitrarily taken as zero volt at all temperatures and is the reference point for all potential measurements.

## Secondary reference electrodes

Because of the difficulties involved in the use of standard hydrogen electrode as reference electrode, some other electrodes constant electrode potential, referred to as secondary reference electrodes.

(i) calomel electrode (ii) silver-silver electrode

# Calomel electrode



## Calomel reference electrode

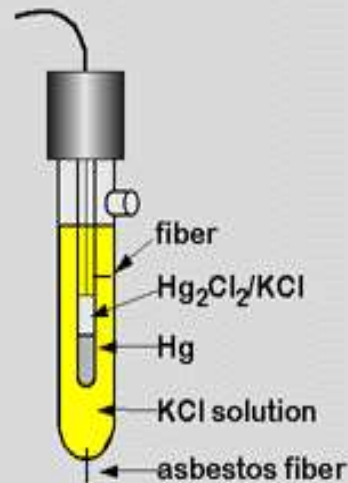
### Calomel electrode (SCE)

A much more common reference electrode.

It much easier to work with - no gas.

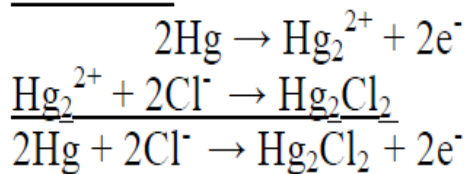
$\text{Hg} / \text{Hg}_2\text{Cl}_{2(\text{sat})}, \text{KCl} //$

KCl is used to maintain constant ionic strength.

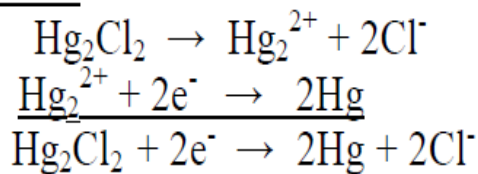


## Calomel electrode

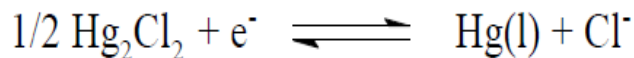
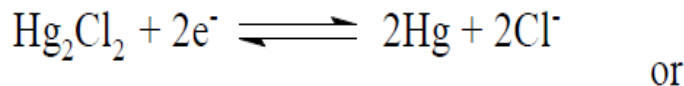
As anode:



As cathode:



The net reversible electrode reaction is



$$\text{Electrode potential } E = E^0 - \frac{2.303 RT}{F} \log [\text{Cl}^-]$$

$$\text{At 298K, } E_{\text{cal}} = E^0_{\text{cal}} - 0.0591 \log [\text{Cl}^-]$$

Since the calomel electrode is reversible with respect to chloride ion its electrode potential depends on the concentration of KCl solution.

