

Resistance of solution : The hinderance provided by solution in the passage of current (R). (R expressed in ohm)

Conductance of solution : The ease provided by solution in the passage of current (C).

$$\therefore C = \frac{1}{R};$$

(C expressed in ohm⁻¹ or mho)

Conductivity : The conducting power of 1 cm³ of a solution (κ).

$$\kappa = \frac{1}{R} \times \frac{l}{a}$$

$$\kappa = C \times \frac{l}{a}$$

(κ expressed in ohm⁻¹cm⁻¹ or mho cm⁻¹ or S cm⁻¹)

where l = length of electrolyte solution in between electrodes,

a = area of cross-section.

The factor $\frac{l}{a}$ is known as **cell constant** expressed in cm⁻¹ or m⁻¹.

Equivalent conductivity : The conducting power of all the ions present in a solution having 1g equivalent of electrolyte (Λ).

$$\Lambda_{eq.} = \kappa \times V_{in mL} = \kappa \times \frac{1000}{N}$$

where V is volume having 1 g equivalent of electrolyte; N is conc. in eq./litre, i.e., normality; λ is expressed in ohm⁻¹cm²eq.⁻¹. In MKS system κ in S m⁻¹ and C_N in eq./m³ and $\Lambda_{eq.}$ in S m²eq.⁻¹ and the expression becomes $\Lambda_{eq.} = \frac{\kappa}{C_N}$.

Molecular conductivity : The conducting power of all the ions present in a solution having 1 mole of electrolyte (Λ). where V is volume containing 1 mole of electrolyte.

$$\Lambda_M = \kappa \times V_{in mL} = \kappa \times \frac{1000}{M}$$

where V is volume having 1 mole of electrolyte; M is concentration in mol/litre, i.e., molarity; Λ is expressed in

ohm⁻¹cm²mol⁻¹. In MKS system κ in S m⁻¹ and C_M in mol/m³ and Λ_M in S m²mol⁻¹ and the expression is

$$\Lambda_M = \frac{\kappa}{C_M}$$

Infinite dilution : It means that the electrolyte is 100% ionised. The λ , Λ values increase with dilution and become constant at infinite dilution.

For weak electrolytes,

$$\text{Degree of dissociation } \alpha' = \frac{\Lambda_v}{\Lambda^\circ}$$

where Λ_v , Λ° are equivalent conductances of electrolyte at dilution v and ∞ or zero concentration respectively.

Important Conversions :

$$1 \text{ S m}^2 \text{ mol}^{-1} = 10^4 \text{ S cm}^2 \text{ mol}^{-1}$$

$$1 \text{ S cm}^2 \text{ mol}^{-1} = 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$$

$$1 \text{ S cm}^{-1} = 10^2 \text{ S m}^{-1}$$

$$1 \text{ S m}^{-1} = 10^{-2} \text{ S cm}^{-1}$$

Kohlrausch law : This law states that at infinite dilution where dissociation of all electrolytes is complete and where all interionic effects disappear, each ion migrates independently of its co-ion and contributes to the total equivalent conductance of an electrolyte a definite share which depends only on its own nature and not at all on the ions with which it is associated. Thus, equivalent conductance at infinite dilution is equal to the sum of ionic conductances of its component ions at infinite dilution.

$$\text{i.e., } \Lambda^\circ_{\text{electrolyte}} = \lambda^\circ_{\text{cation}} + \lambda^\circ_{\text{anion}}$$

where $\lambda^\circ_{\text{cation}}$ and $\lambda^\circ_{\text{anion}}$ are ionic equivalent conductances of cation and anion respectively at infinite dilution expressed in ohm⁻¹cm²eq.⁻¹.

$$\text{Thus, } \Lambda^\circ_{eq. NaCl} = \lambda^\circ_{Na^+} + \lambda^\circ_{Cl^-} \quad \dots(1)$$

$$\Lambda^\circ_{eq. BeCl_2} = \frac{1}{2} \lambda^\circ_{Be^{2+}} + \frac{1}{1} \lambda^\circ_{Cl^-} \quad \dots(2)$$

$$\Lambda^\circ_{eq. AlCl_3} = \frac{1}{3} \lambda^\circ_{Al^{3+}} + \frac{1}{1} \lambda^\circ_{Cl^-} \quad \dots(3)$$

$$\Lambda_{eq. Al_2(SO_4)_3}^\circ = \frac{1}{3} \lambda_{Al^{3+}}^\circ + \frac{1}{2} \lambda_{SO_4^{2-}}^\circ \quad \dots(4)$$

$$\text{Thus, in general } \Lambda_{eq.}^\circ = \frac{1}{n^+} \cdot \lambda_+^\circ + \frac{1}{n^-} \cdot \lambda_-^\circ$$

where n^+ and n^- are charge on each ion furnished by electrolyte

For molar conductance (Λ_M) at infinite dilution

$$\Lambda_{M BaCl_2}^\circ = \lambda_{Ba^{2+}}^\circ + 2\lambda_{Cl^-}^\circ$$

$$\Lambda_{M AlCl_3}^\circ = \lambda_{Al^{3+}}^\circ + 3\lambda_{Cl^-}^\circ$$

$$\Lambda_{M Al_2(SO_4)_3}^\circ = 2\lambda_{Al^{3+}}^\circ + 3\lambda_{SO_4^{2-}}^\circ$$

$$\text{Thus, in general } \Lambda_M^\circ = \gamma_+ \lambda_+^\circ + \gamma_- \lambda_-^\circ$$

where γ_+ and γ_- are the number of +ve and -ve ions furnished by each formula unit of electrolyte.

$$\text{Also, } \lambda_{cation}^\circ = u_{cation}^\circ \times \text{Faraday}$$

$$\lambda_{anion}^\circ = u_{anion}^\circ \times \text{Faraday}$$

where u_{cation}° and u_{anion}° are ionic mobilities of cation and anion at infinite dilution respectively.

Transport no. of cations and anions in an electrolyte:

Transport no. of an ion of an electrolyte in a solution is the fraction of total current carried by that ion in solution.

$$t_{ion} = \frac{\text{Current carried by an ion}}{\text{Total current carried by both the ions}}$$

$$\text{or } t_{cation} = \frac{\text{Current carried by cation}}{\text{Current carried by anion and cation both}}$$

$$t_{anion} = \frac{\text{Current carried by anion}}{\text{Current carried by anion and cation both}}$$

$$\therefore t_{cation} + t_{anion} = 1$$

\therefore Current carried by an ion \propto speed or ionic mobility of that ion $\propto u$

$$\therefore t_{cation} = \frac{u_{cation}}{u_{cation} + u_{anion}}$$

$$\text{and } t_{anion} = \frac{u_{anion}}{u_{cation} + u_{anion}}$$

At infinite dilution

$$\text{Also, } t_{cation}^\infty = \frac{u_{cation}^\infty}{u_{cation}^\infty + u_{anion}^\infty}$$

$$t_{anion}^\infty = \frac{u_{anion}^\infty}{u_{cation}^\infty + u_{anion}^\infty}$$

$$\text{Also, } t_{cation}^\infty \times \lambda_{electrolyte}^\infty = \lambda_{cation}^\circ$$

$$\text{and } t_{anion}^\infty \times \lambda_{electrolyte}^\infty = \lambda_{anion}^\circ$$

● NUMERICAL PROBLEMS ●

- The resistance of a 0.01 *N* solution of an electrolyte was found to be 210 ohm at 298 K using a conductivity cell with a cell constant of 0.88 cm⁻¹. Calculate conductivity and equivalent conductivity of solution.
- The conductivity of *N*/50 solution of a cell of KCl at 25°C is 0.002765 S cm⁻¹. If the resistance of a cell containing this solution is 400 ohm, find out cell constant.
- The resistance of a decinormal solution of a salt occupying a volume between two platinum electrodes 1.80 cm apart and 5.4 cm² in area was found to be 32 ohm. Calculate the conductivity and equivalent conductivity of solution.
- When a certain conductance cell was filled with 0.02 *M* KCl solution (conductivity 0.002768 S cm⁻¹), it had a resistance of 82.4 ohm at 298 K. When filled with 0.005 *N* K₂SO₄, it had a resistance of 324 ohm. Calculate :
 - cell constant.
 - conductance of 0.005 *N* K₂SO₄ solution.
 - conductivity of 0.005 *N* K₂SO₄ solution.
 - equivalent conductivity of 0.005 *N* K₂SO₄ solution.
 - molecular conductivity of 0.005 *N* K₂SO₄.
- At 18°C, the velocity of migration of Ag⁺ ion is 0.00057 cm sec⁻¹ and that of NO₃⁻ is 0.00063 cm sec⁻¹ at infinite dilution. What is the equivalent conductivity of AgNO₃ at infinite dilution?
- The molar conductivity of acetic acid at infinite dilution is 390.7 and for 0.1 *M* acetic acid solution is 5.2 S cm² mol⁻¹. Calculate the :
 - degree of dissociation of acetic acid.
 - [H⁺] in solution.
- 0.04 *N* solution of a weak acid has a conductivity 4.23 × 10⁻⁴ S cm⁻¹. The degree of dissociation of acid at this dilution is 0.0612. Calculate the equivalent conductivity of weak acid at infinite solution.
- The equivalent conductivity of 0.05 *N* solution of a monobasic acid is 15.8 S cm² eq⁻¹. If equivalent conductivity of the acid at infinite dilution is 350 S cm² eq⁻¹, calculate the
 - degree of dissociation of acid.
 - dissociation constant of acid.
- The resistance of a solution 'A' is 50 ohm and that of solution 'B' is 100 ohm, both solutions being taken in the same conductivity cell. If equal volumes of solutions A and B are mixed, what will be the resistance of the mixture using the same cell? (Assume that there is no increase in the degree of dissociation of A and B on mixing)
- A big irregular shaped vessel contained water, the conductivity of which was 2.56 × 10⁻⁵ S cm⁻¹. 500 g of NaCl was then added to the water and the conductivity after the addition of NaCl, was found to be 310 × 10⁻⁵ S cm⁻¹. Find the capacity of the vessel if it is fulfilled with water (Λ[°]_M of NaCl = 149.9).
- The equivalent conductivity of 0.10 *N* solution of MgCl₂ is 97.1 S cm² eq⁻¹ at 25°C. A cell with electrodes that are 1.50 cm² in surface area and 0.50 cm apart is filled with 0.1 *N* MgCl₂ solution. How much current will flow when the potential difference between the electrodes is 5 volts?
- At 18°C the conductance of H⁺ and CH₃COO⁻ at infinite dilution are 315 and 35 S cm² eq⁻¹ respectively. The conductivity of 0.001 *N* solution of acetic acid is 41 × 10⁻⁵ S cm⁻¹ at the same temperature. What is the degree of dissociation of acetic acid?
- The equivalent conductivity of acetic acid at infinite dilution is 387 S cm² eq⁻¹. At the same temperature, 0.001 *M* solution of acetic acid, it is 55 S cm² eq⁻¹. What is the degree of dissociation of 0.1 *N* acetic acid? Assume 1 - α ≈ 1.
- Ionic conductivity at infinite dilution of Al³⁺ and SO₄²⁻ ions are 189 S cm² eq⁻¹ and 160 S cm² eq⁻¹ respectively. Calculate the equivalent and molar conductivity of Al₂(SO₄)₃ at infinite dilution.
- The equivalent conductivity of CH₃COONa, HCl and NaCl at infinite dilution are 91.6, 425.0 and 128.1 S cm² eq⁻¹ respectively. Calculate equivalent conductivity of acetic acid at infinite dilution. Also if degree of dissociation of 0.1 *N* acetic acid is 0.001, find the equivalent conductivity at this concentration of acetic acid.
- Calculate molar conductivity for NH₄OH, given that molar conductivity for Ba(OH)₂, BaCl₂ and NH₄Cl are 523.28, 280.0 and 129.8 S cm² mol⁻¹ respectively.
- Calculate the dissociation constant of water at 25°C from the following data :
Conductivity of H₂O = 5.8 × 10⁻⁸ S cm⁻¹, λ[°]_{H⁺} = 350.0 and λ[°]_{OH⁻} = 198.0 S cm² eq⁻¹.
- The equivalent conductivity of KCl at infinite dilution is 130 S cm² eq⁻¹. The transport no. of Cl⁻ ion in KCl at the same temperature is 0.505. What is the limiting ionic mobility and ionic conductance of K⁺ ion?
- At a certain temperature, the saturated solution of silver chloride has conductivity 1.12 × 10⁻⁶ S cm⁻¹. The ionic conductances of Ag⁺ and Cl⁻ ions at infinite dilution are

