Problem 9-04 Heterogeneous ionic equilibria – solubility product, mean activity coefficient, Debye-Hückel equation

In 1300 cm^3 of saturated lead iodide solution at 26 °C was found 0.905 g of PbI_2 (M = 461 g mol^{-1}). Calculate the solubility product of lead iodide (standard state of infinite dilution, c^{st} = 1 mol dm^{-3}). To determine the mean activity coefficient use the Debye-Hückel relation (A = 1.175 $dm^{3/2}$ $mol^{-1/2}$).

[$K_S = 8.84 \cdot 10^{-9}$]

Solution:

V = 1.3 dm^3
m_{PbI_2} = 0.905 g
M = 461 g mol^{-1}

$$\text{Solubility} = (c_{PbI_2})_{exp} = \frac{m_{PbI_2} / M}{V} = \frac{0.905/461}{1.3} = 1.51 \cdot 10^{-3} \text{ mol dm}^{-3}$$

PbI_2 (s) = Pb^{2+} + 2 I^-

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

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

$\gamma_+^2 \cdot \gamma_-^{} = \gamma_\pm^3$, c^{st} = 1 mol dm^{-3}

$$I = \tfrac{1}{2} \cdot (c_{Pb^{2+}} \cdot 2^2 + c_{I^-} \cdot 1^2) = \tfrac{1}{2} \cdot (4\,c + 2\,c) = 3\,c = 3 \cdot 1.51 \cdot 10^{-3} = 4.53 \cdot 10^{-3} \text{ mol dm}^{-3}$$

$0.001 < I < 0.1$, pro 25°C A = 1.175 $dm^{3/2}$ $mol^{-1/2}$

$$\ln \gamma_\pm = -\frac{|z_K \cdot z_A| \cdot A \cdot \sqrt{I}}{1 + \sqrt{I}} = -\frac{2 \cdot 1 \cdot 1.172 \cdot \sqrt{4.53 \cdot 10^{-3}}}{1 + \sqrt{4.53 \cdot 10^{-3}}} = -0.1478$$

$\gamma_\pm$ = 0.8626

$K_S = 0.8626^3 \cdot 4 \cdot (1.51 \cdot 10^{-3})^3 = 8.84 \cdot 10^{-9}$