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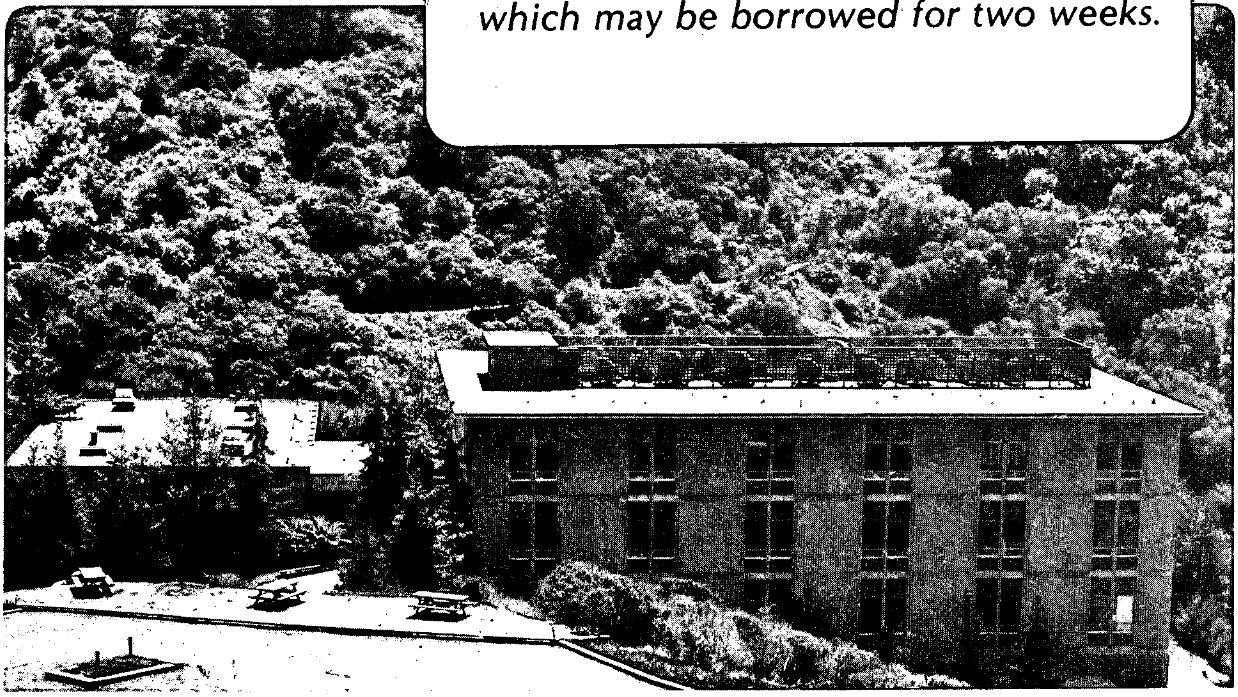

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MOLECULAR THERMODYNAMICS OF FLUID MIXTURES AT LOW AND HIGH DENSITIES

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ABSTRACT

A molecular-thermodynamic framework is proposed to describe phase equilibria over a wide range of densities and compositions. The proposed framework is expressed through a model for the Helmholtz energy that incorporates arbitrary mixing rules at high densities, while at low densities, the model reduces to the correct second-virial-coefficient limit. In effect, this framework provides density-dependent mixing rules.

The proposed framework is illustrated with an equation of state of the Boublik-Mansoori-van der Waals form. Special attention is given to high-pressure vapor-liquid equilibria for systems containing water and hydrocarbons.

INTRODUCTION

Equations of state are commonly used to correlate thermodynamic properties for computer-aided design of chemical processes. When extending equations of state to mixtures for correlation of fluid-phase equilibria, the most important step is the proper formulation of mixing rules for the equation-of-state parameters. Whenever possible, these mixing rules should be consistent with theoretical criteria.

At low densities, an equation of state must not only approach the ideal-gas limit as the density goes to zero but, in addition, it must give a good second virial coefficent; it must give the correct effect of temperature and, for mixtures, it must give a second virial coefficient which is a quadratic function of mole fraction.

At high densities, thermodynamic properties are conveniently represented by perturbation theories based on the van der Waals partition function. These perturbation theories are given as a power series in inverse temperature and inverse volume about the high-temperature, high-density limit. Unfortunately, however, the van der Waals partition function is not reliable for fluids at low densities, especially at low temperatures. Therefore, as discussed elsewhere (e.g. Rowlinson and Swinton, 1982, Sandler, 1985), the van der Waals partition function is not able to correlate fluid-phase behavior for the entire temperature-density space.

We seek a simple, continuous description of fluid properties for densities that range from the ideal-gas limit to liquid-like densities. We have therefore developed a semi-theoretical, molecular-thermodynamic framework for representing the Helmholtz energy of a mixture over a wide density range similar to that described previously (Dimitrelis and Prausnitz, 1982; Prausnitz, 1983, 1985). The framework consists of two parts, one for the low-density and one for the high-density region. For continuity, the framework includes an interpolation function which interpolates between the two density regions. The significant advantage of our framework is that it can incorporate unconventional high-density mixing rules (which are necessary to correlate complex high-pressure fluid-phase behavior) within a molecular-thermodynamic model which also obeys well-established low-density boundary conditions.

Following a suggestion by Kohler and Haar (1981), and following the procedure discussed by Larsen and Prausnitz (1984), we express the molar residual Helmholtz energy a^r as the weighted sum of a low-density second-virial-coefficient term and a high-density van der Waals term. Weighting is achieved through a phenomenological interpolation function of reduced density and temperature that interpolates between the low-density limit and the high-density limit. Mixing rules for the low-density term follow from well-established theory. Mixing rules for the high-density term are determined empirically as indicated e.g. by Wilson (1972), Huron and Vidal (1978) and Peng and Robinson (1980).

Our framework can be applied to any equation of state of the van der Waals form. We present here examples using a Boublik-Mansoori/van der Waals equation of state. (Similar calculations using the perturbed-hard-chain equation of state were presented by Cotterman *et al.* (1986)). Calculated binary phase equilibria for several highly asymmetric mixtures are used to demonstrate the flexibility as well as the limitations of our framework.

Preliminary versions of these concepts have been presented in an earlier publication (Lüdecke and Prausnitz, 1985). Similar work has been proposed by numerous other investigators, notably by Mathias and Copeman (1983), Mollerup (1983), Panagiotopoulos and Reid (1986) and Wogatzki (1988).

RESIDUAL HELMHOLTZ ENERGY

We seek an expression for the molar residual Helmholtz energy a^{r} for a fluid mixture. The residual Helmholtz energy is defined as the Helmholtz energy of a real mixture minus that of an ideal-gas mixture at the same temperature, density and composition. It is most convenient to develop a model for the Helmholtz energy because its derivatives with respect to density and component mole number yield, respectively, the pressure and the chemical potential; these two properties are required to perform isothermal phase-equilibrium calculations.

Following van der Waals, we separate a^{r} into reference and perturbation terms:

$$a^{r} = a^{ref} + a^{per} \tag{1}$$

The reference term includes repulsive intermolecular forces; the perturbation term includes attractive intermolecular forces. We separate the perturbation term into low-density (second-virial) and high-density (dense-fluid) contributions:

$$\boxed{a^{per} = a^{sv}\left(1 - \mathcal{F}\right) + a^{df}\,\mathcal{F}} \tag{2}$$

Function $\mathcal{F}$ interpolates smoothly between the two limits.

The separation shown in Equation (2) allows us to use two independent molecular-thermodynamic models, one for each of the two ends of the density range. On the one hand, we can satisfy the temperature and mole-fraction dependence of the second virial coefficent; on the other, we have the freedom to use a high-density attractive term with whatever mixing rules may be required to correlate highly nonideal fluid-phase behavior at liquid-like densities.

At constant temperature .and composition, Figure 1 shows the low-density and high-density perturbation contributions to the molar residual Helmholtz energy as a function of molar density. Interpolation function $\mathcal{F}$ interpolates between the two contributions.

For the reference contribution a^{ref}, we use the Boublik-Mansoori expression for a hard-sphere mixture (See Appendix I). For the second-virial term a^{sv}, we use

$$a^{sv} = -\rho \sum_{i=1}^{m} \sum_{j=1}^{m} x_i x_j a_{ij}^{sv}(T) \tag{3}$$

where ρ is the molar density, x_i is the mole fraction of component i, m is the number of components in the mixture and $a_{ij}^{sv}(T)$ is an empirical expression for the effect of temperature T on the attractive contribution to the second virial coefficient. For this work, we use for $a_{ij}^{sv}(T)$ the correlation proposed by Tsonopoulos (1974) (See Appendix II).

