Equation of State for Pure Fluids and Mixtures Based on a Truncated Virial Expansion

Andrzej Anderko and Kenneth S. Pitzer
Dept. of Chemistry and Lawrence Berkeley Laboratory, University of California, Berkeley, CA 94720

An accurate, yet simple, equation of state was developed for pure fluids ranging from nonpolar to H_2O and their mixtures. The equation consists of a virial expansion truncated after the fourth virial coefficient and a closed-form term approximating higher coefficients. For nonpolar or weakly polar compounds, the equation is generalized using critical temperature, critical pressure, and acentric factor. Despite its simplicity, the equation represents the P-V-T and saturation properties of pure fluids with a very good accuracy, which is comparable to that of multiparameter, generalized BWR-type equations. For mixture calculations, mixing rules were formulated based on the rigorously known composition dependence of virial coefficients. The equation represents vapor-liquid, gas-gas and liquid-liquid equilibria, as well as volumetric properties of mixtures containing nonpolar components and/or water. Binary parameters can be generalized for series of mixtures containing a common component.

Introduction

Equations of state (EOS) make it possible to represent phase equilibria, *P-V-T* relationships and other properties of pure fluids and mixtures in a compact analytical form. Although there have been efforts to establish mathematical forms of equations of state for over 100 years, a truly satisfactory and not-too-complex solution remains to be developed for wide ranges of temperature, pressure, composition, and molecular variety.

In general, the equation-of-state techniques fall into two classes. The first class encompasses simple, sometimes cubic with respect to volume, van der Waals-type equations. Equations of this type contain a small number (usually 2-4) of temperature-dependent or -independent parameters; if these are fitted to phase equilibrium data, the results for those data can be very accurate. However, the simple van de Waals-type equations are inherently incapable of reproducing the pressure-volume-temperature relationships over large ranges of the *P-V-T* variables. Their inadequacies can be noted especially in the critical and compressed liquid regions.

On the other hand, the multiparameter virial-type equations can reproduce the *P-V-T* properties of pure fluids with very good accuracy. However, extension of the multiparameter equations to mixtures is more difficult because the parameters do not have any clear physical meaning and are frequently strongly correlated with each other. The first method of extending the virial-type equations to mixtures consists of expressing each parameter as a function of composition on the basis of the rigorously known composition dependencies of the second and higher virial coefficients (Benedict et al., 1942; Starling and Han, 1972). However, due to the difficulties mentioned above, the resulting methods are in many cases inferior to the simple van der Waals-type equations when applied to phase equilibrium calculations in mixtures (c.f. a review of Oellrich et al., 1981). In the second widely used method, the equation of state for mixtures is expressed using composition-dependent scaling factors f_{mix} and h_{mix}:

$$z_{\text{mix}} = z\left[\frac{T}{f_{\text{mix}}}, \frac{v}{h_{\text{mix}}}\right] \tag{1}$$

where f_{mix} and h_{mix} are usually defined as quadratic functions of composition

$$f_{\text{mix}}h_{\text{mix}} = \sum_i \sum_j x_i x_j f_{ij} h_{ij} \tag{2}$$

$$h_{\text{mix}} = \sum_i \sum_j x_i x_j h_{ij} \tag{3}$$

and where f_{ij} and h_{ij} are, in general, related to the critical temperature and volume, respectively. It can be easily shown by substituting Eqs. 2-3 into Eq. 1 and employing any virial-type EOS with a realistic temperature dependence for z that the resulting expression will not satisfy the correct composition dependence derived from statistical mechanics for the second and possibly higher virial coefficients (see the Appendix for details). This defect becomes numerically important when the components differ greatly in critical temperature.

The above overview indicates that while the multiparameter virial-type equations of state are advantageous for pure fluids, they become less attractive when applied to mixtures. Therefore, it is worthwhile to examine the possibility of formulating an equation of state for both normal and complex fluids that can be extended to mixtures without violating the requirements of statistical mechanics. It is desirable that the equation be equally accurate for pure fluids and mixtures and its accuracy be comparable to that of multiparameter generalized equations of state.

To enhance the predictive capability of the equation of state, it is worthwhile to generalize it for nonpolar and weakly polar compounds. For this purpose, the acentric factor system (Pitzer, 1955; Pitzer et al., 1955) is very useful. Its success stems mainly from its theoretical background, which makes it possible to indicate the characteristics of molecules conforming to the acentric factor system, and the wide accessibility of experimental information about the slope of the vapor pressure curve, which is used to evaluate the value of the factor.

Numerous equations of state have been generalized using the acentric factor. Recently, Schreiber and Pitzer (1989) have presented a comprehensive acentric factor-based equation for pure fluids. A review (Anderko, 1990) provides a critical evaluation of different methods used in conjunction with the acentric factor system.

In this work, we develop a generalized equation of state for normal (nonpolar or weakly polar) fluids. The same equation can be used for polar fluids (with water as an example) using substance-specific rather than generalized parameters. The functional form of the equation facilitates the application of rigorous mixing rules derived from the virial expansion. The same mixing rules are used for mixtures containing only nonpolar components and for the highly demanding aqueous hydrocarbon mixtures.

Database for Pure Fluids

To establish the generalized equation of state, the database for pure fluids was limited to compounds that can be expected to conform to the three-parameter corresponding states principle. Accordingly, the quantum gases and hydrogen bonding, as well as strongly polar fluids, had to be excluded. For water (as a sample polar fluid), generalization was not attempted and the parameters were fitted individually to the properties of pure water generated from Hill's (1990) EOS. For most fluids, the database covered the reduced densities from 0 to 2.5-3.0, pressures from 0 to approximately 2,000 bar, and reduced temperatures from the triple point to 3, but not exceeding 1,000 K. The database included the saturation and near-critical regions.

As in a previous study (Schreiber and Pitzer, 1989), we used extensive *P-V-T* data for Ar, Kr, Xe, and all of the normal paraffins through octane. Several nonhydrocarbons were also included (for example, CO_2, CF_4, and SF_6). Critically evaluated data were used wherever available, such as those of Rabinovich et al. (1988) for Ar, Kr and Xe and of Younglove and Ely (1987) for alkanes through butane. The IUPAC evaluations were accepted for CO_2, N_2, and propylene (Angus et al., 1976, 1979, 1980). For hydrocarbons from nonane through hexadecane, the available data are less extensive, and therefore only vapor pressures and liquid densities were used. For several fluids (Ar, Kr, Xe, N_2, CH_4 through n-C_5H_{12}, C_7H_{16}, neo-C_5H_{12}, CO_2, CF_4, and SF_6), the data included critical and near-critical isotherms.

The data selected for this study are summarized in Table 1, as well as the values of the critical temperature T_c, critical pressure P_c, and acentric factor ω:

$$\omega = -\log_{10} P_r(\text{at } T_r = 0.7) - 1 \tag{4}$$

Equation of State for Pure Fluids

The equation of state for a pure fluid should be sufficiently flexible to reproduce the extensive *P-V-T* data. On the other hand, it should lend itself to the application of the rigorously known mixing rules derived from the virial expansion. Therefore, it seems advantageous to use explicitly the first few virial terms and to express the remaining terms using the Padé-type approximation. This concept is suited ideally for generalized equations of state, as it is known that various normal fluids accurately conform to the acentric factor system for reduced densities up to about 1.5. The acentric factor system remains a satisfactory approximation at higher reduced densities, but the accuracy is then somewhat lower. Therefore, higher-order virial terms of a generalized EOS can be somewhat less accurate. The above considerations suggest the following form:

$$z = \frac{1 + c\rho_r}{1 - b\rho_r} + \alpha\rho_r + \beta\rho_r^2 + \gamma\rho_r^3 \tag{5}$$

where ρ_r is the reduced density, and b, c, α, β, and γ are parameters. The first term on the righthand side of Eq. 5 resembles approximate forms of repulsive terms in van der Waals-type equations of state. For example, Kim et al. (1986) showed that an expression of similar form,

$$z = \frac{1 + 0.77(b/v)}{1 - 0.42(b/v)} \tag{6}$$

satisfactorily approximated the Carnahan-Starling (1969) expression for hard spheres. It should be noted, however, that the first term on the righthand side of Eq. 5 cannot be regarded as a purely repulsive term because its parameters are empirically adjusted together with the remaining parameters of the EOS.

The functional form of Eq. 5 is in some respects similar to some augmented van der Waals models available in the literature (Bienkowski et al., 1973; Behar et al., 1985; Orbey and Vera, 1986; Soave, 1990). The main difference lies in the evaluation of the parameters of Eq. 5 and, especially, in the method of extending the model to mixtures.

