Problem 10-08 Conductivity, molar conductivity of sparingly soluble salts

The resistance of the conductivity cell filled with KCl solution (molality 0.02 mol kg^{-1}) at 25 °C is 197 Ω. This solution has the conductivity of 0.2765 S m^{-1}. The resistance of the same cell filled with saturated solution of strontium sulphate was 3663 Ω. The conductivity of water used to these measurements was $1.8 \cdot 10^{-4}$ S m^{-1}. Use these data to determination the solubility product of strontium sulphate (standard state infinite dilution, $c^{st} = 1$ mol dm^{-3}) under the assumption that the activities can be replaced by relative concentrations. Limiting molar conductivities of ions are:

$$\lambda^{\infty}_{Sr^{2+}} = 0.0119 \text{ S m}^2 \text{ mol}^{-1}; \quad \lambda^{\infty}_{SO_4^{2-}} = 0.01596 \text{ S m}^2 \text{ mol}^{-1}$$

$[K_S = 2.78 \cdot 10^{-7}]$

Solution:

$SrSO_4 = Sr^{2+} + SO_4^{2-}$

$c_{SrSO4} = c_{SO4^{2-}} = c_{Sr^{2+}}$

$$K_S = a_{Sr^{2+}} \cdot a_{SO_4^{2-}} = \gamma_+ \cdot \frac{c_{Sr^{2+}}}{c^{st}} \cdot (\gamma_- \cdot \frac{c_{SO_4^{2-}}}{c^{st}}) = \gamma_\pm^2 \cdot c^2_{SrSO_4} \quad ; \quad \gamma_\pm = 1$$

Calculation of the concentration of saturated $SrSO_4$ solution from the conductivity:

$R_{KCl} = 197\ \Omega$, $\kappa_{KCl} = 0.2765$ S m^{-1}

$R = 3663\ \Omega$

$\kappa_{water} = 1.8 \cdot 10^{-4}$ S m^{-1}

$$\kappa_{solution} \cdot R = \kappa_{KCl} \cdot R_{KCl}$$

$$\kappa_{solution} = \frac{197 \cdot 0,2765}{3663} = 0.0148705 \text{ S m}^{-1}$$

$$\kappa_{SrSO4} = \kappa_{solution} - \kappa_{water} = 0.0148705 - 0.00018 = 0.0146905 \text{ S m}^{-1}$$

$$\lambda_{SrSO_4} \doteq \lambda^{\infty}_{SrSO_4} = \frac{\kappa_{SrSO_4}}{c_{SrSO_4}} = \lambda^{\infty}_{Sr^{2+}} + \lambda^{\infty}_{SO_4^{2-}} = 0.0119 + 0.01596 = 0.02786 \text{ S m}^2 \text{ mol}^{-1}$$

$$c_{SrSO4} = \frac{\kappa_{SrSO_4}}{\lambda^{\infty}_{SrSO_4}} = \frac{0.0146905}{0.02786} = 0.5273 \text{ mol m}^{-3} = 5.273 \cdot 10^{-4} \text{ mol dm}^{-3}$$

$$\left[\frac{\text{S m}^{-1}}{\text{S m}^2 \text{ mol}^{-1}} = \text{mol m}^{-3} \right]$$

Solubility product:

$$K_S = \gamma_\pm^2 \cdot c^2_{SrSO_4} = 1 \cdot (5.273 \cdot 10^{-4})^2 = 2.78 \cdot 10^{-7}$$