MOLECULAR-THERMODYNAMIC MODEL AT HIGH DENSITY

For the dense-fluid term a^{df}, we use a simple van der Waals expression:

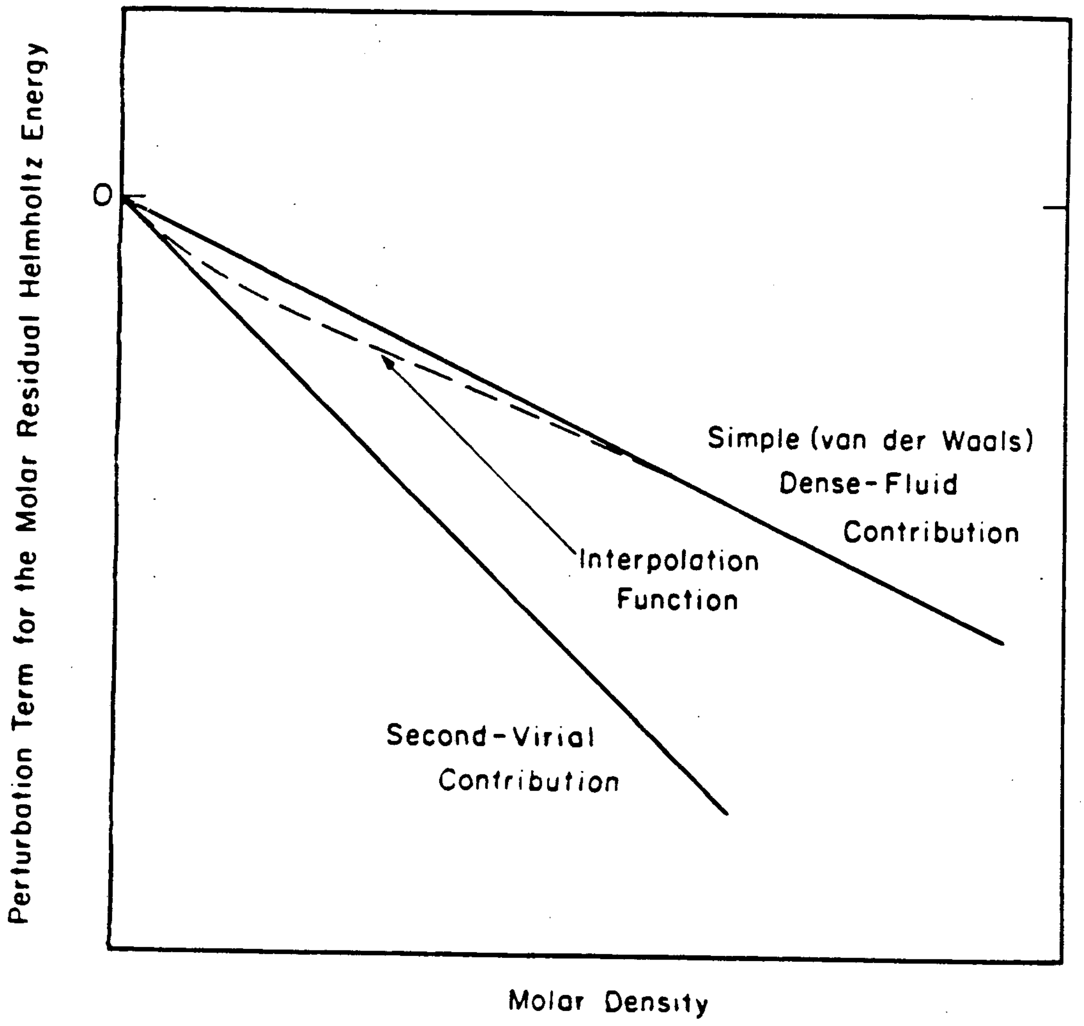

Figure 1. Perturbation Contribution to the Molar Residual Helmholtz Energy According to the Proposed Model as a Function of Density, at Constant Temperature and Composition.

$$\boldsymbol{a}^{df} = -a^{df}(T,\rho,x_i)\rho \tag{4}$$

The attractive-force parameter a^{df} depends, in general, upon temperature, density and composition. For the illustrative purposes of this work, we assume the simplest case where a^{df} depends on temperature and composition only. However, the framework we are proposing is not limited to this case; it can also be used with more complex density-dependent forms for the attractive-force parameter, e.g., with the perturbation term for the Redlich-Kwong equation or the perturbed-hard-chain equation (Cotterman *et al.*, 1986).

The mixing rule for a^{df} is now arbitrary since it does not affect the second virial coefficient. Any empirically successful rule can be used. For the mixtures of interest here, we use a mixing rule which is cubic in mole fraction:

$$\boxed{a^{df}(T,x_i) = \sum_{i=1}^{m}\sum_{j=1}^{m}\sum_{p=1}^{m} x_i x_j x_p a^{df}_{ijp}(T)} \tag{5}$$

where

$$a^{df}_{iii}(T) = a^{df}_i(T) \tag{6}$$

$$a^{df}_{iij}(T) = \frac{1}{3}\left[a^{df}_i(T) + 2a^{df}_{ij}\left(1 - k^{df}_{j,i}\right)\right] \tag{7}$$

$$a^{df}_{ijp}(T) = \frac{1}{6}\{a^{df}_{ij}\left[\left(1-k^{df}_{i,j}\right) + \left(1-k^{df}_{j,i}\right)\right] + a^{df}_{jp}\left[\left(1-k^{df}_{j,p}\right) + \left(1-k^{df}_{p,j}\right)\right] +$$

$$+ a^{df}_{ip}\left[\left(1-k^{df}_{i,p}\right) + \left(1-k^{df}_{p,i}\right)\right]\} \tag{8}$$

and

$$a^{df}_{ij} = \sqrt{a^{df}_i(T)\, a^{df}_j(T)}\ . \tag{9}$$

This mixing rule allows for two adjustable parameters per binary pair, since $k^{df}_{j,i} \neq k^{df}_{i,j}$. The algebraic form of the mixing rule is such that the two binary parameters account for deviations from the geometric-mean combining rule (Equation (9)) at the two opposite ends of the concentration range. Parameter $k^{df}_{i,j}$ is characteristic of the energetic interactions for a molecule i infinitely dilute in molecules j. Similarly, parameter $k^{df}_{j,i}$ depends on the interactions between a molecule j infinitely dilute in molecules i. Therefore, the two parameters are independent.

For mixtures of molecules with similar intermolecular potentials (i.e., when $k^{df}_{j,i} = k^{df}_{i,j} \equiv k^{df}_{ij}$) Equation (5) reduces to the familiar quadratic form

$$a^{df}(T,x_i) = \sum_{i=1}^{m} \sum_{j=1}^{m} x_i x_j \sqrt{a_i^{df}(T)\, a_j^{df}(T)}\,(1 - k^{df}_{ij}) \tag{5a}$$

Mixing rules similar to Equation (5) have been proposed by Mathias and Copeman (1983), Panagiotopoulos and Reid (1986), Stryjek and Vera (1986) and Adachi and Sugie (1986). However, these previous authors have not given as careful attention as we have, toward obtaining the correct effect of composition and temperature on second virial coefficients at low densities.

INTERPOLATION FUNCTION

We determine interpolation function $\mathcal{F}$ empirically, subject to necessary boundary conditions. At zero density, $\mathcal{F}$ must be zero; this boundary condition assures that the interpolation function does <u>not</u> contribute to the second virial coefficient. To demonstrate, we write for the perturbation contribution to the second virial coefficient

$$B^{per} = \frac{1}{RT}\left[\frac{\partial \mathbf{a}^{per}}{\partial \rho}\right]_{\rho=0} \tag{10}$$

where R is the gas constant. Using Equation (2), we obtain

$$B^{per} = \frac{1}{RT}\left[\frac{\partial \mathbf{a}^{sv}}{\partial \rho}\right]_{\rho=0} + \frac{1}{RT}\left[\frac{\partial(\mathbf{a}^{df} - \mathbf{a}^{sv})}{\partial \rho}\right]_{\rho=0} \mathcal{F}(\rho=0) + .$$

$$+ \frac{1}{RT}\{\mathbf{a}^{df}(\rho=0) - \mathbf{a}^{sv}(\rho=0)\}\left[\frac{\partial \mathcal{F}}{\partial \rho}\right]_{\rho=0} \tag{11}$$

If the value for $\mathcal{F}$ at zero density is zero, the second term vanishes. Since the dense-fluid and second-virial contributions to the Helmholtz energy are both zero at zero density, the third term also vanishes. Therefore, the perturbation contribution to the second virial coefficient is determined only by the first term of Equation (11).

At a limiting liquid-like density ρ_L, $\mathcal{F}$ must approach unity. For our purposes here, we define the limit of "liquid-like" density as that density where reduced density ξ is equal to the closed-packed density τ for a cubic face-centered lattice, i.e.

$$\xi_{\rho \to \rho_L} = \tau = \frac{\pi\sqrt{2}}{6} \tag{12}$$

For the reduced density ξ of a mixture, we use

$$\xi = \frac{\rho}{4}\sum_{i=1}^{m} x_i b_i \tag{13}$$

where b is the van der Waals covolume.

The derivative of $\mathcal{F}$ with respect to density at zero density is related to the third virial coefficient. It must be non-zero and finite so that the third virial coefficient may attain physically reasonable values. A zero derivative implies that the third virial coefficient is dictated by the reference term <u>only</u>; this is physically unrealistic. However, at liquid-like densities, the derivative of $\mathcal{F}$ with respect to density must approach zero because we want the contribution of the second-virial-coefficient on pressure to diminish at high densities. Therefore, $\mathcal{F}$ must asymptotically approach unity at liquid-like densities.

Finally, at constant density, $\mathcal{F}$ must decrease with rising temperature so that the molecular-thermodynamic model approaches the random-mixture limit at high temperature.

A simple empirical form for $\mathcal{F}$ which obeys all necessary boundary conditions is shown in Figure 2. Its analytical form is given by

$$\boxed{\mathcal{F} = 1 - \left(1 - \frac{\xi}{\tau}\right)^{\frac{\gamma}{T_r}}} \tag{14}$$

where T_r is the reduced temperature and γ is a universal constant. This constant is obtained from pure-component vapor-pressure and liquid-density data for a variety of fluids. A value of $\gamma = 6$ gives the best overall representation. For a mixture, reduced temperature is defined by

$$T_r = \frac{T}{\sum_{i=1}^{m} \sum_{j=1}^{m} x_i x_j \sqrt{T_{c,i} T_{c,j}}} \tag{15}$$

where $T_{c,i}$ is the critical temperature of component i. For the critical isotherm, interpolation function $\mathcal{F} = 0.5$ at approximately 60% of the critical density, as indicated in Figure 2.

