

Drift speed

When a potential difference of $\Delta\Phi$ is applied between two electrodes a distance l apart, then strength of the field is given by:

$$E = \frac{\Delta\Phi}{l}$$

In such a field, an ion of charge Ze experiences a force of magnitude:

$$F = ZeE = Ze \frac{\Delta\Phi}{l}$$

As an ion moves towards the oppositely charged electrode through the solvent, it experiences a friction or retarding force F' , given by the Stokes law is:

$$F' = 6\pi\eta as$$

where

$a \rightarrow$ radius of the ion

$s \rightarrow$ velocity of the ion

$\eta \rightarrow$ viscosity of the solution.

When these two forces acting in opposite directions become equal, the ion moves at a terminal speed. The terminal speed acquired by an ion in solution when the accelerating force due to electric field is balanced by the opposing viscous drag is called the drift speed.

Thus, when

$$\begin{aligned} F &= F' \\ ZeE &= 6\pi\eta as \\ \Rightarrow s &= \frac{ZeE}{6\pi\eta as} \end{aligned}$$

Drift speed governs the rate at which charge is transported. Hence, with increasing viscosity of the solution and ionic size, conductivity decreases.

Explain: The molar conductivities of the alkali metal ions increase from Li^+ to Cs^+ even though the ionic radii increase.

Ans:

Small ions give rise to stronger electric fields than large ones, so smaller ions are more extensively solvated than big ones. The effective radius of an ion in the solution taking into account all the H_2O molecules it carries in its hydration sphere is called the hydrodynamic radius of the ion. An ion of small ionic radius may have a large hydrodynamic radius because it drags many solvent molecules through the solution as it migrates. So smaller the ion, larger is the hydration sphere and hence lower is the ionic mobility.

Therefore, from Li^+ to Cs^+ , as the ionic size increases, solvation decreases and hence ionic mobility (or molar conductivity) increases.

Ionic mobility (u)

For a given concentration of solution, the drift speed or velocity of an ion is proportional to the strength of the applied field, i.e.

$$s \propto E$$

$$\Rightarrow s = uE$$

where the coefficient of proportionality u is called ionic mobility.

When $E = 1 \text{ Vm}^{-1}$, $s = u$

Therefore, the drift speed (or velocity) with which an ion moves under the application of an electric field of unit strength is called ionic mobility.

Unit:

$$u = \frac{s}{E} = \frac{\text{cms}^{-1}}{\text{Vcm}^{-1}} = \text{cm}^2\text{V}^{-1}\text{s}^{-1}(\text{CGS}) \text{ or } \text{m}^2\text{V}^{-1}\text{s}^{-1}(\text{SI})$$

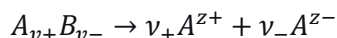
Ionic mobility and molar conductivity of ions

The relation between an ion's mobility and its molar conductivity is:

$$\lambda = z\mu F$$

where z is the charge on the ion, F is Faraday's constant.

For an electrolyte with formula $A_{\nu_+}B_{\nu_-}$, which is dissociated completely to ν_+ positive ions and ν_- negative ions as:



at infinite dilution, molar conductivities of ions are:

$$\lambda_+^\circ = z_+u_+F$$

$$\lambda_-^\circ = z_-u_-F$$

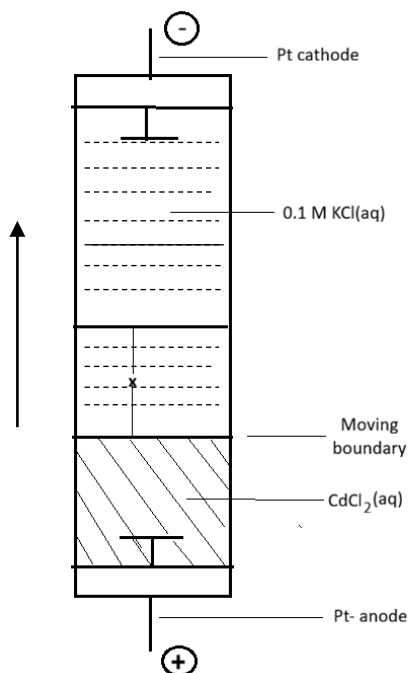
Applying Kohlrausch's law, Λ_m° for $A_{\nu_+}B_{\nu_-}$ is given by

$$\Lambda_m^\circ = \nu_+\lambda_+^\circ + \nu_-\lambda_-^\circ = (z_+u_+\nu_+ + z_-u_-\nu_-)F$$

Greater the mobility of an ion, greater is its contribution towards conductivity.

