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 $m_{Ca^{2+}} = m_{SO_4^{2-}} = 0.005$ 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:

$$I = \frac{1}{2} \sum m_i z_i^2 = \frac{1}{2}(0.005 \times 4 + 0.005 \times 4) = 0.02 \tag{1}$$

At $25°C$, the Debye-Huckel constants are:

A	B	$a_{0,Ca^{2+}}$	$a_{0,SO_4^{2-}}$
0.5085	0.3281×10^{-8}	6×10^8	4×10^8

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 $m_{Ca^{2+}} = m_{SO_4^{2-}} = 0.0085$ 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:

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

The final concentrations are twice as high as our (erroneous) calculation assuming ideality.
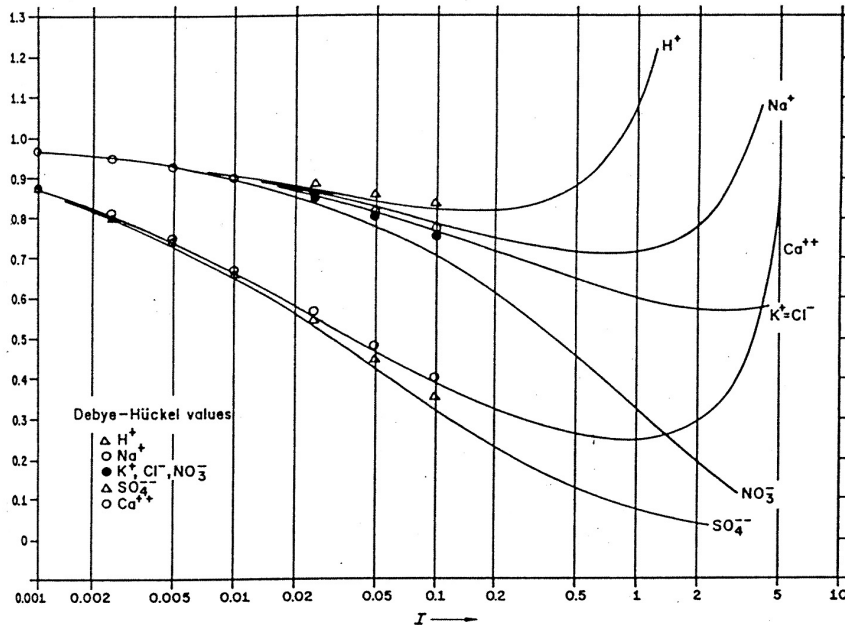
FIG. 2.15. Single ion activity coefficients vs. ionic strength for some common ions. Solid lines represent the values calculated by the mean salt method. Debye-Hückel values were calculated using equation (2.76), with $10^8/\mathring{a}_i = 9$ for H^+; 4 for Na^+; 3 for K^+, Cl^-, NO_3^-; 6 for Ca^{++}; and 4 for SO_4^{--}. The Debye-Hückel Y_i values for the monovalent ions converge, within experimental error, for $I < 0.01$.

TABLE 2.6. Values of Constants for Use in Debye-Hückel Equation (aqueous solution)

Temperature, °C	A	B ($\times 10^{-8}$)
0	0.4883	0.3241
5	0.4921	0.3249
10	0.4960	0.3258
15	0.5000	0.3262
20	0.5042	0.3273
25	0.5085	0.3281
30	0.5130	0.3290
35	0.5175	0.3297
40	0.5221	0.3305
45	0.5271	0.3314
50	0.5319	0.3321
55	0.5371	0.3329
60	0.5425	0.3338

SOURCE: G. G. Manov, R. G. Bates, W. J. Hamer, S. F. Acree, J. Am. Chem. Soc., 65, 1765 (1943).

TABLE 2.7. Values of d_i for Some Individual Ions in Aqueous Solutions

$\mathring{a}_i \times 10^8$	Ion
2.5	Rb^+, Cs^+, NH_4^+, Tl^+, Ag^+
3.0	K^+, Cl^-, Br^-, I^-, NO_3^-
3.5	OH^-, F^-, HS^-, BrO_3^-, IO_4^-, MnO_4^-
4.0–4.5	Na^+, HCO_3^-, $H_2PO_4^-$, HSO_3^-, Hg_2^{++}, SO_4^{--}, SeO_4^{--}, CrO_4^{--}, HPO_4^{--}, PO_4^{3-}
4.5	Pb^{++}, CO_3^{--}, SO_3^{--}, MoO_4^{--}
5.0	Sr^{++}, Ba^{++}, Ra^{++}, Cd^{++}, Hg^{++}, S^{--}, WO_4^{--}
6	Li^+, Ca^{++}, Cu^{++}, Zn^{++}, Sn^{++}, Mn^{++}, Fe^{++}, Ni^{++}, Co^{++}
8	Mg^{++}, Be^{++}
9	H^+, Al^{3+}, Cr^{3+}, trivalent rare earths
11	Th^{4+}, Zr^{4+}, Ce^{4+}, Sn^{4+}

SOURCE: Adapted from I. M. Klotz, Chemical Thermodynamics. Englewood Cliffs, N.J., Prentice-Hall, 1950, p. 331.

Figure 1: Graph shows activity coefficients for various ions from Debye-Huckel theory. We will be concerned only with solutions of ionic strength $\leq 0.1 M/kg$, where the activity-concentration relationships are not too complicated. The tables below give values for constants in the Debye-Huckel equation. All from: *Garrels, RM and Christ CL, Solutions, minerals and equilibria. Harper and Row (1965).*