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Manuscript received October 10, 1978; revision received March 1, and accepted March 25, 1979.

Vapor-Liquid Equilibrium

H. C. VAN NESS
and
M. M. ABBOTT

Department of Chemical and Environmental Engineering
Rensselaer Polytechnic Institute
Troy, New York 12181

A general treatment of fugacities of liquid mixtures yields the proper thermodynamic functions for dealing with nonidealities of liquid phases in equilibrium with vapor mixtures for systems containing supercritical components. The activity coefficients of the supercritical components may be based on standard state fugacities for the hypothetical pure liquids or on Henry's constants. A comparison of the rigorous thermodynamic equations which apply to the liquid phase for the two alternatives shows that they are equivalent.

Part VI. Standard State Fugacities for Supercritical Components

SCOPE

Vapor/liquid equilibrium calculations for systems which include one or more supercritical components (that is, species whose critical temperatures are below the system temperature) are complicated by the fact that these species do not exist as pure liquids at the temperature of the system. Thus one cannot know the vapor pressure or, more fundamentally, the fugacity of the pure liquid upon which the activity coefficient is usually based. Moreover, high pressures are characteristic of such systems, and the usual assumption of pressure independence of the activity coefficients is not satisfactory.

For a supercritical component, two standard state fugacities upon which to base the activity coefficient have been used: first, a value obtained by extrapolation for the hypothetical pure liquid, and second, the value of Henry's constant. The latter has been considered preferable because it can be measured. For binary systems, little difficulty is encountered with the thermodynamic treatment in either case. For multicomponent systems, however, there has been much confusion.

A general treatment is presented here which yields the proper thermodynamic relations for both choices of standard state fugacity. The derivation of appropriate equations for activity coefficients is straightforward, progressing from binary through ternary to multicomponent systems.

CONCLUSIONS AND SIGNIFICANCE

The standard state fugacities for supercritical components of systems in vapor/liquid equilibrium may equally well be taken as Henry's constants or as the fugacities of hypothetical pure liquids. The thermodynamic treatment of liquid phase nonidealities based on activity coefficients for the two cases yields equivalent results. However, use of Henry's constants leads, in practice, to complex equations. The method of Prausnitz and Chueh (1968) as corrected by Abrams et al. (1975) is an example, but it incorporates additional and unnecessary complexity. Activity coefficients based on fugacities of the hypothetical pure liquids as standard state values lead to far simpler equations and have the additional advantage of symmetry. For a supercritical component, fugacities for the standard state of hypothetical pure liquid are as readily determined as are Henry's constants.

With the thermodynamics on a firm theoretical foundation, it becomes clear that treatment through activity coefficients of vapor/liquid equilibria in systems containing supercritical components is severely limited by our inability to take properly into account the effect of pressure on the activity coefficients and to model their composition dependence.

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In Figure 1 we show a schematic diagram of $\ln f$ plotted vs. x_1 for a binary system at constant T and P, where f is the fugacity of the liquid mixture. If values of f have been determined from vapor-liquid equilibrium data at constant T, then P represents a fixed pressure to which the data have been properly corrected. Thus, throughout this treatment, we presume f to be a function of composition only and do not address the problem of how to eliminate the pressure dependency. We simply assume it has been done.

The partial properties corresponding to $\ln f$ are $\ln(\hat{f}_1/x_1)$ and $\ln(\hat{f}_2/x_2)$ and are given by the tangent intercepts, as illustrated in Figure 1. The limiting tangent, drawn at $x_1 = 0$, provides Henry's constant k_1. By definition

$$k_1 = \lim_{x_1 \to 0} \frac{\hat{f}_1}{x_1} = \left(\frac{\hat{f}_1}{x_1}\right)^{\infty} \tag{1}$$

where (∞) signifies a value at infinite dilution. Thus

$$\lim_{x_1 \to 0} \ln \frac{\hat{f}_1}{x_1} = \ln\left(\frac{\hat{f}_1}{x_1}\right)^{\infty} = \ln k_1 \tag{2}$$

We may choose to measure $\ln f$ from any arbitrary reference line which we care to draw on Figure 1, rather than from the base line. In so doing we create new thermodynamic functions

$$\Delta \ln f = \ln f - \ln f^{\text{ref}} \tag{3}$$

In practice, a very limited number of reference lines has been found useful; we consider only two. First let

$$\ln f^{\text{ref}} = x_1 \ln f_1 + x_2 \ln f_2$$

This is the equation of the straight line on Figure 1 drawn between $\ln f_2$ and $\ln f_1$. Combining it with Equation (3), we have

$$\Delta \ln f = \ln f - x_1 \ln f_1 - x_2 \ln f_2 \tag{4}$$

Since $\ln f$ is related to its partial properties by

$$\ln f = \Sigma x_i \ln \frac{\hat{f}_i}{x_i} \tag{5}$$

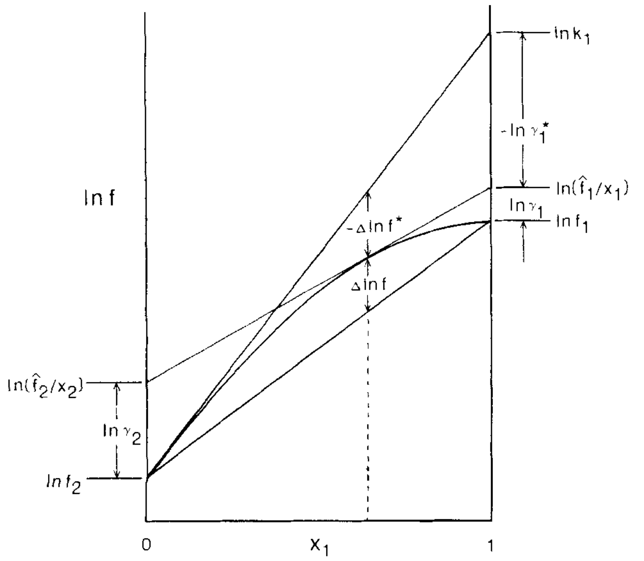

Fig. 1. Schematic diagram showing the relationship of ln f to its partial properties, activity coefficients, and related quantities for a binary system.