## Calomel electrode

KCl concentration	0.1N	1N	Saturated
Electrode potential (V)	0.334	0.281	0.2422

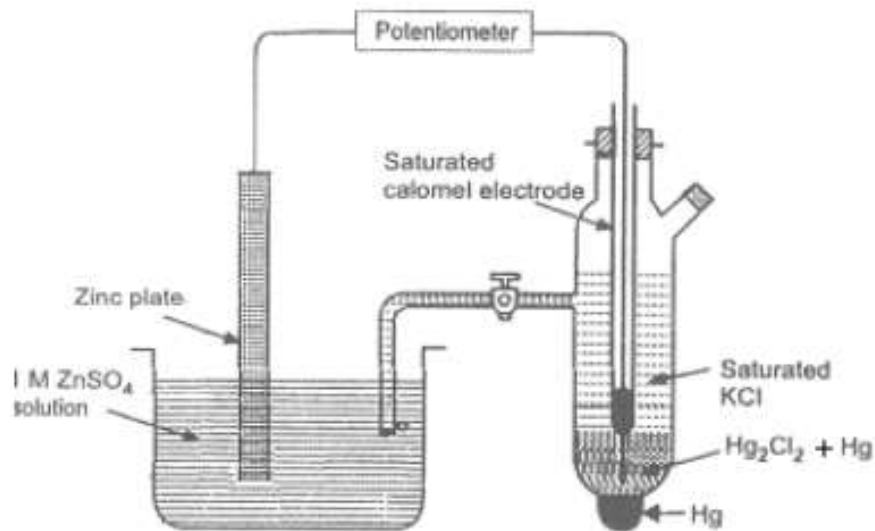
### **Advantages**

- 1. It is very simple in construction.**
- 2. The potential is reproducible and stable over a long period.**
- 3. Its electrode potential will not vary with temperature.**

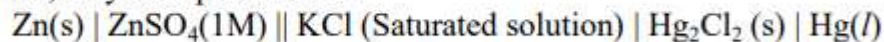
Hence, it is commonly used as secondary reference electrode for potential measurements.

# Determination of single electrode potential using calomel electrode

The test electrode (e.g.,  $\text{Zn}^{2+}/\text{Zn}$ ) is coupled with a saturated calomel electrode



The cell, so formed, may be represented as



## Determination of single electrode potential using calomel electrode

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

$$= E_{\text{cal}} - E_{\text{Zn}^{2+}/\text{Zn}}$$

$$= 0.2422 - E_{\text{Zn}^{2+}/\text{Zn}}$$

$$\text{i.e., } E_{\text{Zn}^{2+}/\text{Zn}} = 0.2422 - E_{\text{cell}}$$



## Determination of Electrode Potential OF Cu electrode:

The potential of Cu electrode can be measured by coupling with standard hydrogen electrode (SHE).