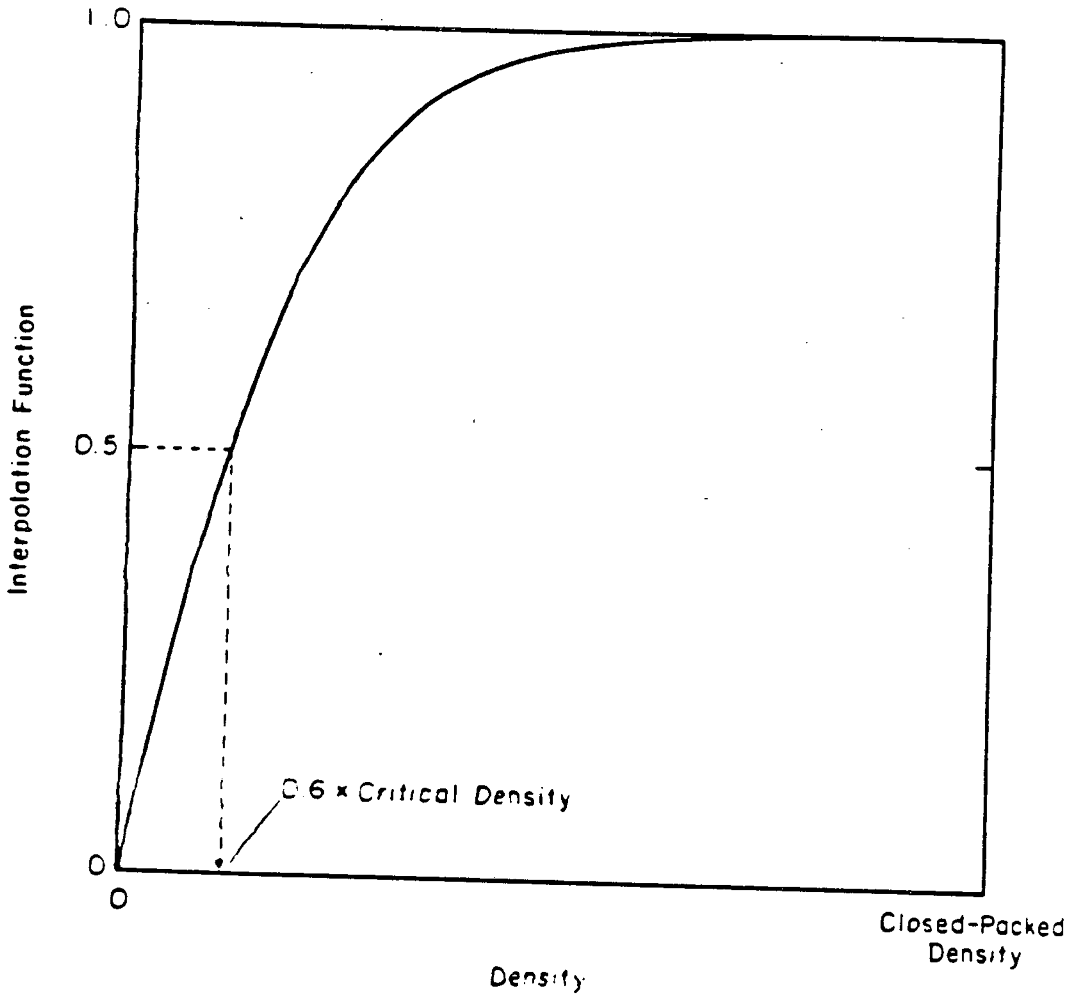

Figure 2. Interpolation Function $\mathcal{F}$.

The advantage of the molecular-thermodynamic framework proposed here follows from its flexibility; while it can incorporate any kind of unconventional high-density mixing rule (e.g., Michel *et al.*, 1989), it nevertheless always gives the correct low-density second-virial-coefficient limit, including the quadratic mole-fraction composition dependence.

Finally, to yield good second virial coefficients, we introduce a small correction term to the Helmholtz energy at low densities to account for the disparity in the value of van der Waals covolume between low and high density. The estimated value for the van der Waals covolume depends upon the density range for the data used for its calculation (Prausnitz, 1985). High-density data give a lower value for b than second-virial-coefficient data. The mathematical form for the correction function is given in Appendix III.

PARAMETER CORRELATION

Pure-component parameters a_i^{df} and b_i depend on temperature according to the empirical relations:

$$a_i^{df} = \frac{R^2 T_{c,i}^2}{P_{c,i}} \frac{a_i^{(0)}}{1+a_i^{(1)}\left(\frac{T}{T_{c,i}}\right)^2} \tag{16}$$

$$b_i = \frac{RT_{c,i}}{P_{c,i}} \frac{b_i^{(0)}}{1+b_i^{(1)}\left(\frac{T}{T_{c,i}}\right)^2} \tag{17}$$

Dimensionless coefficients $a_i^{(0)}$, $a_i^{(1)}$, $b_i^{(0)}$ and $b_i^{(1)}$ are obtained from vapor-pressure, liquid-density and supercritical-density data. Table 1 gives numerical values for the components investigated in this work.

Table 1: Pure-component parameters $a_i^{(0)}, a_i^{(1)}, b_i^{(0)}$ and $b_i^{(1)}$.

Component	$a_i^{(0)}$	$a_i^{(1)}$	$b_i^{(0)}$	$b_i^{(1)}$	Reference
CH_4	0.5205	0.08510	0.1884	0.09499	Angus *et al.* (1978)
C_2H_6	0.6092	0.3761	0.2068	0.3158	Goodwin *et al.* (1976)
C_3H_8	0.6169	0.3847	0.1985	0.2506	Goodwin and Haynes (1982)
n-C_4H_{10}	0.6249	0.4165	0.1943	0.2413	Haynes and Goodwin (1982)
n-C_6H_{14}	0.6528	0.5409	0.1867	0.2506	Vargaftik (1975)
n-$C_{10}H_{22}$	0.7420	0.8277	0.1840	0.3067	Vargaftik (1975)
C_6H_6	0.6327	0.4856	0.1942	0.2955	Institute of Gas Technology (1978)
CH_3OH	0.6810	0.8170	0.1676	0.3505	Radosz (1980) Machado and Streett (1983)
C_2H_5OH	0.8659	1.1345	0.1973	0.4310	Lo and Stiel (1969) Ambrose *et al.* (1970, 1975)
$CH_3CHOHCH_3$	0.9552	1.4104	0.2033	0.4888	Radosz (1980)
$CH_3CHOHC_2H_5$	0.9266	1.3243	0.2069	0.4850	Radosz (1980)
CH_3OCH_3	0.6046	0.3675	0.1884	0.2177	Boublik *et al.* (1984)
CO_2	0.5901	0.3260	0.1811	0.1481	Angus *et al.* (1976)
H_2O	0.5770	0.5803	0.1644	0.3605	Bain (1964)

Binary dense-fluid parameters $k_{i,j}^{df}$ and $k_{j,i}^{df}$ are obtained from vapor-liquid or liquid-liquid equilibria, or Henry's constants. For some highly asymmetric aqueous hydrocarbon mixtures, the dense-fluid parameter describing the dilute aqueous phase is temperature-dependent according to:

$$k^{df}_{i,H_2O} = k^{df,(0)}_{i,H_2O} + \frac{k^{df,(1)}_{i,H_2O}}{T \text{ in K}} \tag{18}$$

Table 2 gives binary parameters for the mixtures investigated in this work. Details concerning the numerical procedure for data reduction are given elsewhere (Topliss *et al.*, 1988).

Table 2: Binary dense-fluid parameters $k^{df}_{i,j}$ and $k^{df}_{j,i}$.

Mixture (i/j)	$k^{df,(0)}_{i,j}$	$k^{df,(1)}_{i,j}$	$k^{df}_{j,i}$	T, K	Reference
CO_2/H_2O	0.32	-145.85	0.091	298-348	Wiebe (1941)
CH_3OCH_3/H_2O	0.45	-226.22	0.064	373-394	Pozo and Streett (1985)
C_3H_8/H_2O	0.29	-163.38	0.45	310-427	Kobayashi and Katz (1953)
n-C_4H_{10}/H_2O	0.29	-175.41	0.48	377-510	Reamer *et al.* (1952)
C_6H_6/H_2O	0.18	-91.73	0.26	313-473	Tsonopoulos and Wilson (1983)
C_2H_5OH/H_2O	-0.095		-0.058	298-343	Mertl (1972)
$CH_3CHOHCH_3/H_2O$	-0.15		-0.085	308-338	Sada and Morishue (1975)
$CH_3CHOHC_2H_5/H_2O$	-0.16		-0.087	333-353	Altsybeeva *et al.* (1964) Moriyoshi *et al.* (1975)
CO_2/CH_3OH	-0.042		-0.0068	298-313	Ohgaki and Katayama (1976)
CO_2/C_2H_5OH	0.051		0.073	308-348	Panagiotopoulos (1986) Gupta *et al.* (1973)
$CO_2/CH_3CHOHCH_3$	0.076		0.056	316-394	Radosz (1986)

CH_4/CH_3OH	-0.10	0.025	250-310	Hong *et al.* (1986)
C_3H_8/CH_3OH	-0.040	0.029	313-373	Galivel-Solastiouk *et al.* (1986)
n-C_6H_{14}/CH_3OH	-0.022	0.099	280-320	Raal *et al.* (1972) Hölscher *et al.* (1986)
C_3H_8/C_2H_5OH	-0.017	-0.044	325-475	Gomez-Nieto and Thodos (1978)
n-C_6H_{14}/C_2H_5OH	0.015	0.11	298-328	Yuan *et al.* (1963)
C_6H_6/C_2H_5OH	0.034	0.10	298-328	Brown and Smith (1954) Smith and Robinson (1970) Yuan *et al.* (1963)

ILLUSTRATIVE RESULTS

Figures 3 and 4 show calculated and experimental (Kobayashi and Katz, 1953; Reamer *et al.*, 1952) phase equilibria for propane/water and *n*-butane/water at two temperatures. The model correlates the phase behavior for these highly asymmetric aqueous hydrocarbon mixtures very well over a wide range of temperature, pressure and concentration (Note the discontinuity in the mole-fraction axis for the hydrocarbon). For these calculations, the dense-fluid binary parameter for the dilute aqueous phase depends on temperature according to Equation (18).

