Electrolysis and Electrical Conductance

→ Water-soluble substances are distinguished as electrolytes or nonelectrolytes.

→ **Electrolytes are electrovalent substances that form ions in solution which conduct an electric current.**

Sodium chloride, copper (II) sulphate and potassium nitrate are examples of electrolytes.

→ **Nonelectrolytes, on the other hand, are covalent substances which furnish neutral molecules in solution.**

Sugar, alcohol and glycerol are typical nonelectrolytes.

→ *Their water-solutions do not conduct an electric current.*

Electrolysis and Electrical Conductance

■ Electrolysis:

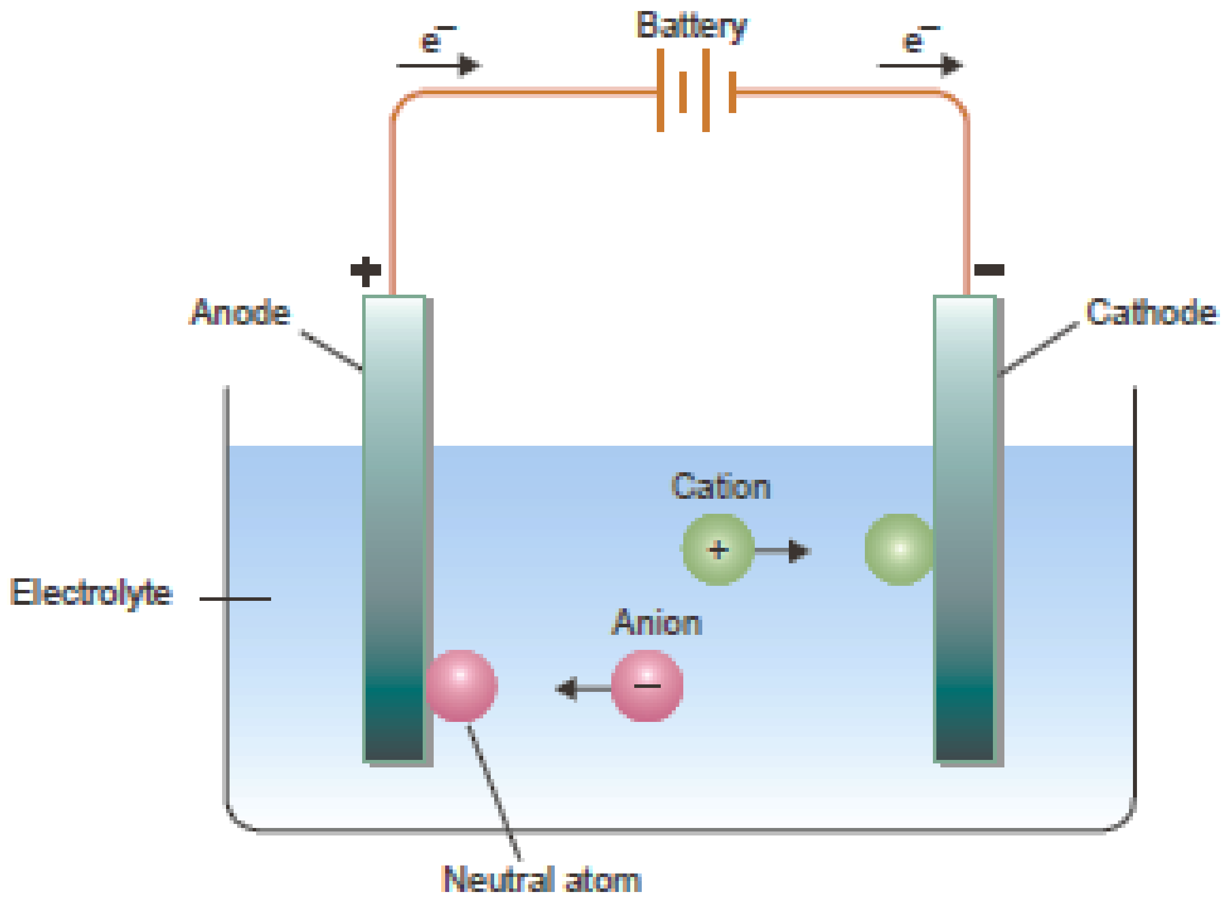
→ **The phenomenon of decomposition of an electrolyte by passing electric current through its solution is termed electrolysis (lyo = breaking).**

→ The process of electrolysis is carried in an apparatus called the **Electrolytic cell. The cell contains water - solution of an** electrolyte in which two metallic rods (electrodes) are dipped**.** These rods are connected to the two terminals of a battery (source of electricity).

→ The electrode connected to the positive terminal of the battery attracts the negative ions (anions) and is called **anode**.

→ The other electrode connected to the negative end of the battery attracts the positive ions (cations) and is called **cathode**.