Equation (4) becomes

$$\Delta \ln f = x_1 \ln \frac{\hat{f}_1}{x_1} + x_2 \ln \frac{\hat{f}_2}{x_2} - x_1 \ln f_1 - x_2 \ln f_2$$

or

$$\Delta \ln f = x_1 \ln \frac{\hat{f}_1}{x_1 f_1} + x_2 \ln \frac{\hat{f}_2}{x_2 f_2} \tag{6}$$

The arguments of the logarithms on the right are by definition activity coefficients; Equation (6) may therefore be written as

$$g \equiv \Delta \ln f = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 \tag{7}$$

where $g \equiv G^E/RT$. These activity coefficients are based on (or normalized with respect to) the fugacities of the pure liquids taken as standard states. Since both components are treated in the same way, the activity coefficients of Equation (7) are said to be symmetrically normalized. This treatment is generally applied to the description of liquid-phase nonidealities for systems in vapor/liquid equilibrium at a temperature below the critical temperatures of all pure constituents. The species are then characterized as subcritical.

An alternative reference line is the one drawn tangent to the $\ln f$ curve of Figure 1 at $x_1 = 0$. The equation for this straight line between $\ln f_2$ and $\ln k_1$ is

$$\ln f^{\text{ref}} = x_1 \ln k_1 + x_2 \ln f_2$$

With Equation (3), this gives

$$\Delta \ln f^* = \ln f - x_1 \ln k_1 - x_2 \ln f_2 \tag{8}$$

where (*) merely identifies this particular function. Substitution for $\ln f$ by Equation (5) leads to

$$\Delta \ln f^* = x_1 \ln \frac{\hat{f}_1}{x_1 k_1} + x_2 \ln \frac{\hat{f}_2}{x_2 f_2}$$

We again identify the arguments of the logarithms on the right with activity coefficients and write

$$g^* \equiv \Delta \ln f^* = x_1 \ln \gamma_1^* + x_2 \ln \gamma_2 \tag{9}$$

where $g^* \equiv (G^E/RT)^*$. Here the activity coefficient for component 1 is based on a fugacity of pure species 1 equal to Henry's constant. Thus the standard state is the hypothetical state of pure species 1 that would obtain were the $\ln f$ vs. x_1 relation of Figure 1 actually provided by the tangent line at $x_1 = 0$. An activity coefficient so defined is denoted by (*), and this sign on the terms to the left of the equal sign of Equation (9) signals an unsymmetric normalization of the activity coefficients.

The second reference line, representing the tangent to the $\ln f$ vs. x_1 curve at $x_1 = 0$ and leading to unsymmetrically normalized activity coefficients, has been used when the liquid phase does not exist for some range of x_1 values adjacent to $x_1 = 1$. This problem arises when T is greater than the critical temperature of component 1, which then is a noncondensable solute in component 2, the solvent. Component 1 is characterized as supercritical. In this event the curve for $\ln f$ must be based on the limited range of data available, as illustrated in Figure 2, where the dashed portion of the curve represents an extrapolation.

Tangents drawn to the $\ln f$ curve of Figure 2 provide intercepts which are values of $\ln(\hat{f}_1/x_1)$ and $\ln(\hat{f}_2/x_2)$. Representative curves for these quantities are shown on Figure 2; indicated also are the line segments which

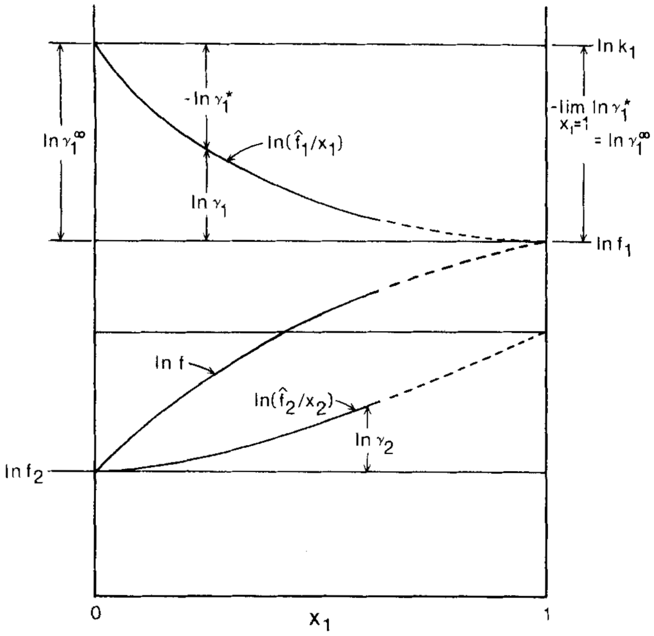

Fig. 2. Schematic diagram of ln f and derived quantities as a function of composition for a binary system. Component 1 is a supercritical solute, and the dashed portions of the curves represent extrapolations.

represent various activity coefficients as a result of their definitions. Note that the extrapolated portion of the curve for $\ln(\hat{f}_1/x_1)$ must have zero slope at $x_1 = 1$ because $\ln(\hat{f}_1/x_1)$ is a partial property with respect to $\ln f$.

We see immediately from Figure 2 that

$$\ln k_1 = \ln f_1 + \ln \gamma_1^\infty \tag{10}$$

and

$$\ln \gamma_1^* = \ln \gamma_1 - \ln \gamma_1^\infty \tag{11}$$

where

$$\ln \gamma_1^\infty = \lim_{x_1\to 0} \ln \gamma_1 = -\lim_{x_1\to 1} \ln \gamma_1^* \tag{12}$$

Although illustrated just for component 1, analogous equations apply to component 2 in a binary system. These equations allow complete interconvertibility between analytical expressions for symmetrically and unsymmetrically normalized activity coefficients.

For an elementary example, assume the available data can be correlated by the simple expression

$$g = Ax_1x_2$$

where parameter A is constant for given T and P. The activity coefficients are then

$$\ln \gamma_1 = Ax_2^2$$

$$\ln \gamma_2 = Ax_1^2$$

By Equation (12)

$$\ln \gamma_1^\infty = A$$

and Equations (10) and (11) yield

$$\ln k_1 = \ln f_1 + A$$

$$\ln \gamma_1^* = \ln \gamma_1 - A = Ax_2^2 - A = A(x_2^2 - 1)$$

In addition, by Equation (9)

$$g^* \equiv \Delta \ln f^* = x_1A(x_2^2 - 1) + x_2Ax_1^2 = -Ax_1^2$$

A value for A may be determined from the data by a variety of methods. Because of the unreliability usually associated with experimental k_1 values, we suggest a method which avoids their use. Since

$$g = x_1 \ln \frac{\hat{f}_1}{x_1} - x_1 \ln f_1 + x_2 \ln \frac{\hat{f}_2}{x_2} - x_2 \ln f_2 = Ax_1x_2$$

we have

$$x_1 \ln \frac{\hat{f}_1}{x_1} + x_2 \ln \frac{\hat{f}_2}{x_2} = x_1 \ln f_1 + x_2 \ln f_2 + Ax_1x_2$$

The data furnish a value for f_2 and values of $\hat{f}_1$ and $\hat{f}_2$ for various mole fractions (x_1, x_2) over the range where the liquid phase exists. The values of f_1 and A which lead to a best fit of the data are found by regression. Were a more complex correlating equation required, additional parameters would be found simultaneously.