- 54.3 and $65.5 \text{ S cm}^2 \text{ eq}^{-1}$ at same temperature. Find the solubility of AgCl in g litre^{-1} at this temperature.
20. Conductivity of a saturated aqueous solution of $\text{Co}_2[\text{Fe}(\text{CN})_6]$ is $2.06 \times 10^{-6} \text{ S cm}^{-1}$. The conductivity of water used to prepare the solution has conductivity $41 \times 10^{-7} \text{ S cm}^{-1}$. If ionic molar conductivities of Co^{2+} and $[\text{Fe}(\text{CN})_6]^{4-}$ are $86 \text{ S cm}^2 \text{ mol}^{-1}$ and $444.0 \text{ S cm}^2 \text{ mol}^{-1}$ respectively. Calculate the solubility product of $\text{Co}_2[\text{Fe}(\text{CN})_6]$.
21. Explain the conducting power order of the following ions:
 $\text{Li}^+(\text{aq.}) < \text{Na}^+(\text{aq.}) < \text{K}^+(\text{aq.}) < \text{Rb}^+(\text{aq.}) < \text{Cs}^+(\text{aq.})$
22. A dilute solution of KCl was placed between two Pt electrodes 10.0 cm apart, across which a potential difference of 6.0 volt was applied. How far would K^+ ions move in 2 hours at 25°C ? Ionic conductivity of K^+ at infinite dilution is $73.52 \text{ S cm}^2 \text{ eq}^{-1}$ at 25°C .
23. The molar conductivities at infinite dilution of AgNO_3 , NaCl and NaNO_3 are 116.5 , 110.3 and $105.2 \text{ S cm}^2 \text{ mol}^{-1}$ respectively. The conductivity of AgCl in water is $2.40 \times 10^{-6} \text{ S cm}^{-1}$ and of water used is $1.16 \times 10^{-6} \text{ S cm}^{-1}$. Find the solubility of AgCl in g litre^{-1} .
24. A water sample of swimming pool shows the resistance of $9.2 \times 10^3 \text{ ohm}$ at 25°C using a conductivity cell. The same cell dipped in 0.02 M KCl has the resistance of 85 ohm . Now 0.5 kg sodium chloride is dissolved in pool and thoroughly stirred. The solution sample now shows the resistance of $7.6 \times 10^3 \text{ ohm}$. If Λ_m° for NaCl and Λ_v for 0.02 M KCl are $126.5 \text{ S cm}^2 \text{ mol}^{-1}$ and $138.0 \text{ S cm}^2 \text{ mol}^{-1}$, calculate the volume of water in pool.
25. At 298 K , the conductivity of pure water is $5.51 \times 10^{-8} \text{ S cm}^{-1}$. The ionic conductances of H^+ and OH^- at this temperature are 349.8 and $198.5 \text{ S cm}^2 \text{ eq}^{-1}$ respectively. Calculate the ionic product of water.
26. A decinormal solution of AgNO_3 was electrolysed between Pt electrodes. After passing a small current for two hour, a fall of concentration of 0.0005124 equivalent occurred in anodic solution. The mass of copper deposited in copper coulometer placed in series was found to be 0.03879 g . Find the transport no. of Ag^+ and NO_3^- in AgNO_3 .
27. A solution of AgNO_3 was electrolysed between silver electrodes. Before electrolysis, 10 g of solution contained 0.01788 g of AgNO_3 . After the experiment, 20.09 g of the anodic solution contained 0.06227 g of AgNO_3 . At the same time, 0.009479 g of Cu was deposited in the copper coulometer placed in series. Calculate transport no. of Ag^+ and NO_3^- .
28. Calculate the transport no. of H^+ and Cl^- ions from the following data obtained by moving boundary method, using CdCl_2 as the indicator electrolyte:
 Concentration of HCl solution = 0.1 N
 Wt. of Ag deposited in coulometer = 0.1209 g
 Movement of boundary = 7.50 cm
 Cross-section of tube = 1.24 cm^2
29. Calculate the conductivity (in $1 \times 10^{-7} \text{ S m}^{-1}$ unit) of a solution prepared by dissolving 10^{-7} mole of AgNO_3 in 1 litre of saturated aqueous solution of AgBr .
 K_{sp} of $\text{AgBr} = 12 \times 10^{-14}$ and $\lambda_{\text{Ag}^+}^\circ$, $\lambda_{\text{Br}^-}^\circ$ and $\lambda_{\text{NO}_3^-}^\circ$ are 6×10^{-3} , 8×10^{-3} and $7 \times 10^{-3} \text{ S m}^2 \text{ mol}^{-1}$ respectively. Neglect the contribution of solvent. (IIT 2006)

SOLUTIONS (Numerical Problems)

- Given for 0.01 N solution;
 $R = 210 \text{ ohm}$, $\frac{l}{a} = 0.88 \text{ cm}^{-1}$
 $\therefore \kappa = \frac{1}{R} \times \frac{l}{a}$
 $\kappa = \frac{1}{210} \times 0.88 = 4.19 \times 10^{-3} \text{ mho cm}^{-1} \text{ or S cm}^{-1}$
 Also, $\Lambda_{eq} = \kappa \times \frac{1000}{N} = 4.19 \times 10^{-3} \times \frac{1000}{0.01}$
 $= 419.05 \text{ S cm}^2 \text{ eq}^{-1}$
- Given for $\frac{N}{50}$ solution; $\kappa = 0.002765 \text{ S cm}^{-1}$, $R = 400 \text{ ohm}$
 $\therefore \kappa = \frac{1}{R} \times \frac{l}{a}$
 $0.002765 = \frac{1}{400} \times \text{cell constant}$
 $\therefore \text{Cell constant} = 1.106 \text{ cm}^{-1}$
- Given, $R = 32 \text{ ohm}$, $l = 1.80 \text{ cm}$, $a = 5.4 \text{ cm}^2$
 $\therefore \kappa = \frac{1}{R} \times \frac{l}{a}$
 $\kappa = \frac{1}{32} \times \frac{1.8}{5.4} = 0.01041 \text{ S cm}^{-1}$
 Also,
 $\Lambda_{eq} = \kappa \times \frac{1000}{N} = 0.01041 \times \frac{1000}{0.1} = 104.1 \text{ S cm}^2 \text{ eq}^{-1}$
- From KCl data : $\kappa = \frac{1}{R} \times \frac{l}{a}$
 $\therefore \frac{l}{a} = \kappa \times R = 0.002768 \times 82.4 = 0.2281 \text{ cm}^{-1}$
 From K_2SO_4 data : $R = 324 \text{ ohm}$
 $\therefore C = \frac{1}{R} = \frac{1}{324} = 3.086 \times 10^{-3} \text{ S}$
 Also, $\kappa = C \times \frac{l}{a} = 3.086 \times 10^{-3} \times 0.2281$
 $= 7.04 \times 10^{-4} \text{ S cm}^{-1}$
 Now, $\Lambda_{eq} = \kappa \times \frac{1000}{N} = 7.04 \times 10^{-4} \times \frac{1000}{0.005}$
 $= 140.80 \text{ S cm}^2 \text{ eq}^{-1}$
 Also, $\Lambda_M = \kappa \times \frac{1000}{M} = 7.04 \times 10^{-4} \times \frac{1000 \times 2}{0.005}$
 $= 281.6 \text{ S cm}^2 \text{ mol}^{-1}$
 $(N = 2M, \text{ because } \text{K}_2\text{SO}_4 \text{ is bivalent})$
- We have, $\lambda_{\text{cation}}^{\circ} = \nu_{\text{cation}}^{\circ} \times \text{Faraday} = 0.00057 \times 96500$
 $\lambda_{\text{Ag}^+}^{\circ} = 55.005 \text{ S cm}^2 \text{ eq}^{-1}$
 Also, $\lambda_{\text{anion}}^{\circ} = \nu_{\text{anion}}^{\circ} \times \text{Faraday} = 0.00063 \times 96500$
 or $\lambda_{\text{NO}_3^-}^{\circ} = 60.795 \text{ S cm}^2 \text{ eq}^{-1}$
 Now from Kohlrausch law,
 $\lambda_{\text{AgNO}_3}^{\circ} = \lambda_{\text{Ag}^+}^{\circ} + \lambda_{\text{NO}_3^-}^{\circ} = 55.005 + 60.795$
 $= 115.8 \text{ S cm}^2 \text{ eq}^{-1}$
- (1) The degree of dissociation ' α ' is given by
 $\therefore \alpha = \frac{\Lambda_v}{\Lambda^{\circ}} = \frac{52}{390.7}$
 $\alpha = 0.0133 \text{ or } 1.33\%$
 (2) $\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$
 Before dissociation 1 0 0
 After dissociation (1- α) α α
 $\therefore [\text{H}^+] = C\alpha = 0.1 \times 0.0133 = 0.00133 \text{ M}$
- Given, $\alpha = 0.0612$
 $\kappa_v = 4.23 \times 10^{-4} \text{ S cm}^{-1}$
 Now, $\Lambda_{eq} = \kappa_v \times \frac{1000}{N} = 4.23 \times 10^{-4} \times \frac{1000}{0.04}$
 $= 10.575 \text{ S cm}^2 \text{ eq}^{-1}$
 Also, $\alpha = \frac{\Lambda_{eq}}{\Lambda_{eq}^{\circ}}$
 $0.0612 = \frac{10.575}{\Lambda_{eq}^{\circ}}$
 $\therefore \Lambda_{eq}^{\circ} = 172.79 \text{ S cm}^2 \text{ eq}^{-1}$
- (1) Degree of dissociation, $\alpha = \frac{\Lambda_{eq}}{\Lambda_{eq}^{\circ}} = \frac{158}{350} = 0.04514$
 (2) For acid of monobasic nature
 $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$
 $K = \frac{C\alpha^2}{(1-\alpha)} = C\alpha^2 = 0.05 \times (0.04514)^2 = 1.019 \times 10^{-4}$
 $= 1.019 \times 10^{-4}$
 Note : Since, $\alpha = 0.04514$ and thus, $1-\alpha = 1$
 Concentration C in mol litre $^{-1}$
 Since, HA is monobasic acid and thus normality = molarity.
- Let κ_1 and κ_2 be the conductivity of the solutions A and B respectively and the constant of the cell be x .
 \therefore For solution A :
 Conductivity = Conductance \times Cell constant
 $\kappa_1 = \frac{1}{50} \times x \quad \dots (1)$
 For solution B : Conductivity, $\kappa_2 = \frac{1}{100} \times x \quad \dots (2)$
 When equal volumes of A and B are mixed, both the solutions get doubly diluted, hence their individual contribution towards the conductivity of the mixture will be $\frac{\kappa_1}{2}$ and $\frac{\kappa_2}{2}$ respectively and the conductivity of the mixture will be $\frac{1}{2}(\kappa_1 + \kappa_2)$.
 \therefore For the mixture : $\frac{1}{2}(\kappa_1 + \kappa_2) = \frac{1}{R} \times x \quad \dots (3)$
 $(R \text{ is the resistance of mixture})$
 From Eqs. (1), (2) and (3),
 $R = 66.67 \text{ ohm}$

