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CALCULATION OF HIGH-PRESSURE VAPOR-LIQUID EQUILIBRIA

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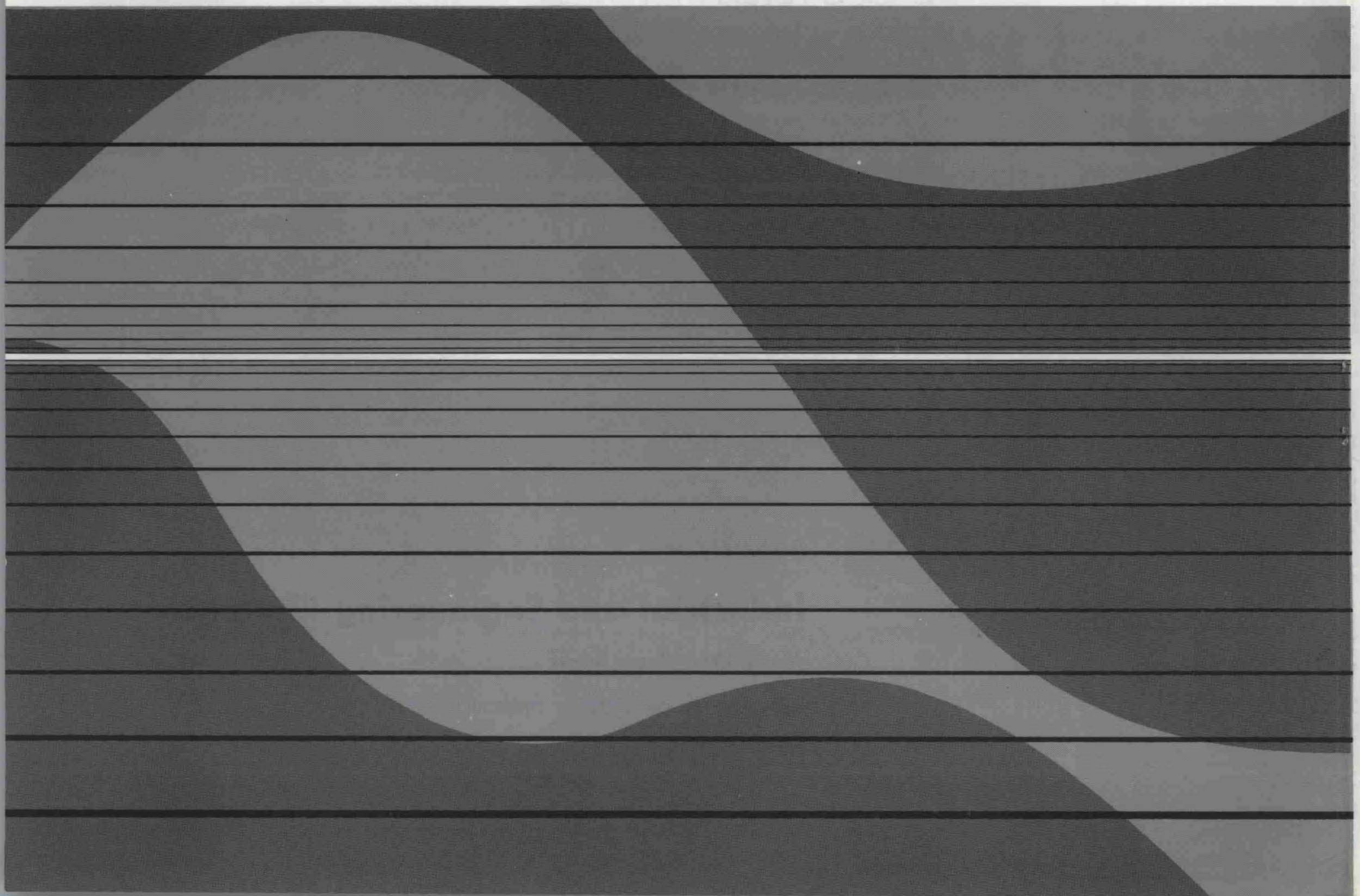
Fugacity coefficients, activity coefficients, and liquid partial molar volumes are the keys to the thermodynamic development of these equilibrium calculations

Although it has been common practice for many years to subject vapor-liquid equilibrium data to thermodynamic analysis, in the past this practice has been largely confined to systems at low or moderate pressures. While many experimental studies of high-pressure vapor-liquid equilibria have been published, little work has been reported on the reduction of such data to thermodynamic functions. However, such reduction is necessary for interpreting and correlating experimental data; thermodynamic analysis is the essential tool whereby experimental data can be generalized to enable prediction of phase behavior under conditions different from those at which the data were obtained. This tool is particularly useful for engineering work where it is often necessary to predict from binary data the behavior of a system containing more than two components.

In this work, we discuss thermodynamic analysis of vapor-liquid equilibria at high pressures, including the critical region. We restrict attention to systems containing nonpolar (or slightly polar) fluids such as those encountered in the petroleum and related industries. In particular, we present equations for reducing raw binary data to thermodynamically significant binary parameters; upon generalizing these equations to systems containing any number of components, we then predict phase behavior of multicomponent mixtures without introducing any ternary (or higher) parameters.



The fundamental equation of vapor-liquid equilibrium is conveniently written in terms of fugacities; for each component i the fugacity in the vapor f_i^V is equal to that in the liquid, f_i^L:

$$f_i^V = f_i^L \tag{1}$$

To facilitate thermodynamic analysis, we introduce two auxiliary functions: the vapor-phase fugacity coefficient ϕ_i and the liquid-phase activity coefficient γ_i:

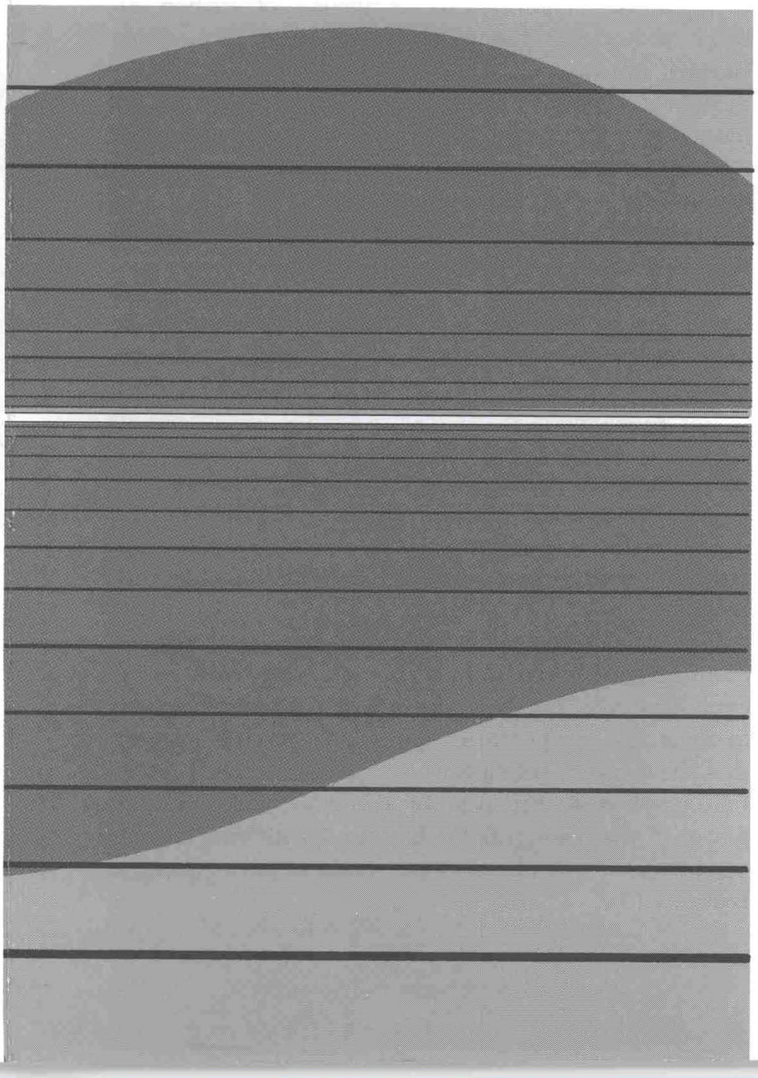
$$f_i^V = \varphi_i y_i P \tag{2}$$

$$f_i^L = \gamma_i x_i f_i^o \tag{3}$$

where y and x are, respectively, mole fractions in the vapor and in the liquid, P is the total pressure, and f_i^o is the standard-state fugacity of component i. Each of these auxiliary functions is discussed separately; Section A considers the fugacity coefficient while Sections B and C consider the activity coefficient. Finally, in Section D we synthesize the analysis of the other sections and compare with experiment some predicted results for several multicomponent systems.

A. Vapor-Phase Fugacity Coefficients

In this section we are concerned with a reliable technique for calculating vapor-phase fugacity coefficients in nonpolar mixtures, including those containing one of the quantum gases. To that end we propose to use the Redlich-Kwong equation with certain modifications.



The Redlich-Kwong equation (*32*) is now nearly 20 years old; recently it has been discussed by several authors (*2*, *12*, *36*, *41*), and it is generally regarded as the best two-parameter equation now available (*40*). For mixtures, however, it often gives poor results, as does the recent modification given by Redlich and coworkers (*31*). The failure of the equation to give consistently good results for mixtures is due to the inflexible mixing rules for the composition dependence of the equation-of-state constants. We propose a modified mixing rule for the constant a; this modification incorporates one characteristic binary constant, and such constants have been reported for 115 binary systems (*8*). Extension to multicomponent systems follows without further assumptions and with no ternary (or higher) constants. A somewhat similar treatment, restricted to paraffin–carbon dioxide mixtures, has been suggested by Joffe and Zudkevitch (*16*). Other modifications of the Redlich-Kwong equation have been reported by Wilson (*41*), Esters and Tully (*12*), Robinson and Jacoby (*36*), and by Barner, Pigford, and Schreiner (*2*).

The Redlich-Kwong equation is:

$$P = \frac{RT}{v - b} - \frac{a}{T^{0.5}v(v + b)} \tag{4}$$

where

$$a = \frac{\Omega_a R^2 T_{c_i}^{2.5}}{P_{c_i}} \tag{5}$$

$$b = \frac{\Omega_b R T_{c_i}}{P_{c_i}} \tag{6}$$

The dimensionless constants Ω_a and Ω_b are, respectively, 0.4278 and 0.0867 if the first and second isothermal derivatives of pressure with respect to volume are set equal to zero at the critical point. In vapor-liquid equilibria, however, we are interested in the volumetric behavior of saturated vapors over a relatively wide range of temperature, rather than in the critical region only. We propose, therefore, to evaluate Ω_a and Ω_b for each pure component by fitting Equation 4 to the volumetric data of the saturated vapor. The temperature range used is that from the normal boiling point to the critical temperature. A list of Ω_a and Ω_b for the saturated vapors of 19 pure substances most often encountered in high pressure vapor-liquid equilibria has been given (*8*).

To apply Equation 4 to mixtures, we need a mixing rule. We propose:

$$b = \sum_{i=1}^{N} y_i b_i \tag{7}$$

where

$$b_i = \frac{\Omega_{b_i} R T_{c_i}}{P_{c_i}} \tag{8}$$

and

$$a = \sum_{i=1}^{N} \sum_{j=1}^{N} y_i y_j a_{ij} \qquad (a_{ij} \neq \sqrt{a_{ii} a_{jj}}) \tag{9}$$

where

$$a_{ii} = \frac{\Omega_{a_i} R^2 T_{c_i}^{2.5}}{P_{c_i}} \tag{10}$$

$$a_{ij} = \frac{(\Omega_{a_i} + \Omega_{a_j}) R^2 T_{c_{ij}}^{2.5}}{2\, P_{c_{ij}}} \tag{11}$$

$$P_{c_{ij}} = \frac{z_{c_{ij}} R T_{c_{ij}}}{v_{c_{ij}}} \tag{12}$$

$$v_{c_{ij}}^{1/3} = \frac{1}{2} \left(v_{c_i}^{1/3} + v_{c_j}^{1/3}\right) \tag{13}$$

$$z_{c_{ij}} = 0.291 - 0.08 \left(\frac{\omega_i + \omega_j}{2}\right) \tag{14}$$

$$T_{c_{ij}} = \sqrt{T_{c_{ii}} T_{c_{jj}}}\,(1 - k_{ij}) \tag{15}$$

The binary constant k_{ij} represents the deviation from the geometric mean for $T_{c_{ij}}$. It is a constant characteristic of the *i-j* interaction; to a good approximation k_{ij} is independent of the temperature, density, and composition. In general, k_{ij} must be obtained from some experimental information about the binary interaction. Good sources of this information are provided by second virial cross coefficients (*28*). Best estimates of k_{ij} have been reported for 115 binary systems (*8*).

