On Solubility and Solubility Product Constants

Babcock and Marion (1) apparently misinterpreted my presentation (6) regarding ionic association and the ion activity solubility product constant \( K_{isp} \). Based on my demonstration of how it is possible to obtain two values of solubility product constant from solubility measurement with and without accounting for ion-pairing, they concluded that I believe in variable \( K_{isp} \)'s. This is not so, as I have stated in the same paper (p. 444) that the thermodynamic \( K_{isp} = \) constant. I also disagree with their implication that solubility studies are presently irrelevant because solubility constants can be calculated from thermodynamic data available in handbooks. Babcock and Marion showed that the stoichiometric constant \( K_1 \) is equal to the thermodynamic solubility constant \( K_2 \), but they did not demonstrate how the constants could be obtained experimentally, nor did their treatment relate directly to the calculation of \( K_2 \).

By using Babcock and Marion's conclusion that \( K_1 = K_2 \), and by relating \( M \) (stoichiometric or analytically measured concentration) and \( m \) (actual concentration of the ionic species) to \( \gamma_+ \) and \( f_+ \) (activity coefficients for the two types of systems defined), the relation of the different variables is \( \gamma_+ = f_+ = \alpha_+ \), where the exponent 2 is missing in their equation [4]; and, by introducing the degree of dissociation \( \alpha \) from their equation [19], where \( \gamma_+ = f_+ = \alpha_+ \), I arrive at \( f_+ = \alpha_+ \gamma_+ = \alpha_+ \). In an earlier report (7) we used a solubility product constant \( K'_1 = \alpha_+^{2+} \gamma_+^{2+} = [\text{Ca}_{2+} \text{SO}_4]_{aq} \) (or \( f_+ = \alpha_+ \gamma_+ = \alpha_+ \)). This also incorporated the essential features of Babcock and Marion's treatment. We further showed how \( \alpha, K_1 \) or \( K_2 \), and \( k \) (dissociation constant of \( \text{CaSO}_4 \)) could be determined simultaneously with the Ca-electrode.

The calculation of the solubility product constant \( K_2 \) by Babcock and Marion from the tabulated material needs elaboration also, particularly the free energy of formation for \( \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \), \( \Delta G^\circ_{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}} = -429.19 \text{ kcal} \). This value in Latimer's text (3) originated from Latimer, Hicks, and Schutz (4). It is based on \( \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \) solubility measurements with the stoichiometric solubility (\( M_+ = M_- = 0.0156 \)) and the activity coefficient for \( \text{Ca}^{2+} \) (\( \gamma_{\text{Ca}^{2+}} = 0.312 \) and letting \( \gamma_{\text{SO}_4^{2-}} = \gamma_{\text{Ca}^{2+}} \) obtained from other investigators. Their computation yielded \( K_1 = [0.0156 \times 0.312]^2 = 2.37 \times 10^{-5} \) or \( \Delta G^\circ_{\text{solution}} = 6.308 \text{ kcal} \). Note that the \( \gamma_{\text{Ca}^{2+}} \) value of Fosbinder (2) which Latimer et al. used did not include the \( \alpha \)-factor and also was based in part on the Debye-Huckel (DH) theory. Thus, we have an example of a stoichiometric measurement and DH activity coefficient combination being used simultaneously. Babcock and Marion objected to this method for getting \( K_2 \), and yet they used the tabulated constant derived from the DH theory and also accounted for a pair such as \( \text{HSO}_4^- \) and \( \text{CaSO}_4^0 \). In my opinion, Osborn's work is invaluable and not wasted effort as implied by Babcock and Marion and Osborn's experimental data and constant \( \alpha = 0.669 \) and \( f_+ = 0.492 \) which yields \( \gamma_{\text{Ca}^{2+}} = 0.312 \). Consequently, \( K_1 = (0.329 \times 1.51 \times 10^{-5})^2 \) which is essentially the same as their \( K_2 \).

An alternative method for computing from Moreno and Osborn's \( K_2 \) will also be demonstrated. The solution equilibrium for \( \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \) pairing is

\[
\text{CaSO}_4(\text{s}) = \text{Ca}^{2+} + \text{SO}_4^{2-} + \text{H}_2\text{O}^+ + 2\text{H}_2\text{O},
\]

where the equilibrium constant is \( K_{aq} \). Moreno and Osborn's \( K_2 = 2.45 \times 10^{-5} \) \( \times 10^{-3} \) \( \Delta G^\circ_{\text{CaSO}_4^0} = 312.6 \text{ kcal} \) and \( \Delta G^\circ_{\text{CaSO}_4^0} = 312.6 \text{ kcal} \), and the balanced mass equation,

\[
2[\text{CaSO}_4 \cdot 2\text{H}_2\text{O}(\text{s})] = \text{Ca}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) + 4\text{H}_2\text{O},
\]

the free energy of formation (\( \Delta G^\circ \)) is

\[
\Delta G^\circ_{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}} = (\Delta G^\circ_{\text{Ca}^{2+}} + \Delta G^\circ_{\text{SO}_4^{2-}} + \Delta G^\circ_{\text{H}_2\text{O}}^0 - 4\Delta G^\circ_{\text{solution}})/2 = -429.19 \text{ kcal}
\]

This \( \Delta G^\circ \) is the same as that listed by Latimer. Agreement appears to be fortuitous compared to the original value reported in the handbook.

Actually, when \( \Delta G^\circ_{\text{solution}} \) of 6.308 kcal for action \( \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \) = \( \text{Ca}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) + 4\text{H}_2\text{O} \), \( \Delta G^\circ \) is \( -429.21 \) instead of \(-429.19 \) kcal as Latimer's text (3).

The reader has the final decision concerning the usefulness of solubility studies. Many times it is not the constant per se which is valuable, but it is the theoretical and experimental approaches used in getting the constant that are invaluable. Because a number of authors does not confirm complete understanding of the particular subject and should not be used as a criterion for judging relevancy for conducting research.

Literature Cited