Since the calculations are near the critical points of the more volatile component, we adjusted the equation-of-state parameters for these components to represent better their pure-component properties in the near-

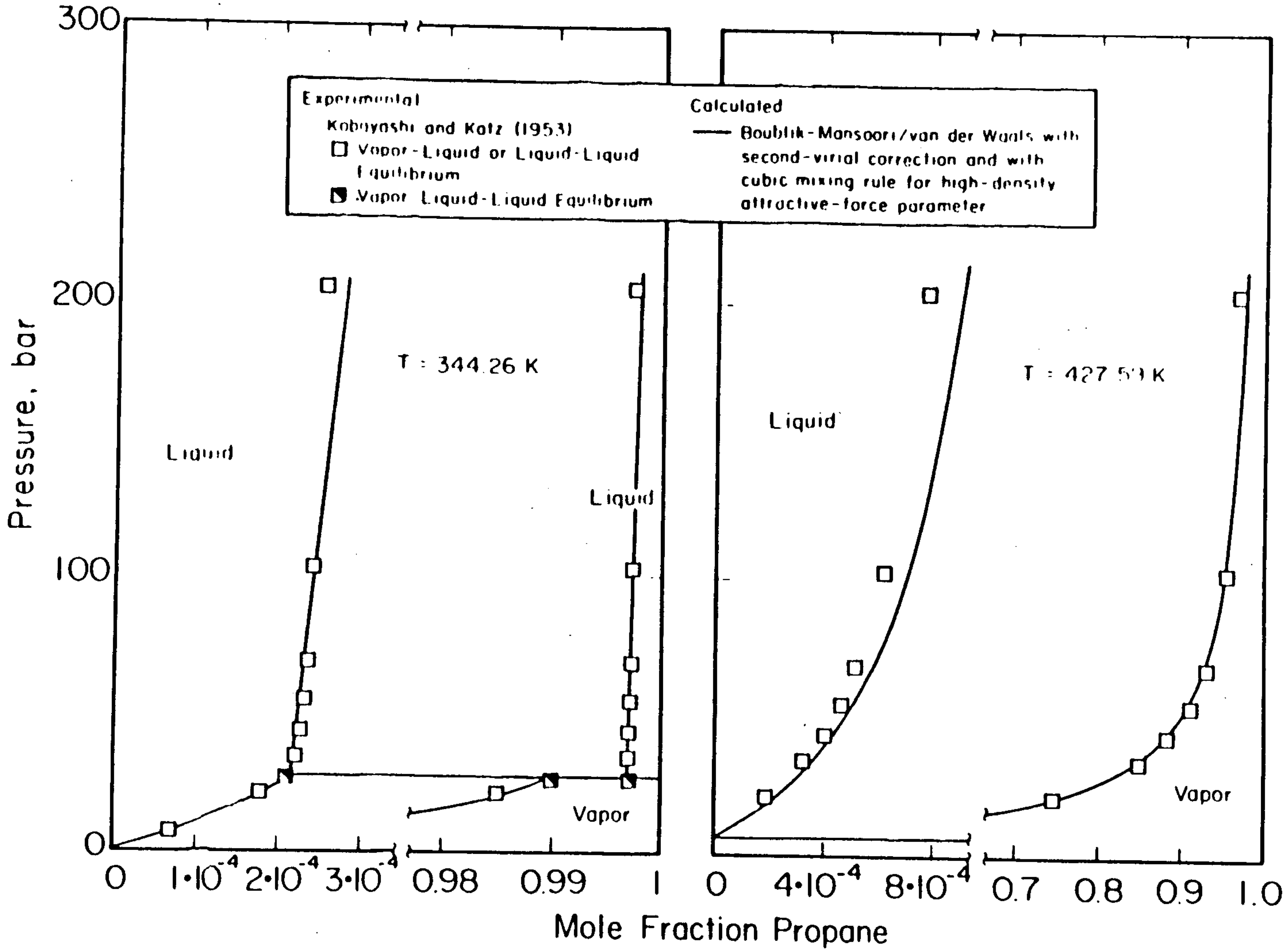

Figure 3. Calculated and Experimental Phase Equilibria for Propane/Water.

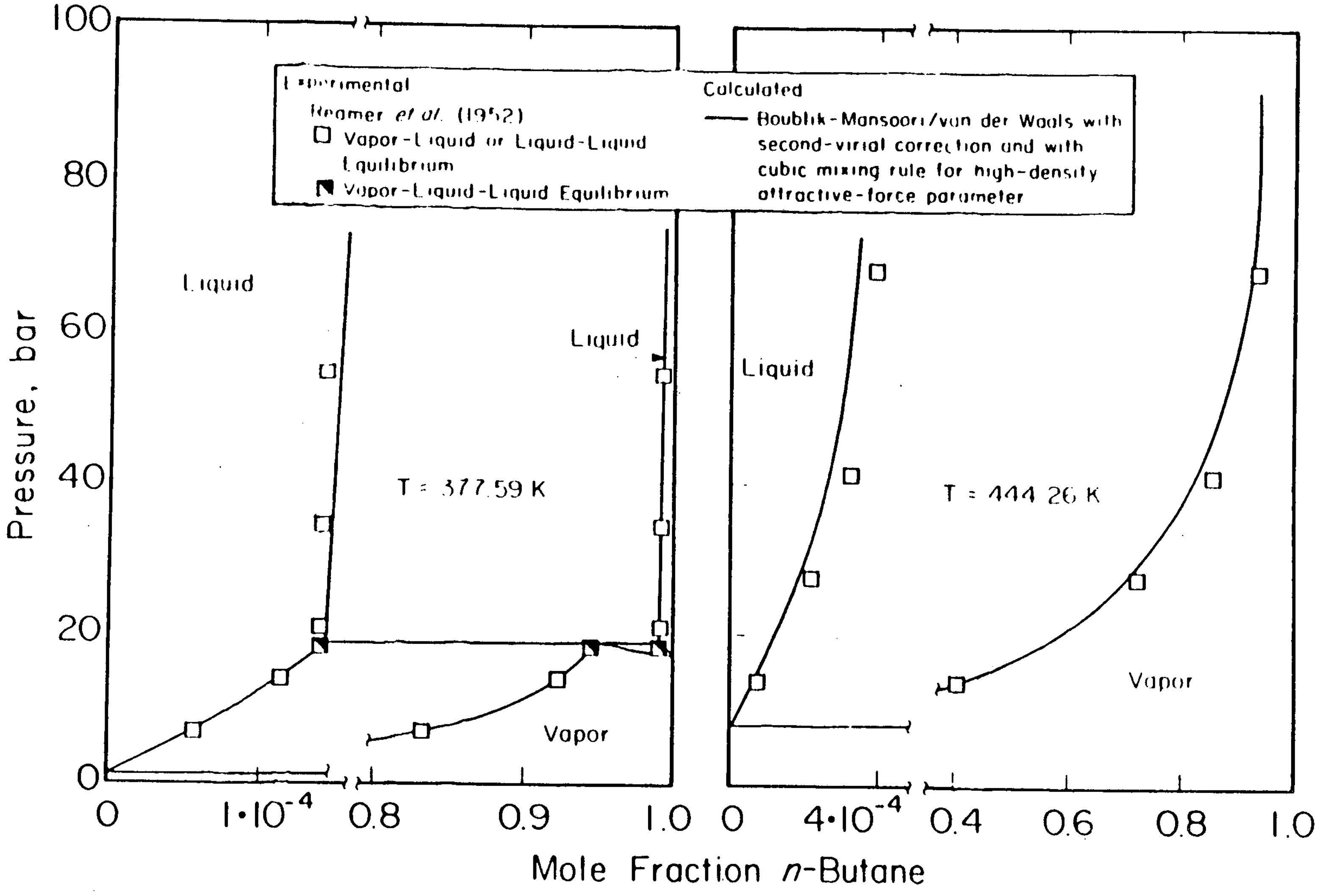

Figure 4. Calculated and Experimental Phase Equilibria for *n*-Butane/Water.

critical region. As discussed in Appendix IV, the choice of equation-of-state parameters has a serious effect on mixture calculations near a component's critical point. Overprediction of the solvent's critical temperature and pressure (even by few degrees or few bars) can adversely affect mixture calculations in the solvent's near-critical region.

Figure 5 shows calculated and experimental (Tsonopoulos and Wilson, 1983) liquid-liquid equilibria at the three-phase pressure for benzene/water. Using a temperature-dependent binary interaction parameter for the aqueous phase, the equation of state reproduces correctly mutual solubilities over a nearly two-hundred-degree (Celsius) temperature range.