Fugacity coefficient. The fugacity of a component i in a gas mixture is related to the total pressure P and its mole fraction y_i through the fugacity coefficient φ_i as shown in Equation 2 of the preceding section.

The fugacity coefficient is a function of pressure, temperature, and gas composition; it is related to the volumetric properties of the gas mixture by the exact relation (*3, 24*):

$$RT \ln \varphi_i = \int_V^\infty \left[\left(\frac{\partial P}{\partial n_i} \right)_{T,V,n_j} - \frac{RT}{V} \right] dV - RT \ln z \tag{16}$$

where V is the total volume of the gas mixture, and z is the compressibility of the gas mixture at T and P.

By substituting Equation 4 and the mixing rules, Equations 7 to 15, into 16, the fugacity coefficient of component k in the mixture becomes:

$$\ln \varphi_k = \ln \frac{v}{v-b} + \frac{b_k}{v-b} - \frac{2 \sum_{i=1}^{N} y_i a_{ik}}{RT^{3/2} b} \ln \frac{v+b}{v} + \frac{a b_k}{RT^{3/2} b^2} \left[\ln \frac{v+b}{v} - \frac{b}{v+b} \right] - \ln \frac{Pv}{RT} \tag{17}$$

The molar volume, v, is that of the gas mixture; it is obtained by solving Equation 4 (which is cubic in v) and taking the largest real root for v.

Figure 1 shows experimental and calculated fugacity coefficients of carbon dioxide in a mixture containing 85 mole per cent *n*-butane at 340° F. The experimental fugacity coefficients of carbon dioxide are obtained from the volumetric data of Olds *et al.* (*22*). The comparison is a rather stringent one since the mole fraction of carbon dioxide is small and the gas mixture is near its critical temperature. The fugacity coefficient of carbon dioxide shows an unusual pressure dependence, going through two inflections and a sharp maximum. Agreement is good considering the uncertainty involved in the numerical differentiation of the experimental data. Also indicated is the poor result obtained when the geometrical mean assumption is used for $T_{c_{12}}$. The Lewis fugacity rule fails badly at all pressures, since the mole fraction of carbon dioxide is small.

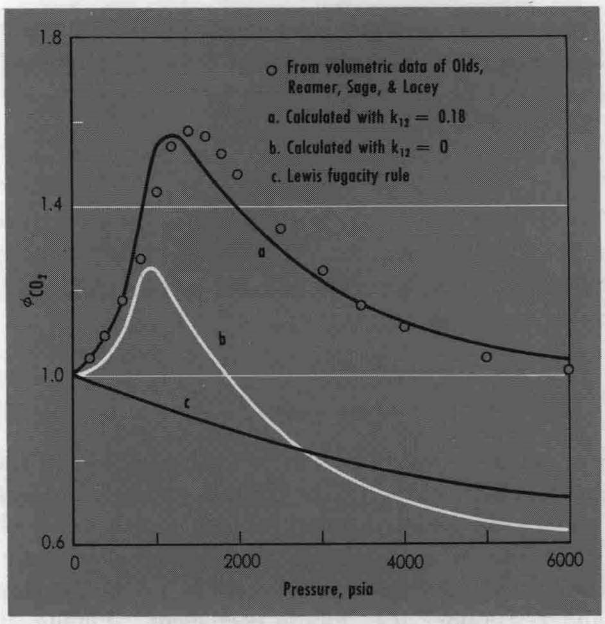


Figure 1. Fugacity coefficients of carbon dioxide in a mixture containing 85 mole per cent n-butane at 340° F. (k_{12} = 0.18 obtained from second virial coefficient data)

The configurational properties of low-molecular-weight gases (hydrogen, helium, neon) are described by quantum, rather than classical, statistical mechanics. As a result, the properties of these gases cannot be given by the same corresponding-states treatment (Equations 8, 10–15) as that used for classical gases when the true critical constants are used as the reducing parameters. It is possible, however, to define temperature-dependent effective critical constants with which the properties of quantum gases can be made to coincide with those for classical gases (*13*).

Figure 2 shows experimental and calculated fugacity coefficients of methane in a mixture with hydrogen at equilibrium with solid methane (*14*). Good agreement at these low temperatures and high pressures suggests that the revised Redlich-Kwong equation can be successfully applied to mixtures of nonpolar and quantum gases. Other examples for fugacity coefficients and for compressibility factors of vapor mixtures have also been reported (*8*).

B. Liquid-Phase Activity Coefficients: Effect of Composition

For isothermal phase equilibria, the liquid-phase activity coefficient depends on the liquid-phase composition and also on the total pressure. For effective thermodynamic analysis and correlation of high-pressure vapor-liquid equilibrium data, it is important to separate the effect of pressure from that of composition. For a binary system, it is useful, therefore, to define two adjusted activity coefficients independent of pressure (*25*) by:

$$\gamma_1^{(P^r)} = \frac{f_1}{x_1 f_{\text{pure }1}^{(P^r)}} \exp \int_P^{P^r} \frac{\bar{v}_1^L}{RT}\, dP \tag{18}$$

and

$$\gamma_2^{*(P^r)} = \frac{f_2}{x_2 H_{2(1)}^{(P^r)}} \exp \int_P^{P^r} \frac{\bar{v}_2^L}{RT}\, dP \tag{19}$$

where subscript 1 refers to the condensable and subscript 2 to the noncondensable component.

The fugacities, f_1 and f_2, are those at the total pressure P of the system. The reference pressure P^r is arbitrary and is most conveniently set equal to zero. As shown elsewhere (*25*), the constant-pressure activity coefficients defined by Equations 18 and 19 satisfy the isothermal, isobaric Gibbs-Duhem equation:

$$x_1 d \ln \gamma_1^{(P^r)} + x_2 d \ln \gamma_2^{*(P^r)} = 0 \tag{20}$$

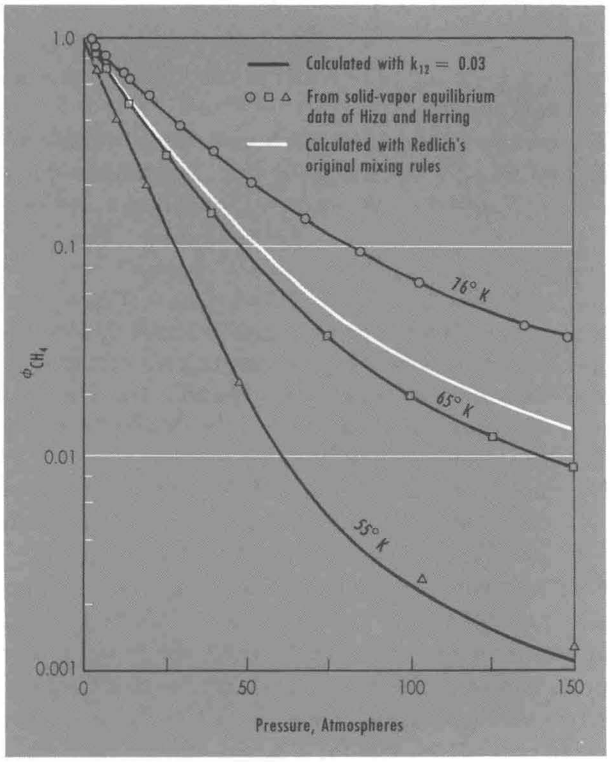


Figure 2. Fugacity coefficients of methane in hydrogen at saturation (k_{12} = 0.03 obtained from second virial coefficient data)

As a result, the composition dependence of these activity coefficients can be represented by an integrated form of Equation 20 (for example, the van Laar equation or the Margules equation) as commonly used in low-pressure vapor-liquid equilibria. Through the exponential factors in Equations 18 and 19 (the Poynting correction), the effect of pressure is separated from the effect of composition, and as a result, interpretation and correlation of high-pressure phase-equilibrium data are very much facilitated (*25*). A technique for calculating partial molar volumes $\bar{v}_1^L$ and $\bar{v}_2^L$, required in Equations 18 and 19, is presented in Section C.

The asterisk (*) in Equation 19 is a reminder that the unsymmetric convention has been used for normalization of activity coefficients. For subcritical component 1 (the temperature T of the solution is well below the critical temperature T_{c_1}), the standard-state fugacity is the fugacity of pure liquid 1 at the temperature of the solution and at the constant reference pressure P^r. For supercritical component 2 (the temperature T of the solution is near or above the critical temperature T_{c_2}), the standard-state fugacity is its Henry's constant in solvent 1 at the temperature of the solution and at P^r. As a result, both activity coefficients approach unity as the liquid solution becomes infinitely dilute with respect to the light component:

$$\gamma_1^{(P^r)} \rightarrow 1 \quad \text{as} \quad x_1 \rightarrow 1 \tag{21}$$

$$\gamma_2^{*(P^r)} \rightarrow 1 \quad \text{as} \quad x_2 \rightarrow 0 \tag{22}$$

The unsymmetric convention of normalization has the advantage that it avoids the use of any ill-defined hypothetical liquid standard state for the noncondensable supercritical component. It has been repeatedly found that no unique reference fugacity exists for such a hypothetical liquid; for a noncondensable supercritical component, the hypothetical pure-liquid fugacities obtained from vapor-liquid equilibria of that component in various solvents may differ considerably from each other. Ambiguity in the standard-state fugacity of a supercritical gas can be avoided by the use of the well-defined and experimentally accessible Henry's constant (*25*). $H_{2(1)}^{(P^r)}$ is given by:

$$H_{2(1)}^{(P^r)} = H_{2(1)}^{(P_1^s)} \exp \int_{P_1^s}^{P^r} \frac{\bar{v}_2^\infty}{RT}\, dP \tag{23}$$

where $H_{2(1)}^{(P_1^s)}$ is evaluated by extrapolating to $x_2 = 0$ a plot of $\ln f_2/x_2$ *vs.* x_2. In Equation 23, P_1^s is the saturation (vapor) pressure of solvent 1 and $\bar{v}_2^\infty$ is the liquid partial molar volume of component 2 infinitely dilute in solvent 1.

Excess Gibbs energy. Following Scatchard (*39*), we define the excess Gibbs energy per mole of solution by

$$\frac{g^{E*}}{RT} = x_1 \ln \gamma_1^{(P^r)} + x_2 \ln \gamma_2^{*(P^r)} \tag{24}$$

Table I. Self-interaction Constants for Some Binary Systems

System	T, °R	$\alpha_{22(1)}$, lb-mole/ft^3	System	T, °R	$\alpha_{22(1)}$, lb-mole/ft^3	System	T, °R	$\alpha_{22(1)}$, lb-mole/ft^3
Methane(2)–ethane(1)	259.7	0.425	Methane(2)-n-pentane(1) contd.	619.7	0.706	Ethane(2)–propane(1)	259.7	0.066
	309.7	0.305		679.7	0.939		309.7	0.059
	359.7	0.182		739.7	1.230		359.7	0.051
	409.7	0.210	Ethylene(2)–ethane(1)	359.7	0.075		409.7	0.043
	459.7	0.333		419.7	0.058		459.7	0.034
	509.7	0.680		459.7	0.039		509.7	0.026
Methane(2)–propane(1)	259.7	0.342		499.7	0.053		559.7	0.025
	309.7	0.322		519.7	0.069		579.7	0.029
	359.7	0.322	Ethylene(2)–acetylene(1)	424.7	0.305		599.7	0.038
	409.7	0.355		459.7	0.270		619.7	0.053
	459.7	0.415		499.7	0.244		639.7	0.099
	491.7	0.462	Ethane(2)–acetylene(1)	424.7	0.538	Propane(2)–*n*-pentane(1)	559.7	0.023
	509.7	0.498		459.7	0.490		619.7	0.032
	559.7	0.593		499.7	0.365		679.7	0.049
	619.7	0.936		519.7	0.277		739.7	0.080
Methane(2)–*n*-pentane(1)	559.7	0.548					799.7	0.141

In view of the unsymmetric normalization, g^{E*} vanishes at infinite dilution with respect to component 2 but not with respect to component 1; that is,

$$g^{E*} \rightarrow 0 \quad \text{as} \quad x_2 \rightarrow 0$$

but (25)

$$g^{E*} \neq 0 \quad \text{as} \quad x_1 \rightarrow 0$$

As defined here, the ideal solution ($g^{E*} = 0$) is one where at constant temperature and pressure the fugacity of the light component is given by Henry's law and that of the heavy component by Raoult's law. In molecular terms this means that g^{E*} is zero whenever the concentration of component 2 in the liquid phase is sufficiently small to prevent molecules of component 2 from interacting with one another.

In a manner analogous to that used by Wohl (*42*), the excess Gibbs energy can be represented by summing interactions of molecules:

$$\frac{g^{E*}}{RT(x_1q_1 + x_2q_2)} = -\alpha_{22(1)}\Phi_2^2 - \ldots \tag{26}$$

where Φ is the effective volume fraction

$$\Phi_2 = \frac{x_2q_2}{x_1q_1 + x_2q_2} \tag{27}$$

where q_i is the effective size of molecule i and where $\alpha_{22(1)}$ is the self-interaction constant of molecules 2 in the environment of molecules 1. In Equation 26 only two-body interactions are considered; higher terms are neglected to keep the number of adjustable parameters to a minimum.