Electrolysis and Electrical Conductance



The mechanism of electrolysis.

Electrolysis and Electrical Conductance

■ Faraday's Laws of Electrolysis:

→ Michael Faraday studied the quantitative aspect of electrolysis. He discovered that there exists a definite relationship between the amounts of products liberated at the electrodes and the quantity of electricity used in the process. In 1834, he formulated two laws which are known as Faraday's Laws of Electrolysis.

→ First Law:

The amount of a given product liberated at an electrode during electrolysis is directly proportional to the quantity of electricity which passes through the electrolyte solution.

If m is the mass of substance (in grams) deposited on electrode by passing Q coulombs of electricity, then

$$m \propto Q \text{ (First Law)}$$

Electrolysis and Electrical Conductance

→ We know that, $Q = I \times t$

where I is the strength of current in amperes and t is the time in second for which the current has been passed. Therefore,

$$m \propto I \times t$$

$$\text{or } m = Z \times I \times t$$

where Z is the constant known as the **Electrochemical equivalent** of the substance (electrolyte).

If $I = 1$ ampere and $t = 1$ second, then, $m = Z$

→ Thus, the **electrochemical equivalent** is the amount of a substance deposited by **1 ampere current** passing for **1 second** (i.e., one coulomb).

Electrolysis and Electrical Conductance

■ Importance of the first law of electrolysis:

→ With the help of the first law of electrolysis we are able to calculate:

(1) the value of electrochemical equivalents of different substances.

(2) the masses of different substances produced by passing a known quantity of electricity through their solutions.

→ Second Law:

When the same quantity of electricity passes through solutions of different electrolytes, the amounts of the substances liberated at the electrodes are directly proportional to their chemical equivalents.

Electrolysis and Electrical Conductance

■ Importance of the second law of electrolysis:

$\rightarrow$ The second law of electrolysis helps to calculate :

(1) the equivalent weights of metals

(2) the unit of electric charge

(3) the Avogadro's number

Electrolysis and Electrical Conductance

■ Conductance of Electrolytes:

→ We have seen that electrolyte solutions conduct electric currents through them by movement of the ions to the electrodes. The power of electrolytes to conduct electric currents is termed conductivity or conductance.

→ Like metallic conductors, electrolytes obey Ohm's law. According to this law, the current **I** flowing through a metallic conductor is given by the relation.

$$I = \frac{E}{R}$$

where E is the potential difference at two ends (in volts); and R is the resistance measured in ohms (or Ω).

Electrolysis and Electrical Conductance

$\rightarrow$ The resistance R of a conductor is directly proportional to its length, l, and inversely proportional the area of its cross-section, A.

$$R \propto \frac{l}{A} \quad \text{or,} \quad R = \rho \times \frac{l}{A}$$

where ρ "rho" is a constant of proportionality and is called **resistivity or specific resistance**. Its value depends upon the material of the conductor. we can write

$$\rho = R \times \frac{A}{l}$$

If l = 1 cm and A = 1 sq cm, then; ρ = R

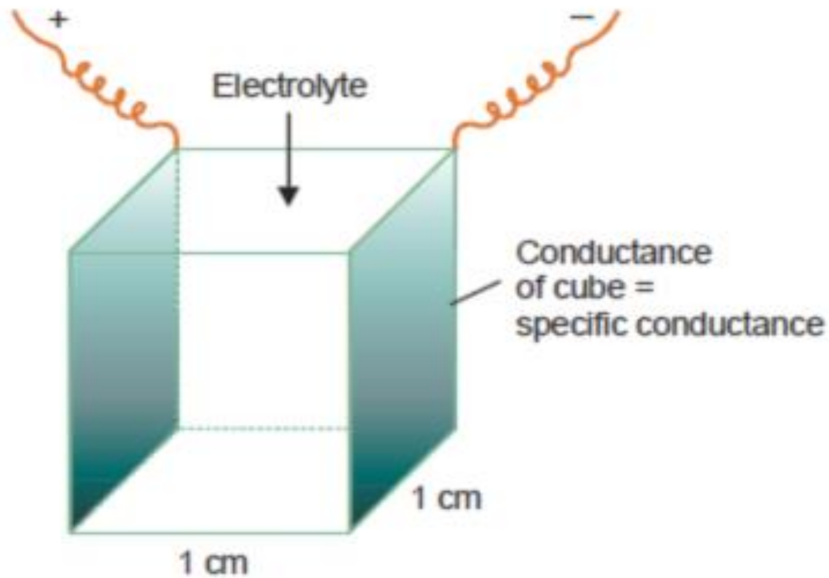
$\rightarrow$ Thus it follows that the **Specific resistance** of a conductor is the resistance in ohms which one centimetre cube of it offers to the passage of electricity.

■ Specific Conductance:

→ The reciprocal of specific resistance is termed Specific conductance or Specific conductivity.