Figure 6 shows predicted Henry's constant for benzene in water. The binary parameters used for these calculations were obtained from liquid-liquid equilibrium data. Agreement with experiment (Tsonopoulos and Wilson, 1983) is excellent. Figure 6 indicates the flexibility of the proposed molecular-thermodynamic framework to correlate high-pressure phase behavior while satisfying low-density boundary conditions.

The above examples represent a class of binary mixtures for which the cubic mixing rule [Equation (5)] is particularly suitable for representing the observed phase behavior. The coexisting phases are very dilute; thus, mutual solubilities are directly related to Henry's constants. Each of the two dense-fluid binary parameters [Equation (7)] affects directly the respective infinite-dilution fugacity coefficient. Therefore, these binary parameters can correlate successfully thermodynamic properties at both ends of the concentration range.

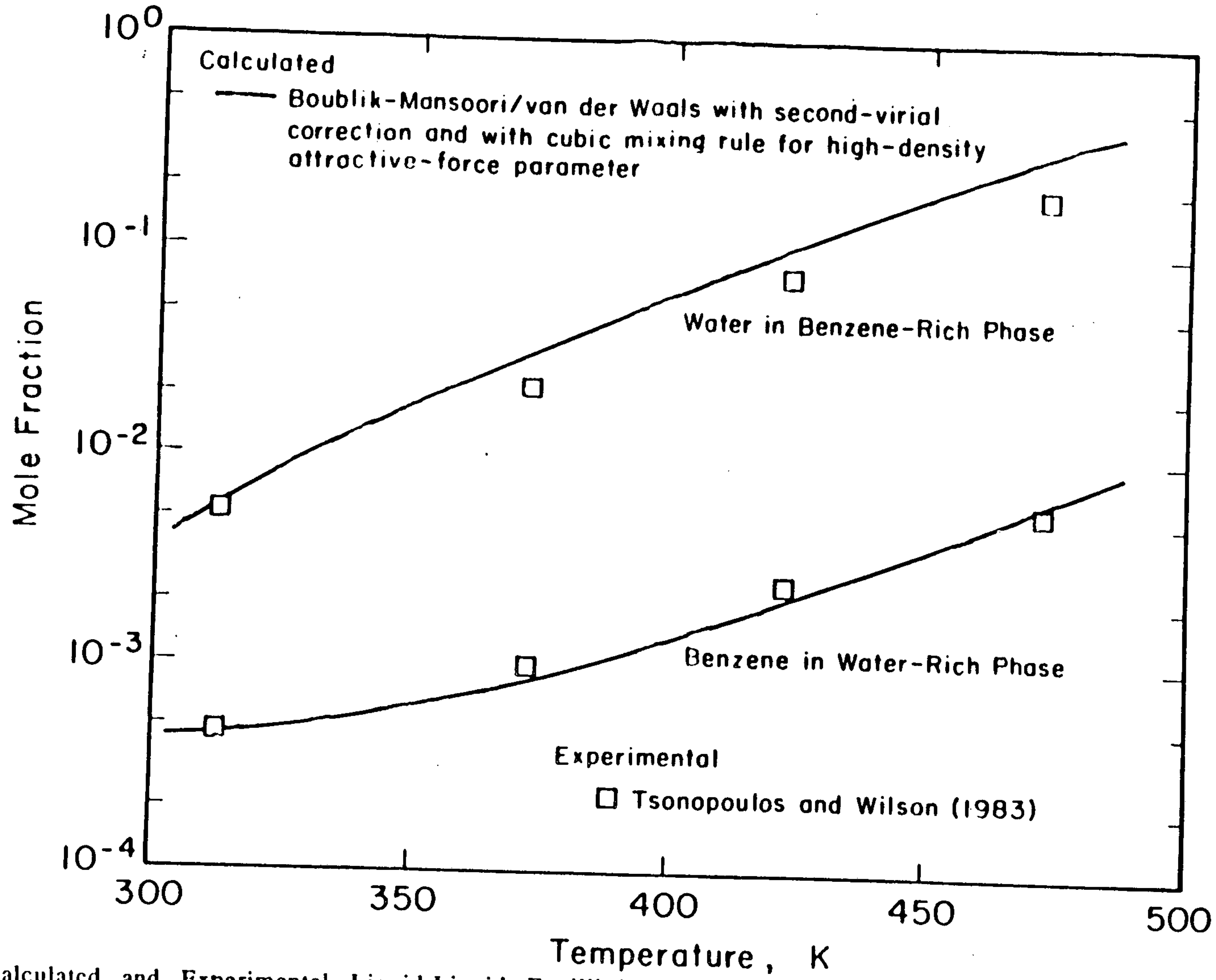

Figure 5. Calculated and Experimental Liquid-Liquid Equilibria for Benzene/Water at Three-Phase Pressure.

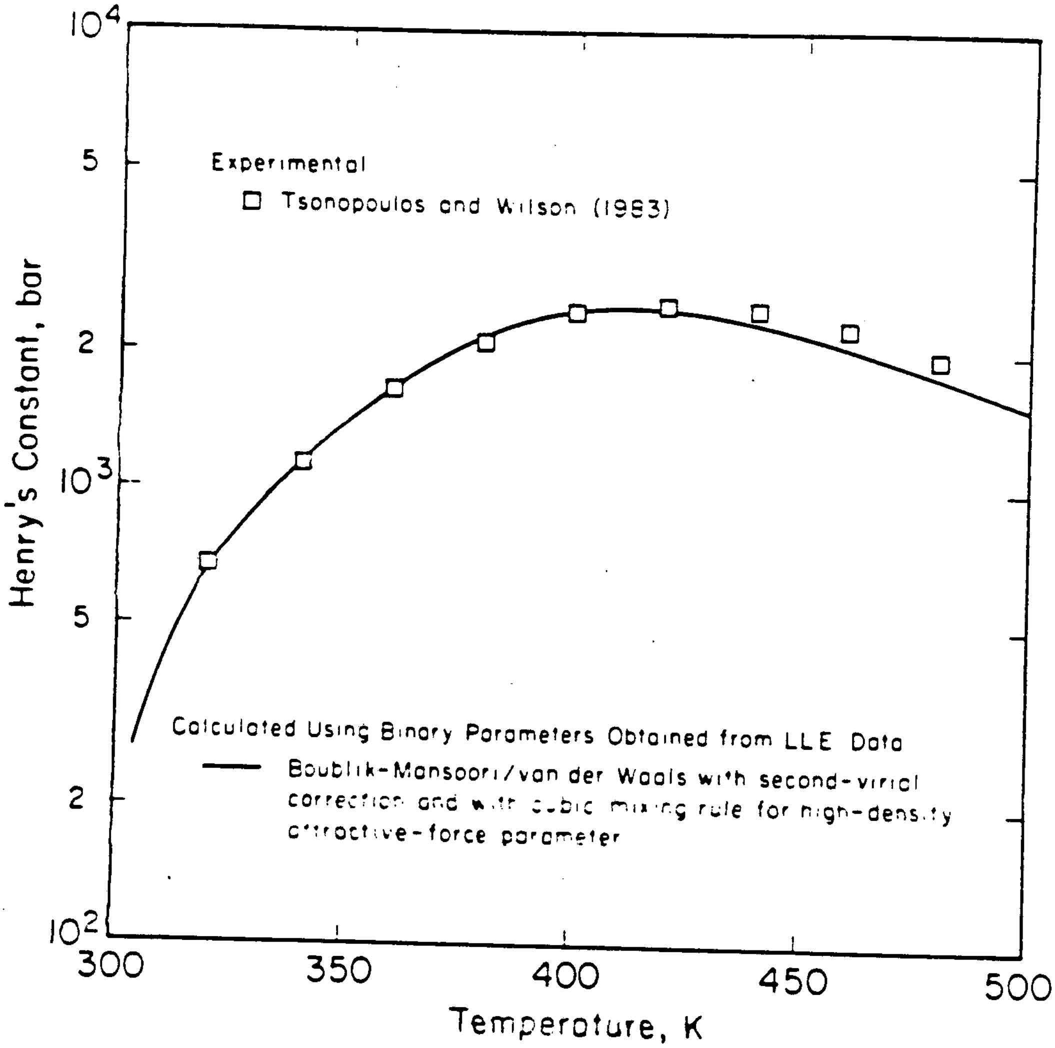

Figure 6. Predicted and Experimental Henry's Constant for Benzene in Water.

Figure 7 shows calculated and experimental (Pozo and Streett, 1984) phase equilibria for dimethyl ether/water. The proposed model correlates the phase behavior very well over a wide range of densities (Note the discontinuity in the pressure axis). Further, while no three-phase data were included in data reduction to obtain the binary parameters, the model predicts the correct three-phase-equilibrium pressure.

Figure 8 shows calculated and experimental (Altsybeeva *et al.*, 1964, Moriyoshi *et al.*, 1975) phase equilibria for the system 2-butanol/water. Using two temperature-independent binary parameters, the model represents well the complex fluid-phase behavior, including the low-pressure azeotrope and three-phase equilibrium as well as the high-pressure liquid-liquid immiscibility over a large pressure range (Note the discontinuity in the pressure axis).

Figure 9 shows calculated and experimental (Wiebe, 1941) vapor-liquid equilibria for carbon dioxide/water. Agreement between experiment and model is excellent including the retrograde region (Note the discontinuity in the mole-fraction axis).

