General Behavior of Dilute Binary Solutions

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Debenedetti and Kumar (1986a) have presented general thermodynamic expressions for the behavior of fugacity coefficients and activity coefficients in dilute solutions by expansion about the infinite dilution limit. They showed that their thermodynamic formalism accurately represented the behavior of dilute solutions of a nonvolatile solid solute in a supercritical solvent. The key result of their development may be summarized in the following expressions:

$$\frac{\phi_1}{\phi_1^\infty} = \frac{\gamma_1}{\gamma_1^\infty} = \exp(-Ky_1) \tag{1}$$

and

$$\frac{\phi_2}{\phi_2^\infty} = \frac{\gamma_2}{\gamma_2^\infty} = \exp[-K(y_1 + \ln y_2)] \tag{2}$$

where

$$K = \left(\frac{\partial^2 \ln \phi 2}{\partial y_2^2}\right)_{T,P,y_2 \to 1} \tag{3}$$

Equations 1 and 2 allow dilute solution properties to be calculated from the infinite dilution fugacity (or activity) coefficients if the partial derivative of Eq. 3 can be determined. The authors show that the temperature and pressure variation of this partial derivative are related to the partial molar enthalpy and partial molar volume, respectively,

$$\left(\frac{\partial K}{\partial T}\right)_P = \frac{\overline{H}_1 - \overline{H}_1^\infty}{y_1RT^2} \tag{4}$$

and

$$\left(\frac{\partial K}{\partial P}\right)_T = -\frac{\overline{V}_1 - \overline{V}_1^\infty}{y_1RT} \tag{5}$$

A somewhat similar approach has been taken by Cochran et al. (1987) in developing a model for dilute solutions of a nonvolatile solid solute in a supercritical solvent. These authors based their approach on the general statistical mechanical theory of solutions of Kirkwood and Buff (1951). From that work the expression for K, analogous to Eq. 3 above, is

$$K = (G_{11}^\infty - G_{12}^\infty)\rho \tag{6}$$

where $G_{\alpha\beta}^\infty$ is the Kirkwood fluctuation integral defined by

$$G_{\alpha\beta} = \int_o^\infty [g_{\alpha\beta}(r) - 1]4\pi r^2 dr \tag{7}$$

at infinite dilution. In Eq. 7 $g_{\alpha\beta}$ is the spatial (i.e., averaged over all molecular orientations) pair correlation function for the $\alpha - \beta$ interaction. Equation 6 is easily derived from Kirkwood-Buff theory (Ben-Naim, 1974). In more recent work Debenedetti and Kumar (1986b) have shown the relationship between their theory of dilute solutions and density fluctuations in the grand ensemble. In this paper we present the basis for modeling using molecular theories of mixtures within the formalism of fluctuation theory.

Physical Meaning of K

Whereas the second partial derivative of the logarithm of the solvent fugacity coefficient with respect to the solvent mole fraction as the solvent mole fraction approaches 1 at constant temperature and pressure (Debenedetti and Kumar's K) is an abstract thermodynamic quantity, the statistical mechanical definition of K in terms of Kirkwood fluctuation integrals lends physical meaning to the quantity. Furthermore, as will be shown below, the statistical mechanical formulation lends itself to the application of various molecular solution approximations. As is the case with the Debenedetti-Kumar representation of K, the statistical mechanical representation is independent of the choice of molecular solution theories and of the choice of equations of state to model the pure solvent.

The fluctuation integral $G_{\alpha\beta}$ represents the excess of molecules of type α about a molecule of type β per unit density of α and has been called the "affinity" of α for β. Lee et al. (1983)

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developed a statistical mechanical definition of local composition in terms of the fluctuation integral. Subsequently, Mansoori and Ely (1985) followed a similar derivation and showed how different mixture theories lead to different approximations for local composition. Pfund et al. (1986) present a similar definition of local composition that avoids the usual difficulties in dealing with long-range interactions (i.e., those beyond the range of local composition). With this definition K can then be expressed in terms of local compositions as follows:

$$K = \frac{n_{11} - n_{12}}{y_1} - \rho(V_{11} - V_{12}) + \frac{n_{11}^{LR} - n_{12}^{LR}}{y_1} \tag{8}$$

where the first term is due to the difference in local compositions, the second term is due to the difference in volumes of the solvation spheres, and the third term is due to the difference in the long-range interactions.

Debenedetti and Kumar's K, then, represents the difference between the excess of solute molecules and solvent molecules about a solute molecule at infinite dilution of the solute, or the affinity of the solute for itself less its affinity for the solvent at infinite dilution.