Experimental Measurement of Ionic Mobility (Moving boundary method)

Ionic mobility is measured directly by measuring the velocity of a visible boundary between two electrolyte solutions. Let us consider that we require to measure the mobility of K^+ ions. Then KCl may be one of the electrolytes (the principal electrolyte). The second electrolyte (the indicator electrolyte) should have the same anion as the first electrolyte (e.g., Cl^-) and its cation should have mobility lower than that of K^+ ion. For KCl as the principal electrolyte, $CdCl_2$ is a suitable indicator electrolyte.



A 0.1 M KCl (aq) solution is held over a solution of similar concentration of $CdCl_2$ in a tube of uniform bore. The anode is placed at the lower end and the cathode at the upper end of the tube as shown in figure. When a small current flows through the cell, the K^+ ions, followed closely by Cd^{2+} ions, move upward. As there will be no gap in between; the boundary will continue to remain sharp. The rate of movement of the boundary will be given by the velocity of K^+ ions.

Let the boundary move x m in t seconds when a field of $E \text{ V m}^{-1}$ is applied, then

$$u = \frac{x}{tE} \text{ m}^2\text{V}^{-1}\text{s}^{-1}$$

Transport number or transference number:

The transport number t is defined as the fraction of total current carried by the ions of a specified type.

For a solution of two kinds of ions, the cation transport number is:

$$t_+ = \frac{I_+}{I}$$

where I^+ is the current carried by the cation and I is the total current through the solution.

Similarly, anion transport number is defined as:

$$t_- = \frac{I_-}{I}$$

Where I^- is the current carried by the anion.

Now,

$$t_+ + t_- = \frac{I_+}{I} + \frac{I_-}{I} = \frac{I^+ + I^-}{I} = \frac{I}{I} = 1$$

or

$$t_+ + t_- = 1$$

Limiting transport number is defined as the fraction of total current carried by the ions of a specified type in the limit of zero concentration.

Now, the current carried by each type of ion is proportional to their conductivity and hence to their ionic mobility, i.e.,

$$I^+ \propto z_+ u_+ \nu_+ F$$

$$I^- \propto z_- u_- \nu_- F$$

$$\therefore t_+ = \frac{I^+}{I^+ + I^-} = \frac{z_+ u_+ \nu_+ F}{z_+ u_+ \nu_+ F + z_- u_- \nu_- F}$$

$$t_- = \frac{I^-}{I^+ + I^-} = \frac{z_- u_- \nu_- F}{z_+ u_+ \nu_+ F + z_- u_- \nu_- F}$$

But electrical neutrality in the compound requires that

$$z_+ \nu_+ = z_- \nu_-$$

$$\therefore t_+ = \frac{u_+}{u_+ + u_-}$$

$$t_- = \frac{u_-}{u_+ + u_-}$$

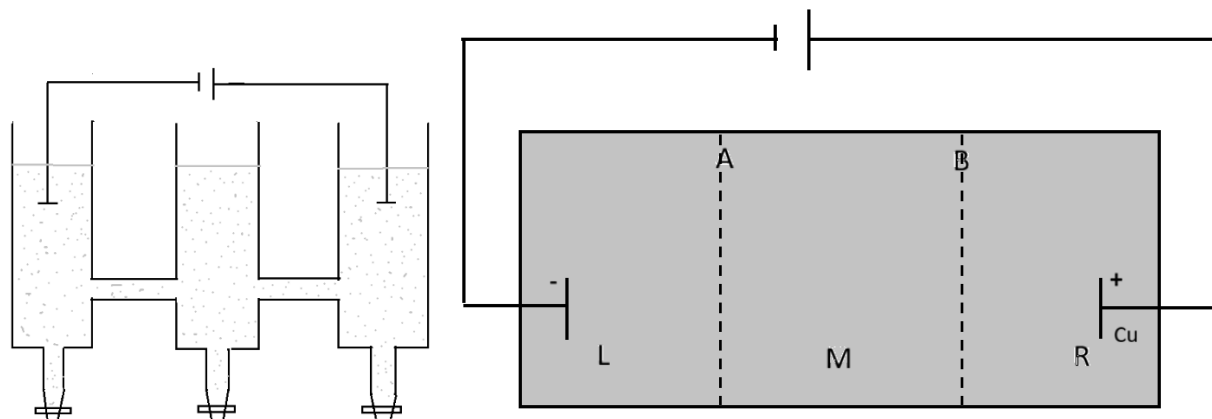
Determination of transport number by Hittorf method:

Principle

When current passes through an electrolyte, cations and anions carry definite fractions of the total current. This leads to unequal changes in concentration near the electrodes. By analyzing these changes, transport numbers can be calculated.

Experimental set up

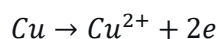
Hittorf apparatus for measuring transport number is shown below:



After electrolysis proceeds for a while, the solutions in each of the compartments are drained and analyzed.

Calculation

Calculations are shown taking the example of electrolysis of $\text{Cu}(\text{NO}_3)_2$ with a Cu anode and an inert cathode. Let a total charge Q flow during the experiment. Then Q/F mole of electrons flow. The anode reaction is



So, $Q/2F$ moles of Cu^{2+} ions enter the right compartment R from the anode. The total number of moles of charge on the ions that pass plane B during the experiment is Q/F . The Cu^{2+} ions carry a fraction t_+ of the current, and the charge on the Cu^{2+} ions moving from R to M is t_+Q . Therefore $t_+Q/2F$ moles of Cu^{2+} ions pass out of R into M during the experiment. The net change in the number of moles of Cu^{2+} ions in compartment R is

$$\Delta n_R(\text{Cu}^{2+}) = \frac{Q}{2F} - \frac{t_+Q}{2F} = (1 - t_+) \frac{Q}{2F} = t_- \frac{Q}{2F}$$

Since NO_3^- carries a fraction t_- of the current, the magnitude of the charge on the nitrate ions moving from M to R during the experiment is t_-Q and t_-Q/F moles of nitrate move into R .

$$\Delta n_R(\text{NO}_3^-) = t_- \frac{Q}{F}$$

The charge on the Cu^{2+} ions passing plane *A* must equal that on the Cu^{2+} ions passing plane *B*. Hence, $t_+Q/2F$ moles of Cu^{2+} ions move from *M* to *L* during the experiment, and there is no change in the number of moles of Cu^{2+} in *M*. Similarly, for NO_3^- :

$$\Delta n_M(Cu^{2+}) = 0, \Delta n_M(NO_3^-) = 0$$

The number of moles of NO_3^- passing through plane *B* equals the number passing through plane *A*, so t_-Q/F moles of nitrate move out of *L* into *M*:

$$\Delta n_L(NO_3^-) = -t_- \frac{Q}{F}$$

We have $t_+Q/2F$ moles of Cu^{2+} ions moving from *M* into *L*. Also, the number of moles of Cu that deposit on the cathode must equal the number that were oxidized at the anode ($Q/2F$). Therefore,

$$\Delta n_L(Cu^{2+}) = \frac{t_+Q}{2F} - \frac{Q}{2F} = (t_+ - 1) \frac{Q}{2F} = -t_- \frac{Q}{2F}$$

The charge *Q* is measured with a coulometer, and chemical analysis gives the Δn 's. Therefore, t_+ and t_- can be found from the above equations.

Determination of transport number by moving boundary method: The method rests on the direct observation of migration of ions in an electric field. Here, the motion of a boundary between two ionic solutions having a common ion is observed as a current flow. A tube has two electrodes fixed at the ends and contains the solutions having an ion in common. Let MX be the salt of interest and NX a salt giving a solution denser than that of MX. The solution of NX is called the indicator solution; it occupies the lower part of the tube. The MX solution, which is called the leading solution, occupies the upper part of the tube. There is a sharp boundary between the two solutions. The boundary is visible because of the difference in refractive indices of the solutions or in some cases due to difference in colour of solutions. The indicator solution must be denser than the leading solution, and the mobility of the M ions must be greater than that of the N ions. Thus, if M ions migrate towards cathode, they will be pulled upwards more rapidly than the N ions around them, and the boundary will move.

