ρ = density
ϕ = solution vector for O.D.E.
ϕ^2 = Thiele modulus
Ω = spatial region

Subscripts

e = equilibrium state
o = initial state
y = derivative with respect to y
z = derivative with respect to z

Superscripts

$*$ = steady state condition

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Use of Molecular Shape Factors in Vapor-Liquid Equilibrium Calculations with the Corresponding States Principle

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Calculation of fugacities of components in a gaseous or liquid solution directly from the corresponding states principle requires an improvement in the pseudo-critical constants for the mixture. The derivation of the pseudo-criticals must take into account deviations from the simple two parameter corresponding states principle which require additional parameters incorporated into the definition of the pseudo-criticals. In this work parameters called molecular shape factors are introduced into the pseudo-criticals. A generalized correlation for these shape factors is presented.

Use of the shape factors greatly improves the calculation of vapor-liquid equilibrium ratios for nonpolar hydrocarbon mixtures with large differences in molecular size and shape. Excellent results are obtained both in the low pressure and in the retrograde region when the pseudo-reduced properties of the vapor and liquid lie within the range of accurately known properties of a reference fluid and the reduced temperatures for each component is greater than approximately 0.6.

Direct calculation of individual component fugacities in a mixture, and of equilibrium vapor-liquid distribution coefficients (K-values) from the corresponding states principle, offers some attractive possibilities in practical solution thermodynamics. In this procedure one defines pseudo-critical values for the mixture and determines the mixture properties from the known properties of a pure reference substance at the same pseudo-reduced conditions. In calculating individual fugacities and K-values one must differentiate the pseudo-critical constants with respect to composition. This requires a great deal more accuracy in the pseudo-critical definitions, than is necessary, to predict total solution properties. Inaccuracies in the definitions of pseudo-criticals arise from three sources:

1. Errors arising from the fact that the partition function and its thermodynamic derivatives for a pure reference cannot always exactly represent the corresponding functions for a mixture of dissimilar molecules, even when

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J. W. Leach is with Ling-Temco-Vought, Inc., Dallas, Texas the individual components obey the simple two parameter corresponding states principle.

2. Uncertainties in the combining rules for the potential between unlike molecular pairs.
3. Difficulties arising when the individual components deviate appreciably from the simple two-parameter corresponding states principle.

This paper proposes a correction for the third source, which is one of the most serious sources of error. All earlier attempts to calculate component fugacities and *K*-values (*9, 16, 29*) did not adequately account for deviations from the two parameter theory and do not work well for mixtures in which these deviations are large. In this study a new method designed especially for use with pseudo-critical expressions is introduced to account for deviations from the simple corresponding states theory. This method uses quantities called molecular shape factors which multiply the individual critical constants in the pseudo-critical equations. Generalized correlations of these factors are presented. A remarkable improvement is obtained in the prediction of *K*-values using these factors.

Errors due to the first source become more serious at low temperatures. An attempt to reduce errors from this source is the subject of a sequel to this paper.

CORRESPONDING STATES PRINCIPLE FOR MIXTURES

The usual derivations of pseudo-critical equations for mixtures (*14, 21, 24, 28*) involve the assumption that force constants in the intermolecular potential function are directly proportional to critical properties with the same proportionality constant for all fluids.

$$\epsilon \propto T_c \qquad\qquad \sigma^3 \propto V_c \tag{1}$$

The theory defines "pseudo-potential" parameters $\overline{\epsilon}$ and $\overline{\sigma}$ which are composition dependent averages. These averages involve the parameters ϵ_{ii} and σ_{ii} describing interactions between like pairs of molecules of the individuals present, and ϵ_{ij} and σ_{ij} describing interactions between unlike molecular pairs. For fluids obeying the simple two parameter corresponding states principle, the proportionalities presented in Equation (1) are exactly correct for all substances. However, for molecules with nonsymmetrical force fields or quantum mechanical effects these simple proportionalities are no longer valid.

The form of the pseudo-critical expression has several possibilities depending on the assumptions made in its derivation. As pointed out previously (*24*), all the various pseudo-critical equations seek to find a pure component reference that can represent a mixture by having the expansion for its configuration integral equivalent to a corresponding expansion for the mixture. In general, equivalence between the two expansions can only be established for a few terms in the expansion. For example, a general result was that proposed by Leland and Mueller (*17*) which defines the pseudo-potential force parameters $\overline{\epsilon}$ and $\overline{\sigma^3}$ for the pure component representing the mixture as:

$$\overline{\epsilon} = \left[\frac{\sum\limits_i \sum\limits_j x_i\, x_j\, (\epsilon^\alpha \sigma^3)_{ij}}{\sum\limits_i \sum\limits_j x_i\, x_j\, (\epsilon^\beta \sigma^3)_{ij}}\right]^{\frac{1}{\alpha-\beta}}$$

$$\overline{\sigma^3} = \left[\frac{\sum\limits_i \sum\limits_j x_i\, x_j\, (\epsilon^\beta \sigma^3)_{ij}}{[\sum\limits_i \sum\limits_j x_i\, x_j\, (\epsilon^\alpha \sigma^3)_{ij}]^{\beta/\alpha}}\right]^{\frac{\alpha}{\alpha-\beta}} \tag{2}$$

The values of α and β depend on the method of carrying out the expansion for the mixture and for the pure component reference which represents it. These values also depend on the approximations involved in attempting to equate the two. An alternative approach is to assume the random mixing approximation as presented by Prigogine (*23*) and Brown (*1*) for a Lennard-Jones potential. This assumption leads to pseudo-potentials in the form:

$$\overline{\epsilon} = \frac{\left(\sum\limits_i \sum\limits_j x_i\, x_j\, \epsilon_{ij}\, \sigma_{ij}^{6}\right)^2}{\left(\sum\limits_i \sum\limits_j x_i\, x_j\, \epsilon_{ij}\, \sigma_{ij}^{12}\right)}$$

$$\overline{\sigma^3} = \left[\frac{\sum\limits_i \sum\limits_j x_i\, x_j\, \epsilon_{ij}\, \sigma_{ij}^{12}}{\sum\limits_i \sum\limits_j x_i\, x_j\, \epsilon_{ij}\, \sigma_{ij}^{6}}\right]^{1/2} \tag{3}$$

The results in Equation (3) are valid only when the molecular sizes are very nearly the same.