Alternatively, the fluctuation integral may be described in terms of the potential of mean force. At a sufficiently high temperature, the fluctuation integral is approximated by the spatial integral of the potential of mean force. In this sense, Debenedetti and Kumar's K represents the spatial integral of the difference in the potential of mean force about a solute molecule due to surrounding solute molecules and that due to surrounding solvent molecules at infinite dilution.

Application of Molecular Solution Approximations

As has been shown elsewhere (Cochran et al., 1987; Pfund et al., 1986), the Kirkwood-Buff formalism permits straightforward application of various molecular solution approximations for prediction of Kirkwood fluctuation integrals in dilute solution or for their accurate correlation. An appropriate equation of state for the pure solvent (in particular, available accurate equations of state) may be used with a chosen molecular solution theory. Equations 9 and 10 illustrate the results of applying two such models. In Eq. 9 the pair correlation functions are assumed to be zero within an excluded volume of diameter $\sigma_{\alpha\beta}$ and to scale in reduced distance, $r/\sigma_{\alpha\beta}$, with the depth of the attractive potential, $\epsilon_{\alpha\beta}$:

$$K = \left[\left(\frac{\epsilon_{11}\sigma_{11}^3 - \epsilon_{12}\sigma_{12}^3}{\epsilon_{22}\sigma_{22}^3}\right)\left(G_{22}^{\infty} + \frac{\pi\sigma_{22}^3}{6}\right) - \frac{\pi}{6}(\sigma_{11}^3 - \sigma_{12}^3)\right]\rho \tag{9}$$

In Eq. 10 the local compositions, defined as in Eq. 8, have been expressed in terms of Wilson's (1964) approximation:

$$K = \frac{4\pi L_{22}^3\rho}{3}\left[\exp\left(\frac{-\lambda_{11}}{kT}\right) - \frac{L_{12}^3}{L_{11}^3}\exp\left(-\frac{\lambda_{12}}{kT}\right)\right] - \frac{4\pi\rho}{3}(L_{11}^3 - L_{12}^3) + G_{22}^{\infty}\rho\left(\frac{\lambda_{11}L_{11}^3 - \lambda_{12}L_{12}^3}{\lambda_{22}L_{22}^3}\right) \tag{10}$$

Other molecular solution approximations may be similarly employed.

Prediction of the solute-solute and the solvent-solute fluctuation integrals at infinite dilution then requires molecular parameters plus an expression for the solvent-solvent fluctuation integral at infinite solute dilution. The latter is readily obtained from an equation of state for the pure solvent by use of Eq. 11, which results from the compressibility equation,

$$G_{22}^{\infty} = (kT\rho_2^{\infty}\chi_2^{\infty} - 1)/\rho_2^{\infty} \tag{11}$$

The molecular parameters in the expressions above may be regressed from data or estimated using various well-known approximations. Because this approach to modeling dilute supercritical solutions has been illustrated elsewhere (Cochran et al., Pfund et al.) this will not be repeated here.

Concluding Remarks

In this note it has been shown that the thermodynamic formalism of Debenedetti and Kumar for fugacity coefficients and activity coefficients in dilute binary solutions can be related to molecular quantities with clear physical meaning through the statistical mechanical theory of solutions of Kirkwood and Buff. In addition, it has been shown that the Kirkwood-Buff formulation permits the introduction of molecular solution models that may permit predictions and accurate correlations to be made. It is hoped that this extension of Debenedetti and Kumar's results may enhance the usefulness of their interesting work.

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Notation

g = spatial pair correlation function, molecules
G = Kirkwood fluctuation integral, Length^3 · molecules^{-1}
H = molar enthalpy, Mass · Length^2 · time^{-2} · mol^{-1}
k = Boltzmann constant, Mass · Length^2 · time^{-2} · molecules^{-1} · Temperature^{-1}
K = Debenedetti-Kumar exponential decay constant
L = diameter of solvation sphere in local composition models,
n = nearest neighbor number in local composition models
P = pressure, Mass · Length^{-1} · time^{-2}
r = radial distance between molecules, Length
R = universal gas constant, Mass · Length^2 · time^{-2} · mol^{-1} · Temperature^{-1}
T = absolute temperature, K
V = volume, Length^3
y = mole fraction

Greek letters

γ = activity coefficient
ϵ = attractive energy parameter, Mass · Length^2 · time^{-2} · molecules^{-1}
λ = parameter in the Wilson approximation, Mass · Length^2 · time^{-2} · molecules^{-1}
ρ = number density, molecules · Length^{-3}
σ = molecular size parameter, Length
ϕ = fugacity coefficient
χ = isothermal compressibility, Length · time · Mass^{-1}

Superscripts

∞ = solute at $y_1 \rightarrow 0$ limit
LR = long-range part
$\overline{}$ = partial molar property

Subscripts

1 = solute
2 = solvent
α, β = indices for arbitrary molecules

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