Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

The Principle of Corresponding States and Prediction of Gas-Liquid Separation Factors and Thermodynamic Properties: A Review

R. A. Mentzer[a]; R. A. Greenkorn[a]; K. C. Chao[a]
[a] SCHOOL OF CHEMICAL ENGINEERING, PURDUE UNIVERSITY, WEST LAFAYETTE, INDIANA

To cite this Article Mentzer, R. A. , Greenkorn, R. A. and Chao, K. C.(1980) 'The Principle of Corresponding States and Prediction of Gas-Liquid Separation Factors and Thermodynamic Properties: A Review', Separation Science and Technology, 15: 9, 1613 — 1678
To link to this Article: DOI: 10.1080/01496398008055612
URL: http://dx.doi.org/10.1080/01496398008055612

SEPARATION SCIENCE AND TECHNOLOGY, 15(9), pp. 1613–1678, 1980

REVIEW

The Principle of Corresponding States and Prediction of Gas–Liquid Separation Factors and Thermodynamic Properties: A Review

R. A. MENTZER, R. A. GREENKORN, and K. C. CHAO*

SCHOOL OF CHEMICAL ENGINEERING
PURDUE UNIVERSITY
WEST LAFAYETTE, INDIANA 47907

Abstract

A review is made of the development of the principle of corresponding states and the utility of the molecular shape factor method for the description of properties of pure fluids and fluid mixtures. From consideration of angle averaging of the potential energy of nonspherical molecules, shape factors were devised to relate the state of an acentric fluid with that of a reference fluid. With the development of correlations for the correspondence of states, an accurate equation of state of the reference fluid is made to apply to many fluids. The method is extended to mixtures with the introduction of van der Waals' combining rules. Extensive calculations show that the use of methane as the reference fluid yields useful results for paraffin hydrocarbons up to about C_7, cyclic hydrocarbons of even higher molecular weight, and nonassociating polar substances. Diverse properties are examined including volumetric properties, vapor pressures, K-values, enthalpies, excess properties of mixing, and transport properties.

INTRODUCTION

A quantitative description of fluid properties is essential to the design of separation equipment for distillation, extraction, and absorption. Methods for estimating thermodynamic properties are necessary, since experimental data are rarely available for a system at the conditions of interest. The principle of corresponding states (PCS) has been found to be a useful

*To whom correspondence should be sent.

method for the prediction of pure fluid and mixture properties from a minimum amount of information.

Van der Waals originated the PCS method in the late 1880s when he wrote his equation of state in reduced form suggesting that all substances obey the same equation of state in terms of reduced variables. Accordingly, the compressibility factor, $z \equiv pV/(nRT)$, can be written as a universal function of the reduced temperature and volume,

$$z = z\left(\frac{T}{T^c}, \frac{V}{V^c}\right) \tag{1}$$

Generalized correlations have been prepared based on the two-parameter form of the PCS, but for practical convenience the reduced pressure, p/p^c, was used in place of the reduced volume, V/V^c, as an independent variable. The two-parameter PCS was found to give accurate results only for simple spherically symmetric molecules, such as the noble gases Ar, Kr, and Xe.

To extend the PCS to a wider range of fluids, two different approaches have been taken, and these may be summarized with the following two equations:

$$z = z\left(\frac{T}{T^c}, \frac{V}{V^c}, a, b, \ldots\right) \tag{2}$$

and

$$z = z\left(\frac{T}{T^c\theta}, \frac{V}{V^c\phi}\right) \tag{3}$$

In the first approach, shown by Eq. (2), various third parameters a have been developed: (a) the Riedel factor, α^c, by Riedel (*1*), (b) the critical compressibility, z^c, by Lydersen et al. (*2*), (c) the molecular length–width ratio by Leland et al. (*3*), (d) the acentric factor, ω, by Pitzer et al. (*4*), and (e) the orientation factor, γ, by Lee and Starling (*5*). Leland et al. (*6*), and Gunn et al. (*7*) have also developed three-parameter approaches to account for quantum effects. Thus a group of molecules (i.e., simple almost spherical nonpolar molecules, light hydrocarbons, etc.) having the same value of a will conform within the group to the PCS. Various fourth parameters, b, have been used so that polar molecules can be included in a corresponding states development. Most notable are developments by Eubank and Smith (*8*), Halm and Stiel (*9*), O'Connell and Prausnitz (*10*), and Harlacher and Braun (*11*).

In the other approach to extend the PCS, indicated by Eq. (3), the reducing temperature and reducing volume do not assume fixed values equal to the critical properties, but are considered scaling factors that vary with

the temperature and volume. Their function is to define the state of the reference fluid that corresponds to the state of the fluid of interest. An accurate equation of state of the reference fluid thus serves to accurately describe many fluids. The scaling factors for mixtures are obtained as combinations of those of the components through the use of combining rules for the scaling temperature and volume. In contrast, combination of the third parameters of Eq. (2) has remained elusive. As a result, the scaling factor method is far more advanced for the description of fluid mixtures. We will deal with the scaling factor approach exclusively in this review.

Leland and Chappelear (*12*) presented an extensive review of the PCS. Gubbins (*13*), in his review of perturbation methods, discussed several corresponding states developments for predicting the properties of liquids. More recently, Rowlinson (*14*, *15*) described the thermodynamics of fluids based on Eq. (3). It is the purpose of this article to present a comprehensive account of the PCS with scaling factors encompassing the theoretical background, working equations, previous calculations, and new results on excess properties of liquid solutions.

THEORETICAL BASIS

Thermodynamic properties of a system can be calculated from the canonical partition function, which completely describes a system with fixed temperature, volume, and number of molecules. Assuming that the translational and intramolecular (vibration, rotation, ...) degrees of freedom are independent, the partition function can be expressed as the product of two terms (Chao and Greenkorn, *16*):

$$Q(N, V, T) = Q^{\text{ext}}(N, V, T)Q^{\text{int}}(N, T) \tag{4}$$

Only the translational contribution, Q^{ext}, depends on the density. Assuming that the translational states can be treated classically, the partition function becomes

$$Q = \frac{1}{N!} Q^{\text{int}} \left(\frac{2\pi mkT}{h^2}\right)^{\frac{3N}{2}} \int \cdots \int \exp\left(-\frac{U}{kT}\right) dr_1 \ldots dr_N \tag{5}$$

where U is the total potential energy. The potential energy is due to the intermolecular forces of all of the molecules in the fluid, and in general depends on the sum of two-body interactions, three-body interactions, etc. The contribution due to intramolecular degrees of freedom, Q^{int}, can be evaluated from ideal gas properties. The description of a real system thus focuses attention on the contribution of the intermolecular potential energy, the only unknown. Eq. (5) is conventionally expressed as

$$Q = \frac{1}{N!} Q^{\text{int}} \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3N}{2}} Q^{\text{conf}} \tag{6}$$

$$Q^{\text{conf}} = \int \cdots \int \exp\left(-\frac{U}{kT} \right) dr_1 \ldots dr_N \tag{7}$$

The quantity Q^{conf} is called the configuration integral. Once this term has been evaluated, the description of a real system is complete.

Direct evaluation of the configuration integral for real fluids is difficult. The physical properties of a real system are therefore rarely calculated this way. The PCS provides an alternate approach. The basic idea behind the PCS is the application of a dimensional analysis technique to the configuration integral. Dimensionless configurational properties, such as the compressibility, fugacity coefficient, or enthalpy departure, are then expressed as universal functions of dimensionless temperature, volume, etc. The known configurational properties for one substance are then used to calculate the same properties for other substances.

The molecular theory of the PCS is based on the consideration of conformal fluids. Two pure fluids are said to be conformal if their intermolecular potentials are of the same functional form. Thus the pairwise interaction potential of fluid α can be expressed in terms of a conformal reference fluid 0 as follows:

$$\varepsilon_{\alpha\alpha}(r) = f_{\alpha\alpha,0} \varepsilon_{00}(r/g_{\alpha\alpha,0}) \tag{8}$$

where

$$f_{\alpha\alpha,0} = \varepsilon_{\alpha\alpha}/\varepsilon_{00}$$

$$g_{\alpha\alpha,0} = \sigma_{\alpha\alpha}/\sigma_{00}$$

The subscript 0 denotes a reference substance whose intermolecular potential, ε_{00}, is known. The intermolecular potential energy for another conformal fluid, $\varepsilon_{\alpha\alpha}$, can be determined once the scaling factors $f_{\alpha\alpha,0}$ and $g_{\alpha\alpha,0}$, called conformal parameters, are known. Rowlinson (*17*) considered N molecules of substance 0 confined to a volume V at a temperature T, and an equal number of molecules of substance α confined to a volume $V(\sigma_{\alpha\alpha}/\sigma_{\alpha\alpha})^3$ at a temperature $T(\varepsilon_{\alpha\alpha}/\varepsilon_{00})$. If the two containers have the same shape, then their linear dimensions are in the ratio $(\sigma_{00}/\sigma_{\alpha\alpha})$. Therefore, for each particular configuration of the first assembly, there is a corresponding configuration for the second such that the potential energy may be written as

$$\frac{U_{\alpha\alpha}[\cdots r_i \cdots]}{kT} = \frac{U_{00}\left[\cdots r_i \frac{\sigma_{\alpha\alpha}}{\sigma_{00}} \cdots \right]}{kT\left(\frac{\varepsilon_{\alpha\alpha}}{\varepsilon_{00}} \right)} \tag{9}$$

In Eq. (9), pairwise additivity is not assumed. Combining Eqs. (7) and (9), the following relation between the configuration integrals is obtained:

$$Q_\alpha^{\text{conf}}[T, V] = g_{\alpha\alpha,0}^{3N} Q_0^{\text{conf}}[T/f_{\alpha\alpha,0}, V/g_{\alpha\alpha,0}^3] \tag{10}$$

The configuration integral of fluid α can therefore be calculated from that of fluid 0. The configurational Helmholtz energy and pressure are found to be

$$A_\alpha[T, V] = f_{\alpha\alpha,0} A_0[T/f_{\alpha\alpha,0}, V/g_{\alpha\alpha,0}^3] - 3NkT \ln (g_{\alpha\alpha,0}) \tag{11}$$

$$p_\alpha[T, V] = (f_{\alpha\alpha,0}/g_{\alpha\alpha,0}^3) p_0[T/f_{\alpha\alpha,0}, V/g_{\alpha\alpha,0}^3] \tag{12}$$

The latter relation expresses the equation of state for fluid α in terms of the equation of state for fluid 0, which is the basis for the PCS. The phase diagram in reduced form is thus identical for all fluids which obey conformal intermolecular potentials.

The molecular requirements for a substance to obey the simple two-parameter PCS were first presented by Pitzer (*18*). They can be summarized as follows (Reed and Gubbins, *19*):

(a) The translational and internal contributions in the canonical partition function are separable, as in Eq. (4).
(b) Only the configurational partition function is dependent on density. The internal energy states therefore assume their ideal gas values.
(c) The translational and configurational portions of the partition function can be treated classically, and Maxwell-Boltzmann statistics applies. This assumption was used to obtain Eq. (5).
(d) The total potential energy of the system can be expressed as the product of a characteristic energy parameter and a common function of dimensionless separation distance.

The first two assumptions are valid at low densities and for simple fluids even at high densities, but may be in error for polyatomic fluids or for associating molecules. The third assumption is satisfactory except for light molecules at low temperatures. The fourth assumption is the most restrictive. The stipulation of separation distance as the only geometric variable rules out any possible angle dependence.

Simple fluids of monatomic molecules such as Ar, Kr, and Xe satisfy all these requirements and follow the PCS to a high degree. Pitzer and co-workers (*4*) and others developed excellent PCS correlations of their properties. But just about all other substances fail to satisfy some of the requirements, and the most common failure is the last assumption due to the nonspherical shape of the molecules.

The intermolecular potential between a pair of nonspherical molecules

is dependent on orientation. The potential is more complex than Eq. (8), and thus does not conform in a simple way to the two-parameter PCS. Pople (*20*) expanded an orientation-dependent potential about a symmetrical contribution in a series of spherical harmonics. The intermolecular potential was separated into a central force term and terms depending on orientation. The angle-dependent contributions were treated as perturbations on the central-force term. Cook and Rowlinson (*21*) showed that for elliptical molecules or slightly polar molecules the orientation-dependent potential reduces to a simple form upon averaging over all orientations. The correct angle-averaged intermolecular potential is a free-energy average (Rushbrooke, *22*). The orientation-dependent potential is thus replaced by a temperature-dependent pair potential, and effective intermolecular parameters $\varepsilon(T)$ and $\sigma(T)$ appear. In certain cases the free-energy averaged potential is of the same functional form as the potential for simple fluids, and therefore will obey the same two-parameter PCS:

$$\varepsilon(r, \theta_1, \theta_2, \phi) \approx \varepsilon(r, T) = \varepsilon_0(T) f\left(\frac{r}{\sigma(T)}\right) \tag{13}$$

Average pair potentials of this form have been determined for various molecular interactions by Cook and Rowlinson (*21*) and Leach (*23*).

Complex fluids whose intermolecular potential can be expressed by Eq. (13) when orientation averaged obey the same two-parameter PCS of simple fluids with effective intermolecular parameters related to critical properties as follows:

$$\begin{aligned} \varepsilon(T) &= akT^c\theta(T) \\ \sigma^3(T) &= bV^c\phi(T) \end{aligned} \tag{14}$$

where a and b are universal constants for all conformal fluids obeying a two-parameter PCS. Molecular shape factors, θ and ϕ, modify the critical constants to give effective reducing parameters θT^c and ϕV^c that are temperature dependent. Since the intermolecular potential function of real molecules is not precisely known, it is most useful to define the shape factors θ and ϕ directly from configurational properties without referring to any specific average pair potential. The shape factors would be on a sound theoretical basis when determined by setting the configurational properties of the nonspherical molecule of interest equal to those of a simple spherical molecule.

To evaluate the molecular shape factors of real substances, Gilbert (*24*) considered the reduced second virial coefficient as a function of reduced temperature:

$$\frac{B}{V^c\phi(T)} = f\left(\frac{T^c\theta(T)}{T}\right) \tag{15}$$

The function f was the reduced second virial coefficient of methane which was selected as the reference fluid. Values of ϕ and θ were determined for the normal paraffins, ethane through n-octane, by forcing their second virial coefficients as correlated by McGlashan and Potter (*25*) to conform to Eq. (15). Gilbert applied the shape factors thus obtained for the calculation of compressibilities and fugacity coefficients. The calculations are in good agreement with experimental data at low pressures, but become poor at higher pressures. At these larger pressures (or densities) the higher order virial coefficients can no longer be made up of the sum of pair interactions. The usefulness of Gilbert's results is thus limited because of the exclusive consideration of the second virial coefficient and the consequent lack of representation of other modes of interaction. Leach (*23*) found that for gases at low densities the shape factors can be determined from second and third virial coefficients. In this region the shape factors depend only on temperature, and the configuration integrals of the two fluids are equal. In general, however, density-independent shape factors cannot be found which would equate the configuration integrals of two fluids with orientation-dependent potentials. If density-dependent shape factors are defined by equating configuration integrals, dimensionless properties derived by differentiation of the integrals with respect to density, such as compressibilities or fugacity coefficients, will not be equal at corresponding reduced conditions. Terms involving $(\partial\theta/\partial V)$ and $(\partial\phi/\partial V)$ must be included in the expressions. On the other hand, the enthalpies and internal energies for two nonsimilar fluids will not be equal at the same reduced conditions, since the shape factor expressions are temperature dependent and these thermodynamic properties involve temperature derivatives of the configuration integral. Only the Helmholtz free energies of the two fluids will be equal. Shape factors determined by equating fugacities and compressibilities are more convenient to use, especially for vapor–liquid equilibrium calculations, than those determined by equating configuration integrals or other configurational thermodynamic properties. Enthalpies and internal energies can then be calculated in either of two ways:

(a) By including the temperature derivatives of the shape factors in the working equations.
(b) Through the use of "second-order" shape factors which are determined by equating the enthalpies or internal energies of two fluids. The second-order shape factors correct the reduced temperature and reduced volume in the same manner as the first-order shape factors.

CORRELATION OF THE CONFORMAL PARAMETERS

Two pure fluids, α and 0, are defined as being in corresponding states when their compressibilities and fugacity coefficients are equal (Leach et al., *26*):

$$z_\alpha[T_\alpha, V_\alpha] = z_0[T_0, V_0] \tag{16}$$

$$\left(\frac{f}{p}\right)_\alpha [T_\alpha, V_\alpha] = \left(\frac{f}{p}\right)_0 [T_0, V_0] \tag{17}$$

These equations map from the T–V space of fluid 0 to the T–V space of fluid α. Some authors write Eq. (17) in terms of either the configurational Helmholtz energy or configurational Gibbs energy (Rowlinson and Watson, *27*; Yuan et al., *28*; and Mollerup, *29*). The logarithm of the fugacity coefficient may be expressed as

$$\ln\left(\frac{f}{p}\right)_\alpha = \frac{G_\alpha}{RT_\alpha} - \ln\left(\frac{p}{kT}\right)_\alpha \tag{18}$$

where G_α is the configurational Gibbs free energy of fluid α. Combining Eqs. (17), (18), and the relation $G = A + pV$, one finds that

$$A_\alpha[T_\alpha, V_\alpha] = f_{\alpha\alpha,0} A_0[T_0, V_0] - RT_\alpha \ln (h_{\alpha\alpha,0}) \tag{19}$$

where

$$f_{\alpha\alpha,0} \equiv T_\alpha/T_0 \tag{20}$$

$$h_{\alpha\alpha,0} \equiv V_\alpha/V_0 \tag{21}$$

Equation (17) is often written in this form. The conformal parameter $h_{\alpha\alpha,0}$ is analogous to $g^3_{\alpha\alpha,0}$. The first subscript refers to the fluid of interest and is doubled for later generalization to mixtures, and the second subscript, 0, refers to the reference substance. Yuan et al. (*28*) used Eq. (21) instead of Eq. (16) when defining two substances as being in corresponding states. These two equations are equivalent.

Substituting Eqs. (20) and (21) into Eqs. (16) and (19), one obtains

$$z_\alpha[T_\alpha, V_\alpha] = z_0\left[\frac{T_\alpha}{f_{\alpha\alpha,0}}, \frac{V_\alpha}{h_{\alpha\alpha,0}}\right] \tag{22}$$

$$A_\alpha[T_\alpha, V_\alpha] = f_{\alpha\alpha,0} A_0\left[\frac{T_\alpha}{f_{\alpha\alpha,0}}, \frac{V_\alpha}{h_{\alpha\alpha,0}}\right] - RT_\alpha \ln (h_{\alpha\alpha,0}) \tag{23}$$

Other thermodynamic properties follow from Eqs. (22) and (23). To perform calculations using these equations, one must know $f_{\alpha\alpha,0}$, $h_{\alpha\alpha,0}$, and the thermodynamic properties of the reference substance. The utility of this approach lies in the ability to generalize the two conformal param-

eters. Noting that the numerical values of $f_{\alpha\alpha,0}$ and $h_{\alpha\alpha,0}$ are close to the ratio of critical temperatures and volumes, one may write

$$f_{\alpha\alpha,0} = \frac{T_\alpha}{T_0} = \frac{T_\alpha^c}{T_0^c}\theta_{\alpha\alpha,0} \tag{24}$$

$$h_{\alpha\alpha,0} = \frac{V_\alpha}{V_0} = \frac{V_\alpha^c}{V_0^c}\phi_{\alpha\alpha,0} \tag{25}$$

In these expressions the ratio of critical temperatures or critical volumes is chosen as a basis for expressing the ratio of temperatures or volumes. The shape factors $\theta_{\alpha\alpha,0}$ and $\phi_{\alpha\alpha,0}$ correct for the departure from the ratio of the critical values. Equations (24) and (25) can be rearranged to illustrate the relationship between the reduced properties of fluids α and 0.

$$T_0^R = \frac{T_0}{T_0^c} = \frac{T_\alpha}{T_\alpha^c\theta_{\alpha\alpha,0}} = \frac{T_\alpha^R}{\theta_{\alpha\alpha,0}} \tag{26}$$

$$V_0^R = \frac{V_0}{V_0^c} = \frac{V_\alpha}{V_\alpha^c\phi_{\alpha\alpha,0}} = \frac{V_\alpha^R}{\phi_{\alpha\alpha,0}} \tag{27}$$

The shape factors are seen to multiply the critical constants of the fluid of interest to form the reduced properties $T_\alpha/(T_\alpha^c\theta_{\alpha\alpha,0})$ and $V_\alpha/(V_\alpha^c\phi_{\alpha\alpha,0})$ which will predict the thermodynamic properties of substance α when substituted into an equation of state for fluid 0.