10. Let the volume of the vessel be
- V
- litre

$$\text{Equivalent of NaCl} = \frac{\text{Mass in grams}}{\text{Eq. mass}} = \frac{500}{58.5} = 8.547$$

Let 8.547 eq. of NaCl be present in V litre

$$\therefore N = \frac{8.547}{V}$$

The conductivity of the NaCl solution (only due to presence of Na^+ and Cl^- ions)

$$\kappa_v = 3.10 \times 10^{-5} - 2.56 \times 10^{-5}$$

$$\kappa_v = 0.54 \times 10^{-5} \text{ S cm}^{-1}$$

$$\Lambda_{M \text{ NaCl}} = 0.54 \times 10^{-5} \times \frac{1000 \times V}{8.547}$$

Since, the vessel is big, the resulting solution may be supposed to be dilute.

$$\therefore \Lambda_{M \text{ NaCl}} = \Lambda_{M \text{ NaCl}}^\circ$$

$$0.54 \times 10^{-5} \times \frac{1000 \times V}{8.547} = 149.9$$

$$V = 2372.5 \times 10^2 \text{ litre} \\ = 2372.5 \times 10^2 \text{ litre}$$

$$11. \text{ Cell constant} = \frac{0.50}{1.50} = \frac{1}{3}$$

$$\therefore \text{Conductivity} = \frac{\text{Equivalent conductivity}}{\text{Volume (cc) containing 1 eq.}} \\ = \frac{97.1 \times 0.1}{1000} = 0.00971 \text{ S cm}^{-1}$$

$$\therefore \text{Conductance} = \frac{\text{Conductivity}}{\text{Cell constant}} \\ = \frac{0.00971}{1/3} \text{ S} = 0.02913 \text{ S}$$

$$\therefore \text{Resistance} = \frac{1}{0.02913} \text{ ohm}$$

$$\therefore \text{Current in ampere} = \frac{\text{Potential difference (by Ohm's law)}}{\text{Resistance (ohm)}} \\ = \frac{5}{1/0.02913} = 0.1456 \text{ ampere}$$

$$12. \Lambda_{eq. \text{ CH}_3\text{COOH}} = \lambda_{\text{H}^+}^\circ + \lambda_{\text{CH}_3\text{COO}^-}^\circ \\ = 315 + 35 = 350 \text{ S cm}^2 \text{ eq.}^{-1}$$

Now given $\kappa = 4.1 \times 10^{-5} \text{ S cm}^{-1}$ for $0.001 \text{ N CH}_3\text{COOH}$

$$\text{Therefore, } \Lambda_{eq.} = \kappa \times \frac{1000}{N} = 4.1 \times 10^{-5} \times \frac{1000}{0.001} \\ = 41 \text{ S cm}^2 \text{ eq.}^{-1}$$

$$\text{Now, degree of dissociation } \alpha = \frac{\Lambda_{eq.}}{\Lambda_{eq.}^\circ} = \frac{41}{350}$$

$$\alpha = 0.117 \text{ or } 11.7\%$$

13. For
- $0.001 \text{ M CH}_3\text{COOH}$

$$\therefore \alpha = \frac{\Lambda_{eq.}}{\Lambda_{eq.}^\circ} \quad \left(\begin{array}{l} \Lambda_{eq.} = 55 \text{ S cm}^2 \text{ eq.}^{-1} \\ \Lambda_{eq.}^\circ = 387 \text{ S cm}^2 \text{ eq.}^{-1} \end{array} \right)$$

$$\therefore \alpha = \frac{55}{387} = 0.142 \text{ or } 14.2\%$$

$$\text{Since, } K_a = \frac{C\alpha^2}{1-\alpha} = \frac{0.001 \times (0.142)^2}{1-0.142}$$

$$K_a = 2.35 \times 10^{-5}$$

$$\therefore \text{Now again } K_a = \frac{C\alpha^2}{1-\alpha} = \frac{0.1 \times \alpha^2}{1-\alpha} = 2.35 \times 10^{-5}$$

and assume $1-\alpha = 1$

$$\therefore \alpha_{at 0.1} = 0.015 \text{ or } 1.5\%$$

$$14. \Lambda_{eq. \text{ Al}_2(\text{SO}_4)_3} = \frac{1}{n^+} \lambda_{\text{Al}^{3+}}^\circ + \frac{1}{n^-} \lambda_{\text{SO}_4^{2-}}^\circ \\ = \frac{1}{3} \times 189 + \frac{1}{2} \times 160 = 143 \text{ S cm}^2 \text{ eq.}^{-1}$$

$$\text{Also, } \Lambda_{M \text{ Al}_2(\text{SO}_4)_3} = 6 \times \Lambda_{eq. \text{ Al}_2(\text{SO}_4)_3} = 6 \times 143 \\ = 858 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\text{or } \Lambda_{M \text{ Al}_2(\text{SO}_4)_3} = \gamma_+ \lambda_{\text{Al}^{3+}}^\circ + \gamma_- \lambda_{\text{SO}_4^{2-}}^\circ \\ = 2 \times 189 + 3 \times 160 = 858 \text{ S cm}^2 \text{ mol}^{-1}$$

15. According to Kohlrausch law

$$\Lambda_{eq. \text{ CH}_3\text{COOH}} = \lambda_{\text{CH}_3\text{COO}^-}^\circ + \lambda_{\text{H}^+}^\circ$$

Given, from Kohlrausch law

$$\Lambda_{eq. \text{ CH}_3\text{COONa}} = 91.6 = \lambda_{\text{CH}_3\text{COO}^-}^\circ + \lambda_{\text{Na}^+}^\circ \quad \dots(1)$$

$$\Lambda_{eq. \text{ HCl}} = 425.0 = \lambda_{\text{H}^+}^\circ + \lambda_{\text{Cl}^-}^\circ \quad \dots(2)$$

$$\Lambda_{eq. \text{ NaCl}} = 128.1 = \lambda_{\text{Na}^+}^\circ + \lambda_{\text{Cl}^-}^\circ \quad \dots(3)$$

Adding Eqs. (1) and (2) and then subtracting Eq. (3),

$$\Lambda_{\text{CH}_3\text{COOH}} = \lambda_{\text{CH}_3\text{COO}^-}^\circ + \lambda_{\text{H}^+}^\circ = \lambda_{\text{CH}_3\text{COONa}}^\circ + \lambda_{\text{HCl}}^\circ - \lambda_{\text{NaCl}}^\circ \\ = 91.6 + 425.0 - 128.1$$

$$\text{or } \Lambda_{eq. \text{ CH}_3\text{COOH}} = 388.5 \text{ S cm}^2 \text{ eq.}^{-1}$$

$$\text{Also, } \alpha = \frac{\Lambda_{eq.}}{\Lambda_{eq.}^\circ}$$

$$0.001 = \frac{\Lambda_{eq.}}{388.5}$$

$$\therefore \Lambda_{eq.} = 0.3885 \text{ S cm}^2 \text{ eq.}^{-1}$$

$$16. \Lambda_{M \text{ Ba(OH)}_2} = \lambda_{\text{Ba}^{2+}}^\circ + 2\lambda_{\text{OH}^-}^\circ = 523.28 \quad \dots(1)$$

$$\Lambda_{M \text{ BaCl}_2} = \lambda_{\text{Ba}^{2+}}^\circ + 2\lambda_{\text{Cl}^-}^\circ = 280.00 \quad \dots(2)$$

$$\Lambda_{M \text{ NH}_4\text{Cl}} = \lambda_{\text{NH}_4^+}^\circ + \lambda_{\text{Cl}^-}^\circ = 129.80 \quad \dots(3)$$

Multiply Eq. (3) by two and subtract from Eq. (2)

$$\lambda_{\text{Ba}^{2+}}^\circ - 2\lambda_{\text{NH}_4^+}^\circ = 280 - 2 \times 129.8 \quad \dots(4)$$

$$\therefore \lambda_{\text{Ba}^{2+}}^\circ - 2\lambda_{\text{NH}_4^+}^\circ = 20.40 \quad \dots(5)$$

Now subtract Eq. (5) from Eq. (1)

$$2\lambda_{\text{NH}_4^+}^\circ + 2\lambda_{\text{OH}^-}^\circ = 502.88$$

$$\therefore \lambda_{\text{NH}_4^+}^\circ + \lambda_{\text{OH}^-}^\circ = \Lambda_{M \text{ NH}_4\text{OH}} = \frac{502.88}{2} \\ = 251.44 \text{ S cm}^2 \text{ mol}^{-1}$$

17. Suppose water contains
- N
- mol/litre or
- N
- eq./litre of
- H^+
- ions or
- OH^-
- ions.

$$\therefore \text{Eq. of } \text{H}^+ = \text{Eq. of } \text{H}_2\text{O}$$

$$\therefore \text{Eq. conductivity of water} = \text{Conductivity} \times \frac{1000}{N}$$

$$= 5.8 \times 10^{-8} \times \frac{1000}{N}$$

Since, water dissociates feebly, i.e., water may be considered to be a dilute solution of H^+ and OH^- ions.

