

# ELECTROCHEMISTRY

by Apni Kaksha ::  
Class XII BOARD EXAMS (Target 100)

These notes have  
been verified by  
CBSE Science Toppers.

Previous 15 year  
Questions have been  
integrated in the  
notes.

↳ No part  
of syllabus  
removed from  
these notes.



Raman  
Dhatarwal

Target 100

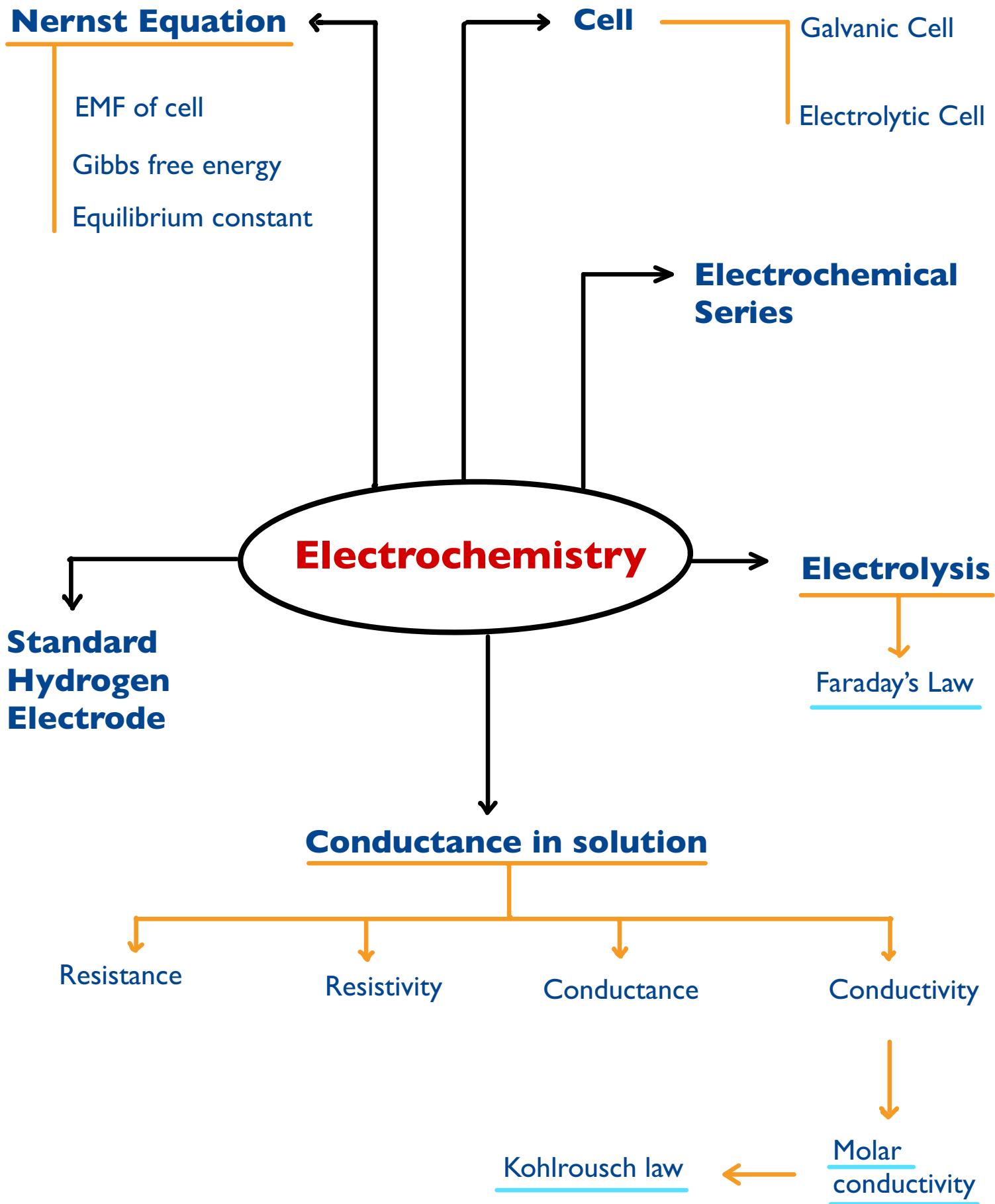
# HOW TO STUDY THE NOTES?

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- Coloured and double sided print
- Revise the notes at least 3-4 time
- Write to revise | 10% rule
- Keep track of previous year qs
- See the marking scheme



## Flow Chart

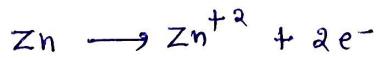


## Electrochemistry

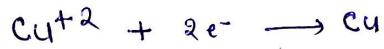
→ It is study of production of electricity from energy which is released during spontaneous chemical reactions and the use of electrical energy to bring about non-spontaneous chemical transformation.

### Some Basic Definitions -:

Oxidation -: Loss of electron



Reduction -: Gain of electron



Electrolyte -: A solution that contains ions is called electrolyte. Electrolyte is an ionic conductor.

Electrode -: Surface at which oxidation or reduction takes place.

Redox Reaction -: An oxidation-reduction (redox) reaction.



### Placing a Zn rod in $\text{CuSO}_4$ solution -:

→  $\text{CuSO}_4$  solution is blue in colour. But if we place a Zn rod in  $\text{CuSO}_4$  solution, colour fades out. This is because of reduction of  $\text{Cu}^{+2} \rightarrow \text{Cu}$ .



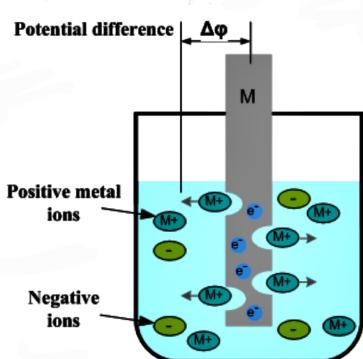
→ Above is a spontaneous reaction. It does not require any external work.



Electrode Potential -: Potential difference between metal and metal ion in which electrode is dipped is called electrode potential.

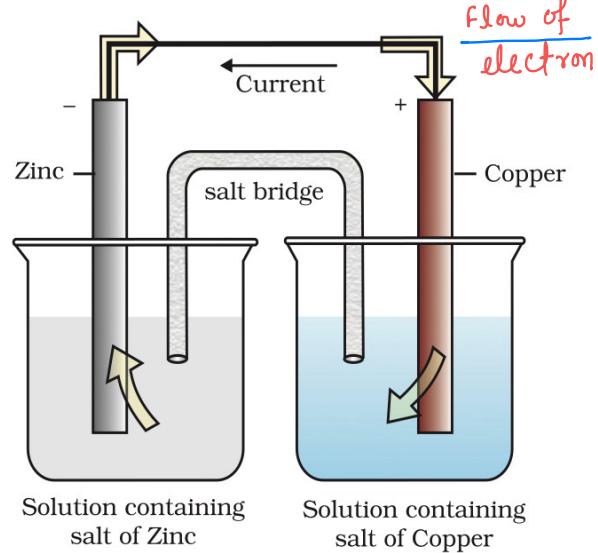
→ Electrode potential of Zn →  $\text{Zn} | \text{ZnSO}_4$

Electrode potential of Cu →  $\text{Cu} | \text{CuSO}_4$



Galvanic or Voltic Cell :- A galvanic cell is a an electrochemical cell that converts the chemical energy of a spontaneous redox reaction into electrical energy.

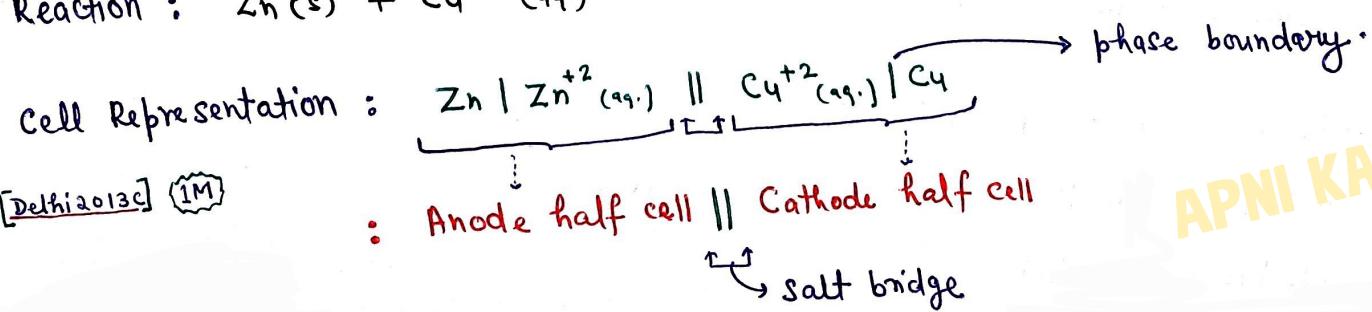
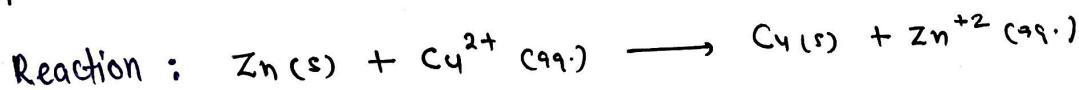
- Spontaneous then  $\Delta G^\circ = \text{OVR}$ .
- In this device  $\Delta G^\circ$  of spontaneous redox reaction is converted into electrical work ( which may be used for running a motor, fan, heater etc.)



