Example 11. The molar conductances at infinite dilution for sodium acetate and hydrogen chloride at 30°C are $91{\cdot}0\times10^{-4}$ and $426{\cdot}16\times10^{-4}$ S m^2 mol^{-1}, respectively. Also for H^+ ion in HCl, t_+ is 0·821 and for CH_3COO^- ion in CH_3COONa, t_- is 0·556. Assuming that $t_\pm = t^\circ_\pm$, calculate Λ°_m for CH_3COOH.

Solution : We know that, $\lambda^\circ_+ = t^\circ_+(\Lambda^\circ_m)$ and $\lambda^\circ_- = t^\circ_-(\Lambda^\circ_m)$ (Eqs. 11 and 12)

Assuming that $t^\circ_+ = t_+$ and $t^\circ_- = t_-$, from the data on HCl, we have

$$\lambda^\circ_+ = 0{\cdot}821\times426{\cdot}16\times10^{-4} = 349{\cdot}88\times10^{-4}\ \text{S m}^2\ \text{mol}^{-1}$$

From the data on CH_3COONa,

$$\lambda^\circ_- = 0{\cdot}556\times91{\cdot}0\times10^{-4} = 50{\cdot}60\times10^{-4}\ \text{S m}^2\ \text{mol}^{-1}$$

Hence, for CH_3COOH, $\Lambda^\circ_m = \lambda^\circ_+ + \lambda^\circ_- = (349{\cdot}88 + 50{\cdot}60)\times10^{-4}\,\text{S m}^2\,\text{mol}^{-1}$

$$= \mathbf{400{\cdot}48\times10^{-4}\ S\ m^2\ mol^{-1}}$$

Example 12. At 25°C, the degree of dissociation (α) of pure water is $1{\cdot}90\times10^{-9}$. Calculate the molar conductance (Λ°_m) and specific conductance (κ) of water at this temperature. The molar ionic conductances of H^+ and OH^- ions are $349{\cdot}83\times10^{-4}$ and $198{\cdot}50\times10^{-4}$ S m^2 mol^{-1}, respectively.

Solution : From Kohlarusch's law,

$$\Lambda^\circ_{mH_2O} = \Lambda^\circ_{H^+} + \lambda^\circ_{OH^-} = (349{\cdot}83 + 198{\cdot}50)\times10^{-4}\ \text{S m}^2\ \text{mol}^{-1} = \mathbf{548{\cdot}33\times10^{-4}\ S\ m^2\ mol^{-1}}$$

The degree of dissociation of a weak electrolyte is given by $\alpha = \Lambda_m/\Lambda^\circ_m$ (Eq. 4)

$\therefore$ $\Lambda_m = \alpha\Lambda^\circ_m = (1{\cdot}90\times10^{-9})(548{\cdot}33\times10^{-4}\,\text{S m}^2\,\text{mol}^{-1}) = 1{\cdot}401\times10^{-10}$ S m^2 mol^{-1}

Further, $\Lambda_m = \kappa/c$ (Eq. 3)

In this case, $c = 1000$ g dm^{-3}/18 g mol^{-1} = 55·56 mol dm^{-3} = $55{\cdot}56\times10^3$ mol m^{-3}

$\therefore$ $\kappa = c\Lambda_m = (55{\cdot}56\times10^3\ \text{mol m}^{-3})\ (1{\cdot}041\times10^{-10}\ \text{S m}^2\ \text{mol}^{-1}) = \mathbf{5{\cdot}78\times10^{-6}\ S\ m^{-1}}$

Example 9. For the strong electrolytes NaOH, NaCl and $BaCl_2$, the molar ionic conductances at infinite dilution are $248 \cdot 1 \times 10^{-4}$, $126 \cdot 5 \times 10^{-4}$ and $280 \cdot 0 \times 10^{-4}$ S m^2 mol^{-1}, respectively. Calculate Λ°_{m} for $Ba(OH)_2$.

