

ELECTROCHEMISTRY

(BSc Part ii)

***Conductance; Equivalent.
conductance ; Molar
conductance***

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***1* Conductance in electrolytic solution**

Electrolytic conductance is flow of electricity through solution of electrolyte . It is due to the Migration of ions when potential difference is applied between the two electrodes “the ease with which electricity flows through a solution is called the conductance of the solution” .

Conductance . *it is defined as the reciprocal of the resistance of the solution*

$$G=1/R , \text{ unit of conductance = Siemen,(S) OR } \Omega^{-1}$$

Resistance: *resistance offered by a uniform conductor to the passage of electricity is directly proportional to the length of the conductor and inversely proportional to the area of cross section of the conductor*

$R \propto 1/a$, $R \propto l$, $R=\rho l/a$ (l =length , a =area, ρ =Specific Resistance)

$\rho = R \times (a/l)$ **unit of R and ρ are Ω (ohm) and Ωcm respectively**

Specific resistance depend on nature of material . It is defined as the resistance (ohm) offered by a conductor or other substance of 1 cm length and having a unit area of cross section

Specific conductance: the reciprocal of specific resistance is called specific conductance

$$K = 1/\rho$$

$$K = l/(R \times a)$$

$$K = G \times (l/a) \text{ unit of } k = \Omega^{-1}\text{cm}^{-1}$$

Term l/a consider as cell constant and its unit is cm^{-1}

Equivalent conductance(Λ_{eq}):

It is defined as the conducting power of all the ions produced by 1 gram equivalent of an electrolyte in a given solution.

$\Lambda_{eq} = k \times v$, v is the volume of the solution in C.C containing 1 gram equivalent of the electrolyte

$$\Lambda_{eq} = k \times 1000/\text{normality}$$

$$\text{Unit: } \Omega^{-1}\text{cm}^2\text{eq}^{-1}$$

Molar conductance(Λ_m):

the conducting power of all the ions produced by one mole of an electrolyte in a given solution

$$\Lambda_m = k \times 1000/\text{molarity} \text{ Unit-ohm}^{-1}\text{cm}^2\text{mol}^{-1}$$

Question1>

Specific conductance of a decimolar solution of KCl at 18°C is 1.12Sm⁻¹. The Resistance of a conductivity cell containing the solution at 18°C was found to be 55 ohm . What is the cell constant

$$R=55\Omega, \quad G=(1/55)S, \quad k=1.12Sm^{-1}$$

$$K_{cell}= k/G= 1.12/(1/55)=61.6m^{-1} \text{ or } .0616cm^{-1}$$

Question 2. The Resistance of 0.5M solution of an electrolyte in a cell was found to be 45 ohm. Calculate the molar conductance of the solution if the electrodes in the are 2.2 cm apart and have an area of 3.8 cm²

$$R = 45\Omega, \quad G = 1/R, \quad G = (1/45) S$$

$$K_{cell} = l/a = 2.2/3.8 = 0.5789 \text{ cm}^{-1} = 57.89 \text{ m}^{-1}$$

$$\kappa = G \times K_{cell} = 1/(45) \times 0.5789 = 0.01286 \text{ Scm}^{-1} = 1.286 \text{ S m}^{-1}$$

$$\Lambda_m = (k \times 1000)/M, \quad M = \text{molarity}$$

$$= 0.01286 \times 1000/.5 = 25.72 \text{ S cm}^2 \text{ mol}^{-1}$$

Question 3. The Resistance of a cell containing (i) .100 N potassium chloride solution and (ii) .100 N silver nitrate solution, was 307.62 and 362.65 ohms respectively at 25° C . The specific conductance of 0.100 N potassium chloride was 0.01286 ohm⁻¹cm⁻¹ at 25° C.