For molecules with appreciable size differences it is much better to make the approximation leading to Equation (2) in terms of approximate radial distribution functions expanded about a hard sphere model (*16, 24*) and consider only the leading terms; the result gives Equation (2) with:

$$\alpha = 1 \qquad\qquad \beta = 0 \tag{4}$$

This assumption becomes better at higher temperatures. In an attempt to improve the assumption, Leland and Mueller (*17*) set $\beta = 0$ and correlated α empirically as a function of the dimensionless ratio:

$$\left[\frac{P \sum\limits_i x_i\, T_{ci}}{T \sum\limits_i x_i\, P_{ci}}\right] \tag{5}$$

Othmer and Chen (*20*) have recently completed a new correlation of α with $[P \sum_i x_i T_{ci}/(T \sum_i x_i P_{ci})]$ which appears to be an improvement over the correlation originally proposed. This type of correlation, however, must account empirically for the combination of errors due to all the sources discussed in the introduction. This paper examines systems at temperatures for which Equation (4) is a good choice and errors due to the first source are minimized. It then corrects primarily for errors due to the third source. There is some reason to believe that this correction will also remove some of the uncertainties due to the second source.

MOLECULAR SHAPE FACTORS

Pseudo-criticals for fluids which obey the simple corresponding states principle are obtained by using Equation (1) to replace ϵ and σ^3 values in equations such as (2) or (3). The common proportionality constant in Equation (1) means that $\overline{\epsilon}$ may be replaced directly by the pseudo-critical T_c' and $\overline{\sigma^3}$ by the pseudo-critical volume, V_c'. Individual ϵ_{ii} and $\sigma^3{}_{ii}$ values are replaced directly with T_{ci} and V_{ci} values.

For mixtures with different structural or quantum deviations from the simple corresponding states principle, the hypothetical pure fluid which represents the mixture cannot be described by using only the two parameters $\bar{\epsilon}$ and $\bar{\sigma}$ of the simple two parameter corresponding states theory. An improvement is to use the molecular shape factors θ and ϕ which replace Equation (1) with:

$$\epsilon \propto \theta\, T_c$$
$$\sigma^3 \propto \phi\, V_c \tag{6}$$

The proportionality constants applicable to $\theta\ T_c$ and $\phi\ V_c$ implied by Equation (6) are now considered to be the same for all substances. The theoretical basis and properties of these shape factors to account for structural and quantum mechanical effects have been discussed (*3, 5, 14*) and a preliminary analytical correlation of their values has been completed (*14, 15*). Cook and Rowlinson (*3*) have derived temperature dependent factors which play the same role as those in Equation (6) and have shown their relationship to molecular properties such as polarizability and dipole moments which cause nonsymmetric force fields.

This paper presents a new generalized correlation for the shape factors θ and ϕ in terms of the acentric factor, ω, as defined by Pitzer (*21*) and also the critical compressibility factor, Z_c. In this manner, the shape factors introduce both a third and fourth parameter into the corresponding states principle. Through Equation (6) they serve as a means of converting the pseudo-potential parameters $\bar{\epsilon}$ and $\bar{\sigma}^3$ expressed in terms of individual force parameters into pseudo-criticals in terms of individual critical constants. The common proportionality constant for all fluids in Equation (6) means that the individual ϵ and σ^3 terms in an equation such as Equation (2) may be replaced directly with $\theta\ T_c$ and $\phi\ V_c$. The average force parameters $\bar{\epsilon}$ and $\bar{\sigma}^3$ now become new pseudo-criticals for complex fluid mixtures. A few of the properties of these factors important in *K*-value calculations are summarized as follows:

1. The factors are temperature dependent and, to a limited extent, depend slightly on density. For gases the factors are completely independent of density in regions which can be described by second and third virial coefficients. In dense gaseous regions which require more than three virials and in liquid regions, the density dependence becomes important.

2. The shape factors useful in *K*-value calculations are defined most conveniently in a relative sense. That is, they may be regarded as factors which modify the criticals of a substance *i* so that its properties can be predicted from a corresponding states tabulation, or correlation of the properties of a structurally dissimilar reference substance *k*. Consequently, the shape factors are conveniently written with two subscripts. The first refers to any given molecule and the second refers to the reference substance used to predict the properties of the given molecule. For example, the reduced equation of state function which gives the compressibility factor of the reference substance *k* might be designated as Z_k. The compressibility factor for a dissimilar fluid *i* at a temperature T_i and volume V_i is then:

$$Z_i = Z_k\left(\frac{T_i}{\theta_{ik}\,T_{ci}}, \frac{V_i}{\phi_{ik}\,V_{ci}}\right) \tag{7}$$

3. The factors θ_{ik} and ϕ_{ik} may be combined to produce a factor ψ_{ik} which modifies the critical pressure P_{ci}. The result may be shown to be (*14*)

$$\psi_{ik} = \left(\frac{Z_{ck}}{Z_{ci}}\right)\left(\frac{\theta_{ik}}{\phi_{ik}}\right) \tag{8}$$

and an alternative way to obtain Z_i from the reduced equation of state for *k* is

$$Z_i = Z_k\left(\frac{T_i}{\theta_{ik}\,T_{ci}}, \frac{P_i}{\psi_{ik}\,P_{ci}}\right) \tag{9}$$

For pure components, whenever *i* and *k* conform to the same reduced corresponding states function, then all of the factors θ_{ik}, ϕ_{ik}, and ψ_{ik} become unity.

4. As a consequence of the temperature dependence of the shape factors, it is important to note that the factors θ_{ik} and ϕ_{ik} which predict compressibility factors and fugacity pressure ratios are not the proper factors to use in predicting $(U^* - U)/(RT)$ or $(H^* - H)/(RT)$. A separate class of shape factors called second order shape factors has been defined for this purpose (*5, 14, 15*). It is also possible to show how incorrect values of $(U^* - U)/(RT)$ and $(H^* - H)/(RT)$ calculated by using the first order factors θ_{ik} and ϕ_{ik} defined to predict compressibility factors may be corrected to give the proper result (*6*). However, it can be shown (*12*) that the $(U^* - U)/(\mathrm{RT})$ or $(H^* - H)/(RT)$ value which appears in the fugacity function $f_i/(x_iP)$ for a component in a mixture is not the true value for the mixture, but the apparent value, obtained by using the first order shape factors which predict compressibilities and fugacities. Consequently, in calculating *K*-values only first-order shape factors are needed.

