Problem 10-07 Conductivity, molar conductivity of sparingly soluble salts

The conductivity of saturated lead iodide solution at the temperature of 18 °C was found to be $3.742 \cdot 10^{-2}$ S m^{-1}, the conductivity of the water used for conductivity measurements was $1.8 \cdot 10^{-4}$ S m^{-1}. Calculate the solubility product of PbI_2 for the standard state of infinite dilution, c^{st} = 1 mol dm^{-3}. You can assume that activities can be replaced by relative concentrations. Limiting molar conductivities of ions are λ^{∞} (Pb^{2+}) = 0.0139 S m^2 mol^{-1} , λ^{∞} (I^-) = 0.00769 S m^2 mol^{-1}.

[K_S (PbI_2) = $8.23 \cdot 10^{-9}$]

Solution:

$PbI_2 = Pb^{2+} + 2\ I^-$

$c_{PbI2} = 2\ c_{I^-} = c_{Pb^{2+}}$

c^{st} = 1 mol dm^{-3}; $\gamma_{\pm} = 1$

$$K_S = a_{Pb^{2+}} \cdot a_{I^-}^2 = \gamma_+ \cdot \frac{c_{Pb^{2+}}}{c^{st}} \cdot \left(\gamma_- \cdot \frac{c_{I^-}}{c^{st}}\right)^2 = \gamma_{\pm}^3 \cdot 4 \cdot c_{PbI_2}^3$$

Calculation of the concentration of the saturated solution:

$\kappa_{solution} = 4.32 \cdot 10^{-2}$ S m^{-1},

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

$\kappa_{PbI2} = \kappa_{solution} - \kappa_{water} = 3.742 \cdot 10^{-2} - 1.8 \cdot 10^{-4} = 3.724 \cdot 10^{-2}$ S m^{-1}

λ^{∞} (Pb^{2+}) = 0.0139 S m^2 mol^{-1}

λ^{∞} (I^-) = 0.00769 S m^2 mol^{-1}

$\lambda^{\infty}_{PbI_2} = \lambda^{\infty}_{Pb^{2+}} + 2\ \lambda^{\infty}_{I^-} = 0.0139 + 2 \cdot\ 0.00769 = 0.02928$ S m^2 mol^{-1}

$$\lambda_{PbI_2} \doteq \lambda^{\infty}_{PbI_2} = \frac{\kappa_{PbI_2}}{c_{PbI_2}} \quad \Rightarrow \quad c_{PbI_2} = \frac{\kappa_{PbI_2}}{\lambda^{\infty}_{PbI_2}} = \frac{0.03724}{0.02928} = 1.27186 \text{ mol m}^{-3}$$

$= 1.27186 \cdot 10^{-3}$ mol dm^{-3}

Solubility product:

$K_S = 4 \cdot (1.27186 \cdot 10^{-3})^3 = 8.23 \cdot 10^{-9}$