

Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures

HENRI RENON and J. M. PRAUSNITZ

University of California, Berkeley, California

A critical discussion is given of the use of local compositions for representation of excess Gibbs energies of liquid mixtures. A new equation is derived, based on Scott's two-liquid model and on an assumption of nonrandomness similar to that used by Wilson. For the same activity coefficients at infinite dilution, the Gibbs energy of mixing is calculated with the new equation as well as the equations of van Laar, Wilson, and Heil; these four equations give similar results for mixtures of moderate nonideality but they differ appreciably for strongly nonideal systems, especially for those with limited miscibility. The new equation contains a nonrandomness parameter α_{12} which makes it applicable to a large variety of mixtures. By proper selection of α_{12} , the new equation gives an excellent representation of many types of liquid mixtures while other local composition equations appear to be limited to specific types. Consideration is given to prediction of ternary vapor-liquid and ternary liquid-liquid equilibria based on binary data alone.

Interpolation and extrapolation of thermodynamic data for liquid mixtures are common necessities in chemical engineering. The model of ideal solutions is useful for providing a first approximation and a reference, but deviations from ideality are frequently large. These deviations are expressed by excess functions which depend on the concentrations of the components and on the temperature.

As shown by Wohl (25), excess functions have commonly been expressed by algebraic expansions of mole fractions with arbitrary, temperature-dependent coefficients which are obtained by fitting experimental data. In these expansions, as many terms and parameters as necessary are introduced in order to represent the experimental data.

A few years ago Wilson (24) showed that the excess Gibbs energy could be conveniently expressed by an algebraic function of local composition and in his final equation Wilson used local volume fractions. Subsequently Orye (11) showed that Wilson's equation is useful for representing equilibrium data for a wide variety of liquid mixtures.

While Wilson's equation represents one particular example of using local compositions, other examples can be readily constructed; for example, Heil (7) recently showed how a modified form of Wilson's equation can be used successfully to represent equilibria in polymer solutions.

We present here a critical discussion of the use of local compositions, derive a new equation based on Scott's two-liquid model theory, and compare experimental data with results calculated from several models. We consider both vapor-liquid and liquid-liquid equilibria, including ternary systems.

THE WILSON AND HEIL EQUATIONS

To take into account nonrandomness in liquid mixtures, Wilson (24) suggested a relation between local mole fraction x_{11} of molecules 1 and local mole fraction x_{21} of molecules 2 which are in the immediate neighborhood of molecule 1:

$$\frac{x_{21}}{x_{11}} = \frac{x_2}{x_1} \frac{\exp(-g_{21}/RT)}{\exp(-g_{11}/RT)} \quad (1)$$

where g_{21} and g_{11} are, respectively, energies of interaction between a 1-2 and 1-1 pair of molecules ($g_{12} = g_{21}$). The overall mole fractions in the mixture are x_1 and x_2 .

Wilson obtained an expression for the excess Gibbs energy by analogy with the Flory-Huggins expression for athermal mixtures, where he replaces overall volume fractions by local volume fractions:

$$g^E/RT = x_1 \ln(\xi_{11}/x_1) + x_2 \ln(\xi_{22}/x_2) \quad (2)$$

where the local volume fractions ξ_{11} and ξ_{22} are derived from Equation (1):

$$\xi_{11} = \frac{x_1}{x_1 + x_2 (v_2/v_1) \exp(-(g_{21} - g_{11})/RT)} \quad (3)$$

and

$$\xi_{22} = \frac{x_2}{x_2 + x_1 (v_1/v_2) \exp(-(g_{12} - g_{22})/RT)} \quad (4)$$

In these equations the v 's are the molar volumes.

Heil (7) pursued the original analogy further and proposed an expression for the excess Gibbs energy similar to the Flory-Huggins equation for nonathematic mixtures. The Heil equation was derived for polymer solutions; it has the following form for solutions of small molecules:

$$g^E/RT = x_1 \ln(\xi_{11}/x_1) + x_2 \ln(\xi_{22}/x_2) + \frac{g_{21} - g_{11}}{RT} x_1 \xi_{21} + \frac{g_{12} - g_{22}}{RT} x_2 \xi_{12} \quad (5)$$

where $\xi_{21} = 1 - \xi_{11}$ and $\xi_{12} = 1 - \xi_{22}$.

Both Equations (2) and (5) are useful, semiempirical relations for thermodynamic excess functions; both equations contain only two adjustable parameters per binary, ($g_{21} - g_{11}$) and ($g_{12} - g_{22}$), and both are readily generalized to solutions containing any number of components.

However, the derivations of both equations contain two essentially arbitrary steps: the relation between the local mole fractions, Equation (1), and the introduction of local compositions into the Flory-Huggins equation. A somewhat more satisfactory way to define and use local compositions is shown below. We shall return later to the Wilson and Heil equations.

THE NONRANDOM, TWO-LIQUID EQUATION

To define the local composition, we make an assumption similar to that of the quasichemical theory of Guggenheim

(6). To obtain an expression for the excess Gibbs energy, we use Scott's two-liquid theory of binary mixtures.

To take into account nonrandomness of mixing, we assume that the relation between the local mole fractions x_{21} and x_{11} is given by a modification of Equation (1):

$$\frac{x_{21}}{x_{11}} = \frac{x_2}{x_1} \frac{\exp(-\alpha_{12}g_{21}/RT)}{\exp(-\alpha_{12}g_{11}/RT)} \quad (6)$$

where α_{12} is a constant characteristic of the nonrandomness of the mixture. Interchanging subscripts 1 and 2, we also have

$$\frac{x_{12}}{x_{22}} = \frac{x_1}{x_2} \frac{\exp(-\alpha_{12}g_{12}/RT)}{\exp(-\alpha_{12}g_{22}/RT)} \quad (7)$$

The local mole fractions are related by

$$x_{21} + x_{11} = 1 \quad (8)$$

$$x_{12} + x_{22} = 1 \quad (9)$$

To show the similarity of our assumption with that of the quasichemical theory, we take the product of Equations (6) and (7) (noting that $g_{12} = g_{21}$) and obtain

$$\frac{x_{21}}{x_{11}} \frac{x_{12}}{x_{22}} = \exp(-\alpha_{12}(2g_{12} - g_{11} - g_{22})/RT) \quad (10)$$

Equations (8) and (9), substituted into Equation (10), yield

$$x_{21}x_{12} = \frac{(1 - x_{21})(1 - x_{12}) \exp(-\alpha_{12}(2g_{12} - g_{11} - g_{22})/RT)}{(1 - x_{21})(1 - x_{12})} \quad (11)$$

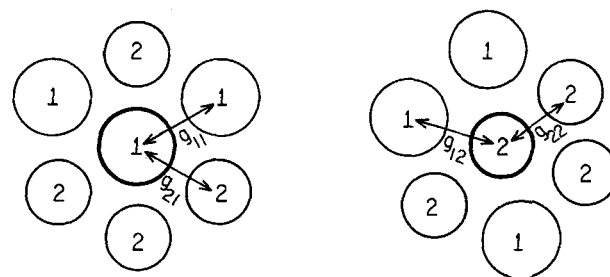
On the other hand, the assumption of nonrandomness in the quasichemical theory of Guggenheim (6) can be written as*

$$x_{21}x_{12} = \frac{(1 - x_{21})(1 - x_{12}) \exp\left(-\frac{1}{z}(2W_{12} - W_{11} - W_{22})/RT\right)}{(1 - x_{21})(1 - x_{12})} \quad (12)$$

where z is the coordination number of the lattice and W_{12} , W_{11} , W_{22} are, respectively, the molar potential energies of interaction of 1-2, 1-1, and 2-2 pairs.