Solution : $BaCl_2 + 2NaOH \longrightarrow Ba(OH)_2 + 2NaCl$

Thus, according to Kohlrausch's law of independent migration of ions,

$$\Lambda^{\circ}_{mBa(OH)_2} = \Lambda^{\circ}_{mBaCl_2} + 2\Lambda^{\circ}_{mNaOH} - 2\Lambda^{\circ}_{mNaCl}$$

$$= (280 + 2 \times 248 \cdot 1 - 2 \times 126 \cdot 5) \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$$

$$= 523 \cdot 2 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$$

Example 10. The molar ionic conductance at infinite dilution of lithium halide (LiX) is found to be $89 \cdot 2 \times 10^{-4}$ S m^2 mol^{-1}. What would be the molar ionic conductance of the halide ion if the molar ionic conductance of Li^+ ion is $38 \cdot 70 \times 10^{-4}$ S m^2 mol^{-1} ?

Solution : According to Kohlrausch's law

$$\Lambda^{\circ}_{m} = \lambda^{\circ}_{+} + \lambda^{\circ}_{-}$$

$$\lambda^{\circ}_{-} = \Lambda^{\circ}_{m} - \lambda^{\circ}_{+} = (89 \cdot 20 - 38 \cdot 70) \times 10^{-4} = 50 \cdot 5 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$$

Example 5. **The specific conductance of 0·01 M solution of acetic acid was found to be 0·0163 S m^{-1} at 25°C. Calculate the degree of dissociation of the acid. Molar conductance of acetic acid at infinite dilution is 390·7×10^{-4} S m^2 mol^{-1} at 25°C.**

Solution :

$$\kappa = 0{\cdot}0163 \text{ S m}^{-1}; \quad c = 0{\cdot}01 \text{ mol dm}^{-3} = 10 \text{ mol m}^{-3}$$

$$\Lambda_m = \frac{\kappa}{c} = \frac{0{\cdot}0163 \text{ S m}^{-1}}{10 \text{ mol m}^{-3}} = 16{\cdot}3 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$$

$$\Lambda_m^{\circ} = 390{\cdot}7 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1} \text{ (given)}$$

$$\alpha = \frac{\Lambda_m}{\Lambda_m^{\circ}} = \frac{16{\cdot}3 \times 10^{-4} \text{S m}^2 \text{ mol}^{-1}}{390{\cdot}7 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}} = \mathbf{0{\cdot}0472}$$

Example 13. **The molar ionic conductance at infinite dilution of silver ions is $61{\cdot}92\times10^{-4}$ S m^2 mol^{-1} at 25° C. Calculate the ionic mobility of silver ions at 25°C at infinite dilution.**

Solution : $\lambda^\circ_+ = 61{\cdot}92\times10^{-4}$ S m^2 mol^{-1}

$u^\circ_+ = \lambda^\circ_+/F$ (Eq. 18)

$$\therefore \quad u^\circ_+ = \frac{61{\cdot}92\times10^{-4}\ \text{S m}^2\ \text{mol}^{-1}}{96485\ \text{C mol}^{-1}}$$

$= \mathbf{6{\cdot}417\times10^{-8}\ m^2\ V^{-1}\ s^{-1}}$ ($\because$ C = A s = V S s)

Example 14. **A dilute solution of potassium chloride was placed between two platinum electrodes 10·0 cm apart, across which a potential of 6·0 volts was applied. How far would the K^+ ion move in 2 hours at 25°C ? Molar ionic conductance of K^+ ion at infinite dilution at 25°C is known to be $73{\cdot}52\times10^{-4}$ S m^2 mol^{-1}**

Solution : Molar ionic conductance of K^+ ion at infinite dilution = $73{\cdot}52\times10^{-4}$ S m^2 s^{-1}

$u^\circ_+ = \lambda^\circ_+/F$ (Eq. 18)

$$u^\circ_+ = \frac{73\cdot52\times10^{-4}\ \text{S m}^2\ \text{mol}^{-1}}{96493\ \text{C mol}^{-1}}$$

$= 7{\cdot}619\times10^{-4}$ m^2 V^{-1} s^{-1} ($\because$ C = V S s)