$$\therefore \Lambda_{eq. H_2O} = \Lambda_{eq. H_2O}^{\circ} = \lambda_{H^+}^{\circ} + \lambda_{OH^-}^{\circ}$$

$$\therefore 5.8 \times 10^{-8} \times \frac{1000}{N} = 350 + 198 = 548$$

$$\therefore N = 1.058 \times 10^{-7}$$

$$\therefore [H^+] = [OH^-] = 1.058 \times 10^{-7}$$

For the equilibrium, $H_2O \rightleftharpoons H^+ + OH^-$

$$\text{Equilibrium constant } (K) = \frac{[H^+][OH^-]}{[H_2O]}$$

$$\begin{aligned} \text{or } K_w &= K \times [H_2O] = [H^+][OH^-] \\ &= 1.058 \times 10^{-7} \times 1.058 \times 10^{-7} \\ &= 1.119 \times 10^{-14} \end{aligned}$$

$$\therefore K = \frac{K_w}{[H_2O]} = \frac{1.119 \times 10^{-14}}{55.5} = 2 \times 10^{-16} \text{ mol/litre}$$

$$\left[[H_2O] = \frac{1000}{18} = 55.5 \text{ mol/litre} \right]$$

Alternate solution

Molarity of water is 55.6 mol litre⁻¹. Also for the dissociation



$$\therefore \text{Equivalent conductivity of water} = 5.8 \times 10^{-8} \times \frac{1000}{55.6}$$

$$\begin{aligned} \text{Also, } \Lambda_{eq. H_2O}^{\circ} &= \lambda_{H^+}^{\circ} + \lambda_{OH^-}^{\circ} \\ &= 350.0 + 198.0 = 548 \end{aligned}$$

$$\text{Now, } \alpha_{H_2O} = \frac{\Lambda_{eq. H_2O}}{\Lambda_{eq. H_2O}^{\circ}} = \frac{5.8 \times 10^{-8} \times 1000}{55.6 \times 548} = 1.9 \times 10^{-9}$$

$$\begin{aligned} \text{Also for } H_2O &\rightleftharpoons H^+ + OH^- \\ K_{eq} &= \frac{C\alpha \cdot C\alpha}{C(1-\alpha)} = C\alpha^2 = 55.6 \times (1.9 \times 10^{-9})^2 \\ &= 2.0 \times 10^{-16} \text{ mol litre}^{-1} \end{aligned}$$

$$18. \text{ Transport no. } t_{Cl^-} = 0.505$$

$$\therefore t_{K^+} + t_{Cl^-} = 1 \quad \therefore t_{K^+} = 1 - 0.505 = 0.495$$

Also we have,

$$\begin{aligned} \text{Ionic conductance } \lambda_{K^+}^{\circ} &= \lambda_{KCl}^{\circ} \times t_{K^+}^{\circ} \\ &= 130 \times 0.495 = 64.35 \end{aligned}$$

$$\text{Also, } \lambda_{K^+}^{\circ} = u_{K^+}^{\circ} \times F$$

$$\begin{aligned} \therefore \text{Limiting ionic mobility } (u_{K^+}^{\circ}) &= \frac{64.35}{96500} \\ &= 6.67 \times 10^{-4} \text{ cm}^2 \text{ sec}^{-1} \text{ volt}^{-1} \end{aligned}$$

$$19. \text{ Given, } \lambda_{Ag^+}^{\circ} = 54.3$$

$$\lambda_{Cl^-}^{\circ} = 65.5$$

$$\begin{aligned} \therefore \Lambda_{eq. AgCl}^{\circ} &= \lambda_{Ag^+}^{\circ} + \lambda_{Cl^-}^{\circ} \\ &= 54.3 + 65.5 = 119.8 \text{ S cm}^2 \text{ eq.}^{-1} \end{aligned}$$

$$\text{We also have, } \Lambda_{eq.} = \kappa \times V = \kappa \times \frac{1000}{N}$$

$$(\because \Lambda_{eq.} = \Lambda_{eq.}^{\circ} \text{ for sparingly soluble salts})$$

$$\therefore 119.8 = 1.12 \times 10^{-6} \times \frac{1000}{N}$$

$$\therefore N = \frac{1.12 \times 10^{-3}}{119.8} \text{ eq./litre}$$

$$S = \frac{1.12 \times 10^{-3}}{119.8} \times 143.5 \text{ g/litre}$$

$$S = 1.34 \times 10^{-3} \text{ g/litre}$$

Note: In case of sparingly soluble salts $\Lambda_v = \Lambda^{\circ}$, since solubility is very low and electrolyte is assumed to be 100% ionised at normal conditions.

20. The complex forming saturated solution is assumed to be 100% ionised, i.e., the condition at infinite dilution. Thus, For, $Co_2[Fe(CN)_6] \rightleftharpoons 2Co^{2+} + \Lambda_{Fe(CN)_6}^{\circ}$

$$= 2 \times 86 + 444 = 616 \text{ S cm}^2 \text{ mol}^{-1}$$

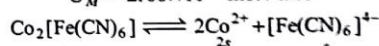
$$\begin{aligned} \text{Also, } \kappa_{\text{complex}} &= \kappa_{\text{sol}} - \kappa_{H_2O} = 2.06 \times 10^{-6} - 0.41 \times 10^{-6} \\ &= 1.65 \times 10^{-6} \text{ S cm}^{-1} \end{aligned}$$

If C_M is molarity then

$$\therefore \Lambda_M^{\circ} = \kappa \times \frac{1000}{C_M}$$

$$616 = \frac{1.65 \times 10^{-6} \times 1000}{C_M}$$

$$\therefore C_M = 2.68 \times 10^{-6} \text{ mol/litre}$$



$$\begin{aligned} K_{sp} &= 4s^3 = 4 \times (2.68 \times 10^{-6})^3 \\ &= 7.699 \times 10^{-17} \end{aligned}$$

21. The size of ions is $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$, thus smallest ion should move more rapidly, however ionic mobility shows the reverse trend because smaller ions are more easily hydrated and thus hydrated ion size for these ions is $Li^+(aq.) > Na^+(aq.) > K^+(aq.) > Rb^+(aq.) > Cs^+(aq.)$. Thus, ionic mobility of $Li^+(aq.)$ is minimum.

$$22. \lambda_{K^+}^{\circ} = 73.52$$

$$\begin{aligned} \text{Ionic mobility, } u_{K^+}^{\circ} &= \frac{\lambda_{K^+}^{\circ}}{F} = \frac{73.52}{96500} \\ &= 7.619 \times 10^{-4} \text{ cm}^2 \text{ sec}^{-1} \text{ volt}^{-1} \end{aligned}$$

$$\text{Potential gradient applied} = \frac{6.0}{10} = 0.6 \text{ volt cm}^{-1}$$

$$\begin{aligned} \therefore \text{Speed of } K^+ &= \text{ionic mobility} \times \text{potential gradient} \\ &= 7.619 \times 10^{-4} \times 0.6 \text{ cm sec}^{-1} \\ &= 45714 \times 10^{-5} \text{ cm sec}^{-1} \end{aligned}$$

$$\begin{aligned} \therefore \text{Distance travelled by } K^+ \text{ in 2 hours} \\ &= 45714 \times 2 \times 60 \times 60 \times 10^{-5} = 3.292 \text{ cm} \end{aligned}$$

23. For monovalent electrolytes

Equivalent conductance = Molar conductance

$$\text{Given, } \Lambda_M^{\circ} AgNO_3 = 116.5 = \lambda_{Ag^+}^{\circ} + \lambda_{NO_3^-}^{\circ} \quad \dots (1)$$

$$\Lambda_{M,NaCl}^{\circ} = 110.3 = \lambda_{Na^+}^{\circ} + \lambda_{Cl^-}^{\circ} \quad \dots(2)$$

$$\Lambda_{M,NaNO_3}^{\circ} = 105.2 = \lambda_{Na^+}^{\circ} + \lambda_{NO_3^-}^{\circ} \quad \dots(3)$$

$$\therefore \Lambda_{M,AgCl}^{\circ} = (1) + (2) - (3) = 116.5 + 110.3 - 105.2$$

$$= 121.6 \text{ S cm}^2 \text{ mol}^{-1}$$

For sparingly soluble salt $\Lambda_M = \Lambda_M^{\circ}$

$$\therefore \Lambda_{M,AgCl} = 121.6 \text{ S cm}^2 \text{ mole}^{-1}$$

$$\text{Now, } \kappa_{AgCl + \text{water}} = 2.40 \times 10^{-6} \text{ S cm}^{-1}$$

$$\kappa_{\text{water}} = 1.16 \times 10^{-6} \text{ S cm}^{-1}$$

$$\therefore \kappa_{AgCl} = (2.40 - 1.16) \times 10^{-6} \text{ S cm}^{-1}$$

$$= 1.24 \times 10^{-6} \text{ S cm}^{-1}$$

$$\text{Therefore, } \Lambda_M = \kappa \times \frac{1000}{N}$$

$$121.6 = 1.24 \times 10^{-6} \times \frac{1000}{M}$$

$$\therefore M = N = \frac{1.24 \times 10^{-3}}{121.6} \text{ mol/litre}$$

$$= \frac{1.24 \times 10^{-3}}{121.6} \times 143.5 \text{ g/litre}$$

$$\text{Solubility of AgCl} = 1.463 \times 10^{-3} \text{ g litre}^{-1}$$

$$24. \quad \Lambda_{M,KCl} = \kappa \times \frac{1000}{M}$$

$$138 = \kappa \times \frac{1000}{0.02}$$

$$\therefore \kappa = 2.76 \times 10^{-3}$$

$$\text{Also, } \kappa_{KCl} = C \times \frac{l}{a}$$

$$2.76 \times 10^{-3} = \frac{1}{85} \times \frac{l}{a} \quad \left(C = \frac{1}{R} = \frac{1}{85} \right)$$

$$\therefore \text{Cell constant } \frac{l}{a} = 0.2346 \text{ cm}^{-1}$$

$$C_{\text{pool water}} = \frac{1}{9.2 \times 10^3} = 1.087 \times 10^{-4} \text{ S}$$

(Note: Conductivity is an additive property but not resistance.)