Construction :- It consist of two metallic electrodes dipping in electrolytic solution. The solution in two compartment is connected through an inverted U shaped tube containing a mixture of agar-agar jelly and an electrolyte like  $\text{KCl}$ ,  $\text{KNO}_3$  etc. This tube is called salt bridge.

- Salt bridge is necessary because
  - [Delhi 2011] i) It connects the solution of two half cells, thus completes the cell circuit.
  - ii) It prevents diffusion of solutions from one compartment to other.
- In representation of cell, salt bridge is represented by ||.
- In galvanic cell : Oxidation at Anode [ negative plate]  
Reduction at cathode [ positive plate]

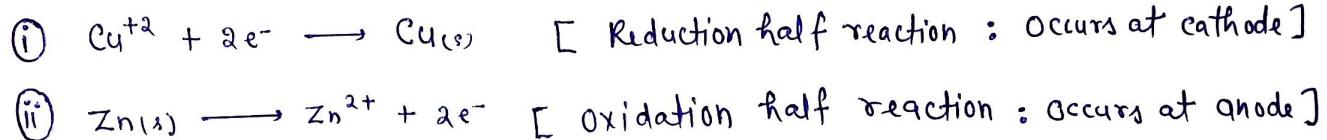
Daniell Cell :- Among the galvanic cells when cell is designed in such a manner to make the use of spontaneous reaction between  $\text{Zn}$  and  $\text{Cu}^{+2}$  ion to produce an electric current, that cell is called Daniell cell.



→  $\text{Zn}$  : Anode (oxidation) and  $\text{Cu}$  : Cathode (reduction)

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→ The two half cell reactions are



### Electrochemical Cell

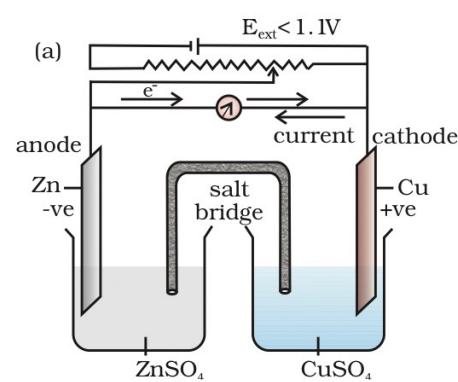
#### i) Galvanic Cell

→ Chemical Energy → Electrical Energy

→  $\Delta G = \ominus Vc$  Spontaneous Reaction

→ Power is produced.

→ a)



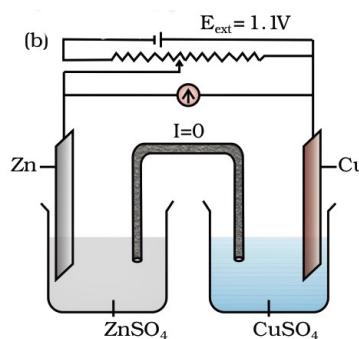
When  $E_{\text{ext}} < 1.1 \text{ V}$

- (i) Electrons flow from Zn rod to Cu rod hence current flows from Cu to Zn.
- (ii) Zn dissolves at anode and copper deposits at cathode.

#### ii) Reversible

→ No Net reaction

b)



- When  $E_{\text{ext}} = 1.1 \text{ V}$
- (i) No flow of electrons or current.
  - (ii) No chemical reaction.

#### iii) Electrolytic Cell

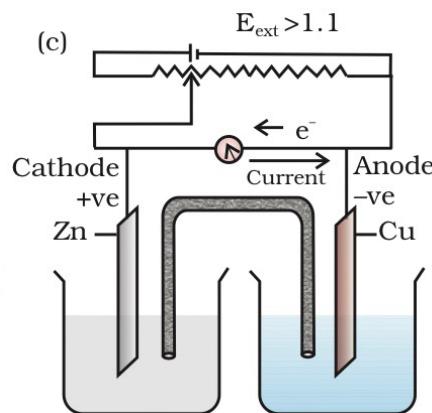
→ Electrical energy → Chemical energy

→ Non spontaneous Reaction

[ $\Delta G = +Vc$ ]

→ Power is consumed.

c)



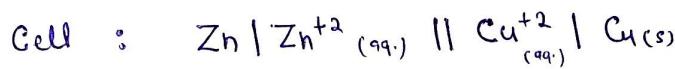
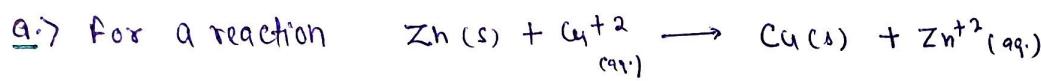
- When  $E_{\text{ext}} > 1.1 \text{ V}$
- (i) Electrons flow from Cu to Zn and current flows from Zn to Cu.
  - (ii) Zinc is deposited at the zinc electrode and copper dissolves at copper electrode.

→ functioning of Daniell cell when external voltage ( $E_{\text{ext}}$ ) opposing the cell potential is applied.

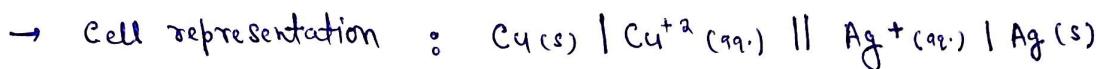
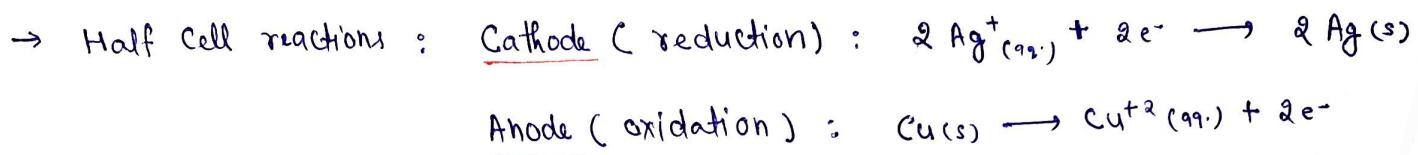
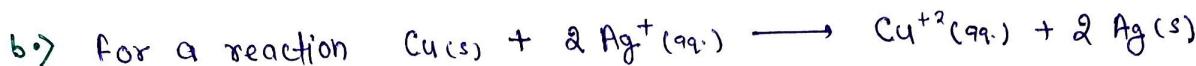
NOTE :- i) When the concentration of all the species involved in a half cell is unity then the electrode potential is known as Standard Electrode Potential.

ii) IUPAC Convention : Standard Reduction Potential (SRP) is S.E.P.  
iii) Cell Potential :- The potential difference between the two electrodes of a galvanic cell is called the cell potential and is measured in Volts.