Potential gradient in this case = 6·0 volts/10 cm = 0·6 volt cm^{-1} = $0{\cdot}6\times10^2$ volt m^{-1}

$\therefore$ Speed of K^+ ion = $7{\cdot}619\times10^{-8}$ m^2 s^{-1} volt$^{-1}\times0{\cdot}6\times10^2$ volt m^{-1} = $7{\cdot}619\times10^{-8}\times0{\cdot}6\times10^2$ m s^{-1}

$\therefore$ Distance moved by K^+ ion in 2 hours = $7{\cdot}619\times10^{-8}\times0{\cdot}6\times10^2$ m s^{-1} ($2\times60\times60$ s) = $\mathbf{3{\cdot}291\times10^{-2}\ m}$

Example 15. Calculate the molar conductance at infinite dilution of an aqueous solution of NaCl at room temperature, given that the mobilities of Na^+ and Cl^- ions at this temperature are $4{\cdot}26\times10^{-8}$ and $6{\cdot}80\times10^{-8}$ m^2 V^{-1} s^{-1}, respectively.

Solution : According to Eq. 18,

$\lambda^\circ_+ = Fu^\circ_+$

$= (96493$ C mol^{-1}) ($4{\cdot}26\times10^{-8}$ m^2 V^{-1} s^{-1}) = $41{\cdot}10\times10^{-4}$ S m^2 mol^{-1}

$$\lambda^{\circ}_{-} = (96493\ \text{C mol}^{-1})\ (6{\cdot}80 \times 10^{-8}\ \text{m}^2\ \text{V}^{-1}\ \text{s}^{-1}) = 65{\cdot}61 \times 10^{-4}\ \text{S m}^2\ \text{mol}^{-1}$$

$$\Lambda^{\circ}_{m} = \lambda^{\circ}_{Na^+} + \lambda^{\circ}_{Cl^-} = (41{\cdot}10 + 65{\cdot}61) \times 10^{-4}\ \text{S m}^2\ \text{mol}^{-1}$$

$$= \mathbf{106{\cdot}71 \times 10^{-4}\ S\ m^2\ mol^{-1}}$$

Example 18. **The molar conductances of sodium acetate, hydrochloric acid and sodium chloride at infinite dilution are $91 \cdot 0 \times 10^{-4}$, $426 \cdot 16 \times 10^{-4}$ and $126 \cdot 45 \times 10^{-4}$ S m^2 mol^{-1}, respectively, at 25°C. Calculate the molar conductance at infinite dilution for acetic acid.**

Solution :

$$\overset{\circ}{\Lambda}_{mCH_3COONa} = \overset{\circ}{\lambda}_{CH_3COO^-} + \overset{\circ}{\lambda}_{Na^+} = 91 \cdot 0 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$$

$$\overset{\circ}{\Lambda}_{mHCl} = \overset{\circ}{\lambda}_{H^+} + \overset{\circ}{\lambda}_{Cl^-} = 426 \cdot 16 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$$

$$\overset{\circ}{\Lambda}_{mNaCl} = \overset{\circ}{\lambda}_{Na^+} + \overset{\circ}{\lambda}_{Cl^-} = 126 \cdot 45 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$$

$$\overset{\circ}{\lambda}_{CH_3COO^-} + \overset{\circ}{\lambda}_{H^+} = \overset{\circ}{\lambda}_{CH_3COO^-} + \overset{\circ}{\lambda}_{Na^+} + \overset{\circ}{\lambda}_{H^+} + \overset{\circ}{\lambda}_{Cl^-} - \overset{\circ}{\lambda}_{Na^+} - \overset{\circ}{\lambda}_{Cl^-}$$

or

$$\overset{\circ}{\Lambda}_{mCH_3COOH} = \overset{\circ}{\Lambda}_{mCH_3COONa} + \overset{\circ}{\Lambda}_{mHCl} - \overset{\circ}{\Lambda}_{mNaCl}$$

$$= (91 \cdot 00 + 426 \cdot 16 - 126 \cdot 45) \times 10^{-4} = 390 \cdot 71 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$$

Example 19. Calculate the transport numbers of Li^+ and Br^- ions when a current flows through an infinitely dilute aqueous solution of LiBr at 25°C, given the ionic mobilities of Li^+ and Br^- ions at infinite dilution are $4{\cdot}01\times10^{-8}$ and $8{\cdot}09\times10^{-8}$ $m^2\ V^{-1}\ s^{-1}$, respectively.