When a current *I* is passed for a time Δt , the boundary moves from AB. All the M ions in the volume *V* between AB and CD must have passed through the plane CD during the time Δt . If *c* is the molar concentration of MX solution, then the number of M ions passed is cVN_A .

∴ Charge they transfer through CD plane is $ZecVN_A$.

where $N_A \rightarrow$ Avogadro's constant.

∴ Current transferred by M ions in the interval Δt :

$$t_M = \frac{zecVN_A}{\Delta t}$$

Therefore, fraction of the total current carried by M ions is

$$\begin{aligned} t_M &= \frac{zecVN_A}{I\Delta t} \\ &= \frac{zcVF}{I\Delta t} \quad (\because N_A e = F) \end{aligned}$$

Hence by measuring V from the distance moved, t_M can be determined.

Relationship between ionic conductance and transport numbers at infinite dilution

Limiting transport numbers are given by

$$\begin{aligned} \therefore t_+^\circ &= \frac{z_+ u_+ v_+}{z_+ u_+ v_+ + z_- u_- v_-} \\ t_-^\circ &= \frac{z_- u_- v_-}{z_+ u_+ v_+ + z_- u_- v_-} \end{aligned}$$

Multiplying and dividing the right-hand side by Faraday constant F ,

$$\therefore t_+^\circ = \frac{z_+ u_+ v_+ F}{z_+ u_+ v_+ F + z_- u_- v_- F}$$

Now, molar ionic conductance of ions at infinite dilution are given by

$$\begin{aligned} \lambda_+^\circ &= z_+ u_+ F \\ \lambda_-^\circ &= z_- u_- F \\ \therefore t_+^\circ &= \frac{v_+ \lambda_+^\circ}{v_+ \lambda_+^\circ + v_- \lambda_-^\circ} \end{aligned}$$

$$\Rightarrow t_+^\circ = \frac{v_+ \lambda_+^\circ}{\Lambda_m^\circ}$$

Similarly, for the anion,

$$t_-^\circ = \frac{v_- \lambda_-^\circ}{\Lambda_m^\circ}$$

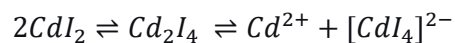
Because we can measure transport number of an ion, using above equations we can compute the individual ionic conductivities and hence ionic mobilities.

Abnormal Transference Number:

Transference numbers vary with concentration of the solution and temperature. It has been found that transference number of cadmium ion decreases with increasing concentration of Cd^{2+} ion, and at higher

concentration, it becomes negative. In such a case, the transport number is called abnormal transport number. A negative transport number means that Cd^{2+} ions migrate towards the anode.

This abnormal behaviour can be explained by postulating a complex formation in fairly concentrated solution of CdI_2 :



Concentration of the dynamic complex $[\text{CdI}_4]^{2-}$ increases with the high concentration of CdI_2 in solution.

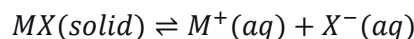
Cd^{2+} ions migrate out of the anode compartment while being simultaneously repelled by $[\text{CdI}_4]^{2-}$ ions.

When the concentrations of Cd^{2+} and $[\text{CdI}_4]^{2-}$ are equal, then $t^+=0$; and when concentration of $[\text{CdI}_4]^{2-}$ is higher than that of Cd^{2+} , $t^+ < 0$.