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} = E_{\text{right}} - E_{\text{left}} \quad [\text{Cell : Anode half || Cathode half cell}]$$



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

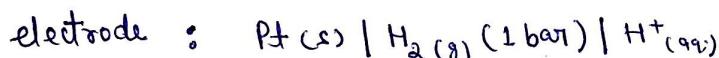


$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}}$$

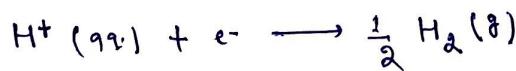
$$= E_{\text{Ag}^{+}/\text{Ag}} - E_{\text{Cu}^{+2}/\text{Cu}}$$

### Standard Hydrogen Electrode :-

→ Representation of half cell for standard hydrogen electrode :

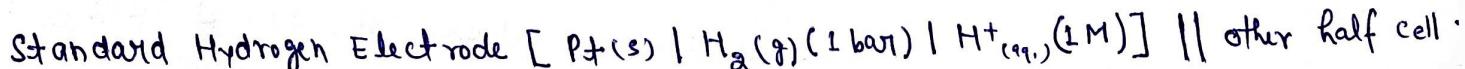


→ According to convention, a half cell called standard hydrogen electrode is assigned a zero potential at all temperatures corresponding to the reaction



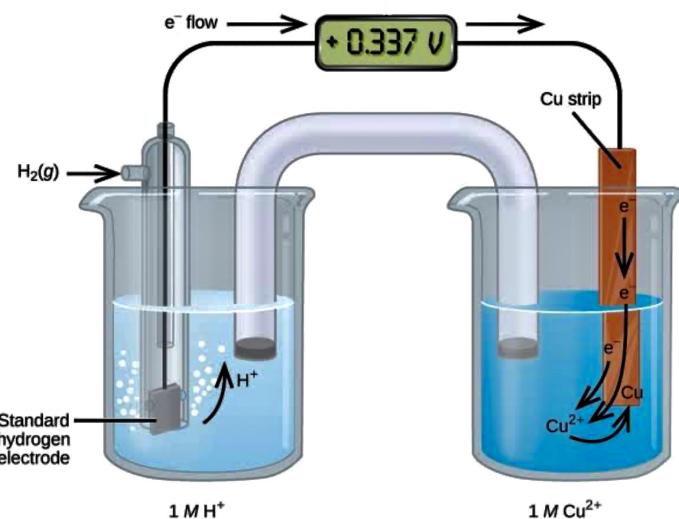
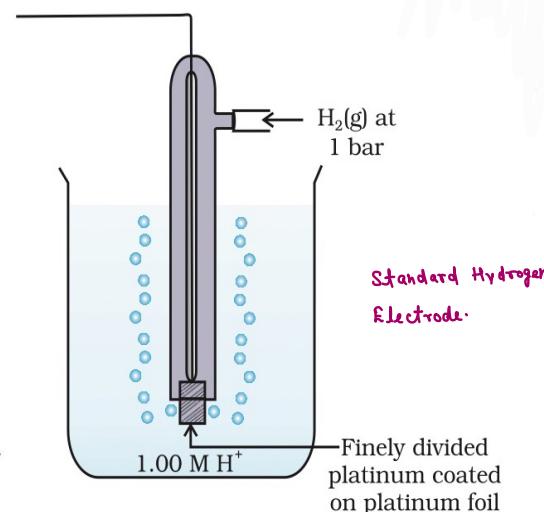
### Measurement of electrode potential :-

→ Construct a cell by taking standard hydrogen electrode as anode (reference half cell) and other half cell as cathode, gives the reduction potential of other half cell.



→ If the concentrations of the oxidised and the reduced forms of species in the right hand half cell are unity. Then the cell potential is equal to standard electrode potential ( $E^\circ_R$ ) of the given half cell.  $E^\circ = E^\circ_R - E_L = E^\circ_R - 0 = E^\circ_R$

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*i* → To calculate  $E^\circ_{\text{Cu}^{+2}/\text{Cu}}$ , make a cell  $\text{Pt(s)} \mid \text{H}_2(\text{g}) \text{ (1 bar)} \mid \text{H}^+(\text{aq.}) \text{ 1M} \parallel \text{Cu}^{+2}(\text{aq.}) \text{ 1M} \mid \text{Cu}$

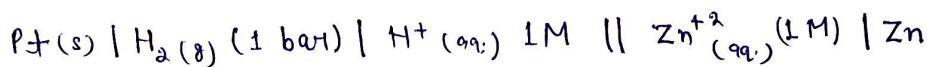
→ EMF of this cell = 0.34V

$$E^\circ_{\text{cell}} = E^\circ_{\text{Cu}^{+2}/\text{Cu}} - E^\circ_{\text{HSE}}$$

$$0.34\text{V} = E^\circ_{\text{Cu}^{+2}/\text{Cu}} - 0 \quad \text{then} \quad \boxed{E^\circ_{\text{Cu}^{+2}/\text{Cu}} = 0.34\text{V}}$$

Similarly;  $E^\circ_{\text{Zn}^{+2}/\text{Zn}}$  can be calculated by following cell.

*ii*



$$\rightarrow E^\circ_{\text{cell}} = -0.76\text{V}$$

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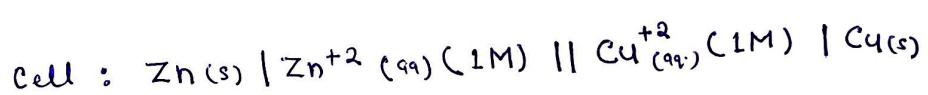
$$E^\circ_{\text{cell}} = E^\circ_{\text{Zn}^{+2}/\text{Zn}} - E^\circ_{\text{SHE}} = E^\circ_{\text{Zn}^{+2}/\text{Zn}} - 0$$

$$\text{then} \quad \boxed{E^\circ_{\text{Zn}^{+2}/\text{Zn}} = -0.76\text{V}}$$

→ In first case, +ve value of SEP indicates that  $\text{Cu}^{+2}$  get reduced more easily than  $\text{H}^+$ , means we can say that  $\text{H}_2$  gas can reduce  $\text{Cu}^{+2}$  ion.

→ In second case, -ve value of SEP indicates that Zn get oxidised by  $\text{H}^+$  ion.

EMF of Daniell Cell :-



$$E^\circ_{\text{cell}} = E^\circ_{\text{Cu}^{+2}/\text{Cu}} - E^\circ_{\text{Zn}^{+2}/\text{Zn}} = 0.34\text{V} - (-0.76\text{V}) = 1.10\text{V}$$

Inert Electrode :- Metals like platinum or gold are used as inert electrode. They do not participate in the reaction but provide their surface for oxidation or reduction reactions and for conduction of electrons.

For example :- Hydrogen Electrode :  $\text{Pt(s)} \mid \text{H}_2(\text{g}) \mid \text{H}^+(\text{aq.})$

Bromine Electrode :  $\text{Pt(s)} \mid \text{Br}_2(\text{aq.}) \mid \text{Br}^-(\text{aq.})$

Nernst Equation :- It gives relation between electrode potential, temperature and concentration of metal ions.

for reaction  $\text{M}^{n+}_{(\text{aq.})} + n\text{e}^- \longrightarrow \text{M(s)}$

$n \rightarrow$  No. of electrons

$$\rightarrow E^\circ_{\text{M}^{n+}/\text{M}} = E^\circ_{\text{M}^{n+}/\text{M}} - \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]}$$

$$\rightarrow \boxed{E^\circ_{\text{M}^{n+}/\text{M}} = E^\circ_{\text{M}^{n+}/\text{M}} - \frac{0.059}{n} \log \frac{1}{[M^{n+}]}}$$

$$\left\{ \begin{array}{l} R = \text{Gas constant} = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \\ F = \text{Faraday's constant} = 96407 \text{ C mol}^{-1} \\ T = 298 \text{ K} \quad \text{and} \quad [M] = 1 = [\text{solid}] \end{array} \right.$$

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→ In Daniell Cell : Electrode potential for any given concentration of  $\text{Cu}^{+2}/\text{Zn}^{+2}$

For Cathode :  $E_{\text{Cu}^{+2}/\text{Cu}} = E_{\text{Cu}^{+2}/\text{Cu}}^{\circ} - \frac{0.059}{2} \log \frac{1}{[\text{Cu}^{+2}_{(\text{aq.})}]}$

For Anode :  $E_{\text{Zn}^{+2}/\text{Zn}} = E_{\text{Zn}^{+2}/\text{Zn}}^{\circ} - \frac{0.059}{2} \log \frac{1}{[\text{Zn}^{+2}_{(\text{aq.})}]}$

Cell Potential  $E_{\text{cell}} = E_{\text{Cu}^{+2}/\text{Cu}} - E_{\text{Zn}^{+2}/\text{Zn}}$

$$= [E_{\text{Cu}^{+2}/\text{Cu}}^{\circ} - E_{\text{Zn}^{+2}/\text{Zn}}^{\circ}] - \frac{0.059}{2} \log \frac{[\text{Zn}^{+2}_{(\text{aq.})}]}{[\text{Cu}^{+2}_{(\text{aq.})}]}$$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.059}{2} \log \frac{[\text{Zn}^{+2}_{(\text{aq.})}]}{[\text{Cu}^{+2}_{(\text{aq.})}]} - [\#]$$

Question :- for the cell  $\text{Zn(s)} | \text{Zn}^{+2}(2\text{M}) \parallel \text{Cu}^{+2}(0.5\text{M}) | \text{Cu(s)}$

[Delhi 2011C] 3M

(i) Write the equation for each half cell.