5. An advantage of the use of shape factors is that it is relatively easy to convert shape factors evaluated for one reference to factors relative to another reference.

For pure components, the value of θ_{ik} for substance *i* relative to reference *k* for use in modifying T_{ci} is equal to the reciprocal of θ_{ki} for substance *k*, relative to a reference *i* but evaluated at a different temperature. The other factors are related similarly. This facility for changing references is useful because it is always advantageous to use a reference as similar to the components of the mixture as possible. Equations for changing references in this manner are presented in this paper.

6. There is a slight effect of composition on the shape factors used for a component in a mixture. This is caused by the effect of differences in environment between pair interactions in a mixture and in a pure component. This effect may be taken into account by writing the factors evaluated from pure component data in terms of reduced temperature T_{R_i} and reduced volume V_{R_i} of the component. For shape factors in a mixture it is shown here that T_{R_i} must be replaced by $\theta_{ik}(T_R)_k$ and V_{R_i} must be replaced by $\phi_{ik}(V_R)_k$ where:

$$(T_R)_k = \frac{T_M}{T'_{c_k}} \text{ and } (V_R)_k = \frac{V_M}{V'_{c_k}} \tag{10}$$

The subscript *k* refers to the reference substance for the shape factors in the pseudo-criticals T_c' and V_c' and the pure substance whose properties at reduced conditions $(T_R)_k$ and $(V_R)_k$ give the properties of the mixture. The subscript *M* refers to mixture properties. The analytical equations for the shape factors in a mixture thus become nonlinear functions that require an iteration for solution. This iteration, however, converges rapidly and is explained below.

ANALYTICAL CORRELATION OF THE FIRST-ORDER SHAPE FACTORS

Empirical relations for the first-order shape factors which predict compressibility factors and fugacity pressure ratios in pure components, when methane is the reference substance are as follows:

$$\theta_{i1} = 1 + (\omega_i - \omega_1)\,[0.0892 - 0.8493 \ln T_{R_i} + (0.3063 - 0.4506/T_{R_i})\,(V_{R_i} - 0.5)] \quad (11)$$

$$\phi_{i1} = \{1 + (\omega_i - \omega_1)\,[0.3903\,(V_{R_i} - 1.0177) - 0.9462\,(V_{R_i} - 0.7663) \ln T_{R_i}]\} \left(\frac{Z_{c1}}{Z_{ci}}\right) \quad (12)$$

In these equations, the acentric factor for methane is $\omega_1 = 0.0050$.

For pure components:

$$T_{R_i} = T_i/T_{ci} \text{ and } V_{R_i} = V/V_{ci}$$

For pure components and in pseudo-critical equations for mixtures V_{R_i} is set equal to the constant value of 2.0 in Equations (11) and (12) for all V_{R_i} conditions $\geqq 2.0$. V_{R_i} is set equal to the constant value of 0.5 in Equations (11) and (12) for all V_{R_i} conditions $\leqq 0.5$. T_{R_i} is set equal to 2.0 for all T_{R_i} values $\geqq 2.0$. The development of Equations (11) and (12) is discussed in more detail by Leach (*12*).

At low densities, indicated here by $V_{R_i} \geqq 2.0$, the shape factors become completely independent of density and they become very close to those obtained by solving equations which equate the second and third virial coefficients of the component and its reference. In earlier work shape factor equations at low densities were based on the McGlashan-Potter (*19*) equation for the second virial coefficient. Equations (11) and (12) with the indicated restrictions apply to all densities. At reduced volumes $\leqq 0.5$ in the liquid and dense fluid region the factors again become independent of density.

At very low temperatures shape factors have not been accurately determined at this time due to uncertainties in the pure component data. Work is continuing in this region and the applicability of these equations for shape factors at very low temperatures is still to be tested. It is recommended for the present that Equations (11) and (12) be used at T_R values above 0.6.

In Equations (11) and (12) the reference substance is methane, indicated by assigning a value of 1 to the k subscript on the shape factors, and these equations apply only for a methane reference. The procedure for changing references is given below.

EXPERIMENTAL EVALUATION OF SHAPE FACTORS AND PSEUDO-CRITICAL EQUATIONS

The shape factors for pure components may be evaluated experimentally in their density dependent regions by simultaneous solution of:

$$Z_i = Z_k \left(\frac{T_i}{\theta_{ik} T_{ci}}, \frac{V_i}{\phi_{ik} V_{ci}}\right) \quad (13)$$

$$(f/P)_i = F_k \left(\frac{T_i}{\theta_{ik} T_{ci}}, \frac{V_i}{\phi_{ik} V_{ci}}\right) \quad (14)$$

The function F_k represents the reduced fugacity pressure ratio function for the reference k and Z_k represents the compressibility function for the reference. Simultaneous solution will give θ_{ik} and ϕ_{ik} as functions of (T/T_{ci}) and (V/V_{ci}). At low densities the solution becomes dependent on T/T_{ci} alone and is identical to the solution of equations which relate the second and third reduced virial coefficients of substance i and the reference k (*14*). Both the high and low density solutions for liquids as well as gases are represented by the empirical correlations in Equations (11) and (12).

In a similar manner the form of the pseudo-critical equations may be tested by simultaneous solution of similar equations for a mixture:

$$Z_M = Z_k \left(\frac{T_M}{T'_{ci}}, \frac{V_M}{V'_{ck}}\right) \quad (15)$$

$$(f/P)_M = F_k \left(\frac{T_M}{T'_{ck}}, \frac{V_M}{V'_{ck}}\right) \quad (16)$$

Equations (15) and (16) were solved for T'_{ck} and V'_{ck} using experimental Z and f/P data for mixtures and an equation of state for the reference substance. The experimental mixture data were the methane-n-butane and the methane-n-pentane systems of Sage and Lacey (*27*). Excellent agreement, obtained by simultaneous solution, was found between the T'_{ck} and V'_{ck} and the values calculated from Equations (2), (4), and (6), when the simple Lorentz-Berthelot combining rules were used for the unlike pair interactions in Equation (2). Replacing force parameters in Equation (2) with criticals multiplied by shape factors gives the results

$$V'_{ck} = \sum_i \sum_j x_i\, x_j\, b_{ijk} \quad (17)$$

$$T'_{ck} = \frac{\sum_i \sum_j x_i\, x_j\, a_{ijk}}{\sum_i \sum_j x_i\, x_j\, b_{ijk}} \quad (18)$$