Activity coefficients can be found from the exact relations

$$\ln \gamma_1^{(P^r)} = \left(\frac{\partial n_T g^{E*}/RT}{\partial n_1}\right)_{T,P,n_2} \tag{28}$$

$$\ln \gamma_2^{*(P^r)} = \left(\frac{\partial n_T g^{E*}/RT}{\partial n_2}\right)_{T,P,n_1} \tag{29}$$

where n_1 is the number of moles of component 1 and n_T is the total number of moles.

Dilated van Laar model for binary liquid mixtures. Equations 26, 27, and 28 yield the classical van Laar equations (for unsymmetric normalization) as reported previously (*25*). Muirbrook (*20*) has shown that these equations, containing two adjustable parameters, are unsatisfactory for describing the properties of some systems which are at a temperature much above the critical temperature of the light component or near the critical temperature of the heavy component. In addition, Muirbrook found that the three-suffix Margules equations were also unsatisfactory (*20*).

The probable reason for the failure of the classical van Laar treatment is due to van Laar's assumption that q_1 and q_2 are constants independent of composition. The q's are parameters which reflect the cross sections, or sizes, or spheres of influence of the molecules; at conditions remote from critical, where the liquid molar volumes is close to a linear function of the mole fraction, it is reasonable to assume that the q's are composition independent. However, for a liquid mixture of a noncondensable component 2 with a subcritical liquid 1, the molar volume of the mixture is a highly nonlinear

Table II. Dilation Constants of Some Binary Systems

System	T, ° R	$\eta_{2(1)}$
Methane(2)–propane(1)	407.7	0.31
	499.7	1.46
	559.7	4.12
	619.7	28.35
Methane(2)–*n*-pentane(1)	559.7	1.19
	619.7	1.62
	679.7	2.25
	739.7	8.39
Propane(2)–*n*-pentane(1)	679.7	0.27
	739.7	1.23
	799.7	26.24
Methane(2)–ethane(1)	359.7	0.90
	409.7	1.29
	459.7	3.06
	509.7	27.10
Ethane(2)–propane(1)	559.7	1.30
	599.7	4.41
	619.7	12.28
	639.7	43.54

Table III. Henry's Constants of Some Solutes in Solvents

System	T, ° R	$H_{2(1)}^{(PO)}$ psia
Methane(2)–ethane(1)	359.7	690
	409.7	1029
	459.7	1330
	509.7	1500
Methane(2)–propane(1)	359.7	870
	409.7	1360
	459.7	1800
	491.7	2044
	509.7	2130
	559.7	2141
	619.7	1844
Methane(2)–*n*-pentane(1)	559.7	2821
	619.7	3185
	679.9	3256
	739.7	2943
Ethane(2)–propane(1)	559.7	449
	579.7	503
	599.7	573
	619.7	616
	639.7	631
Propane(2)–*n*-pentane(1)	619.7	289
	679.7	447
	739.7	610
	799.7	750

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function of the mole fraction, especially in the vicinity of the critical composition. The liquid solution dilates as x_2 rises, and van Laar's model must be modified to take this effect into account.

For practical reasons (since experimental data are usually not plentiful), it is desirable to derive equations for the constant-pressure activity coefficients which contain no more than two parameters. Because of this limitation, we assume that whereas q_1 and q_2 depend on composition, their ratio does not. Since the van Laar treatment is a two-body (quadratic) theory, we assume that q_1 and q_2 are given by a quadratic function of the effective volume fraction:

$$q_1 = v_{c_1}[1 + \eta_{2(1)}\Phi_2^2] \tag{30}$$

$$q_2 = v_{c_2}[1 + \eta_{2(1)}\Phi_2^2] \tag{31}$$

(From Equations 30 and 31, it follows that the volume fraction Φ_i is given by $\Phi_i = x_i v_{c_i}/\Sigma_i x_i v_{c_i}$.)

In Equations ~~B-13~~ 30 and ~~B-14~~ 31 we have arbitrarily used the pure-component critical volumes as our measure of the molecular cross sections at infinite dilution, when $\Phi_2 = 0$. Some other constant (for example, van der Waals b or Leonard-Jones σ^3) could just as easily be used. The dilation constant $\eta_{2(1)}$ is a measure of how effectively the light component dilates (swells) the liquid solution.

When Equations 30 and 31 are substituted into Equation 26, the pressure-independent activity coefficients are

$$\ln \gamma_1^{(P^r)} = A\Phi_2^2 + B\Phi_2^4 \tag{32}$$

$$\ln \gamma_2^{*(P^r)} = A\left(\frac{v_{c_2}}{v_{c_1}}\right)(\Phi_2^2 - 2\,\Phi_2) + B\left(\frac{v_{c_2}}{v_{c_1}}\right)\left(\Phi_2^4 - \frac{4}{3}\,\Phi_2^3\right) \tag{33}$$

where

$$A \equiv \alpha_{22(1)} v_{c_1} \tag{34}$$

$$B \equiv 3\,\eta_{2(1)}\alpha_{22(1)} v_{c_1} \tag{35}$$

Equations 32 and 33 are the desired two-parameter equations. These equations provide accurate representation of the constant-pressure activity coefficients of nonpolar binary mixtures from the dilute region up to the critical composition. To illustrate, Figures 3 and 4 present typical results of data reduction for two binary systems, propane-methane (*30*) and carbon dioxide–nitrogen (*21*).

Self-interaction constants, dilation constants, and Henry's constants for some binary systems are given in Tables I, II, and III. The magnitude of the dilation constant shows a consistent and meaningful variation with respect to the temperature and the properties of the constituent components; the dilation constants are

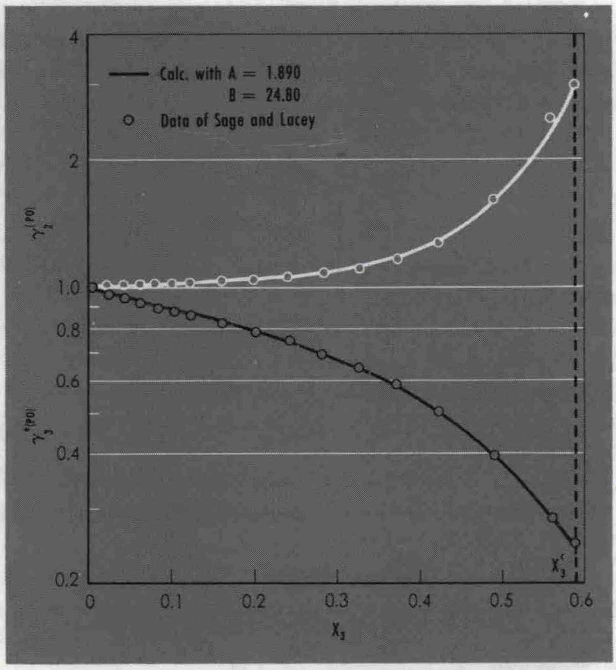

Figure 3. Activity coefficients for the propane(2)–methane(3) system at 100° F.

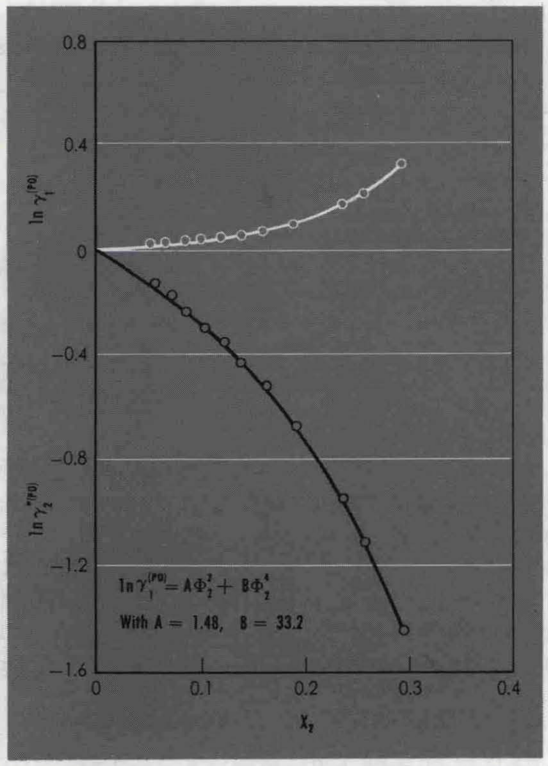

Figure 4. Activity coefficients for the carbon dioxide(1)–nitrogen(2) system at 32° F.

larger for those systems at temperatures approaching the critical temperature of the heavy component (component 1); also, they are larger for those systems in which the light component is highly supercritical. This behavior of dilation constants is in agreement with their physical significance in the dilated van Laar model—i.e., the liquid phase is swelled or dilated most when the subcritical heavy component itself is near its critical temperature, or when the light component is far above its critical temperature. Under these conditions the liquid molar volume increases sharply with dissolved gas.

Plots of ln $\eta^{1/2}$ *vs.* $1/T$ show a similar shape for all systems. It has been possible to unify all the curves into a single reduced plot, as shown in Figure 5. The curve can be represented by

$$\ln (\eta/\eta^{\ddagger})^{1/2} = -30.2925 + 39.1396\,(T^{\ddagger}/T) - 17.2182\,(T^{\ddagger}/T)^2 + 2.81464\,(T^{\ddagger}/T)^3 - 2.78571/(T^{\ddagger}/T) - 5.26736 \ln (T^{\ddagger}/T - 0.9) \quad (36)$$

where $\eta^{\ddagger}$ is a constant characteristic of the light component and $T^{\ddagger}$ is a constant characteristic of the binary system. Some values of $\eta^{\ddagger}$ and $T^{\ddagger}$ are given in Figure 5.

Mixtures of condensable components. At temperatures sufficiently lower than the critical temperature of the light component (component 2), the dilation constant η obtained from data reduction becomes so small that it can be effectively equated to zero. Under these conditions, the constant-pressure activity coefficients of both components can be correlated with only one parameter, α. We found empirically that this occurs for T_{R_2} less than 0.93. Therefore, components with a reduced temperature smaller than 0.93 are treated as heavy components (solvent), and those with T_R larger than 0.93 are treated as light components (solute). Systems for which both T_{R_1} and T_{R_2} are smaller than 0.93 are correlated with $\eta = 0$ and only one parameter, α. Systems for which the critical temperatures of the two components are very close (such as acetylene–ethane) are also analyzed with only one parameter, α, even though T_{R_2} is larger than 0.93; the terms "heavy" and "light" component lose their conventional meaning for such systems. In fact, it sometimes happens that the component with the higher critical temperature ("heavy") may actually have a higher vapor pressure and critical pressure than the component with the lower critical temperature ("light").

For those systems where both components can exist in the pure liquid state, it is not necessary to use the unsymmetric convention for normalization of activity coefficients. Instead, such a system can be analyzed with a one-parameter, symmetric-convention expression for the excess Gibbs energy:

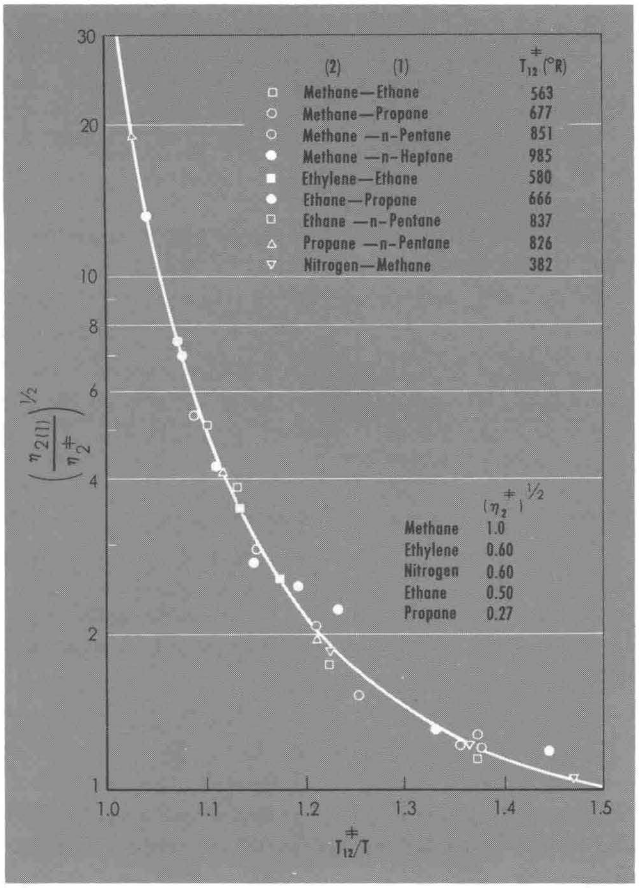

Figure 5. Correlation of dilation constants $\eta_{2(1)}$ *for some binary systems*

$$\frac{g^E}{RT(x_1v_{c_1} + x_2v_{c_2})} = \alpha_{12}\Phi_1\Phi_2 \qquad (37)$$

From Equations 28 and 29 we obtain

$$\ln \gamma_1^{(P^r)} = v_{c_1}\alpha_{12}\Phi_2^2 \qquad (38)$$

$$\ln \gamma_2^{(P^r)} = v_{c_2}\alpha_{12}\Phi_1^2 \qquad (39)$$

where $\gamma_1^{(P^r)}$ is given by Equation 18 and $\gamma_2^{(P^r)}$ by

$$\gamma_2^{(P^r)} = \frac{f_2}{x_2 f_{\text{pure }2}^{(P^r)}} \exp \int_P^{P^r} \frac{\bar{v}_2^L}{RT}\, dP \qquad (40)$$

It can be shown (*5, 26*) that for the case when both components are subcritical and the excess Gibbs energy can be represented by Equation 37, or by Equation 26 with $q_1 = v_{c_1}$, $q_2 = v_{c_2}$—i.e., $\eta = 0$—there exist rigorous relationships between the constants in the two conventions, viz.:

$$\alpha_{22(1)} = \alpha_{12} \qquad (41)$$

$$\ln H_{2(1)}^{(P^r)} = \ln f_{\text{pure }2}^{(P^r)} + v_{c_2}\alpha_{12} \qquad (42)$$

Dilated van Laar model for a multicomponent liquid mixture. Extension of the dilated van Laar model to the multicomponent case is best illustrated for a four-component system containing two solvents and two solutes. The results may then be generalized for a solution containing any number of solutes and solvents as shown elsewhere (*26*).

