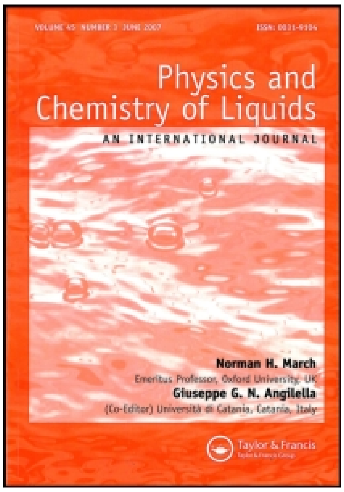

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Letter

Comment on "Solubility and Enhanced Tension of Solute in Solution"

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The paper, "Solubility and Enhanced Tension of Solute in Solution," by H. T. Hammel,[1] describes solution properties in terms of "tension" between solute molecules. While the utility of this approach over conventional thermodynamics is certainly debatable, this comment will deal primarily with the thermodynamic validity of several equations contained in that paper.

The difference in chemical potential between a pure solid and liquid at a particular temperature and pressure is correctly given in Eqs (9) and (10):

$$\mu_B^{l_0}(T, P) - \mu_B^{s_0}(T, P) = \int_T^{T_{Bm}^0} (\bar{S}_B^{l_0} - \bar{S}_B^{s_0})\,\mathrm{d}T \tag{9}$$

in which superscripts (l_0, s_0) refer to the pure liquid and solid, and T_{Bm}^0 is the melting point of the solid at the specified pressure. The integral of Eq. (9) must be evaluated at a constant value of the specified pressure (which also specifies T_{Bm}^0), since this equation is derived from the partial derivative of chemical potential with respect to temperature at constant pressure, and the equivalence of chemical potentials of solid and liquid in equilibrium. Equation (11) is also correct:

$$(\bar{S}_B^{l_0} - \bar{S}_B^{s_0}) = \Delta\bar{H}_B^{ls_0}/T \tag{11}$$

but only for equilibrium conditions of temperature and pressure defined by the Clapeyron Equation:

$$\mathrm{d}P/\mathrm{d}T = (\bar{S}_B^{lo} - \bar{S}_B^{so})/(\bar{V}_B^{lo} - \bar{V}_B^{so}) = (\bar{H}_B^{lo} - \bar{H}_B^{so})/T(\bar{V}_B^{lo} - \bar{V}_B^{so})$$

Thus, for even a small change of temperature, the validity of Eq. (11) requires a very large change of pressure because of the very small change of volume for the fusion process. Substitution of Eq. (11) into the integral of Eq. (9), which must be evaluated at constant pressure, violates the condition of validity of Eq. (11):

$$\mu_B^{lo}(T, P) - \mu_B^{so}(T, P) \neq \int_T^{T_{Bm}^0} (\Delta\bar{H}_B^{lso}/T)\,\mathrm{d}T \tag{12}$$

The correct form of Eq. (12) is:

$$\mu_B^{lo}(T, P) - \mu_B^{so}(T, P) = -T\int_{T_{Bm}^0}^{T} (\Delta\bar{H}_B^{lso}/T^2)\,\mathrm{d}T$$

with the enthalpy of fusion evaluated at the specified pressure, and varying only with temperature.

Equation (14) correctly describes the osmotic equilibrium condition for any component B as a pure liquid separated from a solution by a rigid membrane permeable only to B:

$$\mu_B^{l}(T, P, X_B^l) = \mu_B^{lo}(T, P - \pi_B) \tag{14}$$

The application of this equality to all partial molar quantities

$$\bar{Z}_B^{l}(T, P, X_B^l) = \bar{Z}_B^{lo}(T, P - \pi_B) \tag{14a}$$

is incorrect. Relationships between other partial molar properties must be based on partial differentiation of Eq. (14) with respect to temperature or pressure, while maintaining correctness of Eq. (14) or under the condition

$$\mathrm{d}\mu_B^{l}(T, P, X_B^l) = \mathrm{d}\mu_B^{lo}(T, P - \pi_B)$$

In the case of entropy, Eq. (14) is differentiated with respect to temperature at constant pressure and composition, thus requiring a change in the osmotic pressure;

$$\bar{S}_B^{l}(T, P, X_B^l) = \bar{S}_B^{lo}(T, P - \pi_B) + \bar{V}_B^{lo}(T, P - \pi_B)(\partial\pi_B/\partial T)_{P,X}$$