Comparison of Equations (11) and (12) shows the similarity between the two assumptions; α_{12} is the substitute for $1/z$. However, the energies g_{ij} in Equation (11) are Gibbs energies, whereas the energies W_{ij} in Equation (12) are potential energies.

As discussed by Guggenheim, the quasichemical theory underestimates the effect of nonrandomness in solutions. Since z is of the order 6-12, we expect that α_{12} is a positive constant of the order 0.1 or 0.3. Although the similarity between Equations (11) and (12) suggests a theoretical basis for our assumption [Equations (6) and (7)], it is, however, different from Guggenheim's assumption because we do not use a lattice model, and we consider α_{12} as an empirical constant, independent of temperature. The physical significance of α_{12} becomes obscure when α_{12} exceeds (approximately) 0.3. Empirically, we find values of α_{12} larger than 0.3 for some mixtures, especially for associated mixtures for which Guggenheim's theory is not applicable.



MOLECULE 1 AT CENTER MOLECULE 2 AT CENTER
Fig. 1. Two types of cells according to Scott's two-liquid theory of binary mixtures.

From Equations (6) and (8), we obtain for the local mole fraction

$$x_{21} = \frac{x_2 \exp(-\alpha_{12}(g_{21} - g_{11})/RT)}{x_1 + x_2 \exp(-\alpha_{12}(g_{21} - g_{11})/RT)} \quad (13)$$

and similarly from Equations (7) and (9)

$$x_{12} = \frac{x_1 \exp(-\alpha_{12}(g_{12} - g_{22})/RT)}{x_2 + x_1 \exp(-\alpha_{12}(g_{12} - g_{22})/RT)} \quad (14)$$

We now introduce Equations (13) and (14) into the two-liquid theory of Scott (18) which assumes that there are two kinds of cells in a binary mixture: one for molecules 1 and one for molecules 2, as shown in Figure 1. For cells containing molecules 1 at their centers, the residual Gibbs energy (that is, compared with the ideal gas at the same temperature, pressure, and composition) is the sum of all the residual Gibbs energies for two-body interactions experienced by the center molecule 1. The residual Gibbs energy for a cell containing molecule 1 at its center is $g^{(1)}$ and it is given by

$$g^{(1)} = x_{11}g_{11} + x_{21}g_{21} \quad (15)$$

If we consider pure liquid 1, $x_{11} = 1$ and $x_{21} = 0$. In this case, the residual Gibbs energy for a cell containing a molecule 1 at its center, $g_{\text{pure}}^{(1)}$, is

$$g_{\text{pure}}^{(1)} = g_{11} \quad (16)$$

Similarly, for a cell containing a molecule 2 at its center

$$g^{(2)} = x_{12}g_{12} + x_{22}g_{22} \quad (17)$$

and

$$g_{\text{pure}}^{(2)} = g_{22} \quad (18)$$

The molar excess Gibbs energy for a binary solution is the sum of two changes in residual Gibbs energy: first, that of transferring x_1 molecules from a cell of the pure liquid 1 into a cell 1 of the solution, $(g^{(1)} - g_{\text{pure}}^{(1)})x_1$, and second, that of transferring x_2 molecules from a cell of the pure liquid 2 into a cell 2 of the solution, $(g^{(2)} - g_{\text{pure}}^{(2)})x_2$. Therefore

$$g^E = x_1(g^{(1)} - g_{\text{pure}}^{(1)}) + x_2(g^{(2)} - g_{\text{pure}}^{(2)}) \quad (19)$$

Substituting Equations (8), (9), (15), (16), (17), and (18) into Equation (19), we obtain

$$g^E = x_1x_{21}(g_{21} - g_{11}) + x_2x_{12}(g_{12} - g_{22}) \quad (20)$$

where x_{21} and x_{12} are given by Equations (13) and (14).

We call Equation (20), coupled with Equations (13) and (14), the NRTL (nonrandom, two-liquid) equation.

* Equation (4.09.1) in reference 6, p. 38, is:
 $X^2 = (N_1 - X)(N_2 - X) \exp(-2w/zkT)$ (12.1)
where N_1, N_2 are the number of molecules 1 and 2 in the solution, (Xz) the number of 1-2 interactions, w the interchange energy defined by

$$2w = z(2w_{12} - w_{11} - w_{22})$$

where, in turn, w_{12} , w_{11} , and w_{22} are the potential energies for interactions 1-2, 1-1, and 2-2 on the lattice. The term (zw_{11}) is the energy of interaction of a molecule 1 with all its neighbors in pure liquid 1. Equation (12) is obtained by dividing both sides of Equation (12.1) by N_1N_2 and introducing molar quantities in the exponential.

The activity coefficients for the NRTL equation are found by differentiation of Equation (20) they are

$$\ln \gamma_1 = x_2^2 \left(\tau_{21} \frac{\exp(-2\alpha_{12}\tau_{21})}{[x_1 + x_2 \exp(-\alpha_{12}\tau_{21})]^2} + \tau_{12} \frac{\exp(-\alpha_{12}\tau_{12})}{[x_2 + x_1 \exp(-\alpha_{12}\tau_{12})]^2} \right) \quad (21)$$

$$\ln \gamma_2 = x_1^2 \left(\tau_{12} \frac{\exp(-2\alpha_{12}\tau_{12})}{[x_2 + x_1 \exp(-\alpha_{12}\tau_{12})]^2} + \tau_{21} \frac{\exp(-\alpha_{12}\tau_{21})}{[x_1 + x_2 \exp(-\alpha_{12}\tau_{21})]^2} \right) \quad (22)$$

where

$$\tau_{12} = (g_{12} - g_{22})/RT \quad (23)$$

$$\tau_{21} = (g_{21} - g_{11})/RT \quad (24)$$

with $g_{12} = g_{21}$.

GENERAL FUNDAMENTAL EQUATION

For comparison, it is convenient to generalize the Wilson, Heil, and NRTL equations. To simplify the notation, let

$$G_{12} = \rho_{12} \exp(-\alpha_{12}\tau_{12}) \quad (25)$$

$$G_{21} = \rho_{21} \exp(-\alpha_{12}\tau_{21}) \quad (26)$$

The generalized expression for the excess Gibbs energy of a binary mixture is

$$\frac{g^E}{RT} = -q [x_1 \ln(x_1 + x_2 G_{21}) + x_2 \ln(x_2 + x_1 G_{12})] + p x_1 x_2 \left[\frac{\tau_{21} G_{21}}{x_1 + x_2 G_{21}} + \frac{\tau_{12} G_{12}}{x_2 + x_1 G_{12}} \right] \quad (27)$$

The Wilson, Heil, and NRTL equations follow from Equation (27) by substituting for p , q , ρ_{12} and α_{12} the values indicated in Table 1, taking $i = 1$ and $j = 2$.