The subscripts i and j refer to components in the mixture and the subscript k denotes the reference fluid to which the shape factors apply and designates the pure fluid whose properties represent the mixture at the pseudo-reduced conditions $T_M/(T_c')_k$ and $V_M/(V_c')_k$. In Equations (17) and (18):

$$b_{ijk} = \tfrac{1}{2}\,(\phi_{ik}\, V_{ci} + \phi_{jk}\, V_{cj}) \quad (19)$$

and

$$a_{ijk} = b_{ijk}\sqrt{\theta_{ik}\, T_{ci}\quad \theta_{jk}\, T_{cj}} \quad (20)$$

It is interesting to note that when Equations (17) and (19) are combined the result is

$$V'_{ck} = x_1\, \phi_{1k}\, V_{c1} + x_2\, \phi_{2k}\, V_{c2} + x_3\, \phi_{3k}\, V_{c3} + \ldots \quad (21)$$

Equation (21) is Kay's Rule for pseudo-critical volumes with the inclusion of the appropriate shape factors.

The familiar Lorentz-Berthelot combination rules used in Equations (19) and (20) were intended for simple spherical molecules and their theoretical basis is restricted to molecules of this type. The role of the shape factors is to replace complex molecules with a spherical average. Consequently, their insertion should improve these rules for complicated molecules. In this manner some of the uncertainties discussed in the second source of the introduction are also removed.

THE *K*-VALUE EQUATION

The fugacity of a component in solution determined by the corresponding states principle has been derived earlier by Joffe (*9*). The result is

$$\ln\left(\frac{f_i}{x_i P}\right) = \ln\left(\frac{f}{P}\right)_k - \left(\frac{H^* - H}{RT}\right)_k \left[\frac{n}{T'_{ck}}\left(\frac{\partial T'_{ck}}{\partial n_i}\right)_{T,P,nj}\right]$$

$$- (Z_k - 1) \left[\frac{n}{P'_{ck}} \left(\frac{\partial P'_{ck}}{\partial n_i} \right)_{T,P,n_j} \right]$$

Also, by utilizing the equality:

$$\frac{1}{P'_{ck}} \left(\frac{\partial P'_{ck}}{\partial n_i} \right)_{T,P,n_j} = \frac{1}{T'_{ck}} \left(\frac{\partial T'_{ck}}{\partial n_i} \right)_{T,P,n_j} - \frac{1}{V'_{ck}} \left(\frac{\partial V'_{ck}}{\partial n_i} \right)_{T,P,n_j}$$

One obtains

$$\ln \left(\frac{f_i}{x_i P} \right) = \ln \left(\frac{f}{P} \right)_k - \left(\frac{U^* - U}{RT} \right)_k \left[\frac{n}{T'_{ck}} \left(\frac{\partial T'_{ck}}{\partial n_i} \right)_{T,P,n_j} \right] - (1 - Z_k) \left[\frac{n}{V'_{ck}} \left(\frac{\partial V'_{ck}}{\partial n_i} \right)_{T,P,n_j} \right] \quad (22)$$

P'_{ck} and V'_{ck} are related by:

$$P'_{ck} = Z_{ck} \; R \; T'_{ck}/V'_{ck}$$

The subscript k represents the reference substance and the values $(f/P)_k$ and Z_k are properties of the total solution which are obtained by evaluating properties of pure substance k at the pseudo-reduced conditions. The n term which appears is the total number of moles in the solution. If the mole fractions on which the pseudo-criticals T_c' and P_c' depend are changed to ratios of moles and the differentiations performed, the n term then cancels and does not appear in the final expression.

The K-value is obtained from

$$\ln K_i = \ln \left(\frac{f_i}{x_i P} \right)_L - \ln \left(\frac{f_i}{y_i P} \right)_V \quad (23)$$

The subscripts L and V refer to liquid and vapor phases.

In the evaluation of Equations (22) and (23) the proper pseudo-critical equations must give accurate properties of the mixture. Without the shape factors this cannot be done when the components of the mixture are dissimilar. K-value calculations depend strongly on the thermodynamic properties of the reference fluid; therefore, accurate reference data is of primary importance and, since derivatives of the pseudo-critical expressions appear in the K-value equations, extreme accuracy is needed in their functional representation.

Since the shape factors of a component in a mixture depend on the composition, this composition dependence must be taken into account in the differentiation of V'_c and T'_c. The functions

$$(n/V'_{ck}) (\partial V'_{ck}/\partial n_i)_{T,P,n_j} \text{ and } (n/T'_{ck}) (\partial T'_{ck}/\partial n_i)_{T,P,n_j}$$

in Equation (22) are as follows:

$$\frac{n}{V'_{ck}} \left(\frac{\partial V'_{ck}}{\partial n_i} \right)_{T,P,n_j} = -1 + \left\{ \phi_{ik} \; V_{ci} + n \sum_{r=1}^{n} x_r \; V_{cr} \left(\frac{\partial \phi_{rk}}{\partial n_i} \right)_{T,P,n_j} \right\} \frac{1}{V'_{ck}} \quad (24)$$

$$\frac{n}{T'_{ck}} \left(\frac{\partial T'_{ck}}{\partial n_i} \right)_{T,P,n_j} = -2 + \left\{ 2 \sum_{r=1}^{n} x_r \; a_{irk} + n \sum_r \sum_s x_r \; x_s \left(\frac{\partial a_{rsk}}{\partial n_i} \right)_{T,P,n_j} \right\} \frac{1}{T'_{ck} V'_{ck}} - \frac{n}{V'_{ck}} \left(\frac{\partial V'_{ck}}{\partial n_i} \right)_{T,P,n_j} \quad (25)$$