Once we have values for f_1 and the correlating parameters, the data may be equally well represented by an expression for g^* with unsymmetrically normalized activity coefficients or by an expression for g with symmetrically normalized activity coefficients. Given either expression, the value of γ_1^∞ is provided by Equation (12), and Equations (10) and (11) then relate k_1 to f_1 and γ_1 to γ_1^*. The extrapolations shown in Figure 2 conform to equations with parameters found by a fit to the available data as represented by the solid lines.

Because of the interconvertibility between equations based on different standard states, there is no inherent advantage to the use of standard states based on Henry's law or of unsymmetrically normalized activity coefficients. Henry's law itself can, of course, be applied regardless of the choice of standard states. Henry's law and a standard state based on Henry's constant are two separate and distinct concepts. Henry's law merely states that

$$\hat{f}_i = k_ix_i$$

Given the value of f_i and an expression for γ_i, we can always evaluate Henry's constant by Equation (10):

$$k_i = f_i\gamma_i^\infty$$

Thus, an alternative expression of Henry's law is

$$\hat{f}_i = f_ix_i\gamma_i^\infty$$

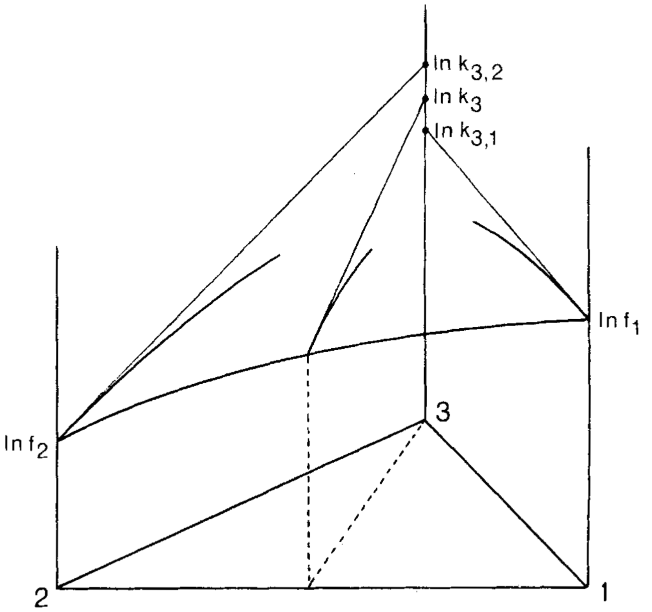

Fig. 3. Schematic representation of the ln f surface for a ternary system in which component 3 is supercritical. Intersections on the $x_3 = 1$ axis of tangents drawn to the surface at $x_3 = 0$ provide Henry's constants for component 3.

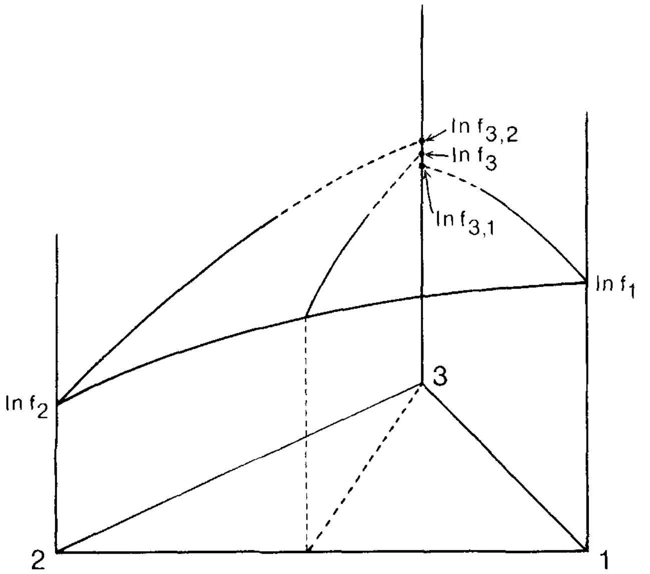

Fig. 4. Extrapolations of curves in the ln *f* surface for a ternary system yield fugacities for component 3 in hypothetical liquid states.

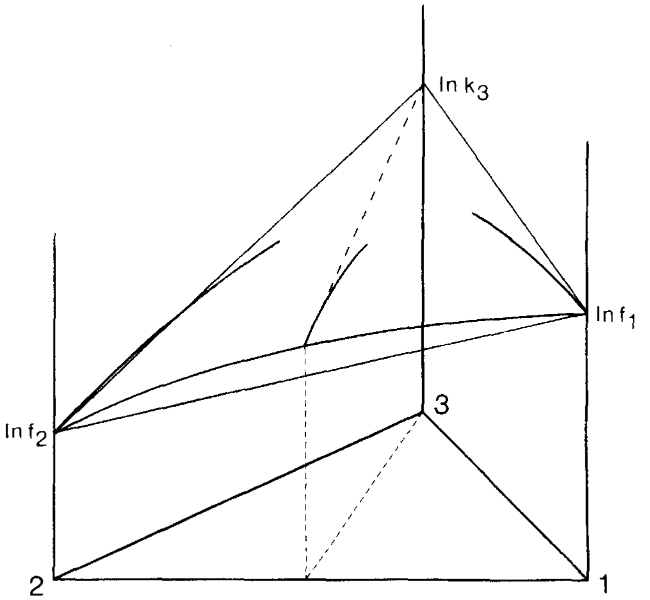

Fig. 5. Reference plane for the ln *f* surface passing through the points ln f_1, ln f_2, and ln k_3. Only the dashed line is a tangent to the ln *f* surface.

Since the exact expression is

$$\hat{f}_i = f_i x_i \gamma_i$$

Henry's law is inexact to the extent that γ_i differs from γ_i^∞.