We use the following notation:

Components 1 and 2	Solvents ($T_{R_i} \leq 0.93$)
Components 3 and 4	Solutes ($T_{R_i} > 0.93$)

In the subsequent discussion of excess Gibbs energy we consider only the excess energy due to the interaction of solute molecules in the mixed solvent—i.e., the excess Gibbs energy is taken relative to a solution infinitely dilute with respect to components 3 and 4 in the mixed solvent and does not include the excess Gibbs energy due to the nonideality of the solute-free solvent mixture.

The reference fugacity of component 3 is Henry's constant for 3 in the mixed solvent; and similarly for component 4. The reference fugacity of component 1 (or 2) is not the fugacity of the pure liquid, but is modified by the activity coefficient of component 1 (or 2) in the solute-free mixed solvent (see Equations 65 and 66).

According to our solution model, we write for the excess Gibbs energy due to interactions of solute molecules in the mixed solvent:

$$\frac{g^{E*}_{(\text{MS})}}{RT(x_1q_1 + x_2q_2 + x_3q_3 + x_4q_4)} = - \alpha_{33(\text{MS})}\Phi_3^2 - \alpha_{44(\text{MS})}\Phi_4^2 - 2\,\alpha_{34(\text{MS})}\Phi_3\Phi_4 \qquad (43)$$

where

$$q_i = v_{c_i}[1 + (\eta_{3(\text{MS})}\Phi_3^2 + \eta_{4(\text{MS})}\Phi_4^2 + 2\,\eta_{34(\text{MS})}\Phi_3\Phi_4)] \quad (i = 1, 2, 3, 4) \qquad (44)$$

and subscript (MS) refers to mixed solvent. Here, $\alpha_{33(\text{MS})}$ is the self-interaction constant of solute molecules 3 in the environment of mixed solvent, and $\eta_{3(\text{MS})}$ is the dilation constant of solute molecules 3 in the mixed solvent. By introducing as before (*6*) the assumptions

$$\alpha_{34(\text{MS})} = \sqrt{\alpha_{33(\text{MS})}\alpha_{44(\text{MS})}} \qquad (45)$$

$$\eta_{34(\text{MS})} = \sqrt{\eta_{3(\text{MS})}\eta_{4(\text{MS})}} \qquad (46)$$

Equation 43 can then be rearranged to read

$$\frac{g^{E*}_{(\text{MS})}}{RT} = -(\alpha_{33(\text{MS})}^{1/2}\Phi_3 + \alpha_{44(\text{MS})}^{1/2}\Phi_4)^2 \times [1 + (\eta_{3(\text{MS})}^{1/2}\Phi_3 + \eta_{4(\text{MS})}^{1/2}\Phi_4)^2](x_1v_{c_1} + x_2v_{c_2} + x_3v_{c_3} + x_4v_{c_4}) \qquad (47)$$

The self-interaction constant of solute molecules in an environment of mixed solvent is assumed to be given by a linear average in the solute-free solvent mole fraction; results are not sensitive to this combination rule since, in most cases, the components in the mixed solvent are similar in their behavior toward the particular solute. Thus,

$$\alpha_{33(\mathrm{MS})}{}^{1/2} = \frac{\Phi_1\alpha_{33(1)}{}^{1/2} + \Phi_2\alpha_{33(2)}{}^{1/2}}{\Phi_1 + \Phi_2} \tag{48}$$

and similarly,

$$\ln\left(\frac{\eta_{3(\mathrm{MS})}}{\eta_3{}^{\ddagger}}\right)^{1/2} = f_\eta\left(\frac{T_{3(\mathrm{MS})}{}^{\ddagger}}{T}\right) \tag{49}$$

where

$$T_{3(\mathrm{MS})}{}^{\ddagger} = \frac{\Phi_1 T_{3(1)}{}^{\ddagger} + \Phi_2 T_{3(2)}{}^{\ddagger}}{\Phi_1 + \Phi_2} \tag{50}$$

and f_η is given by Equation 36. The activity coefficients can be obtained by differentiating Equation 47. They are:

$$\ln \gamma_{1(\mathrm{MS})}{}^{(P^r)} = v_{c_1}\{\Phi_\alpha{}^2(1 + 3\ \Phi_\eta{}^2 + 2\ DM_1\Phi_\eta) - 2\ AM_1\Phi_\alpha(1 + \Phi_\eta{}^2)\} \tag{51}$$

$$\ln \gamma_{2(\mathrm{MS})}{}^{(P^r)} = v_{c_2}\{\Phi_\alpha{}^2(1 + 3\ \Phi_\eta{}^2 + 2\ DM_2\Phi_\eta) - 2\ AM_2\Phi_\alpha(1 + \Phi_\eta{}^2)\} \tag{52}$$

$$\ln \gamma_3{}^*{}_{(\mathrm{MS})}{}^{(P^r)} = v_{c_3}\{\Phi_\alpha{}^2(1 + 3\ \Phi_\eta{}^2 - 2\ \eta_{3(\mathrm{MS})}{}^{1/2}\Phi_\eta) - 2\ \alpha_{33(\mathrm{MS})}{}^{1/2}\Phi_\alpha(1 + \Phi_\eta{}^2)\} \tag{53}$$

$$\ln \gamma_4{}^*{}_{(\mathrm{MS})}{}^{(P^r)} = v_{c_4}\{\Phi_\alpha{}^2(1 + 3\ \Phi_\eta{}^2 - 2\ \eta_{4(\mathrm{MS})}{}^{1/2}\Phi_\eta) - 2\ \alpha_{44(\mathrm{MS})}{}^{1/2}\Phi_\alpha(1 + \Phi_\eta{}^2)\} \tag{54}$$

where

$$\Phi_\alpha = \alpha_{33(\mathrm{MS})}{}^{1/2}\Phi_3 + \alpha_{44(\mathrm{MS})}{}^{1/2}\Phi_4 \tag{55}$$

$$\Phi_\eta = \eta_{3(\mathrm{MS})}{}^{1/2}\Phi_3 + \eta_{4(\mathrm{MS})}{}^{1/2}\Phi_4 \tag{56}$$

$$AM_l = \frac{(\alpha_{33(l)}{}^{1/2} - \alpha_{33(\mathrm{MS})}{}^{1/2})\Phi_3 + (\alpha_{44(l)}{}^{1/2} - \alpha_{44(\mathrm{MS})}{}^{1/2})\Phi_4}{\Phi_1 + \Phi_2} \quad (l = 1, 2) \tag{57}$$

$$DM_l = \Phi_3 DN_{3(l)} + \Phi_4 DN_{4(l)} \quad (l = 1, 2) \tag{58}$$

$$DN_{j(l)} = \frac{DS_j}{T}\,\frac{T_{j(\mathrm{MS})}{}^{\ddagger} - T_{j(l)}{}^{\ddagger}}{v_{c_l}(\Phi_1/v_{c_1} + \Phi_2/v_{c_2})},\ (j = 3, 4) \tag{59}$$

$$DS_j = \eta_j{}^{\ddagger 1/2}\left[\frac{\partial(\eta/\eta^{\ddagger})^{1/2}}{\partial(T^{\ddagger}/T)}\right]_{T^{\ddagger} = T_{i(\mathrm{MS})}{}^{\ddagger}} \tag{60}$$

The fugacity of each component is given by:

$$f_1{}^{(P)} = \gamma_{1(\mathrm{MS})}{}^{(P^r)}x_1 f_{1(\mathrm{MS})}{}^{o(P^r)} \exp \int_{P^r}^{P} \frac{\bar{v}_1{}^L}{RT}\,dP \tag{61}$$

$$f_2{}^{(P)} = \gamma_{2(\mathrm{MS})}{}^{(P^r)}x_2 f_{2(\mathrm{MS})}{}^{o(P^r)} \exp \int_{P^r}^{P} \frac{\bar{v}_2{}^L}{RT}\,fP \tag{62}$$

$$f_3{}^{(P)} = \gamma_{3(\mathrm{MS})}{}^{*(P^r)}x_3 H_{3(\mathrm{MS})}{}^{(P^r)} \exp \int_{P^r}^{P} \frac{\bar{v}_3{}^L}{RT}\,dP \tag{63}$$

$$f_4{}^{(P)} = \gamma_{4(\mathrm{MS})}{}^{*(P^r)}x_4 H_{4(\mathrm{MS})}{}^{(P^r)} \exp \int_{P^r}^{P} \frac{\bar{v}_4{}^L}{RT}\,dP \tag{64}$$

The reference fugacities $f_{1(\mathrm{MS})}{}^{o(P^r)}$ and $f_{2(\mathrm{MS})}{}^{o(P^r)}$ in Equations 61 and 62 are given by (reference *26*):

$$f_{1(\mathrm{MS})}{}^{o(P^r)} = \gamma_{1(\mathrm{SF})}{}^{(P^r)} f_{\mathrm{pure}\ 1}{}^{(P^r)} \tag{65}$$

$$f_{2(\mathrm{MS})}{}^{o(P^r)} = \gamma_{2(\mathrm{SF})}{}^{(P^r)} f_{\mathrm{pure}\ 2}{}^{(P^r)} \tag{66}$$

where $\gamma_{1(\mathrm{SF})}{}^{(P^r)}$ and $\gamma_{2(\overset{SF}{\cancel{\mathrm{MS}}})}{}^{(P^r)}$ are the activity coefficients of components 1 and 2 in the solute-free (SF) mixed solvent, as given by:

$$\ln \gamma_{1(\mathrm{SF})}{}^{(P^r)} = v_{c_1}\alpha_{12}\Psi_2{}^2 \tag{67}$$

$$\ln \gamma_{2(\mathrm{SF})}{}^{(P^r)} = v_{c_2}\alpha_{12}\Psi_1{}^2 \tag{68}$$

where α_{12} is the interaction constant of solvent molecules 1 and 2, and Ψ is the solute-free solvent volume fraction,

$$\Psi_1 = \frac{\Phi_1}{\Phi_1 + \Phi_2},\ \Psi_2 = \frac{\Phi_2}{\Phi_1 + \Phi_2} \tag{69}$$

As shown elsewhere (*26*), Henry's constants $H_{3(\mathrm{MS})}{}^{(P^r)}$ and $H_{4(\mathrm{MS})}{}^{(P^r)}$ are related to Henry's constants in the pure solvents by

$$\ln H_{3(\mathrm{MS})}{}^{(P^r)} = \Psi_1 \ln H_{3(1)}{}^{(P^r)} + \Psi_2 \ln H_{3(2)}{}^{(P^r)} - v_{c_3}\alpha_{12}\Psi_1\Psi_2 \tag{70}$$

$$\ln H_{4(\mathrm{MS})}{}^{(P^r)} = \Psi_1 \ln H_{4(1)}{}^{(P^r)} + \Psi_2 \ln H_{4(2)}{}^{(P^r)} - v_{c_4}\alpha_{12}\Psi_1\Psi_2 \tag{71}$$

Figure 6 presents calculated activity coefficients for the ternary system *n*-pentane(1)–propane(2)–methane-(3) at 220° F; only binary constants were used in these calculations. At 220° F, there are one solvent, *n*-pentane, and two solutes, propane and methane. This case is the same as the one discussed previously (*6*). In this case the mixed-solvent reference state discussed above automatically reduces to the simple case of a single-reference solvent discussed before (*6*).

