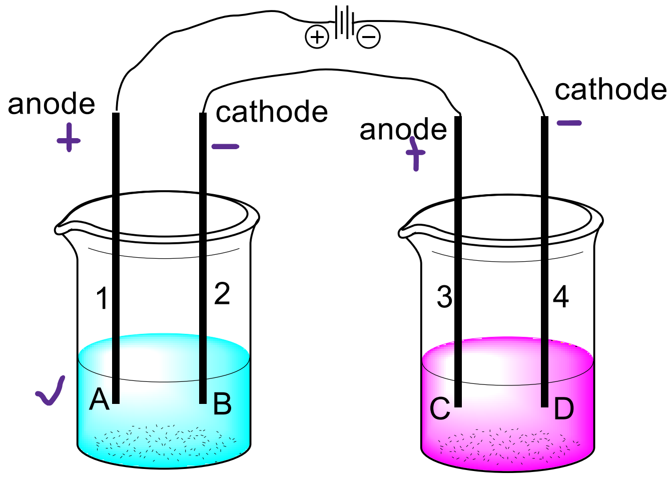
Faradays Second Law of Electrolysis

For two or more electrolytic cells connected in series, the ratio of the mass of the products deposited/evolved at each respective electrode is equal to the ratio of the equivalent masses of the products evolved.

OR

The masses of different products liberated at the electrodes, when the same amount of electricity is passed through different electrolytes are directly proportional to their equivalent masses



Two electrolytic cells connected in series

Proof:

$W = Z \times I \times t$

Then,

$W_A : W_B : W_c : W_D$

$= Z_A \times I \times t : Z_B \times I \times t : Z_C \times I \times t : Z_D \times I \times t$

$= Z_A : Z_B : Z_C : Z_D$

$= E_A/F : E_B/F : E_C/F : E_D/F$

$= E_A : E_B : E_C : E_D$

For series connection, current is same for both the cells (I = constant)

Time = constant

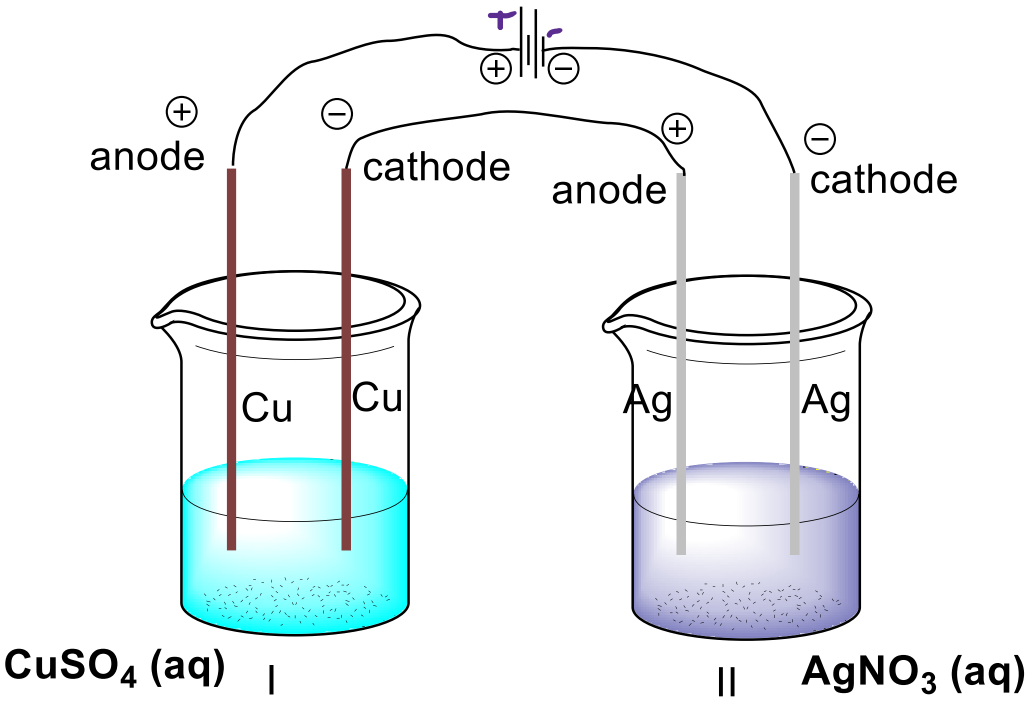
Therefore,
$Q = I \times t =$ constant

Let **A, B, C and D** be the materials deposited/evolved at the electrodes **1, 2, 3 and 4** respectively during electrolysis.

Let $\mathbf{W_A, W_B, W_c, W_D}$ be the masses of **A, B, C, D** deposited/evolved during electrolysis.

According to the Faraday's 2nd law of electrolysis,

$$\mathbf{W_A : W_B : W_c : W_D = E_A : E_B : E_c : E_D}$$



In **cell I**, $\mathbf{W_{Cu}}$ mass of Cu deposited at the cathode
In **cell II, $\mathbf{W_{Ag}}$** mass of Ag is deposited at the cathode

