B.Sc. (Honours) Part-II
Paper-III

Topic: Conductance

UG
Subject-Chemistry

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The conductance is the property of the conductor (metallic as well as electrolytic) which facilitates the flow of electricity through it. It is equal to the reciprocal of resistance, *i.e.*,

$$\text{Conductance} = \frac{1}{\text{Resistance}} = \frac{1}{R} \qquad \text{... (i)}$$

It is expressed in the unit called reciprocal ohm (ohm^{-1} or mho) or siemens.

Specific Conductance or Conductivity

The resistance of any conductor varies directly as its length (l) and inversely as its cross-sectional area (a), *i.e.*,

$$R \propto \frac{l}{a} \text{ or } R = \rho \frac{l}{a} \qquad \text{... (ii)}$$

where, ρ is called the specific resistance.

If $l = 1\,\text{cm}$ and $a = 1\,\text{cm}^2$, then

$$R = \rho \qquad \text{... (iii)}$$

The specific resistance is, thus, defined as the resistance of one centimetre cube of a conductor.

The reciprocal of specific resistance is termed the **specific conductance** or it is the conductance of one centimetre cube of a conductor.

It is denoted by the symbol κ. Thus,

$$\kappa = \frac{1}{\rho}, \quad \kappa = \text{kappa—The specific conductance} \qquad \text{... (iv)}$$

Specific conductance is also called conductivity.

From eq. (ii), we have

$$\rho = \frac{a}{l} \cdot R \quad \text{or} \quad \frac{1}{\rho} = \frac{l}{a} \cdot \frac{1}{R}$$

$$\kappa = \frac{l}{a} \times C \qquad \left(\frac{l}{a} = \text{cell constant}\right)$$

or Specific conductance = conductance × cell constant

In the case of electrolytic solutions, the specific conductance is defined as the conductance of a solution of definite dilution enclosed in a cell having two electrodes of unit area separated by one centimetre apart as shown in Fig. 12.2.

The unit of specific conductance is $\text{ohm}^{-1}\ \text{cm}^{-1}$.

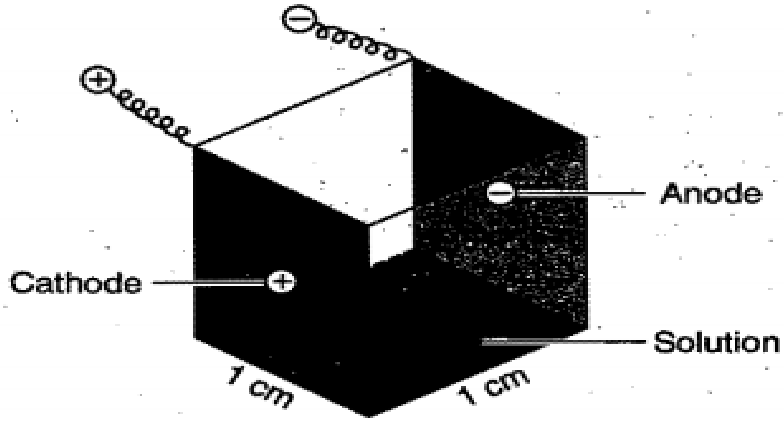

Fig. 12.2 Representation of specific conductance

Equivalent Conductance

One of the factors on which the conductance of an electrolytic solution depends, is the concentration of the solution. In order to obtain comparable results for different electrolytes, it is necessary to take equivalent conductances.

Equivalent conductance is defined as the conductance of all the ions produced by **one gram-equivalent** of an electrolyte in a given solution. It is denoted by Λ.