where

$$\left(\frac{\partial a_{rsk}}{\partial n_i} \right)_{T,P,n_j} = a_{rsk} \left\{ \left[\frac{1}{\theta_{rk}} \left(\frac{\partial \theta_{rk}}{\partial n_i} \right) + \frac{1}{\theta_{sk}} \left(\frac{\partial \theta_{sk}}{\partial n_i} \right) \right] \frac{1}{2} + \frac{V_{c_r} \left(\frac{\partial \phi_{rk}}{\partial n_i} \right) + V_{c_s} \left(\frac{\partial \phi_{sk}}{\partial n_i} \right)}{\phi_{rk} V_{cr} + \phi_{sk} V_{cs}} \right\} \quad (26)$$

$$\left(\frac{\partial \phi_{sk}}{\partial n_i} \right)_{T,P,n_j} = \left(\frac{\partial \phi_{sk}}{\partial T_{R_s}} \right)_{V_{R_s}} \left(\frac{\partial T_{R_s}}{\partial n_i} \right)_{T,P,n_j} + \left(\frac{\partial \phi_{sk}}{\partial V_{R_s}} \right)_{T_{R_s}} \left(\frac{\partial V_{R_s}}{\partial n_i} \right)_{T,P,n_j} \quad (27)$$

$$\left(\frac{\partial \theta_{sk}}{\partial n_i} \right)_{T,P,n_j} = \left(\frac{\partial \theta_{sk}}{\partial T_{R_s}} \right)_{V_{R_s}} \left(\frac{\partial T_{R_s}}{\partial n_i} \right)_{T,P,n_j} + \left(\frac{\partial \theta_{sk}}{\partial V_{R_s}} \right)_{T_{R_s}} \left(\frac{\partial V_{R_s}}{\partial n_i} \right)_{T,P,n_j} \quad (28)$$

$$\left(\frac{\partial T_{R_s}}{\partial n_i} \right)_{T,P,n_j} = \theta_{sk} \frac{T_M}{T'_{ck}} \left[\frac{1}{\theta_{sk}} \left(\frac{\partial \theta_{sk}}{\partial n_i} \right)_{T,P,n_j} - \frac{1}{T'_{ck}} \left(\frac{\partial T'_{ck}}{\partial n_i} \right)_{T,P,n_j} \right] \quad (29)$$

$$\left(\frac{\partial V_{R_s}}{\partial n_i} \right)_{T,P,n_j} = \phi_{sk} \frac{V_M}{V'_{ck}} \left[\frac{1}{\phi_{sk}} \left(\frac{\partial \phi_{sk}}{\partial n_i} \right)_{T,P,n_j} + \frac{1}{n} \left(\frac{\overline{V}_i}{V_M} - 1 \right) - \frac{1}{V'_{ck}} \left(\frac{\partial V'_{ck}}{\partial n_i} \right)_{T,P,n_j} \right] \quad (30)$$

The a_{rsk} terms which appear are given in Equation (20). As in Equation (20), the index k indicates the reference fluid used for the shape factors while the indices r and s indicate interacting components in the mixture.

$\overline{V}_i$ is the partial molal volume of component i and V_M is the molal volume of the mixture. They are given by:

$$\overline{V}_i = V_M \left\{ 1 + \left[\frac{P_{Rk}}{Z_k \; V_{Rk} \left(\frac{\partial P_{Rk}}{\partial V_{Rk}} \right)_{T_{R_k}}} \right] \left[V_{Rk} \left(\frac{\partial Z_k}{\partial V_{Rk}} \right)_{T_{R_k}} \left(\frac{n}{V'_{ck}} \frac{\partial V'_{ck}}{\partial n_i} \right)_{T,P,n_j} + T_{Rk} \left(\frac{\partial Z_k}{\partial T_{Rk}} \right)_{V_{R_k}} \left(\frac{n}{T'_{ck}} \frac{\partial T'_{ck}}{\partial n_i} \right)_{T,P,n_j} \right] \right\} \quad (30a)$$

Equations (24) through (30) are a complete tabulation of the results of differentiating the pseudo-criticals V'_c and T'_c with respect to the number of moles of a given component. The complexity of these results stems from the inclusion of the shape factors which are themselves slightly dependent on composition when applied to mixtures. It is possible that numerical methods can be used to evaluate the differentials in Equations (24) and (25) more easily.

Two iteration procedures are required for the solution of these equations. One iteration determines the molal volume of the mixture from the given T, P, and assumed argument V_R in the shape factors. After convergence of this iteration a second iteration is started by changing the volume argument in the shape factors and their derivatives to agree with the calculated volume of the mixture. When this is done the original iteration is repeated and a second mixture volume is calculated. These iterations are repeated until there is no appreciable change in the calculated mixture volume. Convergence of the iterations is rapid, due to the fact that θ and ϕ are relatively weak functions of reduced volume and composition.

TRANSFORMATIONS OF THE RELATIVE SHAPE FACTORS

Relative shape factors which allow predictions of thermodynamic properties of one complex fluid from known thermodynamic data of another obey some important relations as derived below.

A complex fluid identified by the subscript i has the same reduced properties as a simple reference fluid k when:

$$\left\{ \frac{T_i}{[\theta_{ik}(T_{R_i}, V_{R_i})]T_{ci}} \right\} = T_{R_k}$$

and

$$\left\{ \frac{V_i}{[\phi_{ik}(T_{R_i}, V_{R_i})]V_{ci}} \right\} = V_{R_k} \tag{31}$$

Another complex fluid j with temperature T_j and volume V_j also has reduced properties identical to those of the reference k when:

$$\left\{ \frac{T_j}{[\theta_{jk}(T_{R_j}, V_{R_j})]T_{cj}} \right\} = T_{R_k}$$

and

$$\left\{ \frac{V_j}{[\phi_{jk}(T_{R_j}, V_{R_j})]V_{cj}} \right\} = V_{R_k} \tag{32}$$

Therefore, the two complex fluids i and j also have identical reduced properties at condition:

$$\frac{T_i}{[\theta_{ik}(T_{R_i}, V_{R_i})]T_{ci}} = \frac{T_j}{[\theta_{jk}(T_{R_j}, V_{R_j})]T_{cj}} = T_{R_k} \tag{33}$$

and

$$\frac{V_i}{[\phi_{ik}(T_{R_i}, V_{R_i})]V_{ci}} = \frac{V_j}{[\phi_{jk}(T_{R_j}, V_{R_j})]V_{cj}} = V_{R_k} \tag{34}$$