While the proposed model is useful for correlating the properties of several asymmetric mixtures, it suffers from a deficiency common to all van-der-Waals models: it fails to represent phase equilibria near mixture-critical points, overestimating or underestimating the observed phase envelope. This failure becomes particularly important when the liquid-liquid critical locus is in close proximity to the two-phase vapor-liquid region. A small underprediction of the liquid-liquid mixture critical pressure yields an incorrect liquid-liquid immiscibility region when calculating nearby vapor-

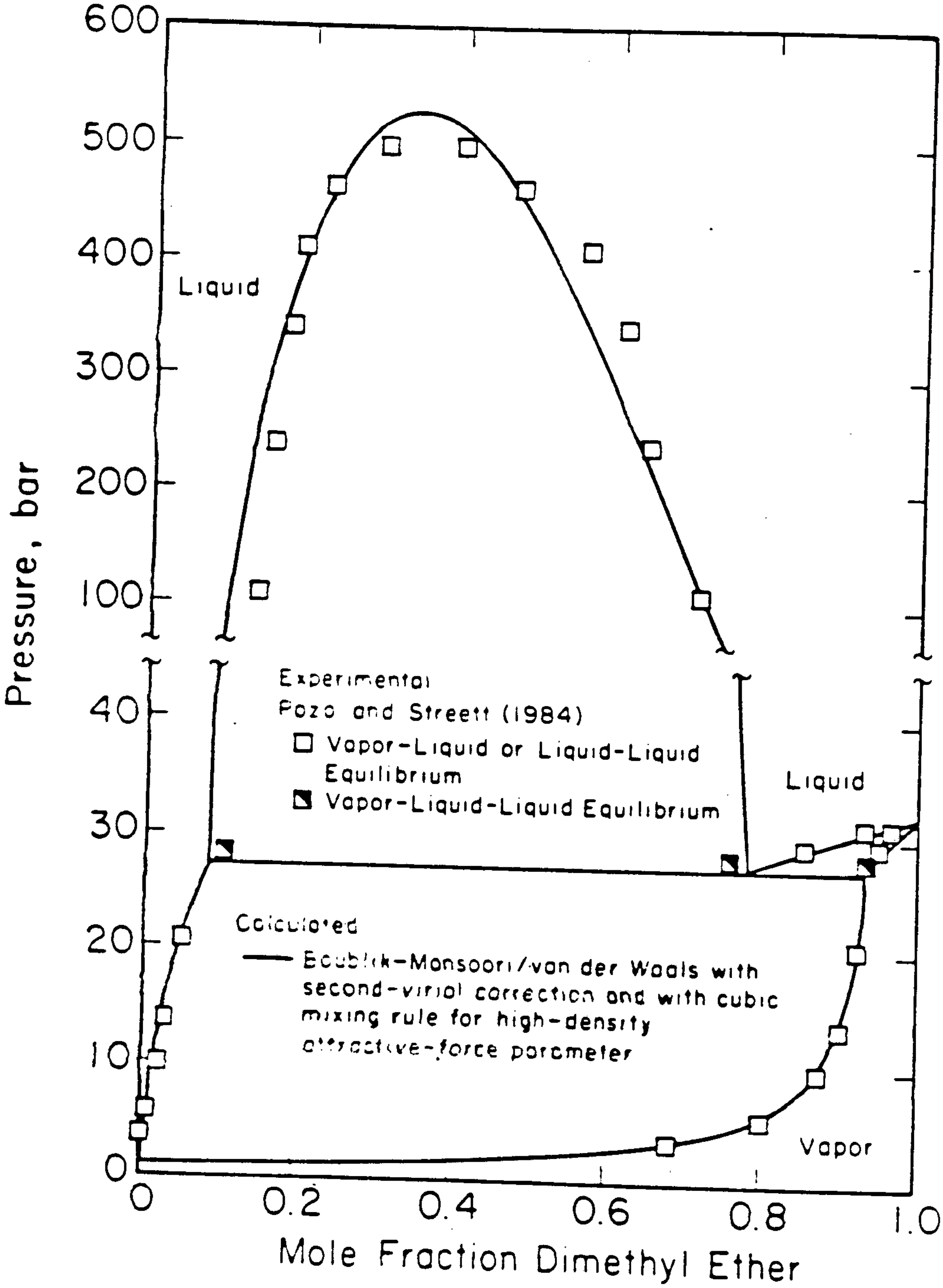

Figure 7. Calculated and Experimental Phase Equilibria for Dimethyl Ether/Water at 373.3 K.

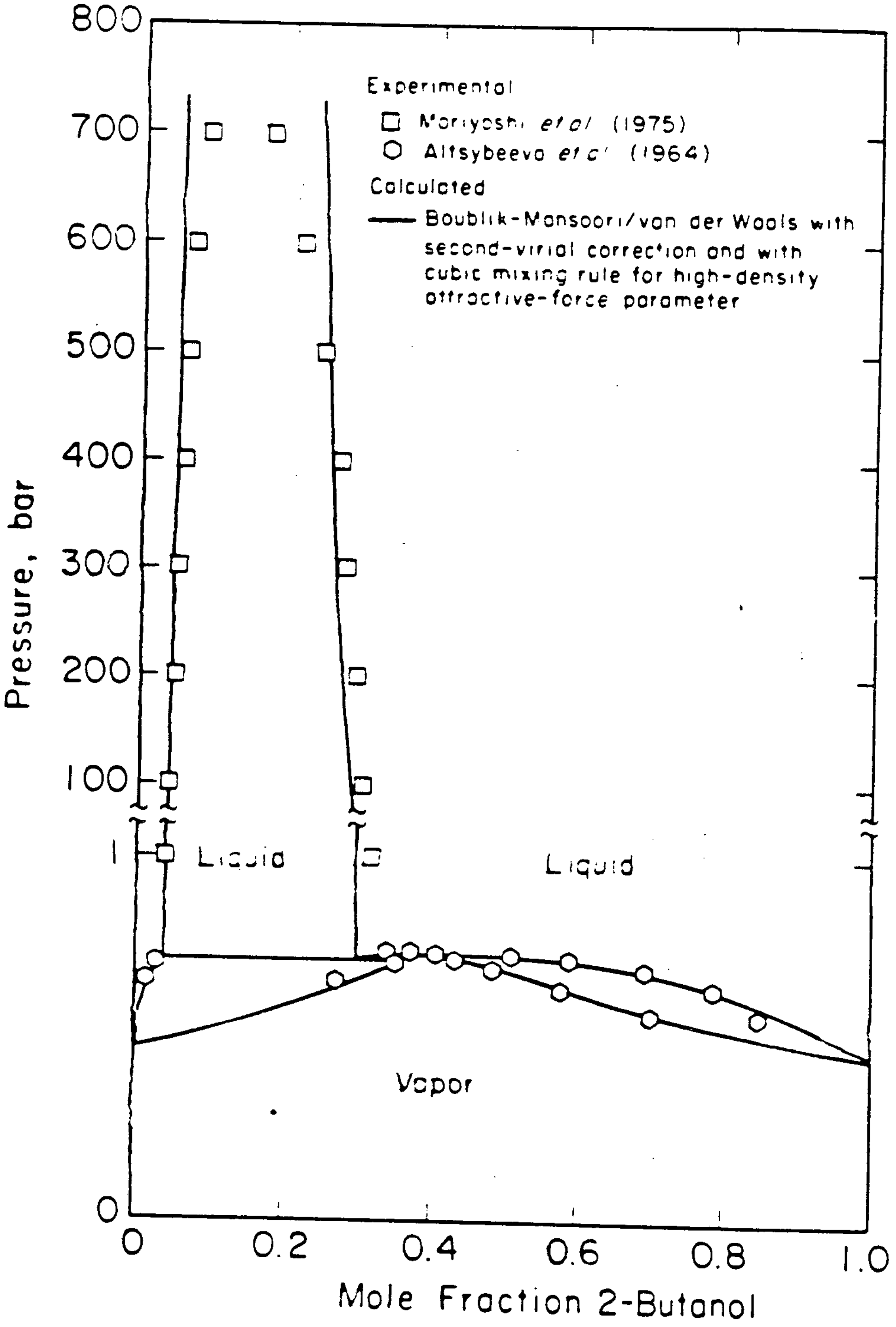

Figure 8. Calculated and Experimental Phase Equilibria for 2-Butanol/Water at 353.15 K.