TERNARY SYSTEMS

All this is preliminary to the treatment of multicomponent systems; consider first a ternary system for which components 1 and 2 are miscible solvents and component 3 is a noncondensable solute. The situation is illustrated schematically in Figure 3, which shows the ln f surface for the liquid mixture on a triangular grid representing mole fractions. This surface is incomplete because no experimental values exist in the neighborhood of pure component 3, the solute. Tangents drawn at $x_3 = 0$ are shown for the two binaries 3-1 and 3-2. The intercepts on the $x_3 = 1$ axis determine Henry's constants $k_{3,1}$ and $k_{3,2}$ for the two constituent binaries. Also shown is the tangent drawn at $x_3 = 0$ for an intermediate solvent composition. It is drawn in the vertical plane representing a constant ratio x_1/x_2 and intersects the $x_3 = 1$ axis at the value ln k_3, yielding Henry's constant for component 3 in the mixed solvent of composition:

$$x_1' = x_1/(x_1 + x_2) \quad \text{and} \quad x_2' = x_2/(x_1 + x_2) \qquad (13)$$

These solute free compositions obey the relations

$$x_1' + x_2' = 1 \quad \text{and} \quad x_1'/x_2' = x_1/x_2 \qquad (14)$$

Henry's constant k_3 is a function of x_1' and has the limiting values $k_{3,1}$ at $x_1' = 1$ and $k_{3,2}$ at $x_1' = 0$.

If we make independent extrapolations of the ln f curves as shown in Figure 4, we most likely find three different intercepts on the $x_3 = 1$ axis: ln $f_{3,1}$, ln $f_{3,2}$, ln f_3. For the binaries, Equation (10) with appropriate subscripts relates ln $f_{3,1}$ and ln $f_{3,2}$ to the corresponding Henry's constants:

$$\ln k_{3,1} = \ln \gamma_{3,1}^\infty + \ln f_{3,1} \qquad (15)$$

and

$$\ln k_{3,2} = \ln \gamma_{3,2}^\infty + \ln f_{3,2} \qquad (16)$$

For component 3 we have, by definition of the activity coefficient

$$\ln \frac{\hat{f}_3}{x_3} = \ln \gamma_3 + \ln f_3 \qquad (17)$$

In the limit as x_3 approaches zero

$$\lim_{x_3 \to 0} \ln \frac{\hat{f}_3}{x_3} = \lim_{x_3 \to 0} \ln \gamma_3 + \ln f_3$$

Because $\ln(\hat{f}_3/x_3)$ is a partial property, it represents a derivative with respect to n_3 at constant n_1 and n_2 and by Equation (13) at constant x_1' and x_2'. Therefore its limiting value, ln k_3, defines Henry's constant for the solute as it approaches infinite dilution at a constant composition of the mixed solvent. Thus we have the general relation

$$\ln k_3 = \ln \gamma_3^\infty + \ln f_3 \qquad (18)$$

Equations (15) and (16) are, of course, special cases. Subtraction of Equation (18) from Equation (17) yields

$$\ln \frac{\hat{f}_3}{x_3 k_3} = \ln \gamma_3 - \ln \gamma_3^\infty$$

or

$$\ln \gamma_3^* = \ln \gamma_3 - \ln \gamma_3^\infty \qquad (19)$$

Since ln k_3 is a function of x_1' with limiting values of ln $k_{3,1}$ and ln $k_{3,2}$ at $x_1' = 1$ and $x_1' = 0$, there is no single value of k_3 to characterize a unique standard state for component 3. If standard state fugacities are provided by the values of k_3, then one must abandon the traditional concept of the standard state as a particular state of component 3. Prausnitz and Chueh (1968) took this step.

The thermodynamics of the Prausnitz and Chueh procedure is most readily understood as an extension of the treatment of binary systems. Rather than a reference line, we have here a reference plane passing through the three points ln f_1, ln f_2, and ln k_3, as shown in Figure 5. Points ln f_1 and ln f_2 are fixed, but ln k_3 is a variable. Thus, the tilt of the reference plane depends on x_1' or on x_1/x_2. Reference fugacities are therefore given by

$$\ln f^{\text{ref}} = x_1 \ln f_1 + x_2 \ln f_2 + x_3 \ln k_3$$

and we define the function

$$\Delta \ln f^* = \ln f - x_1 \ln f_1 - x_2 \ln f_2 - x_3 \ln k_3 \quad (20)$$

Elimination of $\ln f$ by Equation (5) gives

$$\Delta \ln f^* = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 + x_3 \ln \gamma_3^* \quad (21)$$

If the right-hand side of this equation is identified with an excess Gibbs function, we can write

$$\Delta \ln f^* = g^* \equiv (G^E/RT)^* \quad (22)$$

One might therefore suppose that the logarithms on the right of Equation (21) are partial properties with respect to $\Delta \ln f^*$ or g^*. This is incorrect, however, as the following treatment shows.

For n moles, Equation (20) becomes

$$n\Delta \ln f^* = n \ln f - n_1 \ln f_1 - n_2 \ln f_2 - n_3 \ln k_3$$

Partial differentiation gives

$$\left[\frac{\partial(n\Delta \ln f^*)}{\partial n_1}\right]_{n2,n3} = \left[\frac{\partial(n \ln f)}{\partial n_1}\right]_{n2,n3} - \ln f_1 - n_3\left(\frac{\partial \ln k_3}{\partial n_1}\right)_{n2,n3}$$

$$\left[\frac{\partial(n\Delta \ln f^*)}{\partial n_2}\right]_{n1,n3} = \left[\frac{\partial(n \ln f)}{\partial n_2}\right]_{n1,n3} - \ln f_2 - n_3\left(\frac{\partial \ln k_3}{\partial n_2}\right)_{n1,n3}$$

$$\left[\frac{\partial(n\Delta \ln f^*)}{\partial n_3}\right]_{n1,n2} = \left[\frac{\partial(n \ln f)}{\partial n_3}\right]_{n1,n2} - \ln k_3$$

Note that $\ln k_3$ is fixed for given values of n_1 and n_2. Each of the quantities $\partial(n \ln f)/\partial n_i$ is the partial property $\ln(\hat{f}_i/x_i)$. Further, we define

$$\ln \gamma_i^R \equiv n_3\left(\frac{\partial \ln k_3}{\partial n_i}\right)_{n_j} \quad (i = 1, 2) \quad (23)$$

The three partial derivatives then become

$$\left[\frac{\partial(n\Delta \ln f^*)}{\partial n_1}\right]_{n2,n3} = \ln \frac{\hat{f}_1}{x_1} - \ln f_1 - \ln \gamma_1^R = \ln \frac{\gamma_1}{\gamma_1^R}$$

$$\left[\frac{\partial(n\Delta \ln f^*)}{\partial n_2}\right]_{n1,n3} = \ln \frac{\hat{f}_2}{x_2} - \ln f_2 - \ln \gamma_2^R = \ln \frac{\gamma_2}{\gamma_2^R}$$

$$\left[\frac{\partial(n\Delta \ln f^*)}{\partial n_3}\right]_{n1,n2} = \ln \frac{\hat{f}_3}{x_3} - \ln k_3 = \ln \gamma_3^*$$

Each of these quantities is evidently a partial property with respect to $\Delta \ln f^*$. Multiplication of each by the appropriate mole fraction and summation therefore gives

$$\Delta \ln f^* = x_1 \ln \frac{\gamma_1}{\gamma_1^R} + x_2 \ln \frac{\gamma_2}{\gamma_2^R} + x_3 \ln \gamma_3^* \quad (24)$$

Comparison of Equations (21) and (24) shows that

$$x_1 \ln \gamma_1^R + x_2 \ln \gamma_2^R = 0 \quad (25)$$

However, the individual terms are not zero.