The adjustable parameters are $(g_{12} - g_{22})$ and $(g_{21} - g_{11})$. We may consider α_{12} as a third adjustable parameter or, as discussed later, set it at a predetermined value. For the Wilson equation, independent specification of liquid molar volumes is not strictly necessary since G_{12} and G_{21} can be taken as adjustable temperature-dependent parameters.

We now indicate some properties of Equation (27). The activity coefficients are found by appropriate differentiation; they are

$$\ln \gamma_1 = q \left[\frac{x_2 G_{21}}{x_1 + x_2 G_{21}} - \frac{x_2 G_{12}}{x_2 + x_1 G_{12}} - \ln(x_1 + x_2 G_{21}) \right] + p x_2^2 \left[\frac{\tau_{21} G_{21}^2}{(x_1 + x_2 G_{21})^2} + \frac{\tau_{12} G_{12}}{(x_2 + x_1 G_{12})^2} \right] \quad (28)$$

$$\ln \gamma_2 = q \left[\frac{x_1 G_{12}}{x_2 + x_1 G_{12}} - \frac{x_1 G_{21}}{x_1 + x_2 G_{21}} - \ln(x_2 + x_1 G_{12}) \right] + p x_1^2 \left[\frac{\tau_{12} G_{12}^2}{(x_2 + x_1 G_{12})^2} + \frac{\tau_{21} G_{21}}{(x_1 + x_2 G_{21})^2} \right] \quad (29)$$

where τ_{12} , τ_{21} , G_{12} , and G_{21} are given, respectively, in Equations (23), (24), (25), and (26).

A condition for phase instability is that for Δg^M , the molar Gibbs energy of mixing

$$\left(\frac{\partial^2 \Delta g^M}{\partial x^2} \right)_{TP} = 0 \quad (30)$$

for at least one value of x_1 in the interval zero to one. Substituting Equation (25) into Equation (30), we obtain

TABLE 1. VALUES OF p , q , ρ_{ij} , AND α_{ij}

Equation	p	q	ρ_{ij}	α_{ij}^a
Wilson	0	1	v_i/v_j	1
Heil	1	1	v_i/v_j	1
NRTL	1	0	1	α_{ij}

^a $\alpha_{ij} = \alpha_{ji}$.

$$\frac{G_{21}^2}{(x_1 + x_2 G_{21})^2} \left(\frac{q}{x_1} - \frac{2p\tau_{21}}{x_1 + x_2 G_{21}} \right) + \frac{G_{12}^2}{(x_2 + x_1 G_{12})^2} \left(\frac{q}{x_2} - \frac{2p\tau_{12}}{x_2 + x_1 G_{12}} \right) + \frac{1-q}{x_1} + \frac{1-q}{x_2} = 0 \quad (31)$$

Equation (31) immediately shows why Wilson's equation is not compatible with phase instability. Substituting the parameters given in the first horizontal row of Table 1, all terms on the left-hand side of Equation (31) are greater than zero and therefore Equation (31) can never be satisfied. As mentioned by Wilson (24), his equation cannot account for partial miscibility.

We now want to compare the Wilson, Heil, and NRTL equations with each other and with the van Laar equation. To facilitate this comparison we consider symmetric systems.

SYMMETRIC SYSTEMS

We call those binary systems symmetric for which the excess Gibbs energy is not changed if we change x to $(1-x)$. We also assume that $v_2 = v_1$. The condition for symmetry in the local composition equations is the equality of the parameters τ_{12} and τ_{21} , and we note

$$\tau_{12} = \tau_{21} = \tau \quad (32)$$

We write the van Laar equation in the form

$$g^E/RT = \frac{2AB x_1 x_2}{Ax_1 + Bx_2} \quad (33)$$

where A and B are temperature-dependent parameters. For a symmetric system $A = B$, Equation (33) is then identical with the two-suffix Margules and Redlich-Kister equations.

For the NRTL equation, we need to specify the constant α_{12} . In our comparison, we consider two values of α_{12} , namely, 0.50 and 0.25; the two corresponding equations are designated, respectively, by NRTL (0.50) and NRTL (0.25).

We define the parameter a as follows:

$$\begin{aligned} a &= A \text{ for the van Laar equation} \\ a &= 2\tau \text{ for Heil's equation} \\ a &= \tau \text{ for Wilson's equation and the NRTL equation} \end{aligned}$$

All these equations become asymptotically equivalent for small values of the parameter a . In each case, the first term in the power series expansion of g^E/RT in terms of a is $2ax_1x_2$.

Figure 2 presents a comparison of the four symmetric equations. In all four equations, the parameters a are selected such that, for each one, at infinite dilution

$$\gamma_1^\infty = \gamma_2^\infty = 11.0$$

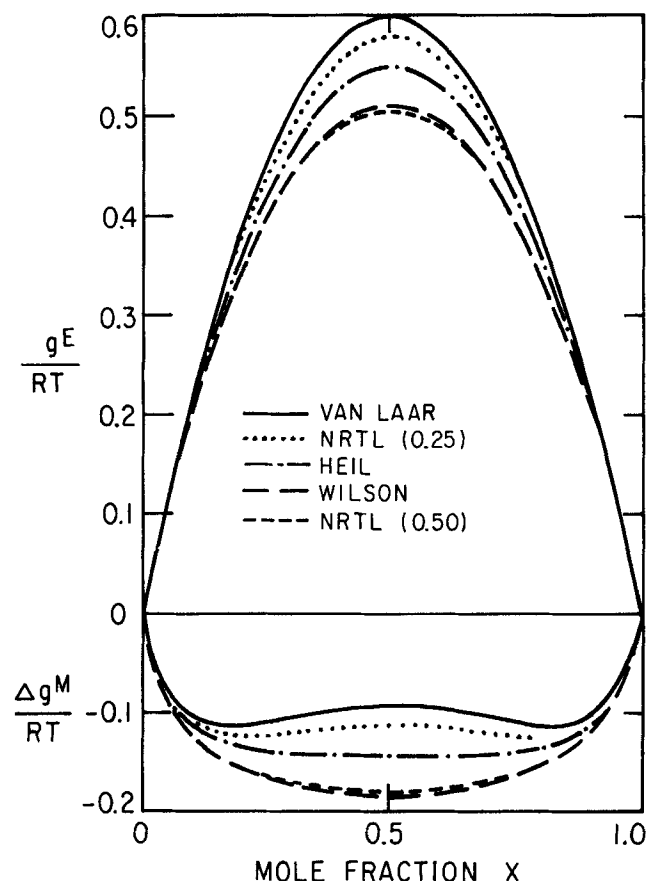


Fig. 2. Excess Gibbs energy and Gibbs energy of mixing for symmetric systems with the same activity coefficients at infinite dilution.

The slopes for $x = 0$ and $x = 1$ are the same for all equations but, as is evident in the central part of the diagram, the excess Gibbs energy decreases in the order: van Laar, NRTL (0.25), Heil, Wilson, NRTL (0.50); in the same order, the curves become more and more flat near the maximum. An important consequence of this tendency is seen in the lower part of Figure 2, where the Gibbs energy of mixing is shown. For the van Laar, NRTL (0.25) and Heil equations, Δg^M presents a maximum and two minima; this indicates that phase splitting occurs. The mu-

tual solubilities are small in the case of the van Laar equation and become larger with the NRTL (0.25) and Heil equations. However, the Wilson and NRTL (0.50) equations do not show phase instability. Although all five equations give the same activity coefficients at infinite dilution, three of them predict the existence of two liquid phases and two of them do not.