Solution : In this case, $u_+^\circ = 4{\cdot}01\times10^{-8}\ m^2\ V^{-1}\ s^{-1}$ and $u_-^\circ = 8{\cdot}09\times10^{-8}\ m^2\ V^{-1}\ s^{-1}$

From Eq. 22,
$$t_+^\circ = \frac{u_+^\circ}{u_+^\circ + u_-^\circ} = \frac{4{\cdot}01\times10^{-8}\ m^2\ V^{-1}\ s^{-1}}{(4{\cdot}01+8{\cdot}09)\times10^{-8}\ m^2\ V^{-1}\ s^{-1}} = \mathbf{0{\cdot}331}$$

Since
$$t_+^\circ + t_-^\circ = 1$$

$\therefore$
$$t_-^\circ = 1 - 0{\cdot}331 = \mathbf{0{\cdot}669}$$

Example 20. Molar ionic conductances at infinite dilution of Na^+ and Cl^- ions are $50{\cdot}11\times10^{-4}$ and $76{\cdot}34\times10^{-4}$ S m^2 mol^{-1}, respectively. Calculate the transport numbers of Na^+ and Cl^- ions.

Solution : According to Eq. 20,
$$t_+^\circ = \frac{\lambda_+^\circ}{\lambda_+^\circ + \lambda_-^\circ} = \frac{50{\cdot}11\times10^{-4}\ S\ m^2\ mol^{-1}}{(50{\cdot}11+76{\cdot}34)\times10^{-4}\ S\ m^2\ mol^{-1}}$$
$$= \frac{50{\cdot}11\times10^{-4}\ S\ m^2\ mol^{-1}}{126{\cdot}45\ S\ m^2\ mol^{-1}} = \mathbf{0{\cdot}396}$$
$$t_-^\circ = \frac{\lambda_-^\circ}{\lambda_+^\circ + \lambda_-^\circ} = \frac{76{\cdot}34\times10^{-4}\ S\ m^2\ mol^{-1}}{(50{\cdot}11+76{\cdot}34)\times10^{-4}\ S\ m^2\ mol^{-1}} = \mathbf{0{\cdot}604}$$

As can be seen, $t_+^\circ + t_-^\circ = 0{\cdot}396 + 0{\cdot}604 = 1$

Example 22. The molar conductance of 0·01 M solution of acetic acid was found to be $16{\cdot}30 \times 10^{-4}$ S m² mol⁻¹ at 25°C. The molar ionic conductances of hydrogen and acetate ions at infinite dilution are $349{\cdot}8 \times 10^{-4}$ and $40{\cdot}9 \times 10^{-4}$ S m² mol⁻¹, respectively, at the same temperature. What percentage of acetic acid is dissociated at this concentration ?

Solution : $$\Lambda^{\circ}_{m\,CH_3COOH} = \lambda^{\circ}_{CH_3COO^-} + \lambda^{\circ}_{H^+} = (40{\cdot}9 + 349{\cdot}8) \times 10^{-4} = 390{\cdot}7 \times 10^{-4}\ \text{S m}^2\,\text{mol}^{-1}$$

$$\alpha = \frac{\Lambda_m}{\Lambda^{\circ}_m} = \frac{16\cdot 30 \times 10^{-4}\ \text{S m}^2\ \text{mol}^{-1}}{390\cdot 7 \times 10^{-4}\ \text{S m}^2\text{mol}^{-1}} = \mathbf{0{\cdot}04172}$$

Thus, 0·01 M acetic acid is **4·172 per cent** dissociated.