Generalized expressions for the first-order shape factors were developed from data on the normal hydrocarbons ethane through pentadecane and isooctane in terms of Eqs. (16) and (17) by Leach et al. (*30*). Methane was chosen as the reference substance, since its volumetric behavior is known very accurately. The following empirical relations were found to represent the shape factors:

$$\theta_{\alpha\alpha,0} = 1 + (\omega_\alpha - \omega_0)[0.0892 - 0.8493 \ln (T_\alpha^R)] + [(0.3063 - 0.4506/T_\alpha^R)(V_\alpha^R - 0.5)] \tag{28}$$

$$\phi_{\alpha\alpha,0} = \{1 + (\omega_\alpha - \omega_0)[0.3903(V_\alpha^R - 1.0177) - 0.9462(V_\alpha^R - 0.7663) \ln (T_\alpha^R)]\}\frac{Z_\alpha^c}{Z_0^c} \tag{29}$$

where for pure fluids $T_\alpha^R = T_\alpha/T_\alpha^c$ and $V_\alpha^R = V_\alpha/V_\alpha^c$. These relations are subject to the following constraints:

when		
	$T_\alpha^R \geq 2.0$	set $T_\alpha^R = 2.0$
	$V_\alpha^R \geq 2.0$	$V_\alpha^R = 2.0$
	$V_\alpha^R \leq 0.5$	$V_\alpha^R = 0.5$

The shape factors are seen to depend on temperature, density (to a limited extent), and the difference between acentric factors and critical compressibilities of the fluid of interest and the reference fluid. It is interesting to note how the commonly employed third parameters ω and z^c are introduced into this methodology. Although Eqs. (28) and (29) were developed from data of the range $0.6 \leq T^R \leq 1.5$, they have been successfully applied to reduced temperatures of 0.3 (Leach, *23*; and Mollerup and Rowlinson, *31*). Generalized correlations for the second-order shape factors of hydrocarbons were also determined by Leach et al. (*30*). These shape factors, which are independent of density, were determined by the simultaneous solution of two reduced internal energy deviation equations on a single isotherm.

Leach et al. (*30*) also developed expressions for the shape factors of quantum fluids. The first-order shape factors were determined by equating the reduced second virial coefficients and compressibilities of a quantum fluid with those of methane, the reference. These shape factors show the same qualitative behavior as those for the hydrocarbons, except at low temperatures where the former exhibit an extremum. Individual density-dependent shape factor correlations were developed for hydrogen, deuterium, and helium. An approximate generalized correlation was also developed, which is independent of density. Second-order shape factors were determined only for hydrogen.

The thermodynamic consistency of the shape factor expressions, Eqs. (28) and (29), has been examined by Canfield and Gunning (*32*) and Gunning (*33*). From classical thermodynamics one knows that the Helmholtz energy and pressure are related as

$$\left(\frac{\partial A}{\partial V}\right)_T = -p \tag{30}$$

Substituting Eq. (23) into Eq. (30), one finds that Eq. (16) will only be obeyed if

$$\{z_0[T_0^R, V_0^R] - 1\} \frac{1}{\phi_{\alpha\alpha,0}} \left(\frac{\partial \phi_{\alpha\alpha,0}}{\partial V_\alpha^R}\right)_{T_\alpha R} = -\frac{U_0[T_0^R, V_0^R]}{RT_0} \frac{1}{\theta_{\alpha\alpha,0}} \left(\frac{\partial \theta_{\alpha\alpha,0}}{\partial V_\alpha^R}\right)_{T_\alpha R} \tag{31}$$

This equation can therefore be used to test the thermodynamic consistency of the shape factor expressions. After examining data for oxygen, nitrogen, and argon it was concluded that the small inequalities of the sides of Eq. (31) do not affect the calculations. As the temperature is lowered below a reduced temperature of one, the equality becomes less precise.

The shape factors obey the following algebraic relationships (Gilbert, *24*; Leach, *23*; Rowlinson and Watson, *27*). According to the reciprocal

rules:

$$\theta_{\alpha\alpha,0}[T_\alpha^R, V_\alpha^R] = \frac{1}{\theta_{00,\alpha}[\theta_{00,\alpha}T_\alpha^R, \phi_{00,\alpha}V_\alpha^R]} \tag{32}$$

$$\phi_{\alpha\alpha,0}[T_\alpha^R, V_\alpha^R] = \frac{1}{\phi_{00,\alpha}[\theta_{00,\alpha}T_\alpha^R, \phi_{00,\alpha}V_\alpha^R]} \tag{33}$$

and according to the ratio rules:

$$\theta_{\alpha\alpha,\beta}[T_\alpha^R, V_\alpha^R] = \frac{\theta_{\alpha\alpha,0}[T_\alpha^R, V_\alpha^R]}{\theta_{\beta\beta,0}\left[\frac{\theta_{\beta\beta,0}}{\theta_{\alpha\alpha,0}}T_\alpha^R, \frac{\phi_{\beta\beta,0}}{\phi_{\alpha\alpha,0}}V_\alpha^R\right]} \tag{34}$$

$$\phi_{\alpha\alpha,\beta}[T_\alpha^R, V_\alpha^R] = \frac{\phi_{\alpha\alpha,0}[T_\alpha^R, V_\alpha^R]}{\phi_{\beta\beta,0}\left[\frac{\theta_{\beta\beta,0}}{\theta_{\alpha\alpha,0}}T_\alpha^R, \frac{\phi_{\beta\beta,0}}{\phi_{\alpha\alpha,0}}V_\alpha^R\right]} \tag{35}$$

These equations are useful for switching reference fluids, since one might want to use a reference substance other than methane. The triple point of methane occurs at a reduced temperature of 0.48. To carry out calculations at lower temperatures, a different reference substance may be chosen. Also, it is advantageous to choose a reference substance which is as similar as possible to the fluid of interest. The change from reference substance 0 to reference β is given by the iterative solution of the nonlinear Eqs. (34) and (35). Leach (*23*) and Fisher and Leland (*34*) have used pentane as a reference substance.

REFERENCE FLUID REPRESENTATION

Calculations using the PCS require that the thermodynamic properties of the reference substance be known very accurately. The properties may be given in tabular form or expressed by an equation of state. Methane is the most commonly used reference because its thermodynamic properties are well known, and it was used as the reference when determining the shape factors.

Yuan et al. (*28*) and Palmer et al. (*35*) chose to represent the thermodynamic behavior of the reference fluid in tabular form. Data tables for benzene and cyclohexane were prepared at temperature intervals of 1 K. This method has the advantage that the data can easily be changed when better data become available without having to refit the equation of state. A large amount of computer space is, however, required to store the data, and integrations and differentations of the data must be carried out numerically.

The choice of an equation of state to represent the phase diagram is

a matter of convenience and accuracy. Leach (*23*) chose to use methane and pentane as reference substances. The available data were fit to within the experimental uncertainty by dividing the phase diagram into four regions: a dilute gas region, two dense fluid regions, and a liquid region. Each region was represented by a different equation of state. Fisher and Leland (*36*) represented the vapor phase of methane with the Vennix-Kobayashi (*37*) equation of state, and the liquid phase with the Tait equation (Hirschfelder et al., *38*). Teja and Rowlinson (*39*) used the Vennix-Kobayashi equation of state for methane as the reference when calculating the critical regions of fluids.

Today several equations of state are available which describe the thermodynamic properties of methane over the entire phase diagram. Recent modifications of the Benedict-Webb-Rubin (BWR) equation of state have been used to represent the reference fluid. This type of function is easy to manipulate due to its analytic nature. Teja and Rice (*40*) used the 20 constant Bender (*41*) equation of state to represent the phase behavior of methane. The 33 constant modified BWR equation of state fit to methane by McCarty (*42*) was used by Haile et al. (*43*) to calculate viscosities, Murad and Gubbins (*44*) to calculate thermal conductivities, and McCarty (*45*) to calculate liquid densities.

Two nonanalytic equations of state for methane developed at the National Bureau of Standards have recieved considerable attention: METHERM4 by Goodwin (*46*) and METHERM5 by Goodwin (*47*). Several shortcomings of the latter equation have been found by Mollerup (*48*) and from our own work. The fugacity coefficients calculated by numerically integrating METHERM5 become greater than 1 at low temperatures as the triple point is approached. The fugacity coefficient of methane should approach 1 at the triple point. Also, the equation becomes indefinite as the density approaches zero. The latter problem has been resolved by Goodwin (*49*) for future use of the equation. The equation of state METHERM4 does not suffer from these problems and is known to describe the thermodynamic behavior of methane very accurately from the triple point of methane up to 700 bars and 500 K. This equation has been used extensively by Mollerup (*48*) and was used in making the new calculations presented here. The equation is given below:

$$\frac{(z-1)}{\rho}T^R = A + B\Phi(T) + C/T^R + D\Psi(\rho, T) \tag{36}$$

where

$$\Phi(T) = T^R[1 - \exp(-b - \beta/T^R)]$$

$$\psi(P, T) = [1 - w \ln(1 + 1/w)]T^R$$

$$w(\rho, T) = \frac{T - \theta(\rho)}{\delta T^c}$$

$$\theta(\rho) = T_s(\rho) \exp\left(-\frac{u(d^R)}{2}\right)$$

$$u(d^R) = \alpha^v[|d^R - 1|^3 - (d^R - 1)^3] + \alpha^l[|d^R - 1|^3 + (d^R - 1)^3]$$

$$T^R = T/T^c, \qquad d^R = d/d^c, \qquad \rho = d/d_t$$

and the coefficients A, B, C, and D are represented by power series in density. The terms b, α^v, α^l, β, and δ are constants. The equation of state requires the single-valued function $T_s(\rho)$ for the saturation temperatures. This function is given by

$$Y(T_s) = U^{8/3}[1 + A_1 \ln(\rho) + (\rho - 1)F(\rho)] \tag{37}$$

where

$$Y(T_s) = \frac{T^c/T_s - 1}{T^c/T_t - 1}$$

$$U(d^R) = \frac{(d^R - 1)}{(d_t{}^R - 1)}$$

and $F(\rho)$ is expressed by a power series in density. Auxiliary equations for the vapor pressure, saturated liquid density, and saturated vapor density as functions of temperature are included in the equation of state package, and are most useful when making calculations at saturated conditions. The equation of state is nonanalytic at the critical point due to the function $\Psi(\rho, T)$. This function was designed to give a large increase in the constant volume heat capacity upon close approach to the critical point, which is consistent with experimental observation. When calculating thermodynamic properties which require integrations, such as the configurational Gibbs free energy, a numerical integration must be used. These integrations increase the computation time. Mollerup (*48*) has decreased the computation time while retaining the accuracy of METHERM4 by storing thermodynamic properties calculated from METHERM4 in tables, and interpolating where necessary. To carry out calculations at reduced temperatures less than the triple point of methane, Mollerup (*48*) has extrapolated the equation into the hypothetical liquid and vapor regions using thermodynamic data of propane. This extrapolation will be used in the low temperature calculations presented here.

Although the reference substance is most commonly a pure fluid, a mixture can also be used as a reference. Chapela-Castañares and Leland (*50*) have developed a procedure, based on conformal solution theory, for calculating the equilibrium ratios in multicomponent systems from

experimental data on binary mixtures. Smoothed binary data for five reference systems serve as the basis for performing the calculations.

PURE FLUID CALCULATIONS

The thermodynamic properties of pure fluids can be calculated once the conformal parameters, $f_{\alpha\alpha,0}$ and $h_{\alpha\alpha,0}$, and a means of representing the reference substance have been specified. Pure fluid calculations require no adjustable parameters. Only the critical properties and acentric factor of a fluid need be known.

Compressibilities

Gunning (*33*) calculated the compressibilities of several fluids from Eq. (22). The Vennix-Kobayashi equation of state was used to represent the vapor phase and the Tait equation was used for the liquid phase of methane. The agreement between the calculations and experimental data is good for the normal hydrocarbons ethane through heptane. The more similar a substance is to the reference, methane, the better the agreement.

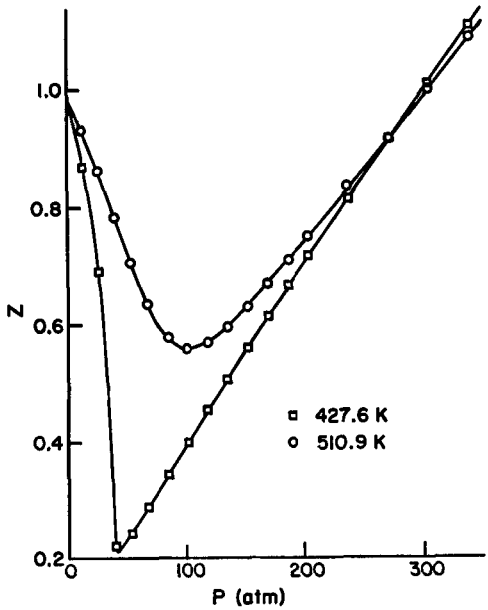

FIG. 1. The calculated compressibility factors of *n*-butane compared with the data of Sage and Lacey (*51*).

The errors are greatest where z is very low and where the isotherms have the greatest slope, as one would expect. In Fig. 1 our calculations for n-butane are compared with the data of Sage and Lacey (*51*). That the results are good for the normal hydrocarbons is not surprising since data for these fluids were used in developing the correlation. The calculations do, however, attest to the accuracy of the shape factor expressions, Eqs. (28) and (29). Gunning (*33*) also calculated the compressibilities of several fluids not used in formulating the shape factor expressions: argon, oxygen, nitrogen, propylene, and toluene. Good results were obtained for all fluids except toluene. These results have been summarized by Gunning and Rowlinson (*52*).

Phase Behavior at Saturation

For a pure fluid with vapor and liquid phases in equilibrium, there is one degree of freedom. Once the temperature or pressure is set, the state of the system is specified. At equilibrium the temperatures, pressures, and fugacities in each phase are equal. The fugacity coefficient may be written

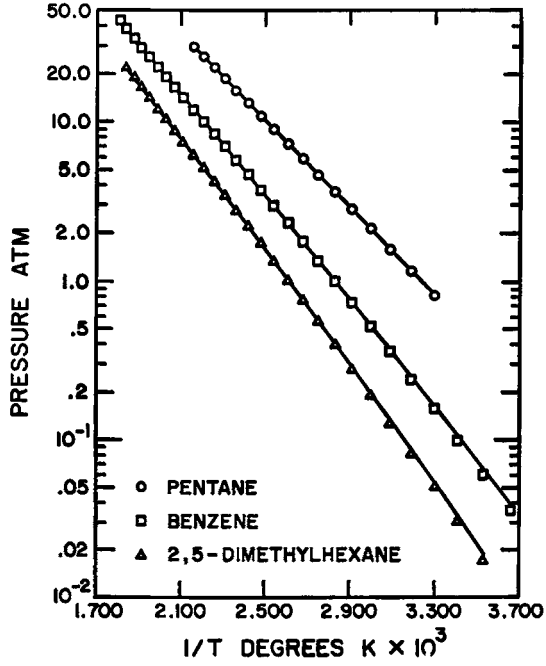

FIG. 2. Vapor pressure calculations at saturation for pentane, benzene, and 2,5-dimethylhexane [Timmermans (*56*)].

in terms of the residual Gibbs energy, which is the difference between the configurational Gibbs free energy of the real substance and a perfect gas. From Eq. (18):

$$\ln\left(\frac{f}{p}\right)_\alpha = \left(\frac{G^{res}}{RT}\right)_\alpha \tag{38}$$

The residual Gibbs free energy is calculated from the equation of state for the reference substance by performing the following integration:

$$\frac{G_0^{res}}{RT_0} = \int_0^{p_0}\left(\frac{z_{0-1}}{p_0}\right) dp_0 \tag{39}$$

For a pure fluid the equality of fugacities may also be expressed as an equality of fugacity coefficients or of residual Gibbs free energies for each phase.

The saturated liquid volumes of several light fluids, which are the principal constitutents of LNG, have been calculated by Mollerup and Rowlinson (*31*) and Mollerup (*53*, *54*). The volumes were calculated for the normal hydrocarbons ethane through pentane, isobutane, nitrogen,

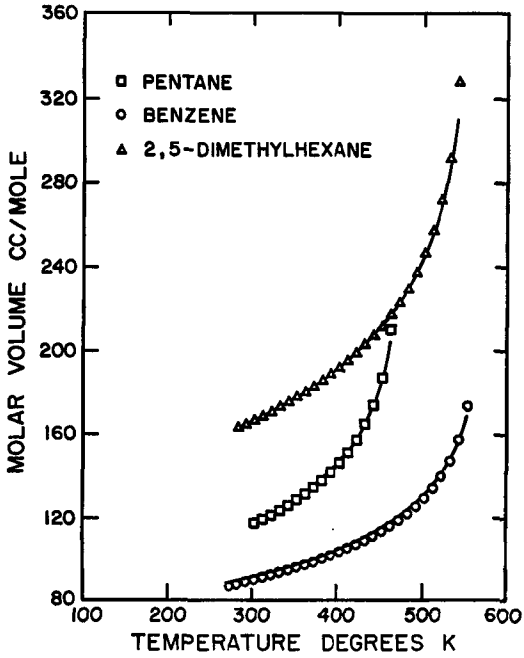

FIG. 3. Liquid molar volume calculations at saturation for pentane, benzene, and 2,5-dimethylhexane [Timmermans (*56*)].

and carbon dioxide by specifying the temperature. The average absolute relative deviations for the fluids ethane, propane, butane, and nitrogen are, respectively, 0.05, 0.04, 0.40, and 0.37% (Mollerup, *54*). The deviations are largest near the critical point, as one would expect. McCarty (*45*) used the PCS to correlate the saturated liquid densities of ethane, propane, butane, isobutane, and nitrogen to within 0.01%. Both the temperature and pressure were specified in the calculations. The numerical constants in the shape factor equations were redetermined, and the acentric factor and critical compressibility of each fluid were estimated from experimental data taken at the National Bureau of Standards and a least squares estimation technique. Calculations have been extended to higher molecular weight hydrocarbons (C_{16}) by Mentzer et al. (*55*). In Figs. 2, 3, and 4 the pressures, liquid molar volumes, and vapor molar volumes are shown as a function of temperature for pentane, benzene, and 2,5-dimethylhexane. It is not surprising that the calculations for pentane are good, since data for pentane were used in developing the shape factor expressions. However, that these expressions permit the accurate determination of vapor–liquid equilibrium (VLE) for other fluids, such as benzene and

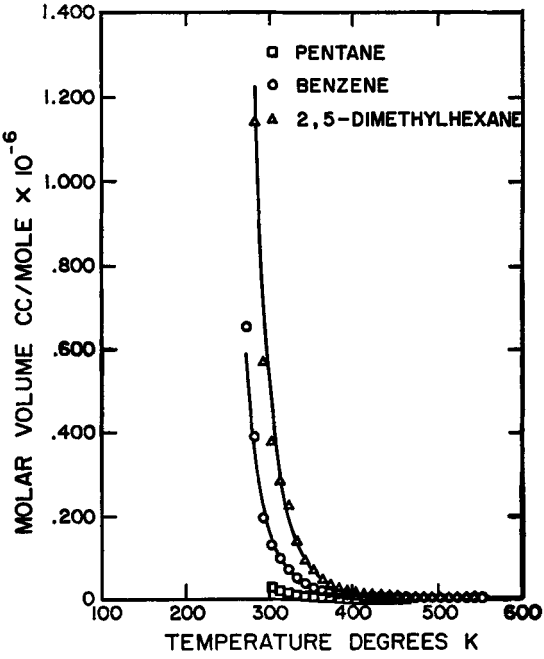

FIG 4. Vapor molar volume calculations at saturation for pentane, benzene, and 2,5-dimethylhexane [Timmermans (*56*)].

2,5-dimethylhexane, indicates the general nature of the shape factor expressions. The VLE calculations for several fluids are summarized in Table 1. The calculations were carried out to a reduced temperature of 0.99, if the data were available. The calculations are surprisingly good considering the differences in size and shape with those of methane, the reference.

