Problem 9-01 Heterogeneous ionic equilibria

The solubility product of silver chloride at 20 °C has the value of $1.26 \cdot 10^{-10}$ and that of calcium fluoride at the same temperature is $3.4 \cdot 10^{-11}$ (both for the standard state of infinite dilution, $c^{st} = 1$ mol dm^{-3}). Which of the previously mentioned substances is more soluble in water? Suppose that activities can be put equal to concentration.

[$c_{AgCl} = 1.122 \cdot 10^{-5}$ mol dm^{-3}, $c_{CaF2} = 2.041 \cdot 10^{-4}$ mol dm^{-3}]

Solution:

$AgCl\,(s) = Ag^+ + Cl^-$; solubility of AgCl = c_{AgCl}

$c_{Ag+}\ (= c_+) = c_{AgCl}$, $c_{Cl-}\ (= c_-) = c_{AgCl}$

$K_S(AgCl) = a_+ \cdot a_- = [\gamma_+ \cdot (c_+/c^{st})] \cdot [\gamma_- \cdot (c_-/c^{st}]$

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

$K_S(AgCl) = c_+ \cdot c_- = c_{AgCl}^2$

$c_{AgCl} = K_S^{1/2} = (1.26 \cdot 10^{-10})^{1/2} = 1.122_5 \cdot 10^{-5}$ mol dm^{-3}

$CaF_2\,(s) = Ca^{2+} + 2\,F^-$; solubility of CaF_2 = c_{CaF_2}

$c_{Ca2+}\ (= c_+) = c_{CaF_2}$, $c_{F-}\ (= c_-) = 2\,c_{CaF_2}$

$$K_S(CaF_2) = a_{Ca^+} \cdot a_{F^-}^2 = \gamma_+ \cdot \frac{c_{Ca^+}}{c^{st}} \cdot \left(\gamma_- \cdot \frac{c_{F^-}}{c^{st}} \right)^2 = \gamma_\pm^3 \cdot \frac{c_{CaF_2}}{c^{st}} \cdot \left(\frac{2\,c_{CaF_2}}{c^{st}} \right)^2 = \gamma_\pm^3 \cdot 4 \left(\frac{c_{CaF_2}}{c^{st}} \right)^3$$

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

$$c_{CaF_2} = \sqrt[3]{\frac{K_S(CaF_2)}{4}} = \sqrt[3]{\frac{3.4 \cdot 10^{-11}}{4}} = 2.041 \cdot 10^{-5} \text{ mol dm}^{-3}$$