Therefore

$$T_{R_i} = \left[\frac{\theta_{ik}(T_{R_i}, V_{R_i})}{\theta_{ik}(T_{R_j}, V_{R_j})} \right] T_{R_j} \tag{35}$$

and

$$V_{R_i} = \left[\frac{\phi_{ik}(T_{R_i}, V_{R_i})}{\phi_{jk}(T_{R_j}, V_{R_j})} \right] V_{R_j} \tag{36}$$

Since T_{R_i} and V_{R_i} are related to T_{R_j} and V_{R_j}, relative shape factors θ_{ij} and ϕ_{ij} can be defined which are functions only of the reduced temperature T_{R_i} and the reduced volume V_{R_i}. These are

$$\theta_{ij}(T_{R_i}, V_{R_i}) = \left[\frac{\theta_{ik}(T_{R_i}, V_{R_i})}{\theta_{jk}(T_{R_j}, V_{R_j})} \right] = \left[\frac{\theta_{ik}(T_{R_i}, V_{R_i})}{\theta_{jk}\left(\dfrac{\theta_{jk}\,T_{R_i}}{\theta_{ik}}, \dfrac{\phi_{jk}\,V_{R_i}}{\phi_{ik}} \right)} \right] \tag{37}$$

and

$$\phi_{ij}(T_{R_i}, V_{R_i}) = \left[\frac{\phi_{ik}(T_{R_i}, V_{R_i})}{\phi_{jk}(T_{R_j}, V_{R_j})} \right] = \left[\frac{\phi_{ik}(T_{R_i}, V_{R_i})}{\phi_{jk}\left(\dfrac{\theta_{jk}T_{R_i}}{\theta_{ik}}, \dfrac{\phi_{jk}V_{R_i}}{\phi_{ik}} \right)} \right] \tag{38}$$

Equations (37) and (38) are nonlinear and must be solved by trial and error.

These equations establish a procedure for changing the reference substance for a given factor. Equations (37) and (38) were designated earlier (*14, 15*) as the ratio rules. If the reference k is chosen as fluid i, so that i and k refer to the same substance, then $\theta_{ik} = \theta_{ii} = 1$ and $\phi_{ik} = \phi_{ii} = 1$. Equations (37) and (38) then become the reciprocal rules, whereby the given component and reference may be interchanged

EQUATION OF STATE FOR REFERENCES

The properties of methane and n-pentane have been correlated to establish two reference equations of state. Methane data, including recent values obtained by Vennix (*31*), have been fitted to an equation of state which represents the data to within a few tenths of 1%. A similar equation has been prepared to correlate the available data for n-pentane. A very accurate representation of the reference fluid properties is essential when individual fugacities and K-values are to be obtained. Furthermore, in calculating mixture properties one must take care to select a reference such that the temperature and pressure of the reference substance fall in a region where accurate data exist, and that the conditions lie within the range of validity of the equation of state. The conditions of the systems studied here are such that a methane reference does not require vapor or liquid properties below the triple point or in other regions where accurate properties are not known. Consequently, methane alone was used as the reference.

In order to fit the data within experimental error, it was necessary to divide the phase diagram into regions and represent each region with a different equation. The phase diagram for the pure reference was divided into four regions, a dilute gas region, two dense fluid regions, and a liquid region.

The dilute gas region was described for methane by the virial equation of state by using the compressibility data of Douslin (*4*) and Hoover (*8*). The dense fluid regions described by the data of Vennix (*31*), and Douslin (*4*) were fitted to a new equation of state. The liquid region was fitted to the Tait (*7*) equation using data of Vennix (*31*), and Van Itterbeek (*30*). The vapor pressure of

Keyes (*11*) and enthalpy data of Jones (*10*) were also used in the equations.

For systems at lower temperatures a reference with a lower reduced triple point temperature is needed. Normal pentane is a possible choice since extensive vapor and liquid properties are available from the work of Brydon, Walen, and Canjar (*2*), Li and Canjar (*18*), Sage and Lacey (*26*), and Sage, Schaafsma, and Lacey (*25*).

For the methane reference used here enthalpy and fugacity data were determined by differentiation and numerical integration of the equation of state. A discussion and presentation of the equation of state functions used and tabulated compressibility factors, fugacity pressure ratios, and enthalpy deviations are presented elsewhere (*12, 13*).

It should be pointed out that it is not absolutely necessary to have an analytical equation of state function for the reference. The reference properties could be furnished equally well by a table of compressibility factors, fugacity pressure ratios, and enthalpy deviations for the reference substance stored in a computer with a program for precise interpolations. An analytical equation of state has the advantage of greater economy in computer storage requirements. However, if a large computer is available, a tabulation of the reference substance properties has the advantage that it can be easily altered or extended as new or better data are obtained without having to refit an analytical equation.

COMPOSITION DEPENDENCE FOR SHAPE FACTORS

The effect on pair interactions, produced by changing their environment from like molecule neighbors in the pure state to the unlike neighbors of a pair in a mixture, produces a composition effect on the shape factors. It is possible to obtain an analytical relationship between shape factors and composition, which is consistent with the requirement that the calculated properties of a solution be independent of the reference substance chosen for the shape factors. This relationship gives good agreement with experimental *K*-values and experimental properties of the solution in vapor and liquid mixtures.

To account for composition effects, it is assumed that for a component i in a mixture, the T_{R_i} and V_{R_i} terms in the shape factor equations are replaced by

$$T_{R_i} = \theta_{ik}\, T_{R_k} = \theta_{ik} \frac{T_M}{T'_{ck}} \tag{39}$$

$$V_{R_i} = \phi_{ik}\, V_{R_k} = \phi_{ik} \frac{V_M}{V'_{ck}} \tag{40}$$

This substitution produces invariance in the calculated mixture properties and *K*-values when the reference fluid is changed. This may be shown as follows.