**At Anode:** Oxidation



**At Cathode:** Reduction

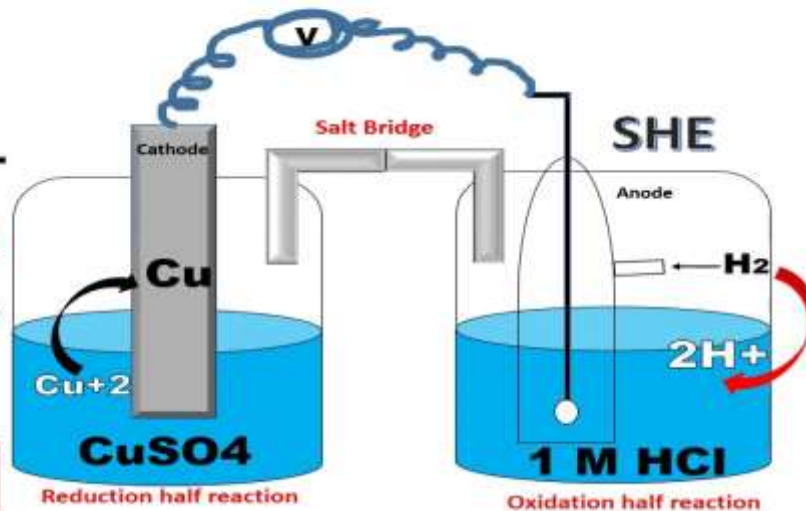


Overall reaction



Electrode reduction potential of Cu = 0.34 volt

Electrode oxidation potential of SHE = 0.00 volt



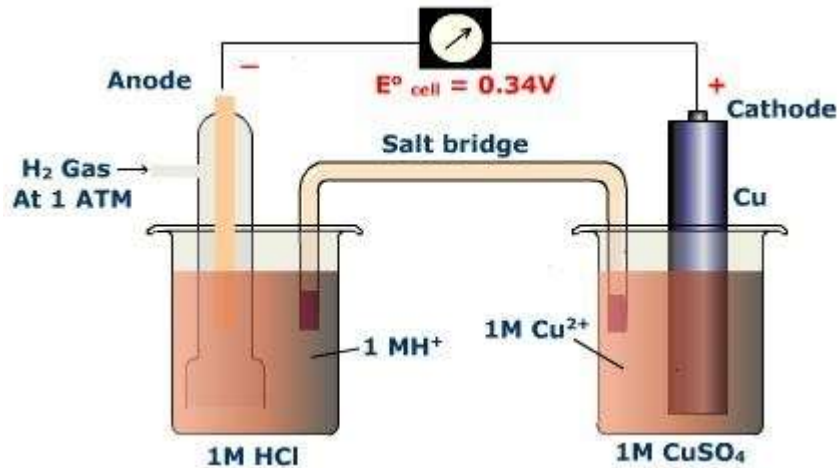
$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

$$E_{\text{cell}} = E_{\text{Cu}} - E_{\text{Hydrogen}}$$

$$E_{\text{Cu}} = E_{\text{cell}} (0.34) + 0$$

$$E_{\text{Cu}} = 0.34\text{V}$$

## Determination of single electrode potential



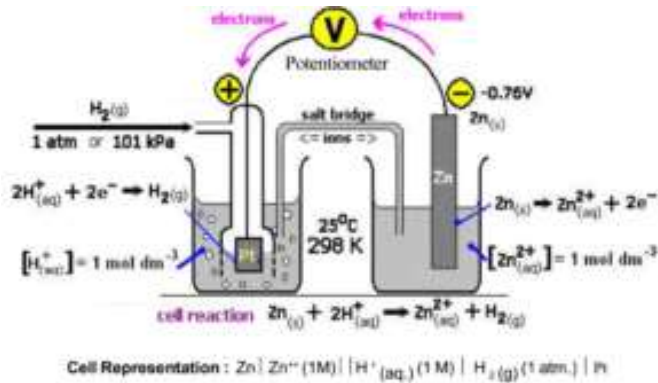
$$E_{cell} = E_{cathode} - E_{anode}$$

$$E_{cell} = E_{Cu} - E_{Hydrogen}$$

$$E_{Cu} = E_{cell} (0.34) + 0$$

$$E_{Cu} = 0.34V$$

# Determination of single electrode potential



$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

$$E_{\text{cell}} = E_{\text{H}^+} - E_{\text{Zn}^{+2}/\text{Zn}}$$

$$E_{\text{Zn}^{+2}/\text{Zn}} = 0 - E_{\text{cell}}$$

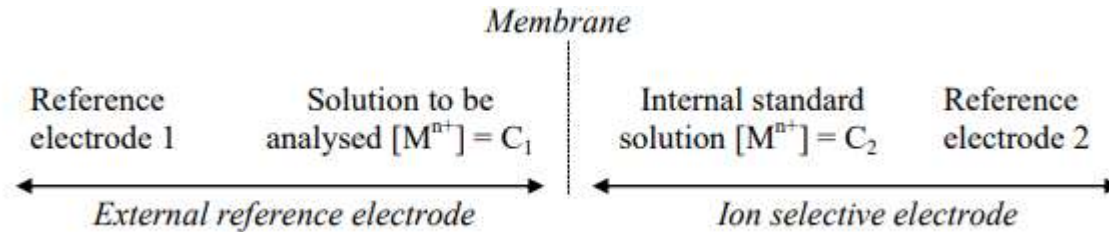
$$E_{\text{Zn}^{+2}/\text{Zn}} = 0 - 0.76$$

$$= -0.76\text{V}$$

# Ion-selective electrodes

Ion-selective electrode is the one which selectively responds to a specific ion in a mixture and potential developed at the electrode is a function of concentration of that ion in the solution. The electrode generally consists of a membrane which is capable of exchanging the specific ions with the solution with which it is in contact.

Therefore these electrodes are also referred to as membrane electrodes



There are three types of membranes

(1) Glass membrane (e.g., glass electrode).