To understand the meaning of equivalent conductance, imagine a rectangular trough with two opposite sides made of metallic conductor (acting as electrodes) exactly 1 cm apart, If $1\ \text{cm}^3$ (1 mL)

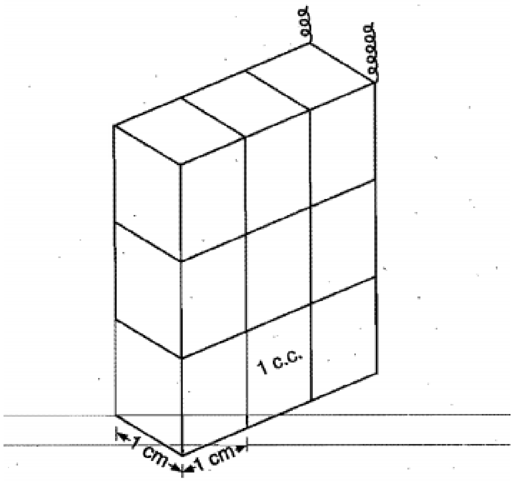

Fig. 12.3

solution containing 1 gram-equivalent of an electrolyte is placed in this container and conductance is measured.

According to definitions,

Conductance = Specific conductance (κ)

= Equivalent conductance (Λ)

If the solution is diluted to say ($9\,\text{cm}^3$) (9 mL), the conductance of the solution will be the same but specific conductance becomes 1/9 th as it contains nine cubes. The conductance is also equal to the equivalent conductance because the solution still has 1 g-equivalent of the electrolyte. This is shown in Fig. 12.3. Thus,

Equivalent conductance $(\Lambda) = 9 \times \kappa$

In general,

$$\Lambda = \kappa \times V \qquad \text{... (v)}$$

where, V is the volume in mL containing 1 g-equivalent of the electrolyte.

In case, if the concentration of the solution is c g-equivalent per litre, then the volume containing 1 g-equivalent of the electrolyte will be $1000/c$.

So, equivalent conductance,

$$\Lambda = \kappa \times \frac{1000}{c} \qquad \text{... (vi)}$$

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

where, N = normality

The unit of equivalent conductance is $\text{ohm}^{-1}\ \text{cm}^2\ \text{eq}^{-1}$.

Molar Conductance

The molar conductance is defined as the conductance of all the ions produced by ionisation of **1 g-mole** of an electrolyte when present in V mL of solution. It is denoted by μ.

$$\text{Molar conductance } \mu = \kappa \times V \qquad \text{... (vii)}$$

where, V is the volume in mL containing 1 g-mole of the electrolyte. If c is the concentration of the solution in g-mole per litre, then

$$\mu = \kappa \times \frac{1000}{c}$$

Cell Constant

Since, the electrodes are not exactly 1 unit apart and may not possess a surface area of 1 square unit, the measured resistance does not give the specific conductance of the solution. Actual measurements of l and a being inconvenient, an indirect method is employed to determine the value of $\frac{l}{a}$ which is a constant quantity for a particular cell and is known as cell constant. We know that,

$$\frac{\text{Specific conductance}}{\text{Conductance}} = \frac{l}{a} = \text{Cell constant}$$

Effect of Dilution on Equivalent Conductance

The value of equivalent conductance increases with dilution. This is due to the fact that degree of ionisation increases with dilution thereby increasing the total number of ions in solution. Solution which contains large number of ions compared to another solution of the same concentration at the same temperature has more conductance and is said to be **stronger electrolyte.** The one which has relatively small number of ions is called a **weak electrolyte.** The number of ions from an electrolyte depends on the degree of dissociation. The curve (Fig. 12.6) shows the variation of the equivalent conductance of some electrolytes with dilution. It shows that electrolytes behave in two ways on dilution:

(i) Electrolytes like KCl have high value of conductance even at low concentration and there is no rapid increase in their equivalent conductance on dilution. Such electrolytes are termed **strong electrolytes.** In the case of strong electrolytes, there is a tendency for equivalent conductance to approach a limiting value when the concentration approaches zero. When the whole of the electrolyte has ionised, further addition of the water does not bring any change in the value of equivalent conductance. This stage is called infinite dilution. The equivalent conductance has a limiting value at infinite dilution and is represented by Λ_{∞}.