Let k and p be two pure component references for the same mixture, M. If this is the case, then:

$$\frac{T_M}{T'_{cp}} = \frac{T_p}{T_{cp}} = \frac{T_k}{\theta_{kp}\, T_{ck}} = \frac{T_M}{\theta_{kp}\, T'_{ck}} \tag{41}$$

In Equation (41), θ_{kp} is the shape factor which gives properties of k from the reference p. It is evaluated at the conditions:

$$T_{R_k} = \frac{T_k}{T_{ck}} = \frac{T_M}{T'_{ck}}$$

$$\tag{42}$$

$$V_{R_k} = \frac{V_k}{V_{ck}} = \frac{V_M}{V'_{ck}}$$

The T'_{cp} and T'_{ck} terms are pseudo-criticals relative to the references p and k, respectively. Equation (41) indicates the relation between T'_{cp} and T'_{ck} which is

$$T'_{cp} = \theta_{kp}\, T'_{ck} \tag{43}$$

In a similar manner:

$$V'_{cp} = \phi_{kp}\, V'_{ck} \tag{44}$$

Equations (43) and (44) may be regarded as conditions which must be fulfilled in order that properties of the mixtures be invariant to changes of the reference substance from k to p.

Let us now consider equations for T'_c which are homogeneous in the first degree in the θ factors for each component, and V'_c equations which are also first degree homogeneous in the ϕ factors for each component. Equations (17) and (18) are pseudo-critical equations of this type. When pseudo-criticals with this type of dependence on the individual component shape factors are transformed from reference k to p by Equations (43) and (44) then the assumption in Equations (39) and (40) means that each individual shape factor in the pseudo-critical is transformed also, in accordance with the ratio rules in Equations (37) and (38). For example, consider the shifting of reference for the V'_c pseudo-critical as defined by Equation (44). The pseudo-critical volume with reference p is

$$V'_{cp} = x_1\, \phi_{1p}\, V_{c1} + x_2\, \phi_{2p}\, V_{c2} + \ldots$$

Transformation to a k reference by Equation (44) gives:

$$V'_{ck} = \frac{V'_{cp}}{\phi_{kp}} = x_1 \left(\frac{\phi_{1p}}{\phi_{kp}} \right) V_{c1} + x_2 \left(\frac{\phi_{2p}}{\phi_{kp}} \right) V_{c2} + \ldots \tag{45}$$

and Equation (45) must be equal to

$$V'_{ck} = x_1\, \phi_{1k}\, V_{c1} + x_2\, \phi_{2k}\, V_{c2} + \ldots \tag{46}$$

Now Equations (39) and (40) are the relationships which must exist between the arguments of shape factors of each component in a mixture when the ratio rules apply. Consequently, the equality between Equations (45) and (46) is obtained by having for each component present in the pseudo-critical equation:

$$\phi_{ik} = \frac{\phi_{ip}}{\phi_{kp}} \tag{47}$$

In Equation (47) the arguments T_{R_i}, V_{R_i} of ϕ_{ip} and ϕ_{ik} are related to the arguments of T_{R_k}, V_{R_k} of ϕ_{kp} in accordance with Equations (39) and (40). Equation (47) is therefore identical with the ratio rule for pure components. In the mixture, however, the arguments T_{R_k} and V_{R_k} have an additional meaning in that they are related to the pseudo-reduced properties, as shown in Equation (42). Since T'_c, as given by Equations (18) and (20), is also homogeneous in the first degree in the θ_i terms, exactly the same procedure may be followed; the equality indicated in Equation (43) is obtained by having each component in the pseudo-critical expression obey the ratio rule:

$$\theta_{ik} = \frac{\theta_{ip}}{\theta_{kp}} \tag{48}$$

In Equation (48) the arguments T_{R_i}, V_{R_i} of θ_{ip} and θ_{ik} are related to the arguments T_{R_k}, V_{R_k} of θ_{kp} in accordance with Equations (39) and (40). Again the T_{R_k} and V_{R_k} values relate to pseudo-reduced values as shown in Equation (42).

In this manner Equations (39) and (40) are the necessary relationships between the arguments of the shape factors that must exist in order for the ratio rules to apply to each component in a mixture as well as to pure components. When the ratio rules thus apply to each component in the mixture, the equalities in Equations (43) and (44) are established and the necessary invariance, with respect to a change of reference substance is obtained. It is assumed that the complete composition dependence of the shape factors may be specified by these changes in T_{R_i} and V_{R_i} alone. This has the proper limiting behavior as the composition approaches the pure state and also has considerable empirical success. It makes the equations describing the shape factors nonlinear in the shape factors and requires an iterative process for their evaluation.

The iteration procedure can be eliminated if the arguments of the shape factors are approximated by

$$V_{R_i} \simeq \frac{V_M}{\sum_i \sum_j x_i x_j V_{c_{ij}}} \tag{49}$$

$$T_{R_i} \simeq T_M \left[\frac{\sum_i \sum_j x_i x_j V_{c_{ij}}}{\sum_i \sum_j x_i x_j T_{c_{ij}} V_{c_{ij}}}\right] \tag{50}$$

where

$$T_{c_{ij}} = \sqrt{T_{ci} T_{cj}} \tag{51}$$

$$V_{c_{ij}} = \left[\frac{V_{ci}^{1/3} + V_{cj}^{1/3}}{2}\right]^3 \tag{52}$$

This approximation gives good results since the shape factors are weak functions of the compositions.

CALCULATED RESULTS

Calculations of K values in hydrocarbon systems were carried out using an IBM 7040 computer. The computation is designed to start with a set of initial trial K-values and a designated temperature, pressure, and overall composition. Initial phase compositions for vapor and liquid are found from a flash calculation using the trial K-values. These compositions are then used to calculate the next set of trial K-values from Equation (22) by using the shape factors given by Equations (11) and (12). Results are shown in Tables 1 and 2 and in Figure 1. In these calculations the experimental values were used as the first trial.

It is significant that these calculations, which utilize only pure component properties and the shape factors, give results which follow the isotherms closely into the retrograde region. This region commonly gives considerable difficulty when using mixture equations of state for K-value calculations. Furthermore, these results are achieved by using only the simplest spherical molecule combining rules for unlike pair interactions. The use of the shape factors considerably extends the range of applicability of these simple rules and the pseudo-critical equations which depend on them. The role of the shape factors is clearly shown by Table 3 in which the same calculations as in Table 1 have been made, except that all shape factors were set at unity.