(2) Solid state membranes

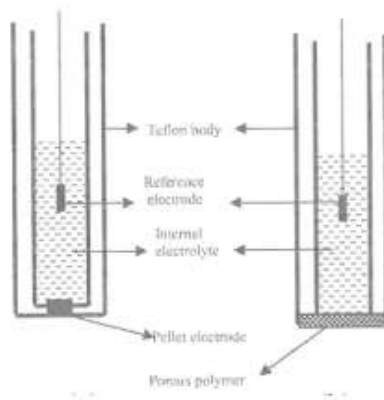
(i) For fluoride ( $F^-$ ) ions- lanthanum trifluoride crystal doped with europium difluoride.

(ii) For chloride ( $Cl^-$ ) ions – pressed pellet of  $Ag_2S + AgCl$ . The electrode has a teflon body and crystal is held in position with epoxy resin.

(3) Liquid state membranes:

(i) For certain alkali and alkaline earth cations-neutral monocyclic crown ethers and phosphate diester.

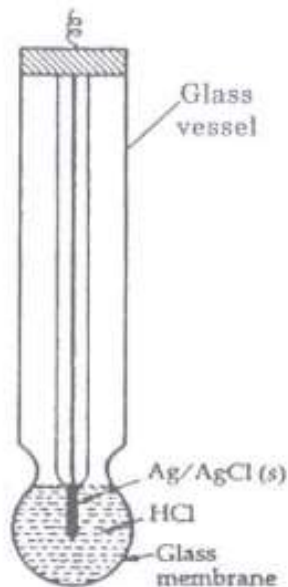
(ii) For anions-iron phenanthrolic complexes. Liquid state membrane is usually obtained by absorbing the active molecules on an inert porous support such as porous polymer.



*Applications:* Ion selective electrodes are used in determining

- (i) The concentration of a number of cations such as  $H^+$ ,  $Li^+$ ,  $Na^+$ ,  $K^+$ ,  $Ag^+$ ,  $NH_4^+$ ,  $Cd^{2+}$ ,  $Pb^{2+}$ ,  $Cu^{2+}$ ,  $Ca^{2+}$  and hardness [ $Ca^{2+} + Mg^{2+}$ ];
- (ii) The concentration of anions such as  $F^-$ ,  $NO_3^-$ ,  $CN^-$ ,  $S^{2-}$  and halide ions;
- (iii) The pH of a solution using glass electrode ( $H^+$  ion-selective electrode) and
- (iv) The concentration of gas using gas sensing electrodes. For example, an electrode which measures the level of  $CO_2$  in blood samples makes use of glass electrode in contact with a very thin  $CO_2$  permeable silicone rubber membrane soaked in a dilute solution of sodium bicarbonate.

# Glass electrode

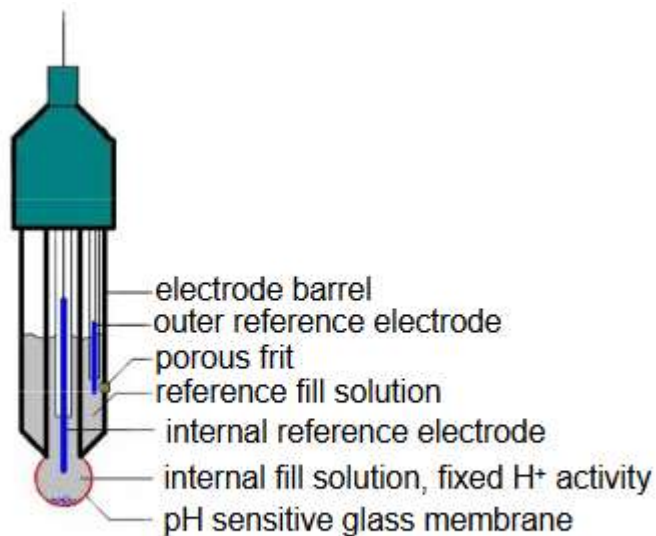


Construction: A glass electrode (Fig.10.) consists of a long glass tube with a thin walled glass bulb at one end. Special glass (Corning glass containing 22%  $\text{Na}_2\text{O}$ , 6%  $\text{CaO}$  and 72%  $\text{SiO}_2$ ) of low melting point and high electrical conductance is used for the purpose. This glass can specifically sense hydrogen ions up to a pH of about 9. The bulb contains 0.1 M HCl and a Ag/AgCl electrode (as internal reference electrode) is immersed into the solution and connected by a platinum wire for electrical contact.