Applications of Conductance Measurements

(i) Determination of Solubility and Solubility Products of Sparingly Soluble Salts:

The solubilities of sparingly soluble salts such as barium sulphate, silver chloride, lead sulphate etc. can be determined by conductance measurements. Let us consider a sparingly soluble salt MX , in contact with its saturated solution, the equilibrium may be represented as



and the solubility product is given by

$$K_{sp} = [M^+][X^-]$$

Let κ_s be the specific conductance of the saturated solution of the salt and κ_{H_2O} be the specific conductance of pure water in which the salt is sparingly soluble. Then the specific conductance of the salt alone is given as

$$\kappa_{salt} = \kappa_s - \kappa_{H_2O}$$

The molar conductivity is then given as

$$\Lambda_m = \frac{\kappa_{salt}}{c}$$

where c is the concentration of the salt in mol/m^3 and hence the solubility. This solution may be regarded as infinitely dilute and hence the molar conductivity would be Λ_m° , i.e.,

$$\Lambda_m^\circ = \frac{\kappa_{salt}}{c}$$

or

$$c = \frac{\kappa_{salt}}{\Lambda_m^\circ}$$

Since the value of Λ_m° can be obtained as the sum of the ionic conductivities:

$$\Lambda_m^\circ = \lambda_+^\circ + \lambda_-^\circ$$

hence

$$c = \frac{\kappa_{salt}}{\lambda_+^\circ + \lambda_-^\circ}$$

Problem

The conductivity of a saturated solution of a sparingly soluble salt MX in water at 298 K is $1.887 \times 10^{-4} \text{ S m}^{-1}$. The molar conductivity of MX at infinite dilution at this temperature is $138.3 \times 10^{-4} \text{ Sm}^{-2} \text{ mol}^{-1}$. Calculate the solubility and the solubility product of MX at this temperature.

Solution: We know that

$$\Lambda_m^\circ = \frac{\kappa_{\text{salt}}}{c}$$

or

$$c = \frac{\kappa_{\text{salt}}}{\Lambda_m^\circ} = \frac{1.887 \times 10^{-4} \text{ Sm}^{-1}}{138.3 \times 10^{-4} \text{ Sm}^2 \text{ mol}^{-1}} = 1.34 \times 10^{-2} \text{ mol m}^{-3} = 1.34 \times 10^{-5} \text{ mol dm}^{-3}$$

Therefore, Solubility product,

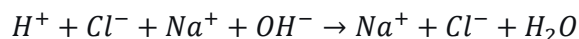
$$K_{sp} = [M^+][X^-] = (1.34 \times 10^{-5} \text{ mol dm}^{-3})^2 = 1.796 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$$

(ii) Conductometric Titrations

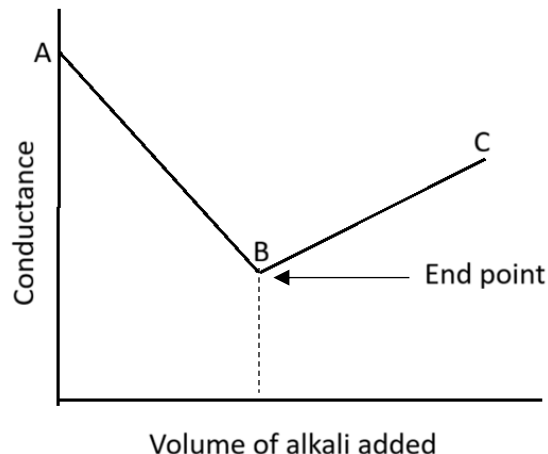
The conductance of a solution depends largely on the number of ions and their mobilities. The variation in conductivity is determined by the variation in conductance of a solution during titration is employed in determining the end point of a titration.

(a) The titration of a strong acid by a strong base

Let us consider the titration of HCl by NaOH . Initially the conductance of the solution is due to hydrogen and chloride ions. When the base is added, the reaction occurring in the vessel is



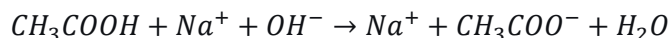
For each mole of hydroxyl ions added, one mole of hydrogen ions is removed. The concentration of hydrogen ions decreases during the titration. The molar conductivity of hydrogen ion at infinite dilution is greater than that of sodium ion. Thus, fast moving hydrogen ions are being replaced by slow moving sodium ions. Consequently, the conductance of the solution decreases. This continues until the equivalence point is reached where all the hydrogen ions from the acid are removed by the hydroxyl ions. At this point, the conductance is due to sodium and chloride ions. Further addition of the base introduces excess of fairly high conducting hydroxyl ions and these cause the conductance to increase rapidly. Hence, in the titration of a strong acid by a strong base, the conductance has a minimum value at the equivalence point. The plot of conductance versus volume of alkali added is shown below.