$$C_{NaCl(aq)} = \frac{1}{7.6 \times 10^3} = 1.316 \times 10^{-4} \text{ S}$$

$$\therefore C_{NaCl} = C_{NaCl(aq)} - C_{\text{pool water}}$$

$$= [1.316 - 1.087] \times 10^{-4} = 2.29 \times 10^{-5}$$

$$\therefore \kappa_{NaCl} = C \times \frac{l}{a} = 2.29 \times 10^{-5} \times 0.2346$$

$$= 5.37 \times 10^{-6} \text{ S cm}^{-1}$$

$$\therefore \Lambda_{NaCl}^{\circ} = \kappa \times \frac{1000}{M}$$

$$\left(M = \frac{500}{58.5 \times V_{(l)}} = \frac{8.55}{V_{(l)}} \right)$$

V is volume of water = volume of solution

$$126.5 = 5.37 \times 10^{-6} \times \frac{1000 \times V_{(l)}}{8.55}$$

$$\therefore V_{(l)} = 2.01 \times 10^5 \text{ litre}$$

$$25. \quad \Lambda_{eq,H_2O}^{\circ} = \lambda_{H^+}^{\circ} + \lambda_{OH^-}^{\circ}$$

$$= 349.8 + 198.5 = 548.3 \text{ S cm}^2 \text{ eq}^{-1}$$

$$\text{Now, } \Lambda_{eq}^{\circ} = \Lambda_{eq}^{\circ} \text{ for water}$$

$$\therefore \Lambda_{eq} = 548.3 \text{ S cm}^2 \text{ eq}^{-1}$$

$$\text{Also, } \Lambda_{eq} = \kappa_v \times \frac{1000}{N}$$

$$548.3 = \frac{5.51 \times 10^{-8} \times 1000}{N}$$

$$\therefore N = 1.005 \times 10^{-7} \text{ eq. litre}^{-1}$$

$$\text{or } [H^+] = [OH^-] = 1.005 \times 10^{-7}$$

$$\text{For water } K_w = [H^+][OH^-] = [1.005 \times 10^{-7}]^2$$

$$K_w = 1.01 \times 10^{-14}$$

$$26. \quad \text{Fall of concentration around anode} = 0.0005124 \text{ eq.}$$

$$\text{Mass of copper deposited in coulometer} = 0.03879 \text{ g}$$

$$\therefore \text{Equivalent of copper deposited in coulometer}$$

$$= \frac{0.03879}{31.8} = 0.001219 \text{ eq.}$$

$$\text{Now transport no. } t_{Ag^+}$$

$$= \frac{\text{No. of equivalent of } Ag^+ \text{ ion lost in anode}}$$

$$\text{No. of equivalent of } Cu^{2+} \text{ deposited in coulometer}$$

$$\text{or total fall in concentration of solution}$$

$$= \frac{0.0005124}{0.001219}$$

$$t_{Ag^+} = 0.4303$$

$$\text{Also, } t_{Ag^+} + t_{NO_3^-} = 1$$

$$\therefore t_{NO_3^-} = 1 - 0.4303 = 0.5697$$

27. After electrolysis:

$$\therefore 20.09 \text{ g of anodic solution contained } 0.06227 \text{ g of AgNO}_3$$

$$\therefore \text{Mass of water in solution} = 20.09 - 0.06227 = 20.02773 \text{ g}$$

$$\text{Thus, } 20.02773 \text{ g H}_2\text{O has } 0.06227 \text{ g AgNO}_3$$

$$= \frac{0.06227}{170} \text{ eq. AgNO}_3$$

$$= 0.0003664 \text{ equivalent AgNO}_3 \text{ or Ag}^+$$

Before electrolysis:

$$\therefore 10.0 \text{ g of solution contained } 0.01788 \text{ g of AgNO}_3$$

$$\therefore \text{Mass of water in solution} = 10 - 0.01788 = 9.98212 \text{ g}$$

$$\text{Thus, } 9.98212 \text{ g water has } 0.01788 \text{ g AgNO}_3$$

$$= \frac{0.01788}{170} \text{ eq. AgNO}_3$$

$$\therefore 20.02773 \text{ g water has } = \frac{0.01788 \times 20.02773}{170 \times 9.98212} \text{ eq. AgNO}_3$$

$$= 0.0002111 \text{ equivalent of AgNO}_3 \text{ or Ag}^+$$

$$\text{Thus, increase in concentration of Ag}^+ \text{ during electrolysis}$$

$$= 0.0003664 - 0.0002111 = 0.0001553 \text{ eq.}$$

$$\text{Also, mass of Cu deposited in coulometer}$$

$$= 0.009479 \text{ g}$$

$$\therefore \text{Eq. of Cu deposited in coulometer} = \frac{0.009479}{31.8}$$

\therefore Eq. of Cu deposited or actual increase around anodic solution = 0.0002982 eq.

(Since, equal equivalents are discharged at either electrode)
Since, Ag^+ has migrated from anode, which brings a fall in concentration around anode but due to attacked electrodes, (i.e., Ag in AgNO_3), apparent increase is noticed.

Thus, fall in concentration of Ag^+ around anode

= Actual increase which would have occur around anode
- Apparent increase in Ag^+ around anode

$$= 0.0002982 - 0.0001553$$

$$= 0.0001429 \text{ equivalent of } \text{Ag}^+$$

\therefore Transport no. of t_{Ag^+}

$$= \frac{\text{Eq. of } \text{Ag}^+ \text{ lost in anodic cell}}{\text{Eq. of } \text{Cu}^{2+} \text{ deposited in coulometer}}$$

$$= \frac{0.0001429}{0.0002982}$$

$$t_{\text{Ag}^+} = 0.4792$$

$$\text{Now, } t_{\text{Ag}^+} + t_{\text{NO}_3^-} = 1$$

$$\therefore t_{\text{NO}_3^-} = 1 - 0.4792 = 0.5208$$

$$28. \text{ Transport no. of } \text{H}^+ \text{ ions} = \frac{l \cdot A \cdot C}{1000Q}$$

l is length of migration = 7.50 cm

A is area of cross-section = 1.24 cm^2

C is concentration of solution = $0.1N$

Q is charge passed = Equivalent of Ag deposited

$$= \frac{0.1209}{108} \text{ Faraday} \quad \left(Q = \frac{W}{E} \right)$$

$$\therefore t_{\text{H}^+} = \frac{7.5 \times 1.24 \times 0.1 \times 108}{0.1209 \times 1000} = 0.8308$$

$$\text{Now, } t_{\text{H}^+} + t_{\text{Cl}^-} = 1$$

$$\therefore t_{\text{Cl}^-} = 1 - 0.8308 = 0.1692$$

29. Solubility of AgBr in presence of 10^{-7} mole of AgNO_3 solution

$$K_{sp} \text{ AgBr} = [\text{Ag}^+][\text{Br}^-]$$

$$12 \times 10^{-14} = [S + 10^{-7}] \times S$$

$$\therefore S = 3 \times 10^{-7} M$$

$$\therefore [\text{Ag}^+] = [3 \times 10^{-7} + 10^{-7}] = 4 \times 10^{-7} M$$

$$[\text{Br}^-] = 3 \times 10^{-7} M$$

$$[\text{NO}_3^-] = 1 \times 10^{-7} M$$

$$\therefore \kappa = \frac{\Lambda^\circ \times M}{1000}$$

$$(\lambda \text{ in } \text{S m}^2 \text{ mol}^{-1} = \lambda \times 10^4 \text{ S cm}^2 \text{ mol}^{-1})$$

$$\therefore \kappa_{\text{Ag}^+} = \frac{6 \times 10^{-3} \times 10^4 \times 4 \times 10^{-7}}{1000}$$

$$= 24 \times 10^{-9} \text{ S cm}^{-1}$$

$$\kappa_{\text{Br}^-} = \frac{8 \times 10^{-3} \times 10^4 \times 3 \times 10^{-7}}{1000} = 24 \times 10^{-9} \text{ S cm}^{-1}$$

$$\kappa_{\text{NO}_3^-} = \frac{7 \times 10^{-3} \times 10^4 \times 10^{-7}}{1000} = 7 \times 10^{-9} \text{ S cm}^{-1}$$

$$\therefore \kappa_{\text{Total}} = \kappa_{\text{Ag}^+} + \kappa_{\text{Br}^-} + \kappa_{\text{NO}_3^-}$$

$$= 24 \times 10^{-9} + 24 \times 10^{-9} + 7 \times 10^{-9}$$

$$= 55 \times 10^{-9} \text{ S cm}^{-1} = 55 \times 10^{-7} \text{ S m}^{-1}$$

In the unit of $1 \times 10^{-7} \text{ S m}^{-1}$, the conductivity is 55.

● SINGLE INTEGER ANSWER PROBLEMS ●

1. The conductance of a 0.0015 M aqueous solution of a weak monobasic acid was determined by using a conductivity cell consisting of platinized Pt electrodes. The distance between the electrodes is 120 cm with an area of cross-section of 1 cm^2 . The conductance of this

solution was found to be $5 \times 10^{-7} \text{ S}$. The pH of the solution is 4. The value of limiting molar conductivity (Λ_M°) of this weak monobasic acid in aqueous solution is $Z \times 10^2 \text{ S cm}^{-1} \text{ mol}^{-1}$. The value of Z is :

[JEE (Main) 2017]

ANSWERS

1. Six

OBJECTIVE PROBLEMS (One Answer Correct)

