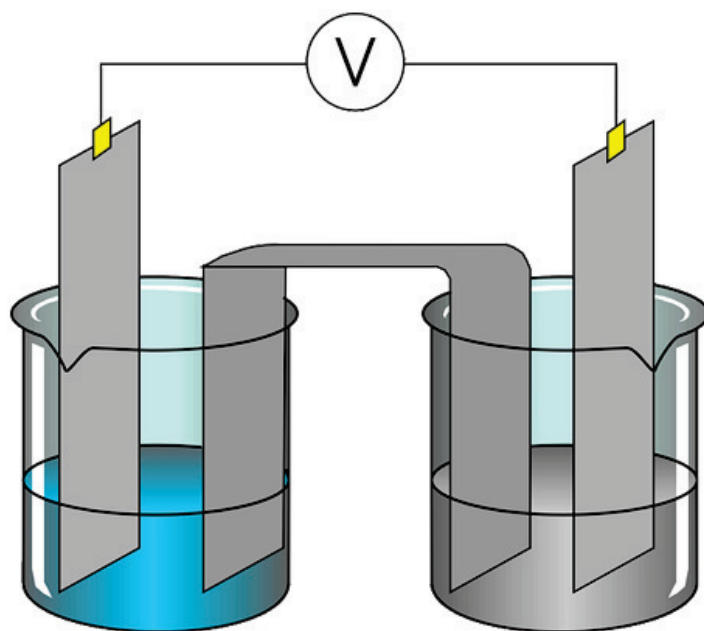


ELECTROCHEMISTRY



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ELECTROCHEMISTRY

Conductivity of Solutions

What is Conductivity?

- Electrical resistance is represented by the symbol 'R', and it is measured in ohm (Ω).
- The electrical resistance of any object is directly proportional to its length (l) and inversely proportional to its area of cross-section (A), i.e.

$$R \propto \frac{l}{A} \quad \text{OR} \quad R = \rho \frac{l}{A}$$

where the constant of proportionality ρ is called resistivity (specific resistance).

- The inverse of resistance, R, is called conductance, G, and we have the relation

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

where the constant κ is called conductivity (specific conductance).

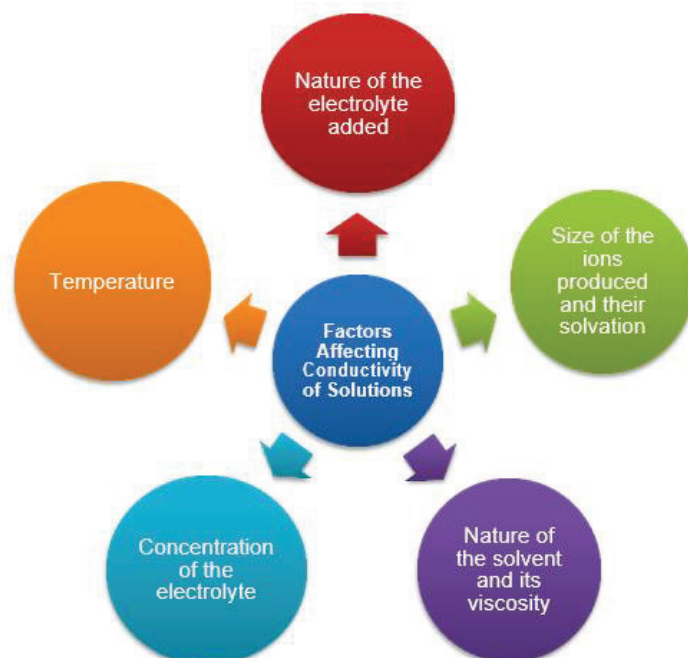
- The SI unit of conductance is Siemens, represented by the symbol 'S', and it is equal to ohm^{-1} (also known as mho) or Ω^{-1} . The SI unit of conductivity (κ) is S m^{-1} .

Conductivity of Electrolytic (Ionic) Solutions

- Very pure water has small amounts of hydrogen and hydroxyl ions ($\sim 10^{-7}\text{M}$) which lend it very low conductivity ($3.5 \times 10^{-5} \text{ S m}^{-1}$).
- When electrolytes are dissolved in water, they dissociate to give their own ions in the solution; hence, its conductivity also increases.

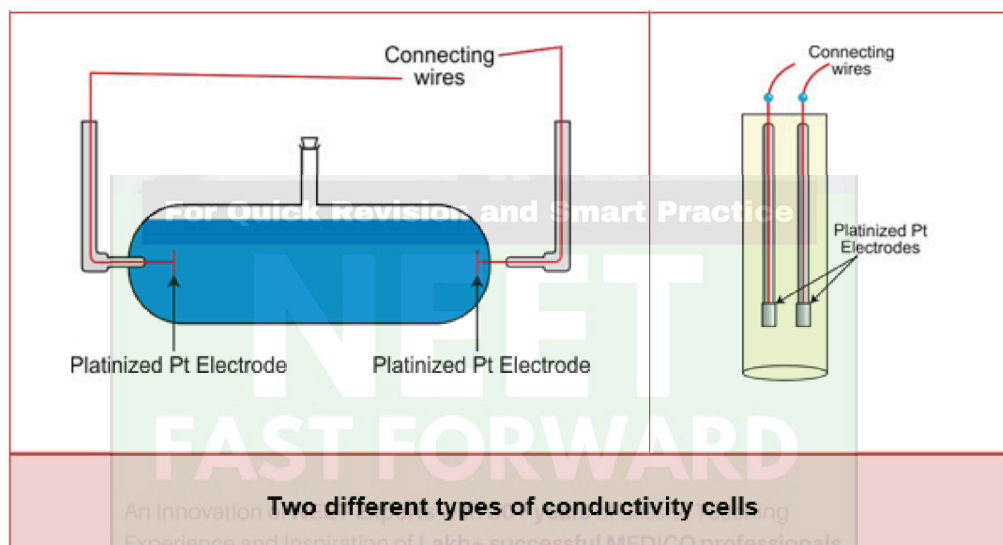
Electrolytic or ionic conductance:

Conductance of electricity by ions present in solutions



Measurement of Conductivity of Ionic Solutions

- We first need to find the resistance of an ionic solution to measure conductivity.
 - We face two problems when measuring the resistance of an ionic solution:
 1. Passing direct current (DC) changes the composition of the solution
 2. A solution cannot be connected to the bridge like a metallic wire or other solid conductor
 - The first difficulty is resolved by using an alternating current (AC) source of power. The second problem is solved by using a specially designed vessel called **conductivity cell**.
- **Conductivity Cell:**



- It consists of two platinum electrodes coated with platinum black (finely divided metallic Pt is deposited on the electrodes electrochemically).
- These have area of cross-section equal to 'A' and are separated by distance 'l'. The resistance of such a column of solution is then given by the equation:

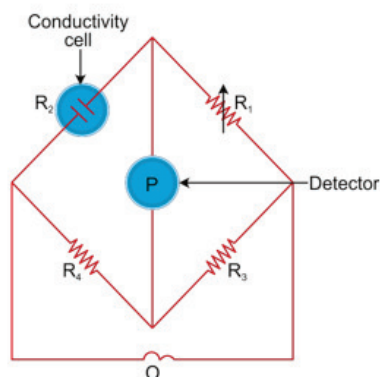
$$R = \rho \frac{l}{A} = \frac{l}{\kappa A}$$

- The quantity 'l/A' is called cell constant and is denoted by the symbol G*. It depends on the distance between the electrodes and their area of cross-section and has the dimension [L⁻¹].
- Hence, the cell constant G* is given by the equation:

$$G^* = \frac{l}{A} = R \kappa$$

- When the cell constant is determined, we can use it for measuring the resistance or conductivity of any solution.
- The set up for the measurement of the resistance is nothing but the well-known

Wheatstone bridge.



Arrangement for measurement of resistance of a solution of an electrolyte

- It consists of two resistances R_3 and R_4 , a variable resistance R_1 and the conductivity cell having the unknown resistance R_2 .
- The Wheatstone bridge is fed by an oscillator O (a source of AC power in the audio frequency range 550–5000 cycles per second).
- P is a suitable detector (a headphone or other electronic device).
- The bridge is balanced when no current passes through the detector.
- Under these conditions,

$$\text{Unknown Resistance, } R_2 = \frac{R_1 R_4}{R_3}$$

- When the cell constant and the resistance of the solution in the cell are determined, the conductivity of the solution is given by the equation:

$$\kappa = \frac{\text{Cell Constant } G^*}{R} = \frac{G^*}{R}$$

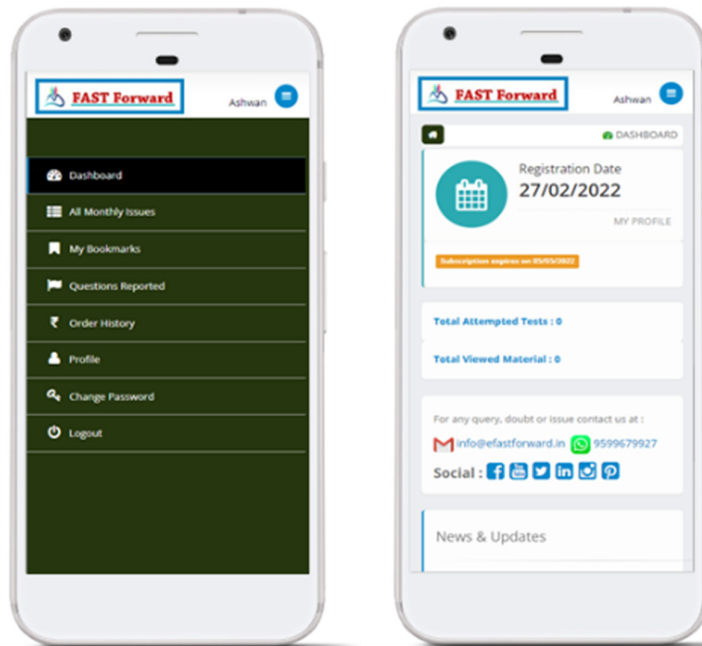
Molar Conductivity

- Conductivity of solutions of different electrolytes in the same solvent and at a given temperature differs due to
 1. Charge and size of ions in which they dissociate
 2. Concentration of ions or ease with which the ions move under a potential gradient
- Therefore, it becomes necessary to define a quantity called molar conductivity denoted by the symbol (λ_m) . It is related to the conductivity of the solution by the equation:

$$\text{Molar Conductivity} = \lambda_m = \frac{\kappa}{C}$$



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