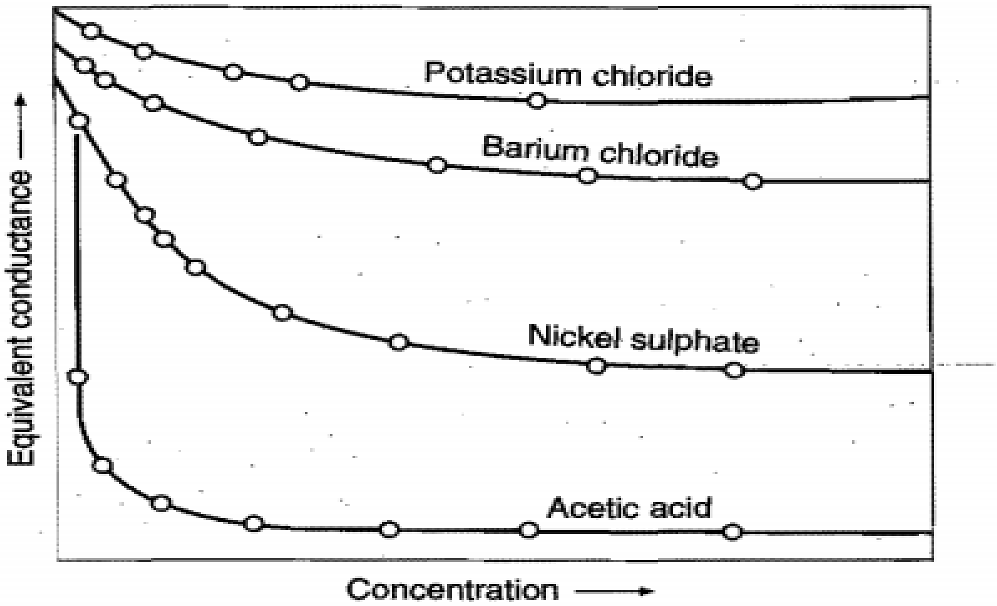

Fig. 12.6 Conductance curve

(ii) Electrolytes like acetic acid have a low value at high concentration and there is a rapid increase in the value of equivalent conductance with dilution. Such electrolytes are termed **weak electrolytes.** There is no indication that a limiting value of equivalent conductance can be attained even when the concentration approaches zero. Thus, graphically, Λ_∞ of weak electrolytes cannot be obtained.

It is thus concluded that equivalent conductance of electrolytes whether strong or weak increases with dilution and reaches to a maximum or limiting value which is termed Λ_∞ (equivalent conductance at infinite dilution). Λ_∞ in the case of strong electrolytes can be obtained by extrapolation of the graph of equivalent conductance to zero concentration but in the case of weak electrolytes it cannot be obtained accurately. An indirect method for obtaining Λ_∞ for weak electrolytes has been given by Kohlrausch.

12.8 KOHLRAUSCH'S LAW

"At infinite dilution, when dissociation is complete, each ion makes a definite contribution towards equivalent conductance of the electrolyte irrespective of the nature of the ion with which it is associated and the value of equivalent conductance at infinite dilution for any electrolyte is the sum of contribution of its constituent ions", *i.e.*, anions and cations. Thus,

$$\Lambda_\infty = \lambda_a + \lambda_c$$

The λ_c and λ_a are called the ionic conductances of cation and anion at infinite dilution respectively. The ionic conductances are proportional to their ionic mobilities. Thus, at infinite dilution,

$$\lambda_c = ku_c$$

and

$$\lambda_a = ku_a$$

where, u_c and u_a are ionic mobilities of cation and anion respectively at infinite dilution. The value of k is equal to 96500 C, *i. e.*, one Faraday.

Thus, assuming that increase in equivalent conductance with dilution is due to increase in the degree of dissociation of the electrolyte; it is evident that the electrolyte achieves the degree of dissociation as unity when it is completely ionised at infinite dilution. Therefore, at any other dilution, the equivalent conductance is proportional to the degree of dissociation. Thus,

Degree of dissociation

$$\alpha = \frac{\Lambda}{\Lambda_\infty} = \frac{\text{Equivalent conductance at a given concentration}}{\text{Equivalent conductance at infinite dilution}}$$

Calculation of absolute ionic mobilities: It has been experimentally found that ionic conductance is directly proportional to ionic mobilities.