Application of Eq. (14a) to the partial molar entropy is then in error by the quantity,

$$\bar{V}_B^{lo}(T, P - \pi_B)(\partial\pi_B/\partial T)_{P,X}$$

This error can be calculated for the special case of an ideal solution of a solute B, with the pure liquid B having negligible coefficients of thermal expansion and isothermal compressibility. In this case,

$$\pi_B \bar{V}_B^{l\circ} = -RT\ln(X_B^l); \qquad \bar{V}_B^{l\circ}(\partial \pi_B/\partial T)_{P,X} = -R\ln(X_B^l)$$

which approaches infinity as the solute approaches infinite dilution. Through similar developments, Eq. (14a) can be shown to be incorrect for all partial molar properties of B except the chemical potential.

Hammel relates the osmotic pressure to the mole fraction of solute:

$$\pi_B = (RT/\bar{V}_B^{l\circ})(1/X_B^l - 1) \tag{19b}$$

While this equation might possibly be valid for some specific value of temperature, pressure, and composition, it cannot be valid for the solute at high dilution. Conventional thermodynamics relates the osmotic pressure to the activity (based on Raoult's Law), again assuming that the pure liquid solute is incompressible:

$$\pi_B = -(RT/\bar{V}_B^{l\circ})\ln(a_B^l)$$

Comparison to Eq. (19b) gives

$$\ln(a_B^l) = 1 - 1/X_B^l; \qquad \mathrm{d}\ln(a_B^l) = \mathrm{d}X_B^l/(X_B^l)^2$$

For a two-component system at constant temperature and pressure, the Gibbs-Duhem Equation,

$$X_A^l\,\mathrm{d}\mu_A + X_B^l\,\mathrm{d}\mu_B = 0$$

gives

$$X_A^l\,\mathrm{d}\ln(a_A^l) = -\mathrm{d}X_B^l/X_B^l; \qquad \mathrm{d}\ln(a_A^l) = \mathrm{d}\ln(X_A^l/X_B^l)$$

As the solute approaches infinite dilution (solvent approaches the pure liquid state), the activity of the solvent then becomes infinite, rather than the value of unity required by the definition of activity.

Hammel's Eqs (12), (14a), and (19b) are inconsistent with conventional thermodynamics, and these inconsistencies must cast doubt on the validity of this solution model, the mathematical relationships derived and/or molecular interpretations based therefrom. As an example to illustrate questionable interpretations that are derived from this model, the author states that $X_A^{l'} = X_A^{l''}$ and $X_B^{l'} = X_B^{l''}$ in a liquid-liquid system. For a binary system, partial miscibility can result only from chemical reactions and/or complexation. While there is possibly some value in Hammel's consideration of "reaction products" or solution complexes for explanation of solution nonideality, one must be careful not to invoke complexation indiscriminately. Partial miscibility occurs in binary mixtures of *n*-heptane and perfluoro-*n*-heptane,[2] and to our knowledge, no one has invoked *n*-heptane "polymers", perfluoro-*n*-heptane "polymers" or heptane-perfluoroheptane complexes to describe the thermodynamic properties of this system. Saturated hydrocarbons are often used as inert solvents in studies involving complexation. The associated solution model, which has been developed thoroughly by Prigogine and DeFay,[3] and reviewed in monographs by Acree[4] and Prausnitz *et al.*,[5] can be traced to Dolezalek.[6] An extensive analysis of this model for the triethylamine + chloroform system has recently been presented by Hepler and co-workers.[7]

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