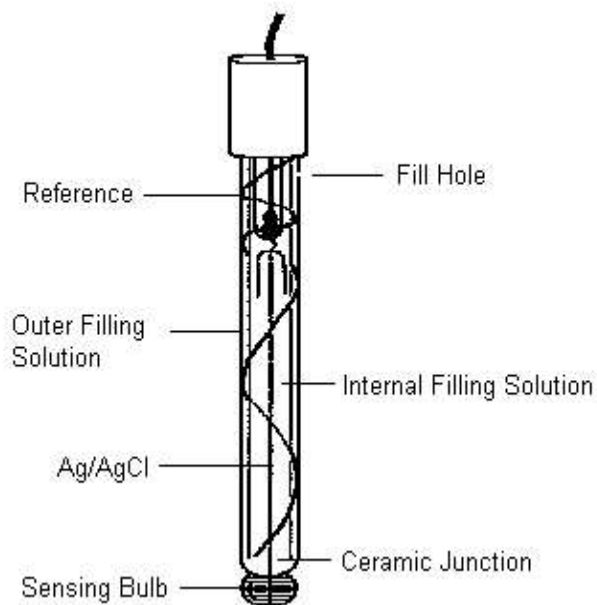
The electrode is represented as,

$\text{Ag} \mid \text{AgCl (s)} \mid \text{HCl (0.1M)} \mid \text{glass.}$

# Glass electrode



[http://upload.wikimedia.org/wikipedia/commons/e/e9/Glass\\_electrode\\_scheme.jpg](http://upload.wikimedia.org/wikipedia/commons/e/e9/Glass_electrode_scheme.jpg)



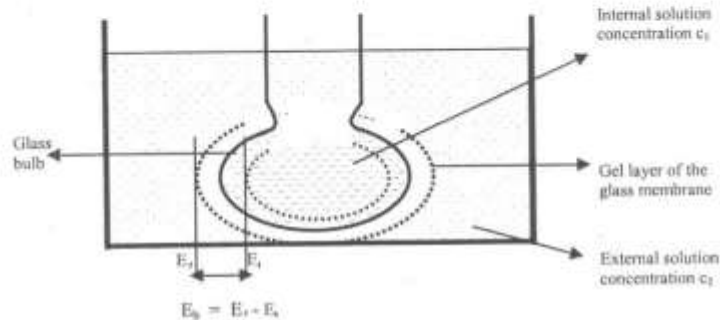


# Electrode potential of glass electrode (Eg)

*Principle:* If a thin walled glass bulb containing an acid is immersed in another solution, the membrane undergoes an ion exchange reaction;  $\text{Na}^+$  ions on the glass are exchanged for  $\text{H}^+$  ions. The potential is developed across the glass membrane (Fig.11).



The potential difference,  $E_b$  at the interface also referred to as the boundary potential is the result of difference in potential ( $E_2 - E_1$ ) developed across the gel layer of glass membrane between the two liquids.