$$\lambda_+ \propto u_+$$

$$\lambda_- \propto u_-$$

where, u_+ and u_- are ionic mobilities of cations and anions.

$$\lambda_+ = Fu_+ \quad \text{where, } F = \text{Faraday}$$

$$\lambda_- = Fu_- \quad\quad = 96500 \text{ coulomb}$$

$$\text{Ionic mobility} = \frac{\text{Ionic velocity}}{\text{Potential gradient}}$$

$$= \frac{\text{Ionic velocity (cm/ sec)}}{\text{Potential difference (volt)/ electrode separation}}$$

Relation between Equivalent and Molar Conductance at Infinite Dilution

$$\Lambda^{\infty} = \frac{1}{z^{+}}\lambda_{+}^{\infty} + \frac{1}{z^{-}}\lambda_{-}^{\infty} \qquad \text{... (i)}$$

where, z^{+} and z^{-} are corresponding charges on the ions,

e.g.,

$$\Lambda_{BaCl_2}^{\infty} = \frac{1}{2}\lambda_{Ba^{2+}}^{\infty} + \frac{1}{1}\lambda_{Cl^{-}}^{\infty} \qquad \text{... (ii)}$$

$$\Lambda_{AlCl_3}^{\infty} = \frac{1}{3}\lambda_{Al^{3+}}^{\infty} + \frac{1}{1}\lambda_{Cl^{-}}^{\infty} \qquad \text{... (iii)}$$

$$\Lambda_{Al_2(SO_4)_3}^{\infty} = \frac{1}{3}\lambda_{Al^{3+}}^{\infty} + \frac{1}{2}\lambda_{SO_4^{2-}}^{\infty} \qquad \text{... (iv)}$$

Molar Conductance at Infinite Dilution

$$\Lambda_m^{\infty} \text{ or } \mu^{\infty} = \text{Molar conductance at infinite dilution}$$

$$= m\lambda_{+}^{\infty} + n\lambda_{-}^{\infty}$$

where, m and n are number of ions formed.

$$\mu_{Al_2(SO_4)_3}^{\infty} = 2\lambda_{Al^{3+}}^{\infty} + 3\lambda_{SO_4^{2-}}^{\infty} = 6\Lambda_{Al_2(SO_4)_3}^{\infty}$$

$$\mu_{BaCl_2} = \lambda_{Ba^{2+}}^{\infty} + 2\lambda_{Cl^{-}}^{\infty} = 2\Lambda_{BaCl_2}^{\infty}$$

12.9 THEORY OF WEAK ELECTROLYTES

(i) Weak electrolytes are not completely ionized when dissolved in a polar medium like water. There exists equilibrium between ions and unionised molecules.

$$AB \rightleftharpoons A^{+} + B^{-}$$

(ii) Concept of chemical equilibrium and law of mass action can be applied to ionic equilibrium also.

$$\begin{array}{llll} & AB & \rightleftharpoons A^{+} & + \; B^{-} \\ t = 0 & C & \quad 0 & \quad 0 \\ t_{eq.} & C - C\alpha & \quad C\alpha & \quad C\alpha \end{array}$$

$$K = \frac{[A^{+}][B^{-}]}{[AB]} = \frac{C\alpha \times C\alpha}{C(1-\alpha)}$$

$$K = \frac{C\alpha^{2}}{1-\alpha} \qquad \text{... (i)}$$

For weak electrolytes, $\alpha << 1$

$$\therefore \qquad (1-\alpha) \approx 1$$

Thus, equation (i) can be written as:

$$K = C\alpha^2$$

$$\alpha = \sqrt{\frac{K}{C}} \qquad \text{... (ii)}$$

From eq. (ii), it is clear that on dilution concentration decreases, as a result of which degree of ionisation 'α' increases. At high degree of ionisation both equivalent and molar conductance increase.

(iii) Degree of ionisation can be calculated as:

$$\alpha = \frac{\Lambda_e^C}{\Lambda_e^\infty} = \frac{\Lambda_m^C}{\Lambda_m^\infty} \qquad \text{... (iii)}$$

Λ_e^C, Λ_m^C = Equivalent and molar conductance at concentration 'C'

$\Lambda_e^\infty, \Lambda_m^\infty$ = Equivalent and molar conductance at infinite dilution.