Given:  $E_{\text{Zn}^{+2}/\text{Zn}}^{\circ} = -0.76\text{V}$

(ii) calculate cell potential at  $25^\circ\text{C}$ .

$E_{\text{Cu}^{+2}/\text{Cu}}^{\circ} = +0.34\text{V}$

Answer :- (i) Anode :  $\text{Zn(s)} \rightarrow \text{Zn}^{+2}_{(\text{aq.})} + 2e^-$   
[2M]

Cathode :  $\text{Cu}^{+2}_{(\text{aq.})} + 2e^- \rightarrow \text{Cu(s)}$   
(0.5M)

(ii)  $E_{\text{cell}}^{\circ} = E_{\text{Cu}^{+2}/\text{Cu}}^{\circ} - E_{\text{Zn}^{+2}/\text{Zn}}^{\circ} = 0.34\text{V} - (-0.76\text{V}) = 1.10\text{V}$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.059}{2} \log \frac{[\text{Zn}^{+2}]}{[\text{Cu}^{+2}]} \Rightarrow 1.10\text{V} - \frac{0.059}{2} \log \frac{2}{0.5}$$

$$E_{\text{cell}} = 1.10\text{V} - \frac{0.059}{2} \times 0.602\text{V} = 1.10\text{V} - 0.0178\text{V} = 1.0822\text{V}$$

Question :- A Zn rod is dipped in  $0.1\text{M}$  solution of  $\text{ZnSO}_4$ . The salt is 95% dissociated at its dilution at  $298\text{K}$ . calculate the electrode potential.

[Delhi 2012C] 2M

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

Answer :- Reaction  $\text{Zn}^{+2} + 2e^- \rightarrow \text{Zn}$   $n=2$

By using Nernst equation, we get  $E_{\text{Zn}^{+2}/\text{Zn}} = E_{\text{Zn}^{+2}/\text{Zn}}^{\circ} - \frac{0.059}{2} \log \frac{1}{[\text{Zn}^{+2}]}$

$$\rightarrow [\text{Zn}^{+2}] = \frac{95}{100} \times 0.1 = 0.095\text{M}; \quad E_{\text{Zn}^{+2}/\text{Zn}} = -0.76\text{V} - \frac{0.059}{2} \log \frac{1}{0.095} = -0.7901\text{V}$$

Question :- Calculate the emf of the following cell at 298 K.



(3M)

Given :  $E^\circ_{\text{Cr}^{+3}/\text{Cr}} = -0.74\text{V}$        $E^\circ_{\text{Fe}^{+2}/\text{Fe}} = -0.44\text{V}$

[Delhi 2016]

Answer :- Half cell reactions :- At anode :  $[\text{Cr} \longrightarrow \text{Cr}^{3+} + 3e^-] \times 2$

At cathode :  $[\text{Fe}^{+2} + 2e^- \longrightarrow \text{Fe}] \times 3$

$$\rightarrow E^\circ_{\text{cell}} = E^\circ_{\text{Fe}^{+2}/\text{Fe}} - E^\circ_{\text{Cr}^{+3}/\text{Cr}}$$

then  $n = 6$

$$= -0.44\text{V} - (-0.74\text{V})$$

$$\rightarrow E^\circ = E^\circ - \frac{0.059}{n} \log \frac{[\text{Cr}^{+3}]^2}{[\text{Fe}^{+2}]^3}$$

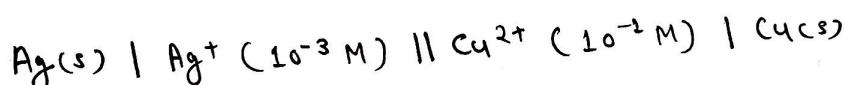
$$= 0.3\text{V}$$

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$$E^\circ_{\text{cell}} = 0.3\text{V} - \frac{0.059}{6} \log \frac{(0.01)^2}{(0.1)^3}$$

$$E^\circ_{\text{cell}} = 0.31\text{V}$$

Question :- Calculate the emf of the following cell at 25°C



(3M)

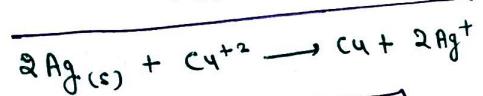
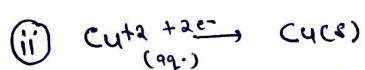
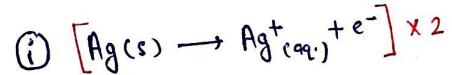
[CBSE 2013]

Given  $\rightarrow E^\circ_{\text{cell}} = +0.46\text{V}$  and  $\log 10^n = n$

Answer :-  $E^\circ_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.059}{2} \log \frac{[\text{Ag}^{+}]^2}{[\text{Cu}^{2+}]}$

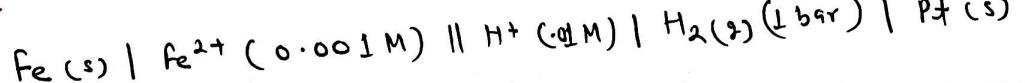
$$E^\circ_{\text{cell}} = 0.46\text{V} - \frac{0.059}{2} \log \frac{(10^{-3})^2}{(10^{-1})}$$

$$E^\circ_{\text{cell}} = 0.608\text{V}$$



$n=2$

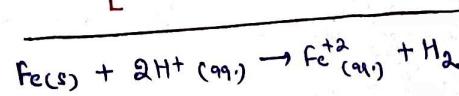
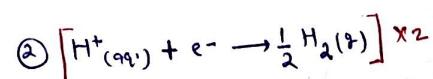
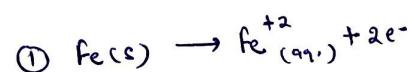
Question :- Calculate the emf of the following cell at 298 K (25°C)



(3M)

[Delhi 2013/2015]

Given  $\rightarrow E^\circ_{\text{cell}} = 0.44\text{V}$  (or  $E^\circ_{\text{Fe}^{+2}/\text{Fe}} = -0.44\text{V}$  and  $E^\circ_{\text{H}^{+}/\text{H}_2} = 0\text{V}$ )



$n=2$

Answer :-  $E^\circ_{\text{cell}} = E^\circ_{\text{H}^{+}/\text{H}_2} - E^\circ_{\text{Fe}^{+2}/\text{Fe}} = 0.44\text{V}$

$$E^\circ_{\text{cell}} = E^\circ - \frac{0.059}{2} \log \frac{[\text{Fe}^{+2}]}{[\text{H}^{+}]^2} = 0.44\text{V} - \frac{0.059}{2} \log \frac{(10^{-3})}{(10^{-1})^2}$$

$$E^\circ_{\text{cell}} = 0.44 - \frac{0.059}{2} = 0.4104\text{V.}$$

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Equilibrium Constant from Nernst Equation :- for a general reaction →



→ Nernst equation can be written as  $E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{RT}{nF} \ln Q$  Q → Reaction Quotient

→ At equilibrium  $E_{\text{cell}} = 0$   $0 = E_{\text{cell}}^{\circ} - \frac{RT}{nF} \ln K_c$

and  $Q = K_c = \text{Equilibrium Constant}$

$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

→ At 25°C  $T = 298\text{K}$

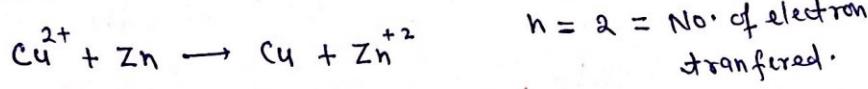
$$f = 96487 \text{ C mol}^{-1}$$

$$R = 0.001987 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$E_{\text{cell}}^{\circ} = \frac{2.303 RT}{nF} \log K_c$$

$$E_{\text{cell}}^{\circ} = \frac{0.059}{n} \log K_c$$

Example :- for Daniell cell  $E_{\text{cell}}^{\circ} = 1.1\text{V}$  then  $1.1\text{V} = \frac{0.059}{2} \log K_c$



$n = 2 = \text{No. of electrons transferred.}$

$$\log K_c = 37.288$$

$$K_c = 2 \times 10^{37}$$

Relation between  $E_{\text{cell}}$  and Gibbs energy of reaction :-

$$\Delta G = -nF E_{\text{cell}}$$

[ Electrical work done in one second is equal to electrical potential multiplied by total charge ( $E_{\text{cell}} \times nF$ ) ]

→ Work done by galvanic cell is equal to decrease in Gibbs energy.