$E_b$  can be related to the difference in the hydrogen ion concentration of the two solutions by the relation,

$$E_b = E_2 - E_1 = \frac{RT}{nF} (\ln C_2 - \ln C_1) \quad \dots\dots(1)$$

Where  $C_1$  is the concentration of  $H^+$  ions of acid solution inside the glass bulb and  $C_2$  is the concentration of the acid solution into which the glass bulb is dipped.

$$E_b = - \frac{RT}{nF} \ln C_1 + \frac{RT}{nF} \ln C_2 \quad \dots\dots(2)$$

If the concentration  $C_1$  of the solution inside the glass bulb is constant, then the first term on the R.H.S. of equation (2) is constant. Therefore

$$E_b = \text{constant} + \frac{RT}{nF} \ln C_2$$

Substituting the value of R and F at 298K

$$E_b = L + 0.0591 \log C_2 \quad \dots\dots\dots(3)$$

Where L is a constant which depends primarily on the pH of the solution taken in the bulb and glass electrode assembly. Since  $C_2 = [H^+]$  of the solution, Equation (3) written as,

$$E_b = L - 0.0591 \text{ pH} \quad \dots\dots\dots(4)$$

The boundary potential established is mainly responsible for the glass electrode potential  $E_g$  and is given by

$$E_g = E_b + E_{Ag/AgCl} \quad \dots\dots\dots(5)$$

From equation (1),  $E_b = 0$  when  $C_1 = C_2$ . But in practice, it has been observed that even when  $C_1 = C_2$ , a small potential is developed. This is called asymmetric potential ( $E_{asy}$ ). Hence, Equation (5) can be written as

$$E_g = E_b + E_{Ag/AgCl} + E_{asy}$$

$$E_g = L - 0.0591 \text{ pH} + E_{Ag/AgCl} + E_{asy}$$

$$E_g = E_g^0 - 0.0591 \text{ pH} \dots \dots \dots (6)$$

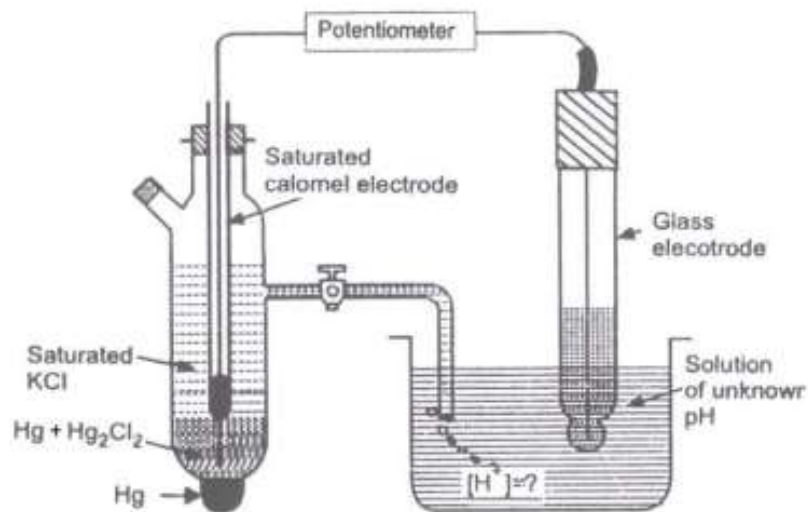
Where  $E_g^0$  is a constant equal to  $L + E_{Ag/AgCl} + E_{asy}$

# Determination of pH using glass electrode

The glass electrode is immersed in the solution, the pH of which is to be determined. It is combined with a reference electrode such as a calomel electrode through a salt bridge.

The cell assembly is represented as,

$\text{Hg}(l) \mid \text{Hg}_2\text{Cl}_2(s) \mid \text{KCl}(\text{Saturated solution}) \parallel \text{Solution of unknown pH} \mid \text{glass} \mid \text{HCl}(0.1\text{M}) \mid \text{AgCl}(s) \mid \text{Ag}(s)$