→ It is defined as : the conductance of one centimetre cube (cc) of a solution of an electrolyte. The specific conductance is denoted by the symbol κ (kappa). Thus,

$$\kappa = \frac{1}{\rho} = \frac{1}{R} \times \frac{l}{A}$$



Diagrammatic illustration of definition of specific conductance.

■ Equivalent Conductance:

→ It is defined as the conductance of an electrolyte obtained by dissolving one gram-equivalent of it in Vcc of water.

→ The equivalent conductance is denoted by Λ . It is equal to the product of **the specific conductance, κ** and the **volume V in cc containing one gram-equivalent of the electrolyte at the dilution V**.

$$\Lambda = \kappa \times V$$

→ In general, if an electrolyte solution contains N gram-equivalents in 1000 cc of the solution, the volume of the solution containing 1 gram-equivalent will be 1000/N. Thus,

$$\Lambda = \frac{\kappa \times 1000}{N}$$

■ Molar Conductance:

→ It is another quantity which helps in comparing the conductivities of electrolytes. It is defined as **: the conductance of all ions produced by one mole (one gram-molecular weight) of an electrolyte when dissolved in a certain volume V cc.**

→ Molar conductance is denoted by μ. Its value is obtained by multiplying the specific conductance, κ, by the volume in cc containing one mole of the electrolyte.

→ Thus, Molar conductance, $\mu = k \times V$ where V is the volume of the solution in cc containing one mole of the electrolyte.

Related problems:

SOLVED PROBLEM 1. 0.1978 g of copper is deposited by a current of 0.2 ampere in 50 minutes. What is the electrochemical equivalent of copper?

SOLUTION

Here $t = 50$ minutes $= 50 \times 60$ seconds; $I = 0.2$ ampere. Quantity of electricity used is

$$Q = I \times t = 0.2 \times 50 \times 60 = 600 \text{ coulombs}$$

$$\text{Amount of copper deposited by 600 coulombs} = 0.1978 \text{ g}$$

$$\text{Amount of copper deposited by 1 coulomb} = \frac{0.1978}{600} \text{ g} = 0.0003296 \text{ g}$$

$$\therefore \quad \text{Electrochemical equivalent of copper} = 0.0003296$$

SOLVED PROBLEM 2. What current strength in amperes will be required to liberate 10 g of iodine from potassium iodide solution in one hour?

SOLUTION

$$\text{127 g of iodine (1 g eqvt) is liberated by} = 96{,}500 \text{ coulomb}$$

$$\therefore \quad \text{10g of iodine is liberated by} = \frac{96{,}500}{127} \times 10 \text{ coulomb}$$

$$\text{Let current strength be} = I$$

$$\text{Time in seconds} = 1 \times 60 \times 60$$

We know that the quantity of electricity, Q, used is given by the expression

$$Q = I \times \text{time in seconds}$$

$$\therefore \quad \text{Current strength, } I = \frac{Q}{t} = \frac{96{,}500 \times 10}{127 \times 60 \times 60}$$

$$= \mathbf{2.11 \text{ ampere}}$$

Electrolysis and Electrical Conductance

SOLVED PROBLEM 1. 0.5 Normal solution of a salt placed between two platinum electrodes, 20 cm apart and of area of cross-section 4.0 sq cm has a resistance of 25 ohms. Calculate the equivalent conductance of the solution.

SOLUTION

Calculation of specific conductance

$l = 20$ cm $\quad A = 4.0$ sq cm $\quad R = 25$ ohms

$$\text{Specific conductance } \kappa = \frac{1}{R} \times \frac{l}{A}$$

$$= \frac{1}{25} \times \frac{20}{4}$$

$$= 0.2 \text{ ohm}^{-1} \text{ cm}^{-1}$$

Calculation of Equivalent conductance

$$\text{Equivalent conductance } = \kappa \times \frac{1000}{N} = \frac{0.2 \times 1000}{0.5}$$

$$= 400 \text{ ohm}^{-1} \text{ cm}^2 \text{ eqvt}^{-1}$$

SOLVED PROBLEM 2. The resistance of a N/10 solution of a salt is found to be 2.5×10^3 ohms. Calculate the equivalent conductance of the solution. Cell constant = 1.15 cm^{-1}.

SOLUTION

Calculation of Specific conductance

$$\text{Specific conductance } \kappa = \frac{1}{R} \times \text{cell constant}$$

$$= \frac{1}{2.5 \times 10^3} \times 1.15$$

Calculation of Equivalent conductance

$$\text{Equivalent conductance } = \frac{\kappa \times 1000}{N}$$

$$= \frac{1.15 \times 1000}{2.5 \times 10^3 \times 0.1} = \frac{115}{25}$$

$$= 4.60 \text{ ohm}^{-1} \text{ cm}^2 \text{ eqvt}^{-1}$$