

Procedure for the Calculation of the Gibbs Energies of Hydration for Volatile Solutes from Solubility Data

J.L. Alvarez and R.J. Fernandez-Prini^{C,S}

Comision Nacional de Energia Atomica, UAQ, Buenos Aires, Argentina
rfprini@cnea.gov.ar

The determination of the Gibbs energy of hydration $\Delta_{\text{hyd}}G_2^\infty$ of volatile nonpolar solutes is frequently accomplished through Henry's constant k_H which in turn, for gaseous solutes, is calculated with the solubility of the solutes. The solubility of nonpolar or slightly polar simple gases in water under ambient conditions and liquid-vapor coexistence has been determined experimentally with extreme precision. However when the solvent's vapour pressure is appreciable corrections for nonideality has to be taken into account and they become increasingly important as the critical temperature of water is approached.

In order to obtain $\Delta_{\text{hyd}}G_2^\infty$ at high temperatures, the experimentally measured solubility has to be processed by careful iterations that require the use of equations for model systems. We have employed a perturbation method to express the chemical potential of the solute and the corresponding equations for the partial molar volume at infinite dilution and the activity coefficient of a hard-sphere equivalent solute. The different steps in the complete procedure to calculate $\Delta_{\text{hyd}}G_2^\infty$ will be analyzed as well as the uncertainty generated on the final value.

If the gaseous solute is relatively soluble in water, e.g. CO_2 , even under ambient conditions the need to consider nonideality (solute's activity coefficient) will limit the possibility of accessing to $\Delta_{\text{hyd}}G_2^\infty$ using only solubility data.