Calculate (a) the cell constant, and (b) the equivalent conductance of a 0.100 N solution of silver nitrate

Conductance of 0.100 KCl = (1/307.62) ohm⁻¹

Cell constant = 0.01286 / (1/307.62) = 3.955 cm⁻¹

Conductance of 0.100 N AgNO₃ solution = 1/(362.65) ohm⁻¹

Specific conductivity (k) = 3.955 x 1/362.65 = 0.010905

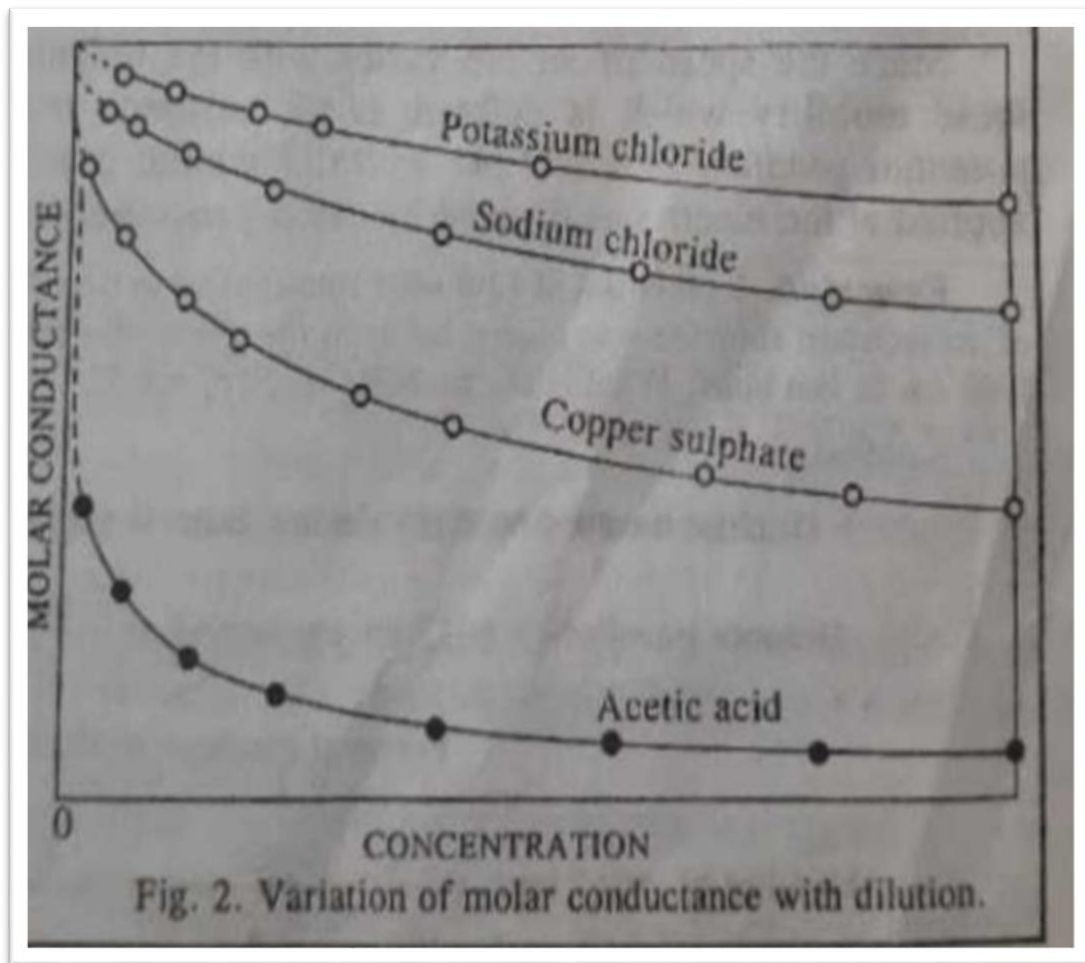
$$\begin{aligned}\Lambda_e &= (k \times 1000)/N \\ &= 0.010905 \times 1000/0.1 \\ &= 109.05 \text{ ohm}^{-1} \text{ cm}^2 \text{ g equiv}^{-1}\end{aligned}$$

Effect of dilution on conductivities *the conductivity of a solution depends upon the number of ions present in it . As on dilution, the degree of ionization of an electrolyte increases i.e., number of ions increases, hence all the conductivities should increase on dilution. But it has been seen that specific conductivity decrease with dilution because on dilution volume of solution increases so , the number of ions per c.c. of the solution decrease and since the specific conductivity depends upon the number of ions per c.c. of the solution , so specific conductivity decrease with dilution*

*Molar conductance **and** Equivalent conductance is the product of specific conductivity and volume. But the decrease in specific conductivity on dilution is more than compensated by the increase in volume, the net result, therefore, is that Equivalent*

and molar conductivity increase on dilution or as the concentration of the electrolyte decreases.