- The resistance of 0.05 *N* solution of an electrolyte A_aB_b was found to be 210 ohm at 300 K. If cell constant is 0.88 cm^{-1} , the molar conductivity is in $\text{S m}^2 \text{ mol}^{-1}$ is :
 (a) $83.81 \times (a+b)$ (b) $83.81 \times (a+b) \times 10^{-4}$
 (c) $83.81 \times (a \cdot b)$ (d) $83.81 \times (a \cdot b) \times 10^{-4}$
- If Λ_M of a solution is $419 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$ for an electrolyte K_2SO_4 at 300 K. The resistance offered by the solution with cell constant 0.88 m^{-1} is 210 ohm, the molarity of K_2SO_4 solution is :
 (a) $1 \times 10^{-4} \text{ M}$ (b) 0.02 M
 (c) 0.05 M (d) 0.03 M
- The molar conductivity of LiNO_3 at infinite dilution is $10^5 \text{ S cm}^2 \text{ mol}^{-1}$. If 0.02 *M* solution shows conductance 0.158 ohm^{-1} using cell of cell constant 1 cm^{-1} . The concentration of Li^+ ion in g litre $^{-1}$ is :
 (a) 0.01106 (b) 0.1106
 (c) 11.06 (d) 0.2212
- One needs some experimental data to determine $\Lambda_{\text{H}_2\text{C}_2\text{O}_4}^\circ$. Which value is also needed in addition of $\Lambda_{\text{HNO}_3}^\circ$ and $\Lambda_{\text{K}_2\text{C}_2\text{O}_4}^\circ$?
 (a) $\Lambda_{\text{NaCl}}^\circ$ (b) $\Lambda_{\text{KNO}_3}^\circ$
 (c) $\Lambda_{\text{KCl}}^\circ$ (d) $\Lambda_{\text{Na}_2\text{C}_2\text{O}_4}^\circ$
- The transport number of Ag^+ in AgNO_3 is 0.4 and of NO_3^- in KNO_3 is 0.4. The ratio of transport number of NO_3^- in AgNO_3 and KNO_3 is:
 (a) 1 (b) 1.5
 (c) 2.0 (d) 2.5
- The absolute velocity of Ag^+ and NO_3^- are 5.7×10^{-4} and $6.9 \times 10^{-4} \text{ cm sec}^{-1}$ respectively. Assuming complete dissociation of AgNO_3 , calculate the molar conductivity of AgNO_3 at infinite dilution:
 (a) $121.59 \text{ S cm}^2 \text{ mol}^{-1}$ (b) $141.59 \text{ S cm}^2 \text{ mol}^{-1}$
 (c) $131.59 \text{ S cm}^2 \text{ mol}^{-1}$ (d) none of these
- The conductivity of 20 mL of 0.2 *N* NaOH solution is *a* S cm^{-1} . If 10 mL of 0.4 *N* HCl solution is added to this solution, the conductivity decreases by *b* S cm^{-1} . The resultant solution has equivalent conductivity in $\text{S cm}^2 \text{ eq}^{-1}$ is :
 (a) *a* - *b* (b) $\frac{(a-b) \times 30}{4}$
 (c) $\frac{(a-b) \times 3 \times 10^4}{4}$ (d) $\frac{(a-b) \times 4}{3}$
- Molar conductivity of AgNO_3 , HCl and HNO_3 at infinite dilution are *a*, *b*, *c* $\text{S cm}^2 \text{ mol}^{-1}$ respectively. If the conductivity of saturated AgCl solution is *ZS cm}^{-1}, then K_{sp} of AgCl will be :
 (a) $\frac{1000Z}{a+b-c}$ (b) $\left[\frac{1000Z}{a+b-c} \right]^2$
 (c) $\left[\frac{a+b-c}{Z} \right]$ (d) $\left[\frac{a+b-c}{Z \times 1000} \right]^2$*
- Which of the following correctly represents the equivalent conductance of $\text{Al}_2(\text{SO}_4)_3$ at infinite dilution :
 (a) $2\lambda_{\text{Al}^{3+}}^\infty + 3\lambda_{\text{SO}_4^{2-}}^\infty$ (b) $2\lambda_{\text{Al}^{3+}}^\infty + \lambda_{\text{SO}_4^{2-}}^\infty$
 (c) $[\lambda_{\text{Al}^{3+}}^\infty + \lambda_{\text{SO}_4^{2-}}^\infty] \times 6$ (d) $\frac{1}{3}\lambda_{\text{Al}^{3+}}^\infty + \frac{1}{2}\lambda_{\text{SO}_4^{2-}}^\infty$
- The best conductor of electricity in 0.1*M* aqueous solution :
 (a) Boric acid (b) Sulphuric acid
 (c) Acetic acid (d) Propionic acid
- An increase in equivalent conductivity of strong electrolytes with dilution is mainly due to :
 (a) increase in ionic molality of ions
 (b) 100% ionisation of electrolyte at normal dilution
 (c) increase in both i.e., molality and ionisation
 (d) increase in number of ions
- The molar conductivity of 1*M* HCl is greater than 1*M* NaCl at a particular temperature. This is due to :
 (a) molar mass of HCl < molar mass of NaCl
 (b) ionic mobility of H^+ > ionic mobility of Na^+
 (c) HCl being an acid has lower pH
 (d) degree of ionisation of HCl > degree of ionisation of NaCl
- SI Unit of ionic mobility is :
 (a) $\text{m}^2 \text{ volt}^{-1} \text{ sec}^{-1}$ (b) $\text{cm}^2 \text{ volt}^{-1} \text{ sec}^{-1}$
 (c) $\text{cm} \text{ volt}^{-1} \text{ sec}^{-1}$ (d) $\text{cm}^2 \text{ volt}^{-1} \text{ sec}^{-1}$
- Molten sodium chloride conducts electricity due to the presence of :
 (a) Free electrons
 (b) Free ions
 (c) Free molecules
 (d) Atoms of sodium and chlorine
- Which of the following is always an additive property :
 (a) Conductance (b) Resistance
 (c) Surface tension (d) Viscosity
- Which of the following ion has exceptionally higher values of Λ_∞ :
 (a) H^+ (b) K^+
 (c) NH_2^- (d) NH_4^+
- At infinite dilution the solution of CH_3COOH does not contain :
 (a) H^+ (b) CH_3COO^-
 (c) CH_3COOH (d) None of these

18. Select the correct statement :

- (a) Λ^∞ of strong electrolytes can be obtained only by Kohlrausch's law
 (b) Mobility of ions depends only on nature of ions
 (c) Speed of ions depends only on nature of ion
 (d) Conductance of solution decreases with increase in temperature

19. The molar conductivity of NaCl, KCl and K_2SO_4 at 25°C and infinite dilution are 126.45, 149.84, 306.60

$S\text{cm}^2\text{mol}^{-1}$ respectively. If $\lambda_{Na^+}^\circ$ at 25°C is 50.11 $S\text{cm}^2\text{mol}^{-1}$, what is $\lambda_{SO_4^{2-}}^\circ$ (in $S\text{cm}^2\text{mol}^{-1}$) at 25°C.

- (a) 159.6 (b) 209.77
 (c) 259.82 (d) 359.82

20. Ionic mobility of which of the following alkali metal ions is lowest when aqueous solution of their salts are put under an electric field?

- (a) Na (b) K
 (c) Rb (d) Li

SOLUTIONS (One Answer Correct)

$$1. (d) \Lambda_M = \kappa \times \frac{1000}{C_M} \quad (C_M \text{ in mol/litre}) \quad \left(\kappa = C \times \frac{l}{a} \right)$$

$$= \frac{0.88 \times 10^2}{210} \times \frac{1000}{0.05} \times 10^{-6}$$

$$= 83.81 \times a \times b \times 10^{-4} S\text{m}^2\text{mol}^{-1}$$

$$2. (a) \Lambda_M = \kappa \times \frac{1}{c}$$

(where, c in mol m^{-3} and κ in $\text{ohm}^{-1}\text{m}^{-1}$)

$$419 \times 10^{-4} = \frac{0.88}{210} \times \frac{1}{c}$$

$$C = 0.1 \text{ mol m}^{-3}$$

$$C = 1 \times 10^{-4} M$$

$$3. (a) \Lambda_v = \frac{\kappa \times 1000}{M}$$

$$= \frac{0.158 \times 1000}{0.02}$$

$$= 7900 S\text{cm}^2\text{mol}^{-1}$$

Also, $\alpha = \frac{\Lambda_v}{\Lambda_\infty} = \frac{7900}{10^5} = 0.079$

$$\therefore [Li^+] = c\alpha = 0.02 \times 0.079 = 1.58 \times 10^{-3}$$

$$\therefore w_{Li^+} = 1.58 \times 10^{-3} \times 7 = 0.01106 \text{ g/litre}$$

$$4. (b) \Lambda_{H_2C_2O_4}^\circ = 2\Lambda_{H^+}^\circ + \Lambda_{C_2O_4^{2-}}^\circ$$

$$= 2\Lambda_{HNO_3}^\circ - \Lambda_{K_2C_2O_4}^\circ - 2\Lambda_{KNO_3}^\circ$$

$$5. (b) t_{NO_3^-} \text{ in } Ag^+ = 1 - 0.4 = 0.6$$

$$t_{NO_3^-} \text{ in } K^+ = 0.4$$

$$\therefore \frac{t_{NO_3^-} \text{ in } Ag^+}{t_{NO_3^-} \text{ in } K^+} = \frac{0.6}{0.4} = 1.5$$

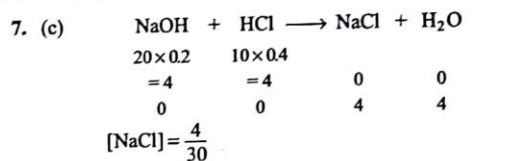
$$6. (a) \lambda_{Ag^+}^\circ = 5.7 \times 10^{-4} \times 96500 \quad (\lambda^\circ = u^\circ \times F)$$

$$\lambda_{NO_3^-}^\circ = 6.9 \times 10^{-4} \times 96500$$

$$\therefore \Lambda_{MAgNO_3}^\circ = \lambda_{Ag^+}^\circ + \lambda_{NO_3^-}^\circ$$

$$= (5.7 \times 10^{-4} + 6.9 \times 10^{-4}) \times 96500$$

$$= 121.59 S\text{cm}^2\text{mol}^{-1}$$



$$\therefore \Lambda_{eq} = \kappa \times \frac{1000}{N} = \frac{(a-b) \times 1000 \times 30}{4}$$

$$= \frac{(a-b)}{4} \times 3 \times 10^4 S\text{cm}^2\text{eq}^{-1}$$

$$8. (b) \Lambda_{AgNO_3}^\circ = \Lambda_{Ag^+}^\circ + \Lambda_{NO_3^-}^\circ = a$$

$$\Lambda_{HCl}^\circ = \Lambda_{H^+}^\circ + \Lambda_{Cl^-}^\circ = b$$

$$\Lambda_{HNO_3}^\circ = \Lambda_{H^+}^\circ + \Lambda_{NO_3^-}^\circ = c$$

$$\text{Also, } \Lambda_{AgCl}^\circ = \Lambda_{Ag^+}^\circ + \Lambda_{Cl^-}^\circ = (a+b-c)$$

$$\text{Also, } \Lambda_{AgCl}^\circ = \kappa \times \frac{1000}{M}$$

$$(a+b-c) = Z \times \frac{1000}{M}$$

$$\therefore M = \frac{1000Z}{(a+b-c)}$$

$$\text{Now, } K_{sp} = [Ag^+][Cl^-] = M^2 = \left[\frac{1000Z}{a+b-c} \right]^2$$

9. (d) Follow Kohlrausch law
 10. (b) H_2SO_4 is strong electrolyte and furnishes maximum no. of ions.
 11. (a) Ionic mobility increases with dilution
 12. (b) Ionic mobility of H^+ is maximum because of lightest ion
 13. (a) Ionic mobility = $\frac{\text{Speed of ion}}{\text{Potential gradient}} = \frac{m \times m}{\text{sec} \times \text{volt}}$
 14. (b) $NaCl_{\text{fused}} \longrightarrow Na^+ + Cl^-$
 15. (a) $C_{\text{solution}} = C_{\text{electrolyte}} + C_{\text{water}}$
 16. (a) Due to smallest size
 17. (c) At infinite dilution $\alpha = 1$
 $CH_3COOH \longrightarrow CH_3COO^- + H^+$
 18. (b) Mobility is speed of ion under unit potential gradient.

$$19. (a) \Lambda_{Na_2SO_4}^\circ = 2\Lambda_{NaCl}^\circ + \Lambda_{K_2SO_4}^\circ - 2\Lambda_{KCl}^\circ$$

$$= 2 \times 126.45 + 306.60 - 2 \times 149.84$$

$$= 259.82$$

$$\lambda_{SO_4^{2-}}^\circ = \Lambda_{Na_2SO_4}^\circ - 2\lambda_{Na^+}^\circ$$

$$= 259.82 - 2 \times 50.11$$

$$= 159.6 S\text{cm}^2\text{mol}^{-1}$$

Numerical Chemistry

20. (d) Enthalpy of hydration of Li^+ is maximum among given species.

$$\text{Size of ion: } r_{Li^+} < r_{Na^+} < r_{K^+} < r_{Rb^+}$$

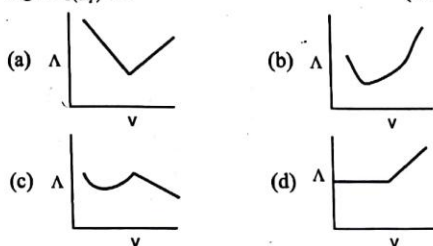
Size of hydrated ion :

$$r_{Li^+(aq)} > r_{Na^+(aq)} > r_{K^+(aq)} > r_{Rb^+(aq)}$$

Thus, ionic mobility will be minimum for Li_{aq}^+ .

