Problem 9-06 Heterogeneous ionic equilibria – solubility in the presence of other ions

The solubility product of lead chloride at 25 °C has the value of $2 \cdot 10^{-5}$ (standard state of infinite dilution, $c^{st} = 1$ mol dm^{-3}). Calculate the solubility of $PbCl_2$ in pure water and compare it with its solubility in NaCl solution (0.1 mol dm^{-3}).

[solubility in water: 0.017 mol dm^{-3}, solubility in NaCl is by one order lower, 0.002 mol dm^{-3}]

Solution:

$PbCl_2\,(s) = Pb^{2+} + 2\,Cl^-$

$c_{Pb^{2+}} = c_{PbCl_2}$

$c_{Cl^-} = 2\,c_{PbCl_2}$

$$K_S = a_{Pb^{2+}} \cdot a_{Cl^-}^2 = \gamma_+ \cdot \frac{c_{Pb^{2+}}}{c^{st}} \cdot \left(\gamma_- \cdot \frac{c_{Cl^-}}{c^{st}} \right)^2 = \gamma_\pm^3 \cdot \frac{c_{PbCl_2}}{c^{st}} \cdot \left(\frac{2\,c_{PbCl_2}}{c^{st}} \right)^2 = \gamma_\pm^3 \cdot 4 \cdot \left(\frac{c_{PbCl_2}}{c^{st}} \right)^3$$

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

1. $c_0 = c_{PbCl_2}$ – solubility in pure water

   $c_{Pb^{2+}} = c_0$

   $c_{Cl^-} = 2\,c_0$

   $$K_S = 4 \cdot c_0^3 \quad \Rightarrow \quad c_0 = \left(\frac{K_S}{4} \right)^{1/3} = \left(\frac{2 \cdot 10^{-5}}{4} \right)^{1/3} = 0.0171 \text{ mol dm}^{-3}$$

2. In the presence of NaCl

   $PbCl_2\,(s) = Pb^{2+} + 2\,Cl^-$

   $NaCl = Na^+ + Cl^-$

$c_{Pb^{2+}} = c_{PbCl_2} = c_1$

$c_{Cl^-} = 2\,c_{PbCl_2} + c_{NaCl} = 2\,c_1 + c_{NaCl}$

$$K_S = c_{Pb^{2+}} \cdot c_{Cl^-}^2 = c_{PbCl_2} \cdot (2\,c_{PbCl_2} + c_{NaCl})^2 \doteq c_{PbCl_2} \cdot c_{NaCl}^2 = c_1 \cdot c_{NaCl}^2$$

Approximation: $2\,c_{PbCl_2} << c_{NaCl}$

$$c_1 \doteq \frac{K_S}{c_{NaCl}^2} = \frac{2 \cdot 10^{-5}}{0.1^2} = 0.002 \text{ mol dm}^{-3}$$