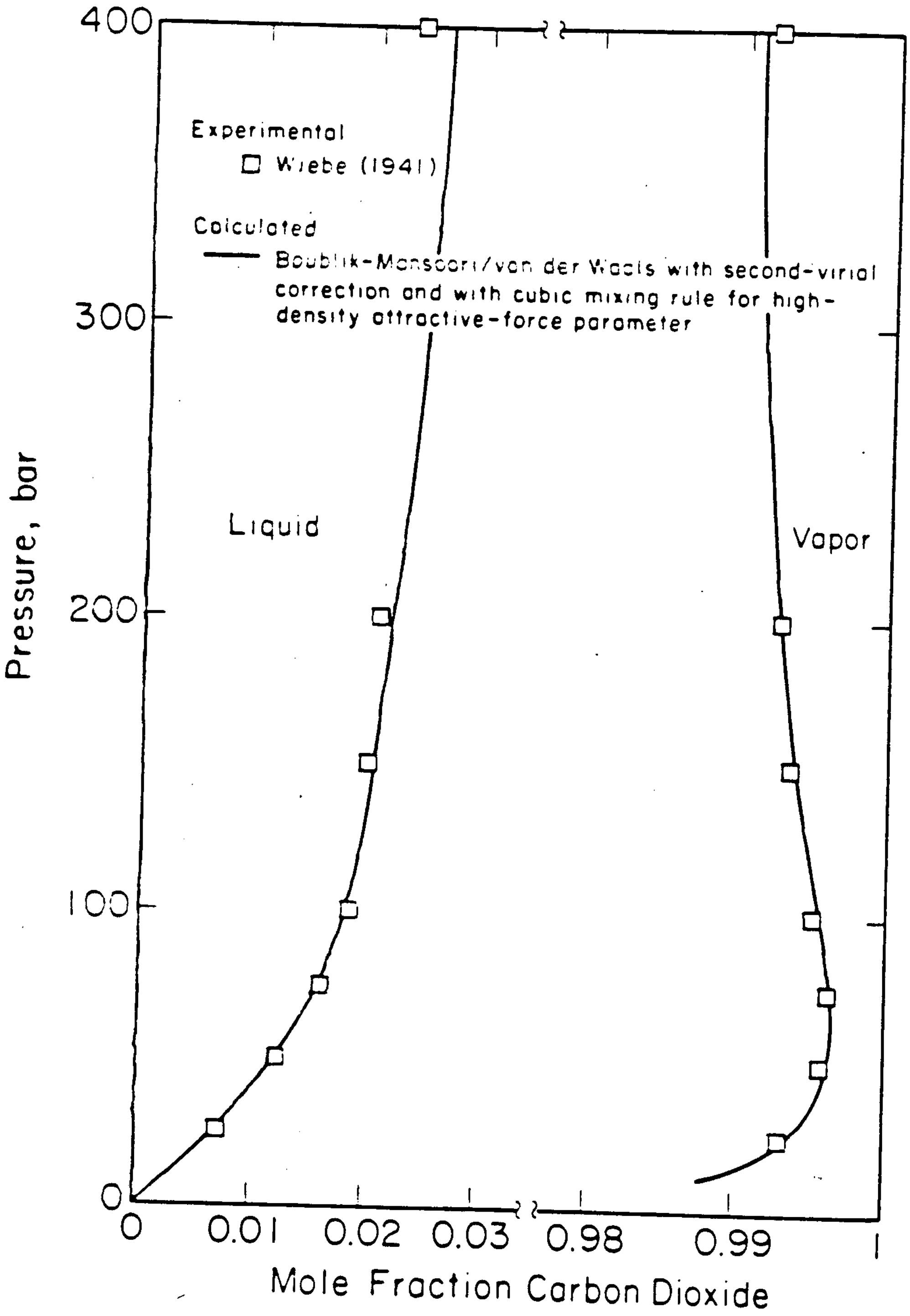

Figure 9. Calculated and Experimental Vapor-Liquid Equilibria for Carbon Dioxide/Water at 323.15 K.

liquid phase equilibria. To illustrate, Appendix V gives results for the propane/methanol mixture.

EFFECT OF THE SECOND VIRIAL COEFFICIENT ON PHASE-EQUILIBRIUM CALCULATIONS

When calculating phase equilibria at low or intermediate densities, it may be important to use a molecular-thermodynamic model which not only reduces to the correct ideal-gas limit but also yields the correct second virial coefficient.

For mixture calculations, the important thermodynamic property is not the absolute value of the second virial coefficient but its derivative with respect to component mole number. This derivative, which is closely related to the cross-second virial coefficient, determines the fugacity coefficient at low densities. Statistical mechanics requires that the mixing rules for equation-of-state parameters must be such that they yield a quadratic mole-fraction dependence for the second virial coefficient. Molecular-thermodynamic models which violate this requirement necessarily give an erroneous composition dependence for the fugacity coefficient of a component in a mixture at modest densities. For a heavy component, dilute in a mixture at modest densities, the fugacity coefficient is often far removed from unity.

Figure 10 shows calculated and experimental (Angus *et al.*, 1976, Hemmaplardh and King, 1972, Kell and McLaurin, 1969, Kudchadker and Eubank, 1970, Lazalde-Crabtree *et al.*, 1980,) second virial coefficients for the system carbon dioxide/methanol. The solid lines indicate calculations using the model proposed here. Tsonopoulos' correlation gives excellent results to

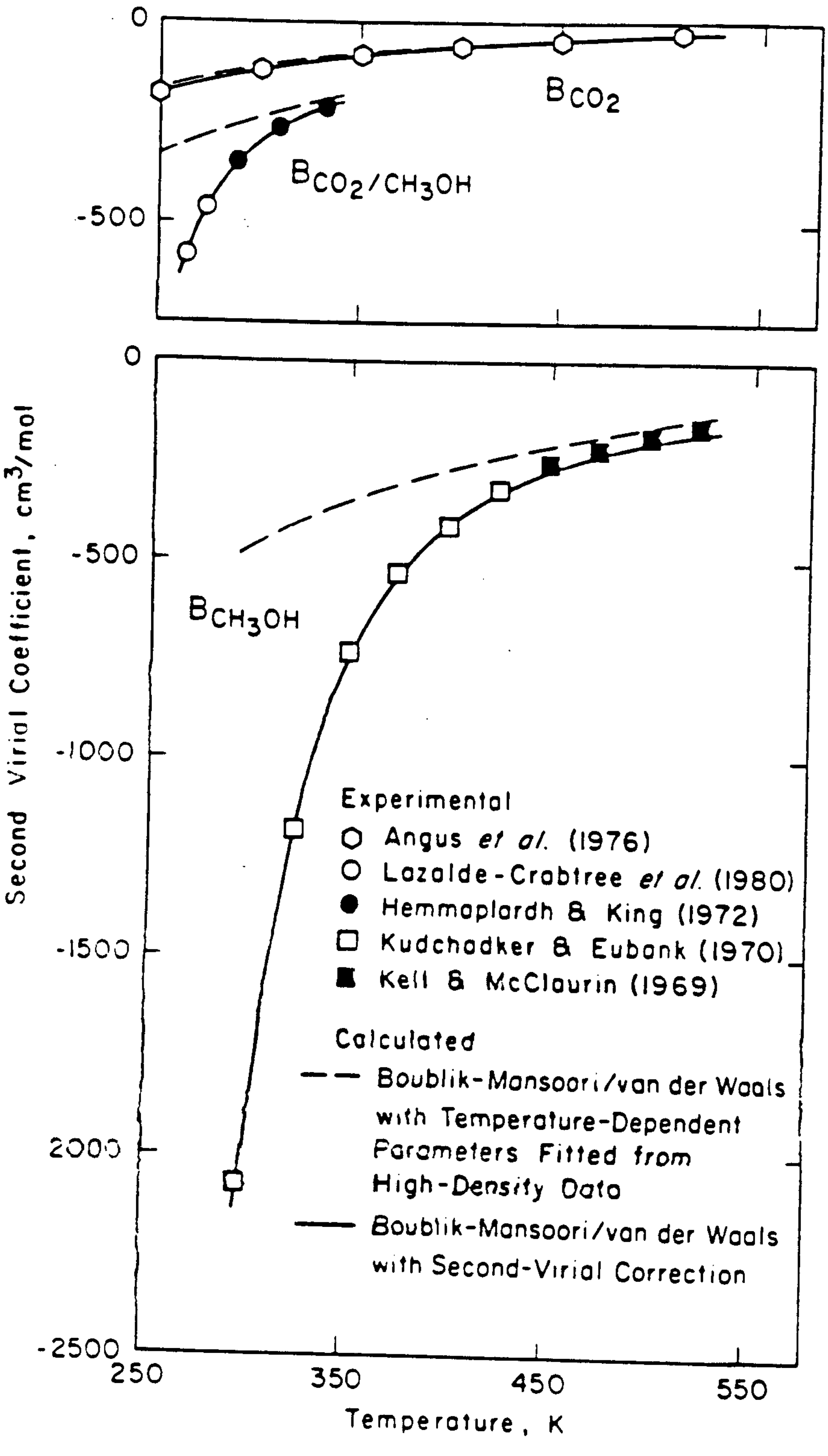

Figure 10. Calculated and Experimental Second Virial Coefficient for the System Carbon Dioxide/Methanol.

very low temperatures. The dashed lines show calculations for the case where we discard the proposed interpolation between low and high densities, that is, where $\mathcal{F}=1$ in Equation (2). In that event, the model becomes a conventional Boublik-Mansoori/van der Waals equation (Dimitrelis and Prausnitz, 1986). We call this the diminutive form of our model. Using equation-of-state parameters obtained at high density [with the quadratic mixing rule for a^{df} (Equation (5a))], we calculate a second virial coefficient which deviates significantly from the observed value, particularly at lower temperatures.

Figure 11 shows the importance of using a model which reduces to the correct second virial coefficient at low densities. Calculated and experimental (Newitt *et al.*, 1956; Lazalde-Crabtree *et al.*, 1980) phase equilibria for the carbon dioxide/methanol system are shown at 263.15 and 273.15 K. We use in this calculation the quadratic mixing rule for the high-density attractive-force parameter [Equation (5a)]. For both sets of calculations shown in Figure 11, binary parameter k_{ij}^{df} is adjusted from solubility data for carbon dioxide in the methanol-rich liquid phase; no vapor-phase data were used for the parameter estimation. The diminutive form of the model underpredicts the observed vapor-phase solubility of methanol while the proposed model represents the phase behavior correctly.

Figure 12 shows the effect observed when we use molecular-thermodynamic terms with physical significance. Calculations and experimental measurements (Olds *et al.*, 1942) are presented for vapor-phase mole fractions for water in methane at 310.93 K over a large pressure range. We show four calculations: first, we use the diminutive form for our model and the quadratic mixing rule for the attractive-force parameter [Equation (5a)]; we then obtain an overprediction of the observed vapor-phase solubilities.

