Chemical effect of current: We know that when two electrodes are immersed in a liquid and a suitable potential difference is applied between the electrodes the molecules of the liquid dissociate to form positive and negative ions. The positive ions flows towards the electrode of negative potential and the negative ions flows towards the electrode of positive potential. The flow of ions inside the liquid constitutes a current and is known as electrolytic conduction. This phenomenon is known as electrolysis and the liquid undergoing electrolysis is known as electrolyte, the container is known as Voltammeter.

Copper Voltammeter: A solution of $CuSO_4$ is taken in a glass jar. Two copper plates are immersed in that, $CuSO_4$ solution dissociates to form copper ion and sulphate ion. The Cu^{++} being positive move towards the copper plate at the cathode. The SO_4^{-} ions move towards anode i.e. copper plate at positive potential reaching the anode the SO_4^{-} reacts with the copper plant and produce $CuSO_4$ solution which dissolves into the solution.

Thus due to electrolysis the mass of copper plate at the cathode increases due to the deposition of copper ions where as the mass of the copper plate at the anode decreases as it loses copper ions. But the mass of copper sulphate in the solution remains unchanged.

Faraday's laws of electrolysis:

Faraday from his experimental observation gave the following two laws for Electrolysis:

(1) The mass of ions deposited at the electrode is proportional to the quantity of charge (electricity) that has been passed through the given electrolyte.

(2) When same amount of charge is passed through different electrolytes the mass of ions deposited at the different electrodes is proportional to their respective chemical equivalents.

Explanation:

Let i = current passed through the electrolyte for t sec

Q = i x t = the amount of charge that has been passed through the electrolyte.

Let W = mass of ions deposited at the electrode.

According to the first law: $W \propto Q$ or $W \propto it$ or $W = Zit \rightarrow (1)$

Where Z is constant of proportionality and is known as electro chemical equivalent (E.C.E) of the element. If i = 1 amp, t = 1 sec W = Z, thus the electro chemical equivalent of an element is defined as the mass of ions of that element deposited when 1 amp current is passed through the electrolyte for 1 sec. i.e. One column charge flows through the electrolyte. Unit of E.C.E = kg/coulomb

Second law: Let a constant current i amp be passed through two different electrolytes for t sec.

Q = i x t coulomb = charge passed through the electrolyte.

Let W_1 & W_2 be the mass of ions of the two elements deposited at the electrodes.

E_1 and E_2 are the chemical equivalent of these two elements respectively.

According to second law:

$$\frac{W_1}{W_2} = \frac{E_1}{E_2} \rightarrow (2) \text{ when Q is constant i.e.} W \propto E$$

From the first law we get

$$W_1 = Z_1 Q$$

$$W_2 = Z_2 Q$$

where Z_1, Z_2 are the electro chemical equivalent of the two elements respectively.

$$\frac{W_1}{W_2} = \frac{Z_1 Q}{Z_2 Q} = \frac{Z_1}{Z_2} \rightarrow (3)$$

From equation (2) and (3)

$$\frac{E_1}{E_2} = \frac{Z_1}{Z_2} \rightarrow (4)$$

From equation (4) we find that the ration of chemical equivalent of two elements is equal to the ratio of their electro chemical equivalent. We now combine the 1st and 2nd law. Let a charge Q be passed through an electrolyte and W be the mass of ion deposited.

From first law : $W \propto Q$ when E is constant

From second law : $W \propto E$ when Q is constant

Combining these two $W \propto QE$ when Q is constant

$$W = \frac{1}{F} QE$$

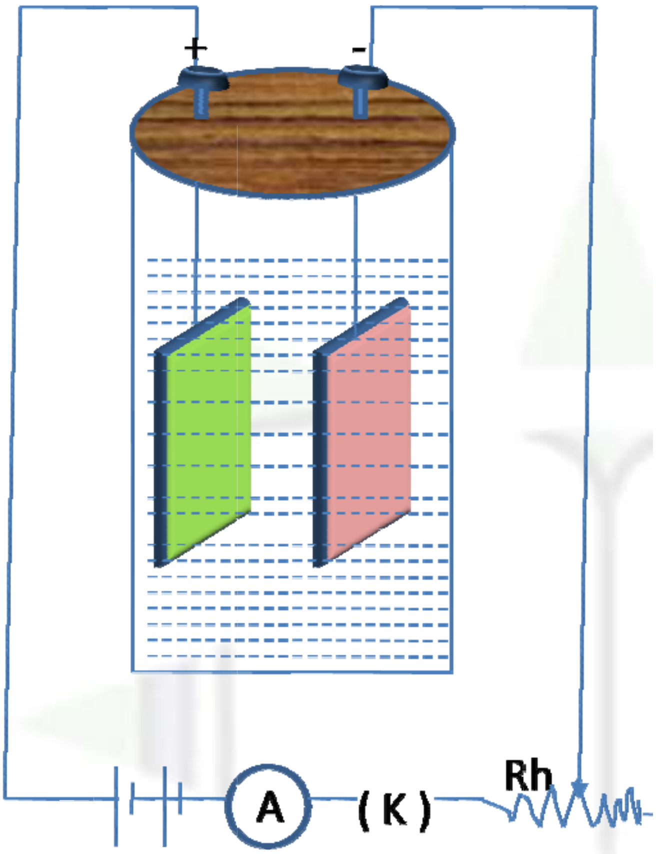
Where $\frac{1}{F}$ is a constant of proportionality & F is known as Faradays number.

