Problem 10-12 Conductivity, molar conductivity, dissociation constant

420 cm^3 of ammonia at the temperature of 25 °C and pressure of 100.7 kPa was dissolved in 2 dm^3 of water (conductivity $5.3\cdot10^{-4}$ S m^{-1}). At these conditions the ammonia can be taken as an ideal gas. The conductivity of the resulting solution was $1.095\cdot10^{-2}$ S m^{-1}. Calculate the dissociation constant of ammonia in aqueous solution (standard state infinite dilution, c^{st} = 1 mol dm^{-3}, activity coefficients for all species can be taken as equal to one). Limiting molar conductivities:

$$\lambda^\infty(NH_4^+) = 0.00737\ \mathrm{S\ m^2\ mol^{-1}}\ ,\ \lambda^\infty(OH^-) = 0.01976\ \mathrm{S\ m^2\ mol^{-1}}.$$

[$K = 1.81\cdot10^{-5}$ ($c_0 = 8.531\cdot10^{-3}$ mol dm^{-3}, $\alpha = 0.045$)]

Solution:

$$\left.\begin{aligned} p &= 100.7\ \mathrm{kPa} \\ T &= 298.15\ \mathrm{K} \\ V_{NH_3} &= 420\ \mathrm{cm^3} \end{aligned}\right\} n_{NH_3} = \frac{pV_{NH_3}}{\boldsymbol{RT}} = \frac{100.7\cdot420\cdot10^{-3}}{8.314\cdot298.15} = 17.062\cdot10^{-3}\ \mathrm{mol}\ \ \text{dissolved in 2 dm}^3\text{ of water}$$

Initial concentration of the solution: $c_0 = \dfrac{n_{NH_3}}{V_{\text{water}}} = \dfrac{17.062\cdot10^{-3}}{2} = 8.531\cdot10^{-3}\ \mathrm{mol\ dm^{-3}}$

Disociation constant apply for the reaction

$$NH_3 + H_2O = NH_4^+ + OH^-$$

$$K = \frac{a_{NH_4^+}\cdot a_{OH^-}}{a_{NH_3}} = \frac{\gamma_+\cdot c_{NH_4^+}\cdot\gamma_-\cdot c_{OH^-}}{\gamma_{NH_3}\cdot c_{NH_3}}\cdot\frac{1}{c^{st}} = \frac{\gamma_\pm^2\cdot c_{NH_4^+}\cdot c_{OH^-}}{c_{NH_3}\cdot c^{st}}$$

$$= \frac{\gamma_\pm^2\cdot(c_0\cdot\alpha)^2}{c_0\cdot(1-\alpha)}\quad ,\quad \gamma_{NH3} = 1,\ \gamma_\pm = 1,\ \ c^{st} = 1\ \mathrm{mol\ dm^{-3}}$$

Balance:
$$c_{NH_3} = c_0\cdot(1-\alpha)$$
$$c_{NH_4^+} = c_0\cdot\alpha$$
$$c_{OH^-} = c_0\cdot\alpha$$
$$\alpha = \frac{\lambda}{\lambda^\infty}\quad ,\quad \lambda = \frac{\kappa_{\text{solution}} - \kappa_{\text{water}}}{c_0\cdot10^3}\qquad (c_0\ \text{- initial concentration of the solution in mol dm}^{-3})$$

κ_{water} = $5.3\cdot10^{-4}$ S m^{-1}
κ_{solution} = $1.095\cdot10^{-2}$ S m^{-1}

$\lambda^\infty(NH_4^+)$ = 0.00737 S m^2 mol^{-1} , $\lambda^\infty(OH^-)$ = 0.01976 S m^2 mol^{-1}.

$$\lambda^\infty = \lambda^\infty_{NH_4^+} + \lambda^\infty_{OH^-} = 0.00737 + 0.01976 = 0.02713\ \ \mathrm{S\,m^2\ mol^{-1}}$$

$$\lambda = \frac{\kappa_{\text{solution}} - \kappa_{\text{water}}}{c_0\cdot10^3} = \frac{1.095\cdot10^{-2} - 5.3\cdot10^{-4}}{8.531\cdot10^{-3}\cdot10^3} = 1.221427\cdot10^{-3}\ \ \mathrm{S\,m^2\ mol^{-1}}$$

$$\alpha = \frac{1.221427\cdot10^{-3}}{0.02713} = 0.04502$$

$$K = \frac{c_0\cdot\alpha^2}{(1-\alpha)} = \frac{8.531\cdot10^{-3}\cdot(0.04502)^2}{1-0.04502} = 1.8105\cdot10^{-5}$$