TABLE 1

Pure Fluid Calculations at Saturation for Nonpolar Compounds

System	T range (K)	No. of data points	Property	AAPD[a]	BIAS[b]	Ref.
Pentane, C_5H_{12}	303–463	17	P	0.5	0.3	Timmermans (*56*)
	303–463	17	V^l	0.7	0.1	〃 〃
	303–463	17	V^v	2.6	2.4	〃 〃
Benzene, C_6H_6	273–553	29	P	2.3	1.6	〃 〃
	273–553	29	V^l	1.6	1.3	〃 〃
	273–553	29	V^v	3.6	1.3	〃 〃
Cyclohexane, C_6H_{12}	333–553	22	P	1.3	−0.9	API 44 (*57*) International Critical Tables (*58*)
	333–553	22	V^l	2.1	−2.1	〃 〃
	353–553	20	V^v	5.3	4.5	〃 〃
2,3-Dimethylbutane, C_6H_{14}	273–493	23	P	1.1	0.6	Timmermans (*56*)
	273–493	23	V^l	0.7	−0.7	〃 〃
	273–493	23	V^v	2.8	0.5	〃 〃
Heptane, C_7H_{16}	273–533	27	P	1.6	0.0	〃 〃
	273–533	27	V^l	0.9	0.1	〃 〃
	273–533	27	V^v	4.7	2.8	〃 〃
Octane, C_8H_{18}	303–563	27	P	2.5	0.3	〃 〃
	303–563	27	V^l	1.3	0.6	〃 〃
	303–563	27	V^v	7.0	3.0	〃 〃
2,5-Dimethylhexane, C_8H_{18}	283–543	27	P	3.0	1.5	〃 〃
	283–543	27	V^l	0.8	−0.6	〃 〃
	283–543	27	V^v	7.3	5.4	〃 〃
Decane, $C_{10}H_{22}$	373–618	28	P	4.0	−3.6	API 44 (*57*)
	373–618	28	V^l	2.8	−2.5	〃 〃 〃
	618	1	V^v	4.4	4.4	〃 〃 〃
Diphenylmethane, $C_{13}H_{12}$	491–700	26	P	1.1	−0.4	Timmermans (*56*) Simnick et al. (*59*)

[a] $\text{AAPD} = \frac{1}{N}\sum_{I=1}^{N}\left|\frac{\text{predicted} - \text{experimental}}{\text{experimental}}\right|_I \times 100\%$

[b] $\text{BIAS} = \frac{1}{N}\sum_{I=1}^{N}\left(\frac{\text{predicted} - \text{experimental}}{\text{experimental}}\right)_I \times 100\%$

As previously mentioned, pure fluid calculations require no adjustable parameters. Various schemes, however, have been proposed to improve the calculations by expressing the acentric factor as a function of temperature. Gunning and Rowlinson (*52*) adjusted the acentric factor at each temperature to fit the known vapor pressures of each pure fluid in their VLE calculations. This procedure, however, often leads to large errors in the prediction of pure fluid densities. Singh and Teja (*60*) developed generalized linear equations for the temperature dependence of the acentric factors for the normal alkanes from liquid density data. Although the liquid density calculations are improved, large errors occur when vapor pressures or vapor densities are calculated. It has been our experience that these functions do not improve the accuracy of saturated liquid density calculations for fluids other than the normal alkanes. If both the vapor pressure and density calculations are to be improved, it is essential that the temperature dependence of the acentric factor be based on both measurements. In the work of Mollerup and Rowlinson (*31*) the acentric factor was chosen to give a good fit of both the saturation pressure and density when the saturation temperature is specified, and an equally good fit of the saturation temperature and density when the saturation pressure is specified. For carbon dioxide and ethane, elliptical equations were developed to express the temperature dependence of the acentric factors. For all other fluids a constant value of the acentric factor was chosen. Although the temperature-dependent acentric factors for ethane and carbon dioxide improve the pure fluid calculations, they do not markedly affect mixture calculations. In our work we have chosen to use a constant value for the acentric factor for all fluids as given by the original definition of Pitzer et al. (*4*):

$$\omega = -1 - \log P^R \qquad \text{at } T^R = 0.7 \tag{40}$$

It was mentioned earlier that polar fluids can be shown to obey the same form of the PCS as nonpolar fluids when the dipole-dipole interaction term in the potential energy expression is free-energy averaged. This assumes, however, that the fluids are not highly polar and do not associate. Although the shape factor equations were not developed for polar fluids, the phase behavior of several polar fluids at saturation was calculated using these equations. The results are summarized in Table 2. For polar fluids which do not associate, such as ethers, ketones, and sulfur compounds, the calculations are good. The predictions for amines are surprisingly good, since all but tertiary amines are known to hydrogen bond. The calculations were found to be poor for acetone, heavy ketones, and alcohols. It is not surprising that the calculations were in poor agreement with experiment for alcohols since they are highly polar and hydrogen

TABLE 2

Pure Fluid Calculations at Saturation for Polar Compounds

System	T range (K)	No. of data points	Property	AAPD	BIAS	Ref.
Dimethyl ether, C_2H_6O	250–400	19	P	2.8	2.8	International Critical Tables (*58*)
	250–400	19	V^l	2.5	−2.4	〃 〃
	250–400	19	V^v	7.3	3.0	〃 〃
Diethyl ether, $C_4H_{10}O$	308–467	19	P	1.0	−0.7	〃 〃
	308–467	19	V^l	1.9	1.0	〃 〃
	308–467	19	V^v	9.2	9.2	〃 〃
2-Pentanone, $C_5H_{10}O$	283–373	10	P	0.9	0.9	Meyer and Wagner (*61*)
	283–373	10	V^l	0.4	0.4	〃 〃
2-Nonanone, $C_9H_{18}O$	343–433	10	P	3.8	−3.8	〃 〃
	343–433	10	V^l	3.1	−3.1	〃 〃
Hydrogen sulfide, H_2S	284–373	13	P	1.0	−1.0	Sage and Lacey (*62*)
	284–373	13	V^l	3.9	−3.8	〃 〃 〃
	284–373	13	V^v	7.0	7.0	〃 〃 〃
Ethyl mercaptan, C_2H_6S	308–499	21	P	1.3	−0.9	International Critical Tables (*58*)
	308–499	21	V^l	2.9	0.5	〃 〃
Ethyl amine, C_2H_7N	289–456	11	P	2.8	−1.2	Timmermans (*56*)
	411–420	2	V^l	0.1	0.0	〃 〃
	302–457	11	V^v	9.3	6.7	〃 〃
Quinoline, C_9H_7N	431–724	20	P	2.3	−2.2	Sebastian et al. (*63*)
	431–511	3	V^l	1.1	−1.1	Lumdsen (*64*)
m-Cresol, C_7H_8O	388–662	19	P	2.9	−0.4	Simnick et al. (*65*); TRC (*66*)
	388–662	19	V^l	2.3	−2.3	TRC (*66*)
Carbon tetrachloride, CCl_4	253–556	31	P	2.6	1.6	Timmermans (*56*)
	323–553	23	V^l	0.9	0.3	〃 〃
	343–553	21	V^v	3.1	3.1	〃 〃
Chlorobenzene, C_6H_5Cl	273–632	30	P	3.5	3.0	〃 〃
	273–632	30	V^l	2.9	2.2	〃 〃
	443–543	11	V^v	1.2	1.0	〃 〃
Carbon dioxide, CO_2	218–304	19	P	1.9	−1.9	Din (*67*)
	218–304	19	V^l	3.3	−3.3	〃 〃
	218–304	19	V^v	7.7	−7.7	〃 〃

bond. Calculations for several additional polar fluids have been summarized by Mentzer et al. (*55*). Although the calculated properties of many polar fluids are in reasonable agreement with experimental data, little work has been done in this area. The calculations could undoubtedly be improved if a reduced dipole dependence were added to the shape factor expressions.

Compressed Liquid Densities

The density of a compressed liquid is calculated by specifying both the temperature and pressure. Mollerup (*53*, *54*) has compared liquid density calculations off the saturation curve with experimental data for several light substances. The accuracy is comparable to that found for the liquid density calculations at saturation conditions.

Enthalpies

The calculation of enthalpies requires a temperature derivative of the free energy, and therefore some loss in accuracy is expected. Most investigators have calculated enthalpies through the use of first-order shape factors and their temperature derivatives, rather than using second-order shape factors. The working equation is Eq. (96), which will be discussed latter with the mixture calculations. Fisher and Leland (*34*) calculated residual enthalpies, $(H - H^*)$, for nitrogen and pentane on a single isotherm at various pressures. For nitrogen at 255 K the average deviation between the calculations and experimental data was 2.8 Btu/lb over a pressure range of 70–270 atm. The pentane calculations differed from the data by an average of -0.7 Btu/lb at 344 K over a pressure range of 135 to 205 atm. Gunning (*33*) calculated the configurational enthalpies of argon and pentane. The calculated configurational enthalpies of argon are in excellent agreement with experimental data from 20 to 300 atm. The results for pentane are good, except near the critical region. Mollerup (*29*, *48*) has calculated the residual enthalpies of ethane and propane. In Table 3 the calculated residual enthalpies of *n*-butane are compared with the values presented by Sage and Lacey (*51*). The calculations are in good agreement with the literature values.

Yuan et al. (*28*) used the conformal parameters determined from configurational Gibbs energy and molar volume data to calculate configurational enthalpies. That these parameters also accurately predict pure fluid enthalpies attests to the validity of conformal solution theory. Enthalpies were calculated for carbon tetrachloride, hexane, and heptane at 25, 50, and 75°C with an average absolute relative error of 0.8%, using benzene as the reference fluid.

TABLE 3

Comparison of the Calculated Residual Enthalpies of *n*-Butane with the Values Reported by Sage and Lacey (*51*)

	$-(H - H^*)$, (J/mole)					
	427.6 K		460.9 K		510.9 K	
P (atm)	Expt	Calc	Expt	Calc	Expt	Calc
13.6	1,662	1,581	1,424	1,324	1,169	1,040
27.2	3,887	3,823	3,130	2,945	2,393	2,202
40.8	12,745	13,279	5,269	5,106	3,706	3,512
54.4	14,482	14,468	8,160	8,430	5,142	4,971
68.1	15,031	14,900	11,671	11,523	6,651	6,538
85.1	15,369	15,225	12,966	12,793	8,419	8,430
102.1	15,566	15,414	13,626	13,374	9,880	9,835
119.1	15,686	15,549	13,973	13,739	10,859	10,601
136.1	15,760	15,643	14,212	13,968	11,470	11,307
153.1	15,808	15,697	14,382	14,130	11,886	11,699
170.1	15,835	15,724	14,505	14,252	12,180	11,982
187.1	15,846	15,738	14,593	14,333	12,398	12,199
204.1	15,846	15,724	14,654	14,387	12,561	12,361
238.2	15,813	15,697	14,713	14,455	12,784	12,563
272.2	15,752	15,616	14,721	14,441	12,930	12,685

Joule-Thomson Coefficients

The isothermal and adiabatic Joule-Thomson coefficients are defined as

$$\phi = \left(\frac{\partial H}{\partial p}\right)_T \tag{41}$$

$$\eta = \frac{(\partial H/\partial p)_T}{(\partial H/\partial T)_p} \tag{42}$$

respectively. This type of calculation requires an additional differentation of the Gibbs energy and is thus a most rigid test of the calculation procedure. Experimental Joule-Thomson coefficient data are not plentiful and are often inconsistent. Gunning (*33*) calculated Joule-Thomson coefficients numerically for carbon dioxide, propane, butane, and pentane, and compared them with experimental data. The agreement between the calculations and data is mixed. The calculated adiabatic Joule-Thomson coefficients for carbon dioxide were found to be in good agreement with the measurements of Roebuck et al. (*68*), which are thought to be reliable. The results agree to within 5%, except at low pressures. The computed isothermal Joule-Thomson coefficients of carbon dioxide were also found to be in good agreement with experimental data.

Transport Properties

Haile et al. (*43*) correlated the viscosities of light hydrocarbons and simple inorganic gases by determining shape factors from compressibility and viscosity data. This method is similar in principle to that used by Yuan et al. (*28*) and Palmer et al. (*35*) in that the conformal parameters are determined from pure fluid data for use in correlating mixture data. The procedure has not been generalized, since pure fluid data are needed to determine the shape factors for each fluid.

Thermal conductivities of dense fluids were correlated by Murad and Gubbins (*44*) by determining the shape factors needed to equate the compressibilities and reduced thermal conductivities of various fluids with those of methane, the reference. Generalized shape factor correlations were developed for use in calculating the thermal conductivities of hydrocarbons up to hexane, carbon dioxide, and nitrogen. The calculations are stated to be accurate to 4%, which is the usual experimental uncertainty for thermal conductivities. In Fig. 5 the thermal conductivities of hexane calculated from the correlation are compared with the data of Tsederberg (*69*). The agreement is seen to be quite good.

MIXTURE MODELS

The PCS can be utilized to calculate mixture properties. The pure fluid framework is applied to mixtures through the use of mixing rules for the conformal parameters. Reid and Leland (*70*) have shown how several of the commonly used mixing rules can be obtained by making various

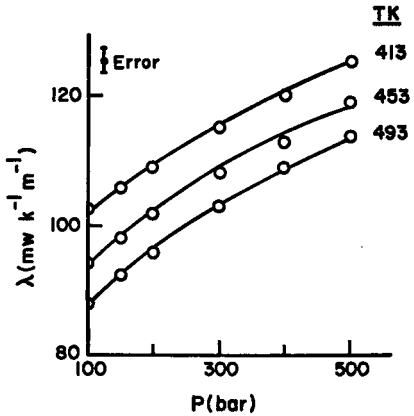

FIG. 5. Thermal conductivity calculations by Murad and Gubbins (*44*) for hexane compared with data from Tsederberg (*69*).

assumptions about unlike pair interactions and the radial distribution function. Mixing rules have been derived for so-called "random mixtures" where all the molecular species are of the same size, and therefore the probability of finding a molecule of one species at a given distance from a neighbor is the same for all species (Rowlinson, *17*). In practice, however, the components of a mixture have different sizes and shapes, and therefore do not mix randomly.

The most successful mixing rules, and the ones for which there are the best theoretical arguments, are those known as the van der Waals mixing rules. This model is in no way dependent on the validity of the van der Waals equation of state. The van der Waals one-fluid model has been shown to be superior to the random mixture model for mixtures of molecules of different sizes (Leland et al., *71*). With this model a pseudopure fluid, denoted by x, is defined whose Gibbs free energy differs from that of the mixture only by the ideal energy change of mixing. The configurational Gibbs free energy of the mixture can therefore be written as

$$G_m[T, p, x] = G_x[T, p, x] + RT \sum_\alpha x_\alpha \ln (x_\alpha) \tag{43}$$

where

$$G_x = f_{x,0} G_0[T/f_{x,0}, ph_{x,0}/f_{x,0}] - RT \ln (h_{x,0}) \tag{44}$$

The latter equation is written for the pseudofluid x and is obtained from Eq. (23) and the relation $G = A + pV$. In terms of the conformal parameters, the mixing rules are

$$h_{x,0} = \sum_\alpha \sum_\beta x_\alpha x_\beta h_{\alpha\beta,0} \tag{45}$$

$$f_{x,0} h_{x,0} = \sum_\alpha \sum_\beta x_\alpha x_\beta f_{\alpha\beta,0} h_{\alpha\beta,0} \tag{46}$$

The unlike pair conformal parameters are usually represented as follows:

$$f_{\alpha\beta,0} = \zeta_{\alpha\beta} (f_{\alpha\alpha,0} f_{\beta\beta,0})^{1/2} \tag{47}$$

$$h_{\alpha\beta,0} = \frac{1}{8} \eta_{\alpha\beta} (h_{\alpha\alpha,0}^{1/3} + h_{\beta\beta,0}^{1/3})^3 \tag{48}$$

where $\zeta_{\alpha\beta}$ and $\eta_{\alpha\beta}$ are binary interaction parameters which must be determined from experimental data. They are assumed to be independent of temperature, pressure, and composition. If nothing is known of a binary mixture, $\zeta_{\alpha\beta}$ and $\eta_{\alpha\beta}$ can either be estimated from those of similar mixtures or set equal to unity by adopting the Lorentz-Berthelot assumption. It is important to note that only binary parameters appear in Eqs. (45) and (46), and thus they are all that are needed for multicomponent mixture calculations.

Leland et al. (*72*) developed a van der Waals two-fluid model in an attempt to account for departures from randomness due to differences in size and intermolecular energy of the species. Instead of replacing the entire mixture with a single hypothetical pure fluid, each component of the mixture is replaced by a pseudocomponent and then assumed to mix ideally to form the mixture. The two-fluid model may be more appropriately called a multifluid model, since each real component is replaced by an equivalent component. The configurational Gibbs free energy may thus be written (Rowlinson and Watson, *27*):

$$G_m[T, p, x] = \sum_\alpha x_\alpha \{G_\alpha'[T, p, x_\alpha] + RT \ln (x_\alpha)\} \tag{49}$$

where

$$G_\alpha'[T, p, x_\alpha] = f_{\alpha,0} G_0 \left[\frac{T}{f_{\alpha,0}}, \frac{p h_{\alpha,0}}{f_{\alpha,0}}\right] - RT \ln (h_{\alpha,0}) \tag{50}$$

The van der Waals mixing rules become for the two-fluid model:

$$h_{\alpha,0} = \sum_\beta x_\beta h_{\alpha\beta,0} \tag{51}$$

$$f_{\alpha,0} h_{\alpha,0} = \sum_\beta x_\beta f_{\alpha\beta,0} h_{\alpha\beta,0} \tag{52}$$

The unlike pair interactions may be represented by Eqs. (47) and (48), as for the one-fluid model. Difficulties arise when calculating the thermodynamic properties of a mixture whose components have very different critical temperatures. In this instance the component with the lower critical temperature may have a reduced temperature larger than unity, such that no liquid state can exist (Mollerup and Fredenslund, *73*). Fisher and Leland (*36*) have described a variation of this two-fluid model. Instead of replacing each component in a mixture with a pseudocomponent, each phase of a mixture is split into a light and heavy hypothetical fluid. The thermodynamic properties of each pseudofluid are then calculated using two different reference substances. The thermodynamic properties of a phase are obtained by combining the properties of the two pseudofluids weighted by their respective mole fractions.

There appears to be some confusion in the literature with respect to the term "two-fluid" as applied to the calculation of thermodynamic properties. In the preceding paragraph a two-fluid mixture model is described for calculating the properties of mixtures. The conformal parameters for each pseudocomponent, or hypothetical fluid, are given by Eqs. (51) and (52), and therefore yield different reduced temperatures and volumes for each pseudocomponent or hypothetical fluid. Yesavage (*74*) and Johnson and Clover (*75*) have developed a two-fluid method of calcu-

lating thermodynamic properties which is applicable to both pure fluids and mixtures. By this method a thermodynamic property is calculated with two reference fluids using the same reduced variables. The two results are then each weighted by a factor which is a function of a characteristic parameter of the two reference substances and fluid of interest (i.e., ω), and linearly combined to give the property for the system of interest. Starling (*76*) and Chapela-Castañares and Leland (*50*) have also obtained good results using this method.

For mixture calculations the shape factors have a slight composition dependence. The composition dependence accounts for the different environment which a molecule is subjected to in a mixture as compared to a pure fluid. The arguments in the shape factor equations are:

$$f_{\alpha\alpha,0} = \frac{T_\alpha^c}{T_0^c}\theta_{\alpha\alpha,0}\left[\frac{T\theta_{\alpha\alpha,0}}{T_0^c f_{x,0}}, \frac{V\phi_{\alpha\alpha,0}}{V_0^c h_{x,0}}\right] \tag{53}$$

$$h_{\alpha\alpha,0} = \frac{V_\alpha^c}{V_0^c}\phi_{\alpha\alpha,0}\left[\frac{T\theta_{\alpha\alpha,0}}{T_0^c f_{x,0}}, \frac{V\phi_{\alpha\alpha,0}}{V_0^c h_{x,0}}\right] \tag{54}$$

These arguments are necessary if the calculations are to be independent of the reference substance used. For pure fluids they become $T_\alpha^R = T_\alpha/T_\alpha^c$ and $V_\alpha^R = V_\alpha/V_\alpha^c$. It is important to note that the quantities $\theta_{\alpha\alpha,0}$ and $\phi_{\alpha\alpha,0}$ in pure fluid calculations are not the same as the pure fluid contributions $\theta_{\alpha\alpha,0}$ and $\phi_{\alpha\alpha,0}$ in the van der Waals mixing rules. Mixture calculations require an iterative solution procedure. In practice, the iterations are found to converge rapidly. Leach et al. (*26*) have developed an approximation for the arguments of the shape factors which eliminates the iteration procedure.