Figure 2 indicates a very important property of the local composition equations. Compared with the van Laar equation, and for the same nonideality at infinite dilution, the local composition equations have lower maxima of the excess Gibbs energy, thereby reducing the tendency toward immiscibility.

Figure 3 shows how the change of curvature of the excess Gibbs energy is related to the degree of nonideality of the mixture. To characterize the nonideality, we plot on the abscissa the logarithm of the activity coefficient at infinite dilution, while on the ordinate we plot the logarithm of the activity coefficient for either component in an equimolar mixture. A decrease of the activity coefficient in an equimolar mixture corresponds to a flatter excess Gibbs energy curve in Figure 2. The general trend shown in Figure 2 remains; the equations give flatter curves in the order: van Laar, NRTL (0.25), Heil, Wilson, and NRTL (0.50). This effect is not significant for nearly ideal solutions but it becomes appreciable when $\ln \gamma^\infty = 1.4$ and it becomes increasingly important as the degree of nonideality rises. When the activity coefficient at infinite dilution becomes very large, the activity coefficient in an equimolar mixture increases linearly with γ^∞ in the van Laar equation, reaches a maximum in the Heil and NRTL equations and an asymptotic limit in the Wilson equation.

In Figure 3 unstable liquid phases at equimolar concentration are indicated by dashed lines. The minimum activity coefficient at infinite dilution required for phase instability is lowest in the van Laar equation ($\ln \gamma^\infty = 2$) followed by the Heil equation ($\ln \gamma^\infty = 2.18$); it is variable in the case of the NRTL equation, increasing from $\ln \gamma^\infty = 2$ when $\alpha_{12} = 0$ to $\ln \gamma^\infty = 2.94$ when $\alpha_{12} = 0.426$. For $\alpha_{12} > 0.426$ phase instability does not occur at all.

The activity coefficient at infinite dilution is a monotonic, increasing function of a for all the equations considered here; therefore the parameter a is also a measure of the degree of nonideality of the mixture. Figure 4 shows the variation with a of the activity coefficient of an equimolar mixture, indicating also the minimum value of a which is required for phase splitting. In Figure 4 the

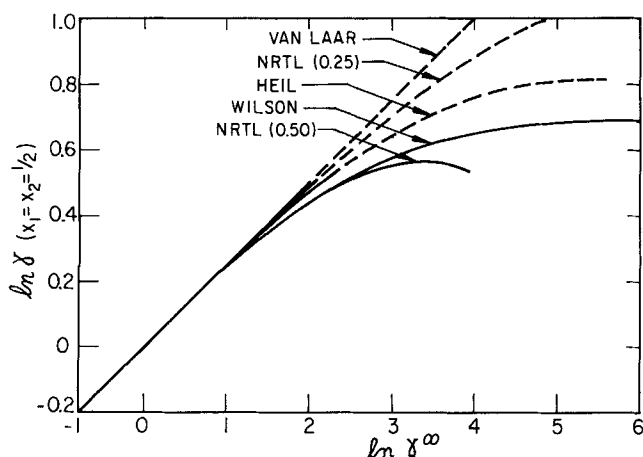


Fig. 3. Activity coefficient for symmetric equimolar mixture as a function of activity coefficient at infinite dilution.

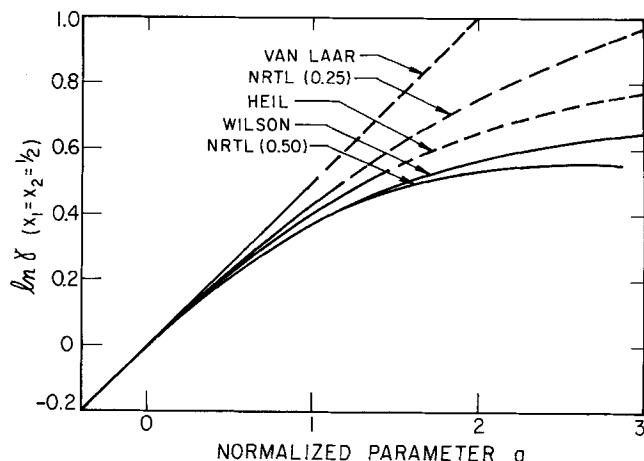


Fig. 4. Activity coefficient for symmetric mixture as a function of normalized parameter a .

relative position of the curves representing the NRTL equation for different values of α_{12} illustrates the effect of nonrandomness. For the same value of a , the lower excess Gibbs energy for equimolar mixtures if α_{12} is larger, is due only to the reduction of the number of 1-2 interactions caused by the reduction of nonrandomness. According to the position of their curves in Figure 4, we can say that nonrandomness is taken into account more seriously by Wilson's equation than by Heil's equation.

NONSYMMETRIC SYSTEMS

For the NRTL equation, unsymmetric systems are those where τ_{12} is different from τ_{21} , and for the Wilson equation unsymmetric behavior results when G_{12} is different from G_{21} . For the Heil equation, lack of symmetry can be caused either by different molar volumes or by unequal τ_{12} and τ_{21} . For the van Laar equation, unsymmetric systems are those where A is different from B . All equations can satisfactorily represent unsymmetric systems; however, the van Laar equation cannot represent systems where the logarithms of the activity coefficients at infinite dilution have different signs. As for symmetric systems, the four equations are not equivalent for unsymmetric systems even when these equations are normalized such that for each component i , γ_i^∞ is the same for each equation.

Turning again to the NRTL equation, the activity coefficient at infinite dilution γ_1^∞ depends primarily on τ_{21} , while γ_2^∞ depends primarily on τ_{12} . For $\gamma_2^\infty > \gamma_1^\infty$, it is necessary that $\tau_{12} > \tau_{21}$ and vice versa. Therefore we can say that the lack of symmetry of a system (more precisely, the skewness of the Gibbs energy curve) is related to the difference between τ_{12} and τ_{21} , while, for moderately unsymmetric systems, the degree of nonideality is related mainly to their sum. The flatness of the Gibbs energy curve is related to α_{12} .

REPRESENTATION OF BINARY VAPOR-LIQUID DATA

We now turn to a comparison of calculated results with experimental data and we first consider binary mixtures. The most strongly nonideal mixtures provide the best test because the equations then differ most.

Vapor-liquid data at low pressure for selected systems were fitted with each of the equations to show their relative advantages. Vapor-phase nonideality corrections were calculated from an empirical correlation for the second virial coefficient (10). In all calculations the saturation pressures of the pure components were those reported in the articles from which the data are taken; they are given elsewhere, together with the value of the parameters (16, Appendix G). To obtain the parameters, a nonlinear least-squares fitting program was used which minimizes the

sum-of-squares of relative deviation in pressure plus the sum-of-squares of deviations in vapor phase mole fraction (whenever available) for all data points. The calculation method used is similar to the one suggested by Prausnitz et al. (13).

Since deviations come from both the scatter of the data and from the inadequacy of the equation, they cannot provide directly a measure of the adequacy of the equation. Only a comparison of the deviations obtained from different equations with the same set of data gives an indication of relative adequacy of different equations.