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Example 23. At 25°C the specific conductance of carefully distilled water is $58{\cdot}0\times10^{-7}$ S m^{-1} and the λ_m° values for H^+ and OH^- ions are $349{\cdot}8\times10^{-4}$ and $198{\cdot}5\times10^{-4}$ S m^2 mol^{-1}, respectively. Assuming that Λ_m differs very little from Λ_m°, calculate the ionic product of water at 25°C.

Solution :

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$K_w = [H^+][OH^-] = (c)\ (c) = c^2 \qquad \ldots(i)$$

where c is the concentration of each of the ionic speices.

From Kohlraush's law, $\Lambda_m^\circ = \lambda_{H^+}^\circ + \lambda_{OH^-}^\circ = (349{\cdot}8 + 198{\cdot}5)\times10^{-4}$ S m^2 mol^{-1}

$$= 548{\cdot}3\times10^{-4} \text{ S m}^2 \text{ mol}^{-1} \approx \Lambda_m \text{ (Given)}$$

Since $\Lambda_m = \kappa/c$ (Eq. 3)

$$\therefore \quad c = \kappa/\Lambda_m = \frac{58{\cdot}0 \times 10^{-7}\text{ S m}^{-1}}{548{\cdot}5 \times 10^{-4}\text{ S m}^2\text{ mol}^{-1}} = 1{\cdot}06 \times 10^{-4} \text{ mol m}^{-3}$$

$$= 1{\cdot}06\times10^{-7} \text{ mol dm}^{-3}$$

Hence, from Eq. (i), $K_w = c^2 = (1{\cdot}06\times10^{-7} \text{ mol dm}^{-3})^2 = \mathbf{1{\cdot}12\times10^{-14}\ mol^2\ dm^{-6}}$

Example 24. The specific conductance of a saturated solution of silver chloride at 25°C after subtracting the specific conductance of water is $2{\cdot}28\times10^{-4}$ S m^{-1}. Calculate the solubility of silver chloride in grams per dm^3 at this temperature. $\Lambda^\circ_{mAgCl} = 138{\cdot}3\times10^{-4}$ S m^2 mol^{-1} and $M_{(AgCl)} = 143{\cdot}5$ g mol^{-1}

Solution : $\kappa = 2{\cdot}28\times10^{-4}$ S m^{-1}

Let the solubility of AgCl be x mol m^{-3}

$$\therefore \quad \Lambda_m = \kappa/c = 2{\cdot}28\times10^{-4} \text{ S m}^{-1}/x$$

$$2{\cdot}28\times10^{-4} \text{ S m}^{-1}/x = 138{\cdot}3\times10^{-4} \text{ S m}^2 \text{ mol}^{-1}$$

$$x = \frac{2{\cdot}28\times10^{-4}\text{ S m}^{-1}}{138{\cdot}3\times10^{-4}\text{ S m}^2\text{ mol}^{-1}} = 1{\cdot}648\times10^{-2}\text{ mol m}^{-3} = 1{\cdot}648\times10^{-5}\text{ mol dm}^{-3}$$

$$= 143{\cdot}5 \text{ g mol}^{-1} \times 1{\cdot}648\times10^{-5}\text{ mol dm}^{-3} = \mathbf{2{\cdot}365\times10^{-3}\text{ g dm}^{-3}}$$

Example 25. At 25°C, the specific conductance of a saturated solution of AgCl is $2{\cdot}68\times10^{-4}$ S m^{-1} and that of water with which the solution was made is $0{\cdot}86\times10^{-4}$ S m^{-1}. If molar conductances at infinite dilution of $AgNO_3$, HNO_3 and HCl are, respectively, $133{\cdot}0\times10^{-4}$, $421{\cdot}0\times10^{-4}$ and $426{\cdot}0\times10^{-4}$ S m^2 mol^{-1}, calculate the solubility of AgCl in grams per dm^3 in water at the given temperature.