Wheeler and Smith (*77*) suggested the following mixing rules for the conformal parameters:

$$f_{x,0} = \sum_\alpha \sum_\beta w_f(\alpha, \beta) f_{\alpha\beta,0} \tag{55}$$

$$h_{x,0} = \sum_\alpha \sum_\beta w_h(\alpha, \beta) h_{\alpha\beta,0} \tag{56}$$

where a general weighting function is defined as

$$w(\alpha, \beta) = \frac{x_\alpha x_\beta S_\alpha S_\beta I(\alpha, \beta)}{\sum_\alpha \sum_\beta x_\alpha x_\beta S_\alpha S_\beta I(\alpha, \beta)} \tag{57}$$

The terms S_α and S_β are measures of the size and shape of molecules α and β, while the quantity $I(\alpha, \beta)$ is a measure of the strength of interaction between these two molecules relative to other pairs. In general, the size–shape and interaction effects for each molecule and binary pair will be different in Eqs. (55) and (56). If the S's and I's are set to unity, the

weighting factors take on the random mixing form. If the S's and I's are set to unity for w_h, and the S's are set to unity while the I's are set equal to $h_{\alpha\alpha}$, $h_{\alpha\beta}$, and $h_{\beta\beta}$ for w_f, Eqs. (55) and (56) reduce to the van der Waals one-fluid model.

Several investigators have sought to modify the van der Waals mixing rule for $f_{x,0}$. Various values for the exponent δ on the weighting factor h have been recommended:

$$f_{x,0} = \frac{\sum_\alpha \sum_\beta x_\alpha x_\beta f_{\alpha\beta,0} h_{\alpha\beta,0}^\delta}{h_{x,0}^\delta} \tag{58}$$

Leland and Chappelear (*12*) have shown that the conventional van der Waals mixing rule ($\delta = 1$) follows from certain assumptions concerning the radial distribution function of a pair of molecules in a mixture. When the critical volumes of the two components are equal, the exponent δ is of no importance and may thus be set to zero. Plöcker et al. (*78*) empirically found a value of 0.25 to be best for mixtures of molecules which differ appreciably in size. Teja (*79*) compared the critical state predictions of binary mixtures using values of δ equal to 0.0, 0.25, and 1.0. A value of unity was found to be best. In our work on equilibrium ratios and excess properties we also chose to use a value of unity.

MIXTURE CALCULATIONS

The thermodynamic properties of mixtures can be calculated once mixing rules for the conformal parameters have been specified. Binary interaction parameters may or may not be used to represent the unlike pair interactions, as in Eqs. (47) and (48), depending on the nonideality of the mixture and the desired accuracy.

Compressibilities

The compressibility of a mixture is calculated from the equation of state for the reference fluid by

$$z(T, V) = z_0(T/f_{x,0}, V/h_{x,0}) \tag{59}$$

Fisher and Leland (*34*) calculated the compressibilities of hydrocarbon mixtures with the van der Waals one-fluid model. Equation (47), with $\zeta_{\alpha\beta}$ set to unity, was used to represent $f_{\alpha\beta,0}$, while $h_{\alpha\beta,0}$ was calculated from

$$h_{\alpha\beta,0} = \frac{1}{2}(h_{\alpha\alpha,0} + h_{\beta\beta,0}) \tag{60}$$

In this equation the volumes are thought of as being additive instead of

the effective molecular diameters as in Eq. (48). The compressibilities of methane + propane mixtures were predicted with an average absolute error of 1.0% on a 100°F isotherm over a pressure range of 200 to 2,500 psia. For methane + decane mixtures at the same temperature, and pressure from 695 to 3,000 psia the predicted compressibilities agreed with experimental data to within 3.1%. The poorer agreement for the latter system is to be expected due to the greater dissimilarity between the components of the mixture. Gunning (*33*) calculated the compressibilities of several mixtures with one interaction parameter, $\zeta_{\alpha\beta}$, used to characterize each binary pair. Compressibilities were calculated within 1.0% for the mixtures methane + hydrogen sulfide, methane + carbon dioxide, and air. The agreement was poorer for the system toluene + hexane. Comparisons between the compressibilities of air using the one-fluid and two-fluid van der Waals models showed the latter to be no more accurate than the former, except possibly at low temperatures.

Compressed Liquid Densities

The density of a compressed mixture is calculated from the specified temperature, pressure, and composition by

$$V[T, p, x] = h_{x,0} V_0[T/h_{x,0}, ph_{x,0}/f_{x,0}] \tag{61}$$

The formulation of the PCS considered here is well-suited for the calculation of densities of mixtures of light components. Mollerup has demonstrated that the densities of LNG, LPG, and related mixtures can be calculated with an accuracy of about 0.2% (Mollerup and Rowlinson, *31*; Mollerup, *53*, *54*; Mollerup et al., *80*). This is more accurate than any other existing correlation. Mixtures were described by the van der Waals one-fluid model and Eqs. (47) and (48). Calculation of liquid densities is very sensitive to the parameter $\eta_{\alpha\beta}$. The procedure has been applied with good results to a reduced temperature of 0.3. It is not surprising that this method is well-suited for the prediction of the densities of mixtures of light molecules, since methane is the reference fluid. The advantage over other methods, however, is that it can handle heavier hydrocarbons and nitrogen very well. This method also covers a larger temperature, pressure, and composition range than most other methods.

Teja and Rice (*40*) fit the densities of binary mixtures of benzene with *n*-hexane, *n*-heptane, *n*-decane, and *n*-hexadecane at 25 and 50°C with one interaction parameter, $\zeta_{\alpha\beta}$, per binary pair. The average absolute deviation ranged from 0.4% for benzene + *n*-heptane mixtures to 1.8% for benzene + *n*-hexadecane mixtures. These results are not as accurate as those for mixtures of lighter molecules. Perhaps the calculations could

be improved if the interaction parameter $\eta_{\alpha\beta}$ instead of $\zeta_{\alpha\beta}$ was used to characterize each binary interaction.

Vapor-Liquid Equilibrium

Two phases are at equilibrium when the temperature and pressure in each phase are the same, and the fugacity of each component in each phase is the same. According to the Gibbs phase rule, for a binary mixture with a vapor and a liquid phase there are two degrees of freedom. Thus the state of the system is fixed once two variables are specified such as the temperature and pressure, the temperature and composition of one phase, etc.

The equilibrium ratio of component α, $K_\alpha \equiv y_\alpha/x_\alpha$, is obtained as follows (Mollerup, *29*):

$$\ln (K_\alpha) = \ln\left(\frac{f_\alpha}{x_\alpha p}\right)_{\text{liq}} - \ln\left(\frac{f_\alpha}{y_\alpha p}\right)_{\text{vap}} \tag{62}$$

$$= \left(\frac{\bar{G}_\alpha^{\text{res}}}{RT}\right)_{\text{liq}} - \left(\frac{\bar{G}_\alpha^{\text{res}}}{RT}\right)_{\text{vap}} \tag{63}$$

An expression for the residual Gibbs energy of component α in a mixture is found by subtracting the Gibbs energy of component α in a perfect gas mixture from the Gibbs energy of component α in a real mixture. Both of these terms are partial molar quantities which can be written in terms of the configurational Gibbs energy as follows:

$$\bar{G}_\alpha = G_x + \left(\frac{DG_x}{Dx_\alpha}\right)_{T,p} - \sum_\beta x_\beta \left(\frac{DG_x}{Dx_\beta}\right)_{T,p} \tag{64}$$

where the differential operator (D/Dx_α) denotes a differentiation with respect to x_α where all the other mole fractions are held constant (Rowlinson, *17*). This operator is necessary because the mole fractions in a mixture are not independent. The residual Gibbs energy of component α in either phase of the mixture is found to be

$$\bar{G}_\alpha^{\text{res}} = G_x + \left(\frac{DG_x}{Dx_\alpha}\right)_{T,p} - \sum_\beta x_\beta \left(\frac{DG_x}{Dx_\beta}\right)_{T,p} - RT \ln\left(\frac{p}{kT}\right) \tag{65}$$

The configurational Gibbs energy of the pseudofluid, G_x, is written in terms of the residual Gibbs energy of the reference fluid by combining Eq. (44) with the definition of the residual Gibbs free energy:

$$G_x = f_{x,0} G_0^{\text{res}}[T/f_{x,0}, ph_{x,0}/f_{x,0}] + RT \ln\left(\frac{p}{kT}\right) \tag{66}$$

The quantity G_0^{res} is determined from the PVT properties of the reference substance by Eq. (39). The derivative of G_x with respect to composition,

required in Eq. (65), is calculated from Eq. (44):

$$\left(\frac{DG_x}{Dx_\alpha}\right)_{T,p} = U_0\left(\frac{Df_{x,0}}{Dx_\alpha}\right)_{T,p} + (z_0 - 1)RT_0\left(\frac{f_{x,0}}{h_{x,0}}\right)\left(\frac{Dh_{x,0}}{Dx_\alpha}\right)_{T,p} \quad (67)$$

where U_0 is the configurational energy of the reference substance. The working equations for calculating equilibrium ratios are in a different form than those used by Leach et al. (*26*), but can be shown to be equivalent. The derivatives of the conformal parameters with respect to composition for the one-fluid van der Waals mixing rules have been determined from Eqs. (45) and (46) by Rowlinson and Watson (*27*) and Mollerup (*46*):

$$\left(\frac{Dh_{x,0}}{Dx_j}\right)_{T,p} = 2\sum_\alpha x_\alpha h_{\alpha j,0} + \sum_\alpha \sum_\beta x_\alpha x_\beta \left(\frac{Dh_{\alpha\beta,0}}{Dx_j}\right)_{T,p} \quad (68)$$

$$\left(\frac{Df_{x,0}}{Dx_j}\right)_{T,p} h_{x,0} + \left(\frac{Dh_{x,0}}{Dx_j}\right)_{T,p} f_{x,0} = 2\sum_\alpha x_\alpha f_{\alpha j,0} h_{\alpha j,0} + \sum_\alpha \sum_\beta x_\alpha x_\beta \left[\left(\frac{Df_{\alpha\beta,0}}{Dx_j}\right)_{T,p} h_{\alpha\beta,0} + \left(\frac{Dh_{\alpha\beta,0}}{Dx_j}\right)_{T,p} f_{\alpha\beta,0}\right] \quad (69)$$

To determine the derivatives of the unlike pair conformal parameters with respect to composition, we write by analogy with Eqs. (53) and (54):

$$f_{\alpha\beta,0}[T^R_{\alpha\beta,0}, V^R_{\alpha\beta,0}] = \frac{T^C_{\alpha\beta}}{T^C_0}\theta_{\alpha\beta,0}\left[\frac{T\theta_{\alpha\beta,0}}{T^C_0 f_{x,0}}, \frac{V\phi_{\alpha\beta,0}}{V^C_0 h_{x,0}}\right] \quad (70)$$

$$h_{\alpha\beta,0}[T^R_{\alpha\beta,0}, V^R_{\alpha\beta,0}] = \frac{V^C_{\alpha\beta}}{V^C_0}\phi_{\alpha\beta,0}\left[\frac{T\theta_{\alpha\beta,0}}{T^C_0 f_{x,0}}, \frac{V\phi_{\alpha\beta,0}}{V^C_0 h_{x,0}}\right] \quad (71)$$

These equations are only used to determine partial derivatives. The quantities $f_{\alpha\beta,0}$ and $h_{\alpha\beta,0}$ for use in the combining rules are determined from Eqs. (47) and (48). Applying the differential operator to Eqs. (70) and (71):

$$\left(\frac{Dh_{\alpha\beta,0}}{Dx_j}\right)_{T,p} = \frac{h_{\alpha\beta,0}}{\phi_{\alpha\beta,0}}\left(\frac{D\phi_{\alpha\beta,0}}{Dx_j}\right)_{T,p} \quad (72)$$

$$\left(\frac{Df_{\alpha\beta,0}}{Dx_j}\right)_{T,p} = \frac{f_{\alpha\beta,0}}{\theta_{\alpha\beta,0}}\left(\frac{D\theta_{\alpha\beta,0}}{Dx_j}\right)_{T,p} \quad (73)$$

The derivatives of the shape factors with respect to composition are found by the chain rule of partial differentiation through the use of the independent variables as written in Eqs. (70) and (71):

$$\left(\frac{D\phi_{\alpha\beta,0}}{Dx_j}\right)_{T,p} = \left(\frac{D\phi_{\alpha\beta,0}}{DV^R_{\alpha\beta,0}}\right)_{T^R_{\alpha\beta,0}}\left(\frac{DV^R_{\alpha\beta,0}}{Dx_j}\right)_{T,p} + \left(\frac{D\phi_{\alpha\beta,0}}{DT^R_{\alpha\beta,0}}\right)_{V^R_{\alpha\beta,0}}\left(\frac{DT^R_{\alpha\beta,0}}{Dx_j}\right)_{T,p} \quad (74)$$

$$\left(\frac{D\theta_{\alpha\beta,0}}{Dx_j}\right)_{T,p} = \left(\frac{D\theta_{\alpha\beta,0}}{DV^R_{\alpha\beta,0}}\right)_{T^R_{\alpha\beta,0}} \left(\frac{DV^R_{\alpha\beta,0}}{Dx_j}\right)_{T,p} + \left(\frac{D\theta_{\alpha\beta,0}}{DT^R_{\alpha\beta,0}}\right)_{V^R_{\alpha\beta,0}} \left(\frac{DT^R_{\alpha\beta,0}}{Dx_j}\right)_{T,p} \tag{75}$$

To determine the derivatives of the unlike pair shape factors, the expressions for the shape factors, Eqs. (28) and (29), are written in terms of the unlike pair quantities $T^R_{\alpha\beta,0}$, $V^R_{\alpha\beta,0}$, $\omega_{\alpha\beta}$, and $z_{\alpha\beta}{}^c$, and differentiated. The arguments of these derivatives, $T^R_{\alpha\beta,0}$ and $V^R_{\alpha\beta,0}$, are determined from Eqs. (70) and (71) by iteration, since they are composition dependent. To evaluate $\theta_{\alpha\beta,0}$ and $\phi_{\alpha\beta,0}$, we assume that

$$\omega_{\alpha\beta} = (\omega_\alpha + \omega_\beta)/2 \tag{76}$$

$$z_{\alpha\beta}{}^c = (z_\alpha{}^c + z_\beta{}^c)/2 \tag{77}$$

It is important to note that $\theta_{\alpha\beta,0}$ and $\phi_{\alpha\beta,0}$ are determined from Eqs. (70) and (71) so that the independent variables of these shape factors will be known and the derivatives of the unlike pair shape factors evaluated. Finally, the derivatives $(DV^R_{\alpha\beta,0}/Dx_j)_{T,p}$ and $(DT^R_{\alpha\beta,0}/Dx_j)_{T,p}$ must be determined.

$$\frac{\left(\frac{DV^R_{\alpha\beta,0}}{Dx_j}\right)_{T,p}}{V^R_{\alpha\beta,0}} = \frac{\left(\frac{D\phi_{\alpha\beta,0}}{Dx_j}\right)_{T,p}}{\phi_{\alpha\beta,0}} - \frac{\left(\frac{Dh_{x,0}}{Dx_j}\right)_{T,p}}{h_{x,0}} = \frac{\left(\frac{DV}{Dx_j}\right)_{T,p}}{V} \tag{78}$$

$$\frac{\left(\frac{DT^R_{\alpha\beta,0}}{Dx_j}\right)_{T,p}}{T^R_{\alpha\beta,0}} = \frac{\left(\frac{D\theta_{\alpha\beta,0}}{Dx_j}\right)_{T,p}}{\theta_{\alpha\beta,0}} - \frac{\left(\frac{Df_{x,0}}{Dx_j}\right)_{T,p}}{f_{x,0}} \tag{79}$$

In the articles by Rowlinson and Watson (*27*) and Mollerup (*48*), the last term in Eq. (78) was omitted (Mollerup, *81*). The equation is correct in the original work of Leach et al. (*26*), although the nomenclature is different. In practice, the added quantity is of little importance numerically, except for mixtures of very dissimilar molecules at high temperatures and pressures. For some systems the interaction parameters presented by Mollerup (*48*) and Mentzer et al. (*55*) may need to be adjusted if they are to be used in a revised program. The derivative appearing in this term is evaluated from

$$\left(\frac{DV}{Dx_j}\right)_{T,p} = -\frac{RT}{f^2_{x,0}}\left[\frac{T}{p}\left(\frac{\partial z}{\partial T_0}\right)_{p_0} + h_{x,0}\left(\frac{\partial z}{\partial p_0}\right)_{T_0}\right]\left(\frac{\partial f_{x,0}}{\partial x_j}\right)_{T,p} + \frac{RT}{f_{x,0}}\left(\frac{\partial z}{\partial p_0}\right)_{T_0}\left(\frac{\partial h_{x,0}}{\partial x_j}\right)_{T,p} \tag{80}$$

Equations (68), (69), (72)–(75), and (78)–(80) must be solved simultaneously for $(Dh_{x,0}/Dx_j)_{T,p}$ and $(Df_{x,0}/Dx_j)_{T,p}$. The calculation of K-values is

complex and must be performed on a computer. The flow diagram of a computer program for carrying out the calculations has been presented by Mollerup and Rowlinson (*31*). Computer programs have been developed as a part of various studies: program "LNG" by J. Mollerup, and program "PROPERTY" by T. W. Leland Jr. and his colleagues. If the van der Waals two-fluid model is to be used, equations similar to those presented above, but more complex, must be solved (Rowlinson and Watson, *27*; and Mollerup and Fredenslund, *73*).

Equilibrium ratios for binary mixtures of methane with several different paraffins have been predicted by Chappelear et al. (*82*), Leach et al. (*26*), and Fisher et al. (*83*). The van der Waals one-fluid model was used, along with Eqs. (47) and (60), to describe the mixture. No binary interaction parameters were used in the calculations. Good results were obtained even into the retrograde region. Fisher et al. (*83*) predicted *K*-values for the ternary mixture methane + ethane + propane and for a multicomponent natural gas mixture. The deviations from the experimental data were generally found to be greatest for the heavy components. At low temperatures the one-fluid mixture model was found to be a poor approximation. Leach (*23*) developed an empirical expression to correct the conformal parameter $f_{x,0}$ at low temperatures. A two-fluid van der Waals model has also been employed to improve the VLE predictions at low reduced temperatures ($T^R < 0.6$). Watson and Rowlinson (*84*) calculated the VLE behavior for the system nitrogen + oxygen + argon and its associated binaries with both the one-fluid and two-fluid van der Waals models. A single reference substance, methane, was used and one interaction parameter, $\zeta_{\alpha\beta}$, was employed to represent each pair interaction. They found the two-fluid model to be marginally the best. Upon further examination the two-fluid model was found to be no more accurate than the one-fluid model, except at low temperatures and high densities (Gunning and Rowlinson, *52*). Little has been reported on the use of the two-fluid model with two different reference substances. Fisher and Leland (*36*) have used the two-fluid van der Waals model with methane and pentane as the reference substances. Each phase of the mixture was split into a light hypothetical fluid and a heavy hypothetical fluid. Thermodynamic properties of the light phase are then calculated with the methane reference and properties of the heavy phase with the pentane reference. This procedure follows from the observation that it is best to use a reference substance as similar to the fluid of interest as possible.

Bubble point and dew point calculations were made by Gunning (*33*) for several systems consisting of from two to ten components. Both mixtures of relatively small molecules and mixtures in which the components are different in size and shape were examined. The van der Waals

one-fluid model was used, and the unlike pair interactions were represented by Eqs. (47) and (48), with $\eta_{\alpha\beta}$ set to unity. The values of ω were adjusted at each temperature to fit the known vapor pressure of each component in a mixture. This leads to a good correlation of bubble points or dew points, but often results in large deviations for density predictions. For mixtures of molecules which are very different in size, Teja (*85*) found it necessary to use an interaction parameter for volume, $\eta_{\alpha\beta}$.