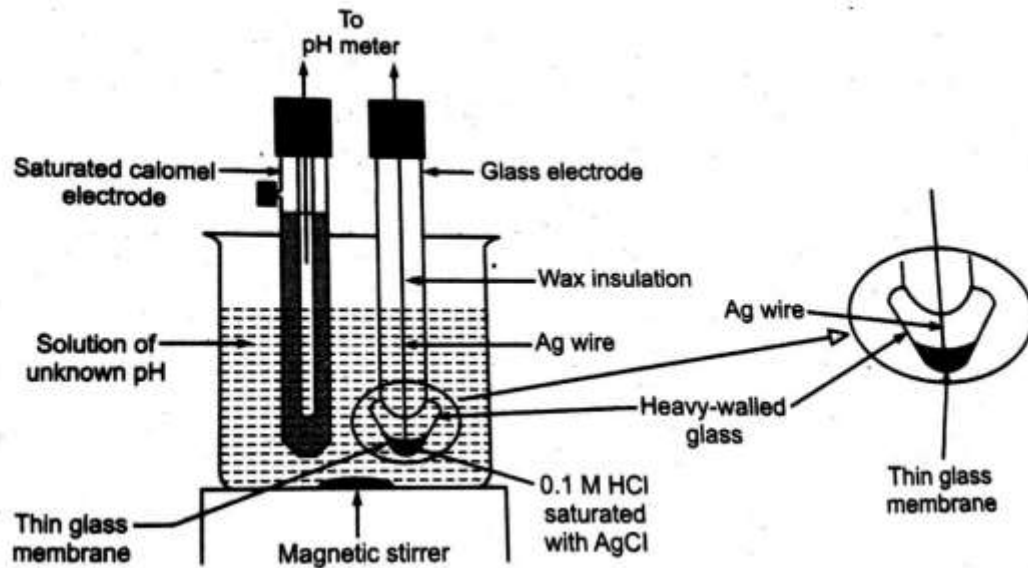
The emf of the above cell,  $E_{\text{cell}}$  is measured using an electronic voltmeter with a null type potentiometer circuit (or a pH meter) (An ordinary potentiometer with a low resistance of the galvanometer is not used because of high internal resistance of the glass electrode).

$E_{\text{cell}}$  measured is the difference between the calomel electrode ( $E_{\text{cal}}$ ) and  $E_g$  .

$$E_{\text{cell}} = E_g - E_{\text{cal}}$$

$$= [E_g^0 - 0.0591 \text{ pH}] - E_{\text{cal}}$$

$$\text{Therefore, pH} = \frac{E_g^0 - E_{\text{cal}} - E_{\text{cell}}}{0.0591}$$



*Advantages of glass electrode:*

- (i) Glass electrode can be employed in the presence of strong oxidizing or reducing substances and metal ions.
- (ii) It is not poisoned easily.
- (iii) Accurate results are obtained between pH range 1-9. However, by using special glass electrodes, pH 1-13 can be measured.
- (iv) It is simple to operate, can be used in portable instruments and therefore extensively used in chemical, industrial, agricultural and biological laboratories.

## Some Ions Measured with Ion-Specific Electrodes

Species Detected	Typical Sample
$\text{NH}_3/\text{NH}_4^+$	Industrial wastewater, seawater
$\text{CO}_2/\text{HCO}_3^-$	Blood, groundwater
$\text{F}^-$	Drinking water, urine, soil, industrial stack gases
$\text{Br}^-$	Grain, plant tissue
$\text{I}^-$	Milk, pharmaceuticals
$\text{NO}_3^-$	Soil, fertilizer, drinking water
$\text{K}^+$	Blood serum, soil, wine
$\text{H}^+$	Laboratory solutions, soil, natural waters



*Limitations of glass electrode:*

- (i) In strongly acidic solutions of  $\text{pH} < 1$ , the salt effect due to anions is observed.
- (ii) It can be used upto a  $\text{pH}$  of 13 but being sensitive to  $\text{Na}^+$  ions above a  $\text{pH}$  of 9, the linear relationship between glass electrode altered. So an alkaline error is introduced beyond a  $\text{pH}$  of 9, which should be taken into consideration.
- (iii) It does not function properly in some organic solvents like pure alcohol.