Solution : $\kappa_{solution} = \kappa_{AgCl} + \kappa_{water}$

$$\therefore \quad \kappa_{AgCl} = \kappa_{solution} - \kappa_{water} = (2{\cdot}68 - 0{\cdot}86)\times10^{-4}\text{ S m}^{-1} = 1{\cdot}82\times10^{-4}\text{ S m}^{-1}$$

Since AgCl is formed according to the reaction

$$AgNO_3 + HCl \longrightarrow AgCl + HNO_3$$

hence, using Kohlrauch's law,

$$\Lambda^\circ_{mAgCl} = \Lambda^\circ_{mAgNO_3} + \Lambda^\circ_{mHCl} - \Lambda^\circ_{mHNO_3} = (133{\cdot}0 + 426{\cdot}0 - 421{\cdot}0)\times10^{-4}\text{ S m}^2\text{ mol}^{-1}$$

$$= 138{\cdot}0\times10^{-4}\text{ S m}^2\text{ mol}^{-1}$$

$\Lambda_m = \kappa/c$ and for the saturated solution of the sparingly soluble salt, $\Lambda_m = \Lambda^\circ_m$

$$\therefore \quad c = \frac{\kappa}{\Lambda^\circ_m} = \frac{1{\cdot}82\times10^{-4}\text{ S m}^{-1}}{138{\cdot}0\times10^{-4}\text{ S m}^2\text{mol}^{-1}} = 1{\cdot}32\times10^{-2}\text{ mol m}^{-3}$$

$$= 1{\cdot}32\times10^{-5}\text{ mol dm}^{-3}$$

$$\therefore \quad \text{Solubility of AgCl} = (1{\cdot}32\times10^{-5}\text{ mol dm}^{-3})(143{\cdot}5\text{ g mol}^{-1}) = \mathbf{1{\cdot}89\times10^{-3}\text{ g dm}^{-3}}$$

Example 26. Calculate the solubility product of the sparingly soluble salt CaF_2 from the following data : The molar ionic conductances (at infinite dilution) of Ca^{2+} and F^- ions are 104×10^{-4} and 48×10^{-4} S m^2 mol^{-1}, respectively. The specific conductance of the saturated solution of CaF_2 at room temperature is $4{\cdot}25\times10^{-3}$ S m^{-1} and the specific conductance of water used for preparing the solution is 2×10^{-4} S m^{-1}.

Solution : Let c mol dm^{-3} be the solubility of CaF_2. Accordingly, the solubility equilibrium may be written as

$$\underset{}{CaF_2\,(s)} \rightleftharpoons \underset{c}{Ca^{2+}(aq)} + \underset{2c}{2F^-(aq)}$$

Then, at equilibrium, the solubility product of CaF_2 is given by

$$K_{sp} = [Ca^{2+}][F^-]^2 = (c)(2c)^2 = 4c^3 \quad \ldots(i)$$

Specific conductance due to CaF_2 alone

$$= \kappa\text{ (soln)} - \kappa\text{ (water)} = (4{\cdot}25\times10^{-3} - 2{\cdot}0\times10^{-4})\text{ S m}^{-1} = 4{\cdot}05\times10^{-3}\text{ S m}^{-1}$$

$$\Lambda^\circ_{m(CaF_2)} = \lambda^\circ_{(Ca^{2+})} + 2\lambda^\circ_{(F^-)} = (104 + 2\times48)\times10^{-4}\text{ S m}^2\text{ mol}^{-1} = 200\times10^{-4}\text{ S m}^2\text{ mol}^{-1}$$

For saturated solution of sparingly soluble salt, $\Lambda_m \approx \Lambda^\circ_m$. Also, $\Lambda_m = \kappa/c$

$$\therefore \qquad c = \frac{k}{\Lambda_m} = \frac{4 \cdot 05 \times 10^{-3}\ \text{S m}^{-1}}{200 \times 10^{-4}\ \text{S m}^2\ \text{mol}^{-1}} = 2 \cdot 025 \times 10^{-1}\ \text{mol m}^{-3} = 2 \cdot 025 \times 10^{-4}\ \text{mol dm}^{-3}$$

Hence, from Eq. (*i*), $K_{sp} = 4c^3 = 4(2 \cdot 025 \times 10^{-4}\ \text{mol dm}^{-3})^3 = \mathbf{3 \cdot 32 \times 10^{-11}\ mol^3\ dm^{-9}}$