Following the procedure proposed by Schreiber and Pitzer (1989), the reduced density ρ_r for the normal fluids was calculated using T_c and P_c rather than ρ_c:

$$\rho_r = \rho(z_c^* R T_c / P_c) \tag{7}$$

Table 1. Pure-Component Database and Representation of Liquid Volumes V_L (for Reduced Densities $\rho_R > 1.8$), Vapor Pressures P_{sat}, and Pressures P outside saturation region (for $\rho_R < 1.8$)*

Fluid	Ref.	T_c, K	P_c, bar	ω	$\delta(V_L)$	$\delta(P_{sat})$	$\delta(P)$		
							This Study	Yamada (1973)	Schreiber & Pitzer (1989)
Argon	1-3	150.86	48.979	−0.004	1.85	0.58	1.17	0.71	0.46
Krypton	1	209.39	54.96	−0.002	0.50	0.45	0.31	0.27	0.36
Xenon	1, 4	289.74	58.40	0.002	0.62	2.96	1.20	0.65	0.34
Methane	2, 5	190.53	45.9797	0.011	0.53	0.76	0.87	0.78	0.29
Nitrogen	6	126.20	34.00	0.037	2.71	0.79	0.68	—	—
Ethylene	7, 8	282.3452	50.403	0.087	1.17	1.58	0.62	0.65	0.34
Ethane	5, 9	305.34	48.7143	0.100	0.75	0.80	0.82	0.61	0.35
Propane	5	369.85	42.4766	0.153	1.14	0.94	0.52	0.21	0.40
Tetrafluoromethane	11, 12, 13	227.527	37.45	0.177	8.87	—	2.34	3.01	2.15
Neopentane	14, 15	433.75	31.963	0.197	2.48	1.08	1.48	1.36	0.59
n-Butane	5, 16	425.15	37.96	0.200	1.26	1.10	1.05	0.57	0.41
Sulfor hexafluoride	17, 19	318.70	37.590	0.208	5.10	—	2.29	—	—
Carbon dioxide	18-20	304.21	73.825	0.223	1.16	0.63	1.09	1.65	0.55
n-Pentane	21-24	469.69	33.64	0.252	0.63	1.15	2.00	1.11	0.98
n-Hexane	25-27, 32	507.85	30.58	0.303	2.62	1.22	3.40	2.53	2.38
n-Heptane	28, 29, 32	540.15	27.36	0.350	0.43	0.96	1.91	1.13	0.83
n-Octane	30-32	568.76	24.87	0.398	0.90	0.84	1.02	—	—
n-Decane	32	617.7	21.2	0.489	1.38	0.96	—	—	—
n-Dodecane	32, 33	658.2	18.2	0.575	1.73	0.88	—	—	—
n-Hexadecane	32, 33	722.0	14.1	0.742	3.14	0.88	—	—	—
Water	34	647.07	221.2	—	0.16	0.65	0.99	—	—

*The average absolute deviations $\delta(Q)$, where $Q = V_L$ or P_{sat} or P, are defined by Eq. 17.

1. Rabinovich et al. (1988)
2. Gielen et al. (1973)
3. Verbeke et al. (1969)
4. Habgood and Schneider (1954)
5. Younglove and Ely (1987)
6. Angus et al. (1979)
7. McCarty and Jacobsen (1981)
8. Levelt-Sengers et al. (1984)
9. Beattie et al. (1939a)
10. Angus et al. (1980)
11. Calado et al. (1986)
12. Douslin et al. (1961)
13. Rubio et al. (1985)
14. Dawson et al. (1973)
15. Beattie et al. (1952a)
16. Beattie et al. (1939b)
17. Ulybin and Zherdev (1970)
18. Angus et al. (1976)
19. Wentorf (1956)
20. Michels et al. (1937)
21. Beattie et al. (1952b)
22. Gehrig and Lentz (1979)
23. Kratzke et al. (1985)
24. Beattie et al. (1951)
25. Dymond et al. (1979)
26. Griskey and Canjar (1959)
27. Kelso and Felsing (1940)
28. Smith et al. (1937)
29. Beattie and Kay (1937)
30. Benson and Winnick (1971)
31. Felsing and Watson (1942)
32. Reid et al. (1987)
33. Boelhouwer (1960)
34. Hill (1990)

where z_c^* is the value of the critical compressibility factor calculated from the equation:

$$z_c^* = 0.2905 - 0.0787\omega \qquad (8)$$

As the uncertainty of ω is small, Eq. 8 provides a set of standardized estimates of the compressibility factor. Equations 7-8 make it possible to avoid the use of experimental values of critical density which is not directly measured and is subject to considerably greater uncertainty than T_c or P_c.

For water, the actual critical density was used because it is known with good accuracy, and the acentric factor-based correlations are not valid.

To ensure the correct behavior of Eq. 5 at low densities, it is worthwhile to constrain it to accurately reproduce the second virial coefficient. For this purpose, the expression developed by Schreiber and Pitzer (1989) has been used for nonpolar compounds:

$$B_r = B\frac{P_c}{RT_c z_c^*} = d_1 + d_2 T_r^{-1} + d_3 T_r^{-2} + d_4 T_r^{-6} \qquad (9)$$

where

$$d_i = d_{i,0} + \omega d_{i,1}, \; i = 1, \ldots, 4 \qquad (10)$$

The parameters $d_{i,0}$ and $d_{i,1}$ are collected in Table 2. To constrain Eq. 5 for the reproduction of the second virial coefficient, the parameter α was expressed in further calculations as:

$$\alpha = B_r - b - c \qquad (11)$$

Equations 9-10 provide an accurate representation of second virial coefficients of normal fluids as demonstrated by Schreiber and Pitzer (1989).

To obtain a complete generalized equation of state, the parameters of Eq. 5 have been first adjusted to reproduce the data for methane. Methane has been selected as a model simple fluid following the results of Schreiber and Pitzer, who analyzed the conformity of simple fluids (those with $\omega \approx 0$) to the two-parameter corresponding states principle and concluded that methane showed the intermediate behavior among the four simple fluids analyzed (Ar, Kr, Xe, and CH_4).

An analysis of the PVT data for methane made it possible to determine the temperature dependence of the parameters of Eq. 5:

$$b = e_1 \qquad (12)$$

$$c = e_2 + e_5/T_r + e_8/T_r^2 \qquad (13)$$

Table 2. Parameters of the Equation for Second Virial Coefficients (Eqs. 9-10) and the Complete Equation of State (Eqs. 12-16)

	Generalized EOS				Water
i	$d_{i,0}$	$d_{i,1}$	$e_{i,0}$	$e_{i,1}$	e_i
1	0.442259	0.725650	0.252433	0.0487884	0.210866
2	−0.980970	0.218714	−0.0906396	−0.879256	1.821081
3	−0.611142	−1.24976	0.0827465	−0.516256	−0.550987
4	−0.00515624	−0.189187	0.108346	0.816731	−0.002947
5	—	—	1.810233	0.671581	0
6	—	—	−0.622962	−0.319606	0.328445
7	—	—	−0.267383	−0.742537	−0.307798
8	—	—	−0.389954	−0.226976	0
9	—	—	0.708662	1.27043194	0.742716
10	—	—	−0.102484	−0.295499	−0.033229
11	—	—	0.00988093	0.273364	0.00531296
12	—	—	−0.00209377	−0.0711799	−0.00147727
13	—	—	—	—	−1.555869
14	—	—	—	—	−0.539968
15	—	—	—	—	−1.451764
16	—	—	—	—	−0.00228129

$$\beta = e_3 + e_6/T_r + e_9/T_r^2 + e_{11}/T_r^6 \qquad (14)$$

$$\gamma = e_4 + e_7/T_r + e_{10}/T_r^2 + e_{12}/T_r^6 \qquad (15)$$

The generalized equation was developed by the addition of acentric-factor-dependent terms to the equation for the simple fluid. A linear acentric factor dependence sufficed

$$e_i = e_{i,0} + e_{i,1}(\omega - \omega_{CH_4}),\ i = 1, \ldots, 12 \qquad (16)$$

The values of the parameters of the resulting equation are shown in Table 2.

In the case of water (and more generally other polar fluids), it is not justified to use the generalized expression for the second virial coefficient (Eqs. 9-10). Therefore, the parameter α was calculated using adjustable constants $e_{13}, \ldots e_{16}$:

$$\alpha = e_{13} + e_{14}/T_r + e_{15}/T_r^2 + e_{16}/T_r^6 \qquad (11a)$$

At the same time, the parameter c (Eq. 13) was treated as independent of temperature ($e_5 = e_8 = 0$). The parameters for water are given in Table 2 along with those for the generalized EOS.

Deviations of pure-component properties in Table were calculated from Eqs. 5 and 12-16 from experimental data. The deviations are defined as:

$$\delta(Q) = \frac{100}{N}\sum_{i=1}^{N}\left|1 - \frac{Q_i^{\text{cal}}}{Q_i^{\text{exp}}}\right| \qquad (17)$$

where Q is either the liquid volume V_L (at reduced densities higher than $\rho_R = 1.8$) or vapor pressure P_{sat} or pressure P outside the saturation region (at $\rho_R < 1.8$). Our results were compared in Table 1 with those obtained from the generalized equations of state of Yamada (1973) and Schreiber and Pitzer (1989). It is evident that the results obtained from the present equation are comparable to those obtained from Yamada's and Schreiber and Pitzer's equations. Although the number of adjustable constants has been reduced to 24 (compared to 44 for Yamada's and 49 for Schreiber-Pitzer's EOS), the overall accuracy is not much reduced in most cases.

Although an extensive array of near critical data was included in our database, we did not constrain our equation to exactly reproduce the critical coordinates. Due to the simple mathematical form of the P-V-T relationship, the critical constraints would lead to an appreciable deterioration of the quality of the overall fit. Nevertheless, the calculated critical temperatures are slightly overestimated only (usually by 2-3 K). The overestimation of T_c is typical when analytical equations of state are fitted to PVT data without imposing the critical constraints (c.f. Vidal, 1984).

Since the equation has been constrained to accurately reproduce the second virial coefficients, it is also worthwhile to examine the third virial coefficients. The third virial coefficient calculated from Eq. 5 is:

$$C = b(b + c) + \beta \qquad (18)$$

Figure 1 shows the third virial coefficients predicted for methane from the present equation (solid line), the EOS of Schreiber and Pitzer (dashed line) and the correlation of Orbey and Vera (1983). The latter correlation was based exclusively on experimental third virial coefficient data and is believed to be closest to reality, although it should be noted that the uncertainty of third virial coefficients is at least an order of magnitude larger than that of second virial coefficients. As shown in Figure 1, the discrepancies are largest at low reduced temperatures and are influenced only moderately by the flexibility of the equation. It is not possible to reproduce the maximum of C at low, reduced temperatures when the equation of state is obtained from extensive PVT data, including the high liquid density region. The predicted third virial coefficients, however, are reasonable at higher, reduced temperatures.