The difference between Equations (21) and (24) is that the logarithms on the right of Equation (24) are related to $\Delta \ln f^*$ or g^* as partial properties, whereas those of Equation (21) are not. Thus, if we write an equation to model $\Delta \ln f^*$ or g^*, the derived **equations** for the partial properties represent the logarithms on the right of Equation (24) rather than those on the right of Equation (21).

We must have some means by which to determine the composition dependence of k_3. Since we cannot presume this to be given by experiment, we must rely on some sort of mixing rule that relates k_3 to quantities characteristic of the constituent binaries, for which data are assumed available. To establish this mixing rule, we *define* $\ln f_3$ (see Figure 4) by

$$\ln f_3 = x_1' \ln f_{3,1} + x_2' \ln f_{3,2} \quad (26)$$

In combination with Equation (18), this gives

$$\ln k_3 = \ln \gamma_3^{\infty} + x_1' \ln f_{3,1} + x_2' \ln f_{3,2} \quad (27)$$

Equations for $\ln \gamma_1^R$ and $\ln \gamma_2^R$ now follow from the definition of Equation (23) in combination with Equation (27):

$$\ln \gamma_1^R = n_3\left(\frac{\partial \ln \gamma_3^{\infty}}{\partial n_1}\right)_{n2,n3} + \frac{x_2' x_3}{x_1 + x_2} \ln \frac{f_{3,1}}{f_{3,2}} \quad (28)$$

and

$$\ln \gamma_2^R = n_3\left(\frac{\partial \ln \gamma_3^{\infty}}{\partial n_2}\right)_{n1,n3} + \frac{x_1' x_3}{x_1 + x_2} \ln \frac{f_{3,2}}{f_{3,1}} \quad (29)$$

An expression for $\ln \gamma_3^{\infty}$ comes from the equation chosen to model the data. Once this choice is made, Equations (28) and (29) allow evaluation of the γ_i^R.

Since Equation (27) for $\ln k_3$ is based on an arbitrary mixing rule, it does not inherently yield values of k_3 consistent with its experimental definition:

$$k_3 = \lim_{x_3 \to 0} \frac{\hat{f}_3}{x_3}$$

By the definition of γ_3^*

$$\frac{\hat{f}_3}{x_3} = k_3 \gamma_3^*$$

In the limit as $x_3 \to 0$ for a particular solvent composition, we have

$$\lim_{x_3 \to 0} \frac{\hat{f}_3}{x_3} = k_3 \lim_{x_3 \to 0} \gamma_3^*$$

Thus, if k_3 is to retain its fundamental experimental significance, the equation chosen to model the data must always yield the limiting value

$$\lim_{x_3 \to 0} \gamma_3^* = 1$$

The method just described is a complete treatment of the thermodynamics applicable to the liquid phase for a ternary system when Henry's constants serve as standard state fugacities for the single solute. It is therefore based on an unsymmetrical normalization of activity coefficients.

The treatment of Chueh and Prausnitz (1968) as corrected by Abrams et al. (1975) incorporates this method but adds an entirely superfluous step. They subtract from Equation (24) another function defined as

$$\Delta \ln f' = x_1 \ln \gamma_1' + x_2 \ln \gamma_2' \quad (30)$$

This gives

$$\Delta \ln f^* - \Delta \ln f' = x_1 \ln \frac{\gamma_1}{\gamma_1^R \gamma_1'} + x_2 \ln \frac{\gamma_2}{\gamma_2^R \gamma_2'} + x_3 \ln \gamma_3^* \quad (31)$$

where (′) makes reference to the solute-free 1-2 binary mixture of solvents. By definition

$$\gamma_i' = \frac{\hat{f}_i'}{x_i' f_i} \quad (i = 1, 2)$$

where $\hat{f}_i'$ is the fugacity of i in the solute-free binary system at $x_3 = 0$. The relation of x_i' to x_1 and x_2 is given by Equation (13).

The Gibbs-Duhem equation for this binary system is certainly valid:

$$x_1' d \ln \gamma_1' + x_2' d \ln \gamma_2' = 0$$

In accord with Equation (13), multiplication by $x_1 + x_2$ gives

$$x_1 d \ln \gamma_1' + x_2 d \ln \gamma_2' = 0$$

Therefore, Equation (30) also conforms to the Gibbs-Duhem equation, and so does Equation (31).

We may rewrite Equation (31) as

$$\Delta \ln f^+ = x_1 \ln \gamma_1^+ + x_2 \ln \gamma_2^+ + x_3 \ln \gamma_3^*$$

where (+) identifies quantities relevant to the Prausnitz-Chueh-Abrams treatment. Comparison with the original equation shows

$$\gamma_i \equiv \frac{\hat{f}_i}{x_i f_i} = \gamma_i^+ \gamma_i^R \gamma_i' \quad (i = 1, 2)$$

Thus, the traditional activity coefficient γ_i is given as the product of three other quantities. Such complexity is neither necessary nor advantageous; we pursue this treatment no further.

HYPOTHETICAL STANDARD STATE FUGACITIES

An alternative to the use of Henry's constants for standard state fugacities of the solute is use of values of f_3, the fugacity of hypothetical pure liquid 3. As shown by Figure 4, we again have no single value to characterize a unique standard state for the solute. Rather, we have a whole range of hypothetical pure liquid solutes and an extrapolated surface that terminates in a vertical line on the $x_3 = 1$ axis. We assume the same mixing rule as before and define $\ln f_3$ by Equation (26).