Mollerup has made extensive calculations on the thermodynamic properties of mixtures consisting of light molecules, such as LNG and LPG (Mollerup and Rowlinson, *31*; Mollerup, *29*, *48*, *53*, *54*, *80*, *86*; Mollerup and Fredenslund, *87*; Mollerup et al., *88*). The van der Waals one-fluid model was used to represent each mixture, and two interaction parameters were employed to characterize each pair interaction. Values for the interaction parameters were determined from bubble point pressures and liquid densities. Acentric factors were chosen to give a good fit

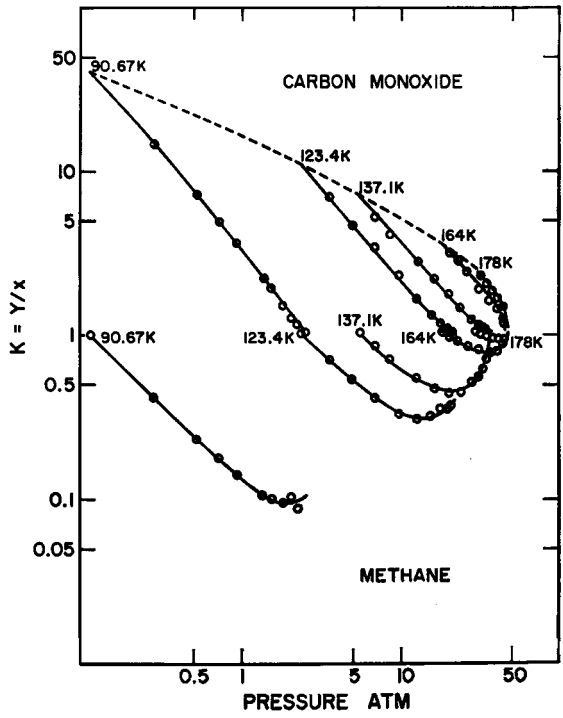

FIG. 6. The *K*-value calculations of Mollerup et al. (*88*) for methane + carbon monoxide mixtures compared with the data of Christiansen et al. (*89*) and Sprow and Prausnitz (*90*).

of the *PVT* behavior of each pure fluid at saturation. In Fig. 6 the predicted equilibrium ratios are shown as a function of pressure for the system methane + carbon monoxide. The calculations are accurate both in the normal and the critical regions of the phase diagram. Equilibrium ratios for the system carbon dioxide + pentane are compared with experimental data in Fig. 7. The lighter the components of the mixture are, the more accurate the calculations tend to be. For mixtures related to LNG or LPG, calculated *K*-values are generally accurate to within a few percent. In Table 4 calculated *K*-values for the ternary system methane + ethane + propane at 213.71 K are compared with experimental data. The calculated values in this table are true predictions, since the interaction parameters were determined solely from binary data. Saturated liquid densities can also be predicted quite accurately. In Table 5 the experimental and calculated molar volumes for several LPG mixtures are summarized. The correlation predicts LNG densities to within 0.1 % and LPG densities to within 0.2%. An extensive tabulation of the interaction parameters

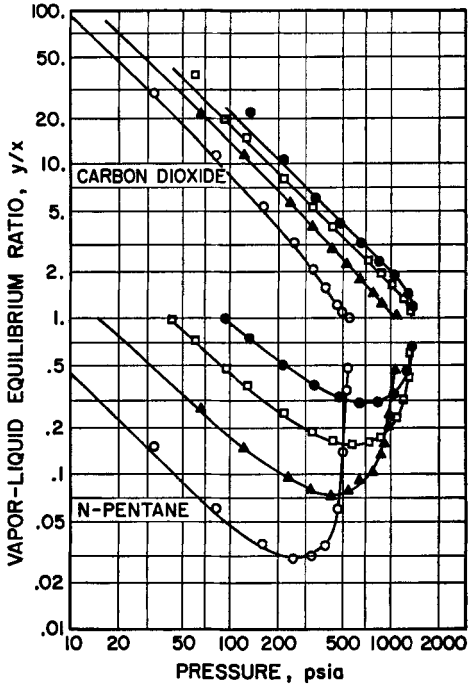

FIG. 7. Equilibrium ratios for the carbon dioxide + pentane system calculated by Mollerup (*53*) compared with the data of Besserer and Robinson (*91*): (○) 40.1°F, (▼) 100.2°F, (□) 159.8°F, (●) 220°F, (—) predicted.

TABLE 4

Equilibrium Ratios for the Ternary Mixture Methane + Ethane + Propane at 213.71 K Calculated by Mollerup (*29*) Compared with the Data of Wichterle and Kobayashi (*92*)

Mole fractions (liquid)			Experimental values				Predicted values			
CH_4	C_2H_6	C_3H_8	P (atm)	K_1	K_2	K_3	P (atm)	K_1	K_2	K_3
.0813	.2052	.7135	6.80	10.1	.615	.0789	7.00	10.2	.566	.0780
.0583	.7770	.1650	6.80	8.63	.61	.0812	6.84	9.05	.593	.0842
.0533	.9008	.0459	6.80	8.6	.608	.085	6.87	8.66	.593	.0859
.1777	.1834	.6389	13.6	5.08	.352	.0499	13.8	5.11	.328	.0495
.1667	.6943	.1390	13.6	4.48	.352	.052	13.7	4.52	.344	.0544
.1624	.7963	.0413	13.6	4.40	.356	.0523	13.5	4.43	.349	.0563
.3720	.1412	.4868	27.2	2.54	.244	.0442	27.1	2.55	.226	.0419
.3725	.5193	.1082	27.2	2.33	.245	.0530	26.6	2.33	.243	.0485
.5453	.0971	.3576	40.85	1.76	.241	.0531	38.8	1.76	.221	.0515
.5826	.3427	.0747	40.85	1.55	.263	.0740	40.4	1.56	.251	.0684
.7711	.0512	.1777	54.45	1.24	.348	.133	55.2	1.25	.314	.118
.7796	.1795	.0409	54.45	1.18	.413	.206	54.6	1.19	.379	.168
.7840	.2037	.0123	54.45	1.16	.449	.207	54.5	1.17	.407	.192

TABLE 5

Comparison between the Experimental LPG Molar Volumes and Those Calculated by Mollerup (*86*)

Mixture no.	X_{CH_4}	$X_{C_2H_6}$	$X_{C_3H_8}$	$X_{nC_4H_{10}}$	No. of data points	T (K)	P (atm)	$\Delta V\%$	Ref.
1		0.3700	0.6300		37	278–328	23–137	0.12	Thomlinson (*93*)
2		0.4989	0.5011		19	283–325	28–103	0.10	〃 〃
3		0.7171	0.2829		37	278–322	36–138	0.17	〃 〃
4		0.8997	0.1003		29	283–322	44–147	0.28	〃 〃
5	0.0231	0.7005	0.2764		24	280–322	38–138	0.24	〃 〃
6	0.0323	0.4828	0.4849		29	278–328	33–138	0.16	〃 〃
7	0.0218	0.6952	0.2747	0.0083	21	280–322	42–138	0.15	〃 〃
8			1.000		40	278–328	10–138	0.10	Manley and Swift (*94*)
9			1.000		19	244–333	20–109	0.08	〃 〃 〃 〃
10			1.000		40	291–323	10–137	0.10	Thomlinson (*93*)

needed to predict the thermodynamic properties of mixtures containing methane, ethane, ethylene, propane, propylene, butane, isobutane, pentane, isopentane, nitrogen, carbon monoxide, carbon dioxide, and hydrogen sulfide has been presented by Mollerup (*48*).

McCarty (*45*) compared several models for the prediction of LNG densities. The models examined were:

(a) The formulation of the PCS considered here
(b) The hard sphere model of Rodosevich and Miller (*95*)
(c) The cell model of Albright (*96*)
(d) The empirical method of Klosek and McKinley (*97*).

The PCS was found to be the only correlation which could correlate LNG densities to within 0.1 %. He concluded that the PCS has the widest range of temperature, pressure, and composition, but is complex to use and is sensitive to the values of the interaction parameters.

The applicability of the PCS to calculate the thermodynamic behavior of light components and their mixtures at saturation has been discussed extensively in the literature. Very little work, however, has been reported

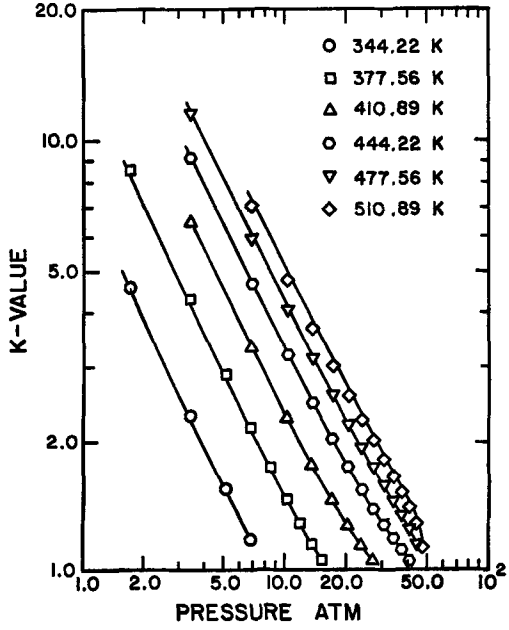

FIG. 8. *K*-value of butane versus pressure for the mixture butane–decane [Reamer and Sage (*98*)].

on the use of this procedure to calculate the properties of mixtures of larger molecules. Mentzer et al. (*55*) have carried out bubble point calculations on mixtures of methane, carbon dioxide, hydrogen, and hydrogen sulfide with various hydrocarbons up to *n*-hexadecane. The van der Waals one-fluid mixture model with two interaction parameters per binary pair was used. These parameters were determined to obtain the best agreement between calculated and experimental bubble point pressures and equilibrium ratios. Liquid density data were not used to determine the interaction parameters, ζ and η, since little data are available for several of the systems under consideration. In Figs. 8 and 9 the calculated equilibrium ratios for the system butane + decane are compared with experimental data. The calculations are in excellent agreement with the data as the critical region is approached. Only at the lowest temperature do the calculated *K*-values of decane begin to deviate from the data. The equilibrium ratios for carbon dioxide + heptane mixtures are shown in Figs. 10 and 11. The calculations do not show quite the correct temperature dependence for the *K*-values of carbon dioxide, while the calculated *K*-values of heptane are in good agreement with the data. The shape factor

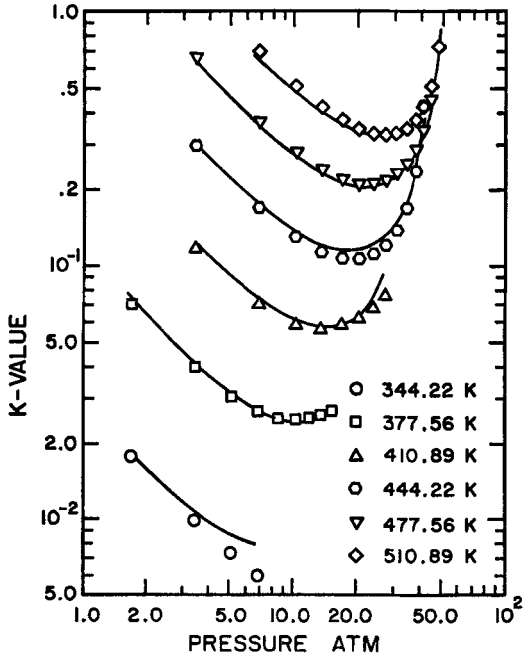

FIG. 9. *K*-value of decane versus pressure for the mixture butane–decane [Reamer and Sage (*98*)].

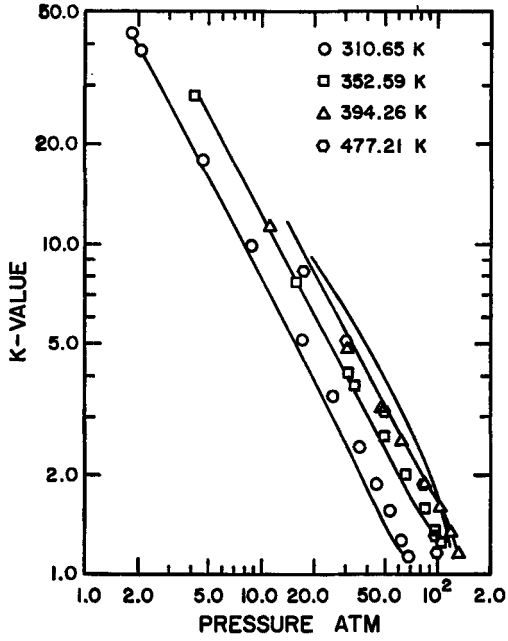

FIG. 10. *K*-value of carbon dioxide as a function of pressure for the mixture carbon dioxide + heptane [Kalra et al. (*99*)].

expressions for quantum fluids developed by Leach (*23*) are not convenient to use when calculating VLE for mixtures of quantum fluids and hydrocarbons. The difficulty arises when cross-term shape factors need to be computed in Eqs. (72) and (73). Because of these problems, and since the mixtures containing a quantum fluid (hydrogen) were at relatively high temperatures, only the hydrocarbon shape factor expressions were used to calculate the *K*-values of mixtures containing hydrogen. Equilibrium ratios for the system hydrogen + benzene were calculated and are compared with experimental data in Figs. 12 and 13. The agreement is quite good. A comparison between the VLE calculations and experimental data for several binary systems is presented in Table 6. Optimum values of the interaction parameters are reported. The calculations are most accurate for mixtures containing methane or carbon dioxide with paraffins up to about *n*-hexane. Good results are also obtained with heavier substances if they have a cyclic molecular structure. In general, the more dissimilar the components of the mixture are, the poorer the results. This limitation of the procedure is due to the fact that the pure fluid calculations tend to be less accurate for the paraffins beyond C_7, and the one-fluid model gives

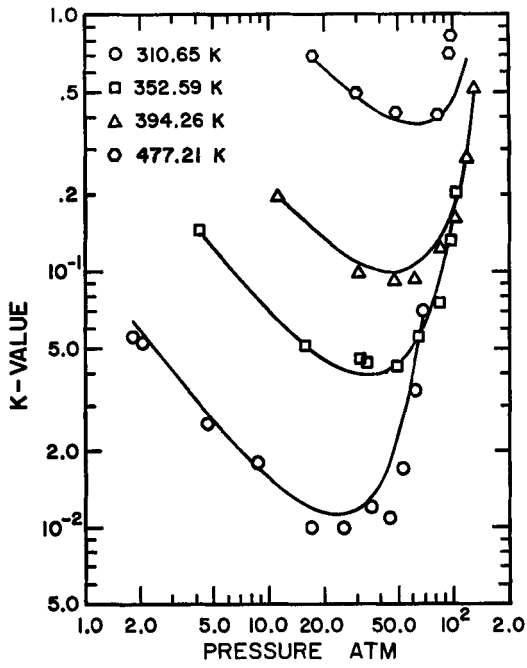

FIG. 11. *K*-value of heptane as a function of pressure for the mixture carbon dioxide + heptane [Kalra et al. (*99*)].

a poor representation of mixtures of highly dissimilar components. The calculations for hydrogen mixtures are the least accurate. Whereas for some systems the calculations are in good agreement with data, for others the agreement is quite poor. In Table 7 predicted bubble point pressures and *K*-values for the ternary system methane + butane + decane are compared with the experimental data of Reamer et al. (*114–116*). The agreement is satisfactory, considering the dissimilarity of the components. Although the binary interaction parameters were determined from bubble point pressures and *K*-values, they can be used to predict other thermodynamic properties such as densities. In Table 8 the predicted liquid and vapor densities for several binary mixtures at saturation are summarized. The predicted saturated liquid densities exhibit deviations of a few percent, while the saturated vapor densities are not quite as accurate.

The calculation of azeotropic and critical lines using the PCS formulation described here has been investigated by Teja and Rowlinson (*39*) and Teja (*117*). Calculations of this type are a severe test of the PCS due to their inherent complexity. Critical and azeotropic states are defined in terms of the Helmholtz energy and its derivatives with respect to volume

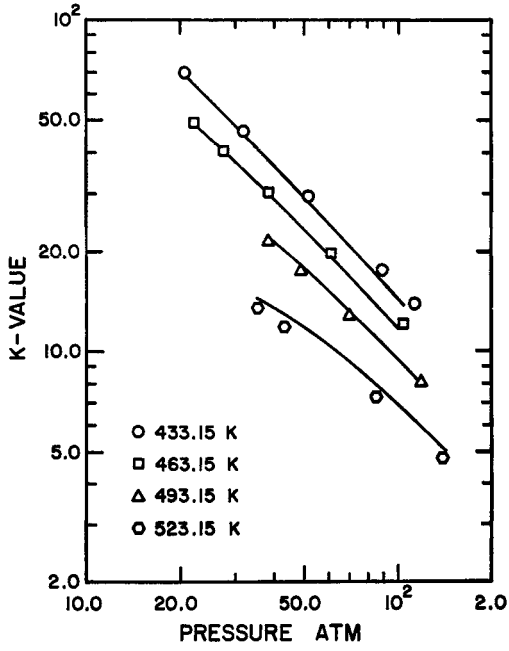

FIG. 12. *K*-value of hydrogen versus pressure for the mixture hydrogen + benzene [Connolly (*100*)].

and composition. Critical loci, upper and lower critical end points, and azeotropic lines for binary and multicomponent mixtures were calculated with generally only one interaction parameter, $\zeta_{\alpha\beta}$, per binary pair. The agreement between the calculations and experimental data is quantitative for mixtures of methane, ethane, propane, and carbon dioxide with the *n*-alkanes up to hexane. The PCS has also been shown to describe the behavior of systems where azeotropism occurs in the critical region, such as in the system carbon dioxide + ethane (Teja and Kropholler, *118*). For mixtures of molecules with greater dissimilarity in size and chemical type, the calculations exhibit the correct topology of the critical loci only in a qualitative manner. Critical states of mixtures containing a polar molecule have also been calculated (Teja, *79*). The agreement between the calculations and experimental data is not quite as good as that for nonpolar mixtures due to errors in the representation of the pure polar fluids. Good results have, however, been obtained for the following systems: ammonia + isooctane, ammonia + butane, hydrogen sulfide + ethane, and hydrogen sulfide + propane. That the van der Waals one-fluid mixture model gives good results for systems containing ammonia is surprising, since

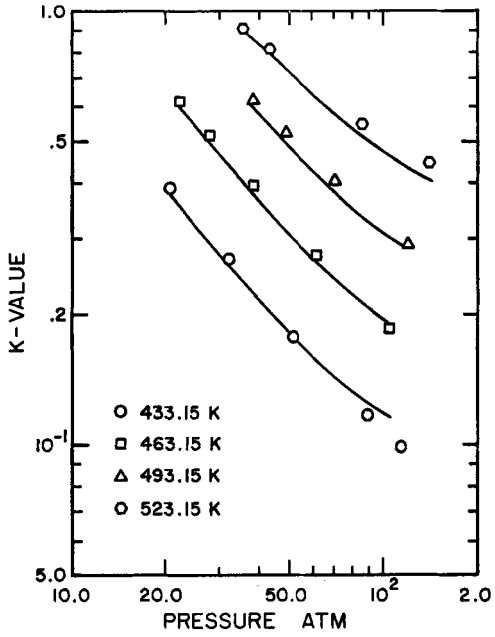

FIG. 13. *K*-value of benzene versus pressure for the mixture hydrogen + benzene [Connolly (*100*)].

Palmer et al. (*35*), Murad and Gubbins (*44*), and Mentzer (*119*) found these missing rules not to hold for mixtures containing a strongly polar component.