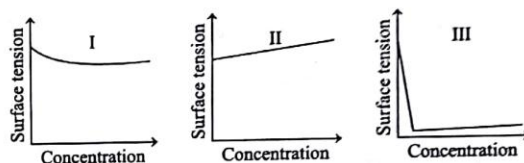
● PREVIOUS YEARS PROBLEMS ●

- The correct order of equivalent conductivity at infinite dilution of LiCl, NaCl and KCl is : (IIT 2001)
 (a) $\text{LiCl} > \text{NaCl} > \text{KCl}$ (b) $\text{KCl} > \text{NaCl} > \text{LiCl}$
 (c) $\text{NaCl} > \text{KCl} > \text{LiCl}$ (d) $\text{LiCl} > \text{KCl} > \text{NaCl}$
- $\text{AgNO}_3(\text{aq})$ was added to an aqueous KCl solution gradually and the conductivity of the solution was measured. The plots of conductance Λ vs volume of $\text{AgNO}_3(\text{aq})$ is : (IIT 2011)



- Resistance of 0.2 M solution of an electrolyte is 50 Ω . The specific conductance of the solution is 1.4 S m^{-1} . The resistance of 0.5 M solution of the same electrolyte is 280 Ω . The molar conductivity of 0.5 M solution of the electrolyte in $\text{S m}^2 \text{mol}^{-1}$ is : [JEE (Main) 2014]
 (a) 5×10^{-4} (b) 5×10^{-3}
 (c) 5×10^3 (d) 5×10^2

- The equivalent conductance of NaCl at concentration C and at infinite dilution are λ_C and λ_∞ respectively. The correct relationship between λ_C and λ_∞ is given as : (where the constant B is positive) [JEE (Main) 2014]
 (a) $\lambda_C = \lambda_\infty + (B)C$ (b) $\lambda_C = \lambda_\infty - (B)C$
 (c) $\lambda_C = \lambda_\infty - (B)\sqrt{C}$ (d) $\lambda_C = \lambda_\infty + (B)\sqrt{C}$
- The qualitative sketches I, II and III given below show the variation of surface tension with molar concentration of three different aqueous solution of KCl, CH_3OH and $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3^-\text{Na}^+$ at room temperature. The correct assignment of the sketches is: [JEE (Advanced) II 2016]



- I : KCl; II : CH_3OH ; III : $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3^-\text{Na}^+$
- I : $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3^-\text{Na}^+$; II : CH_3OH ; III : KCl
- I : KCl; II : $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3^-\text{Na}^+$; III : CH_3OH
- I : CH_3OH ; II : KCl; III : $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3^-\text{Na}^+$

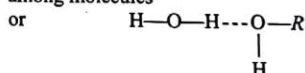
SOLUTIONS (Previous Year Problems)

- (b) More is the size of hydrated ion ($\text{Li}^+_{\text{aq}} > \text{Na}^+_{\text{aq}} > \text{K}^+_{\text{aq}}$) lesser is conductance.
- (d) Initial conductance (Λ) of solution was due to K^+_{aq} and Cl^-_{aq} . On addition of $\text{AgNO}_3(\text{aq})$, the reaction occurs
 $\text{AgNO}_3(\text{aq}) + \text{KCl}(\text{aq}) \longrightarrow \text{AgCl} + \text{KNO}_3(\text{aq})$
 $\Lambda_{\text{KCl}} = \Lambda_{\text{KNO}_3}$ till complete precipitation and then increases with further addition of AgNO_3 .
- (a) $\kappa = \frac{1}{R} \times \frac{l}{a}$
 For given 0.2 M electrolyte solution
 $\kappa = 1.4 \text{ S m}^{-1} = 1.4 \times 10^{-2} \text{ S cm}^{-1}$
 $\therefore \frac{l}{a} = 1.4 \times 10^{-2} \times 50 \text{ cm}^{-1}$
 For 0.5 M electrolyte solution
 $\Lambda_m = \frac{\kappa \times 1000}{C} = \frac{1}{R} \times \frac{l}{a} \times \frac{1000}{C}$
 $= \frac{1}{280} \times \frac{1.4 \times 10^{-2} \times 50 \times 1000}{0.5} = 5 \text{ S cm}^2 \text{mol}^{-1}$
 $= 5 \times 10^{-4} \text{ S m}^2 \text{mol}^{-1}$
- (c) This is called onsager's equation.
- (c) Substance like detergents $[\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3^-\text{Na}^+]$ decreases the surface tension sharply due to

micellization. Those like alcohol (e.g., CH_3OH , $\text{C}_2\text{H}_5\text{OH}$) lower the surface tension slightly due to their lower dielectric constant and the mixture produced acquires lower dielectric constant than water. Dielectric constant is directly proportional to surface tension.

or

Soluble inorganic impurities present in bulk of a liquid such as KCl slightly increase the surface tension of water. Usually ionic solute furnish ions and the solution of ions give rise to increase in molecular attraction leading to slight increase in surface tension. Addition of H_2O to CH_3OH decreases the interaction among molecules



bonding is weaker than $\text{H}-\text{O}-\text{H} \cdots \text{H}-\text{O}-\text{H}$

A decrease in molecular attraction leads to decrease in surface tension (remember $\text{H}-\text{OH}-\text{CH}_3\text{OH}$ shows positive deviation from Raoult's law).

OBJECTIVE PROBLEMS (More Than One Answer Correct)

- Which one is correct statement?
 - Conductance is an additive property
 - Conductance order : $\text{Li}^+_{(aq.)} < \text{Na}^+_{(aq.)} < \text{K}^+_{(aq.)} < \text{Rb}^+_{(aq.)}$
 - Molar conductivity of NH_4^+ in liquid NH_3 is higher than in H_2O
 - At infinite dilution all the interionic attractions vanishes
- Which relations are correct about conductances?
 - $\kappa_b = \frac{C \Lambda_v^2}{\Lambda^\circ (\Lambda^\circ - \Lambda_v)}$
 - $\alpha = \frac{\Lambda_v}{\Lambda_\infty}$ for strong electrolytes
 - $\Lambda^\circ_{M_{A_xB_y}} = x \Lambda^\circ_{A^+} + y \Lambda^\circ_{B^-}$
 - $\Lambda_M = \kappa \times \frac{1000}{M}$
- Select the correct statements :
 - Λ°_M for weak electrolytes depends upon degree of dissociation of electrolyte, ionic mobility and nature of ion
 - Λ°_M for strong electrolytes depends upon ionic mobility and nature of ion
 - The SI unit of Λ_M is $\text{S m}^2 \text{mol}^{-1}$
 - $1 \text{ S m}^2 \text{mol}^{-1} = 1 \times 10^4 \text{ S cm}^2 \text{mol}^{-1}$
- A graph plotted for $\log(i-1)$ vs. $\log \Lambda_v$, where i is van't Hoff factor of given uni-univalent electrolyte having molar conductance Λ_v at dilution v , then which are correct?
 - Slope = $-\log \Lambda^\circ$; intercept = -1
 - Slope = 1 ; intercept = $-\log \Lambda^\circ_M$
 - Slope = 1 ; intercept = $\log \Lambda^\circ_M$
 - Slope = $\log \Lambda^\circ_M$; intercept = $+1$
- Λ°_M and Λ°_E are molar and equivalent conductivity at infinite dilution and λ° is ionic conductance at infinite dilution, then for potash alum:
 - $\Lambda^\circ_M = 2 \times \lambda^\circ_{\text{K}^+} + 2 \times \lambda^\circ_{\text{Al}^{3+}} + 4 \times \lambda^\circ_{\text{SO}_4^{2-}}$
 - $\Lambda^\circ_E = \frac{1}{8} \times \Lambda^\circ_M$
 - $\Lambda^\circ_E = \frac{1}{4} \times \lambda^\circ_{\text{K}^+} + \frac{1}{4} \times \lambda^\circ_{\text{Al}^{3+}} + \frac{1}{2} \times \lambda^\circ_{\text{SO}_4^{2-}}$
 - $\Lambda^\circ_M = \lambda^\circ_{\text{K}^+} + \lambda^\circ_{\text{Al}^{3+}} + \lambda^\circ_{\text{SO}_4^{2-}}$
- An ion travels 0.4 cm in 1 minute under the influence of 2 volt potential difference when electrodes are 3 cm apart. Which one are correct?
 - Speed of ion = $6.67 \times 10^{-3} \text{ cm s}^{-1}$
 - Ionic mobility = $1 \times 10^{-6} \text{ m}^2 \text{volt}^{-1} \text{sec}^{-1}$
 - Ionic mobility = $1.0 \times 10^{-3} \text{ cm}^2 \text{volt}^{-1} \text{sec}^{-1}$
 - Ionic mobility = $4.44 \times 10^{-3} \text{ cm}^2 \text{volt}^{-1} \text{sec}^{-1}$
- The increase in ionic mobility of strong electrolytes with dilution is due to :
 - Increase in degree of dissociation
 - Increase in number of ions
 - Relaxation or Assymetric effect
 - Solution or Electrophoretic effect
- The formula, $\alpha = \frac{\Lambda_v}{\Lambda_\infty}$ does not hold good for :
 - CH_3NH_2
 - H_2SO_4
 - HClO_4
 - NH_4Cl
- In a solution of NH_4OH , at infinite dilution, which are present :
 - NH_4OH
 - NH_4^+
 - OH^-
 - None of these
- The term infinite dilution refers for :
 - All interionic effect disappears
 - Weak electrolytes are 100% dissociated
 - The Kohlrausch law becomes valid for weak and strong electrolytes both
 - Ionic mobility becomes constant
- Which are correct for super conductors ?
 - possess zero resistivity
 - possess infinite conductivity
 - Metals and their alloys at 0 to 15 K
 - Ceramic materials and mixed oxides at 0 to 150 K
- Which one is incorrect ?
 - $1 \text{ J} = 1 \text{ N} \times 1 \text{ m}$
 - $1 \text{ J} = 1 \text{ volt-coulomb}$
 - $1 \text{ J} = 1 \text{ watt} \times 1 \text{ sec}$
 - $1 \text{ J} = 1 \text{ volt} \times 1 \text{ ampere} \times 1 \text{ sec}$
- Molar conductivity of NH_4^+ and NH_2^- are usually higher in liquid NH_3 than in water due to :
 - Grothus conductance
 - Auto protolysis of solvent
 - Higher dielectric constant of NH_3
 - High conducting nature of NH_3
- Which of the following will increase the conductivity of solution :
 - Temperature
 - Dielectric constant of solvent
 - Decrease in viscosity of solvent
 - Decrease in solvation of ion