From Faraday's 2nd law

$$\frac{W_{Cu}}{W_{Ag}} = \frac{E_{Cu}}{E_{Ag}}$$

Electrolytic refining

At cell II, Ag^+ will move towards the cathode

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

Ag anode of cell **II** will oxidize

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

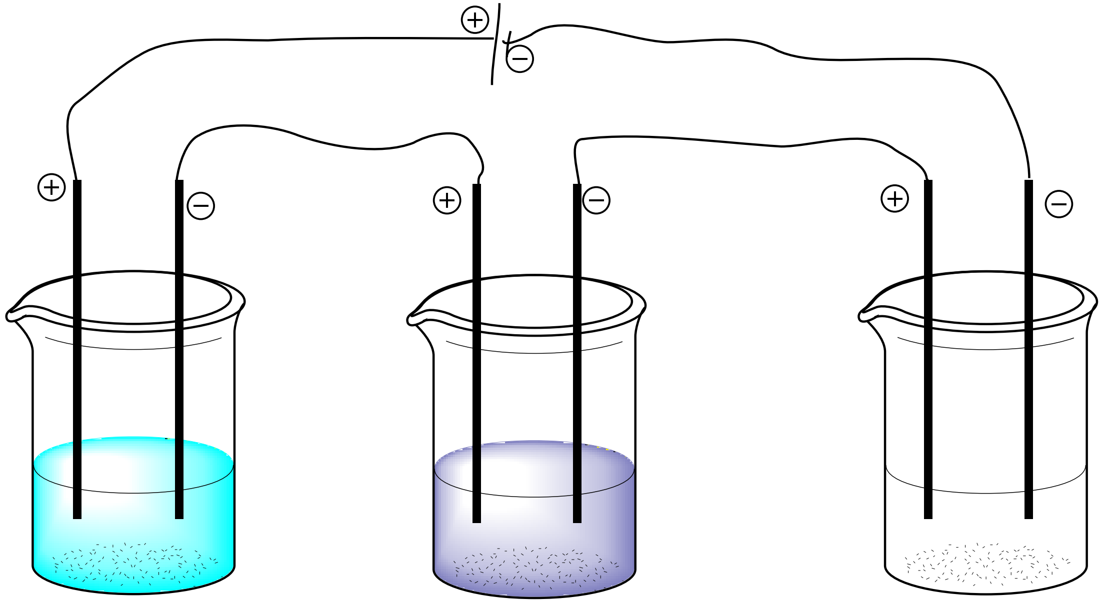
At cell I, Cu^{2+} from the solution will move towards the cathode

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

Cu anode of **cell I** will undergo oxidation

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

Q1.Three electrolytic cells A,B,C containing solutions of ZnSO4 , AgNO3 and CuSO4 , respectively are connected in series. A steady current of 1.5 amperes was passed through them until 1.45 g of silver deposited at the cathode of cell B. How long did the current flow? What mass of copper and zinc were deposited?



$1Ag^+ + 1e^- \rightarrow 1\ Ag\ (s)$

1 mol of Ag is deposited by 1 mol of electrons

$\Rightarrow$ 108 g silver is deposited by 1F charge

$\Rightarrow$ 108 g silver is deposited by 96500 C charge.

$\Rightarrow$ Charge required to deposit 1.45 g Silver = (1.45 x 96500) /108 C

$\Rightarrow$ Charge required to deposit 1.45 g silver = 1295.6 C

Current = 1.5 A

Q = I x t => t = Q/I = 1295.6/1.5 s = 864.85 s

From Faradays second Law :

$W_{Zn} : W_{Ag} : W_{Cu} = E_{Zn} : E_{ag} : E_{cu}$

For Zn

$W_{Zn}/W_{Ag} = E_{Zn}/E_{Ag}$ => W_{Zn}/1.45 g = 32.67g/108g => W_{Zn} = (32.67 x 1.45)/108 = 0.43 g

$W_{Ag}/W_{cu} = E_{Ag}/E_{cu}$ => 1.45g/W_{cu} = 108/32 => W_{cu} = 0.42 g

Chemical Cell

- A chemical cell is a device that converts chemical energy into electrical energy. Most batteries are chemical cells. A chemical reaction takes place inside a chemical cell which results in the flow of electric current.

EMF of a cell

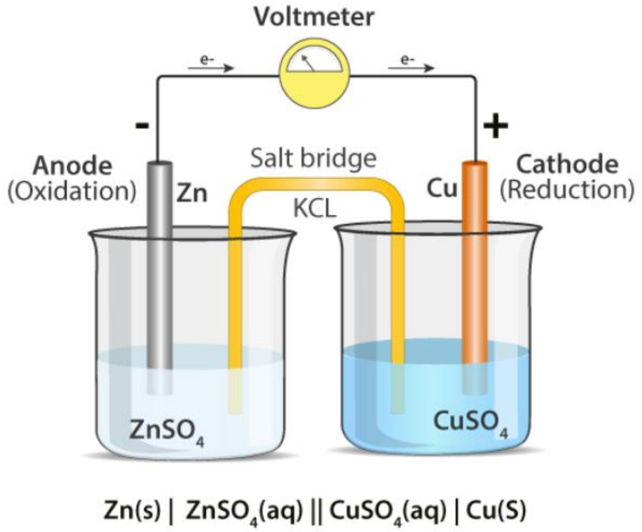
It is the potential difference across the terminals of a cell when no current is being drawn from it.

Standard EMF of a cell (E^o_{Cell})

$Zn\ (s) |\ Zn^{2+}_{(aq)} ||\ Cu^{2+}_{(aq)} |\ Cu_{(s)}$

$E^o_{cell} = E^o_{Cu2+/Cu} - E^o_{Zn2+/Zn}$

$E^o_{cell} = E^o_{red} - E^o_{oxid}$



- The potential difference across the terminals of a cell when the concentration of the species taking part in the electrode reactions is unity (1 Molar), if any gas appears in the reaction, it is said to have a pressure of 1 bar and further the reaction is carried out at 298 K is called **standard cell potential.**

That means, when the concentration of the species taking part in the cell reaction is not 1 M, then the cell potential is not equal to the standard cell potential.

It varies with the concentration of the species as:

$$\mathbf{E_{cell} = E^{o}{}_{cell} - \frac{RT}{nF} \ln Q}$$