Extension of the EOS to Mixtures

In considering the application of Eq. 5 to mixtures, we first

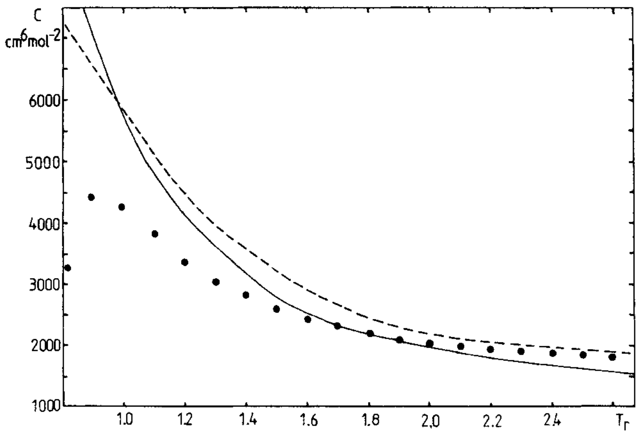

Figure 1. Third virial coefficients of methane calculated.

From the proposed equation of state (———); from the equation of Schreiber and Pitzer (1989) (– – – –); and from the correlation of Orbey and Vera (1983) (●).

rewrite the equation in terms of density ρ, instead of reduced density ρ_r

$$z=\frac{1+cv_c\rho}{1-bv_c\rho}+\alpha v_c\rho+\beta v_c^2\rho+\gamma v_c^3\rho \tag{19}$$

Thus, the quantities to be defined for a mixed fluid are (bv_c), (cv_c), ..., (γv_c^3). Next, we consider the virial expansion of Eq. 19.

$$z=1+B\rho+C\rho^2+D\rho^3+E\rho^4+\cdots \tag{20}$$

$$B=bv_c+cv_c+\alpha v_c \tag{21}$$

$$C=(bv_c)^2+(bv_c)(cv_c)+\beta v_c^2 \tag{22}$$

$$D=(bv_c)^3+(bv_c)^2(cv_c)+\gamma v_c^3 \tag{23}$$

$$E=(bv_c)^4+(bv_c)^3(cv_c) \tag{24}$$

According to statistical mechanics, the second virial coefficient B should be a quadratic function of composition, the third virial coefficient C—a cubic one, the fourth virial coefficient D—a quartic one, etc. This implies that the composition dependence of b can only be linear. A quadratic expression for b would be acceptable for the second virial coefficient, but would violate composition dependencies for all higher coefficients. According to the same criterion, c and α should be quadratic, β = cubic, and γ = quartic functions of composition. Therefore, the mixing rules for the parameters are:

$$bv_c=\sum_i x_i b_i v_{ci} \tag{25}$$

$$cv_c=\sum_i\sum_j x_i x_j c_{ij} v_{cij} \tag{26}$$

$$\alpha v_c=\sum_i\sum_j x_i x_j \alpha_{ij} v_{cij} \tag{27}$$

$$\beta v_c^2=\sum_i\sum_j\sum_k x_i x_j x_k \beta_{ijk} v_{cijk}^2 \tag{28}$$

$$\gamma v_c^3=\sum_i\sum_j\sum_k\sum_\ell x_i x_j x_k x_\ell \gamma_{ijk\ell} v_{cijk\ell}^3 \tag{29}$$

where v_{ci} is the calculated critical volume for component i given by:

$$v_c=RT_c z_c^*/P_c \tag{30}$$

Among the above mixing rules, only that for b does not require arbitrary assumptions. For the remaining parameters, it is necessary to postulate specific combining rules.

For the effective critical volume for the (ij) pair, the combining rule is defined as:

$$v_{cij}=[(v_{ci}^{1/3}+v_{cj}^{1/3})/2]^3 \tag{31}$$

Equation 31 generates analogous combining rules for triplets (ijk) and quadruplets $(ijk\ell)$:

$$v_{cijk}=[(v_{ci}^{1/3}+v_{cj}^{1/3}+v_{ck}^{1/3})/3]^3 \tag{32}$$

$$v_{cijk\ell}=[(v_{ci}^{1/3}+v_{cj}^{1/3}+v_{ck}^{1/3}+v_{c\ell}^{1/3})/4]^3 \tag{33}$$

The combining rule for the α_{ij} parameter is expressed as:

$$\alpha_{ij}=(\alpha_i\alpha_j)^{1/2}k_{1,ij} \tag{34}$$

To postulate a combining rule for the β_{ijk} parameters, we note that a triplet (ijk) is made up of three pairs: (ij), (jk), and (ik). Therefore, β_{ijk} can be expressed as:

$$\beta_{ijk}=(\beta_{ij}\beta_{jk}\beta_{ik})^{1/3} \tag{35}$$

Assuming that expressions for β_{ij}, β_{jk}, and β_{ik} are similar to that for α_{ij}, Eq. 35 can be rewritten using binary interaction parameters for the (ij), (jk), and (ik) pairs:

$$\beta_{ijk}=\beta_i^{1/3}\beta_j^{1/3}\beta_k^{1/3}(k_{2,ij}k_{2,jk}k_{2,ik})^{1/3} \tag{36}$$

where $k_{2,ij}=1$ for $i=j$. Analogously, we note that a quadruplet $(ijk\ell)$ can be decomposed into six pairs: (ij), (jk), $(k\ell)$, (ik), $(i\ell)$, and $(j\ell)$. This assumption yields the following combining rule

$$\begin{aligned}\gamma_{ijk\ell}&=(\gamma_{ij}\gamma_{jk}\gamma_{k\ell}\gamma_{ik}\gamma_{i\ell}\gamma_{j\ell})^{1/6}\\&=\gamma_i^{1/4}\gamma_j^{1/4}\gamma_k^{1/4}\gamma_\ell^{1/4}(k_{3,ij}k_{3,jk}k_{3,k\ell}k_{3,ik}k_{3,i\ell}k_{3,j\ell})^{1/6}\end{aligned} \tag{37}$$

Finally, the combining rule for c is given by:

$$c_{ij}=[(c_i+c_j)/2]k_{4,ij} \tag{38}$$

The above formulation is applicable to mixtures containing any number of components. Although only binary parameters have been employed, parameters such as $\beta_{ijk}\,(i\neq j\neq k)$ can be optionally treated as freely adjustable ternary constants.

In this article, the above formalism will be applied only to binary mixtures. In this case, Eqs. 36–37 simplify to:

$$\beta_{iij}=\beta_i^{2/3}\beta_j^{1/3}k_{2,ij}^{2/3} \tag{39}$$

$$\gamma_{iiij}=\gamma_i^{3/4}\gamma_j^{1/4}k_{3,ij}^{1/2} \tag{40}$$

$$\gamma_{iijj}=\gamma_i^{1/2}\gamma_j^{1/2}k_{3,ij}^{2/3} \tag{41}$$

Table 3. Vapor-Liquid Equilibria and Volumetric Properties of Mixtures Containing Methane and Nonpolar or Weakly Polar Components*

Component	Ref.	Temp. Range K	Pres. Range Bar	Parameters of Individual Correlation				$\delta(x)$	$\delta(y)$	$\delta(V_L)$	$\delta(V_V)$
				a_1	a_2	a_3	a_4				
Propane	1	277-361	5-101	1.112	−0.933	−0.197	2.756	0.69 [2.10]	0.95 [1.32]	2.0 [4.4]	2.6 [2.7]
Isobutane	2	311-378	5-116	1.055	−0.548	−0.142	2.009	0.28 [1.29]	0.57 [0.71]	1.2 [3.5]	1.0 [2.0]
Neopentane	3	298	12-150	1.043	−1.184	−0.140	2.600	0.86 [1.41]	1.19 [1.16]	2.7 [2.1]	2.8 [2.4]
Butane	4	294-394	2-132	1.053	−1.155	−0.135	2.695	0.56 [1.00]	0.64 [0.65]	0.9 [0.9]	2.7 [2.9]
Cyclohexane	5	294-444	13-282	1.030	−1.146	−0.126	2.482	1.12 [2.04]	0.31 [0.53]	1.2 [1.8]	0.9 [1.0]
Benzene	6, 7	338-501	6-330	1.016	−1.073	−0.085	2.435	0.45 [1.83]	1.12 [1.06]	—	—
Pentane	8	311-444	1-169	1.009	−1.161	−0.088	2.661	0.23 [0.63]	0.45 [0.54]	0.7 [0.8]	1.0 [1.2]
Hexane	9	298-423	0.2-196	1.003	−1.178	−0.127	2.619	0.76 [1.24]	1.05 [1.06]	0.9 [1.0]	3.2 [3.3]
Heptane	10	311-511	0.4-248	0.993	−1.226	−0.119	2.670	0.80 [0.86]	0.36 [0.35]	1.4 [1.5]	1.7 [1.7]
Octane	11	298-423	10-273	0.984	−0.727	−0.210	2.003	0.82 [2.14]	0.22 [0.28]	0.9 [0.9]	1.2 [1.2]
Nonane	12	298-423	10-323	1.030	−0.697	−0.190	2.133	1.38 [2.58]	0.59 [0.51]	1.8 [1.6]	1.3 [1.3]
Decane	13	311-511	1-361	0.968	−0.881	−0.155	2.270	0.88 [1.52]	0.47 [0.53]	1.7 [1.3]	1.4 [1.3]
Hexadecane	14	462-704	20-252	0.972	−0.645	−0.439	1.925	1.97 [2.95]	0.67 [0.81]	—	—

*The average absolute deviations δ are defined by Eqs. 17 and 46. The values in brackets denote the deviations obtained from the generalized correlation (Eqs. 47-48).