Substituting the values of 'α' from eq. (iii) in eq. (i), we get

$$K = \frac{C \times \left(\frac{\Lambda_e^C}{\Lambda_e^\infty}\right)^2}{1 - \frac{\Lambda_e^C}{\Lambda_e^\infty}} = \frac{C(\Lambda_e^C)^2}{\Lambda_e^\infty\ (\Lambda_e^\infty - \Lambda_e^C)} \qquad \text{... (iv)}$$

Similarly,

$$K = \frac{C(\Lambda_m^C)^2}{\Lambda_m^\infty\ (\Lambda_m^\infty - \Lambda_m^C)} \qquad \text{... (v)}$$

Equations (iv) and (v) are called **Ostwald equations.**

Molar Conductance. It is customary to express electrolytic conductance in terms of molar conductance, which is defined as the conducting power of all the ions produced by one mole of the electrolyte in a given solution. It is denoted by Λ_m.

Let us consider a solution containing c moles of an electrolyte in one cubic metre of the solution. The volume of the solution containing 1 mole of the electrolyte would be $1/c$ cubic metre.

$$\Lambda_m = \text{conductance of 1 m}^3\text{ of the solution} \times \text{volume of the solution in m}^3\text{ containing 1 mole of the electrolyte}$$

$$= \text{specific conductance} \times 1/c$$

$$= \kappa/c \qquad ...(3)$$

Since units of κ are S m^{-1} and those of c are mol m^{-3}, hence the units of Λ_m are S m^2 mol^{-1}.

4. Conductometric Titrations. Conductance measurements are frequently employed to find the end points of acid-alkali and other titrations. The principle involved is that *electrical conductance depends upon the number and mobility of ions.*

Consider, in the first instance, the titration of a strong acid, like hydrochloric acid, with a strong base, like sodium hydroxide. The acid is taken in the conductivity vessel and the alkali in the burette. The conductance of hydrochloric acid is due to the presence of hydrogen and chloride ions. As alkali is added gradually, the hydrogen ions are replaced by slow moving sodium ions, as represented below :

$$H^+(aq) + Cl^-(aq) + [Na^+(aq) + OH^-(aq)] \longrightarrow Na^+(aq) + Cl^-(aq) + \underset{\text{(unionised)}}{H_2O(l)}$$

Hence, on continued addition of sodium hydroxide, the conductance will go on decreasing until the acid has been completely neutralized. Any subsequent addition of alkali will result in introducing fast moving hydroxyl ions. The conductance, therefore, after reaching a certain minimum value, will begin to increase. On plotting the conductance against the volume of alkali added, the points will lie on two straight lines *AB* and *CD* (Fig. 7). The point of intersection *X* of these two lines gives the volume of alkali required for the neutralization.

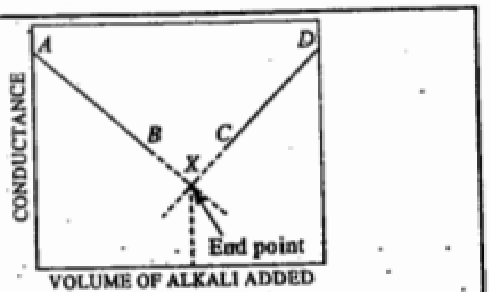

Fig. 7. Titration of a strong acid against a strong base.

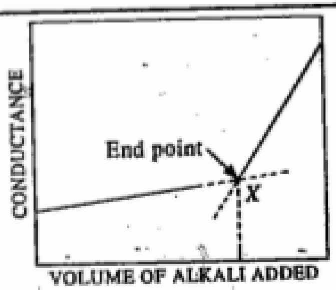

Fig. 8. Titration of a weak acid against a strong base.

