Chapter-1- Faraday's Laws

1.1. Introduction

In 1833, Michael Faraday (1791-1867) assumed that during the passage of an electric current through a solution (**Figure 1**) the flow of electricity is associated with the movement of particles of matter carrying either positive or negative charges called ions.

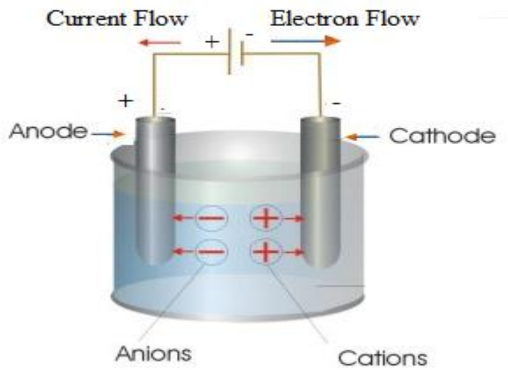


Figure 1 Electrolytic solution

- ✓ The cations carrying positive charges move in the direction of the current, *i.e.*, towards the cathode.
- ✓ The anions carrying negative charge move in the opposite direction of the current, *i.e.*, towards the anode.

It is apparent that charges which are transferred through solution and across electrode/solution interfaces are 'atomic' in nature.

Faraday summarized the quantitative aspects of **electrolysis experiments** in two statements known as **Faraday's laws of electrolysis**:

The number of reactant molecules involved in an electrode reaction is related stoichiometrically to the number of charges (electrons) flowing in the circuit. This is the basic argument of the laws formulated by Michael Faraday.

1.2. Faraday's first law

In electrolysis, the mass of an element deposited (plated) on the cathode, or liberated (or dissolved) on anode during passage of current through a solution of the metal salt is directly proportional to the charge, Q which passed through the electrolytic solution; and the equivalent weight (atomic weight/oxidation number) of the metal (**Figure 2**).

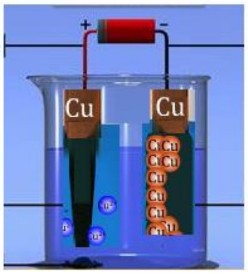


Figure 2 Electrolysis of electrodes

If m is the mass of a substance deposited or liberated at an electrode due to the passage of charge Q, then according to Faraday's first law of electrolysis:

$$\mathbf{m \propto Q \quad or \quad m \propto I \times t \quad or \quad m = e\,Q = e \times I \times t} \qquad (\mathbf{1.1})$$

where I is the current in amperes (A), which passes for time 't' in second (s); and e is a constant of proportionality called **electrochemical equivalent** of the substance.

if $Q = 1C$, then $m = e$

Hence, **electrochemical equivalent, e** of a substance is the mass (or weight) of the substance liberated or deposited in electrolysis by the passage of 1 coulomb of charge (This means when 1A of current passed for one second). Its SI unit is expressed in Kg/C.

Example 1.1

Calculate the mass of copper metal deposited on the cathode electrode when a current of 0.5 amperes passed through an electrolyte solution of $CuSO_4$ for one hour time?

Data: Electrochemical equivalent of Cu, e = 3.294×10^{-4} Kg/C

Answer:

$$\mathrm{m} = \mathrm{e} \times \mathrm{I} \times \mathrm{t}$$

$$\mathrm{m} = 5.929 \times 10^{-7}\ \mathrm{Kg\,C^{-1}} \times 0.5\ A \times 3600\ s$$

$$\mathrm{m} = 5.929 \times 10^{-4}\ \mathrm{Kg} = 0.5929\ \mathrm{g}$$

1.3 Faraday's second law

The masses of different substances deposited at or dissolved (or liberated) from electrodes, when the same quantity of electricity is passed through different electrolytes, connected in series are proportional to their chemical equivalents.

The chemical equivalent, E of an element is numerically equal to its relative atomic mass in grams divided by its ion valency.

$$\mathbf{E} = \frac{\textbf{Atomic mass of an element}}{\textbf{valency of the element}} \qquad (\mathbf{1.2})$$

Thus, Faraday's second law of electrolysis can also be stated as: "The mass of different substances liberated or deposited by the same quantity of electricity is proportional to the atomic masses divided by the valency of their ions".