→ If concentration of all the reacting species is unity then  $E_{\text{cell}} = E_{\text{cell}}^{\circ}$ .

$$\Delta G^{\circ} = -nF E_{\text{cell}}^{\circ}$$

→ By measuring  $E_{\text{cell}}^{\circ}$ , we can calculate  $\Delta G^{\circ}$  and equilibrium constant ( $\Delta G^{\circ} = -RT \ln K$ )

Example :- for Daniell cell  $E_{\text{cell}}^{\circ} = 1.1\text{V}$  then value of  $\Delta G^{\circ} = ?$  If  $f = 96500 \text{ C mol}^{-1}$

$$\hookrightarrow n=2$$

$$\Delta G^{\circ} = -nF E^{\circ} = -2 \times 96500 \times 1.1$$

[CBSE 2013  
Delhi 2013]

$$\Delta G^{\circ} = -212300 \text{ J mol}^{-1}$$

2M

Question :- Calculate  $\Delta G^{\circ}$  and  $\log K_c$  for the following reaction :



CBSE 2019

3M

Given :  $E_{\text{Cd}^{2+}/\text{Cd}}^{\circ} = -0.403\text{V}$  ,  $E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} = -0.763\text{V}$

Answer -:  $E_{\text{cell}}^{\circ} = E_{\text{Cd}^{2+}/\text{Cd}}^{\circ} - E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} = (-0.403) - (-0.763) = 0.36 \text{ V}$

$n = 2 = \text{No. of mole of electron used}$ ,  $F = 96500 \text{ C mol}^{-1}$

$$\textcircled{1} \rightarrow \Delta G^{\circ} = -nF^{\circ}F = -2 \times 96500 \times 0.36 \text{ V} = \underline{69480 \text{ J mol}^{-1}}$$

$$\textcircled{2} \rightarrow E_{\text{cell}}^{\circ} = \frac{0.059}{n} \log K_c \quad \text{then} \quad \log K_c = \frac{n E_{\text{cell}}^{\circ}}{0.059} = \frac{2 \times 0.36}{0.059} = \underline{12.18}$$

Question :- A copper-silver cell is set up. The copper ion concentration is  $0.10 \text{ M}$ . The concentration of silver ion is not known. The cell potential when measured was  $0.422 \text{ V}$ . Determine the concentration of silver ions in the cell. (3M)

Given:  $E_{\text{Ag}^{+}/\text{Ag}}^{\circ} = 0.80 \text{ V}$ ,  $E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} = 0.34 \text{ V}$

[Delhi 2010]

Answer -: Cell Reaction :  $\text{Cu}_{(\text{s})} + 2 \text{Ag}_{(\text{aq})}^{+} \longrightarrow \text{Cu}_{(\text{aq})}^{2+} + 2 \text{Ag}_{(\text{s})}$

$$E_{\text{cell}}^{\circ} = E_{\text{Ag}^{+}/\text{Ag}}^{\circ} - E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} = 0.80 \text{ V} - 0.34 \text{ V} = 0.46 \text{ V}$$

By using Nernst equation :  $E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.059}{n} \log \frac{[\text{Cu}^{2+}]}{[\text{Ag}^{+}]^2}$   $n=2 = \text{No. of electron taking part}$

$$(E_{\text{cell}} = 0.422 \text{ V})$$

$$([\text{Cu}^{2+}] = 0.1 \text{ M})$$

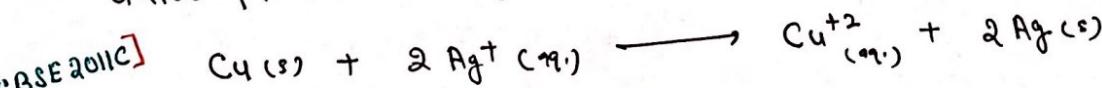
$$0.422 \text{ V} = 0.46 \text{ V} - \frac{0.059}{2} \log \frac{0.1}{[\text{Ag}^{+}]^2}$$

$$\log \frac{0.1}{[\text{Ag}^{+}]^2} = 1.288 \Rightarrow \frac{0.1}{[\text{Ag}^{+}]^2} = \text{antilog } 1.288 \\ = 19.41$$

$$\rightarrow \frac{0.1}{19.41} = [\text{Ag}^{+}]^2 = 0.00515$$

$$\rightarrow [\text{Ag}^{+}] = 0.0717 = 7.17 \times 10^{-2} \text{ M}$$

Question :- i) Write the formulation for the galvanic cell in which the reaction takes place. Identify the cathode and the anode reactions in it.



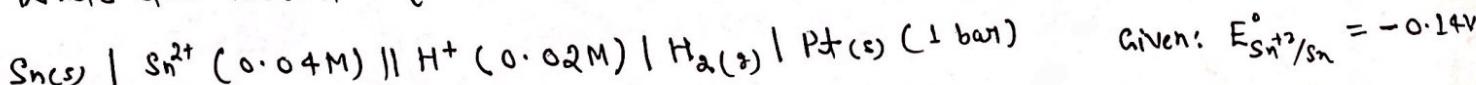
5M

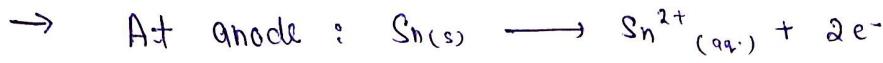
Answer -: At anode:  $\text{Cu}_{(\text{s})} \longrightarrow \text{Cu}_{(\text{aq})}^{2+} + 2e^-$

At cathode:  $2 \text{Ag}_{(\text{aq})}^{+} + 2e^- \longrightarrow 2 \text{Ag}_{(\text{s})}$

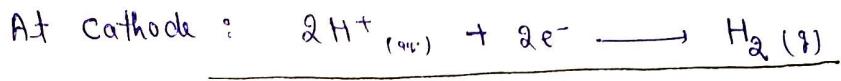
[Delhi 2010C] (1M)

ii) Write the Nernst equation and calculate the emf of the following cell.

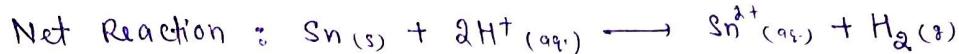




$n=2$



$$\begin{aligned} \rightarrow E_{cell}^\circ &= E_{\text{H}^+/\text{H}_2}^\circ - E_{\text{Sn}^{2+}/\text{Sn}}^\circ \\ &= 0\text{V} - (-0.14\text{V}) \\ &= 0.14\text{V} \end{aligned}$$



$$\rightarrow E_{cell} = E_{cell}^\circ - \frac{0.059}{n} \log \frac{[\text{Sn}^{2+}]}{[\text{H}^+]^2}$$

$$= 0.14\text{V} - \frac{0.059}{2} \log \frac{0.04}{(0.02)^2} = 0.14\text{V} - \frac{0.059}{2} \log \left(\frac{4}{100}\right) \left(\frac{100}{2}\right)^2$$