If W = E then F = Q

Hence Faraday's number can be defined as the amount of charge which when passed through the electrolyte would deposit ions of that element of mass equal to the chemical equivalent of that element.

Experimental verification of Faraday's laws of electrolysis

Verification of first law:



A copper voltammeter is taken and by trial rheostat is adjusted so that suitable constant current flows through the circuit as shown. The copper plate connected to the negative terminal i.e. the plate acting as cathode is thoroughly cleaned dried and weighed and then again placed in its position.

The experiment consists of two parts:

Part I: (i) By closing the key K a constant current say i_1 amp recorded from the ammeter is passed for t sec and the mass of ion deposited at the cathode is measured by taking out the cathode drying and weighing it.

(ii) The same is repeated for different values of current say i_2 amp by changing with the rheostat for the same time interval t sec.

Let W_1 and W_2 be the mass of ions deposited when current i_1 & i_2 amp flow for t sec respectively. From this recorded values it is found

$$\frac{W_1}{W_2} = \frac{i_1}{i_2} \text{ or } W \propto i \text{ when t is constant}$$

Part II : This time a constant current say i amp is passed for two different time t_1 sec and t_2 sec and in each case the mass of ions deposited at the electrodes is measured. Let W_3 and W_4 be the mass of ions deposited when i am flows for t_1 and t_2 sec respectively. From the recorded values it is found that

$$\frac{W_3}{W_4} = \frac{t_1}{t_2} \text{ or } W \propto t \text{ when i is constant}$$

Combining the two experimental results

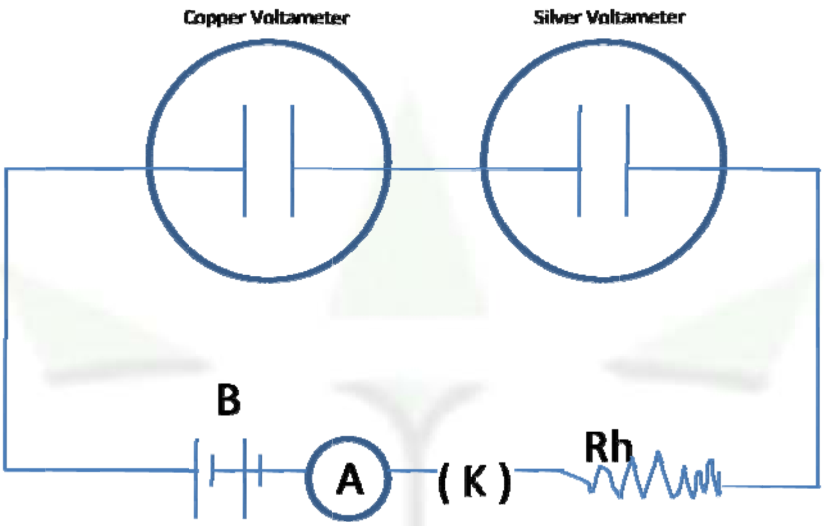
$W \propto it$ when both i & t varies

or $W \propto Q$

First law is verified.

Verification of Second law:

Two different voltameter say a copper voltameter and a silver voltameter are connected in series to a battery an ammeter a key and rheostat



The electrodes which acts as cathode from both the voltameters are taken out cleaned dried and weighed and are again placed in their position. Closing the key K a constant current is passed through the series circuit for a given time interval. The electrodes at the cathode are taken out dried and weighed and then the mass of ions deposited are calculated.

Let W_{cu} & W_{Ag} be the mass of copper and silver deposited respectively.

E_{Cu} & E_{Ag} be the values of chemical equivalent of copper and silver respectively.

From the measured and known values it is found that

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

$$W \propto E$$

Second law verified.