C. Liquid-Phase Activity Coefficients: Effect of Pressure

As indicated in the previous section, a useful thermodynamic analysis of high-pressure vapor-liquid equilibria requires information on the effect of pressure on liquid-phase fugacities; this information is given by partial molar volumes in the liquid mixture.

At low or moderate pressures, liquid-phase activity coefficients are weakly dependent on pressure and, as a result, it has been customary to assume that, for practical purposes, activity coefficients depend only on temperature and composition. In many cases this is a good assumption but for phase equilibria at high pressures, especially for those near critical conditions, it can lead to serious error.

When the standard-state fugacity is defined at a constant pressure, for any component i, the pressure de-

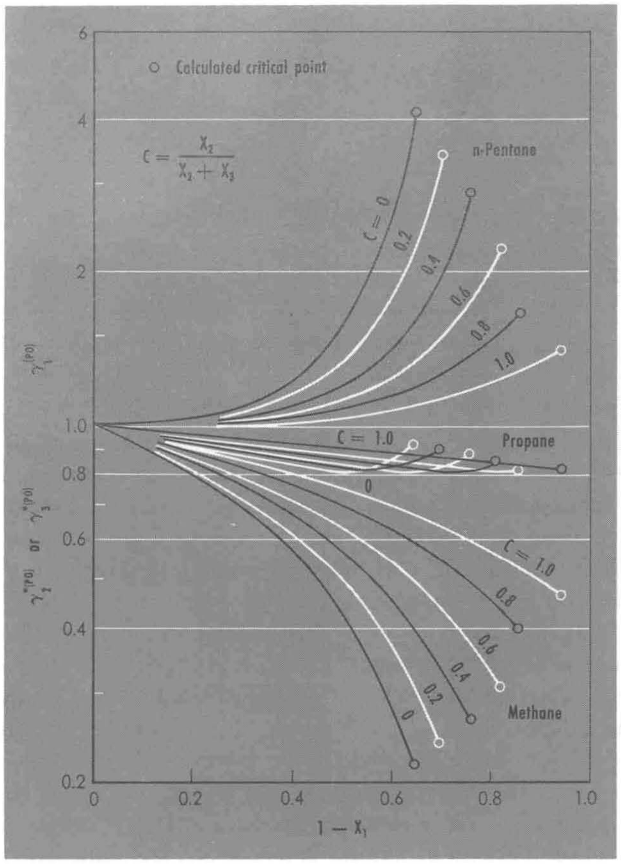

Figure 6. Calculated activity coefficients for the ternary system n-pentane(1)–propane(2)–methane(3) at 220° F.

pendence of the activity coefficient γ_i is given exactly by:

$$\left(\frac{\partial \ln \gamma_i}{\partial P}\right)_{T,x} = \frac{\bar{v}_i}{RT} \tag{72}$$

At high pressures in the critical region, $\bar{v}_i$ is usually a strong function of composition, especially for heavy components where $\bar{v}_i$ frequently changes sign as well as magnitude.

Experimental data for partial molar volumes are rare for binary systems and for multicomponent systems there are essentially none. Since thermodynamic analysis or prediction of multicomponent high-pressure phase equilibria requires partial molar volumes, we require a reliable method for calculating partial molar volumes from a minimum of experimental information.

Partial molar volume from an equation of state. The partial molal volume of component k in a mixture of N components is defined by

$$\bar{v}_k = \left(\frac{\partial V}{\partial n_k}\right)_{P,T,n_j(i\neq k)} \tag{73}$$

The partial molar volume can be evaluated from a suitable equation of state for the liquid mixture. Since most equations of state are explicit in pressure rather than in volume, it is convenient to rewrite Equation 73:

$$\bar{v}_k = \frac{-\left(\frac{\partial P}{\partial n_k}\right)_{T,V,n_j(i\neq k)}}{\left(\frac{\partial P}{\partial V}\right)_{T,n_i\ (\text{all } i)}} = f(x_1 \ldots\ldots, T, v) \tag{74}$$

With an equation of state, Equation 74 gives $\bar{v}_k$ as a function of the composition, temperature, and molar volume v of the liquid mixture. Pressure does not appear explicitly in Equation 74 but is implicit in the volume which depends on the pressure.

For practical applications in vapor-liquid equilibria, we require partial molar volumes at saturation; therefore, we need the saturated molar volume of the liquid mixture in Equation 74. The saturated molar volume of a liquid mixture can be calculated by extending to mixtures the corresponding-states correlation of Lyckman and Eckert (*17*) who slightly revised Pitzer's tables (*23*) for the saturated liquid volume of pure substances for the reduced temperature region 0.56–1.00. Pseudocritical rules are required for applications to mixtures. Such rules have been proposed (*7*) for the region in which the pseudoreduced temperature of the mixture is less than 0.93. In the critical region ($T_R > 0.93$), it has been found necessary to modify the pseudocritical rules in order that they converge to the true critical constants of the mixture at the critical point. To this end, we have developed correlations for true critical temperatures and volumes of mixtures and, also, an equation-of-state method for calculating the true critical pressures of mixtures. For reduced temperatures less than 0.56 other modifications are required. Details and results of these calculations are given elsewhere (*7*, *26*).

In Equation 74, besides the saturated molar volume of the liquid mixture, we need an explicit form of the function f. For this, we need an equation of state for liquid mixtures.

Equation of state for liquid mixtures. For nonpolar liquids, an equation of the van der Waals type provides a reasonable description of volumetric properties. Since the Redlich-Kwong equation (*33*) represents a useful modification of the van der Waals equation, we propose to use this equation for liquid mixtures with certain alterations. The Redlich-Kwong equation of state is given by Equation 4, and, for any pure fluid, the two constants a and b can be related to the critical properties of that fluid by Equations 5 and 6. As noted in Section A, if the conditions at the critical point are imposed, $\Omega_a = 0.4278$ and $\Omega_b = 0.0867$ for all fluids. Adoption of these values is equivalent to fitting the equation of state to derivatives in the critical region which, although the most sensitive, does not provide the best fit over a wide range of conditions. This is particularly true when the equation is applied to the liquid

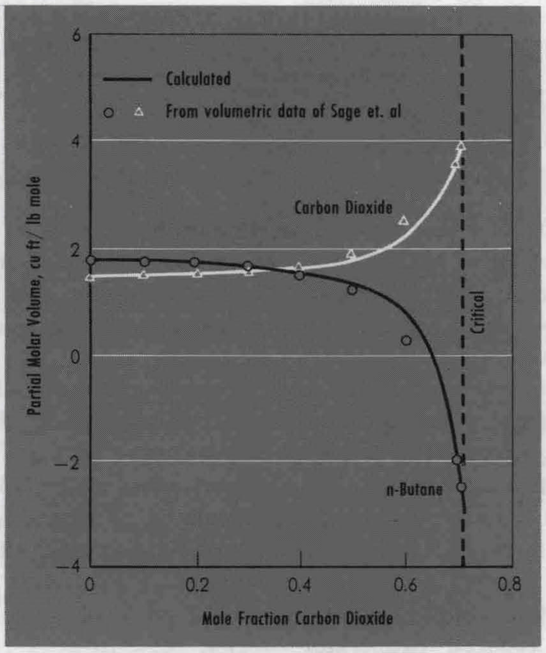

Figure 7. Partial molal volumes in the saturated liquid phase of the n-butane–carbon dioxide system at 160° F.

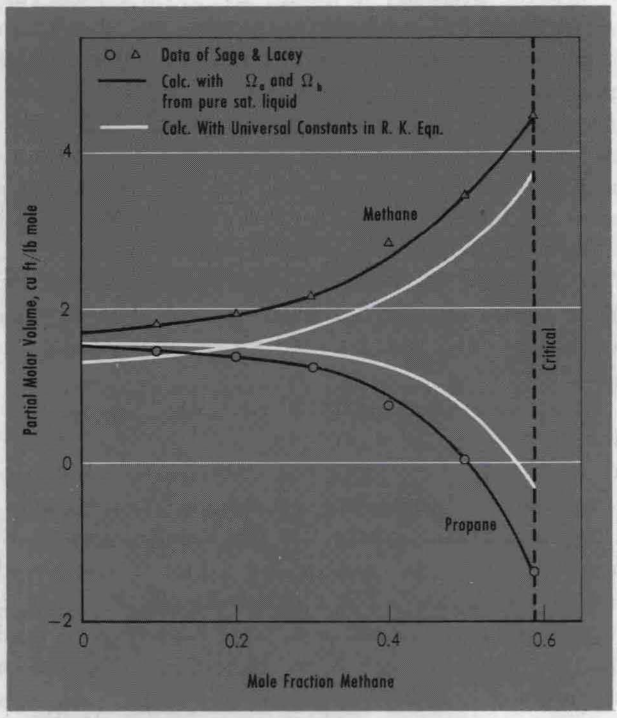

Figure 8. Partial molar volumes in the saturated liquid phase of the propane–methane system at 100° F.

phase. If we accept universal values for Ω_a and Ω_b, we are, in effect, subscribing to a two-parameter theorem of corresponding states. However, Pitzer and others (*19, 23, 34, 37*) have shown that the theorem of corresponding states requires a third parameter to be applicable to a wide class of substances. We propose, therefore, for each pure liquid, to fit the Redlich-Kwong equation to the *P-V-T* data of the saturated liquid and to evaluate the best Ω_a and Ω_b for each pure component. Fortunately, such data are readily available; results are given elsehwere (*26*) for 19 common liquids. They differ slightly from the universal values and show a trend with respect to an acentric factor.

For application to mixtures, we use the same mixing rules as given by Equations 7 through 15, except that the cube-root average for $v_{c_{ij}}$, Equation 13, is replaced by the arithmetic mean of v_{c_i} and v_{c_j}; this is done to weight the larger molecule slightly more heavily in the liquid phase. The binary constant k_{ij}, which represents the deviation from the geometric mean for $T_{c_{ij}}$, is the same for both vapor and liquid phases; to a good approximation k_{ij} is independent of the temperature, density, and composition. Special precautions are needed for mixtures containing hydrogen or helium (*26*).

Partial molar volumes. The partial molar volume can be obtained after performing the partial differentiation indicated in Equation 74:

$$\bar{v}_k = \frac{\dfrac{RT}{v-b}\left(1+\dfrac{b_k}{v-b}\right) - \dfrac{2\left(\sum_i^N x_i a_{ki}\right) - \dfrac{ab_k}{v+b}}{v(v+b)T^{1/2}}}{\dfrac{RT}{(v-b)^2} - \dfrac{a}{T^{1/2}}\left[\dfrac{2v+b}{v^2(v+b)^2}\right]} \tag{75}$$

With v, the saturated liquid molar volume of the mixture, calculated from a corresponding states correlation, the partial molar volume of each component in a multicomponent liquid mixture can be readily calculated from Equation 75. A computer program for performing the calculation is given elsewhere (*26*).

Figures 7 and 8 show calculated partial molar volumes in the saturated liquid phase of the systems *n*-butane–carbon dioxide and propane–methane, including the critical region. The calculated values are compared with those computed from the volumetric data of Sage and Lacey (*38*); agreement between calculated and experimental values is quantitative for both systems. The partial molar volumes of the lighter component (supercritical in these cases) and the heavier component show very different behavior in the critical region even for a system as simple as propane–methane. The partial molar volume of the lighter component approaches a large positive value due to its "dilative" effect, and that of the heavier component approaches a large negative

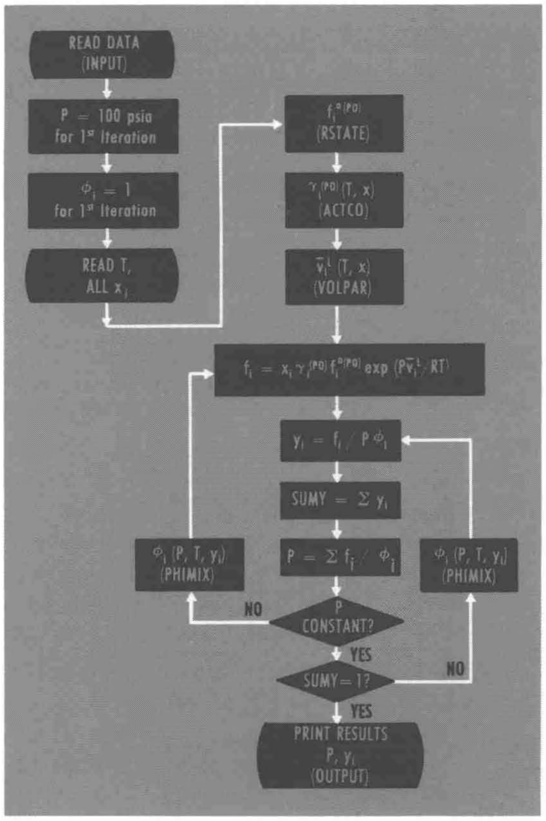

Figure 9. Schematic diagram of bubble-pressure program

value, due to its "condensing" effect. As a result, pressure has exactly opposite effects on the activity coefficients of the lighter component and the heavier component, as indicated by Equation 72. The simple approximation of using partial molar volumes at infinite dilution leads to large error near the critical region.