$$\rightarrow E_{cell} = 0.0909\text{V}$$

### Table of S.E.P at 298K

Reaction (Oxidised form + ne <sup>-</sup> → Reduced form)	E°/V
F <sub>2</sub> (g) + 2e <sup>-</sup> → 2F <sup>-</sup>	2.87
Co <sup>3+</sup> + e <sup>-</sup> → Co <sup>2+</sup>	1.81
H <sub>2</sub> O <sub>2</sub> + 2H <sup>+</sup> + 2e <sup>-</sup> → 2H <sub>2</sub> O	1.78
MnO <sub>4</sub> <sup>-</sup> + 8H <sup>+</sup> + 5e <sup>-</sup> → Mn <sup>2+</sup> + 4H <sub>2</sub> O	1.51
Au <sup>3+</sup> + 3e <sup>-</sup> → Au(s)	1.40
Cl <sub>2</sub> (g) + 2e <sup>-</sup> → 2Cl <sup>-</sup>	1.36
Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup> + 14H <sup>+</sup> + 6e <sup>-</sup> → 2Cr <sup>3+</sup> + 7H <sub>2</sub> O	1.33
O <sub>2</sub> (g) + 4H <sup>+</sup> + 4e <sup>-</sup> → 2H <sub>2</sub> O	1.23
MnO <sub>2</sub> (s) + 4H <sup>+</sup> + 2e <sup>-</sup> → Mn <sup>2+</sup> + 2H <sub>2</sub> O	1.23
Br <sub>2</sub> + 2e <sup>-</sup> → 2Br <sup>-</sup>	1.09
NO <sub>3</sub> <sup>-</sup> + 4H <sup>+</sup> + 3e <sup>-</sup> → NO(g) + 2H <sub>2</sub> O	0.97
2Hg <sup>2+</sup> + 2e <sup>-</sup> → Hg <sub>2</sub> <sup>2+</sup>	0.92
Ag <sup>+</sup> + e <sup>-</sup> → Ag(s)	0.80
Fe <sup>3+</sup> + e <sup>-</sup> → Fe <sup>2+</sup>	0.77
O <sub>2</sub> (g) + 2H <sup>+</sup> + 2e <sup>-</sup> → H <sub>2</sub> O <sub>2</sub>	0.68
I <sub>2</sub> + 2e <sup>-</sup> → 2I <sup>-</sup>	0.54
Cu <sup>+</sup> + e <sup>-</sup> → Cu(s)	0.52
Cu <sup>2+</sup> + 2e <sup>-</sup> → Cu(s)	0.34
AgCl(s) + e <sup>-</sup> → Ag(s) + Cl <sup>-</sup>	0.22
AgBr(s) + e <sup>-</sup> → Ag(s) + Br <sup>-</sup>	0.10
2H <sup>+</sup> + 2e <sup>-</sup> → H <sub>2</sub> (g)	0.00
Pb <sup>2+</sup> + 2e <sup>-</sup> → Pb(s)	-0.13
Sn <sup>2+</sup> + 2e <sup>-</sup> → Sn(s)	-0.14
Ni <sup>2+</sup> + 2e <sup>-</sup> → Ni(s)	-0.25
Fe <sup>2+</sup> + 2e <sup>-</sup> → Fe(s)	-0.44
Cr <sup>3+</sup> + 3e <sup>-</sup> → Cr(s)	-0.74
Zn <sup>2+</sup> + 2e <sup>-</sup> → Zn(s)	-0.76
2H <sub>2</sub> O + 2e <sup>-</sup> → H <sub>2</sub> (g) + 2OH <sup>-</sup> (aq)	-0.83
Al <sup>3+</sup> + 3e <sup>-</sup> → Al(s)	-1.66
Mg <sup>2+</sup> + 2e <sup>-</sup> → Mg(s)	-2.36
Na <sup>+</sup> + e <sup>-</sup> → Na(s)	-2.71
Ca <sup>2+</sup> + 2e <sup>-</sup> → Ca(s)	-2.87
K <sup>+</sup> + e <sup>-</sup> → K(s)	-2.93
Li <sup>+</sup> + e <sup>-</sup> → Li(s)	-3.05

Increasing strength of oxidising agent

Increasing strength of reducing agent

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- For  $F_2$  gas SEP is highest in table indicating that  $F_2$  has maximum tendency to get reduced to  $F^-$ :  $F_2$  is the strongest oxidising agent.
- Li has lowest SEP indicating that  $Li^+$  is a weakest oxidising agent and Li metal is the most powerful reducing agent.
- As value of SRP decreases for metal ion  $\Rightarrow$  Reducing power of metal increases

Example -: Arrange following metals in an increasing order of their reducing power.

SRP of metals are -

i) $K^+   K = -2.93V$	ii) $Ag^+   Ag = 0.80V$
iii) $Cu^{2+}   Cu = 0.34V$	iv) $Mg^{2+}   Mg = -2.37V$
v) $Cr^{+3}   Cr = -0.74V$	vi) $Fe^{+2}   Fe = -0.47V$

# Reducing Power of metal  $\propto \frac{1}{\text{Reduction Potential}}$

[CBSE 2010]

2M

# Order of reducing power :  $Ag < Cu < Fe < Cr < Mg < K$

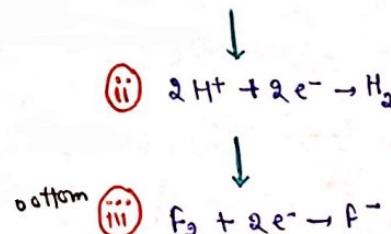
Electrochemical Series :- If SRP values of different electrodes are arranged in a series in increasing order, then series is called <sup>Top</sup>i)  $Li^+ + e^- \rightarrow Li$   
electrochemical series.

Application of series - :

i) SRP  $\downarrow \Rightarrow$  Reducing Power  $\uparrow$   
 $\Rightarrow$  Oxidising Power  $\downarrow$

ii) Anode : Oxidation  $\rightarrow$  Electrode higher up in series.

Cathode : Reduction  $\rightarrow$  Lower in series with respect to anode.



for Daniell cell  
Anode : Zn  
Cathode : Cu

iii) Metals which are higher up in series can displace metals in lower in series from their salt solution.



$$E^\circ_{Zn^{+2}/Zn} = -0.76V$$



$$E^\circ_{Cu^{+2}/Cu} = 0.34V$$

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iv) Metals placed above than hydrogen can release  $H_2$  gas on reaction with dilute acid solution.



### Conductance of electrolytic solutions and its measurement :-

Resistance :- Resistance is the hindrance provided by a conductor in the passage of current.

→  $R \propto$  length of conductor ( $l$ )

$$\propto \frac{1}{\text{cross sectional area} (A)}$$

$$R \propto \frac{l}{A} \Rightarrow R = \rho \frac{l}{A}$$

$$\rightarrow \rho = R \frac{A}{l} = \text{Resistivity.}$$

Resistivity :- Resistivity is defined as the resistance offered by a conductor of unit length and unit cross sectional area.

[If  $A = 1 m^2$  and  $l = 1 m$  then  $\rho = R$ .]

→ Unit of resistivity [Specific Resistance] = Ohm - metre [ $\Omega m$ ]

Conductance :- The ease with which current flows through a conductor.

→ Conductance [ $G$ ] =  $\frac{1}{R} = \frac{A}{\rho l} = K \frac{A}{l} = \text{conductivity} \times \frac{1}{\text{cell constant}}$

→ Conductivity ( $K$ ) =  $\frac{1}{\rho} = \frac{1}{\text{Resistivity}}$

→ Cell constant =  $\frac{l}{A}$   
( $C^*$ )

Unit of cell constant =  $m^{-1}$

Unit of conductance =  $\Omega m^{-1} = \text{Siemens}$  (S)

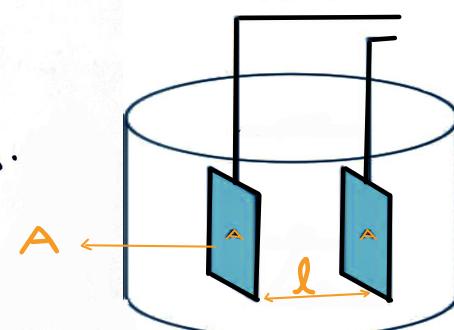
Unit of conductivity =  $S m^{-1}$   
=  $\Omega m^{-1} m^{-1}$

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# In case of conductance of a solution :-

$l \rightarrow$  length between the electrodes

$A \rightarrow$  cross sectional area of electrodes.



Molar Conductivity :- [ $\Lambda_m$  or  $\Lambda_m^{\circ}$ ] The conductance of solution kept between the electrodes at unit distance apart and having area of cross section large enough to accomodate sufficient volume of the solution that contains 1 mole of electrolyte.

→ If  $V$  volume of solution contains 1 mole of electrolyte, then

$$\text{molar conductivity } \Lambda_m = K \frac{A}{l} = \boxed{K \cdot V = \Lambda_m}$$

[Since  $l=1$  then  $V = l \times A = A$ ]

→ Molar conductivity  $\uparrow$  with  $\downarrow$  in concentration (means dilution). This is because the total volume  $V$  of solution containing 1 mole of electrolyte increases on dilution.

→ Relation between  $\Lambda_m$  and Molarity (M) :-

$$\Lambda_m = \frac{K \times 1000}{M}$$

→ Unit of  $\Lambda_m = \text{sm}^2 \text{ mol}^{-1}$  or  $\text{scm}^2 \text{ mol}^{-1}$

Limiting Molar conductivity :- When concentration  $\rightarrow 0$  Then  $\Lambda_m = \Lambda_m^{\circ}$

When concentration approaches zero, the molar conductivity reaches a limiting value known as limiting molar conductivity ( $\Lambda_m^{\circ}$ ). [CBSE 2010] 1M

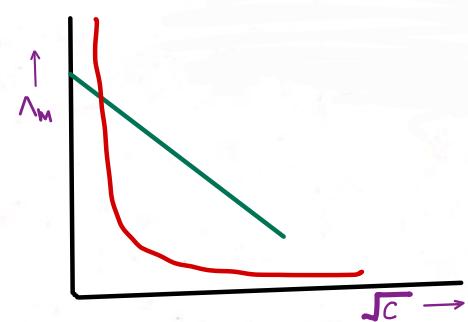
→ For strong electrolytes [KCl],  $\Lambda$  increases slowly with dilution and can be represented by DHO Equation (Debye - Huckle - Onsager equation).

$$\Lambda_m = \Lambda_m^{\circ} - A c^{1/2}$$

$c$  → concentration of electrolyte.

