Le Chatelier's Principle, Solubility, and Deja Vu

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In recent years at least four substantial articles have appeared in this journal dealing with the application of Le Chatelier's principle to the prediction of the temperature dependency of solubility (1 - 4). The gist of these articles is that naive use of tabulated values of $\Delta H_{sol}°$ at infinite dilution in the van't Hoff relation can lead to errors, the proper value being $\Delta H_{sol}°$ for the saturated solution, which may differ in sign from the value at infinite dilution. In addition, when calculating $\Delta H_{sol}°$ for the saturated solution, one must take care to use the solid actually in equilibrium with the solution at that point. This is often a hydrate rather than the anhydrous solid taken from the shelf to make the solution in the first place.

In light of the interest shown in this subject and the space that has been devoted to it in the journal, I was struck by a strong sense of *deja vu* upon accidentally coming across the following statement in the 1895 English edition of Wilhelm Ostwald's *Outlines of General Chemistry* and thought it would be of interest to the readers of the journal as well (5):

> Attention should be paid to the fact that it is the sign of the heat of solution in the almost saturated solution which determines the sense of the change of solubility with temperature. Substances which dissolve to a large extent in water usually have their heat of solution smaller the more concentrated the solution becomes, and it is not impossible that such substances, having a small negative heat of solution in dilute solutions, may acquire a positive heat in more concentrated solutions, so that only the sign in the almost saturated solutions is of use in the application of the above principle [i.e., van't Hoff's relation].

Ostwald's books served as the prototypes for succeeding generations of "P Chem" texts and were, for the most part, based directly on the primary literature. Consequently, it is of interest to note that his caveat on the relationship between $\Delta H_{sol}°$ and the temperature dependency of solubility is already missing from most second generation texts, though many of these were written by his own students (6 - 8). Indeed, this example illustrates the fate of many discoveries on passing from the primary literature into the textbook literature. First generation texts are usually based on the primary literature and generally comment on difficulties and limitations. Succeeding generations, on the other hand, are based more and more on other textbooks and in the process gradually simplify and idealize things until, in some cases, they are simply incorrect and the difficulties and limitations must be recovered again from the primary literature - a recovery process in which the *Journal of Chemical Education* often plays an important role, as the above articles testify.

References and Notes

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Publication History

Published in *J. Chem. Educ.*, **1987**, *64*, 287.