The plane of reference for $\ln f$ is now chosen to pass through the fixed points $\ln f_1$ and $\ln f_2$ and through the variable point $\ln f_3$. Reference fugacities are therefore given by

$$\ln f^{\text{ref}} = x_1 \ln f_1 + x_2 \ln f_2 + x_3 \ln f_3$$

This provides the function

$$\Delta \ln f = \ln f - x_1 \ln f_1 - x_2 \ln f_2 - x_3 \ln f_3 \tag{32}$$

Proceeding exactly as in the development of Equation (24), we find

$$\Delta \ln f = x_1 \ln \frac{\gamma_1}{\gamma_1^F} + x_2 \ln \frac{\gamma_2}{\gamma_2^F} + x_3 \ln \gamma_3 \tag{33}$$

where for each component

$$\gamma_i = \frac{\hat{f}_i}{x_i f_i}$$

and

$$\ln \gamma_i^F = n_3 \left(\frac{\partial \ln f_3}{\partial n_i} \right)_{n_j} \quad (i = 1, 2) \tag{34}$$

With Equation (26), this yields

$$\ln \gamma_1^F = \frac{x_2' x_3}{x_1 + x_2} \ln \frac{f_{3,1}}{f_{3,2}} \tag{35}$$

and

$$\ln \gamma_2^F = \frac{x_1' x_3}{x_1 + x_2} \ln \frac{f_{3,2}}{f_{3,1}} \tag{36}$$

These equations clearly satisfy the relation

$$x_1 \ln \gamma_1^F + x_2 \ln \gamma_2^F = 0$$

Equation (33) can therefore also be written as

$$\Delta \ln f = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 + x_3 \ln \gamma_3 \tag{37}$$

Again, we can identify $\Delta \ln f$ with an excess Gibbs function:

$$\Delta \ln f = g \equiv G^E/RT \tag{38}$$

The partial properties with respect to this function are the logarithms on the right of Equation (33), not those of Equation (37).

As an elementary example, consider the case for which the constituent binaries can be modeled by equations of the form $g_{ij} = A_{ij} x_i x_j$ and the ternary by

$$g = g_{12} + g_{13} + g_{23}$$

Then

$$g \equiv \Delta \ln f = A_{12} x_1 x_2 + A_{13} x_1 x_3 + A_{23} x_2 x_3 \tag{39}$$

From this equation we get

$$\left[\frac{\partial (ng)}{\partial n_1} \right]_{n2,n3} = A_{12} x_2 + A_{13} x_3 - g$$

$$\left[\frac{\partial (ng)}{\partial n_2} \right]_{n1,n3} = A_{12} x_1 + A_{23} x_3 - g$$

$$\left[\frac{\partial (ng)}{\partial n_3} \right]_{n1,n2} = A_{13} x_1 + A_{23} x_2 - g$$

These partial properties are identified with the logarithms on the right of Equation (33). Therefore, with Equations (35) and (36), we get

$$\ln \gamma_1 = A_{12} x_2 + A_{13} x_3 - g + \frac{x_2' x_3}{1 - x_3} \ln \frac{f_{3,1}}{f_{3,2}} \tag{40}$$

$$\ln \gamma_2 = A_{12} x_1 + A_{23} x_3 - g + \frac{x_1' x_3}{1 - x_3} \ln \frac{f_{3,2}}{f_{3,1}} \tag{41}$$

$$\ln \gamma_3 = A_{13} x_1 + A_{23} x_2 - g \tag{42}$$

These equations provide values of the activity coefficients once A_{12}, A_{13}, A_{23}, $f_{3,1}$, and $f_{3,2}$ are evaluated from data for the binary systems. The fugacities are given by

$$\hat{f}_i = x_i \gamma_i f_i$$

where for component 3, f_3 is evaluated by Equation (26). The procedure based on symmetrically normalized activity coefficients is simple and direct.

By contrast, we find the procedure based on unsymmetrically normalized activity coefficients far from simple. First, we need an expression for $g^* \equiv \Delta \ln f^*$. Combination of Equations (19), (21), and (37) shows that

$$g^* \equiv \Delta \ln f^* = \Delta \ln f - x_3 \ln \gamma_3^\infty \tag{43}$$

We can get an expression for $\ln \gamma_3^\infty$ from Equation (42) when evaluated at $x_3 = 0$, $x_1 = x_1'$, and $x_2 = x_2'$:

$$\ln \gamma_3^\infty = A_{13} x_1' + A_{23} x_2' - A_{12} x_1' x_2' \tag{44}$$

Combining Equations (39), (43), and (44), we find after reduction

$$g^* \equiv \Delta \ln f^* = A_{12}x_1'x_2'(1 - x_1x_3 - x_2x_3) - A_{13}x_1'x_3^2 - A_{23}x_2'x_3^2$$

The partial properties with respect to this function are identified with the logarithms on the right of Equation (24). Thus we find

$$\ln \gamma_1 = \frac{x_2'x_3}{(1 - x_3)} \left\{ \left[\frac{(1 - x_1)(1 - x_3)^2}{x_3} + x_2' - x_1' \right] A_{12} + \left[\frac{(1 - x_1)(1 - x_3)^2}{x_2} - 1 \right] A_{13} + x_3(2 - x_3)A_{23} \right\} + \ln \gamma_1^R \quad (45)$$

$$\ln \gamma_2 = \frac{x_1'x_3}{(1 - x_3)} \left\{ \left[\frac{(1 - x_2)(1 - x_3)^2}{x_3} + x_1' - x_2' \right] A_{12} + \left[\frac{(1 - x_2)(1 - x_3)^2}{x_1} - 1 \right] A_{23} + x_3(2 - x_3)A_{13} \right\} + \ln \gamma_2^R \quad (46)$$

$$\ln \gamma_3^* = x_3(2 - x_3)(x_1'x_2'A_{12} - x_1'A_{13} - x_2'A_{23}) \quad (47)$$

Note that this model always gives $\gamma_3^* = 1$ when $x_3 = 0$, thus preserving the physical significance of Henry's constants. The quantities $\ln \gamma_1^R$ and $\ln \gamma_2^R$ are given by Equations (28) and (29), which in conjunction with Equation (44) yield

$$\ln \gamma_1^R = \frac{x_2'x_3}{1 - x_3} \left[A_{13} - A_{23} - (x_2' - x_1')A_{12} + \ln \frac{f_{3,2}}{f_{3,1}} \right] \quad (48)$$

$$\ln \gamma_2^R = \frac{x_1'x_3}{1 - x_3} \left[A_{23} - A_{13} - (x_1' - x_2')A_{12} + \ln \frac{f_{3,1}}{f_{3,2}} \right] \quad (49)$$

Equations (45) and (48) together provide values of the activity coefficient γ_1; similarly, Equations (46) and (49) yield values of γ_2. From these

$$\hat{f}_i = x_i\gamma_i f_i \quad (i = 1, 2)$$

Equation (47) gives γ_3^*, from which

$$\hat{f}_3 = x_3\gamma_3^* k_3$$

with k_3 evaluated by Equation (27) with $\ln \gamma_3^\infty$ given by Equation (44).