Also shown in Figure 8 are the partial molar volumes calculated with the universal values $\Omega_a = 0.4278$ and $\Omega_b = 0.0867$. The results are much less satisfactory, indicating the need for evaluating Ω_a and Ω_b for each pure saturated liquid.

All of the above equations for the calculation of partial molar volumes in saturated liquid mixtures are applicable to multicomponent systems without any further assumptions.

With partial molar volumes, the effect of pressure on liquid-phase activity coefficients can be taken into account. By separating the effect of pressure from that of composition, experimental liquid-phase activity coefficients can be subjected to rigorous thermodynamic analysis. Such analysis permits meaningful intepretation and correlation of binary, high-pressure, vapor-liquid equilibrium data and facilitates prediction of multicomponent-phase behavior.

D. Prediction of Mulicomponent-Phase Equilibria

For vapor-liquid equilibria of an N-component system, the variables of interest are the temperature, total pressure, $N - 1$ independent liquid-phase mole fractions and $N - 1$ independent vapor-phase mole fractions. Since there are 2 N variables but only N variables may be independently specified, the other N variables must be determined by solving the N simultaneous equations. They are the N equations of equilibrium:

$$f_i^V = f_i^L \qquad \text{for } i = 1, 2, \ldots, N \tag{76}$$

In the N equations of equilibrium expressed in Equation 76, the vapor-phase fugacities are given by:

$$f_i^V = \varphi_i y_i P \tag{77}$$

and the liquid-phase fugacities are given by:

$$f_i^L = \gamma_i^{(P^r)} x_i f_i^{o(P^r)} \exp \frac{(P - P^r)\bar{v}_i^L}{RT} \tag{78}$$

The solution of the N equations of equilibrium must satisfy the two stoichiometric relations

$$\sum_{i=1}^{N} x_i = 1 \tag{79}$$

and

$$\sum_{i=1}^{N} y_i = 1 \tag{80}$$

The phase-equilibrium calculations most often encountered in the design of separation processes are bubble-point and dew-point calculations. In the first case, pressure (or temperature) and all of the liquid-phase mole fractions are given; the temperature (or pressure) and the vapor-phase mole fractions are to be calculated. In the second case, pressure (or temperature) and all of the vapor-phase mole fractions are given, and the temperature (or pressure) and the liquid-phase mole fractions are desired. The calculations involve the simultaneous solution of the N equations given by Equation 76 which satisfies Equations 79 and 80. These calculations are most conveniently performed by iteration schemes.

The solution of each of these four problems involves the same thermodynamic quantities and relationships; only the order of calculation and the convergence technique are different. It is, therefore, convenient to calculate those thermodynamic quantities in separate subroutines which can then be used with all of the main programs. The fugacity coefficients are calculated in subroutine PHIMIX, the activity coefficients $\gamma_i^{(PO)}$ in subroutine ACTCO, the reference fugacities in the subroutine RSTATE, and the partial molar volumes, $\bar{v}_i^L$, are calculated in subroutine VOLPAR. Details of the computer programs are given elsewhere (*26*).

BUBL P program. The main program, BUBL P, performs a bubble pressure calculation. The temperature and the liquid-phase mole fractions are given. The program finds the equilibrium pressure and vapor-phase mole fractions.

Figure 9 shows a schematic diagram of the method of solution used in the BUBL P program. The itera-

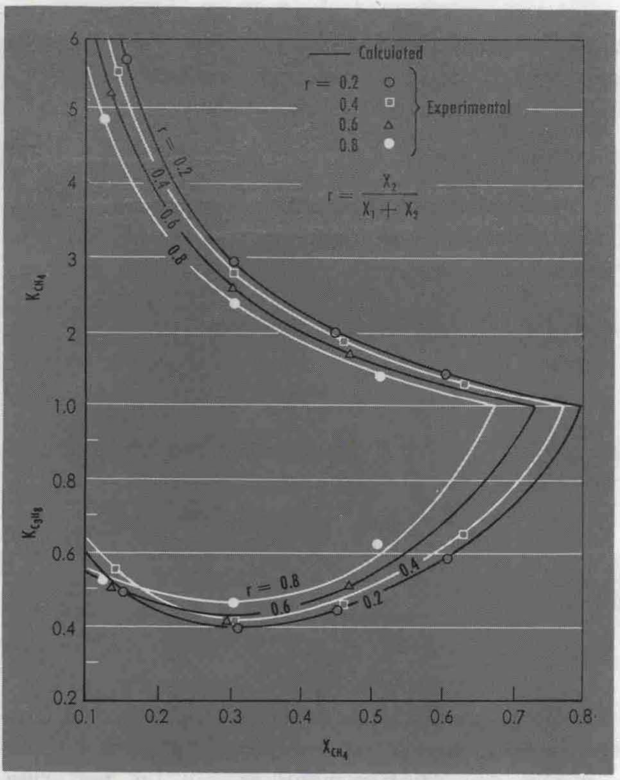

Figure 10. Vapor-liquid equilibrium constants for the n-pentane(1)–propane(2)–methane(3) system at 100° F.

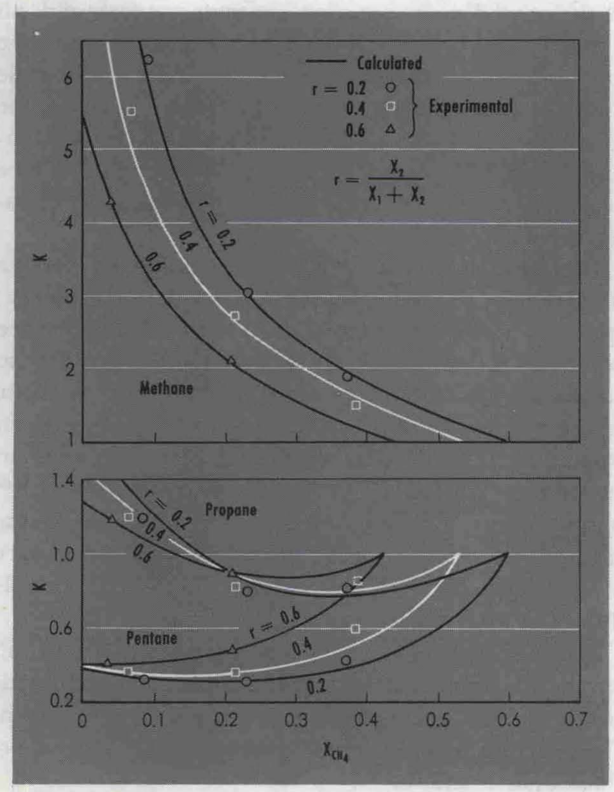

Figure 11. Vapor-liquid equilibrium constants for the n-pentane(1)–propane(2)–methane(3) system at 220° F.

tion scheme used is essentially the same as that discussed elsewhere (27). Data are read in by subroutine INPUT. Initial guesses for pressure and fugacity coefficients are then made for the first iteration. It is important that the solution be always approached from the ideal-gas side—i.e., a sufficiently low pressure and $\varphi_i = 1$. Use of an unreasonably high pressure as the first guess may cause divergence due to the large effect of a large Poynting correction. For this reason, each bubble-pressure calculation must always start from a low-pressure first guess; it is important not to use the result from a previous, unrelated bubble-pressure calculation which may have converged to a very high equilibrium pressure. We arbitrarily set the first guess of pressure at 100 psia. The speed of convergence is essentially independent of this value; however, neither a value of zero nor a very high value should be used.

Next, the main program reads in the known variable T and all x_i's. Subroutines RSTATE, ACTCO, and VOLPAR and then called to calculate those thermodynamic quantities which depend only on the known temperature and liquid-phase compositions.

Calculation of the liquid-phase fugacities begins the loop of iteration. The vapor-phase compositions are calculated, for the first time, by

$$y_i = f_i / P\varphi_i \qquad (81)$$

and pressure is calculated by

$$P = \sum_{i=1}^{N} f_i / \varphi_i \qquad (82)$$

The new pressure is then compared to the former value and, if it has changed, the vapor-phase fugacity coefficients (subroutine PHIMIX) are recalculated using the new pressure and vapor-phase compositions (after normalizing by SUMY). The loop is then re-entered by the recalculation of liquid-phase fugacity using Equation 78.

When an unchanging value of the pressure is achieved (within some small tolerance) the stoichiometry $\Sigma y_i = 1$ is tested. Usually this is satisfied when the pressure has attained an unchanging value. If $\sum y_i$ is not satisfied, the vapor-phase fugacity coefficients are recalculated and the loop is re-entered at the calculation of vapor-phase compositions. When the two conditions of unchanging pressure and $\sum y_i$ are met, the equations are all satisfied and the equilibrium results are printed out. Usually, convergence is attained after several iterations, taking a total time of about half a second on an IBM 7094 computer (for a ternary system).

Figures 10 to 13 and Tables IV to IX give examples of predicted bubble pressures and vapor compositions for some multicomponent systems uging binary data only. In the calculation for the ternary system acetylene–

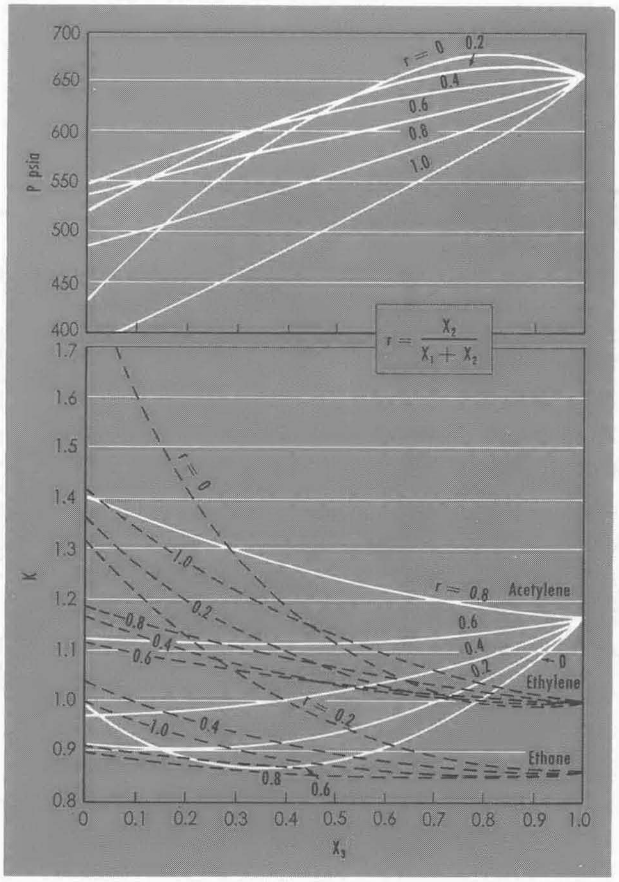

Figure 12. Calculated vapor-liquid equilibrium constants and bubble pressures for the acetylene(1)–ethane(2)–ethylene(3) system at 40° F.

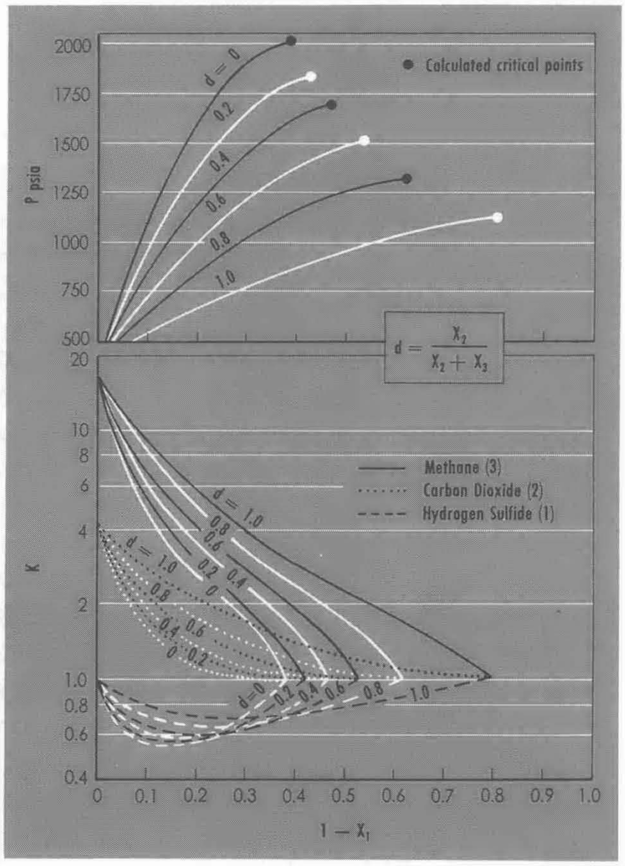

Figure 13. Calculated vapor-liquid equilibrium constants and bubble pressures for the hydrogen sulfide(1)–carbon dioxide(2)–methane(3) system at 100° F.

ethane–ethylene, all three components are treated as solvents, using only one parameter, α, per binary, as explained in Section B.