1. Reamer et al. (1950)
2. Olds et al. (1942)
3. Rogers and Prausnitz (1971)
4. Sage et al. (1940)
5. Reamer et al. (1958)
6. Lin et al. (1979)
7. Elbishlawi and Spencer (1951)
8. Sage et al. (1942)
9. Shim and Kohn (1962)
10. Reamer et al. (1956)
11. Kohn and Bradish (1964)
12. Shipman and Kohn (1966)
13. Reamer et al. (1942)
14. Lin et al. (1980)

The subscript ij in the symbols $k_{1,ij}, \ldots, k_{4,ij}$ will be omitted in further parts of this work, as it is superfluous for binary mixtures. Other combining rules are obviously possible, but the above prescriptions are recommended on the basis of their empirical effectiveness.

Mixtures of Nonpolar and Weakly Polar Compounds

The above combining rules contain at most four binary parameters $k_1, \ldots, k_4$. Analysis of several data sets for mixtures of nonpolar and weakly polar compounds has shown that two of these parameters can be left constant.

$$k_3 = k_4 = 1 \qquad (42)$$

while for the remaining two, a simple temperature dependence is sufficient:

$$k_1 = a_1 + a_3/T_r^5 \qquad (43)$$

$$k_2^{2/3} = a_2 + a_4/T_r^{1.5} \qquad (44)$$

For mixture calculations using Eqs. 43-44, the reduced temperature is defined as:

$$T_r = T/(T_{c1}T_{c2})^{1/2} \qquad (45)$$

The above mixing and combining rules have been applied to calculate vapor-liquid equilibria and volumetric properties of mixtures. Emphasis was put on mixtures formed by components with vastly different sizes and critical temperatures. For such asymmetric mixtures, the equations of state that are customarily used for engineering-oriented computations are less satisfactory than for more symmetric mixtures (c.f. Han et al., 1988). Mixtures containing methane and nitrogen as lighter components, as well as the krypton + neon mixture, have been selected to verify the method. First, the phase equilibrium compositions and saturated volumes have been simultaneously correlated for individual mixtures. The parameters $a_1, \ldots, a_4$ have been determined by minimizing the residuals between calculated and experimental K-factors and liquid and vapor volumes. Tables 3 and 4 show the results for the methane and nitrogen mixtures, as well as deviations in phase equilibrium composition defined by

$$\delta(q) = \frac{100}{N}\sum_{i=1}^{N} |q_i^{\text{cal}} - q_i^{\text{exp}}|, \; q = x \text{ or } y \qquad (46)$$

and deviations in volumes defined by Eq. 17. It is preferable

Table 4. Vapor-Liquid Equilibria and Volumetric Properties of Mixtures Containing Nitrogen and Nonpolar or Weakly Polar Components*

Component	Ref.	Temp. Range K	Pres. Range Bar	Parameters of Individual Correlation a_1	a_2	a_3	a_4	$\delta(x)$	$\delta(y)$	$\delta(V_L)$	$\delta(V_V)$
Isobutane	1	255-311	2-207	0.947	−2.310	0.006	3.702	0.54 [2.77]	0.58 [1.88]	1.9 [3.7]	4.0 [3.5]
Butane	2, 3	311-411	3-285	1.136	1.731	−0.923	−2.840	0.34 [1.05]	0.49 [2.09]	2.2 [4.8]	2.5 [2.3]
Cyclohexane	4	366-411	1-276	1.157	1.549	−0.915	−1.788	0.30 [0.38]	0.26 [1.19]	0.8 [0.8]	1.6 [1.2]
Carbon dioxide	5, 6	270-273	31-123	1.157	1.129	−0.700	−1.500	0.13 [0.53]	0.43 [1.69]	—	—
Pentane	7	277-377	2-207	1.006	−0.907	−0.279	1.780	1.73 [3.81]	0.90 [2.32]	1.6 [2.2]	—
Hexane	8	311-444	17-344	1.143	1.790	−0.849	−2.183	0.65 [1.80]	0.58 [1.40]	—	—
Heptane	9	305-455	70-691	1.057	0.833	−0.425	−0.433	0.93 [1.28]	0.92 [1.24]	2.2 [3.0]	3.5 [4.2]
Decane	10	311-411	34-344	1.160	2.167	−0.994	−2.165	1.68 [1.93]	0.46 [0.34]	—	—

* The average absolute deviations δ are defined by Eqs. 17 and 46. The values in brackets denote the deviations obtained from the generalized correlation (Eqs. 49-51).

1. Kalra et al. (1978)
2. Malewski and Sandler (1989)
3. Shibata and Sandler (1989a)
4. Shibata and Sandler (1989b)
5. Yorizane et al. (1971)
6. Somait and Kidnay (1978)
7. Kalra et al. (1977)
8. Poston and McKetta (1966)
9. Akers et al. (1954)
10. Azarnoosh and McKetta (1963)

to list deviations of the x and y values calculated at fixed T and P, because P vs. x curves are very steep in many cases.

It is evident that the proposed method yields an excellent simultaneous representation of equilibrium-phase compositions and volumes. A particularly interesting example is provided by the krypton-neon mixture (Trappeniers and Schouten, 1974). As shown in Figure 2, the thermodynamic behavior of this system includes a region of typical vapor-liquid equilibrium at higher temperatures and a region of fluid-fluid equilibrium extending to very high pressures at lower temperatures. At certain intermediate temperatures, a region of smooth transition exists. In this region, two critical pressures are observed. It is remarkable that the proposed equation of state reproduces these phenomena with experimental accuracy.

The correlation of individual data sets is equally satisfactory for systems containing methane or nitrogen as the lighter component. As heavier components, straight chain or branched aliphatic hydrocarbons as well as benzene, cyclohexane and carbon dioxide have been selected. Among the mixtures studied, those containing components with vastly different volatilities (methane or nitrogen + decane or hexadecane) provide a stringent test for the model.

To enhance the predictive capability of the method, generalized correlations have been established for the k_1 and k_2 parameters. The correlations have been separately developed for mixtures containing methane and nitrogen by analyzing variations of the $a_1, \ldots, a_4$ parameters (Eqs. 43-44) within both series. After assigning suitably averaged values for the $a_2, \ldots, a_4$ parameters, a_1 has been found to vary linearly with the acentric factor of the heavier component.

For mixtures containing methane, the generalized correlation is:

$$k_1 = 1.113 - 0.317\omega - 0.14/T_r^5 \qquad (47)$$

$$k_2^{2/3} = -1.09 + 2.5/T_r^{1.5} \qquad (48)$$

where ω is the acentric factor of the heavier component. This correlation has been established for $\omega \leq 0.742$ (the value for hexadecane).

For the nitrogen mixtures the correlation had to be split into two acentric factor ranges:

$$k_1 = 1.517 - 1.081\omega - 0.7/T_r^5 \text{ for } \omega \geq 0.252 \qquad (49)$$

$$k_1 = 1.332 - 0.552\omega - 0.7/T_r^5 \text{ for } \omega \leq 0.223 \qquad (50)$$

and

$$k_2^{2/3} = 1.6 - 1.5/T_r^{1.5} \text{ for both ranges} \qquad (51)$$

Splitting of the correlation into two ranges is deemed more reliable than expressing a_1 as a higher order (for example, quadratic) function of the acentric factor.

The results of calculating phase equilibria and volumetric properties using the generalized equations (Eqs. 41-42) or (Eqs. 43-45) are listed in Tables 3 and 4 in brackets. Although the deviations are somewhat larger than those obtained from the individual correlation of the data, they are reasonably low for all systems. Therefore, the generalized correlations can be used with confidence to predict vapor-liquid equilibria and volumetric properties of mixtures containing methane or nitrogen. Similar expressions can be established for other series of mixtures with a common component.

Aqueous Hydrocarbon Mixtures

Aqueous hydrocarbon systems pose a challenge for the existing fluid state theories, and their consistent thermodynamic representation over wide ranges of P, T, and x is difficult. Among the more successful methods, the complex EOS of Lee and Chao (1988) is accurate at higher temperatures. The authors did not present results of calculations at lower temper-

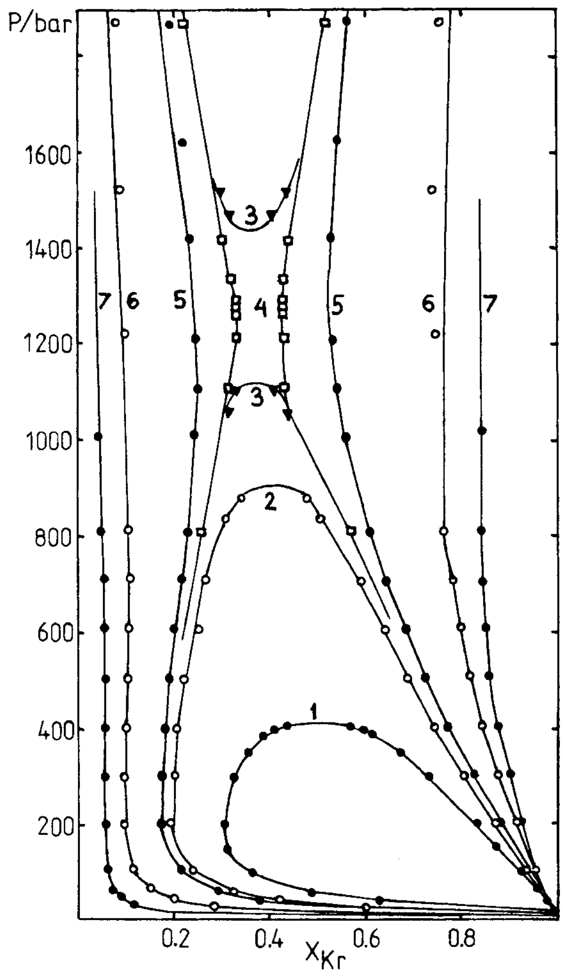

Figure 2. Vapor-liquid and gas-gas equilibria in the neon-krypton system.