We call δy the root-mean-square deviation of experimental from calculated vapor phase mole fractions, and δP the root-mean-square relative deviation of calculated from experimental pressures. We have calculated δP and δy for a large number of isothermal vapor-liquid data and some isobaric data; the detailed results (16, Appendix G) are summarized in Table 2, where we have grouped the systems in the categories described below.

Type I includes those systems where deviations from ideality are not large, although they may be positive or negative.

$$|g^E \text{ (maximum)}| < 0.35 RT \quad (33)$$

Most of the currently available vapor-liquid data fall in this category. We distinguish three subtypes:

Type Ia includes most mixtures of nonpolar substances such as hydrocarbons and carbon tetrachloride, but mixtures of fluorocarbons and paraffins are excluded.

Type Ib includes some mixtures of nonpolar and polar nonassociated liquids, for example, *n*-heptane-methylethylketone, benzene-acetone, and carbon tetrachloride-nitroethane.

Type Ic includes some mixtures of polar liquids: some with negative excess Gibbs energy, for example, acetone-chloroform and chloroform-dioxane, and some with positive, but not large, excess Gibbs energy, for example, acetone-methyl acetate and ethanol-water.

Table 2 shows δy and δP for each of these subtypes. The comparison indicates that all the equations are equally good for these systems. For the NRTL equation, the root-mean-square deviations are not affected by the value selected for α_{12} in the range 0.2 to 0.5; vapor-liquid data are usually not precise enough to indicate the nonrandomness of mixtures of this type because the effect of nonrandomness on the shape of the excess Gibbs energy curve is not strong. We recommend $\alpha_{12} = 0.30$.

Type II includes mixtures of saturated hydrocarbons with polar nonassociated liquids, as, for instance, *n*-hexane-acetone or isooctane-nitroethane. Phase splitting occurs at a relatively low degree of nonideality and the nonrandomness, as measured by α_{12} , is small. Values of δy and δP for nine mixtures, given in Table 2, show that

TABLE 2. COMPARISON BETWEEN LOCAL COMPOSITION AND VAN LAAR EQUATION FOR REPRESENTATION OF BINARY VAPOR-LIQUID DATA

Type	Root-mean-square average deviation in vapor-phase mole fraction × 1000				Root-mean-square average relative deviation in pressure × 1000				α_{12}	No. of systems
	van Laar	Heil	Wilson	NRTL	van Laar	Heil	Wilson	NRTL		
Ia	4	4	4	4	3	3	3	3	0.30	8
Ib	7	7	7	7	6	6	6	6	0.30	10
Ic	7	7	7	7	9	9	9	9	0.30	11
II	7	8	13	6	8	10	21	8	0.20	9
III	15	7	11	7	15	4	8	4	0.40	3
IV	26	22	10	14	34	28	11	24	0.47	13
V	13	10	5	5	16	11	4	5	0.47	2
VI	10	10	13	10	16	16	21	16	0.30	2
VII	—	—	—	—	12	13	15	13	0.47	2

both the NRTL (0.20) and the van Laar equations give a good representation of these data; Heil's equation is also quite good, but Wilson's equation is only fair. To fit these data we recommend $\alpha_{12} = 0.20$.

Type III includes mixtures of saturated hydrocarbons and the homolog perfluorocarbons such as *n*-hexane-perfluoro-*n*-hexane. Table 2 shows that the Heil and NRTL (0.40) equations give the best representation of the data. We recommend $\alpha_{12} = 0.40$.

Type IV includes mixtures of a strongly self-associated substance, such as an alcohol with a nonpolar substance, like a hydrocarbon or carbon tetrachloride. The excess Gibbs energy curve presents a flat shape near its maximum, and phase splitting occurs only if the activity coefficients are very large. Values of δy and δP for thirteen mixtures of this type show that Wilson's equation gives a very good fit but the Heil and van Laar equations do not. These systems present a high degree of nonrandomness and are best represented by high values of α_{12} in the NRTL equation; the fitting is very sensitive to the value of α_{12} and it is best to use α_{12} as an adjustable parameter. The optimum values of α_{12} are between 0.40 and 0.55. However, in Table 2 we have selected a common value of α_{12} for all systems of this type in order to reduce the number of fitting parameters to two. When experimental data are insufficient to justify three parameters, we recommend $\alpha_{12} = 0.47$ for fitting this type of mixture.*

Suitable data for strongly nonideal systems, besides the types already considered, are scarce. However, we tentatively identify three more types:

Type V is represented by two systems of polar substances (acetonitrile and nitromethane) with carbon tetrachloride which present a high degree of nonrandomness and are best fitted by the NRTL (0.47) equation and the Wilson equation. We recommend $\alpha_{12} = 0.47$.

Type VI is represented by two systems of water plus a polar, nonassociated substance (acetone and dioxane); they are best represented by the van Laar and the NRTL (0.30) equations. We recommend $\alpha_{12} = 0.30$.

Type VII is represented by two systems of water plus a polar self-associated substance (butyl-glycol and pyridine); they present a high degree of nonrandomness and we recommend $\alpha_{12} = 0.47$.

We can draw the following conclusions about representation of binary vapor-liquid equilibria.

The Wilson equation is especially suitable for alcohol-hydrocarbon systems, but it can never predict phase splitting. The Heil equation can predict phase splitting but provides only a small improvement over the van Laar equation.

The NRTL equation gives the best fit for all types of mixtures by proper selection of the constant α_{12} , taking into account only the nature of the binary system. It is the simplest of the local composition equations (it contains no logarithmic term in the expression of g^E) and has perhaps the best semitheoretical basis. When justified by the data, it can be used as a three-parameter equation for highly non-ideal systems, but it can also be used as a two-parameter equation by using for α_{12} the values recommended and listed in Table 2.

PROBABLE ERROR AND TEMPERATURE DEPENDENCE OF PARAMETERS

As determined from vapor-liquid data and shown elsewhere (16), the probable error in the parameters of the Heil equation is such that, for good data, the error on the

sum of the parameters $S = (g_{12} - g_{22}) + (g_{21} - g_{11})$ is of the order of 10 cal./mole and the error in the difference between the parameters $D = (g_{12} - g_{22}) - (g_{21} - g_{11})$ is of the order of 50 cal./mole. The orders of the errors in S and D are, respectively, 20 and 100 cal./mole for the parameters of the Wilson and NRTL equations.

With the assumption that Heil's parameters from reduction of vapor-liquid data are independent of temperature, calculated and experimental enthalpies agree only qualitatively. Therefore the parameters are temperature dependent. Fortunately, however, they are only weak functions of temperature, and, in many cases, isobaric data can be used to obtain useful, temperature-averaged parameters. These conclusions, discussed in more detail elsewhere (16), also hold for the Wilson and NRTL equations.

LIQUID-LIQUID EQUILIBRIA

While the Wilson equation is not applicable to liquid-liquid systems, the Heil and the NRTL equations ($\alpha_{12} < 0.426$) can be used to represent thermodynamic properties of binary mixtures with two liquid phases. It is possible to calculate the parameters from experimental compositions of the two equilibrated liquid phases.

Parameters for the Heil and for the NRTL (0.20) equations were determined over a large range of temperature up to the critical solution temperature for twelve liquid-liquid systems containing a polar substance and a hydrocarbon (they are given in reference 16); in all cases, the temperature dependence of the parameters is linear and the parameters are consistent with parameters derived from vapor-liquid data. Therefore, for this type of mixture, it is possible to predict vapor-liquid equilibria by linear extrapolation with temperature of the parameters obtained from liquid-liquid data at lower temperature.

