Ionic strength and non-ideal solutions

ESS 312 - Spring 2011

Let’s look at the effect of ionic strength on our estimate of gypsum solubility.

Remember that, by assuming \( a_i = m_i \) we estimated that a saturated solution of gypsum should contain \( m_{Ca^{2+}} = m_{SO_4^{2-}} = 0.005 \text{ mol/kg} \).

We can use this as a starting point to estimate the ionic strength of the solution, and check whether our assumption of ideality was valid:

\[
I = \frac{1}{2} \sum i z_i^2 = \frac{1}{2} (0.005 \times 4 + 0.005 \times 4) = 0.02 \tag{1}
\]

At 25\(^\circ\)C, the Debye-Huckel constants are:

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>( a_{0, Ca^{2+}} )</th>
<th>( a_{0, SO_4^{2-}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5085</td>
<td>0.3281 \times 10^{-8}</td>
<td>6 \times 10^8</td>
<td>4 \times 10^8</td>
</tr>
</tbody>
</table>

Hence:

\[
\log_{10} \gamma_{Ca^{2+}} = \frac{-A z_{Ca^{2+}}^2 \sqrt{I}}{1 + B a_{0, Ca^{2+}} \sqrt{I}} = -0.225 \tag{2}
\]

giving:

\[
\gamma_{Ca^{2+}} = 0.596 \tag{3}
\]
\[
\gamma_{SO_4^{2-}} = 0.572 \tag{4}
\]

Now we can go back and re-write the equilibrium constant expression:

\[
K_{sp} = a_{Ca^{2+}} \times a_{SO_4^{2-}} = (0.596 \times m_{Ca^{2+}}) \times (0.572 \times m_{SO_4^{2-}}) = 10^{-4.61} \tag{5}
\]

Stoichiometry still requires \( m_{Ca^{2+}} = m_{SO_4^{2-}} \), hence:

\[
m_{Ca^{2+}} = \sqrt{\frac{10^{-4.61}}{0.596 \times 0.572}} = 0.0085 = m_{SO_4^{2-}} \tag{6}
\]

Which is 70% higher than we (incorrectly) estimated by assuming the solution would be ideal. Unfortunately we’re not done yet, because ...

If \( m_{Ca^{2+}} = m_{SO_4^{2-}} = 0.0085 \text{ mol/kg} \), then \( I = 0.034 \), and \( \gamma_{Ca^{2+}} \) and \( \gamma_{SO_4^{2-}} \) should be lower. Clearly, we need to solve this iteratively: Determine the ionic strength, update the activity coefficients and then re-calculate the concentrations. Repeat with each new set of concentrations, until the values converge, at:

\[
I = 0.04; \gamma_{Ca^{2+}} = 0.51; \gamma_{SO_4^{2-}} = 0.475; m_{Ca^{2+}} = m_{SO_4^{2-}} = 0.0101 \text{ mol/kg} \tag{7}
\]

The final concentrations are twice as high as our (erroneous) calculation assuming ideality.
Figure 1: Graph shows activity coefficients for various ions from Debye-Hückel theory. We will be concerned only with solutions of ionic strength \( \leq 0.1 \text{M/kg} \), where the activity-concentration relationships are not too complicated. The tables below give values for constants in the Debye-Hückel equation. All from: Garrels, RM and Christ CL, Solutions, minerals and equilibria. Harper and Row (1965).