Points are the experimental data of Trappeniers and Schouten (1974), and lines denote the results of calculations using the proposed EOS. Numbers denote isotherms: 1, 178.15 K; 2, 166.15 K; 3, 164.92 K; 4, 164.66 K; 5, 163.15 K; 6, 148.15 K; and 7, 133.16 K.

atures where the solubilities in both aqueous and hydrocarbon phases are very low and equation-of-state methods are difficult to apply. A very simple equation proposed by Anderko (1991) is accurate at low temperatures, but is not valid at pressures higher than approximately 200 bar.

The present equation of state can be applied to aqueous hydrocarbon mixtures using the same two-parameter mixing rules described for nonpolar mixtures. We selected mixtures containing methane, ethane, and propane as examples. Phase equilibria for the latter mixture include vapor-liquid and liquid-liquid equilibrium regions separated by a three-phase liquid-liquid vapor region. Remarkably, the present equation reproduces both VLE and LLE essentially within experimental uncertainty. The results are given in Table 5. The temperature dependence of the binary parameters for aqueous mixtures is somewhat more complex than for nonpolar mixtures.

Case of $H_2O + CH_4$:

$$k_1 = 0.6496 + 0.4749q \tag{52}$$

$$k_3 = 0.9892 + 0.6370q - 1.1333q^2 + 1.9556q^3 - 2.9816q^5 + 5.3007q^7 \text{ for } 310.93 \leq T \leq 523.15 \text{ K} \tag{53}$$

$$k_1 = 0.9746 + 1.7234q \tag{54}$$

$$k_3 = 1.4414 - 1.7864q \text{ for } 523.15 \leq T \leq 633.15 \text{ K} \tag{55}$$

Case of $H_2O + C_2H_6$:

$$k_1 = 0.6407 + 0.1677q \tag{56}$$

$$k_3 = 1.0098 + 0.0249q - 0.8384q^2 + 1.9190q^3 \text{ for } 310.93 \leq T \leq 444.26 \text{ K} \tag{57}$$

Case of $H_2O + C_3H_8$:

$$k_1 = 0.6253 + 0.20478q \tag{58}$$

$$k_3 = 1.0402 - 0.0284q \text{ for } 310.93 \leq T \leq 427.59 \text{ K} \tag{59}$$

where $q = T/310.93 - 1$ and $k_2 = k_4 = 1$ in all cases.

In the case of the $H_2O + CH_4$ mixture, the data of Sultanov et al. (1972, 1972) and Price (1979) are not in agreement at high temperatures (above 523.15 K). Therefore, Eqs. 54-55 should be treated with caution. Figures 3-7 show the high quality of correlation for the methane + water and propane + water mixtures.

Multicomponent Mixtures

While only binary mixtures have been considered in detail,

Table 5. Vapor-Liquid (VLE) and Liquid-Liquid (LLE) Equilibria in Aqueous Hydrocarbon Mixtures*

Hydrocarbon	Ref.	Temp. Range K	Pres. Range bar	Equilibrium	k_1	k_3	$\delta(x)$	$\delta(y)$	$\delta(K_1)$	$\delta(K_2)$
Methane	1-4	310.93-523.15	0-980	VLE	Eq. 52	Eq. 53	0.019	0.21	4.3	3.5
	3	523.15-633.15	98-980	VLE	Eq. 54	Eq. 55	0.168	1.5	3.4	7.8
Ethane	5-6	310.93-444.26	0-690	VLE	Eq. 56	Eq. 57	0.004	0.11	6.0	4.2
Propane	7	310.93-426.59	0-207	VLE	Eq. 58	Eq. 59	0.001	0.34	6.0	5.1
		310.93-369.65	27-207	LLE	Eq. 58	Eq. 59	0.002	0.18	3.9	7.3
		310.93-427.59	0-207	VLE + LLE	Eq. 58	Eq. 59	0.002	0.23	5.6	6.8

* The average absolute deviations δ are defined by Eqs. 17 and 46. Subscripts 1 and 2 denote water and a hydrocarbon, respectively.

1. Culberson and McKetta (1951)
2. Olds et al. (1942)
3. Sultanov et al. (1971, 1972)
4. Price (1979)
5. Culberson and McKetta (1950)
6. Reamer et al. (1943)
7. Kobayashi and Katz (1953)

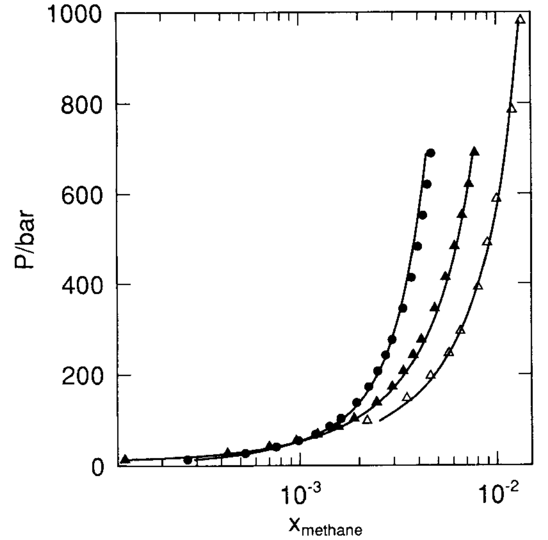

Figure 3. Pressure-composition relationships for the aqueous phase in the water + methane binary.

At 310.93 K (●); at 444.26 K (▲); and at 473.15 K (△). The lines denote the results obtained from the EOS.

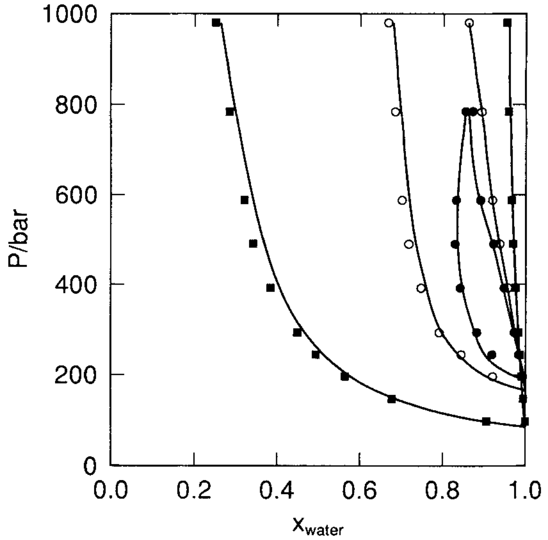

Figure 5. Vapor-liquid equilibria in the water + methane mixture.

At 573.15 K (■); at 623.15 K (○); and at 633.15 K (●). The lines denote the results obtained from the EOS.

the formulation of the equation for a mixed fluid is fully consistent with the requirements for mixtures with any number of components. Thus, Eqs. 19–34, 38, and 45 require no modification; in particular, Eqs. 34 and 38 relate to the second virial coefficient and in turn to binary interactions between molecules. It is only for the third or higher virial coefficients that ternary or higher molecular interactions enter. Thus, Eq. 35 can have an additional term β'_{ijk} related to the ternary interaction of molecules i, j, and k; this yields

$$\beta_{ijk} = (\beta_{ij}\beta_{ik}\beta_{jk})^{1/3} + \beta'_{ijk} \qquad (60)$$

The corresponding change can be made in Eq. 36, and appropriate terms for both ternary and quaternary interactions can be added to Eq. 37.

Since ternary and quaternary interactions also occur in pure fluids and binary mixtures, the correction term β'_{ijk} relates to the difference between the i-j-k interaction and the appropriate mean of i-i, j-j, k-k, i-j, i-k and j-k interactions, and this difference may be very small. Thus, in many cases there may be no need to modify Eqs. 35–37, and then the properties of more complex mixtures can be predicted from knowledge of all of the component binaries.

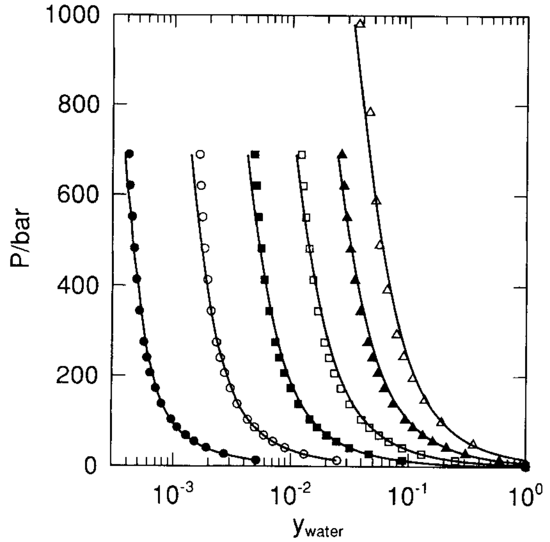

Figure 4. Pressure-composition relationships for the methane-rich phase in the water + methane binary.