Figure 5 shows the variation of the parameters with

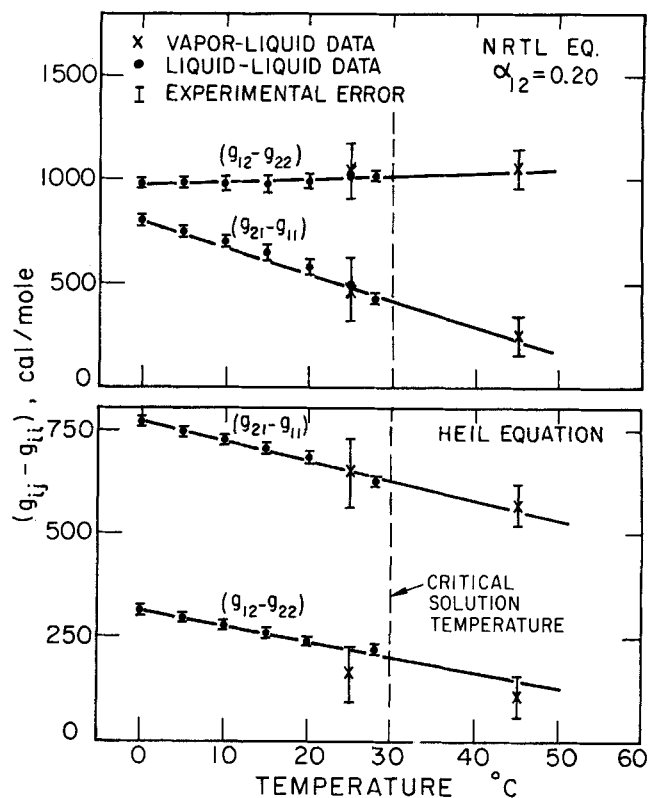


Fig. 5. Parameters for nitroethane (1)-isooctane (2) system calculated from vapor-liquid and liquid-liquid data.

* As Wilson's, the NRTL (0.47) equation does not allow phase splitting, but it offers generally a good representation of vapor-liquid data of Type IV mixtures in the miscible regions.

TABLE 3. COMPARISON OF PREDICTION OF TERNARY VAPOR-LIQUID EQUILIBRIA WITH EQUATIONS USING TWO PARAMETERS PER BINARY SYSTEM AND NO TERNARY CONSTANT

System	Temp., °C. or pressure, mm. Hg	No. of data points	Mean arithmetic deviation in vapor mole fraction y for individual component $\times 1,000$			95 % Confidence limit in y $\times 1,000$ NRTL	Mean relative deviation in pressure $\times 1,000$			95 % Confidence limit in relative pressure $\times 1,000$ NRTL	Ref.
			Heil	Wilson	NRTL*		Heil	Wilson	NRTL*		
<i>n</i> -Hexane	70	21	-2	-2	-2	4					
Cyclohexane			3	3	3	4	-8	-8	-7	2	22
Benzene			-1	-1	-1	5					
<i>n</i> -Octane	35	25	5	1	4	4					
Isooctane			0	7	0	10	16	14	-6	13	4
Nitroethane			-5	-8	-4	8					
<i>n</i> -Heptane	760	39	3	3	3	2					
Toluene			2	2	2	1	15	14	11	33	20
Methylethyl ketone			-5	-5	-5	2					
<i>n</i> -Heptane	760	47	5	4	4	3					
Benzene			6	2	2	4	4	14	13	5	23
Ethanol			-11	-6	-6	6					
<i>n</i> -Heptane	400	50	7	4	5	7					
Benzene			9	4	3	4	-15	4	4	9	9
Ethanol			-16	-8	-7	9					
<i>n</i> -Heptane	760	8	1	-2	-5	4					
Toluene			-2	-2	-3	5	3	-1	-7	9	2
Methanol			1	4	+8	8					
Benzene	35	6	-1	0	-1	5					
Carbon tetra- chloride			-3	-3	-3	4	9	4	3	9	17
Methanol			4	3	4	7					
Benzene	55	8	-3	-1	-3	3					
Carbon tetra- chloride			-6	-2	-2	4	11	0	2	6	17
Methanol			9	3	5	7					
<i>n</i> -Hexane	760	16	-1	0	-1	4					
Hexene-1			4	3	4	4	-11	-10	-12	9	21
1,4-Dioxane			-3	-3	-3	6					
Acetone	50	30	-5	-5	-5	4					
Chloroform			-3	-3	-3	4	23	21	23	16	19
Methanol			8	8	8	3					
Acetone	50	35	-4	-4	-4	3					
Methanol			1	1	1	7	12	13	12	12	19
Methyl acetate			3	3	3	5					
Ethanol	760	96	0	10	-4	7					
Ethyl acetate			1	-7	5	22	6	-9	9	8	5
Water			-1	-3	-1	17					

* α_{12} is selected for each binary mixture according to the values given in Table 3.

temperature for a typical binary system. The temperature range extends from below to above the critical solution temperature. The probable errors in the parameters are indicated by the vertical lines in Figure 5. For liquid-liquid data this error is smaller than for vapor-liquid data. It is of the order of 10 cal./mole for Heil's parameters and 20 cal./mole for parameters in the Wilson and NRTL equations. The temperature dependence of the parameters cannot be neglected in this case. Within experimental error, however, the parameters derived from vapor-liquid data are consistent with those derived from liquid-liquid data.

GENERALIZATION OF THE EQUATIONS TO MULTICOMPONENT SYSTEMS

The equations for binary solutions, presented earlier, are readily generalized to solutions containing any number of components. The generalization requires no additional assumption; all the local composition equations considered here take into account only two-body interactions and therefore the assumptions needed for 3, 4, ... component solutions are the same as those for binary solutions.

For a multicomponent solution, let x_{ji} stand for the local mole fraction of molecule j and let x_{ki} stand for the local mole fraction of molecule k in the immediate neighborhood

of molecule i . These two local mole fractions are related by

$$\frac{x_{ji}}{x_{ki}} = \frac{x_j}{x_k} \frac{\exp(-\alpha_{ij}g_{ji}/RT)}{\exp(-\alpha_{ik}g_{ki}/RT)} \quad (34)$$

For a multicomponent solution, the excess Gibbs energy is

$$\frac{g^E}{RT} = -q \sum_{i=1}^N x_i \ln \left(\sum_{j=1}^N G_{ji}x_j \right) + p \sum_{i=1}^N x_i \frac{\sum_{j=1}^N \tau_{ji}G_{ji}x_j}{\sum_{k=1}^N G_{ki}x_k} \quad (35)$$

where N is the number of components in the system and

$$\tau_{ji} = (g_{ji} - g_{ii})/RT \quad (36)$$

$$G_{ji} = \rho_{ji} \exp(-\alpha_{ji}\tau_{ji}) \quad (37)$$

We can obtain the Wilson, Heil, and the NRTL equations for multicomponent solutions by giving the values listed in Table 1 to p , q , ρ_{ij} and α_{ij} .