Henry's Constants

Henry's constant for substance α dissolved in solvent β is defined as

$$H_{\alpha,\beta} = \lim_{x_\alpha \to 0}\left(\frac{f_\alpha}{x_\alpha}\right) \tag{81}$$

Mollerup and Fredenslund (*87*) have shown that $H_{\alpha,\beta}$ may be expressed in terms of the residual Gibbs energy of solute α at infinite dilution by

$$H_{\alpha,\beta}^{(p)} = p \exp\left[\lim_{x_\alpha \to 0}\left(\frac{\bar{G}_\alpha^{\,res}}{RT}\right)\right] \tag{82}$$

where $\bar{G}_\alpha^{\,res}$ is given by Eq. (65). Generally Henry's constants are given at the saturation pressure of the solvent. Using values of $\zeta_{\alpha\beta}$ and $\eta_{\alpha\beta}$ determined from bubble point pressures and liquid density data, Fredenslund and Graus (*120*) predicted Henry's constants for several systems. Their

TABLE 6

Comparison of Vapor–Liquid Equilibrium Calculations with Experimental Data for Binary Mixtures

System	T (K)	P (atm), max	No. of data points	$\Delta P\%$ AAPD (BIAS)	$\Delta K_1\%$ AAPD (BIAS)	$\Delta K_2\%$ AAPD (BIAS)	ξ	η	Ref.
Methane + hexane	311–411	17	16	1.9 (0.7)	1.1 (0.9)	4.0 (0.3)	1.001	1.092	Gunn et al. (*101*)
Methane + octane	298–423	70	33	8.6 (1.0)	0.2 (0.0)	16.8 (13.6)	0.945	0.987	Kohn and Bradish (*102*)
Methane + cyclohexane	294–444	277	54	6.7 (2.2)	1.4 (1.4)	8.1 (−7.5)	0.984	1.056	Reamer et al. (*103*)
Methane + *m*-xylene	461–582	200	23	8.7 (−3.8)	3.5 (1.2)	6.3 (−4.2)	1.063	1.102	Simnick et al. (*104*)
Methane + 1-methylnaphthalene	464–704	250	28	7.4 (0.1)	2.2 (1.9)	10.1 (2.5)	1.042	1.134	Sebastian et al. (*105*)
Methane + diphenylethane	462–703	250	25	8.5 (−2.0)	1.3 (1.0)	5.7 (−0.1)	1.102	1.125	〃 〃
Ethane + heptane	339–450	84	32	2.4 (1.3)	0.8 (−0.5)	6.6 (1.9)	0.970	1.059	Mehra and Thodos (*106*)
Butane + decane	311–511	48	61	1.6 (0.2)	0.8 (0.3)	6.8 (1.2)	0.984	1.023	Reamer and Sage (*98*)
Carbon dioxide + heptane	311–477	130	34	8.8 (0.7)	1.8 (1.2)	11.3 (−0.1)	0.838	1.124	Kalra et al. (*99*)
Carbon dioxide + hexadecane	463–664	50	16	14.5 (5.5)	2.0 (1.5)	14.6 (6.0)	0.901	1.227	Chao et al. (*107*)
Carbon dioxide + cyclohexane	473–533	100	31	9.0 (−8.9)	7.6 (6.2)	3.3 (−1.5)	0.934	1.234	Krichevskii and Sorina (*108*)
Carbon dioxide + methylcyclohexane	311–477	147	31	7.7 (4.9)	1.6 (1.1)	17.1 (4.1)	0.820	1.120	Robinson and Ng (*109*)
Carbon dioxide + *m*-cresol	463–665	50	14	3.3 (0.3)	4.4 (4.2)	6.7 (0.6)	0.995	1.235	Chao et al. (*107*)
Carbon dioxide + 1-methylnaphthalene	463–704	50	15	5.8 (3.1)	4.1 (3.7)	11.6 (2.7)	0.867	1.197	〃 〃
Hydrogen + butane	328–394	166	60	3.1 (−1.5)	3.6 (2.5)	8.9 (0.7)	1.527	1.044	Klink et al. (*110*)
Hydrogen + octane	463–543	123	50	4.5 (−4.0)	5.4 (4.8)	5.5 (−1.8)	1.822	1.101	Connolly and Kandalic (*111*)
Hydrogen + cyclohexane	311–411	612	53	12.4 (4.4)	0.2 (0.0)	9.6 (4.3)	0.944	0.841	Berty et al. (*112*)
Hydrogen + benzene	433–533	153	49	2.7 (−2.1)	3.8 (3.2)	5.4 (−0.9)	1.730	1.079	Connolly (*100*)
Hydrogen sulfide + pentane	278–444	75	37	2.0 (−1.7)	4.5 (−2.4)	8.1 (1.7)	0.885	1.050	Reamer et al. (*113*)

TABLE 7

Comparison of Vapor–Liquid Equilibrium Calculations for the System Methane + Butane + Decane with the Experimental Data of Reamer et al. (*114–116*)

Liquid mole fractions			Experimental values				Predicted values			
CH_4	C_4H_{10}	$C_{10}H_{22}$	P (atm)	K_1	K_2	K_3	P (atm)	K_1	K_2	K_3
					Values at 277.6 K					
0.331	0.267	0.401	68.0	2.98	0.050	0.0015	56.9	2.96	0.076	0.0001
					Values at 344.3 K					
0.104	0.358	0.538	27.2	8.59	0.293	0.0032	25.4	8.19	0.409	0.0026
0.153	0.339	0.508	40.8	5.95	0.263	0.0033	37.5	5.81	0.323	0.0024
0.197	0.482	0.321	54.4	4.43	0.263	0.0053	52.1	4.38	0.281	0.0032
0.239	0.457	0.304	68.0	3.68	0.260	0.0066	63.9	3.67	0.267	0.0038
					Values at 410.9 K					
0.0006	0.199	0.795	6.8	37.4	3.61	0.067	6.2	35.6	3.63	0.075
0.013	0.395	0.592	13.6	17.4	1.91	0.047	12.7	17.8	1.89	0.050
0.037	0.386	0.577	20.4	11.7	1.42	0.037	18.9	12.4	1.36	0.038
0.060	0.377	0.563	27.2	8.94	1.19	0.033	25.1	9.62	1.09	0.032
0.084	0.366	0.550	34.0	7.25	1.02	0.030	31.8	7.75	0.911	0.028
0.108	0.356	0.536	40.8	6.12	0.899	0.029	38.7	6.48	0.794	0.027
0.155	0.336	0.509	54.4	4.71	0.759	0.029	52.7	4.94	0.658	0.025
0.198	0.320	0.482	68.0	3.86	0.688	0.031	66.4	4.04	0.587	0.026

TABLE 8

Comparison of Liquid and Vapor Molar Volume Predictions with Experimental Data

System	T(K)	P(atm), max	No. of data points	ΔV^l% AAPD (BIAS)	ΔV^v% AAPD (BIAS)	Ref.
Methane + octane	298–423	70	33	1.2 (−1.0)	—	Kohn and Bradish (*102*)
Methane + cyclohexane	294–444	277	54	1.8 (−1.5)	—	Reamer et al. (*103*)
Carbon dioxide + heptane	311–477	130	28	2.7 (2.4)	11.7 (8.1)	Kalra et al. (*99*)
Carbon dioxide + cyclohexane	473–533	100	31	6.0 (5.9)	14.5 (12.9)	Krichevskii and Sorina (*108*)
Hydrogen + cyclohexane	311–411	612	53	3.1 (−3.1)	—	Berty et al. (*112*)
Hydrogen sulfide + pentane	278–444	75	37	1.4 (0.7)	5.1 (0.3)	Reamer et al. (*113*)

TABLE 9

Comparison between Experimental Henry's Constants and Those Calculated by Fredenslund and Grauso (*120*)

System: Solvent–solute	T_1 (K)	ξ_{12}	η_{12}	$H_{1,2}$(calc), (atm)	$H_{1,2}$(expt), (atm)	Deviation (%)	Ref.
C_2H_6–CO_2	293.2	0.902	1.023	59.0	61.5	−4.2	Fredenslund and Mollerup (*121*)
CH_4–CO	137.1	0.980	1.005	36.8	32.8	10.9	Christiansen et al. (*89*)
	164.0			62.8	55.8	11.1	〃 〃 〃
	178.0			73.1	67.9	7.1	〃 〃 〃
Ar–Co	137.1	0.990	1.010	28.2	27.2	3.5	〃 〃 〃
CH_4–Ar	150.7	0.969	1.018	36.9	38.0	−3.0	〃 〃 〃
	164.0			48.8	42.0	13.9	〃 〃 〃
	178.0			60.4	56.5	6.5	〃 〃 〃
C_3H_8–CH_4	192.3	0.993	1.024	50.7	47.0	7.3	Wichterle and Kobayashi (*122*)
	213.7			74.0	73.8	0.3	〃 〃 〃
H_2S–CO	233.2	0.980	1.020	2380	2040	14.3	Fredenslund and Mollerup (*123*)
	263.2			1850	1924	−4.0	〃 〃 〃
	293.3			1450	1494	−3.0	〃 〃 〃
n-C_5H_{12}–CO_2	311.1	0.844	1.070	83	85	−2.4	Besserer and Robinson (*91*)
	344.2			114	118	−3.5	〃 〃 〃
	377.6			141	149	−5.7	〃 〃 〃
n-C_5H_{12}–N_2	311.1	0.960	1.020	607	608	−0.2	Robinson (*124*)
	344.2			578	576	0.3	〃 〃
	377.6			530	455	16.5	〃 〃
Mixed CH_4–Ar solvent:							
CH_4–Ar–Co[a]	137.1	[c]	[c]	29.3	31.4	−7.2	Christiansen and Fredenslund (*125*)
CH_4–Ar–CO[b]	137.1	[c]	[c]	27.8	27.0	2.9	〃 〃 〃

[a] $x_{CH_4} = 0.482$, $x_{Ar} = 0.518$, $x_{CO} = 0$, $P = 10$ atm.

[b] $x_{CH_4} = 0.138$, $x_{Ar} = 0.862$, $x_{CO} = 0$, $P = 20$ atm.

[c] ξ_{ij} and η_{ij} are those given above for the constituent binaries.

results are in excellent agreement with experimental data, as can be seen in Table 9. Henry's constants for carbon monoxide in a mixed solvent of argon and methane are included in the table. Mollerup et al. (*80*) calculated the Henry's constants as a function of temperature for several binary mixtures of nitrogen and an alkane up to pentane. Henry's constants at 1 atm are known for a few of the systems listed in Table 6. Using the values of $\zeta_{\alpha\beta}$ and $\eta_{\alpha\beta}$ determined from equilibrium ratios and bubble point pressures, Henry's constants were predicted for the following binary mixtures: methane + 1-methylnaphthalene, carbon dioxide + 1-methylnapthalene, and carbon dioxide + hexadecane. The predictions are compared with experimental data in Fig. 14.

Excess Gibbs Free Energies and Activity Coefficients

The excess Gibbs free energy of a solution is that free energy in excess of that of an ideal solution at the same temperature, pressure, and composition. The excess Gibbs free energy can be expressed in terms of total, configurational, or residual Gibbs free energies of the mixture and its pure components. One can thus write that

$$G^E[T, p, x] = G_m^{\text{res}}[T, p, x] - \sum_\alpha x_\alpha G_\alpha^{\text{res}}[T, p] \tag{83}$$

where

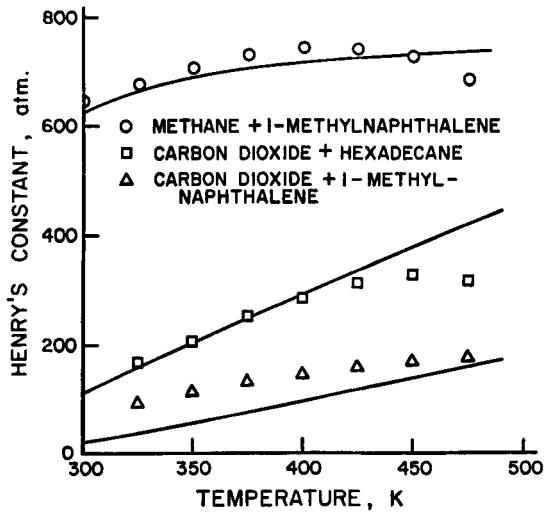

FIG. 14. Henry's constants as a function of temperature for several binary systems whose components differ greatly in size and shape: (○) Chappelow and Prausnitz (*126*), (△) Tremper and Prausnitz (*127*).

$$G_\alpha^{res} = G_\alpha^{conf} - G_{-\alpha}^{conf,P.G.}$$
$$= f_{\alpha\alpha,0} G_0[T/f_{\alpha\alpha,0}, ph_{\alpha\alpha,0}/f_{\alpha\alpha,0}] \quad (84)$$

and

$$G_m^{res} = \sum_\alpha x_\alpha \bar{G}_\alpha^{res} \quad (85)$$

The quantity $\bar{G}_\alpha^{res}$ is evaluated from Eq. (65). Activity coefficients are related to the excess Gibbs free energy by

$$G^E = RT \sum_\alpha x_\alpha \ln \gamma_\alpha \quad (86)$$

Differentiating this equation we find that

$$\ln \gamma_\alpha = \frac{1}{RT}\left(\frac{\partial(nG^E)}{\partial n_\alpha}\right)_{T,p,n_\beta} \quad (87)$$

Substituting Eq. (83) into Eq. (87), one finds that the activity coefficient of component α is obtained by subtracting the residual Gibbs free energy of pure fluid α from the residual Gibbs free energy of component α in the mixture at the same temperature and pressure (Mollerup and Fredenslund, *73*):

$$RT \ln \gamma_\alpha = \bar{G}_\alpha^{res}[T, p, x_\alpha] - G_\alpha^{res}[T, p] \quad (88)$$

Combining Eqs. (65), (84), and (88), the working equation for calculating activity coefficients is obtained:

$$RT \ln \gamma_\alpha = G_x + \left(\frac{DG_x}{Dx_\alpha}\right)_{T,p} - \sum_\beta x_\beta \left(\frac{DG_x}{Dx_\beta}\right)_{T,p}$$
$$- f_{\alpha\alpha,0} G_0[T/f_{\alpha\alpha,0}, ph_{\alpha\alpha,0}/f_{\alpha\alpha,0}] + RT \ln h_{\alpha\alpha,0} \quad (89)$$

Little work has been reported on the calculation of excess free energies and activity coefficients using the PCS methodology presented here. The calculation of excess properties is a severe test of a solution theory because the errors are magnified by the subtraction of numbers of equal orders of magnitude, such as in Eq. (83). However, because the shape factors are based on fugacity coefficient data (residual Gibbs free energies), reasonable estimates of excess free energies are expected for mixtures of hydrocarbons, primarily the lighter ones.

Activity coefficients for the mixtures argon + methane, ethane + ethylene, and ethylene + carbon dioxide have been calculated both in the normal and critical regions using the PCS (Mollerup and Fredenslund, *128*). The working equations have been presented by Mollerup and Fredenslund (*73*). A simple two-constant equation of state was used to calculate the configurational Gibbs energy and its derivatives with respect

to temperature and volume. The two equation of state constants were determined from data at one isotherm, and then used to predict activity coefficients at other temperatures. Although a simple equation of state was chosen to express the configurational Gibbs energy and its derivatives, the PVT behavior of the reference substance was represented by an equation of state given by Leach (*23*). The van der Waals two-fluid mixture model was used, and the unlike pair conformal parameters were given by Eqs. (47) and (48). Only one interaction parameter, $\zeta_{\alpha\beta}$, was used, and values for it were obtained from the literature. In the critical region the activity coefficients were correlated by the unsymmetric convention to avoid the use of hypothetical standard states. The calculated activity coefficients for the system argon + nitrogen were found to be in close agreement with the data. The agreement for the other two systems was not as good. Also, the values of $\zeta_{\alpha\beta}$ were found to be temperature dependent. To avoid the errors incurred when experimental data are converted to activity coefficients, Mollerup (*129*) calculated the equilibrium ratios for several simple mixtures (argon + nitrogen, methane + carbon monoxide, argon +

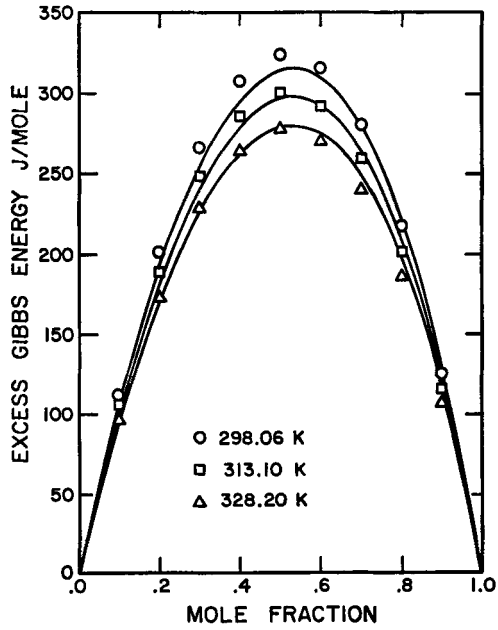

FIG. 15. Calculated excess Gibbs free energies for the system benzene (l) + cyclohexane as a function of the mole fraction of benzene compared with the experimental data of Mentzer (*119*). The curves represent the calculations with $\zeta = 0.973$ and $\eta = 1.095$.

methane, and argon + carbon monoxide) using the same methodology. The correlation of K-values on one isotherm yielded two temperature-independent equation of state constants which accurately predicted the data on other isotherms. This procedure, however, was found to give less satisfactory results for systems containing larger molecules.

We have correlated the activity coefficients and excess Gibbs free energies of several binary mixtures of hydrocarbons, with from six to eight carbon atoms, using the van der Waals one-fluid model. The configurational Gibbs energies required in Eqs. (83) and (89) were determined directly from the equation of state for the reference (METHERM4). Two interaction parameters were used to characterize each binary pair. Calculated excess Gibbs energies for the system benzene + cyclohexane are compared with the experimental data of Mentzer (*119*) in Fig. 15. The calculated and experimental activity coefficients at 39.95°C are shown in Fig. 16. Recalling that data for neither benzene nor cyclohexane were used in the evaluation of the shape factors, the calculations are seen to

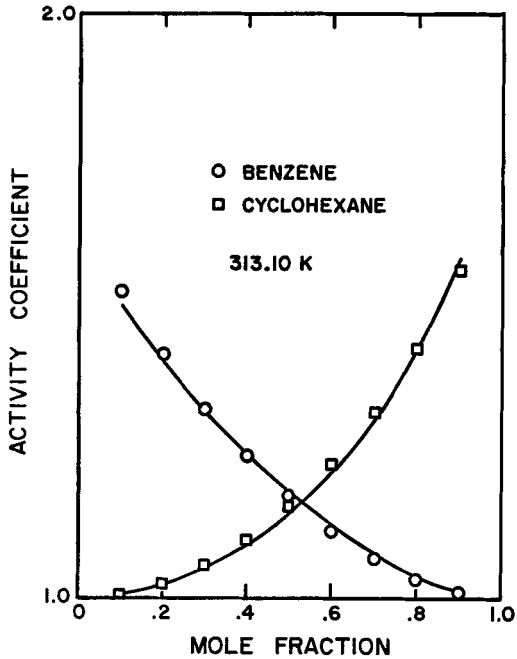

FIG. 16. Calculated activity coefficients for the system benzene(l) + cyclohexane as a function of the mole fraction of benzene compared with the data of Mentzer (*119*). The curves represent the calculations with $\zeta = 0.973$ and $\eta = 1.095$.

be quite good. Experience has shown, however, that in general the PCS cannot correlate excess Gibbs free energies over a large temperature range with two temperature-independent interaction parameters. In Fig. 17 calculated excess Gibbs energies for the system benzene + *n*-heptane are compared with the experimental data of Werner and Schuberth (*130*), Fu and Lu (*131*), and Brown (*132*) at 20.0, 75.0, and 80.0°C, respectively. The calculations do not exhibit the correct temperature dependence over this larger temperature range. Although the use of temperature-dependent interaction parameters would result in better agreement between the calculations and data, this remedy to the problem is artificial. At least part of the problem lies in the inability of the PCS to precisely predict the Gibbs free energies of the pure components (Mentzer, *119*). The values of ζ and η, which on a theoretical level should solely reflect the unlike pair interactions, in practice are influenced by both the errors in the prediction of the pure fluid properties and the unlike pair interactions. The PCS with shape factors is only capable of accurately correlating the activity coeffi-

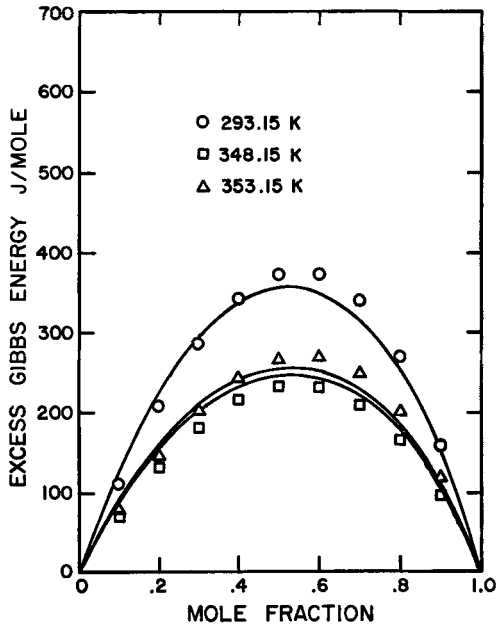

FIG. 17. Calculated excess Gibbs free energies for the system benzene(l) + *n*-heptane as a function of the mole fraction of benzene compared with the data of Werner and Schuberth (*130*) at 293.15 K, Fu and Lu (*131*) at 348.15 K, and Brown (*132*) at 353.15 K. The curves represent the calculations with $\zeta = 0.963$ and $\eta = 1.191$.

cients and excess Gibbs free energies of mixtures of this type over a narrow temperature range.

The PCS with shape factors has been used to correlate excess Gibbs energies and activity coefficients for binary mixtures which contain a polar component. Preferably the polar components should not associate. Calculated excess Gibbs free energies for the system methyl ethyl ketone + ethylbenzene from 55.0 to 75.0°C are compared with the experimental data of Kraus and Linek (*133*) in Fig. 18. The activity coefficients at 65.0°C are shown in Fig. 19. The agreement between the calculations and data is quite good. Mentzer (*119*) found that although the excess free energies and activity coefficients of several polar binary mixtures could be correlated over a narrow temperature range, quite often the composition dependence of the free energies was not correctly represented with the one-fluid van der Waals mixing rules.

