

Taken from Daniel C. Harris, *Quantitative Chemical Analysis*, 6th ed., New York: W. H. Freeman, 2003.

8-3 Using Activity Coefficients

We now examine illustrations of the use of activity coefficients in equilibrium calculations. The general prescription is trivial: *Write each equilibrium constant with activities in place of concentrations. Use the ionic strength of the solution to find the activity coefficients.*

A Simple Solubility Problem

In the first example, we calculate the concentration of Ca^{2+} in a 0.050 M solution of NaClO_4 saturated with CaF_2 . The relevant equilibrium is



The equilibrium expression is set up with the aid of a little table:

	$\text{CaF}_2(s) \rightleftharpoons \text{Ca}^{2+} + 2\text{F}^-$		
Initial concentration	solid	0	0
Final concentration	solid	x	$2x$

$$\begin{aligned} K &= \mathcal{A}_{\text{Ca}^{2+}} \mathcal{A}_{\text{F}^-}^2 = [\text{Ca}^{2+}] \gamma_{\text{Ca}^{2+}} [\text{F}^-]^2 \gamma_{\text{F}^-}^2 \\ &= [x] \gamma_{\text{Ca}^{2+}} [2x]^2 \gamma_{\text{F}^-}^2 \end{aligned} \quad (8-9)$$

To find values of γ for Equation 8-9, we first calculate the ionic strength, which is due to dissolved NaClO_4 and the dissolved CaF_2 . However, K_{sp} for CaF_2 is small, so we start by guessing that the contribution of CaF_2 to the ionic strength will be negligible. The ionic strength of 0.050 M NaClO_4 is 0.050 M. At $\mu = 0.050$ M in Table 8-1, we find $\gamma_{\text{Ca}^{2+}} = 0.485$ and $\gamma_{\text{F}^-} = 0.81$. Substituting into Equation 8-9 gives

$$\begin{aligned} 3.9 \times 10^{-11} &= [x](0.485)[2x]^2(0.81)^2 \\ x &= [\text{Ca}^{2+}] = 3.1 \times 10^{-4} \text{ M} \end{aligned}$$

Our assumption was correct; the contribution of CaF_2 to the ionic strength ($3 \times 3.1 \times 10^{-4} = 9.3 \times 10^{-4}$ M) is negligible compared with the ionic strength from 0.050 M NaClO_4 .

The Common Ion Effect

Now let's find the concentration of Ca^{2+} in 0.050 M NaF saturated with CaF_2 . The ionic strength is again 0.050 M, this time from NaF .

	$\text{CaF}_2(s) \rightleftharpoons \text{Ca}^{2+} + 2\text{F}^-$		
Initial concentration	solid	0	0.050
Final concentration	solid	x	$2x + 0.050$

Assuming that $2x \ll 0.050$, we solve the problem as follows:

$$\begin{aligned} K_{\text{sp}} &= [\text{Ca}^{2+}] \gamma_{\text{Ca}^{2+}} [\text{F}^-]^2 \gamma_{\text{F}^-}^2 \\ 3.9 \times 10^{-11} &= (x)(0.485)(0.050)^2(0.81)^2 \\ x &= [\text{Ca}^{2+}] = 4.9 \times 10^{-8} \quad (\text{Yes! } 2x \ll 0.050) \end{aligned}$$

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Note that both $[\text{F}^-]$ and γ_{F^-} are squared.

Question What is the value of μ , including the contribution of CaF_2 ?

Question Why is the solubility of CaF_2 lower in NaF solution than in NaClO_4 solution?

Be sure to turn over the page!

A Problem That Requires an Iterative Solution

As a final example, we calculate the solubility of LiF in distilled water:



The ionic strength is determined by the concentration of dissolved LiF. But we do not know that concentration. As a first approximation, we calculate $[\text{Li}^+]$ and $[\text{F}^-]$ by neglecting activity coefficients. Calling x_1 our first approximation for $[\text{Li}^+]$ (and $[\text{F}^-]$), we write

$$K_{\text{sp}} \approx [\text{Li}^+][\text{F}^-] = x_1^2 \Rightarrow x_1 = [\text{Li}^+] = [\text{F}^-] = 0.041$$

For a second approximation, we assume that $\mu = 0.041$ M, which is the result of our first approximation. Interpolating in Table 8-1 gives $\gamma_{\text{Li}^+} = 0.851$ and $\gamma_{\text{F}^-} = 0.830$ for $\mu = 0.041$ M. Putting these values into the expression for K_{sp} gives

$$\begin{aligned} K_{\text{sp}} &= [\text{Li}^+]\gamma_{\text{Li}^+}[\text{F}^-]\gamma_{\text{F}^-} \\ &= [x_2](0.851)[x_2](0.830) \Rightarrow x_2 = 0.049 \text{ M} \end{aligned}$$

As a third approximation, we assume that $\mu = 0.049$ M. Using this new ionic strength to find new values of activity coefficients in Table 8-1 gives

$$K_{\text{sp}} = [x_3](0.837)[x_3](0.812) \Rightarrow x_3 = 0.050 \text{ M}$$

This is a method of *successive approximations*. Each cycle of calculations is called one *iteration*.

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As LiF dissolves, it increases the ionic strength and increases its own solubility.

Using $\mu = 0.050$ M gives a fourth approximation:

$$K_{\text{sp}} = [x_4](0.835)[x_4](0.81) \Rightarrow x_4 = 0.050 \text{ M}$$

The fourth answer is the same as the third answer. We have reached a self-consistent result, which must therefore be correct.