The activity coefficient is obtained by appropriate differentiation of Equation (35):

$$\ln \gamma_i = q \left(1 - \ln \sum_{j=1}^N x_j G_{ji} - \sum_{j=1}^N \frac{x_j G_{ij}}{\sum_{k=1}^N G_{kj}x_k} \right) + p \left[\frac{\sum_{j=1}^N \tau_{ji}G_{ji}x_j}{\sum_{k=1}^N G_{ki}x_k} + \sum_{j=1}^N \frac{x_j G_{ij}}{\sum_{k=1}^N G_{kj}x_k} \left(\tau_{ij} - \frac{\sum_{l=1}^N x_l \tau_{lj} G_{lj}}{\sum_{k=1}^N G_{kj}x_k} \right) \right] \quad (38)$$

PREDICTION OF TERNARY VAPOR-LIQUID EQUILIBRIA

With the local composition equations, prediction of the properties of multicomponent systems is possible without any additional ternary or higher order parameters. For the NRTL equation, the excess Gibbs energy is derived from the two-liquid theory by taking into account only two-body interactions; there is no need to introduce higher-order interactions in the treatment of multicomponent systems when they were neglected for binary mixtures.

Table 3 presents a comparison of experimental vapor-phase mole fractions and total pressures with calculated results using only two fitting parameters determined from each of the binary data. For the NRTL equation, the values of α_{12} are selected according to the rules given earlier.

We compare the mean arithmetic deviations in the vapor mole fractions (absolute) and total pressures (relative) for the three local composition equations. These quantities are a measure of the accuracy of the prediction of the ternary equilibria. We indicate also 95% confidence limits for the NRTL equation, as suggested recently by Adler et al. (1).

The results indicated in Table 3 lead to conclusions which parallel those reached from fitting binary systems.

For systems of type I, where the deviations from ideality are not too large, all equations give similar results. In Table 3 systems belonging to this type are *n*-hexane-cyclohexane-benzene, *n*-hexane-hexene-1-dioxane, *n*-heptane-toluene-methylethylketone, acetone-chloroform-methanol, and acetone-methanol-methylacetate.

For type II systems, which have immiscible regions, the Heil equation and the NRTL equation are better than the Wilson equation. In Table 3 systems belonging to this type are *n*-octane-isooctane-nitroethane and ethanol-ethylacetate-water.

For systems of type IV, mixtures of alcohols and non-polar liquids, the Wilson and NRTL equations give the best predictions. In Table 3 systems of this type are *n*-heptane-benzene-ethanol, *n*-heptane-toluene-methanol, and benzene-carbon tetrachloride-methanol.

From these results we conclude that the NRTL equation is a good and general equation for prediction of ternary vapor-liquid equilibria using only data for binary mixtures; a suitable value of α_{12} can be selected independently for each binary system.

Table 4 shows a comparison of the NRTL equation with the Wohl equation. The results for the Wohl equation are taken from Adler et al. (1). These authors use a three-parameter Wohl equation of the Margules type for fitting the binary data. When they use the best ternary constant to fit the experimental ternary data, they obtain the results listed in Table 4. (They show that it is also possible to use the same value of the ternary constant for all these

TABLE 4. COMPARISON OF NRTL AND WOHL EQUATIONS FOR PREDICTION OF TERNARY VAPOR-LIQUID EQUILIBRIA

System	Mean arithmetic deviation in individual components vapor mole fraction $\times 1000$		95% Confidence limits in vapor mole fraction $\times 1000$	
	NRTL (with no ternary constant)	Wohl (with best ternary constant)	NRTL (with no ternary constant)	Wohl (with best ternary constant)
<i>n</i> -Heptane	3	3	2	8
Toluene	2	-4	1	5
Methyl-ethyl ketone	-5	1	2	8
<i>n</i> -Heptane	4	0	3	4
Benzene	2	8	4	7
Ethanol	-6	-8	6	8
760 mm. Hg				
<i>n</i> -Heptane	5	0	7	4
Benzene	3	-5	4	7
Ethanol	-7	5	9	8
400 mm. Hg				
<i>n</i> -Heptane	-5	8	4	14
Toluene	-3	-2	5	8
Methanol	8	-6	8	19
Benzene	-1	-13	5	22
Carbon tetrachloride	-3	3	4	20
Methanol 35°C.	4	10	7	39
Benzene	-3	-15	3	21
Carbon tetrachloride	-2	7	4	13
Methanol 55°C.	5	8	7	29
Acetone	-5	-11	4	18
Chloroform	-3	11	4	8
Methanol	8	0	3	12
Acetone	-4	-9	3	12
Methanol	1	8	7	15
Methyl acetate	3	1	5	8
Ethanol	-4	-6	7	22
Ethyl acetate	5	1	22	57
Water	1	5	17	49

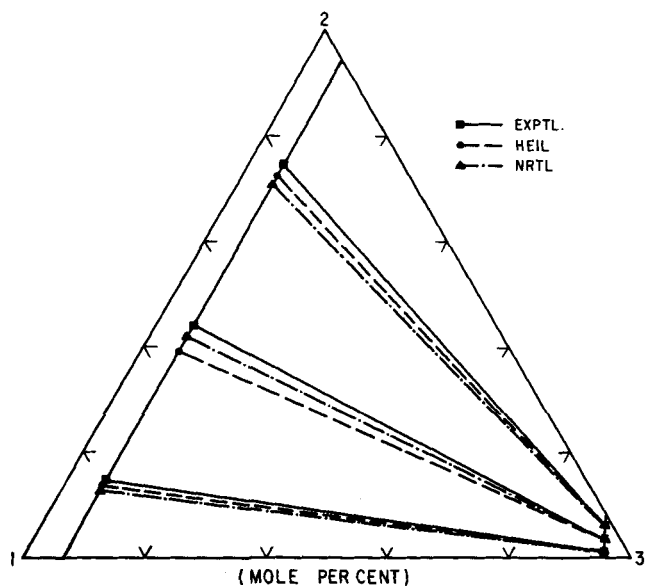


Fig. 6. Calculated and observed liquid-liquid equilibria for the system isooctane (1)-*n*-hexane (2)-furfural (3) at 30°C.

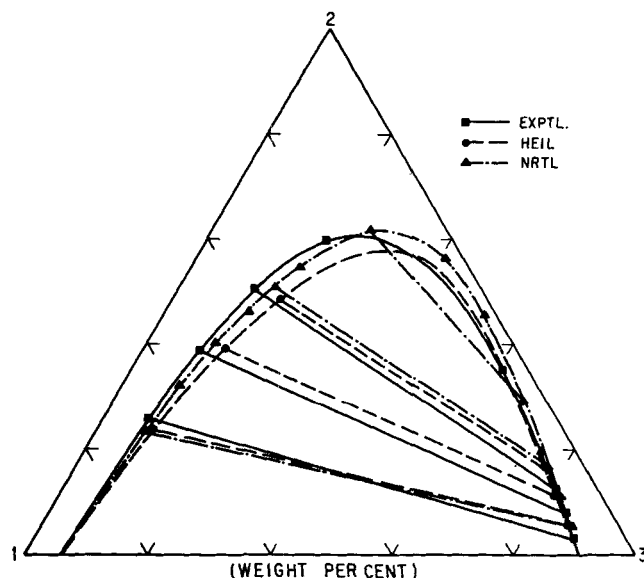


Fig. 8. Calculated and observed liquid-liquid equilibria for the system *n*-octane (1)-octene-1 (2)-nitroethane (3) at 0°C.

systems usually with a small loss of accuracy in the predictions.) For the NRTL equation only two fitting parameters are used for the binaries and no ternary constant is introduced. As shown in Table 4, both the mean arithmetic deviations and the confidence limits are better for the NRTL equation than for the Wohl equation even with optimized ternary constants.

