

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  $\text{Ca}^{2+}$  in a 0.050 M solution of  $\text{NaClO}_4$  saturated with  $\text{CaF}_2$ . 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	$x$	$2x$

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

To find values of  $\gamma$  for Equation 8-9, we first calculate the ionic strength, which is due to dissolved  $\text{NaClO}_4$  and the dissolved  $\text{CaF}_2$ . However,  $K_{\text{sp}}$  for  $\text{CaF}_2$  is small, so we start by guessing that the contribution of  $\text{CaF}_2$  to the ionic strength will be negligible. The ionic strength of 0.050 M  $\text{NaClO}_4$  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

$$3.9 \times 10^{-11} = [x](0.485)[2x]^2(0.81)^2$$

$$x = [\text{Ca}^{2+}] = 3.1 \times 10^{-4} \text{ M}$$

Our assumption was correct; the contribution of  $\text{CaF}_2$  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  $\text{NaClO}_4$ .

#### The Common Ion Effect

Now let's find the concentration of  $\text{Ca}^{2+}$  in 0.050 M  $\text{NaF}$  saturated with  $\text{CaF}_2$ . The ionic strength is again 0.050 M, this time from  $\text{NaF}$ .

	$\text{CaF}_2(s) \rightleftharpoons \text{Ca}^{2+} + 2\text{F}^-$		
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:

$$K_{\text{sp}} = [\text{Ca}^{2+}] \gamma_{\text{Ca}^{2+}} [\text{F}^-]^2 \gamma_{\text{F}^-}^2$$

$$3.9 \times 10^{-11} = (x)(0.485)(0.050)^2(0.81)^2$$

$$x = [\text{Ca}^{2+}] = 4.9 \times 10^{-8} \quad (\text{Yes! } 2x \ll 0.050)$$

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

**Question** What is the value of  $\mu$ , including the contribution of  $\text{CaF}_2$ ?

**Question** Why is the solubility of  $\text{CaF}_2$  lower in  $\text{NaF}$  solution than in  $\text{NaClO}_4$  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  $K_{\text{sp}}$  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.