Derivation of the Three-Parameter Wilson Equation for the Excess Gibbs Energy of Liquid Mixtures

HENRI RENON
Institut Francais du Petrole, Rueil-Malmaison, France
and J. M. PRAUSNITZ
University of California, Berkeley, California

In 1964, Wilson (*6*) proposed a new equation for g^E, the molar excess Gibbs energy of a liquid mixture; for a binary:

$$\frac{g^E}{RT} = -x_1 \ln(1 - ax_2) - x_2 \ln(1 - bx_1) \tag{1}$$

where x_1 and x_2 are the mole fractions of components 1 and 2 and a, b are adjustable parameters. Wilson showed that his equation can be obtained by substitution of local volume fractions for overall volume fractions in the Flory-Huggins equation.

In Wilson's derivation, local mole fractions x_{ji} and x_{ki} are related to overall mole fractions x_j and x_k by

$$\frac{x_{ji}}{x_{ki}} = \frac{x_j \exp(-g_{ji}/RT)}{x_k \exp(-g_{ki}/RT)} \tag{2}$$

where x_{ji} is the local mole fraction of j around i and g_{ji} is an energy parameter characterizing the interaction between molecules i and j.

A study by Orye (*2*) indicated that Wilson's equation, using only two adjustable parameters, is useful for representing excess Gibbs energies of a wide variety of liquid mixtures including strongly nonideal mixtures. However, as pointed out by Wilson (*4, 6*), Equation (1) is not applicable to liquid mixtures which are only partially miscible. When Equation (1) is substituted into the classical equations for phase instability, it is not possible to obtain a solution which permits the existence of two liquid phases.

For partially miscible systems, Wilson suggested that Equation (1) be multiplied by an arbitrary constant c which depends on the binary system. Wilson and Scatchard showed (*4*) that for the partially miscible system n-butyl glycol-water a good representation of the liquid-liquid equilibria could be obtained with $c = 1.465$.

We want to show here that Equation (1), multiplied by constant c, can be derived on the basis of well-defined assumptions by introducing the concept of local composition into Scott's two-liquid theory of mixtures (*5*).

In a manner similar to that used in our derivation of the NRTL (Non-Random, Two-Liquid) equation (*3*) we write for the excess enthalpy:

$$h^E = x_1\, x_{21}\, (h_{21} - h_{11}) + x_2\, x_{12}\, (h_{12} - h_{22}) \tag{3}$$

where h_{ij} is a parameter characterizing the interaction between molecule i and molecule j; $h_{12} = h_{12}$.

We relate the local mole fractions to the overall mole fractions by

$$\frac{x_{21}}{x_{11}} = \frac{x_2}{x_1}\, e^{-\nu_{21}/c} \tag{4}$$

$$\frac{x_{12}}{x_{22}} = \frac{x_1}{x_2}\, e^{-\nu_{12}/c} \tag{5}$$

where

$$\nu_{12} = (h_{12} - h_{22})/RT \tag{6}$$

and

$$\nu_{21} = (h_{21} - h_{11})/RT \tag{7}$$

Upon comparing Equation (3) with Guggenheim's quasi-chemical lattice theory (*1, 3*) we find that $c = z/2$ where z is the coordination number (number of nearest neighbors about one molecule) of the liquid.

To obtain an expression for g^E, we use the Gibbs-Helmholtz equation,

$$\frac{\partial \dfrac{g^E}{T}}{\partial \dfrac{1}{T}} = h^E \tag{8}$$

Equation (3) is now substituted into Equation (8) and integrated with respect to $1/T$. Following Guggenheim (*1*), we assume that $(h_{21} - h_{11})$ and $(h_{12} - h_{22})$ are independent of temperature. At the lower limit of integration, $1/T = 0$, the quantities ν_{12} and ν_{21} vanish and the local mole fractions are equal to the overall mole fractions; at $1/T = 0$, therefore, the mixture is completely random. Integration yields

$$\frac{g^E}{RT} = c\left(x_1 \ln\frac{x_{11}}{x_1} + x_2 \ln\frac{x_{22}}{x_2} \right) \tag{9}$$

Equation (9) can be shown to be equivalent to Wilson's three-parameter equation as follows: From Equation (4) and the conservation relation $x_{11} + x_{21} = 1$ we write

$$x_{11} = \frac{x_1}{x_1 + x_2 \exp(-\nu_{21}/c)} = \frac{x_1}{1 - x_2[1 - \exp(-\nu_{21}/c)]} \tag{10}$$

Then

$$\ln\frac{x_{11}}{x_1} = -\ln[1 - x_2[1 - \exp(-\nu_{21}/c)]] \tag{11}$$

Similarly,

$$\ln\frac{x_{22}}{x_2} = -\ln[1 - x_1[1 - \exp(-\nu_{12}/c)]] \tag{12}$$

Substitution of Equations (11) and (12) into Equation (9) yields

$$\frac{g^E}{RT} = -c\,[x_1 \ln(1 - ax_2) + x_2 \ln(1 - bx_1)] \tag{13}$$

where $a = 1 - \exp(-\nu_{21}/c)$ and $b = 1 - \exp(-\nu_{12}/c)$. The special case $c = 1$ corresponds to a coordination number of 2 which is unreasonably low; for typical liquids z is in the range 6–12.

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