LIQUID-LIQUID TERNARY EQUILIBRIA

Using the Heil equation, we can predict ternary liquid-liquid equilibria (solubility curve and tie lines) from binary data (vapor-liquid or liquid-liquid) in a limited number of cases. Good prediction is obtained when mutual solubilities are not too small ($> 5\%$ mole fraction). Plait points are predicted within about 10% mole fraction. Because of the maximum indicated in Figure 3, the Heil equation (for monomeric systems) does not apply when

two components of strongly nonideal mixtures have very small mutual solubilities (for example, water and hydrocarbons).

The NRTL equation, on the contrary, is generally applicable. It is possible to predict liquid-liquid ternary equilibria from binary data if the best value of α_{12} for each binary is chosen.

If binary vapor-liquid data are used, the resulting prediction depends on the quality of the data and on the right selection of α_{12} . For binary systems whose components are essentially immiscible, α_{12} has to be estimated. It appears that $\alpha_{12} = 0.20$ is suitable for such systems. Generally, the precision of the parameters obtained from vapor-liquid equilibria is not sufficient to predict accurately the tie lines, because, as we have seen, the error in the difference of the parameters is large. Liquid-liquid data are much more sensitive to the values of the parameters (and especially to the difference between the parameters) than are vapor-liquid data. Therefore the use of tie-line data to calculate some binary parameters is preferable because the precision is better; also experimental determination is easier. Whenever possible, parameters obtained from reliable mutual solubilities are preferred for the prediction of multicomponent phase equilibria. Liquid-liquid ternary results are also rather sensitive to the value of α_{12} chosen for the most nonideal binaries.

Figure 6 to 8 illustrate typical agreement between experimental data (12, 8, 15) and results calculated with the NRTL equation and, when applicable, with the Heil equation. In all cases, α_{12} is selected according to the rules given above. The solubility curve and the tie lines are calculated with the use of binary parameters only.

CONCLUSION

Two major conclusions result from our comparison of the local composition equations for the representation of the excess Gibbs energy of liquid mixtures.

Considering, at first, binary mixtures, it appears that binary data for many different types of mixtures cannot be represented with the same two-parameter equation. Even if the activity coefficients at infinite dilution are the same for two different mixtures, it does not follow that the activity coefficients at other concentrations are even approximately the same if the mixtures belong to different types. A very sensitive test of mixture type is provided by

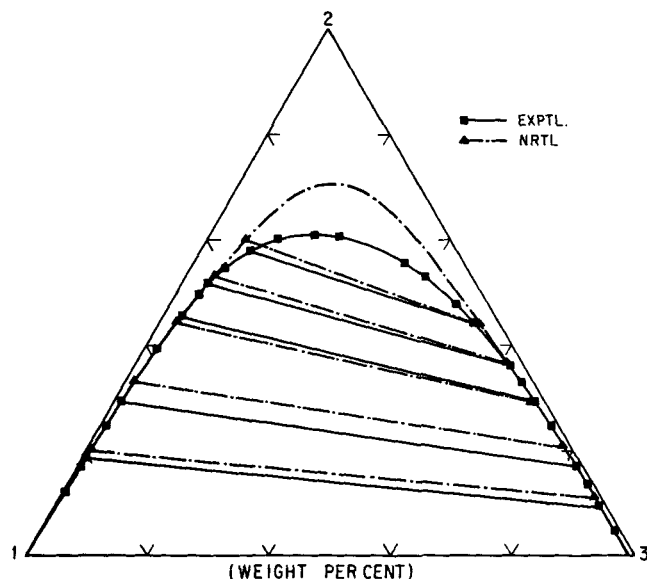


Fig. 7. Calculated and observed liquid-liquid equilibria for the system chloroform (1)-acetone (2)-water (3) at 25°C.

the existence or nonexistence of immiscibility for a given level of nonideality of the dilute solutions. In order to obtain a satisfactory representation of the properties of binary liquid mixtures, many authors have proposed empirical or semiempirical equations with three or more adjustable parameters; for example, Wohl (25), Redlich-Kister (13), and Black (3) have given expressions with three (or more) adjustable parameters to provide a classification of liquid mixtures. However, the precision of the experimental data frequently does not justify the use of three adjustable parameters. The NRTL equation uses only two adjustable parameters but it contains a third constant, selected according to the chemical characteristics of the components of the mixture, to provide the flexibility required for representing the shape of the excess Gibbs energy.

Turning to multicomponent mixtures, it is desirable to be able to predict the excess Gibbs energy from binary data alone. This should be possible if, as is probable, two-body interactions make the largest contribution to the excess properties. However, previously recommended expressions based on three-parameter equations for binary systems require either some ternary data or, additional simplifying assumptions. The new equation, based in a semiempirical way on the two-liquid theory of Scott, can be extended to the multicomponent case without introducing any additional assumptions; it appears to predict well ternary vapor-liquid and liquid-liquid equilibria without requiring a ternary constant.

The computation methods used in this work are outlined in Appendix K of reference 16 with a listing of computer programs to obtain the parameters in the NRTL equation for binary mixtures by fitting vapor-liquid data or by using mutual solubilities and to predict multicomponent vapor-liquid equilibria and ternary liquid-liquid equilibria.

NOTATION

a	= normalized parameter for symmetric systems
A, B	= van Laar constants
D	= difference between parameters; $D = (g_{12} - g_{22}) - (g_{21} - g_{11})$
g	= Gibbs energy per mole
$g^{(1)}$	= Gibbs energy for a cell containing molecule 1
g_{ij}	= energies of interaction between an i - j pair of molecules
G_{ji}	= coefficient as defined in Equation (37)
k	= Boltzmann's constant
N	= number of molecules
p	= coefficient (0 or 1) as defined in Table 1
q	= coefficient (0 or 1) as defined in Table 1
R	= gas constant
S	= sum of parameters; $S = (g_{12} - g_{22}) + (g_{21} - g_{11})$
T	= absolute temperature
v	= molar volume
w	= interchange energy
w_{12}	= potential energy for an interaction 1-2 on a lattice
W_{12}	= molar potential energy of interaction
x_i	= overall mole fraction of substance i
x_{ij}	= local mole fraction of molecule i in the immediate neighborhood of molecule j
X	= number of 1-2 interactions divided by z
y	= vapor mole fraction
z	= lattice coordination number

Greek Letters

α_{ij}	= nonrandomness constant for binary ij interactions
Δg^M	= Gibbs energy of mixing per mole

γ	= activity coefficient
δ	= root-mean-square deviation between calculated and experimental property
ξ_{ij}	= local volume fraction of molecule i in the immediate neighborhood of molecule j
ρ_{ij}	= coefficient as defined in Table 1
τ_{ji}	= coefficient as defined in Equation (36)
τ	= normalized parameter for symmetric systems

Superscripts

E	= excess
∞	= infinite dilution

Subscript

i	= component i
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