The variation of molar conductance with dilution in some



common electrolytes is shown in fig .2. As can be seen, in strong electrolytes there is a tendency for molar conductance to approach a certain limiting value when the concentration approaches zero the molar conductance at this point is know as **molar conductance at zero concentration or at infinite dilution.** It is denoted by $\Lambda^{\circ m}$

It may be made clear that by infinite dilution is meant a solution so dilute that it has maximum or limiting molar conductance which does not increase on further dilution. This value, in case of strong electrolytes, is obtained by extrapolating the molar conductance graph to zero concentration.

*But in case of weak electrolytes limiting value can't be obtained by extrapolation. Because degree of ionization of weak electrolytes are directly proportional to square root of volume or dilution (**Ostwald dilution law**)*

Ionic mobility. Although, at infinite dilution, all electrolytes are completely ionized, their molar conductance differ vastly from one another. This is because of differences in the speeds of the ions. Since the speed of an ion varies with the potential applied, it is better to use the term **ionic mobility** which is defined as the distance travelled by an ion per second under a potential gradient of 1 volt per meter

. **Potential gradient** = potential difference applied at the electrodes/ distance between the electrodes

Question 4. A potential of 12.0 volts was applied to two electrodes placed 20 cm apart. A dilute solution of ammonium chloride was placed between the electrodes when NH_4^+ ion was found to cover a distance of 1.60 cm in one hour. What is mobility of NH_4^+ ion ?

Distance travelled by ammonium ion in 1 hour = $1.6 \times 10^{-2}\text{m}$

\therefore Distance travelled by NH_4^+ ion per second = $1.6 \times 10^{-2}/3600$

$$\text{Potential gradient} = 12/20 \text{ V cm}^{-1} = (12 \times 100)/20 \text{ V m}^{-1}$$

Mobility of ions = speed/ potential gradient =

$$(1.6 \times 10^{-2}/3600)/(12 \times 100/20) = 7.41 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$$

Factors Affecting Conductivity

1) Dielectric constant. It is true that greater the dielectric constant of the medium, greater will be the degree of ionization of the electrolyte. Hence, molar and Equivalent conductance increase with increase in dielectric constant of the medium,

2) Viscosity. (Walden law)

Consider a single ion immersed in a liquid and subjected to an electric field, E . As the ion moves through the liquid, its motion is retarded by the viscosity of the liquid. The frictional force, f , acting on a spherical ion of radius r , moving with a velocity v , is given by **Stokes's law**,

$$F = 6 \pi \eta r v \quad \eta = \text{Coefficient of viscosity of liquid}$$

This force is balanced by the electrical force acting on the ion, viz, $z e E$

$$6 \pi \eta r v = z e E \quad z = \text{charge number}, e = \text{electronic charge}$$

Hence, mobility, $u_{(+,-)}$ of the ion is given by

$$u_+ = v/E = ze/6\pi\eta r$$

$$\Lambda^{\circ}_+ = z u^{\circ}_+ F, \text{ now putting value of } u^{\circ}_+$$

$$\Lambda^{\circ}_+ = z^2 e F / 6 \pi \eta_0 r, \quad \eta_0 = \text{viscosity of pure liquid}$$

The only quantity on right -hand side of equation that depends on medium is η_0

$$\Lambda^{\circ}_+ \eta_0 = \text{constant (this called Walden's rule)}$$

As is evident , the larger the viscosity of the medium ,the lesser would be the mobility and hence the lesser would be the conductance of the ion

- *Walden 's rule holds only for large ions such as **tetra methyl ammonium ion $(\text{CH}_3)_4\text{N}^+$** and the **picrate ion $\text{C}_6\text{H}_2(\text{NO}_2)_3\text{O}^-$** . However, if we exclude water, the smaller ions , too , obey Walden's rule , though not **very satisfactorily**. The reason is that the smaller ions are more solvated then larger ions.*

3) Temperature. *In most cases , the conductivity of an electrolyte rises rapidly with temperature , which may be due to (i) fall in viscosity of the solvent , and (ii) decrease in the extent of solvation of ions .*

4) Concentration of electrolytic solution (Discuss above under the topic *effect of dilution on conductivities*)