We have

If Q = 1C => m = e

If Q= 96500 C => E = 96 500 × e = e × F, thus

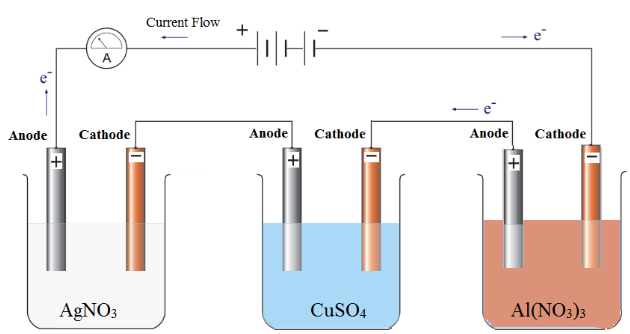
$$\mathbf{m} = \frac{\mathbf{E}}{\boldsymbol{F}} \times \mathbf{I} \times \mathbf{t} \quad (\mathbf{1.3})$$

Example 1.2

Consider three solutions of electrolytes: $AgNO_3$, $CuSO_4$ and $Al(NO_3)_3$ in a series, pass some quantity of electricity through them for the same time. Ag, Cu and Al metals collect at the cathode. Their masses are directly proportional to their equivalent masses. According to Faraday, if 96,500 Coulombs (or 1 Faraday) is passed through these electrolytes, we get

$$Ag\ \frac{108}{1} = 108\ g, \qquad Cu\ \frac{63.5}{2} = 31.75\ g\ and\ \ Al\ \frac{27}{3} = 9\ g,$$

which are the equivalent masses of Ag, Cu and Al respectively.



Thus, when a given current is passed for a given time through a series of electrolyte solutions, the extent of decomposition is always the same when expressed in terms of equivalents.

In this statement lies **the definition of the Faraday constant** which is the amount of electricity required to deposit one equivalent of any ion from a solution and has the value 96 500 coulombs. The current (or the quantity of electricity) of 96500 C is called **Faraday**:

$$\mathbf{1\ Faraday = e\ N_A = 96\,500\ C \quad (1.4)}$$

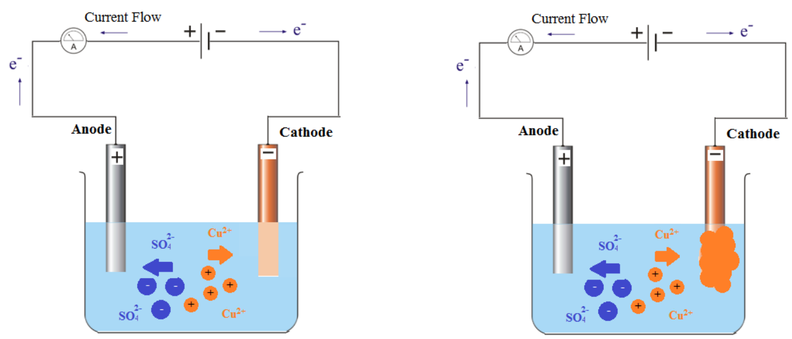
Example 1.3

Consider an electrolytic solution copper sulphate. When the solution is electrolyzed, copper is deposited at the cathode.

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

If a constant current passed for 5 hours and 404 mg of Cu was deposited.

Calculate the current passed through $CuSO_4$ electrolyte?



Solution

The mass of Cu deposited in cathode, m (Cu) = 0.404 g.

Atomic mass of Cu = 63.5 a.m.u

Gain of 2é means 2F electric charge

According to cathode reaction:

63.5 g of Cu is deposited by 2F electric charge, thus 0.404 g of Cu is deposited by

$$= \frac{2}{63.5} \times 0.404 = 0.0127\ \mathrm{F} = 0.0127\ \times 96500\ \mathrm{C} = 1225.6\ \mathrm{C}$$

We know that:

$$\mathrm{I} = \frac{\mathrm{Q}}{\mathrm{t}} = \frac{1225.6}{5 \times 3600} = 6.8\ \times 10^{-2}\mathrm{A}$$