At 310.93 (●); at 344.26 K (○); 377.59 K (■); 410.93 K (□); at 444.26 K (▲); and at 473.15 K (△). The lines denote the results obtained from the EOS.

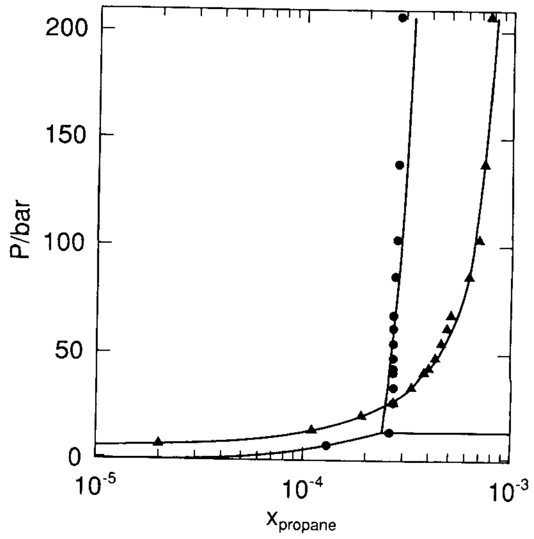

Figure 6. Pressure-composition relationships for the aqueous phase in the water + propane binary.

At 310.93 K (●) and at 427.59 K (▲). The lines denote the results obtained from the EOS. The horizontal lines is a three-phase VLLE locus.

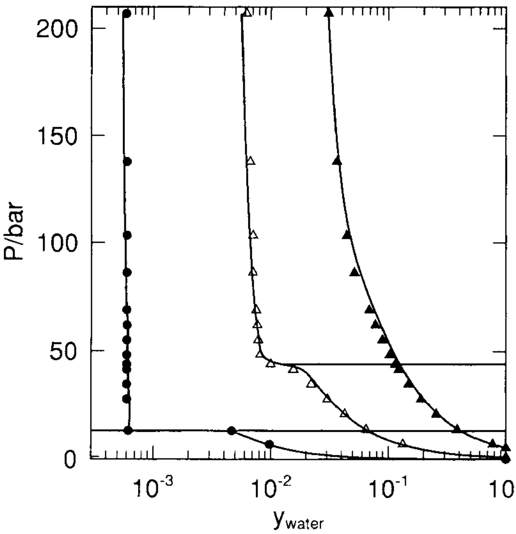

Figure 7. Pressure-composition relationship for the propane-rich phase in the water + propane binary.

At 310.93 K (●); at 369.65 K (△); and at 427.59 K (▲). The lines denote the results obtained from the EOS. The horizontal lines are the three-phase VLLE loci.

Discussion

The simple mathematical form of the equation of state used in this study has been proposed to facilitate the introduction of accurate mixing rules. However, the pure-component properties calculated from this equation are sufficiently accurate to justify the simplifications introduced. In fact, the obtained accuracy is comparable to that of the multiparameter extended BWR-type equations.

The mixing rules are consistent with the rigorously known composition dependence of the virial expansion and make it possible to simultaneously calculate phase equilibria and volumetric properties of mixtures with very high accuracy. Moreover, the binary parameters can be generalized for series of mixtures containing a common component, thus providing a convenient predictive tool.

The proposed equation can be used as a reliable tool for estimating phase equilibria for a mixture when only very limited experimental data are available. To illustrate this, let us adjust the binary parameters $a_1, \ldots, a_4$ (Eqs. 43-44) to just two experimental pairs of points (x, y) for the krypton-neon mixture (Figure 2): the first pair at 178.15 K and 304 bar and the second pair at 123.17 K and 456 bar. After fitting the parameters in this way, the complete set of phase equilibrium data can be predicted with the deviations $\delta(x) = 1.33$ and $\delta(y) = 0.68$ (x denotes the krypton-rich phase and y the neon-rich phase). If the whole experimental data set is used to fit the parameters, the $\delta(x)$ and $\delta(y)$ deviations are 0.72 and 0.43, respectively.

If no experimental information is available about a mixture of interest, its properties can be estimated using data for other mixtures containing a common component. The safest method of doing it is to establish a generalized correlation for mixtures containing a common component, as demonstrated for the methane and nitrogen mixtures. If extensive data are not available, however, information about two mixtures A and B will suffice to predict the behavior of mixture C. A possible algorithm for such calculations is as follows:

Step 1. Correlate the data for mixtures A and B by fitting the parameters $a_1, \ldots, a_4$ (Eqs. 43-44).

Step 2. Take an arithmetic mean of the obtained a_4 parameters and correlate the data again by fitting the parameters $a_1, \ldots, a_3$.

Step 3. Repeat step 2 by taking a mean value of a_3 and by fitting a_1 and a_2. Then, take a mean value of a_2 and fit only a_1 with the values of $a_2, \ldots, a_4$ held constant at their mean values.

Step 4. Finally, take a weighted average of the first parameter, assuming that a_1 is a linear function of ω:

$$a_1 = \frac{\omega - \omega_A}{\omega_B - \omega_A} (a_{1,B} - a_{1,A}) + a_{1,A} \tag{61}$$

The above scheme has been applied to predict the behavior of the nitrogen + carbon dioxide system using experimental data for nitrogen + butane and nitrogen + heptane. The resulting deviations $\delta(x)$ and $\delta(y)$ are equal to 1.07 and 0.80, respectively, and can be regarded as satisfactory. Obviously, this predictive scheme can be applied most easily if the mixtures A, B, and C contain more similar components.

It may be argued that the use of two adjustable parameters (on the isothermal basis) is not justified for nonpolar mixtures. In fact, a similar accuracy of phase equilibrium calculations for the nonpolar methane- and nitrogen-containing mixtures can be obtained using existing one-binary-parameter models. However, the advantage of the present model for nonpolar mixtures lies in the accurate simultaneous representation of phase equilibria and volumetric properties for mixtures as well as pure fluids. Most importantly, the same two-parameter mixing rules are applicable to different classes of mixtures, including the highly demanding aqueous hydrocarbon systems. The agreement with experimental data to high precision over wide ranges of pressure and temperature represents a severe test and recommends the equation for further use for different classes of mixtures.

Acknowledgment

This research was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Division of Chemical Sciences, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

Notation

$a_1, .., a_4$ = parameters of Eqs. 43-44
b = EOS parameter (Eq. 5)
B = second virial coefficient
c = EOS parameter (Eq. 5)
C = third virial coefficient
$d_1, .., d_4$ = parameters of Eqs. 9-10
D = fourth virial coefficient
$e_1, .., e_{16}$ = parameters of Eqs. 12-16
E = fifth virial coefficient
f = corresponding-states scaling factor
h = corresponding-states scaling factor
$k_1, .., k_4$ = binary parameters of the EOS
P = pressure
R = gas constant
T = temperature
v = molar volume
x = mole fraction

y = vapor-phase mole fraction
z = compressibility factor

Greek letters

α = EOS parameter (Eq. 5)
β = EOS parameter (Eq. 5)
γ = EOS parameter (Eq. 5)
δ = deviation defined in Eq. 17 or 46
ρ = density
ω = acentric factor

Subscripts

c = critical value
i, j, k, ℓ = components i, j, k, ℓ
L = liquid
mix = mixture
r = reduced quantity
sat = saturated property
v = vapor

Superscript

* = value calculated from ω and an equation

Literature Cited

Akers, W. W., D. M. Kehn, and C. H. Kilgore, "Volumetric and Phase Behavior of Nitrogen-Hydrocarbon Systems: Nitrogen-*n*-Heptane System," *Ind. Eng. Chem.*, **46**, 2536 (1954).

Anderko, A., "Equation-of-State-Methods for the Modeling of Phase Equilibria," *Fluid Phase Equilib.*, **61**, 145 (1990).

Anderko, A., "Phase Equilibria in Aqueous Systems from an Equation of State Based on the Chemical Approach," *Fluid Phase Equilibr.*, **65**, 89 (1991).

Angus, S., B. Armstrong, and K. M. deReuck, *International Thermodynamic Tables of the Fluid State: Carbon Dioxide*, Pergamon Press, Oxford (1976).

Angus, S., B. Armstrong, and K. M. deReuck, *International Thermodynamic Tables of the Fluid State: 7. Propylene*, Pergamon Press, Oxford (1980).

Angus, S., K. M. deReuck, and B. Armstrong, *International Thermodynamic Tables of the Fluid State: 6. Nitrogen*, Pergamon Press, Oxford (1979).

Azarnoosh, A., and J. J. McKetta, "Nitrogen-*n*-Decane System in the Two-Phase Region," *J. Chem. Eng. Data*, **8**, 494 (1963).

Beattie, J. A., D. R. Douslin, and S. W. Levine, "The Compressibility of and Equation of State for Gaseous Neopentane," *J. Chem. Phys.*, **20**, 1619 (1952a).

Beattie, J. A., and W. C. Kay, "The Normal Boiling Point and Critical Constants of Normal Heptane," *J. Amer. Chem. Soc.*, **59**, 1586 (1937).

Beattie, J. A., S. W. Levine, and D. R. Douslin, "The Vapor Pressure and Critical Constants of Normal Pentane," *J. Amer. Chem. Soc.*, **73**, 4431 (1951).

Beattie, J. A., S. W. Levine, and D. R. Douslin, "The Compressibility of and Equation of State for Gaseous Normal Pentane," *J. Amer. Chem. Soc.*, **74**, 4778 (1952b).

Beattie, J. A., G. L. Simard, and G. J. Su, "The Vapor Pressure and Critical Constants for Normal Butane," *J. Amer. Chem. Soc.*, **61**, 24 (1939b).