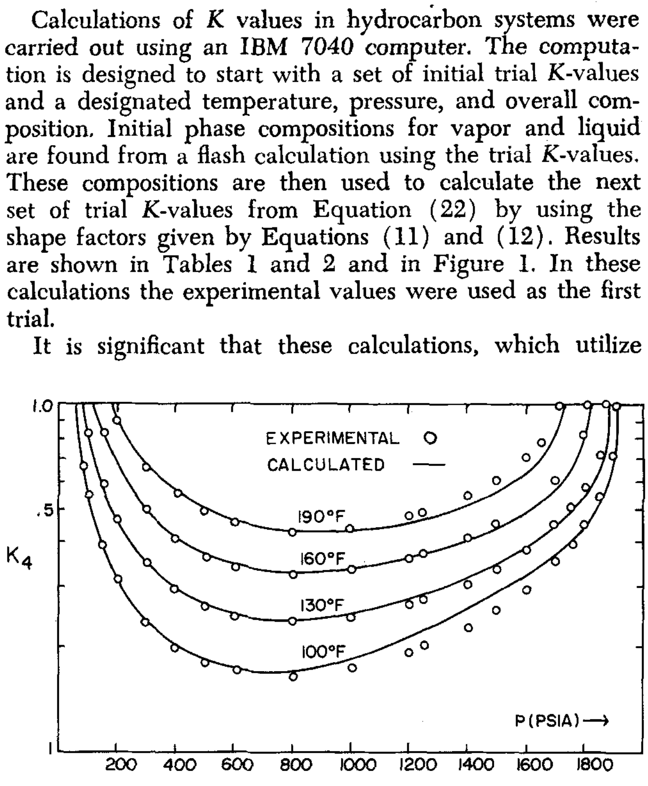

Fig. 1. K_4 vs. Pressure, Methane-n-Butane System.

TABLE 1. METHANE-n-PENTANE SYSTEM K-VALUE CALCULATIONS
(pure methane reference)
at 100°F.

P lb./sq.in.abs.	K_1 exp. (27)	K_1 calc.	K_5 exp. (27)	K_5 calc.
20	139.33	140.12	0.7922	0.8003
60	46.49	47.26	0.2884	0.2847
100	28.40	28.36	0.1876	0.1806
200	14.30	14.12	0.1131	0.1036
300	9.61	9.36	0.0892	0.0795
400	7.27	6.99	0.0776	0.0685
600	4.93	4.62	0.0705	0.0610
1000	3.07	2.75	0.0766	0.0688
1500	2.14	1.84	0.1052	0.1134
2000	1.59	1.37	0.1890	0.2468
		at 220°F.		
100	30.53	30.01	0.9556	0.9525
200	15.68	15.80	0.5442	0.5461
400	7.87	8.04	0.3454	0.3376
600	5.27	5.36	0.2842	0.2762
800	3.97	3.99	0.2645	0.2560
1000	3.18	3.17	0.2695	0.2558
1250	2.53	2.53	0.2909	0.2740
1500	2.08	2.08	0.3331	0.3076
1750	1.66	1.71	0.4444	0.3846
2000	1.31	1.30	0.5941	0.6096

TABLE 2. METHANE-n-BUTANE SYSTEM K-VALUES CALCULATIONS
(pure methane reference)
at 100°F.

P lb./in.sq.abs.	K_1 exp. (27)	K_1 calc.	K_4 exp. (27)	K_4 calc.
80	32.39	31.23	0.6701	0.6741
100	26.26	25.15	0.5500	0.5550
200	13.25	12.71	0.3139	0.3155
400	6.78	6.38	0.2005	0.2013
600	4.56	4.24	0.1698	0.1728
1000	2.78	2.54	0.1744	0.1813
1400	1.96	1.78	0.2293	0.2477
1600	1.66	1.59	0.2959	0.2970
1800	1.35	1.33	0.4558	0.4427
1900	1.10	1.18	0.7719	0.6112
		at 220°F.		
300	9.14	8.16	0.8550	0.8677
400	6.81	6.28	0.7079	0.7292
500	5.36	5.07	0.6293	0.6484
600	4.39	4.22	0.5840	0.5988
800	3.15	3.10	0.5523	0.5532
1000	2.39	2.50	0.5717	0.5397
1200	1.86	1.96	0.6277	0.5764
1250	1.75	1.86	0.6488	0.5912
1300	1.64	1.75	0.6737	0.6104
1450	1.29	1.26	0.8004	0.8222

Studies of systems at lower temperatures and with greater molecular dissimilarity than those in Tables 1 and 2 indicate that there are probably significant errors due to the first source discussed in the introduction which are still to be considered. This will probably require an alteration in the pseudo-critical equations themselves. K-value calculations with the pseudo-criticals [defined in Equations (17) through (20) by using the shape factors] are valid down to reduced temperatures of about 0.6 for each component of the mixture. Work is continuing to extend the shape factor correlation to temperature regions below this value. An IBM Fortran IV card deck[†] has been prepared for distribution which contains the K-value and mixture property calculations using this procedure.

TABLE 3. METHANE-n-PENTANE SYSTEM K-value CALCULATIONS WITH ALL SHAPE FACTORS SET AT UNITY
(Pure Methane Reference)
100°F.

P lb./sq.in.abs.	K_1 calc.	K_5 calc.
60	22.41	0.5830
100	13.75	0.3726
200	7.16	0.2164
400	3.85	0.1455
600	2.747	0.1306
1000	1.866	0.1453
1500	1.407	0.2262
2000	1.025	0.8882

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NOTATION

f = fugacity
F = function
$\frac{H^* - H}{RT}$ = reduced excess enthalpy function, H^* = molal enthalpy of the ideal gas
K = equilibrium vapor-liquid ratio
P = absolute pressure
T = absolute temperature
$\frac{U^* - U}{RT}$ = reduced excess internal energy, U^* = molal internal energy of the ideal gas
V = volume
x,y = mole fraction in liquid and gaseous phases
Z = compressibility factor

Greek Letters

ϵ = maximum attractive intermolecular potential energy
θ = first-order shape factor for critical temperature
σ = effective molecular diameter or closest approach distance without repulsion between centers of molecules
ϕ = first-order volume shape factor for critical volume
ψ = first-order critical pressure shape factor
ω = acentric factor

Superscripts

$'$ = pseudo-condition
* = ideal gas state

Subscripts

L = liquid phase
M = mixture
R = reduced by critical property
V = vapor phase
c = critical
i, j, k, p = pure reference component indices
T = temperature
1 = methane
4 = n-pentane
5 = n-butane

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[†] Directions for obtaining a copy of this deck with its operating instructions can be obtained by correspondence with T. W. Leland at Rice University.