Excess Gibbs free energies for mixtures of simple molecules have been correlated by Wheeler and Smith (*77*), Calvin and Smith (*134*), and Houng and Smith (*135*) using a model based on conformal solution theory.

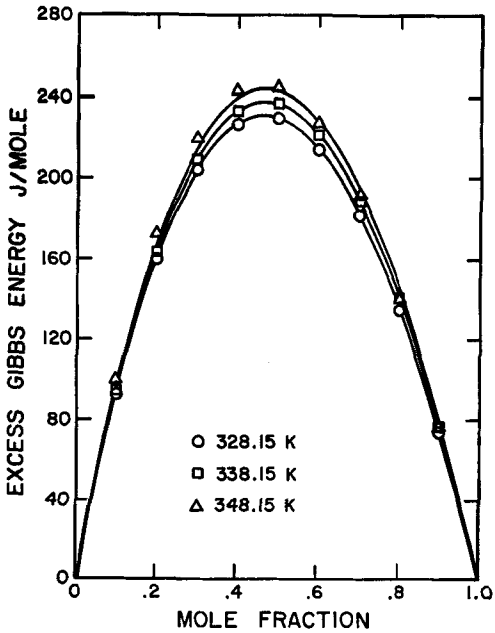

FIG. 18. Calculated excess Gibbs free energies for the system methyl ethyl ketone(l) + ethylbenzene as a function of the mole fraction of methyl ethyl ketone compared with the data of Kraus and Linek (*133*). The curves represent the calculations with $\zeta = 0.975$ and $\eta = 1.058$.

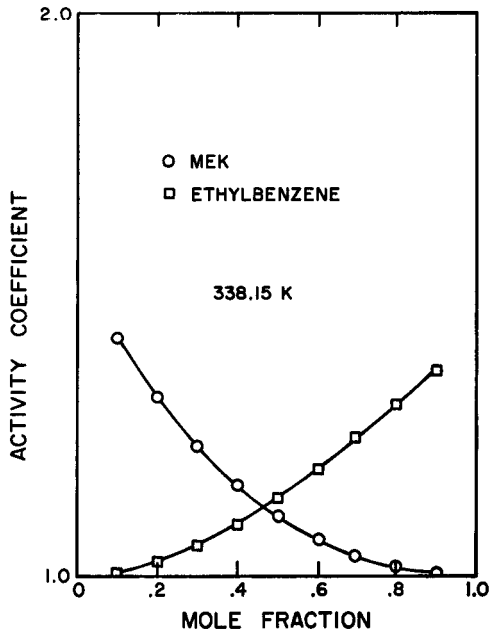

FIG. 19. Calculated activity coefficients for the system methyl ethyl ketone(l) + ethylbenzene as a function of the mole fraction of methyl ethyl ketone compared with the data of Kraus and Linek (*133*). The curves represent the calculations with $\zeta = 0.975$ and $\eta = 1.058$.

While Wheeler and Smith (*77*) expressed the pure component conformal parameters in terms of the critical properties of the fluid of interest and reference fluid, the latter two studies found them to vary with temperature and used enthalpy and density data for their evaluation. The working equation for calculating the excess Gibbs energy was written as a Taylor series expansion about the reference substance in terms of the conformal parameters. Calvin and Smith (*134*) and Houng and Smith (*135*) also correlated excess enthalpies and volumes using Taylor series expansions as the working equations. The difficulty in using an expression of this type is that the conformal parameters must be near unity for the series to converge. The reference substance must therefore by quite similar in nature to the components of interest, which requires an extensive tabulation of physical property data for several reference substances. This procedure was improved upon by Yuan et al. (*28*). The Taylor series expansions were abandoned and excess properties were calculated by subtracting the ideal solution contribution from the contribution of the mixture—as for the excess Gibbs energy in Eq. (83). Excess enthalpies and volumes, as well

as Gibbs free energies, were correlated for several mixtures. The procedure is similar in nature to that of the shape factor approach. However, the pure fluid conformal parameters are not generalized and must be determined from data in terms of fugacities and densities. The pure fluid contributions to the excess free energy and volume are obtained essentially from experimental data. This methodology emphasizes the description of the mixture, and results in an excellent correlation of excess properties since the pure fluid contributions are known accurately. Yuan et al. (*28*) and Stookey and Smith (*136*) used the van der Waals one-fluid model to correlate the excess properties of mixtures of molecules in the C_6 to C_7 boiling range.

The unlike pair conformal parameters were characterized by Eqs. (47) and (48), and the two interaction parameters, $\zeta_{\alpha\beta}$ and $\eta_{\alpha\beta}$, were found to be temperature dependent. An Arrhenius-type function was assumed for each interaction parameter, resulting in four parameters per binary pair. These correlation constants can be determined either from excess free energies and volumes or from excess enthalpies and volumes (Stookey and Smith, *136*). Benzene was primarily used as the reference substance, since it is similar in size to the molecules of interest and is often one of the components of the mixture. In general, the excess properties were correlated to within their experimental uncertainty. That the excess enthalpies are correlated accurately indicates that the temperature dependence of the excess free energies is represented well. Palmer et al. (*35*) used the same procedure to correlate the excess properties of a partially miscible system containing a polar compound: acetonitrile + benzene + heptane. The van der Waals mixing rules were found not to hold for polar fluids, and the general weighting function approach discussed earlier was used. The values of S in the weighting functions w_f and w_h were obtained from the radius of gyration, and the values of I were determined from an identifiable bond model for those molecular pairs with special interactions. An Arrhenius-type function was used to express the temperature dependence of the interaction parameters, as before. To summarize, this methodology is most promising for the correlation of excess properties. Unfortunately, the method is not generalized and an excessive amount of pure fluid data is required. Hopefully, generalized correlations of the pure fluid conformal parameters will be developed such that pure fluid properties can be determined with a high degree of accuracy. In comparing this procedure with that involving shape factors, one finds that:

(a) The conformal parameters in the former method do not have a composition dependence or density dependence, while the shape factors do.

(b) The former procedure uses temperature-dependent interaction parameters while the latter does not.

Enthalpies

Enthalpies can either be calculated through the use of second-order shape factors or via the first-order shape factors and their derivatives with respect to temperature. In practice, the latter procedure has been used most often, since the shape factor expressions are easily differentiated.

The residual enthalpy of a mixture is equal to the configurational enthalpy minus the configurational enthalpy of a perfect gas:

$$\begin{aligned} H_m^{\text{res}} &= H_m - RT \\ &= U_m + pV - RT \end{aligned} \tag{90}$$

The internal energy and Helmholtz energy are related as follows:

$$U_m = A_m - T\left(\frac{\partial A_m}{\partial T}\right)_v \tag{91}$$

From Eqs. (45), (46), and the relation $G = A + pV$, an expression for the Helmholtz energy of the mixture is obtained:

$$A_m[T, V, x] = A_x[T, V, x] + RT\sum_\alpha x_\alpha \ln x_\alpha \tag{92}$$

$$A_x[T, V, x] = f_{x,0}A_0[T/f_{x,0}, V/h_{x,0}] - RT\ln h_{x,0} \tag{93}$$

Combining Eqs. (91) and (92), an expression for U_m in terms of A_x is obtained:

$$U_m = A_x - T\left(\frac{\partial A_x}{\partial T}\right)_v \tag{94}$$

The derivative required in Eq. (94) is obtained by differentiating Eq. (93):

$$\left(\frac{\partial A_x}{\partial T}\right)_v = -S_0 + U_0\left(\frac{\partial f_{x,0}}{\partial T}\right)_v + (p_0V_0 - RT_0)\frac{f_{x,0}}{h_{x,0}}\left(\frac{\partial h_{x,0}}{\partial T}\right)_v - R\ln h_{x,0} \tag{95}$$

where S_0 is the configurational entropy of the reference substance. Combining Eqs. (90) and (93)–(95), the working equation for calculating residual enthalpies is obtained (Mollerup, *29*):

$$\frac{H_m^{\text{res}}}{RT} = \frac{U_0}{RT_0}\left[1 - T_0\left(\frac{\partial f_{x,0}}{\partial T}\right)_v\right] + (z_0 - 1)\left[1 - \frac{T}{h_{x,0}}\left(\frac{\partial h_{x,0}}{\partial T}\right)_v\right] \tag{96}$$

Residual enthalpies for both pure components and mixtures are calculated from this equation. Quite often the enthalpies for mixtures are given in

the literature as excess enthalpies. These are calculated from Eq. (96) as

$$H^E = H_m^{res} - \sum_\alpha x_\alpha H_\alpha^{res} \tag{97}$$

The derivatives of the conformal parameters with respect to temperature at constant volume have been determined by Mollerup (*48*) in terms of the one-fluid van der Waals model:

$$\left(\frac{\partial h_{x,0}}{\partial T}\right)_v = \sum_\alpha \sum_\beta x_\alpha x_\beta \left(\frac{\partial h_{\alpha\beta,0}}{\partial T}\right)_v \tag{98}$$

$$\left(\frac{\partial f_{x,0}}{\partial T}\right)_v h_{x,0} + \left(\frac{\partial h_{x,0}}{\partial T}\right)_v f_{x,0} = \sum_\alpha \sum_\beta x_\alpha x_\beta \left[h_{\alpha\beta,0}\left(\frac{\partial f_{\alpha\beta,0}}{\partial T}\right)_v + f_{\alpha\beta,0}\left(\frac{\partial h_{\alpha\beta,0}}{\partial T}\right)_v\right] \tag{99}$$

The derivatives of the unlike pair conformal parameters with respect to temperature are determined from Eqs. (70) and (71):

$$\left(\frac{\partial h_{\alpha\beta,0}}{\partial T}\right)_v = \frac{h_{\alpha\beta,0}}{\phi_{\alpha\beta,0}}\left(\frac{\partial \phi_{\alpha\beta,0}}{\partial T}\right)_v \tag{100}$$

$$\left(\frac{\partial f_{\alpha\beta,0}}{\partial T}\right)_v = \frac{f_{\alpha\beta,0}}{\theta_{\alpha\beta,0}}\left(\frac{\partial \theta_{\alpha\beta,0}}{\partial T}\right)_v \tag{101}$$

The derivatives of the shape factors with respect to temperature are determined by the chain rule of partial differentiation:

$$\left(\frac{\partial \phi_{\alpha\beta,0}}{\partial T}\right)_v = \left(\frac{\partial \phi_{\alpha\beta,0}}{\partial V^R_{\alpha\beta,0}}\right)_{T^R_{\alpha\beta,0}}\left(\frac{\partial V^R_{\alpha\beta,0}}{\partial T}\right)_v + \left(\frac{\partial \phi_{\alpha\beta,0}}{\partial T^R_{\alpha\beta,0}}\right)_{V^R_{\alpha\beta,0}}\left(\frac{\partial T^R_{\alpha\beta,0}}{\partial T}\right)_v \tag{102}$$

$$\left(\frac{\partial \theta_{\alpha\beta,0}}{\partial T}\right)_v = \left(\frac{\partial \theta_{\alpha\beta,0}}{\partial V^R_{\alpha\beta,0}}\right)_{T^R_{\alpha\beta,0}}\left(\frac{\partial V^R_{\alpha\beta,0}}{\partial T}\right)_v + \left(\frac{\partial \theta_{\alpha\beta,0}}{\partial T^R_{\alpha\beta,0}}\right)_{V^R_{\alpha\beta,0}}\left(\frac{\partial T^R_{\alpha\beta,0}}{\partial T}\right)_v \tag{103}$$

The partial derivatives of the unlike pair shape factors with respect to reduced volume and temperature are determined as described before—from Eqs. (70), (71), (76), and (77). Finally, partial derivatives of the reduced volume and temperature with respect to temperature are determined from

$$\frac{\left(\frac{\partial V^R_{\alpha\beta,0}}{\partial T}\right)_v}{V^R_{\alpha\beta,0}} = \frac{\left(\frac{\partial \phi_{\alpha\beta,0}}{\partial T}\right)_v}{\phi_{\alpha\beta,0}} - \frac{\left(\frac{\partial h_{x,0}}{\partial T}\right)_v}{h_{x,0}} \tag{104}$$

$$\frac{\left(\frac{\partial T^R_{\alpha\beta,0}}{\partial T}\right)_v}{T^R_{\alpha\beta,0}} = \frac{\left(\frac{\partial \theta_{\alpha\beta,0}}{\partial T}\right)_v}{\theta_{\alpha\beta,0}} - \frac{\left(\frac{\partial f_{x,0}}{\partial T}\right)_v}{f_{x,0}} + \frac{1}{T} \tag{105}$$

Equations (98)–(105) are solved analytically for $(\partial h_{x,0}/\partial T)_v$ and $(\partial f_{x,0}/\partial T)_v$.

Residual enthalpies have been calculated for mixtures of low molecular weight hydrocarbons by Leach et al. (*30*), Fisher et al. (*83*), and Fisher and Leland (*34*) using the van der Waals one-fluid model without any binary interaction parameters. The unlike pair conformal parameters were represented by Eqs. (47) and (60). For low temperature calculations the correction to Eq. (46) developed by Leach (*23*) was used. The following mixtures were studied: methane + propane, methane + pentane, methane + ethane + propane, and a natural gas mixture. The average deviation with experimental data was approximately 3 Btu/lb. As one might expect, the deviations decrease as the temperature is increased, pressure is decreased, or methane composition is increased.

Gunning (*33*) introduced one interaction parameter into the procedure for calculating enthalpies through Eq. (47). Equation (48) with $\eta_{\alpha\beta}$ set to unity was used to express the other unlike pair conformal parameter. Calculated configurational enthalpies of air and an equimolar mixture of methane and propane were found to be in good agreement with experimental data. Excess enthalpies were calculated for the system carbon dioxide + nitrogen and found to be in good agreement with experimental data except at high pressures where the excess enthalpy rises rapidly.

Using the binary interaction parameters determined from bubble point pressures and liquid densities, Mollerup has calculated the residual enthalpies of several mixtures (Mollerup, *29*, *48*; Mollerup and Fredenslund, *87*) of light components. Predicted residual enthalpies for the system methane + propane and the ternary mixture methane + ethane + propane are in excellent agreement with experimental data. In Fig. 20 the excess enthalpies calculated by Mollerup (*29*) for mixtures of methane and nitrogen at two different compositions are compared with the experimental data of Eijnsbergen and Beenakker (*137*). The predicted enthalpies agree quite well with the experimental data. For mixtures of light components (natural gas mixtures), calculated liquid phase enthalpies are generally accurate to 1 Btu/lb and vapor phase enthalpies with negligible error.

We have calculated the excess enthalpies for several binary mixtures of hydrocarbons with from six to eight carbon atoms (Mentzer, *119*). Since the temperature dependence of the calculated excess Gibbs free energies for systems of this type was found to be incorrect, and enthalpies are related to the temperature derivative of the Gibbs free energy, accurate excess enthalpy predictions are not expected. In Fig. 21 the predicted excess enthalpies for the system benzene + cyclohexane are compared with the experimental data of Savini et al. (*138*) and Nicholson (*139*) at 25.0 and 90.0°C, respectively. The binary interaction parameters determined from the excess Gibbs free energy data shown in Fig. 15 were used in the

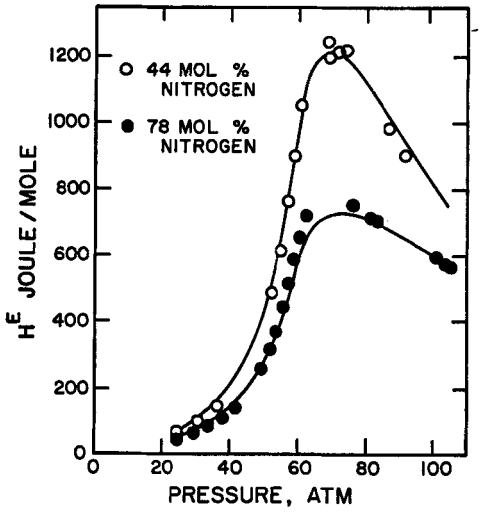

FIG. 20. The excess enthalpy calculations of Mollerup (*29*) for two mixtures of methane and nitrogen at 201.2 K compared with the experimental data by Eijnsbergen and Beenakker (*137*).

calculations. Although the calculations are of the correct order of magnitude, they do not have the correct temperature dependence. The calculations are only marginally improved if the interaction parameters are chosen so as to give a best fit of the excess enthalpy data. To accurately correlate the excess enthalpies at several temperatures, different values of $\zeta_{\alpha\beta}$ and $\eta_{\alpha\beta}$ must be used to represent each isotherm. The conformal solution model developed by Yuan et al. (*28*) is capable of correlating the excess enthalpies for mixtures of this type very accurately.

Joule-Thomson Coefficients

The calculation of Joule-Thomson coefficients from the PCS with shape factors has been examined by Gunning (*33*). A finite difference technique was used to evaluate the coefficients. Adiabatic Joule-Thomson coefficients were calculated for air, and isothermal Joule-Thomson coefficients were calculated for the ternary system methane + ethane + nitrogen. The predictions were found to be in good agreement with available experimental data.

Transport Properties

Leach et al. (*30*) have used the shape factor equations and the generalized

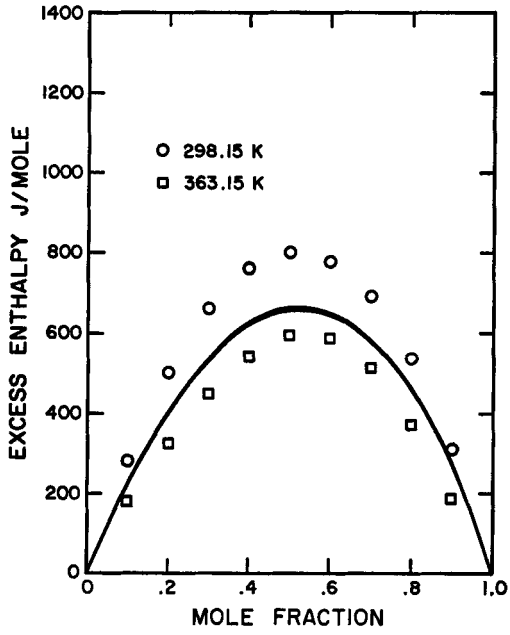

FIG. 21. Calculated excess enthalpies for the system benzene + cyclohexane as a function of the mole fraction of benzene compared with the data of Savini et al. (*138*) and Nicholson (*139*). The interaction parameters were determined from excess Gibbs free energy data.

correlation presented by Hirschfelder et al. (*38*) to calculate viscosities. Shape factors multiplied by the appropriate critical constants and the van der Waals mixing rules were used to determine effective intermolecular parameters which are required in the correlation. The viscosity of a mixture of hydrogen and nitrogen was calculated to within about 1%.

Haile et al. (*43*) and Murad and Gubbins (*44*) used the van der Waals one-fluid model and mixing rules for the reduced mass developed from the Enskog dense gas theory to calculate, respectively, the viscosities and thermal conductivities of mixtures. In the viscosity calculations one unlike pair interaction parameter ($\zeta_{\alpha\beta}$) was used, while two interaction parameters ($\zeta_{\alpha\beta}$ and $\eta_{\alpha\beta}$) were required in the thermal conductivity calculations. In each of the developments, shape factors are defined which enable one to calculate the viscosities and thermal conductivities of pure fluids and mixtures from those of a reference, methane. Viscosities were calculated for hydrocarbon mixtures and a typical LNG mixture. The standard deviation between experimental and calculated values was about 2% for equimolar mixtures. Thermal conductivities of dense gas mixtures were calculated to within about $\pm 4\%$. Both viscosity and thermal conductivity

calculations were found to be poor for mixtures containing strongly polar compounds. The van der Waals mixing rules do not express the correct composition dependence for mixtures of strongly polar molecules.

CONCLUSION

The shape factor method of PCS can predict a variety of thermodynamic properties of fluids and their mixtures. For pure fluid calculations only the critical properties and acentric factor need be known, while for mixture calculations at most two interaction parameters are required per binary pair. The calculations are best for the lower molecular weight hydrocarbons, which are similar to the reference substance, methane. In general, the more a molecule deviates in size and shape from that of methane, the less accurate the calculations. The thermodynamic behavior of pure polar substances which do not associate can also be calculated, although not to quite the same accuracy as nonpolar compounds.