Very near the critical point of the mixture, for the region $0.97 \leq T_R \leq 1.0$ for the liquid mixture, calculated results are extremely sensitive to small errors in any of the thermodynamic quantities involved. Results for this hypersensitive region can be best obtained by interpolating between calculations at a lower T_R and the known condition at the critical point—i.e., $K_i = 1$ for each component and the pressure is equal to the critical pressure of the mixture. Correlations of critical properties of mixtures are given elsewhere (*7, 26*).

In general, agreement between predicted and experimental results is very good. However, in a few instances, significant disagreement was noted, especially

Table IV. Comparison of Calculated and Experimental Results from Program BUBL P

n-Pentane(1)–Propane(2)–Methane(3) System

Given				Calculated				Experimental[a]			
T, ° R	x_1	x_2	x_3	P, psia	y_1	y_2	y_3	P, psia	y_1	y_2	y_3
559.7	0.678	0.170	0.152	495	0.046	0.086	0.868	500	0.049	0.085	0.866
559.7	0.555	0.139	0.306	987	0.040	0.056	0.903	1000	0.043	0.056	0.901
559.7	0.442	0.110	0.448	1448	0.049	0.049	0.902	1500	0.051	0.049	0.900
559.7	0.315	0.079	0.606	1973	0.068	0.047	0.885	2000	0.083	0.046	0.871
619.7	0.701	0.175	0.124	515	0.113	0.143	0.744	500	0.112	0.145	0.743
619.7	0.587	0.147	0.266	1019	0.093	0.086	0.821	1000	0.094	0.080	0.826
619.7	0.482	0.121	0.397	1499	0.103	0.069	0.828	1500	0.103	0.068	0.829
619.7	0.363	0.091	0.546	2070	0.130	0.057	0.813	2000	0.138	0.073	0.789
679.7	0.730	0.182	0.088	495	0.243	0.227	0.529	500	0.238	0.215	0.547
679.7	0.616	0.154	0.230	1000	0.186	0.129	0.685	1000	0.181	0.122	0.697
679.7	0.501	0.125	0.374	1443	0.185	0.093	0.722	1500	0.206	0.099	0.695

[a] References *4, 11.*

Table V. Comparison of Calculated and Experimental Results from Program BUBL P

Acetylene(1)–Ethane(2)–Ethylene(3) System

Given				Calculated				Experimental[a]			
T, ° R	x_1	x_2	x_3	P, psia	y_1	y_2	y_3	P, psia	y_1	y_2	y_3
424.7	0.187	0.330	0.483	197.4	0.203	0.252	0.545	200.3	0.202	0.260	0.538
424.7	0.061	0.316	0.623	199.4	0.073	0.230	0.697	200.3	0.084	0.234	0.682
424.7	0.084	0.104	0.812	218.9	0.084	0.075	0.841	220.0	0.084	0.080	0.836
424.7	0.142	0.630	0.228	170.8	0.205	0.501	0.294	175.1	0.206	0.511	0.283
459.7	0.060	0.204	0.736	356.2	0.069	0.156	0.775	359.9	0.065	0.157	0.778
459.7	0.025	0.437	0.538	316.9	0.035	0.346	0.619	320.2	0.034	0.347	0.619
459.7	0.143	0.795	0.062	277.0	0.237	0.685	0.078	280.1	0.220	0.684	0.096
459.7	0.056	0.464	0.480	315.8	0.079	0.370	0.551	319.7	0.077	0.374	0.549
499.7	0.074	0.767	0.159	466.8	0.113	0.694	0.193	465.5	0.113	0.698	0.189
499.7	0.031	0.741	0.228	461.8	0.048	0.673	0.279	464.8	0.046	0.677	0.277
499.7	0.843	0.082	0.075	510.5	0.771	0.120	0.109	514.4	0.778	0.114	0.108
499.7	0.192	0.658	0.150	515.7	0.252	0.579	0.169	514.4	0.242	0.590	0.168
499.7	0.042	0.426	0.532	542.0	0.055	0.366	0.579	564.4	0.050	0.363	0.587
499.7	0.257	0.493	0.250	558.6	0.299	0.432	0.269	564.4	0.286	0.441	0.273
499.7	0.316	0.202	0.482	619.6	0.319	0.182	0.499	614.4	0.310	0.188	0.502
499.7	0.500	0.041	0.459	621.8	0.448	0.043	0.509	614.4	0.460	0.047	0.493
499.7	0.104	0.067	0.829	650.1	0.114	0.058	0.828	664.4	0.103	0.061	0.836
499.7	0.224	0.032	0.745	668.6	0.224	0.029	0.747	664.4	0.217	0.032	0.751

[a] References *15, 18.*

Table VI. Comparison of Calculated and Experimental Results from Program BUBL P

Propane(1)–Ethane(2)–Methane(3) System

Given				Calculated				Experimental[a]			
T, ° R	x_1	x_2	x_3	P, psia	y_1	y_2	y_3	P, psia	y_1	y_2	y_3
309.7	0.500	0.258	0.242	97	0.003	0.025	0.972	100	0.003	0.028	0.969
309.7	0.153	0.319	0.528	191	0.001	0.021	0.978	200	0.002	0.024	0.974
359.7	0.570	0.320	0.110	103	0.021	0.115	0.864	100	0.025	0.110	0.865
359.7	0.281	0.483	0.236	202	0.007	0.102	0.891	200	0.009	0.098	0.893
359.7	0.262	0.242	0.496	400	0.006	0.042	0.951	400	0.007	0.036	0.956
409.7	0.607	0.268	0.125	202	0.054	0.148	0.798	200	0.056	0.140	0.804
409.7	0.200	0.523	0.277	408	0.014	0.185	0.801	400	0.013	0.188	0.799
409.7	0.293	0.109	0.598	816	0.032	0.048	0.920	800	0.036	0.036	0.928
409.7	0.145	0.089	0.766	968	0.031	0.076	0.893	1000	0.047	0.050	0.903
459.7	0.139	0.724	0.136	407	0.026	0.482	0.492	400	0.028	0.485	0.487
459.7	0.421	0.188	0.391	805	0.075	0.105	0.821	800	0.082	0.094	0.824
459.7	0.308	0.107	0.585	1079	0.086	0.075	0.839	1100	0.099	0.063	0.838
459.7	0.260	0.030	0.710	1221	0.107	0.027	0.866	1300	0.146	0.025	0.829
509.7	0.811	0.160	0.027	200	0.432	0.290	0.278	200	0.441	0.284	0.275
509.7	0.715	0.175	0.110	401	0.246	0.188	0.566	400	0.250	0.193	0.557
509.7	0.593	0.121	0.286	801	0.179	0.093	0.728	800	0.187	0.091	0.722
509.7	0.442	0.169	0.389	975	0.156	0.129	0.715	1000	0.167	0.126	0.707
509.7	0.463	0.037	0.500	1225	0.209	0.030	0.762	1200	0.214	0.030	0.756

[a] Reference 29.

Table VII. Comparison of Calculated and Experimental Results from Program BUBL P

Ethane(1)–Methane(2)–Hydrogen(3) System[a]

Given				Calculated				Experimental[a]			
T, ° R	x_1	x_2	x_3	P, psia	y_1	y_2	y_3	P, psia	y_1	y_2	y_3
209.3	0.720	0.275	0.0046	199.4	0.0002	0.0570	0.9428	195.7	0.00020	0.0431	0.957
209.3	0.353	0.628	0.0192	520.7	0.0001	0.0490	0.9509	502.0	0.00006	0.0461	0.954
209.3	0.328	0.597	0.0754	2436	0.0002	0.0419	0.9579	1990	0.00016	0.0357	0.964
209.3	0.753	0.211	0.0362	2037	0.0002	0.0186	0.9812	1985	0.00035	0.0137	0.986
209.3	0.904	0.0788	0.0168	986.8	0.0001	0.0078	0.9921	981.9	0.00022	0.0054	0.995
209.3	0.905	0.0637	0.0312	2133	0.0002	0.0063	0.9935	1965	0.00026	0.0044	0.996
259.4	0.451	0.518	0.0313	712.8	0.0016	0.1495	0.8489	749.6	0.0017	0.136	0.862
259.4	0.505	0.438	0.0573	1420	0.0016	0.0975	0.9009	1490	0.00161	0.0910	0.907
259.4	0.503	0.440	0.0574	1418	0.0016	0.0979	0.9005	1990[b]	0.00206	0.0535[b]	0.944
259.4	0.673	0.280	0.0473	1476	0.0018	0.0669	0.9313	1500	0.00210	0.0540	0.944
259.4	0.699	0.267	0.0340	1061	0.0018	0.0725	0.9258	1013	0.00196	0.0633	0.935
309.7	0.768	0.203	0.0291	740.7	0.0143	0.1457	0.8400	748.7	0.0137	0.130	0.856
309.7	0.780	0.162	0.0584	1500	0.0108	0.0768	0.9124	1500	0.0114	0.0695	0.919
309.7	0.829	0.100	0.0712	1986	0.0102	0.0422	0.9475	1980	0.0109	0.0356	0.953
309.7	0.901	0.0725	0.0266	745.5	0.0146	0.0534	0.9320	749.0	0.0140	0.0450	0.941
309.7	0.354	0.624	0.0222	489.5	0.0137	0.5348	0.4515	517.4	0.0141	0.492	0.494
309.7	0.517	0.417	0.0660	1234	0.0106	0.2108	0.7786	1485	0.0122	0.188	0.800
359.5	0.544	0.444	0.0122	528.1	0.0683	0.6543	0.2775	521.1	0.0816	0.696	0.222
359.5	0.514	0.411	0.0745	1557	0.0410	0.3038	0.6552	1410	0.047	0.318	0.635
359.5	0.549	0.368	0.0827	1728	0.0398	0.2580	0.7022	1790	0.0469	0.264	0.689
359.5	0.738	0.238	0.0241	643.3	0.0644	0.3180	0.6176	699.2	0.0656	0.318	0.616
433.0	0.590	0.395	0.0148	813.1	0.2359	0.6427	0.1214	837.7	0.240	0.645	0.115
433.0	0.731	0.210	0.0590	1162	0.1975	0.2992	0.5033	1200	0.204	0.300	0.496
433.0	0.704	0.228	0.0676	1283	0.1880	0.3027	0.5093	1400	0.187	0.288	0.525
433.0	0.665	0.245	0.0901	1578	0.1727	0.2850	0.5423	1605	0.187	0.297	0.516
459.7	0.798	0.117	0.0845	1383	0.2698	0.1668	0.5634	1520	0.308	0.169	0.523
459.7	0.640	0.300	0.0595	1287	0.2929	0.4015	0.3057	1217	0.346	0.406	0.248
459.7	0.632	0.266	0.102	1773	0.2721	0.3072	0.4207	1610	0.319	0.339	0.342

[a] Reference 9. [b] Experimental data seem to be in error; compare with the line immediately above. See discussion in the text.

in the pressure. While it is not possible to explain such disagreement with certainty, close scrutiny of the experimental data suggests that for some of the reported points there may be appreciable experimental error. For example, in the system ethane–methane–hydrogen at −200° F, the measured pressure is 1490 psia when the liquid composition is 50.5 mole per cent ethane, 43.8 mole per cent methane, 5.73 mole per cent hydrogen. However, at the same temperature and for a very similar liquid composition (50.3 mole per cent ethane, 44.0 mole per cent methane, 5.74 mole per cent hydrogen) the measured pressure is 1990 psia. It is most unlikely that such a small change in liquid composition could produce such a large change in the total pressure. The reported vapor composition in the first case is 0.161 mole per cent ethane and 9.10 mole per cent methane; in the second case, it is 0.206 mole per cent ethane and 5.35 mole per cent methane. It is not likely that such a small change in liquid composition could account for a factor of nearly 2 in the *K* value of methane. Our calculations suggest that the experimental results for the first case are more reliable than those for the second case.