Suppose, it is required to titrate a weak acid like acetic acid, against a strong base, like sodium hydroxide. The conductance of the acid will be low on account of its poor dissociation. On adding the base, highly ionised sodium acetate is formed and hence the conductance begins to increase.

$$CH_3COOH(aq) + [Na^+(aq) + OH^-(aq)] \longrightarrow CH_3COO^-(aq) + Na^+(aq) + \underset{\text{(unionised)}}{H_2O(l)}$$

When the acid is completely neutralized, further addition of the base introduces excess of fast moving hydroxyl ions. The conductance of the solution, therefore, begins to increase even more sharply than before. On plotting the conductance against the volume of the alkali added, the two lines obtained will be as shown in Fig. 8. The point of intersection *X* gives the end point.

When a mixture of a strong and a weak acid is to be titrated against a strong base, a combination of curves shown in Figs. 7 and 8 is obtained. Suppose a mixture of HCl and CH_3COOH is to be titrated against NaOH. Hydrochloric acid, being a much stronger acid, will get titrated first. The titration of acetic acid will commence only after hydrochloric acid has been completely neutralized. Hence, a combination of curves as mentioned above is obtained. This is represented in Fig. 9. While the point *B* corresponds to the neutralisation of HCl, the point *C* corresponds to the neutralisation of CH_3COOH.

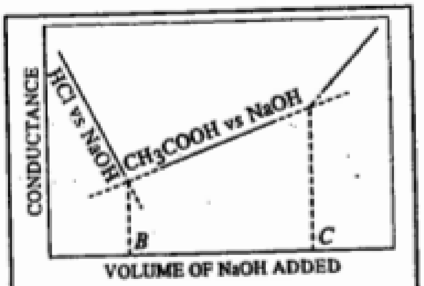

Fig. 9. Titration of a mixture of HCl and CH_3COOH against NaOH.

Finally, suppose it is required to titrate a strong acid like hydrochloric acid, against a weak base, like ammonium hydroxide. The conductance will fall at first due to the replacement of fast moving H^+ ions by slow moving NH_4^+ ions.

$$H^+(aq) + Cl^-(aq) + [NH_4OH] \longrightarrow NH_4{}^+(aq) + Cl^-(aq) + H_2O(l)$$

After neutralisation of the acid, further addition of weakly ionised ammonium hydroxide will not cause any appreciable change in the conductance. The curves obtained will be as shown in Fig. 10.

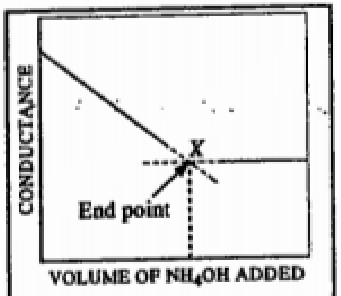

Fig. 10. Titration of a strong acid against a weak base.

5. Precipitation Titrations. The titration of silver nitrate against potassium chloride can also be carried out by this method. The reaction involved may be represented as

$$Ag^+(aq) + NO_3^-(aq) + [K^+(aq) + Cl^-(aq)] \longrightarrow K^+(aq) + NO_3^-(aq) + AgCl(s)$$

Since the mobility of potassium ion is nearly the same as that of silver ion which it replaces, the conductance will remain more or less constant and will begin to increase only after the end point. The curves obtained will be as shown in Fig. 11.

In order to get accurate results, the change of volume during the titration should be as small as possible. For this purpose the titration solution in the burette is usually five to ten times stronger than the solution taken in the conductivity vessel.

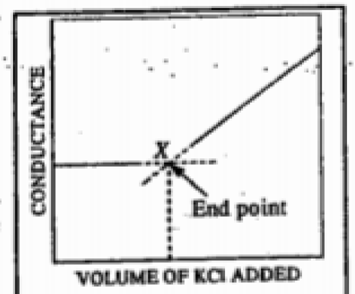

Fig. 11. Titration of silver nitrate against potassium chloride.

Conductometric titrations have several advantages. Coloured solutions, which cannot be titrated by ordinary volumetric methods with the help of indicators, can be successfully titrated conductometrically. The method can also be employed in the case of very dilute solutions and also for weak acids and bases. Further, no special care is necessary near the end point as it is determined graphically.