Beattie, J. A., G. J. Su, and G. L. Simard, "The Critical Constants of Ethane," *J. Amer. Chem. Soc.*, **61**, 924 (1939a).

Behar, E., R. Simonet, and E. Rauzy, "A New Noncubic Equation of State," *Fluid Phase Equilib.*, **21**, 237 (1985).

Benedict, M., G. R. Webb, and L. C. Rubin, "An Empirical Equation for Thermodynamic Properties of Light Hydrocarbons and Their Mixtures: II. Mixtures of Methane, Ethane, Propane and Butane," *J. Chem. Phys.*, **10**, 747 (1942).

Benson, M. S., and J. Winnick, "PVT Properties of Liquid *n*-Octane," *J. Chem. Eng. Data*, **16**, 154 (1971).

Bienkowski, P. R., H. S. Denenholz, and K. C. Chao, "A Generalized Hard-Sphere Augmented Virial Equation of State," *AIChE J.*, **19**, 167 (1973).

Boelhouwer, J. W. M., "PVT Relations for Five Liquid *n*-Alkanes," *Physica*, **26**, 1021 (1960).

Calado, J. C. G., R. G. Rubio, and W. B. Streett, "The Equation of State of Tetrafluoromethane," *ACS Symp. Ser.*, **300**, 60 (1986).

Carnahan, N. F., and K. E. Starling, "Equation of State for Non-Attracting Rigid Spheres," *J. Chem. Phys.*, **51**, 635 (1969).

Culberson, O. L., and J. J. McKetta, Jr., "Phase Equilbria in Hydrocarbon-Water Systems: II. The Solubility of Ethane in Water at Pressures to 10,000 psia," *Petr. Trans. AIME*, **189**, 319 (1950).

Culberson, O. L., and J. J. McKetta, Jr., "Phase Equilbria in Hydrocarbon-Water Systems: III. The Solubility of Methane in Water at Pressures to 1,000 psia," *Petr. Trans. AIME*, **192**, 223 (1951).

Dawson, P. P., I. H. Siberberg, and J. J. McKetta, "Volumetric Behavior, Vapor Pressures and Critical Properties of Neopentane," *J. Chem. Eng. Data*, **18**, 7 (1973).

Douslin, D. R., R. H. Harrison, R. T. Moore, and J. P. McCullough, "Tetrafluoromethane: *P-V-T* and Intermolecular Potential Energy Relations," *J. Chem. Phys.*, **35**, 1357 (1961).

Dymond, J. H., K. J. Young, and J. D. Isdale, "P, ρ, T Behavior of *n*-Hexane + *n*-Hexadecane in the Range 298 to 373 K and 0.1 to 500 MPa," *J. Chem. Thermodyn.*, **11**, 887 (1979).

Elbishlawi, M., and J. R. Spencer, "Equilibrium Relations of Two Methane-Aromatic Binary Systems at 150°F," *Ind. Eng. Chem.*, **43**, 1811 (1951).

Felsing, W. A., and G. M. Watson, "The Compressibility of Liquid *n*-Octane," *J. Amer. Chem. Soc.*, **64**, 1822 (1942).

Gehrig, M., and H. Lentz, "Values of $p(V, T)$ for *n*-Pentane in the Range 5 to 250 MPa and 313 to 643 K," *J. Chem. Thermodyn.*, **11**, 291 (1979).

Gielen, H., V. Jansoone, and O. Verbeke, "Application of an Empirical Equation of State to the Critical Region of Methane and Argon," *J. Chem. Phys.*, **59**, 5763 (1973).

Griskey, R. G., and L. N. Canjar, "Compressibility of *n*-Hexane," *AIChE J.*, **5**, 29 (1959).

Habgood, H. W., and W. G. Schneider, "PVT Measurements in the Critical Region of Xenon," *Can. J. Chem.*, **32**, 98 (1954).

Han, S. J., H. M. Lin, and K. C. Chao, "Vapor-Liquid Equilibrium of Molecular Fluid Mixtures by Equation of State," *Chem. Eng. Sci.*, **43**, 2327 (1988).

Hill, P. G., "A Unified Fundamental Equation for the Thermodynamic Properties of H_2O," *J. Phys. Chem. Ref. Data*, **19**, 1223 (1990).

Kalra, J., H.-J. Ng, R. D. Miranda, and D. B. Robinson, "Equilbrium Phase Properties of the Nitrogen-Isobutane System," *J. Chem. Eng. Data*, **23**, 321 (1978).

Kalra, H., D. B. Robinson, and G. J. Besserer, "The Equilibrium Phase Properties of the Nitrogen-*n*-Pentane System," *J. Chem. Eng. Data*, **22**, 215 (1977).

Kelso, E. A., and W. A. Felsing, "The Pressure-Volume-Temperature Relations of *n*-Hexane and of 2-Methylpentane," *J. Amer. Chem. Soc.*, **62**, 3132 (1940).

Kim, H., W. C. Wang, H. M. Lin, and K. C. Chao, "Cubic Chain of Rotators Equation of State," *Ind. Eng. Chem. Fundam.*, **25**, 75 (1986).

Kobayashi, R., and D. L. Katz, "Vapor-liquid Equilibria for Binary Hydrocarbon-Water Systems," *Ind. Eng. Chem.*, **45**, 440 (1953).

Kohn, J. P., and W. F. Bradish, "Multiphase and Volumetric Equilibria of the Methane-*n*-Octane System at Temperatures between −110°C and 150°C," *J. Chem. Eng. Data*, **9**, 5 (1964).

Kratzke, H., S. Muller, M. Bohn, and R. Kohlen, "Thermodynamic Properties of Saturated and Compressed Liquid Pentane," *J. Chem. Thermodyn.*, **17**, 283 (1985).

Lee, M. J., and K. C. Chao, "Augmented BACK Equation of State for Polar Fluids," *AIChE J.*, **34**, 825 (1988).

Levelt-Sengers, J. M. H., G. A. Olchowy, B. Kamgar-Parsi, and J. V. Sengers, "A Thermodynamic Surface for the Critical Region of Ethylene," National Bureau of Standards Technical Note 1189 (1984).

Lin, H.-M., H. M. Sebastian, J. J. Simnick, and K.-C. Chao, "Gas-Liquid Equilibrium in Binary Mixtures of Methane with *n*-Decane, Benzene, and Toluene," *J. Chem. Eng. Data*, **24**, 146 (1979).

Lin, H.-M., H. M. Sebastian, and K.-C. Chao, "Gas-Liquid Equilibrium in Hydrogen + *n*-Hexadecane and Methane + Hexadecane at Elevated Temperatures and Pressures," *J. Chem. Eng. Data*, **25**, 252 (1980).

Malewski, M. K. F., and S. I. Sandler, "High-Pressure Vapor-Liquid Equilibria of the Binary Mixtures Nitrogen + *n*-Butane and Argon + *n*-Butane," *J. Chem. Eng. Data*, **34**, 424 (1989).

McCarty, R. D., and R. T. Jacobsen, "An Equation of State for Fluid Ethylene," National Bureau of Standards Technical Note 1045 (1981).

Mentzer, R. A., R. A. Greenkorn, and K. C. Chao, "The Principle of Corresponding States and Prediction of Gas-Liquid Separation Factors and Thermodynamic Properties: a Review," *Sep. Sci. Techn.*, **15**, 1613 (1980).

Michels, A., B. Blaisse, and C. Michels, "The Isotherms of CO_2 in the Neighbourhood of the Critical Point and Round the Coexistence Line," *Proc. Roy. Soc.*, London, **A160**, 358 (1937).

Oellrich, L., V. Plöcker, J. M. Prausnitz, and H. Knapp, "Equation-of-State Methods for Computing Phase Equilibria and Enthalpies," *Int. Chem. Eng.*, **21**, 1 (1981).

Olds, R. H., B. H. Sage, and W. N. Lacey, "Methane-Isobutane System," *Ind. Eng. Chem.*, **34**, 1008 (1942).

Olds, R. H., B. H. Sage, and W. N. Lacey, "Composition of the Dew-Point Gas in the Methane-Water System," *Ind. Eng. Chem.*, **34**, 1223 (1942).

Orbey, H., and J. H. Vera, "Correlation for the Third Virial Coefficient Using T_c, P_c and ω as Parameters," *AIChE J.*, **29**, 107 (1983).

Orbey, H., and J. H. Vera, "Rational Construction of an Augmented Hard Core Equation of State for Pure Compounds and Study of its Application to Mixtures," *Chem. Eng. Commun.*, **44**, 95 (1986).

Pitzer, K. S., "The Volumetric and Thermodynamic Properties of Fluids: I. Theoretical Basis and Virial Coefficients," *J. Amer. Chem. Soc.*, **77**, 3427 (1955).

Pitzer, K. S., D. Z. Lippman, R. F. Curl, Jr., C. M. Huggins, and D. E. Petersen, "The Volumetric and Thermodynamic Properties of Fluids: II. Compressibility Factor, Vapor Pressure and Entropy of Vaporization," *J. Amer. Chem. Soc.*, **77**, 3433 (1955).

Poston, R. S., and J. J. McKetta, "Vapor-Liquid Equilibrium in the *n*-Hexane-Nitrogen System," *J. Chem. Eng. Data*, **11**, 364 (1966).

Price, L. C., "Aqueous Solubility of Methane at Elevated Temperatures and Pressures," *AAPG Bull.*, **632**, 1527 (1979).

Rabinovich, V. A., A. A. Vasserman, V. I. Nedostup, and L. S. Veksler, *Thermophysical Properties of Neon, Argon, Krypton and Xenon*, Hemisphere, Washington, DC (1988).