The two methods are, of course, equivalent, producing the same results from the same starting information. However, the complexity of the method based on Henry's constants as standard state fugacities for the solute makes it generally unattractive. Any advantage it might have is not to be found in the thermodynamic treatment.

MULTICOMPONENT SYSTEMS

The treatment based on symmetrically normalized activity coefficients is readily generalized to multicomponent systems. We let subscript s identify the general *solvent* species and subscript σ identify the general *solute* species. Then, by definition

$$g \equiv \Delta \ln f = \ln f - \sum_s x_s \ln f_s - \sum_\sigma x_\sigma \ln f_\sigma \quad (50)$$

and

$$ng \equiv n\Delta \ln f = n \ln f - \sum_s n_s \ln f_s - \sum_\sigma n_\sigma \ln f_\sigma \quad (51)$$

We now differentiate partially with respect to the mole number of each particular species with all other mole numbers n_j (and T and P) held constant. We do this first for a solvent species, letting subscript i denote the specific solvent and subscript k all other solvents. Equation (51) is then written:

$$ng = n \ln f - n_i \ln f_i - \sum_k n_k \ln f_k - \sum_\sigma n_\sigma \ln f_\sigma$$

Differentiation with respect to n_i yields

$$\left[\frac{\partial(ng)}{\partial n_i}\right]_{n_j} = \left[\frac{\partial(n \ln f)}{\partial n_i}\right]_{n_j} - \ln f_i - \sum_\sigma n_\sigma \left(\frac{\partial \ln f_\sigma}{\partial n_i}\right)_{n_j} \quad (52)$$

For a solute species, we let subscript q denote the specific solute and subscript r all other solutes. Equation (51) is then written:

$$ng = n \ln f - \sum_s n_s \ln f_s - n_q \ln f_q - \sum_r n_r \ln f_r$$

Differentiation with respect to n_q gives:

$$\left[\frac{\partial(ng)}{\partial n_q}\right]_{n_j} = \left[\frac{\partial(n \ln f)}{\partial n_q}\right]_{n_j} - \ln f_q \quad (53)$$

This equation depends on a definition of $\ln f_\sigma$ for each solute species that makes it depend solely on the *solvent* composition. This definition is given later.

Each of the first terms on the right of Equations (52) and (53) is a partial property, namely, $\ln(\hat{f}_i/x_i)$ or $\ln(\hat{f}_q/x_q)$; therefore, these equations become

$$\left[\frac{\partial(ng)}{\partial n_i}\right]_{n_j} = \ln \frac{\hat{f}_i}{x_i f_i} - \sum_\sigma n_\sigma \left(\frac{\partial \ln f_\sigma}{\partial n_i}\right)_{n_j} = \ln \gamma_i - \ln \gamma_i^F \quad (54)$$

and

$$\left[\frac{\partial(ng)}{\partial n_q}\right]_{n_j} = \ln \frac{\hat{f}_q}{x_q f_q} = \ln \gamma_q \quad (55)$$

where we define

$$\ln \gamma_i^F \equiv \sum_\sigma n_\sigma \left(\frac{\partial \ln f_\sigma}{\partial n_i}\right)_{n_j} \quad (56)$$

Multiplication of Equations (54) and (55) by the appropriate mole fractions and summation over all components gives

$$g \equiv \Delta \ln f = \sum_s x_s \ln \frac{\gamma_s}{\gamma_s^F} + \sum_\sigma x_\sigma \ln \gamma_\sigma \quad (57)$$

The logarithms on the right are partial properties with respect to the function $g \equiv G^E/RT$. It follows from Equation (50) that

$$g \equiv \sum_s x_s \ln \gamma_s + \sum_\sigma x_\sigma \ln \gamma_\sigma \quad (58)$$

Comparison of Equations (57) and (58) shows that

$$\sum_s x_s \ln \gamma_s^F = 0 \quad (59)$$

We define $\ln f_q$ for any solute species q by

$$\ln f_q = \sum_s x_s' \ln f_{q,s} \tag{60}$$

where $f_{q,s}$ is the fugacity of (hypothetical) pure q for the binary system $q - s$, and x_s' is the mole fraction of solvent s in the all-solute-free solution. Thus, $\ln f_q$ (and in general $\ln f_\sigma$) depends solely on solvent composition. Equation (60) may be written

$$\ln f_q = \sum_s \frac{n_s}{\sum_s n_s} \ln f_{q,s}$$

or

$$\ln f_q = \frac{n_i}{\sum_s n_s} \ln f_{q,i} + \sum_k \frac{n_k}{\sum_s n_s} \ln f_{q,k}$$

Differentiating partially with respect to n_i, we get

$$\left(\frac{\partial \ln f_q}{\partial n_i}\right)_{nj} = \frac{1}{\sum_s n_s}\left[(1 - x_i') \ln f_{q,i} - \sum_k x_k' \ln f_{q,k}\right]$$

Since $1 - x_i' = \sum_k x_k'$, this reduces to

$$\left(\frac{\partial \ln f_q}{\partial n_i}\right)_{nj} = \frac{1}{\sum_s n_s} \sum_k x_k' \ln \frac{f_{q,i}}{f_{q,k}}$$

Because a term for which $k = i$ is identically zero, we may as well sum over all solvents s; thus

$$\left(\frac{\partial \ln f_q}{\partial n_i}\right)_{nj} = \frac{1}{\sum_s n_s} \sum_s x_s' \ln \frac{f_{q,i}}{f_{q,s}}$$

Substitution into Equation (56) gives

$$\ln \gamma_i^F = \sum_\sigma \frac{n_\sigma}{\sum_s n_s} \sum_s x_s' \ln \frac{f_{\sigma,i}}{f_{\sigma,s}}$$

$$= \sum_\sigma \frac{x_\sigma}{\sum_s x_s} \sum_s \frac{x_s}{\sum_s x_s} \ln \frac{f_{\sigma,i}}{f_{\sigma,s}}$$

or, finally

$$\ln \gamma_i^F = \frac{1}{\left(\sum_s x_s\right)^2} \sum_\sigma \sum_s x_\sigma x_s \ln \frac{f_{\sigma,i}}{f_{\sigma,s}} \tag{61}$$

This equation with Equations (54) and (55) allows evaluation of all activity coefficients once one adopts a model equation for $g \equiv G^E/RT$.