SOLUTIONS (More Than One Answer Correct)

- (a,b,c,d) (a) $C_T = \sum C_i + C_{\text{Water}}$
(b) Due to more hydration of small cation and thus size increase and conductance decreases,
(c) Due to greater conductance. Conductance of NH_4^+ in NH_3 is more.
- (a,c,d) $\alpha = \frac{\Lambda_v}{\Lambda^\circ}$ for weak electrolytes.
- (a,b,c,d) These are facts.
- (b) $\alpha = \frac{i-1}{n-1}$ $n = 2$ for AB
 $\therefore \frac{\Lambda_v}{\Lambda_M^\circ} = \frac{i-1}{1}$ or $i-1 = \frac{\Lambda_v}{\Lambda_M^\circ}$
or $\log(i-1) = \log \Lambda_v - \log \Lambda_M^\circ$
 $Y = mx + c$
- (a,b,c) Follow text of Kohlrausch law.
- (a,b) $\text{Speed} = \frac{0.4}{60} = 6.67 \times 10^{-3} \text{ cm sec}^{-1};$
 $= 6.67 \times 10^{-5} \text{ m sec}^{-1}$
 $\text{Ionic mobility} = \frac{\text{Speed}}{\text{Pot. gradient}}$
 $= \frac{6.67 \times 10^{-5} \times 3 \times 10^{-2}}{2}$
 $= 1 \times 10^{-6} \text{ m}^2 \text{ volt}^{-1} \text{ sec}^{-1}$
- (c,d) Follow Debye-Huckel theory of strong electrolytes
- (a) The formula is valid for weak electrolytes
- (b,c) At infinite dilution weak electrolyte is completely dissociated
- (a,b,c,d) All are facts
- (a,b,c,d) These are facts.
- (a,b,c,d) -do-
- (a,b) -do-
- (a,b,c,d) -do-

COMPREHENSION BASED PROBLEMS

Comprehension 1 : Electrolytes that are known as weak electrolytes on the basis of very strong dependence of conductance on concentration give quite constant concentration independent values of dissociation constant (K_a) calculated from degree of dissociation (α) values from measured conductances or from colligative properties. The partial dissociation appears to be a major factor in determining the properties of weak electrolytes and the degree of dissociation for weak electrolyte at dilution v is given by $\alpha = \frac{\Lambda_v}{\Lambda_\infty}$. The strong electrolytes on the otherhand do not obey

this relation and the variation of molar conductivity for strong electrolytes is given by $\Lambda_v = \Lambda_\infty - bc^{1/2}$.

- [1] The slope of the graph $\frac{\Lambda_v^2}{\Lambda_\infty(\Lambda_\infty - \Lambda_v)}$ vs. $\frac{1}{c}$, if Λ_v and Λ_∞ are molar conductivity of weak electrolyte having dissociation constant K_a at concentration c and zero respectively is:
(a) concave downwards
(b) concave upwards
(c) straight line with intercept K_a
(d) straight line with slope K_a
- [2] The numerical value of $\Lambda_{\text{ion}}^\infty$:
(a) is dependent of nature of ion
(b) is called molar conductivity

(c) is obtained by extrapolation of Λ_c vs. \sqrt{c} curves to zero concentration for all electrolytes

(d) is equal to $\frac{\Lambda_v}{\alpha}$ for strong electrolytes

- [3] The van't Hoff factor for weak electrolyte A_xB_y , if $(n = x + y)$ can be given as:
(a) $i = 1 - \alpha + x\alpha + y\alpha$
(b) $i = 1 + (x + y)$ at infinite dilution
(c) $i = (n - 1) \frac{\Lambda_v}{\Lambda_\infty} + 1$
(d) either of these
- [4] The graph plotted for $\log(i - 1)$ vs. $\log \Lambda_v$, where i is van't Hoff factor for uni-univalent electrolyte and Λ_v is its molar conductivity at concentration c does not show the following characteristics:
(a) straight line
(b) slope equal to unity
(c) intercept equal to $\log \Lambda_\infty$
(d) intercept equal to $-\log \Lambda_\infty$
- [5] Which statement is wrong about the variation of molar conductivity with dilution for a given electrolyte?
(a) Depends upon ionic mobility and degree of dissociation of all electrolytes
(b) Depends upon ionic mobility and degree of dissociation of weak electrolytes
(c) Depends upon ionic mobility for strong electrolytes
(d) Depends upon the nature of ion furnished by electrolytes on dissolution

SOLUTIONS

Comprehension 1

$$[1] \text{ (d)} \quad K_a = \frac{c\alpha^2}{(1-\alpha)} = \frac{c\Lambda_v^2}{\Lambda_\infty^2 \left(1 - \frac{\Lambda_v}{\Lambda_\infty}\right)}$$

$$K_a = \frac{c\Lambda_v^2}{\Lambda_\infty(\Lambda_\infty - \Lambda_v)}$$

$$\text{or} \quad \frac{\Lambda_v^2}{\Lambda_\infty(\Lambda_\infty - \Lambda_v)} = \frac{K_a}{c}$$

$$y = m \cdot x \quad \left(x = \frac{1}{c}\right)$$

[2] (a) Λ_∞ depends on nature of ion.

[3] (d) All are correct.

$$i = 1 - \alpha + x\alpha + y\alpha$$

$$\therefore \alpha = \frac{i-1}{(x+y)-1} = \frac{i-1}{\frac{\Lambda_v}{\Lambda_\infty}-1}$$

$$\text{or} \quad \frac{\Lambda_v}{\Lambda_\infty} = \frac{i-1}{n-1}$$

$$\therefore i = (n-1) \frac{\Lambda_v}{\Lambda_\infty} + 1$$

[4] (c) $\therefore n = 2$ for H_2A

$$\therefore i = \frac{\Lambda_v}{\Lambda_\infty} + 1$$

$$\therefore \log(i-1) = \log \Lambda_v - \log \Lambda_\infty$$

$$\therefore \text{slope} = 1 \text{ and intercept} = -\log \Lambda_\infty$$

[5] (a) For strong electrolytes, ' α ' has no effect on Λ_M .

610

Numerical Chemistry

STATEMENT EXPLANATION PROBLEMS

In each sub question given below a statement (S) and explanation (E) is given. Choose the correct answers from the codes (a), (b), (c) and (d) given for each question:

- (a) S is correct but E is wrong
 (b) S is wrong but E is correct
 (c) Both S and E are correct and E is correct explanation of S
 (d) Both S and E are correct but E is not correct explanation of S

1. S: A graph plotted between Λ_v vs. $c^{1/2}$ gives a straight line with slope equal to $-A$ and intercept equal to Λ_∞ .

E: The value of A for a given solvent and temperature depends upon the nature of electrolyte, i.e., charge on cation or anion furnished by electrolyte on dissolution.

2. S: Conductivity of weak electrolytic solution decreases with dilution whereas equivalent conductivity, molar conductivity increases with dilution.

E: On dilution, the ionic mobility and number of ions present in solution increases but number of ions per mL decreases.

3. S: The Λ^∞ for all electrolytes can be obtained by extrapolation of Λ_M curves vs. $\sqrt{\text{concentration}}$ to zero concentration.

E: Λ^∞ for all electrolytes can be obtained by Kohlrausch law.

4. S: The ratio of speeds of cation and anions of an electrolyte under same potential gradient is 2 : 3, the fall in concentration around anodic and cathodic solution will be in the ratio 1 : 1 during the passage of current.

E: The number of ions discharged at either electrode during electrolysis is independent of their relative speed.

5. S: The conductance of ions during passage of current through an electrolyte showing autoprotolysis are abnormally higher.

E: The ions obtained during autoprotolysis show higher values due to Grotthuss conductance.

6. S: Conductance of a solution can be obtained by designing the apparatus based on Wheatstone bridge principle.

E: Meter bridge used to detect the resistance of metal wire can be used to read out the conductance of solutions.

7. S: The conductance measurement of an electrolytic solution is made by using two conductivity cells having different cell constants gives different values of conductance.

E: The conductances of solution obtained will be different but conductivity of solution would be same.

8. S: Speed of ions depends upon nature of ions only.

E: Mobility of ions depends upon mass, charge and size of ions only.

ANSWERS (Statement Explanation Problems)

- (d) Both are facts.
- (c) Explanation is correct reason for statement.
- (b) Λ_c vs. \sqrt{c} curves give Λ^∞ values on extrapolation to zero concentration for strong electrolytes only.
- (b) The number of ions discharged on opposite electrodes is independent of their relative speed, however fall in concentration around any electrode depends upon the speed of ion moving away from it.
- (c) Explanation is correct reason for statement.
- (a) Some modifications such as A.C. in place of D.C., null point detector in place of galvanometer, etc., are to be made in meter bridge.
- (d) Both are correct. The K is same in both cases because number of ions per c.c. remains same.
- (b) Speed of ions depends upon nature of ions and potential gradient.

612

Numerical Chemistry

MATCHING TYPE PROBLEMS

Type I: More Than One Match Are Possible

1. List A

- (A) Λ vs $c^{1/2}$ plots
(B) Kohlrausch law

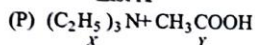
List B

- Λ° for strong electrolyte
- Hyperbolic graph
- Straight line graph
- Λ° for weak electrolyte

2. An aqueous solution of X is added slowly to an aqueous solution of Y as shown in List A. The variation in conductivity of these reactions is given in List B. Match List A with List B and select the correct using the code given below the lists:

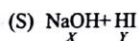
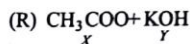
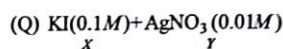
[JEE (Advanced) II 2013]

List A



List B

- (1) Conductivity decreases and then increases



- (2) Conductivity decreases and then does not change much
- (3) Conductivity increases and then does not change much
- (4) Conductivity does not change much and then increases

Codes:

	P	Q	R	S
(a)	3	4	2	1
(b)	4	3	2	1
(c)	2	3	4	1
(d)	1	4	3	2

ANSWERS

1. A-1, 2, 3; B-1, 4

2. a