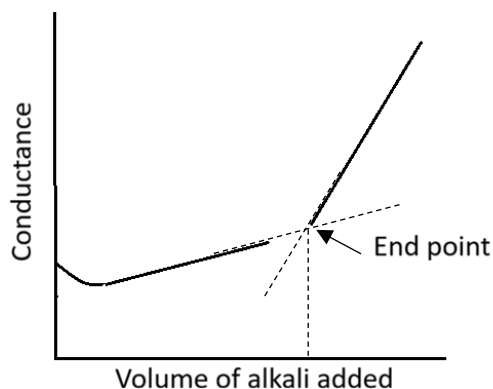
Slope of BC is less than that of AB because hydroxyl ions are less conducting than hydrogen ions. At B neither the hydrogen ions nor the hydroxyl ions are in excess and hence it is the end point or the equivalence point.

(b) The titration of a weak acid by a strong base

When a moderately weak acid such as acetic acid is titrated by a strong base like NaOH, initially the conductance of the solution is low because of suppression of ionization of acetic acid due to common ion effect of completely ionized sodium acetate formed in the reaction.

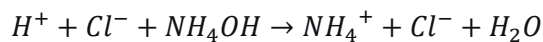


With the addition of the base up to the equivalence point, the conductance gradually increases because of the increase in the concentration of the highly ionized sodium acetate. After the equivalence point, a rapid increase in conductance results due to the excess of fast-moving hydroxyl ions. The titration curve obtained in such cases is shown below:

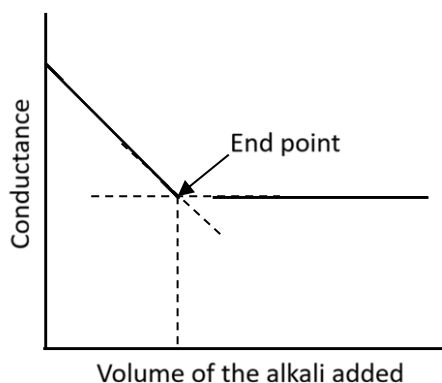


(c) The titration of strong acid and weak base

When a solution of a weak base like NH_4OH is added to a solution of a strong acid like HCl , the following reaction takes place

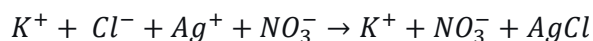


Initially the conductance is high as the acid is completely ionized. As ammonium hydroxide is added from the burette, conductance starts decreasing as fast moving H^+ ions are replaced by slow moving NH_4^+ ions. After the end point, the conductance remains virtually constant as addition of excess of weakly ionized NH_4OH does not change the conductance to any appreciable extent. Due to the presence of the salt NH_4Cl in the solution, the ionization of NH_4OH is further suppressed. Nature of the curve is shown below:

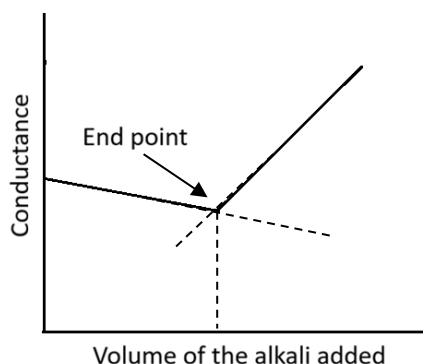


(d) The titration of precipitation reaction

Let us consider the precipitation reaction between potassium chloride and silver nitrate:



When a solution of AgNO_3 is added from a burette to a solution of KCl , Cl^- ions are replaced by NO_3^- ions. Since both the ions have almost equal mobility, during the process conductance decreases very slightly till the end point is reached. After the end point, conductance increases due to the excess of AgNO_3 in the solution. Nature of the curve is shown below:

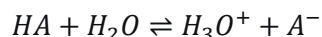


(iii) Degree of Ionization and Ionization Constant of Weak Electrolytes

A weak electrolyte like acetic acid is partially ionized at appreciable concentration and completely ionized at infinite dilution. If Λ_m and Λ_m° are the molar conductivities at the given concentration and at infinite dilution respectively, then the degree of ionization is given as

$$\alpha = \frac{\Lambda_m}{\Lambda_m^\circ}$$

Let us consider the ionization equilibrium of a weak acid:



The ions in solution are in equilibrium with the unionized HA molecules and the ionization constant is given by

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

This ionization constant in terms of α is given by

$$K_a = \frac{\alpha^2 c}{1 - \alpha}$$

Knowing the value of α , we can calculate the value of ionization constant.