The only complication in this procedure is the lack of single values for the $f_{\sigma,s}$, the fugacities of hypothetical pure liquid solutes. If, for a given solute q, all $f_{q,s}$ values are the same, then in Equation (61) $f_{\sigma,i} = f_{\sigma,s}$ for every term of the sum, and all γ_i^F values are unity. This reduces the procedure to that applicable when all species are condensable. The problem is to find a single f_q that satisfactorily correlates the data for all binaries $q - s$ made up of solute q and each of the individual solvents. This requires extrapolations of data for binary systems to a common intercept, as indicated for a ternary system in Figure 6. There is no reason, in principle, why this cannot be done, though it may well require more complex correlating equations than would otherwise be necessary. With modern electronic computers, it might even be possible by regression of sufficient data to establish for noncondensable species standard state fugacities of some general applicability, even to the extent of including the temperature dependency.

We have in this paper dealt only with the formal thermodynamic treatment of liquid solutions that contain supercritical species. Our use of a very simple (and undoubtedly naive) equation by way of an example for the composition dependence of G^E should not suggest that the problem of modeling G^E has been solved. Moreover, as stated at the beginning, this paper is conditioned by the assumption that all data are corrected to a fixed pressure. As shown by Van Ness (1979), the correction of activity coefficients to zero pressure in the manner suggested by Chueh and Prausnitz is not likely to be satisfactory in the critical region. Until we can account properly for both the composition and pressure dependence of the activity coefficients, any general method of dealing with high pressure vapor/liquid equilibria through activity coefficients will lead to uncertain results, no matter how exact the thermodynamic treatment. If these problems remain intractable, then the equation-of-state approach may well prove advantageous.

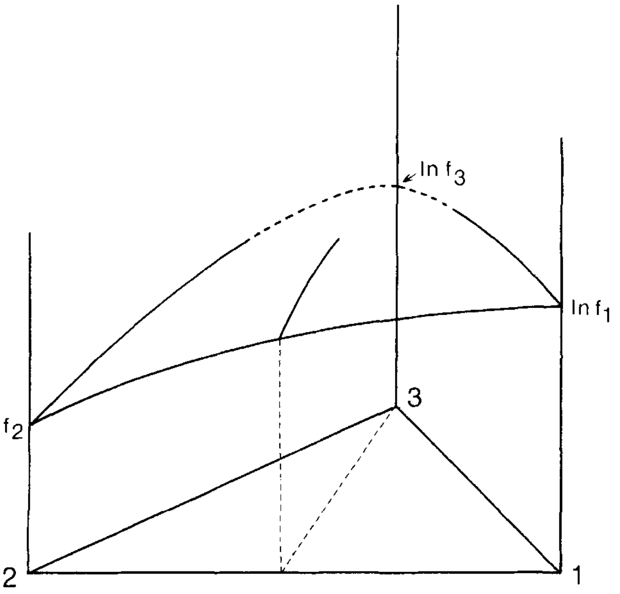

Fig. 6. Schematic diagram of the ln f surface showing extrapolations of the curves for the 1-3 and 2-3 binaries to a common intercept on the $x_3 = 1$ axis.

NOTATION

A = parameter
f = fugacity of a mixture
f_i = fugacity of pure component i in general
$f_{i,j}$ = standard state fugacity of pure i for the $i - j$ binary
$\hat{f}_i$ = fugacity of component i in solution
G^E = excess Gibbs function (free energy)
g = G^E/RT
k_i = Henry's constant for component i in general
$k_{i,j}$ = Henry's constant for component i in the $i - j$ binary
n = total number of moles
n_i = number of moles of component i
P = pressure
R = universal gas constant

T = absolute temperature
x_i = mole fraction of component i in solution
γ_i = activity coefficient of component i in general
$\gamma_{i,j}$ = activity coefficient of component i in the $i - j$ binary
γ_i^F = factor defined by Equation (34) or (56)
γ_i^R = factor defined by Equation (23)

Superscripts

$*$ = unsymmetric normalization of activity coefficients
∞ = value at infinite dilution
$'$ = value for solute-free mixture

Subscripts

s = solvent species
σ = solute species

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Manuscript received January 2, 1979; revision received April 3, and accepted April 18, 1979.

A New Correlation for Saturated Densities of Liquids and Their Mixtures

RISDON W. HANKINSON
and
GEORGE H. THOMSON
308 TRW Building
Technical Systems Development
Phillips Petroleum Company
Bartlesville, Oklahoma 74004

A new correlation has been developed for the densities of saturated liquids and their mixtures. The correlation is relatively easy to use and is applicable to a wide variety of liquids. The saturated liquid density correlation is flexible and consistent and requires only reduced temperature, acentric factor, and a characteristic volume for each pure compound. Mixing rules are given. When tested against a data base of 2 657 points of pure compound liquid density data for 97 hydrocarbons and 1 851 points for 103 other compounds, the new correlation gave an average absolute error of 0.37% compared to 2.14% for the Yen-Woods correlation and 0.50% for the SDR equation as modified by Spencer and Danner. For 2 994 points of liquid mixture density data for 167 mixtures, the new correlation gave an average absolute error of 1.40% compared to 5.64% for the Yen-Woods correlation and 2.95% for the SDR equation. Characteristic volumes are listed for 200 compounds; they are generalized as functions of acentric factor for various types of compounds and are compared to critical volumes.

SCOPE

The objective of this work was to develop and extensively test an equation for the computation of saturated liquid densities of pure compounds and their bubble point mixtures that has the following attributes: sufficiently general to apply to a wide range of compound classes, flexible enough to allow accurate calibration to known pure compound data, predictive in those cases where such data are unavailable or of uncertain accuracy, mathematically consistent in that there are no discontinuities in the value or slope in the range $0.25 < T_R < 0.98$, capable of being calibrated to mixtures for precise work, and simple enough for inclusion in process simulators and on microprocessors. In order to provide extensive testing and evaluation, it was necessary to develop an experimental data base representative of the wide variety of compounds and mixtures of interest.

CONCLUSIONS AND SIGNIFICANCE

A corresponding states equation which explicitly relates the saturated liquid volume of a pure compound to its reduced temperature and a readily available parameter, termed the characteristic volume, has been developed. The characteristic volumes are reported for 200 pure compounds. An evaluated set of mixing rules is presented.

The saturated liquid volumes obtained from the corresponding states liquid density (COSTALD) equation reproduce 4 508 points of experimental data on 190 different compounds to within 0.375 average absolute percent over the reduced temperature range of $0.25 < T_R < 0.98$. For 141 binary systems, 13 ternary systems, and 13 higher multicomponent systems, the 2 994 calculated densities agree with the experimental data to within 1.39 percent. For the 2 069 points of data on hydrocarbons and hydro-

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