[CBSE 2019] 2M

$A$  → constant



Question :-  $\Lambda_m$  of a 1.5 M solution of an electrolyte is found to be  $130.9$   $\text{scm}^2 \text{ mol}^{-1}$ . Calculate the conductivity of this solution. [CBSE 2010/2012] 2M

Answer :-  $M = 1.5 \text{ mol/l}$

We know that  $\rightarrow \Lambda_m = \frac{K \times 1000}{M}$  then  $K = \frac{M \cdot \Lambda_m}{1000} = \frac{(1.5)(130.9)}{1000} = 0.208 \text{ scm}^{-1}$

Question :- The resistance of 0.01 M NaCl solution at 25°C is 200 Ω. The cell constant of the conductivity cell is unity. Calculate molar conductivity of the solution? [CBSE 2014c] 3M

Answer :-  $R = 200 \Omega$ ,  $M = 0.01 \text{ Mole/L}$

$$\text{Cell constant } \frac{l}{A} = 1 \text{ cm}^{-1} \text{ Then conductivity } K = \frac{1}{R} \times \frac{l}{A} = \frac{1}{200} \times 1$$

$$\rightarrow \text{Molar Conductivity } \Lambda_m = \frac{K \times 1000}{M}$$

$$= \frac{(1/200) \times 1000}{0.01} = \underline{\underline{500 \text{ S cm}^2 \text{ mol}^{-1}}}$$

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Question :- The electrical resistance of a column of 0.05 M NaOH solution of diameter 1 cm and the length 50 cm is  $5.55 \times 10^3 \Omega$ . calculate its molar conductivity, conductivity and resistivity? [CBSE 2012] 3M

Answer :- Molarity of NaOH solution = 0.05 M

$$\text{Diameter} = 1 \text{ cm}, \text{ Radius} = 0.5 \text{ cm}, \text{ Area } A = \pi r^2 = (3.14)(0.5)^2$$

$$A = 0.785 \text{ cm}^2$$

$$\rightarrow \text{Resistivity } \rho = \frac{RA}{l} = \frac{(5.55 \times 10^3)(0.785)}{50}$$

$$\text{and length} = 50 \text{ cm.}$$

$$\rho = \underline{\underline{87.135 \Omega \text{ cm}}}$$

$$\rightarrow \text{Conductivity } K = \frac{1}{\rho} = \frac{1}{87.135} = \underline{\underline{1.148 \times 10^{-2} \text{ S cm}^{-1}}}$$

$$\rightarrow \text{Molar conductivity } \Lambda_m = \frac{K \times 1000}{M} = \frac{(1.148 \times 10^{-2})(1000)}{0.05}$$

$$\Lambda_m = \underline{\underline{229.6 \text{ S cm}^2 \text{ mol}^{-1}}}$$

Question :- The resistance of a conductivity cell containing 0.001 M KCl solution at 290K is 1500 Ω. What is the cell constant if the conductivity of 0.001 M KCl solution at 290K is  $0.146 \times 10^{-3} \text{ S cm}^{-1}$ ? [Delhi 2012] 3M

Answer :-  $K = 0.146 \times 10^{-3} \text{ S cm}^{-1}$  and  $R = 1500 \Omega$

$$\boxed{\text{Cell Constant } C^* = K \cdot R} = 0.146 \times 10^{-3} \times 1500 \text{ cm}^{-1} = 0.219 \text{ cm}^{-1}$$

Kohlrausch Law :- "Limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte."

For Strong Electrolyte

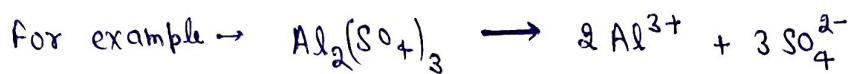
$$\rightarrow \text{for NaCl} : \Lambda^\circ_{\text{NaCl}} = \Lambda^\circ_{\text{Na}^+} + \Lambda^\circ_{\text{Cl}^-}$$

$$\rightarrow \text{CH}_3\text{COOH at infinite dilution } (C \rightarrow 0) : \Lambda^\circ_{\text{CH}_3\text{COOH}} = \Lambda^\circ_{\text{CH}_3\text{COO}^-} + \Lambda^\circ_{\text{H}^+}$$

[Delhi 2010, CBSE 2010]

2M

$\rightarrow$  If an electrolyte on dissociation gives  $n_1$  cations and  $n_2$  anions then its limiting molar conductivity  $\Lambda_m^\circ = n_1 \Lambda_+ + n_2 \Lambda_-$



$$\Lambda_m^\circ [\text{Al}_2(\text{SO}_4)_3] = 2 \Lambda_m^\circ (\text{Al}^{3+}) + 3 \Lambda_m^\circ (\text{SO}_4^{2-})$$

Question :- The value of  $\Lambda_m^\circ$  of  $\text{Al}_2(\text{SO}_4)_3$  is  $0.58 \text{ S cm}^2 \text{ mol}^{-1}$ , while  $\Lambda_m^\circ (\text{SO}_4^{2-})$  is  $160 \text{ S cm}^2 \text{ mol}^{-1}$ . Calculate the limiting ionic conductivity of  $\text{Al}^{3+}$ .

[CBSE 2010]

Answer :-  $\Lambda_m^\circ (\text{Al}_2(\text{SO}_4)_3) = 2 \Lambda_m^\circ (\text{Al}^{3+}) + 3 \Lambda_m^\circ (\text{SO}_4^{2-})$

$$\Lambda_m^\circ (\text{Al}^{3+}) = \frac{\Lambda_m^\circ (\text{Al}_2(\text{SO}_4)_3) - 3 \Lambda_m^\circ (\text{SO}_4^{2-})}{2} = \frac{0.58 - 3 \times 160}{2}$$

$$\Lambda_m^\circ (\text{Al}^{3+}) = 109 \text{ S cm}^2 \text{ mol}^{-1}$$

Question :- Calculate  $\Lambda_m^\circ$  for acetic acid, given that  $\Lambda_m^\circ (\text{H}^+) = 426 \text{ S cm}^2 \text{ mol}^{-1}$

[Delhi 2010] 3M

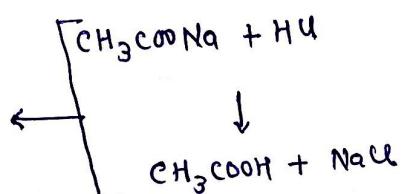
$$\Lambda_m^\circ (\text{NaCl}) = 126 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\Lambda_m^\circ (\text{CH}_3\text{COONa}) = 91 \text{ S cm}^2 \text{ mol}^{-1}$$

Answer :-  $\Lambda_m^\circ (\text{CH}_3\text{COOH}) = \Lambda_m^\circ (\text{CH}_3\text{COO}^-) + \Lambda_m^\circ (\text{H}^+)$

$$\rightarrow \Lambda_m^\circ (\text{CH}_3\text{COONa}) + \Lambda_m^\circ (\text{H}^+) = \Lambda_m^\circ (\text{CH}_3\text{COOH}) + \Lambda_m^\circ (\text{NaCl})$$

$$\rightarrow 91 + 426 = \Lambda_m^\circ (\text{CH}_3\text{COOH}) + 126$$



then  $\Lambda_m^\circ (\text{CH}_3\text{COOH}) = 391 \text{ S cm}^2 \text{ mol}^{-1}$

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- At higher concentration, weak electrolyte (like  $\text{CH}_3\text{COOH}$ ) have lower degree of dissociation. Hence for such electrolytes, the change in  $\Lambda_m$  with dilution is due to increase in degree of dissociation and consequently the number of ions in total volume of solution that contain 1 mole of electrolyte.
- Degree of dissociation :- The ratio of molar conductivity ( $\Lambda_m$ ) at a specific concentration to the molar conductivity at infinite dilution ( $\Lambda_m^\circ$ ) is known as degree of dissociation ( $\alpha$ ). [Delhi 2015C] 2M

$$\alpha = \frac{\Lambda_m}{\Lambda_m^\circ}$$

Question :- calculate the degree of dissociation of acetic acid at 298K, given that  
 $\Lambda_m(\text{CH}_3\text{COOH}) = 11.7 \text{ s cm}^2 \text{ mol}^{-1}$ ,  $\Lambda_m^\circ(\text{CH}_3\text{COO}^-) = 40.9 \text{ s cm}^2 \text{ mol}^{-1}$   
 $\Lambda_m^\circ(\text{H}^+) = 349.1 \text{ s cm}^2 \text{ mol}^{-1}$  [Delhi 2011C] 3M