Reamer, H. H., R. H. Olds, B. H. Sage, and W. N. Lacey, "Phase Equilibria in Hydrocarbon Systems: Methane-Decane System," *Ind. Eng. Chem.*, **34**, 1526 (1942).

Reamer, H. H., R. H. Olds, B. H. Sage, and W. N. Lacey, "Composition of the Dew-Point Gas in the Ethane-Water System," *Ind. Eng. Chem.*, **35**, 790 (1943).

Reamer, H. H., B. H. Sage, and W. N. Lacey, "Phase Equilibria in Hydrocarbon Systems: Volumetric and Phase Behavior of the Methane-Propane System," *Ind. Eng. Chem.*, **42**, 534 (1950).

Reamer, H. H., B. H. Sage, and W. N. Lacey, "Phase Equilibria in Hydrocarbon Systems. Volumetric and Phase Behavior of the Methane-*n*-Heptane System," *Ind. Eng. Chem., Chem. Eng. Data Ser.*, **1**, 29 (1956).

Reamer, H. H., B. H. Sage, and W. N. Lacey, "Phase Equilibria in Hydrocarbon Systems: Volumetric and Phase Behavior of the Methane-Cyclohexane System," *Ind. Eng. Chem., Chem. Eng. Data Ser.*, **3**, 240 (1958).

Rogers, B. L., and J. M. Prausnitz, "High-Pressure Vapor-Liquid Equilibria for Argon + Neopentane and Methane + Neopentane," *J. Chem. Thermodyn.*, **3**, 211 (1971).

Rubio, R. G., J. C. G. Calado, P. Clancy, and W. B. Streett, "A Theoretical and Experimental Study of the Equation of State of Tetrafluoromethane," *J. Phys. Chem.*, **89**, 4637 (1985).

Sage, B. H., B. L. Hicks, and W. N. Lacey, "Phase Equilibria in Hydrocarbon Systems. The Methane-*n*-Butane System in the Two-Phase Region," *Ind. Eng. Chem.*, **32**, 1085 (1940).

Sage, B. H., H. H. Reamer, R. H. Olds, and W. N. Lacey, "Phase Equilibria in Hydrocarbon Systems. Volumetric and Phase Behavior of the Methane-*n*-Pentane System," *Ind. Eng. Chem.*, **34**, 1108 (1942).

Schreiber, D. R., and K. S. Pitzer, "Equation of State in the Acentric Factor System," *Fluid Phase Equilibr.*, **46**, 113 (1989).

Shibata, S. K., and S. I. Sandler, "High-Pressure Vapor-Liquid Equilibria, Involving Mixtures of Nitrogen, Carbon Dioxide and *n*-Butane," *J. Chem. Eng. Data*, **34**, 291 (1989).

Shibata, S. K., and S. I. Sandler, "High-Pressure Vapor-Liquid Equilibria of Mixtures of Nitrogen, Carbon Dioxide and Cyclohexane," *J. Chem. Eng. Data*, **34**, 419 (1989b).

Shim, J., and J. P. Kohn, "Multiphase and Volumetric Equilibria of Methane-*n*-Hexane Binary System at Temperatures Between −110°C and 150°C," *J. Chem. Eng. Data*, **7**, 3 (1962).

Shipman, L. M., and J. P. Kohn, "Heterogeneous Phase and Volumetric Equilibrium in the Methane-*n*-Nonane System," *J. Chem. Eng. Data*, **11**, 176 (1966).

Smith, L. B., J. B. Beattie, and W. C. Kay, "The Compressibilities of Liquid and Gaseous Normal Heptane and an Equation of State for Gaseous Normal Heptane," *J. Amer. Chem. Soc.*, **59**, 1587 (1937).

Soave, G., "A Noncubic Equation of State for *P-V-T* and Phase Equilibrium Calculations (Pure Compounds)," *Fluid Phase Equilibr.*, **56**, 39 (1990).

Somait, F. A., and A. J. Kidnay, "Liquid-Vapor Equilibria at 270.00 K for Systems Containing Nitrogen, Methane, and Carbon Dioxide," *J. Chem. Eng. Data*, **23**, 301 (1978).

Starling, K. E., and M. S. Han, "Thermo Data Refined for LPG: 14. Mixtures," *Hydroc. Process.*, **51**, 129 (1972).

Sultanov, R. G., V. G. Skripka, and A. Yu. Namiot, "Moisture Content of Methane at High Temperatures and Pressures," *Gazovaia Promyshlennost*, 16 (Apr. 6, 1971).

Sultanov, R. G., V. G. Skripka, and A. Yu. Namiot, "Solubility of Methane in Water at High Temperatures and Pressures," *Gazovaia Promyshlennost*, 17 (May 6, 1972).

Trappeniers, N. J., and J. A. Schouten, "Vapour-Liquid and Gas-Gas Equilibria in Simple Systems: III. The System Neon-Krypton," *Physica*, **73**, 546 (1974).

Ulybin, S. A., and E. P. Zherdev, "Density of Sulfur Hexafluoride in the −40 to +200° Range at Pressures to 500 bars," *Dokl. Akad. Nauk SSSR*, **191**, 572 (1970).

Verbeke, O. B., V. Jansoone, R. Gielen, and J. DeBoelpaep, "The Equation of State of Fluid Argon and Calculation of the Scaling Exponents," *J. Phys. Chem.*, **73**, 4076 (1969).

Vidal, J., "Phase Equilibria and Density Calculations for Mixtures in the Critical Range with Simple Equations of State," *Ber. Bunsenges. Phys. Chem.*, **88**, 784 (1984).

Wentorf, Jr., R. H., "Isotherms in the Critical Region of Carbon Dioxide and Sulfur Hexafluoride," *J. Chem. Phys.*, **24**, 607 (1956).

Yamada, T., "An Improved Generalized Equation of State," *AIChE J.*, **19**, 286 (1973).

Yorizane, M., S. Yoshimura, H. Masuoka, and M. Nakamura, "Prediction of High-Pressure Vapor-Liquid Equilibria for Multicomponent Systems by the BWR Equation of State," *J. Chem. Eng. Japan*, **4**, 10 (1971).

Younglove, B. A., and J. F. Ely, "Thermophysical Properties of Fluids: II. Methane, Ethane, Propane, Isobutane and Normal Butane," *J. Phys. Chem. Ref. Data*, **16**, 577 (1987).

Appendix

Statistical mechanics yields rigorous expressions for composition dependency for each virial coefficient. These results are reviewed briefly. It is then explained how this composition dependency is violated by certain corresponding states treatments.

The basic statistical mechanics of fluid as related to the virial series shows that the second virial coefficient relates to interactions of two molecules, the third virial coefficient to interactions of three molecules, and so on. In a binary mixture, this implies 1-1, 1-2, and 2-2 interactions for the second virial coefficient, and so on. After appropriate statistical factors are introduced, the following relationships are obtained:

$$z = 1 + B\rho + C\rho^2 + D\rho^3 + \cdots \tag{A1}$$

with

$$B = x_1^2 B_{11} + 2x_1x_2B_{12} + x_2^2B_{22} \tag{A2a}$$

$$C = x_1^3C_{111} + 3x_1^2C_{112} + 3x_1x_2^2C_{122} + x_2^3C_{222}, \text{ etc.} \tag{A2b}$$

For a simple example, consider just the second virial coefficient and the one-fluid approximation:

$$z(T, \rho, x) = 1 + \rho B(T, x) \tag{A3}$$

Next, assuming equal critical volumes for the two components, $B(T, x)$ takes the form:

$$B(T, x) = v_c B_r(T_r^{\text{mix}}) \tag{A4}$$

The composition-averaged critical temperature frequently used as a scaling factor for T_r^{mix} yields:

$$T_r^{\text{mix}} = T/(x_1^2T_{c,11} + 2x_1x_2T_{c,12} + x_2^2T_{c,22}) \tag{A5}$$

The temperature dependence of B_r is frequently expressed as a series in negative powers of T_r.

$$B_r = C_0 + \frac{C_1}{T_r} + \frac{C_2}{T_r^2} + \cdots + \frac{C_n}{T_r^n} \tag{A6}$$

For accurate representation of real fluid properties, this series must extend beyond the term in T_r^{-2}. Substituting Eqs. A5 and A6 into Eq. A4, we obtain:

$$B(T, x) = v_c\Bigg[C_0 + \frac{C_1(x_1^2T_{c,11} + 2x_1x_2T_{c,12} + x_2^2T_{c,22})}{T} + \frac{C_2(x_1T_{c,11} + 2x_1x_2T_{c,12} + x_2^2T_{c,22})^2}{T^2} + \cdots + \frac{C_n(x_1^2T_{c,11} + 2x_1x_2T_{c,12} + x_2^2T_{c,22})^n}{T^n} \tag{A7}$$

Since the x-dependency of $B(T, x)$ cannot be more complex than quadratic, only the terms in C_0 and C_1 are acceptable. For higher virial coefficients, the relationships are similar, but may be more complex. Because of the higher-order x-dependencies of these virial coefficients, there may or may not be any inconsistency. The above analysis shows that the numerical effects arising from this inconsistency can be large when the critical temperatures of the components are very different.

It is known that corresponding-states treatments of mixed fluids using shape factors lose accuracy seriously as the difference in critical temperatures of the pure components increases (c.f. Mentzer et al., 1980). This inaccuracy is much greater when vapor and liquid densities are considered in addition to phase compositions. The violation of the composition dependencies of the virial coefficients is presumably a major source of this inaccuracy.

Manuscript received Mar. 25, 1991, and revision received Aug. 1, 1991.