

Problem 10-12 Conductivity, molar conductivity, dissociation constant

420 cm³ of ammonia at the temperature of 25°C and pressure of 100.7 kPa was dissolved in 2 dm³ of water (conductivity 5.3·10⁻⁴ S m⁻¹). At these conditions the ammonia can be taken as an ideal gas. The conductivity of the resulting solution was 1.095·10⁻² S m⁻¹. Calculate the dissociation constant of ammonia in aqueous solution (standard state infinite dilution, $c^{\text{st}} = 1 \text{ mol dm}^{-3}$, activity coefficients for all species can be taken as equal to one). Limiting molar conductivities:

$$\lambda^{\infty}(\text{NH}_4^+) = 0.00737 \text{ S m}^2 \text{ mol}^{-1}, \quad \lambda^{\infty}(\text{OH}^-) = 0.01976 \text{ S m}^2 \text{ mol}^{-1}.$$

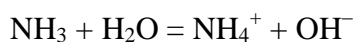
$$[K = 1.81 \cdot 10^{-5} \text{ (} c_0 = 8.531 \cdot 10^{-3} \text{ mol dm}^{-3}, \alpha = 0.045)]$$

Solution:

$$\left. \begin{array}{l} p = 100.7 \text{ kPa} \\ T = 298.15 \text{ K} \\ V_{\text{NH}_3} = 420 \text{ cm}^3 \end{array} \right\} n_{\text{NH}_3} = \frac{pV_{\text{NH}_3}}{RT} = \frac{100.7 \cdot 420 \cdot 10^{-3}}{8.314 \cdot 298.15} = 17.062 \cdot 10^{-3} \text{ mol dissolved in 2 dm}^3 \text{ of water}$$

$$\text{Initial concentration of the solution: } c_0 = \frac{n_{\text{NH}_3}}{V_{\text{water}}} = \frac{17.062 \cdot 10^{-3}}{2} = 8.531 \cdot 10^{-3} \text{ mol dm}^{-3}$$

Dissociation constant apply for the reaction



$$\begin{aligned} K &= \frac{a_{\text{NH}_4^+} \cdot a_{\text{OH}^-}}{a_{\text{NH}_3}} = \frac{\gamma_+ \cdot c_{\text{NH}_4^+} \cdot \gamma_- \cdot c_{\text{OH}^-}}{\gamma_{\text{NH}_3} \cdot c_{\text{NH}_3}} \cdot \frac{1}{c^{\text{st}}} = \frac{\gamma_{\pm}^2 \cdot c_{\text{NH}_4^+} \cdot c_{\text{OH}^-}}{c_{\text{NH}_3} \cdot c^{\text{st}}} \\ &= \frac{\gamma_{\pm}^2 \cdot (c_0 \cdot \alpha)^2}{c_0 \cdot (1 - \alpha)} \quad , \quad \gamma_{\text{NH}_3} = 1, \gamma_{\pm} = 1, c^{\text{st}} = 1 \text{ mol dm}^{-3} \end{aligned}$$

$$\text{Balance: } c_{\text{NH}_3} = c_0 \cdot (1 - \alpha)$$

$$c_{\text{NH}_4^+} = c_0 \cdot \alpha$$

$$c_{\text{OH}^-} = c_0 \cdot \alpha$$

$$\alpha = \frac{\lambda}{\lambda^{\infty}} \quad , \quad \lambda = \frac{\kappa_{\text{solution}} - \kappa_{\text{water}}}{c_0 \cdot 10^3} \quad (c_0 - \text{initial concentration of the solution in mol dm}^{-3})$$

$$\kappa_{\text{water}} = 5.3 \cdot 10^{-4} \text{ S m}^{-1}$$

$$\kappa_{\text{solution}} = 1.095 \cdot 10^{-2} \text{ S m}^{-1}$$

$$\lambda^{\infty}(\text{NH}_4^+) = 0.00737 \text{ S m}^2 \text{ mol}^{-1}, \quad \lambda^{\infty}(\text{OH}^-) = 0.01976 \text{ S m}^2 \text{ mol}^{-1}.$$

$$\lambda^{\infty} = \lambda_{\text{NH}_4^+}^{\infty} + \lambda_{\text{OH}^-}^{\infty} = 0.00737 + 0.01976 = 0.02713 \text{ S m}^2 \text{ mol}^{-1}$$

$$\lambda = \frac{\kappa_{\text{solution}} - \kappa_{\text{water}}}{c_0 \cdot 10^3} = \frac{1.095 \cdot 10^{-2} - 5.3 \cdot 10^{-4}}{8.531 \cdot 10^{-3} \cdot 10^3} = 1.221427 \cdot 10^{-3} \text{ S m}^2 \text{ mol}^{-1}$$

$$\alpha = \frac{1.221427 \cdot 10^{-3}}{0.02713} = 0.04502$$

$$K = \frac{c_0 \cdot \alpha^2}{(1 - \alpha)} = \frac{8.531 \cdot 10^{-3} \cdot (0.04502)^2}{1 - 0.04502} = 1.8105 \cdot 10^{-5}$$