Answer :- Degree of dissociation =  $\alpha = \frac{\Lambda_m}{\Lambda_m^\circ}$

$$\begin{aligned} \Lambda_m^\circ &= \Lambda_m(\text{CH}_3\text{COO}^-) + \Lambda_m^\circ(\text{H}^+) \\ &= 40.9 + 349.1 = 390 \text{ s cm}^2 \text{ mol}^{-1} \end{aligned} \rightarrow \text{Then } \alpha = \frac{11.7}{390} = 3 \times 10^{-2}$$

Question :- conductivity of  $2.5 \times 10^{-4} \text{ M}$  methanoic acid is  $5.25 \times 10^{-5} \text{ s cm}^{-1}$ . calculate its molar conductivity and degree of dissociation. [CBSE 2015] 3M

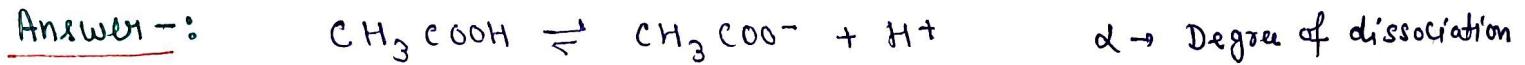
$$\text{Given : } \lambda^\circ(\text{H}^+) = 349.5 \text{ s cm}^2 \text{ mol}^{-1} \text{ and } \lambda^\circ(\text{HCOO}^-) = 50.5 \text{ s cm}^2 \text{ mol}^{-1}$$

$$\text{Answer} - : \quad \Lambda_m = \frac{k \times 1000}{M} = \frac{5.25 \times 10^{-5} \times 1000}{2.5 \times 10^{-4}} = 210 \text{ s cm}^2 \text{ mol}^{-1}$$

$$\Lambda_m(\text{HCOOH}) = \lambda^\circ(\text{H}^+) + \lambda^\circ(\text{HCOO}^-) = 50.5 + 349.5 = 400 \text{ s cm}^2 \text{ mol}^{-1}$$

$$\rightarrow \alpha = \frac{\Lambda_m}{\Lambda_m^\circ} = \frac{210}{400} = 0.525 \quad \text{APNI KAKSHA}$$

Question :- The conductivity of  $0.001 \text{ M}$  acetic acid is  $4 \times 10^{-5} \text{ s cm}^{-1}$  calculate the dissociation constant of acetic acid, if molar conductivity at infinite dilution for acetic acid is  $390 \text{ s cm}^2 \text{ mol}^{-1}$ . [Delhi 2013C] 2M



Initial conc'	C	0	0
After time t,	$C - \alpha$	$\alpha$	$\alpha$

$$\rightarrow \alpha = \frac{\Lambda_m}{\Lambda_m^\circ} \quad \# \quad \Lambda_m^\circ = 390 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\rightarrow \Lambda_m = \frac{K \times 1000}{M} = \frac{(4 \times 10^{-5})(1000)}{0.001}$$

$$\Lambda_m = 40 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\rightarrow \alpha = \frac{\Lambda_m}{\Lambda_m^\circ} = \frac{40}{390} = 0.103$$

Then, dissociation constant

$$K = \frac{\alpha \cdot \alpha}{C - \alpha}$$

$$K = \frac{\alpha^2}{1 - \alpha}$$

# Put value of  $\alpha$  in above equation →

$$K = \frac{(0.001)(0.103)^2}{(1 - 0.103)}$$

$$K = 1.18 \times 10^{-5}$$

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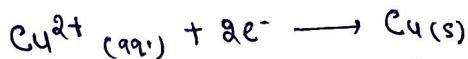
### Electrolysis

→ Electrolytic Cells :— When external potential applied becomes greater than  $E^\circ_{\text{cell}}$  of electrochemical cell, electron flows from Cathode to anode, means that electrochemical cell becomes electrolytic cell. [CBSE 2019 | 2016] 1M

→ In electrolytic cells, electrical energy is used to carry out non-spontaneous chemical reactions and the process which takes place in an electrolytic cell is called electrolysis.

### Purification of impure Copper :-

→  $\text{Cu}^{2+}$  ion discharge at cathode



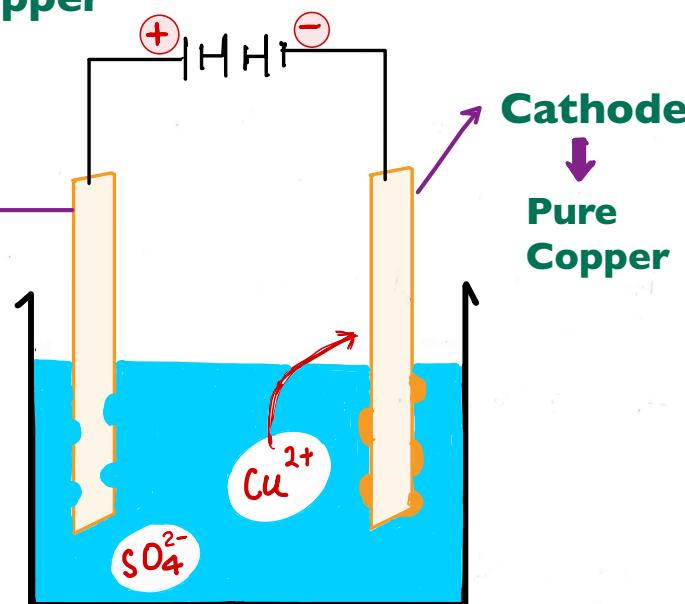
→ copper metal is deposited on the cathode.

→ At anode, copper is dissolved (oxidised).  $\text{Cu(s)} \rightarrow \text{Cu}^{2+} + 2e^-$

→ Impure copper : Anode

→ pure copper : Cathode.

### Impure Copper



## Faraday's Laws of electrolysis [ Quantitative aspects of electrolysis ] -:

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

→ If  $w$  gram of substance gets deposit on passing  $Q$  coulomb of electricity Then

$$w \propto Q \quad \text{or} \quad w = z Q$$

where 
$$z = \frac{E}{F}$$

$$w = z i t$$

$z$  → electrochemical equivalent

$i$  → current [ Ampere ]

$t$  → time [ second ]

ii) Second Law -: The amount of different substances liberated by the same quantity of electricity passing through the electrolytic solution are proportional to their chemical equivalent weights.

→ Equivalent Weights [ atomic mass of metal / no. of electrons required to reduce the cation ]

$$\rightarrow \frac{w_1}{E_1} = \frac{w_2}{E_2}$$

$w$  → mass of substance deposited

$E$  → equivalent weight.

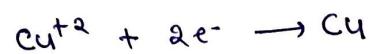
**APNI KAKSHA**

NOTE :-  $\text{Ag}^{+}(aq) + e^- \rightarrow \text{Ag}$  [ one mole of the electron is required for the reduction of one mole of  $\text{Ag}^+$  ion.]

$$\begin{aligned} \rightarrow \text{charge on 1 mole of electron} &= 1 \text{ faraday} = N_A \times (1.6021 \times 10^{-19} \text{ C}) \\ &= (6.02 \times 10^{23} \text{ mol}^{-1}) (1.6021 \times 10^{-19} \text{ C}) \\ &= 96487 \text{ C mol}^{-1} \approx 96500 \text{ C mol}^{-1} \end{aligned}$$

Question :- A solution of  $\text{CuSO}_4$  is electrolysed for 10 minutes with a current of 1.5 amperes. What is the mass of copper deposited at the cathode?

Answer :-  $t = 10 \times 60 = 600 \text{ second}$



2F charge is required for  $\frac{1 \text{ mol Cu}}{63 \text{ g of Cu}}$

→  $2 \times 96500 \text{ C}$  charge for  $= 63 \text{ g of Cu}$

$$1 \text{ C} \quad " \quad " = \frac{63 \text{ g}}{2 \times 96500 \text{ C}}$$

$$\text{then, } 900 \text{ C} \quad " \quad " = \frac{63 \times 900}{2 \times 96500} = 0.2930 \text{ g.}$$

$$\left[ \begin{array}{l} Q = i \cdot t \\ = 1.5 \times 600 = 900 \text{ C} \end{array} \right]$$