In the binary system hydrogen sulfide–carbon dioxide at 100° F, the measured pressure is 600 psia when the liquid composition is 84 mole per cent hydrogen sulfide and 16 mole per cent carbon dioxide. However, in the ternary system hydrogen sulfide–carbon dioxide–methane at 100° F, the measured pressure is again 600 psia even though the liquid now contains 2 mole per cent methane with 81 mole per cent hydrogen sulfide and 17 mole per cent carbon dioxide. Our calculated pressure for this ternary mixture is 744 psia. Since methane is a highly supercritical component at 100° F, we would expect that introduction of 2 mole per cent methane raises the total pressure beyond that for the methane-free binary system. Uncertainties in experimental results are unfortunately, not rare, especially in ternary (and higher) systems, because of severe experimental problems.

Experimental and observed results for the five-component system (Table IX) are generally in good agreement. When the liquid phase is predominantly *n*-pentane, the predicted *K* factor for methane is a little lower than that reported by De Priester (*10*). Our model parameters for methane–*n*-pentane were obtained from the very good data of Sage and Lacey (*38*) which reproduce extremely well the methane–*n*-pentane, and methane–propane–*n*-pentane systems. It appears that De Priester's extrapolated data for the *n*-pentane–methane system disagree somewhat with those of Sage and coworkers.

BUBL T program. The main program, BUBL T, performs a bubble-temperature calculation. The pressure and the liquid-phase compositions are the known variables. The program calculates the equilibrium temperature and vapor compositions. Since the temperature is unknown, all the temperature-dependent thermodynamic quantities enter into the iterative loop.

After the data have been read in by INPUT, the first guess of temperature is made by utilizing the known liquid-phase compositions and total pressure, using approximately seven tenths of the pseudocritical temperature of the mixture. The temperature-dependent quantities are then calculated in subroutines RSTATE, ACTCO, and VOLPAR. The liquid-phase fugacities are then calculated by Equation 78, and vapor-phase compositions are calculated for the first time, using $\varphi_i = 1$. These vapor-phase compositions (after normalization) are then immediately used to recalculate φ_i (subroutine PHIMIX) and new y_i's are calculated. These calculations are repeated until Σy_i attains a constant value. The stoichiometric criterion $\sum y_i = 1$ is then tested and, if not satisfied, the deviation from unity is used to readjust the temperature. The loop is then entered at RSTATE and the iteration repeated until SUMY is constant and equals unity. When these conditions are satisfied, the problem is solved and the equilibrium results are printed out. Table X shows results of predicted ternary bubble temperatures and compositions calculated from binary data only.

Conclusion

In this work, we have described a method for reducing binary vapor-liquid equilibrium data to thermodynamically significant functions. For describing the vapor phase we use a well-known, two-parameter equation of state modified for mixtures to take into account deviations from the geometric mean approximation. For the liquid phase, we define the excess Gibbs energy with reference to a mixture which follows Henry's law; thereby we avoid the use of any arbitrary hypothetical standard states. The composition dependence of the activity coefficients is given by an equation similar to that of van Laar, modified to take into account the tendency of liquid mixtures to dilate in the critical region. Most important, we calculate the pressure dependence of the activity coefficient with realistic estimates of the liquid-phase partial volumes; these quantities, more than any others, provide the key to progress in high-pressure thermodynamics.

Table VIII. Comparison of Calculated and Experimental Results from Program BUBL P

Hydrogen Sulfide(1)–Carbon Dioxide(2)–Methane(3) System at 100° F

Given			Calculated				Experimental[a]			
x_1	x_2	x_3	P, psia	y_1	y_2	y_3	P, psia	y_1	y_2	y_3
0.840	0.160	0.000	624	0.6259	0.3741	0.000	600	0.608	0.392	0.000
0.810	0.170	0.020	744	0.5551	0.3329	0.1120	600[b]	0.660	0.222	0.118
0.937	0.044	0.0190	605	0.6996	0.1190	0.1814	600	0.684	0.115	0.201
0.891	0.101	0.008	601	0.6726	0.2593	0.0681	600	0.644	0.259	0.097
0.870	0.122	0.008	627	0.6430	0.2950	0.0620	600[c]	0.630	0.317	0.053
0.967	0.000	0.033	657	0.6839	0.000	0.3161	600[c]	0.710	0.000	0.290
0.955	0.029	0.016	564	0.7439	0.0850	0.1712	600	0.690	0.066	0.244
0.891	0.000	0.109	1162	0.502	0.000	0.498	1200[c]	0.049	0.000	0.510
0.843	0.042	0.115	1177	0.4856	0.0613	0.4531	1200	0.470	0.095	0.435
0.747	0.137	0.116	1121	0.4614	0.1801	0.3585	1200	0.445	0.201	0.354
0.683	0.213	0.104	1050	0.4494	0.2675	0.2831	1200	0.418	0.278	0.304

[a] Reference 35.

[b] Experimental data seem to be in error; compare with line immediately above. See discussion in the text.

[c] These binary data are somewhat in disagreement with those of Sage's which, in turn, are given correctly by the calculations.

Table IX. Comparison of Calculated and Experimental Results from Program BUBL P

n-Pentane(1)–*n*-Butane(2)–Propane(3)–Ethane(4)–Methane (5)[a]

Given		Calculated		Experimental	
T, ° F	100	*P*, psia	289	*P*, psia	289
x_1	0.488	y_1	0.0424	y_1	0.033
x_2	0.213	y_2	0.0526	y_2	0.044
x_3	0.120	y_3	0.0877	y_3	0.091
x_4	0.115	y_4	0.2371	y_4	0.233
x_5	0.064	y_5	0.5802	y_5	0.599
T, °F	100	*P*, psia	85	*P*, psia	96
x_1	0.802	y_1	0.1678	y_1	0.129[b]
x_2	0.114	y_2	0.0733	y_2	0.068
x_3	0.045	y_3	0.0916	y_3	0.089
x_4	0.023	y_4	0.1499	y_4	0.144
x_5	0.016	y_5	0.5175	y_5	0.570[b]
T, °F	200	*P*, psia	771	*P*, psia	782
x_1	0.356	y_1	0.0913	y_1	0.068
x_2	0.222	y_2	0.1076	y_2	0.097
x_3	0.160	y_3	0.1417	y_3	0.130
x_4	0.126	y_4	0.1860	y_4	0.194
x_5	0.136	y_5	0.4734	v_5	0.511

[a] Reference *10*.
[b] See discussion in the text.

The main use of our equations for data reduction follows from their generalization to multicomponent mixtures. With the help of an electronic computer, it is possible to make good estimates of multicomponent phase behavior including the critical region using only the results of binary data reduction. Details of such calculations, including computer programs, are presented in a forthcoming monograph (*26*).

Since our method requires a considerable amount of binary data, our calculated results for binary systems are almost always more accurate than those obtained by other calculation methods. In a recent review (*1*) it was shown that common calculation methods can predict *K* factors for binary systems containing paraffins and olefins with root-mean-square deviations averaging 7 to 20% and sometimes more, depending on the particular method and on the conditions; in the critical region errors are often much larger.

For systems containing nitrogen, carbon dioxide, acetylene, hydrogen sulfide, or hydrogen, common computational methods frequently give large errors of the order of 20% and sometimes errors exceeding 100% (*1*).

Our method of calculation for binary systems gives *K* factors generally accurate to within a root-mean-square deviation of 3 to 4% provided some good binary experimental data are available for data reduction. This low root-mean-square deviation is only slightly larger for the critical region and for systems containing one or more of the frequently encountered components in petroleum refining outside the paraffin-olefin class.

While it is difficult to generalize, for multicomponent mixtures common calculational methods can predict *K* factors for mixtures containing paraffins or olefins with a root-mean-square deviation of about 15 to 30%, depending on the method and on the conditions (*1*). For systems containing nitrogen, the errors are only slightly larger; however, for systems containing carbon dioxide, acetylene, hydrogen sulfide, or hydrogen, errors are often much larger (*1*) especially if the Benedict-Webb-Rubin equation is used or if the Chao-Seader correlation is used at low temperatures.

We estimate that our predicted *K* factors for multicomponent systems have a root-mean-square deviation between 4 and 8%; the lower figure pertains to systems for which there are good binary data and for the region not immediately in the critical. The higher figure pertains to those systems where binary data are sparse and to the region very close to the critical. The general-

Table X. Comparison of Calculated and Experimental Results from Program BUBL T

n-Pentane(1)–Propane(2)–Methane(3) System

	Given			Calculated				Experimental[a]			
P, psia	x_1	x_2	x_3	*T*, ° R	y_1	y_2	y_3	*T*, ° R	y_1	y_2	y_3
500	0.533	0.355	0.112	619.0	0.092	0.302	0.606	619.7	0.091	0.297	0.612
500	0.362	0.543	0.095	619.9	0.069	0.452	0.479	619.7	0.067	0.461	0.472
500	0.678	0.170	0.152	561.9	0.047	0.087	0.866	559.7	0.049	0.085	0.866
500	0.384	0.577	0.039	679.0	0.152	0.677	0.171	679.7	0.153	0.680	0.167
1000	0.443	0.296	0.261	620.1	0.079	0.178	0.743	619.7	0.080	0.168	0.752
1000	0.298	0.447	0.255	620.3	0.063	0.279	0.658	619.7	0.066	0.277	0.657
1000	0.555	0.139	0.306	564.2	0.043	0.058	0.899	559.7	0.043	0.056	0.901
1000	0.616	0.154	0.230	680.1	0.187	0.129	0.684	679.7	0.181	0.122	0.697
1500	0.482	0.121	0.397	619.9	0.104	0.069	0.828	619.7	0.103	0.068	0.829
1500	0.213	0.320	0.467	558.8	0.037	0.176	0.787	559.7	0.046	0.160	0.794
1500	0.501	0.125	0.374	676.1	0.195	0.095	0.710	679.7	0.206	0.099	0.695

[a] References *4*, *11*.

ity of our method readily permits application without serious loss of accuracy to systems containing nonpolar (or slightly polar) components outside the paraffin-olefin class.

Our calculated results are generally more accurate than those using common techniques for two reasons: first, our method uses to the fullest possible extent all the thermodynamic tools that have recently become available; of these tools, the new technique for estimating liquid partial molar volumes is especially important. Second, our method avoids arbitrary hypothetical standard states and is based on careful reduction of binary experimental data. The literature is already rich with binary data and more binary experimental results are appearing regularly. The philosophical basis of our method follows from our conviction that whereas it is extremely difficult to predict phase behavior from pure-component data alone, we may expect with few exceptions to predict with confidence multicomponent behavior from at least some binary data in addition to pure-component data, provided we are willing to make an effort to take thermodynamics seriously.

Nomenclature

a, b = constants in Redlich-Kwong equation of state
A, B = binary parameters given by Equations 34 and 35
f = fugacity
f^0 = reference fugacity
g^E = excess Gibbs energy in symmetric convention
g^{E*} = excess Gibbs energy in unsymmetric convention
$g^{E*}_{(MS)}$ = excess Gibbs energy (unsymmetric convention) relative to the mixed solvent
$H_{2(1)}$ = Henry's constant for solute 2 in solvent 1
k_{ij} = characteristic constant for i-j interaction
n_i = number of moles of component i
n_T = total number of moles
N = number of components
NS = number of solvent-components
P = total pressure
P_c = critical pressure
P_{cij} = critical pressure characteristic of the i-j interaction
P^r = constant reference pressure
PO = a constant reference pressure of zero
q = effective molar volume
R = gas constant
T = temperature
T_c = critical temperature
T_{cij} = critical temperature characteristic of the i-j interaction
$T^{\ddagger}$ = characteristic constant of a binary system, used in correlating dilation constants
v = molar volume of the vapor phase or liquid phase
V = total volume of the mixture
v_c = critical volume
v_{cij} = critical volume characteristic of the i-j interaction
$\bar{v}^L_i$ = partial molar volume of component i in the liquid mixture
x = mole fraction in the liquid phase
y = mole fraction in the vapor phase
z = compressibility factor
z_c = critical compressibility factor
z_{cij} = critical compressibility factor characteristic of the i-j interaction

Greek Letter

$\alpha_{22(1)}$ = self-interaction constant of molecules 2 in the environment of molecules 1
α_{12} = interaction constant of molecules 1 and 2
γ = activity coefficients for solvent components
γ^* = activity coefficients for solute components (in unsymmetric convention)
$\eta_{2(1)}$ = dilation constant of solute 2 in solvent 1
$\eta^{\ddagger}$ = characteristic constant of a solute, used in correlating dilation constants
φ_i = fugacity coefficient of component i in a gas mixture
Φ = volume fraction as given by Equation 27
Ψ = solute-free solvent volume fraction as given by Equation 69
ω = acentric factor
Ω_a, Ω_b = dimensionless constants in Redlich-Kwong equation

Superscripts

E = excess quantity
L = liquid phase
(P^r) = at constant reference pressure
(PO) = at constant reference pressure of zero
s = at saturation
o = reference state
$*$ = unsymmetric convention of normalization for activity coefficients

Subscripts

c = critical
i = component i
$ii(j)$ = i-i interaction in the environment of j
ij = i-j interaction
(MS) = with reference to mixed solvent
(SF) = solute-free solvent

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