Problem 9-02 Heterogeneous ionic equilibria – mean activity coefficient

The concentration of the saturated solution at 20 °C was found to be $2.45 \cdot 10^{-4}$ mol dm^{-3}. Calculate the mean activity coefficient of CaF_2 in the saturated solution. Compare the result with the previous problem and find out if the assumption, that the mean activity coefficient is equal to one, made there, was justified.

[$\gamma_\pm = 0.833 \neq 1$; the assumption was not justified]

Solution:

$CaF_2\,(s) = Ca^{2+} + 2\,F^-$; solubility of $CaF_2 = c_{CaF_2} = 2.45 \cdot 10^{-4}$ mol dm^{-3}

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

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

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

$$\gamma_\pm = \frac{1}{c_{CaF_2}} \cdot \sqrt[3]{\frac{K_S(CaF_2)}{4}} = \frac{1}{2.45 \cdot 10^{-4}} \cdot \sqrt[3]{\frac{3.4 \cdot 10^{-11}}{4}} = 0.833$$