Problem

The resistance of a 0.02 mol dm^{-3} solution of acetic acid in a cell (cell constant = 0.2063 cm^{-1}) was found to be 888 ohm. What is the degree of ionization of the acid at this concentration? (Given Λ_m° for acetic acid = $387.9 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$).

Solution

Since

$$\kappa = \frac{1}{R} \times \text{cell constant} = \frac{1}{888} \times 0.2063 = 2.324 \times 10^{-4} \text{ S cm}^{-1} = 2.324 \times 10^{-2} \text{ S m}^{-1}$$

$$c = 0.02 \text{ mol dm}^{-3} = 0.02 \times 10^3 \text{ mol m}^{-3}$$

Therefore,

$$\Lambda_m = \frac{\kappa}{c} = \frac{2.324 \times 10^{-2} \text{ S m}^{-1}}{0.02 \times 10^3 \text{ mol m}^{-3}} = 1.162 \times 10^{-3} \text{ S m}^2 \text{ mol}^{-1}$$

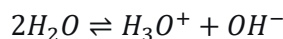
Given

$$\Lambda_m^\circ = 387.9 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$$

$$\therefore \alpha = \frac{\Lambda_m}{\Lambda_m^\circ} = \frac{1.162 \times 10^{-3} \text{ S m}^2 \text{ mol}^{-1}}{387.9 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}} = 0.03$$

(iv) Determination of ionic product of water

Since water is a weak electrolyte and it ionizes as



Ionic product of water is given by

$$K_w = [H_3O^+][OH^-]$$

In pure water

$$[H_3O^+] = [OH^-] = (K_w)^{\frac{1}{2}}$$

At 298 K, the specific conductance of a pure sample of distilled water is $5.8 \times 10^{-6} \text{ Sm}^{-1}$. The density of water at 298 K is 0.997 kg dm^{-3} .

Therefore, molar concentration of water is

$$c = \frac{0.997 \text{ kg dm}^{-3}}{18 \times 10^{-3} \text{ kg mol}^{-1}} = 55.3 \text{ mol dm}^{-3} = 55.3 \times 10^3 \text{ mol m}^{-3}$$

Molar conductivity is

$$\Lambda_m = \frac{\kappa}{c} = \frac{5.8 \times 10^{-6} \text{ Sm}^{-1}}{55.3 \times 10^3 \text{ mol m}^{-3}} = 1.05 \times 10^{-10} \text{ Sm}^2 \text{ mol}^{-1}$$

Molar conductivity of water at infinite dilution is given by Kohlrausch's law as

$$\Lambda_m^\circ = \lambda_{H_3O^+}^\circ + \lambda_{OH^-}^\circ = (349.8 \times 10^{-4} + 198.0 \times 10^{-4}) = 547.8 \times 10^{-4} \text{ Sm}^2 \text{ mol}^{-1}$$

Hence degree of ionization of water is

$$\alpha = \frac{\Lambda_m}{\Lambda_m^\circ} = \frac{1.05 \times 10^{-10} \text{ Sm}^2 \text{ mol}^{-1}}{547.8 \times 10^{-4} \text{ Sm}^2 \text{ mol}^{-1}} = 1.9 \times 10^{-9}$$

Now,

$$[H_3O^+] = [OH^-] = c\alpha = (55.3 \text{ mol dm}^{-3})(1.9 \times 10^{-9}) = 105.07 \times 10^{-9} = 1.05 \times 10^{-7} \text{ mol dm}^{-3}$$

$$\therefore K_w = [H_3O^+][OH^-] = (1.05 \times 10^{-7})(1.05 \times 10^{-7}) = 1.1 \times 10^{-14}$$