Most thermodynamic properties can be calculated to within their experimental uncertainty for relatively light molecules and their mixtures, except for mixtures containing hydrogen. Liquid densities for mixtures of the lower molecular weight hydrocarbons are in excellent agreement with experimental data. Equilibrium ratios, enthalpies, and Henry's constants for these mixtures can also be calculated accurately, but the differentiations required in the calculations result in a loss of accuracy. As the components of the mixture become more dissimilar, the accuracy of the calculations decreases.

The shape factor approach is not well-suited for the correlation of excess Gibbs free energies, excess enthalpies, and activity coefficients. Although these properties can be calculated fairly well for mixtures of light molecules, the accuracy decreases with an increase in molecular size. The conformal solution approach of Yuan et al. (*28*) is an excellent model for the correlation of excess free energies, enthalpies, and volumes, but must be generalized for it to find widespread use.

Acknowledgement

Financial support for this work by the National Science Foundation through Grant ENG 79-12455 is gratefully acknowledged.

SYMBOLS

A (configurational) Helmholtz energy
B second virial coefficient

D differentiation in which the mole fractions are treated as independent
f corresponding states parameter or fugacity
G (configurational) Gibbs free energy
h corresponding states parameter or Planck's constant
H (configurational) enthalpy
k Boltzmann's constant
K equilibrium ratio
m weight of a molecule
n number of moles
N number of molecules
p pressure
Q partition function
r coordinate
R gas constant
S (configurational) entropy
T temperature
U energy of arbitrary configuration
U (configurational) energy
V volume
x mole fraction
y vapor mole fraction
z compressibility

Greek Letters

ε intermolecular energy
ξ, η binary interaction parameters
θ, ϕ shape factors
σ characteristic intermolecular distance
ω acentric factor
λ thermal conductivity

Subscripts

α, β, i, j components
m mixture
0 reference substance
s saturated
t liquid triple point
x pseudofluid

Superscripts

c	critical state
conf	configurational
ext	external
E	excess property
int	internal
l	liquid
P.G.	perfect gas
res	residual
R	reduced
v	vapor
–	partial molar property

REFERENCES

1. L. Riedel, *Chem.-Ing.-Tech.*, *26*, 83 (1954).
2. A. L. Lydersen, R. A. Greenkorn, and O. A. Hougen, *A Generalized Correlation of Thermodynamic Properties of Pure Fluids*, Engineering Experimental Station Report No. 4, University of Wisconsin, Madison, 1955.
3. T. W. Leland, Jr., P. S. Chappelear, and B. W. Gamson, *AIChE J.*, *8*, 482 (1962).
4. K. S. Pitzer, D. Z. Lippmann, R. F. Curl, Jr., C. M. Huggins, and D. E. Petersen, *J. Am. Chem. Soc.*, *77*, 3433 (1955).
5. L. L. Lee and K. E. Starling, *Three-Parameter Conformal Solution Theory for Light Hydrocarbon, Vapor–Liquid Equilibria*, 70th Annual Meeting of the American Institute of Chemical Engineers, New York, November 13–17, 1977, Paper 82b.
6. T. W. Leland, Jr., R. Kobayashi, and W. H. Mueller, *AIChE J.*, *7*, 535 (1961).
7. R. D. Gunn, P. L. Chueh, and J. M. Prausnitz, *Ibid.*, *12*, 937 (1966).
8. P. T. Eubank and J. M. Smith, *Ibid.*, *8*, 117 (1962).
9. R. L. Halm and L. I. Stiel, *Ibid.*, *13*, 351 (1967).
10. J. P. O'Connell and J. M. Prausnitz, *Ind. Eng. Chem., Process Des. Dev.*, *6*, 245 (1967).
11. E. A. Harlacher and W. G. Braun, *Ibid.*, *9*, 479 (1970).
12. T. W. Leland, Jr., and P. S. Chappelear, *Ind. Eng. Chem.*, *60*, 15 (1968).
13. K. E. Gubbins, *AIChE J.*, *19*, 684 (1973).
14. J. S. Rowlinson, *Chem. Eng. (London)*, *291*, 718 (1974).
15. J. Rowlinson, "Prediction of Thermodynamic Properties," in *Phase Equilibria and Fluid Properties in the Chemical Industry* (T. S. Storvick and S. I. Sandler, eds.), ACS Symposium Series, American Chemical Society, Washington, D.C., 1977.
16. K. C. Chao and R. A. Greenkorn, *Thermodynamics of Fluids*, Dekker, New York, 1975.
17. J. S. Rowlinson, *Liquids and Liquid Mixtures*, 2nd ed., Butterworths, London, 1969.
18. K. S. Pitzer, *J. Chem. Phys.*, *7*, 583 (1939).
19. T. M. Reed and K. E. Gubbins, *Applied Statistical Mechanics*, McGraw-Hill, New York, 1973.

20. J. A. Pople, *Proc. R. Soc. London, A221*, 498 (1954).
21. D. Cook and J. S. Rowlinson, *Ibid., A219*, 405 (1953).
22. G. S. Rushbrooke, *Trans. Faraday Soc., 36*, 1055 (1940).
23. J. W. Leach, "Molecular Structure Corrections for Application of the Theory of Corresponding States to Non-Spherical Pure Fluids and Mixtures," Ph.D. Thesis, Rice University, Houston, Texas, 1967.
24. L. L. Gilbert, "Molecular Structure Effects on the Theory of Corresponding States," M. S. Thesis, Rice University, Houston, Texas, 1963.
25. M. L. McGlashan and D. J. B. Potter, *Proc. R. Soc. London, A267*, 478 (1962).
26. J. W. Leach, P. S. Chappelear, and T. W. Leland, *AIChE J., 14*, 568 (1968).
27. J. S. Rowlinson and I. D. Watson, *Chem. Eng. Sci., 24*, 1565 (1969).
28. I. C. Yuan, D. A. Palmer, and B. D. Smith, *Ind. Eng. Chem., Fundam., 11*, 387 (1972).
29. J. Mollerup, *Adv. Cryog. Eng., 20*, 172 (1975).
30. J. W. Leach, P. S. Chappelear, and T. W. Leland, Jr., *Proc. Am. Pet. Inst., Div. Refining, 46*, 223 (1966).
31. J. Mollerup and J. S. Rowlinson, *Chem. Eng. Sci., 29*, 1373 (1974).
32. F. B. Canfield and A. J. Gunning, *Ibid., 26*, 1136 (1971).
33. A. J. Gunning, "Prediction of the Thermodynamic Properties of Multicomponent Mixtures," Ph.D. Thesis, University of London, 1972.
34. G. D. Fisher and T. W. Leland, Jr., *Ind. Eng. Chem., Fundam., 9*, 537 (1970).
35. D. A. Palmer, I. C. Yuan, and B. D. Smith, *Ibid., 11*, 397 (1972).
36. G. D. Fisher and T. W. Leland, "Application of Two-Fluid Method with the Corresponding States Principle," in *National Gas Processors Association, Proceedings of the Annual Convention*, 1969, Technical Paper 48, p. 57.
37. A. J. Vennix and R. Kobayashi, *AIChE J., 15*, 926 (1969).
38. J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids*, Wiley, New York, 1954.
39. A. S. Teja and J. S. Rowlinson, *Chem. Eng. Sci., 28*, 529 (1973).
40. A. S. Teja and P. Rice, *J. Chem. Eng. Data, 21*, 173 (1976).
41. E. Bender, *Kaltetechnik-Klimatisierung, 23*, 258 (1971).
42. R. D. McCarty, *Cryogenics, 14*, 276 (1974).
43. J. M. Haile, K. C. Mo and K. E. Gubbins, *Adv. Cryog. Eng., 21*, 501 (1976).
44. S. Murad and K. E. Gubbins, *Chem. Eng. Sci., 32*, 499 (1977).
45. R. D. McCarty, *A Comparison of Mathematical Models for the Prediction of LNG Densities*, Interagency Report NBSIR 77-867, National Bureau of Standards (U. S.), 1977.
46. R. D. Goodwin, *Natl. Bur. Stand. (U.S.), Rep. 10*, 715 (1971).
47. R. D. Goodwin, *Natl. Bur. Stand. (U.S.), Tech. Note 653* (1974).
48. J. Mollerup, *Adv. Cryog. Eng., 23*, 550 (1978).
49. R. D. Goodwin, "The Nonanalytic Equation of State for Pure Fluids Applied to prepare," in *Equations of State in Engineering and Research* (K. C. Chao and R. L. Robinson, eds.), Advances in Chemistry Series, American Chemical Society, Washington, D.C., 1979.
50. G. A. Chapela-Castañares and T. W. Leland, *AIChE Symp. Ser., 70*, 48 (1974).
51. B. Sage and W. Lacey, *API Research Project 37: Thermodynamic Properties of the Lighter Paraffin Hydrocarbons and Nitrogen*, American Petroleum Institute, New York, 1950.
52. A. J. Gunning and J. S. Rowlinson, *Chem. Eng. Sci., 28*, 521 (1973).
53. J. Mollerup, *Densities of Liquified Natural Gas and Related Mixtures*, Paper

Presented at the CHISA '75 Conference in Praha, Czechoslovakia, August 1975.
54. J. Mollerup, *Ber. Bunsenges. Phys. Chem.*, *81*, 1015 (1977).
55. R. A. Mentzer, R. A. Greenkorn, and K. C. Chao, *The Extended Principle of Corresponding States and Vapor–Liquid Equilibria of Molecular Fluids, and Their Mixtures with Light Gases*, Paper Presented at the 72nd Annual Meeting of the American Institute of Chemical Engineers, San Francisco, November 27, 1979.
56. J. Timmermans, *Physico-Chemical Constants of Pure Organic Compounds*, Elsevier, New York, 1950.
57. American Petroleum Institute Project 44, *Selected Values of Properties of Hydrocarbons and Related Compounds*, Carnegie Press, Pittsburgh, 1953.
58. *International Critical Tables*, Vol. III, McGraw-Hill, New York, 1928.
59. J. J. Simnick, H. M. Sebastian, H. M. Lin, and K. C. Chao, *J. Chem. Eng. Data*, *23*, 339 (1978).
60. A. Singh and A. S. Teja, *Chem. Eng. Sci.*, *31*, 404 (1976).
61. E. F. Meyer and R. E. Wagner, *J. Phys. Chem.*, *70*, 3162 (1966).
62. B. Sage and W. Lacey, *API Research Project 37: Some Properties of the Lighter Hydrocarbons, Hydrogen Sulfide, and Carbon Dioxide*, American Petroleum Institute, New York, 1955.
63. H. M. Sebastian, J. J. Simnick, H. M. Lin, and K. C. Chao, *J. Chem. Eng. Data*, *23*, 305 (1978).
64. J. S. Lumdsen, *J. Chem. Soc.*, *91*, 28 (1907).
65. J. J. Simnick, H. M. Sebastian, H. M. Lin, and K. C. Chao, *J. Chem. Thermodyn.*, *11*, 531 (1979).
66. Thermodynamic Research Center, Texas Experimental Station, Texas A&M University, College Station, Texas, *Thermodynamic Properties of Chemical Compounds of Importance to Processing Lignite*, July 15, 1977.
67. F. Din (ed.), *Thermodynamic Functions of Gases*, Vol. 1, Butterworths, London, 1956.
68. J. R. Roebuck, T. A. Murrell, and E. E. Miller, *J. Am. Chem. Soc.*, *64*, 400 (1942).
69. N. V. Tsederberg, *Thermal Conductivity of Gases and Liquids*, M.I.T. Press, Cambridge, Massachusetts, 1965.
70. R. C. Reid and T. W. Leland, *AIChE J.*, *11*, 228 (1965).
71. T. W. Leland, J. S. Rowlinson, and G. A. Sather, *Trans. Faraday Soc.*, *64*, 1447 (1968).
72. T. W. Leland, J. S. Rowlinson, G. A. Sather, and I. D. Watson, *Ibid.*, *65*, 2034 (1969).
73. J. Mollerup and A. Fredenslund, *Chem. Eng. Sci.*, *28*, 1285 (1973).
74. V. F. Yesavage, "The Measurement and Prediction of the Enthalpy of Fluid Mixtures under Pressure," Ph.D. Dissertation, University of Michigan, Ann Arbor, 1968.
75. D. W. Johnson and C. P. Colver, in *Proceedings of the Natural Gas Processors Association, 49th Annual Convention*, 1970, p. 19.
76. K. S. Starling, *Ibid.*, p. 9.
77. J. D. Wheeler and B. D. Smith, *AIChE J.*, *13*, 303 (1967).
78. V. Plöcker, H. Knapp, and J. Prausnitz, *Ind. Eng. Chem., Process Des. Dev.*, *17*, 324 (1978).
79. A. S. Teja, *Ind. Eng. Chem., Fundam.*, *18*, 435 (1979).
80. J. Mollerup, A. Fredenslund, and L. Grauso, *Prediction of SNG, LPG, and LNG Thermodynamic Properties*, Paper Presented at the Centennial American Chemical Society Meeting, New York, April 1976.

81. J. Mollerup, Instituttet for Kemiteknik, Danmarks Tekniske Hojskole, Private Communication, July 19, 1978.
82. P. S. Chappelear, J. W. Leach, and T. W. Leland, "Thermodynamic Calculations on Paraffin Hydrocarbon Systems Currently Possible by the Rice Corresponding States Principle," *Proc. Nat. Gas Process. Assoc.*, *46*, 28 (1967).
83. G. D. Fisher, P. S. Chappelear, and T. W. Leland, "Some Results of Rice Corresponding States Computer Programs for *K*-Values and Thermodynamic Properties," in *Proceedings of the 47th Annual Convention of the Natural Gas Processors Association*, 1968, p. 27.
84. I. D. Watson and J. S. Rowlinson, *Chem. Eng. Sci.*, *24*, 1575 (1969).
85. A. Teja, Ph.D. Thesis, University of London, 1971.
86. J. Mollerup, "Thermodynamic Properties of LNG and LPG Mixtures," Paper Presented at the JABLONNA conference, November 1975.
87. J. Mollerup and A. Fredenslund, *Inst. Chem. Eng. Symp. Ser.*, *44*, 18 (1976).
88. J. Mollerup, A. Fredenslund, and L. Grauso, *Prediction of SNG, LPG, and LNG Thermodynamic Properties*, Paper Presented at the Centennial American Chemical Society Meeting in New York, April 1976.
89. L. J. Christiansen, A. Fredenslund, and J. Mollerup, *Cryogenics*, *13*, 405 (1973).
90. F. B. Sprow and J. M. Prausnitz, *AIChE J.*, *12*, 780 (1966).
91. G. J. Besserer and D. B. Robinson, *J. Chem. Eng. Data*, *18*, 416 (1973).
92. I. Wichterle and R. Kobayashi, *Ibid.*, *17*, 13 (1972).
93. J. R. Thomlinson, *NGPA Technical Publication TP-1*, Tulsa, Oklahoma, 1970.
94. D. B. Manley and G. W. Swift, *J. Chem. Eng. Data*, *16*, 301 (1971).
95. J. B. Rodosevich and R. C. Miller, *Adv. Cryog. Eng.*, *19*, 339 (1974).
96. M. A. Albright, *A Model for the Precise Calculation of Liquefied Natural Gas Densities*, NGPA Technical Publication TP-3, 1973.
97. J. Klosek and C. McKinley, "Densities of Liquefied Natural Gas and of Low Molecular Weight Hydrocarbons," in *Proceedings of the First International Conference on LNG*. IGT, Chicago, 1968.
98. H. H. Reamer and B. H. Sage, *J. Chem. Eng. Data*, *9*, 24 (1964).
99. H. Kalra, H. Kubota, D. B. Robinson, and H.-J. Ng, *Ibid.*, 23, 317 (1978).
100. J. F. Connolly, *J. Chem. Phys.*, *36*, 2897 (1962).
101. R. D. Gunn, J. J. McKetta, and N. Ata, *AIChE J.*, *20*, 347 (1974).
102. J. P. Kohn and W. F. Bradish, *J. Chem. Eng. Data*, *9*, 5 (1964).
103. H. H. Reamer, B. H. Sage, and W. N. Lacey, *Ind. Eng. Chem., Chem. Eng. Data Ser.*, *3*, 240 (1958).
104. J. J. Simnick, H. M. Sebastian, H. M. Lin, and K. C. Chao, *Fluid Phase Equil.*, *3*, 145 (1979).
105. H. M. Sebastian, J. J. Simnick, H. M. Lin, and K. C. Chao, *J. Chem. Eng. Data*, *24*, 149 (1979).
106. V. S. Mehra and G. T. Thodos, *Ibid.*, *10*, 211 (1965).
107. K. C. Chao and co-workers, Unpublished Data, Purdue University, School of Chemical Engineering, 1979.
108. I. R. Krichevskii and G. A. Sorina, *Russ. J. Phys. Chem.* (*Engl. Trans.*), *34*, 679 (1960).
109. D. B. Robinson and H.-J. Ng, *GPA Report RP-29*, 1978.
110. A. E. Klink, H. Y. Cheh, and E. H. Amick, Jr., *AIChE J.*, *21*, 1142 (1975).
111. J. F. Connolly and G. A. Kandalic, Paper Presented at the API 28th Midyear Meeting, Philadelphia, 1963, Paper 14–63.
112. T. E. Berty, H. H. Reamer, and B. H. Sage, *J. Chem. Eng. Data*, *11*, 25 (1966).

113. H. H. Reamer, B. H. Sage, and W. N. Lacey, *Ind. Eng. Chem.*, *45*, 1805 (1953).
114. H. H. Reamer, J. M. Fiskin, and B. H. Sage, *Ibid.*, *41*, 2871 (1949).
115. H. H. Reamer, B. H. Sage, and W. N. Lacey, *Ibid.*, *43*, 1436 (1951).
116. H. H. Reamer, B. H. Sage, and W. N. Lacey, *Ibid.*, *44*, 1671 (1952).
117. A. S. Teja, *AIChE J.*, *21*, 618 (1975).
118. A. S. Teja and H. W. Kropholler, *Chem. Eng. Sci.*, *30*, 435 (1975).
119. R. A. Mentzer, "Thermodynamic Properties of Fluids—Experimental Determination and Prediction Using the Principle of Corresponding States," Ph.D. Thesis, Purdue University, West Lafayette, Indiana, 1980.
120. A. Fredenslund and L. Graus, *Determination and Prediction of Henry's Constants*, Paper Presented at the IUPAC Fourth International Conference on Chemical Thermodynamics, Montpellier, France, 1975, Paper IV, p. 6.
121. A. Fredenslund and J. Mollerup, *J. Chem. Soc., Faraday Trans. 1.*, *20*, 1653 (1974).
122. I. Wichterle and R. Kobayashi, *J. Chem. Eng. Data*, *17*, 4 (1972).
123. A. Fredenslund and J. Mollerup, *J. Chem. Thermodyn. 7*, 677 (1975).
124. D. B. Robinson, Private Communication to A. Fredenslund and L. Graus 1973.
125. L. J. Christiansen and A. Fredenslund, *Cryogenics*, *14*, 10 (1974).
126. C. C. Chappelow III, and J. M. Prausnitz, *AIChE J.*, *20*, 1097 (1974).
127. K. K. Tremper and J. M. Prausnitz, *J. Chem. Eng. Data*, *21*, 295 (1976).
128. J. Mollerup and A. Fredenslund, *Chem. Eng. Sci.*, *28*, 1295 (1973).
129. J. Mollerup, *Chem. Eng. J.*, *6*, 23 (1973).
130. G. Werner and H. Schuberth, *J. Prakt. Chem.*, *31*, 225 (1966).
131. S. J. Fu and B. C.-Y. Lu, *J. Appl. Chem.*, *16*, 324 (1966).
132. I. Brown, *Aust. J. Sci. Res.*, *A*, *5*, 530 (1952).
133. J. Kraus and J. Linek, *Collect. Czech. Chem. Commun.*, *36*, 2547 (1971).
134. W. J. Calvin and B. D. Smith, *AIChE J.*, *17*, 191 (1971).
135. J. Houng and B. D. Smith, *Ibid.*, *17*, 1102 (1971).
136. D. Stookey and B. D. Smith, *Ind. Eng. Chem., Process Des. Dev.*, *12*, 372 (1973).
137. B. van Eijnsbergen and J. J. M. Beenakker, *Physica*, *39*, 499 (1968).
138. C. G. Savini, D. R. Winterhalter, L. H. Kovack, and H. C. Van Ness, *J. Chem. Eng. Data*, *11*, 40 (1966).
139. D. E. Nicholson, *Ibid.*, *6*, 5 (1961).

Received by editor March 22, 1980