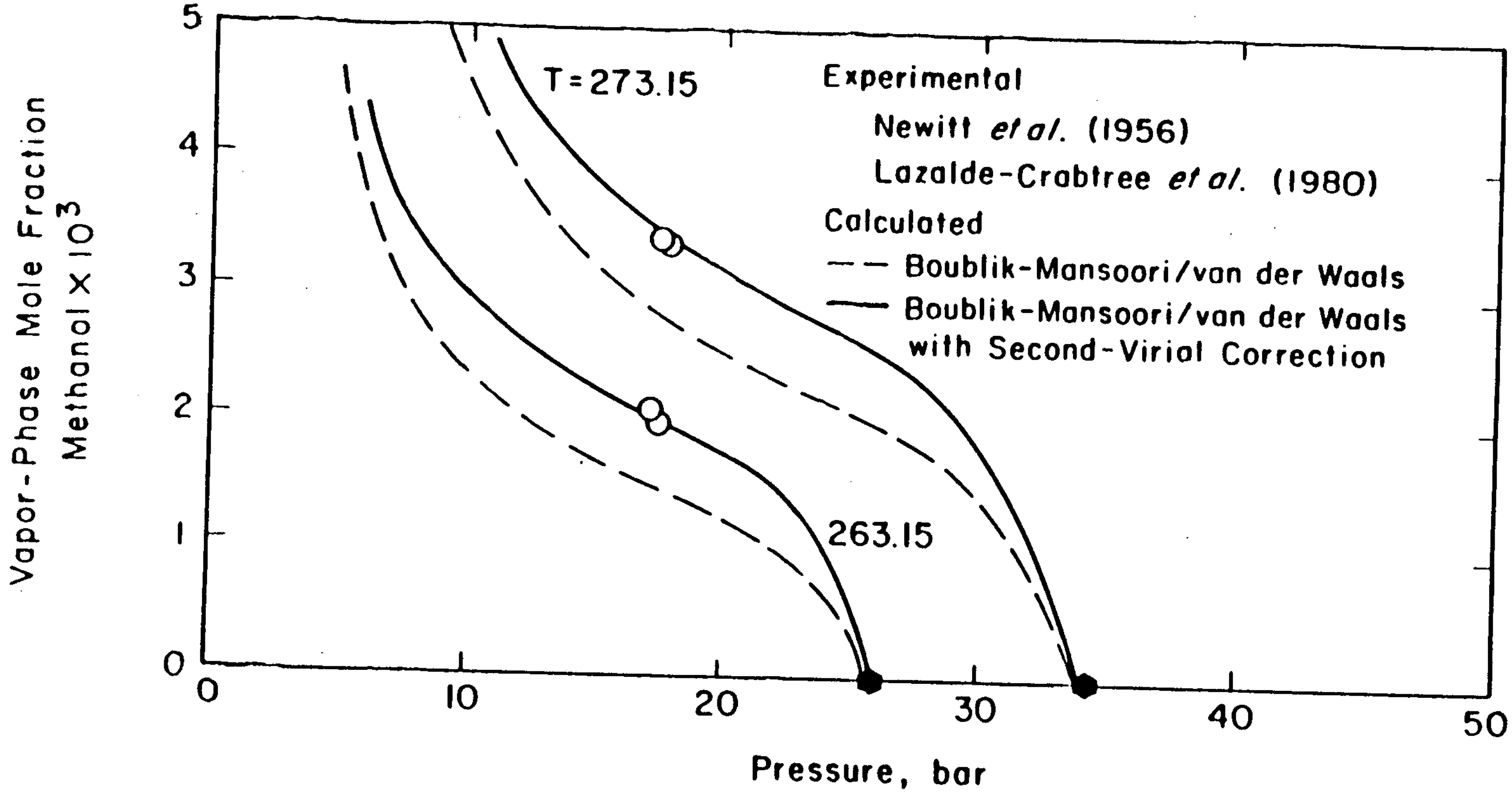

Figure 11. Calculated and Experimental Vapor-Phase Mole Fraction of Methanol in Carbon Dioxide (Binary Interaction Parameter k_{ij}^{df} Adjusted from Solubility Data for Carbon Dioxide in Water).

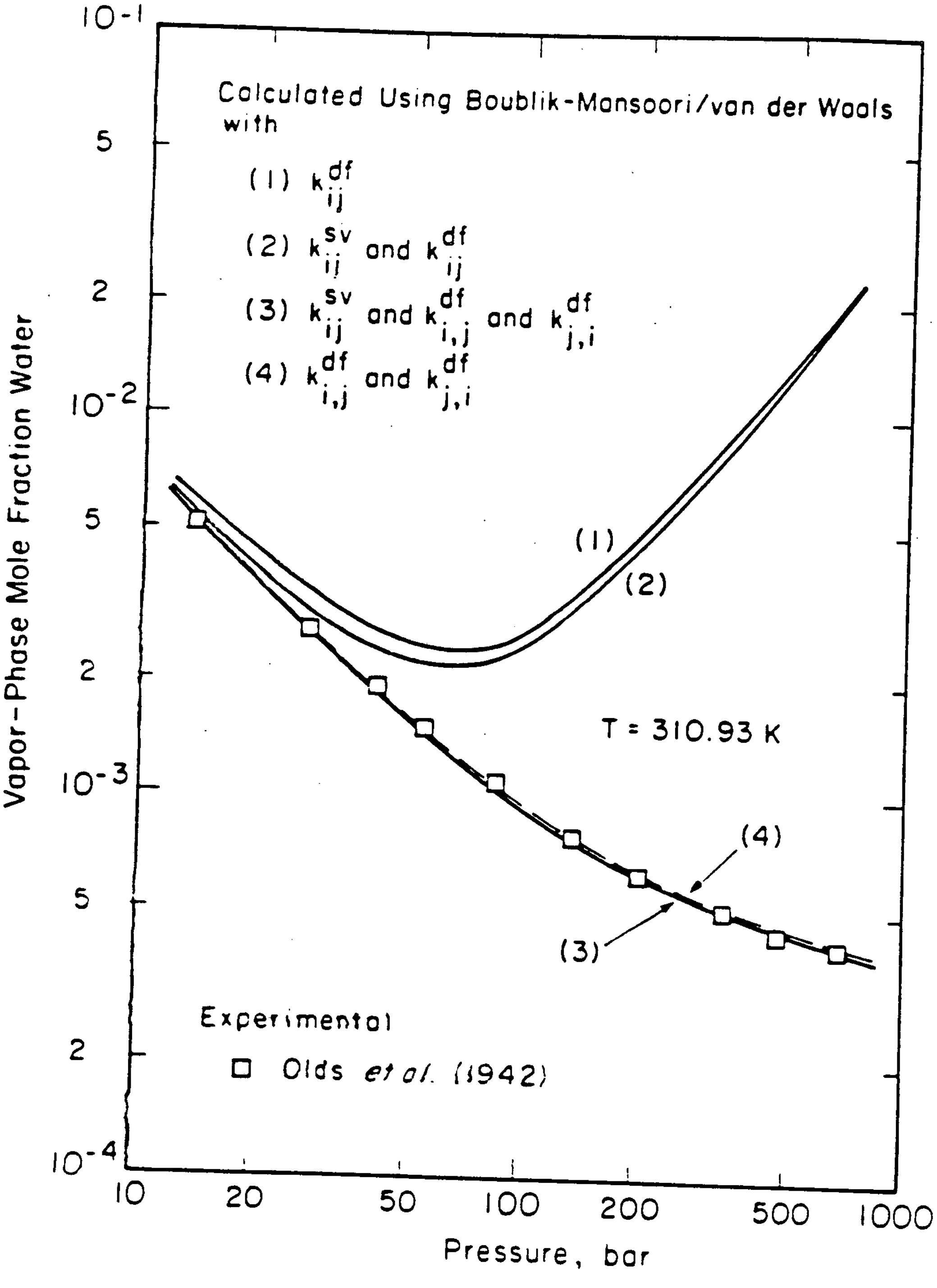

Figure 12. Calculated and Experimental Vapor-Phase Mole Fraction of Water in Methane at 310.93 K (Binary Interaction Parameters Adjusted from K-Factor Data for Both Components at 680 bar).

Second, we include the proposed interpolation between the second-virial and dense-fluid contribution [Equation (2)], while maintaining the simple quadratic mixing rule for the attractive-force parameter [Equation (5a)]. Using the correct second virial coefficient improves the correlation for the vapor-phase mole fraction of water up to 30 bar. When a cubic mixing rule is used for the dense-fluid attractive-force parameter [Equation (5)], calculations are in excellent agreement with observed phase behavior (case 3).

There is no significant deterioration in the calculated results when we use the diminutive form of the model with the cubic mixing rule [Equation (5)] (case (4)). For this case, the representation of the phase behavior is good despite the erroneous cubic-mole-fraction dependence for the second virial coefficient, indicating that in some cases, a theoretically invalid mixing rule may nevertheless give acceptable results. To illustrate, Figure 13 presents cross-second virial coefficents for the methane/water binary as a function of the methane mole fraction for two temperatures. The experimental value (Rigby and Prausnitz, 1968, Smith *et al.*, 1983) is independent of mole fraction as dictated by statistical mechanics. If we use the diminutive model with the cubic mixing rule [Equation (5)], we obtain at low densities a second virial coefficient which is cubic in mole fraction; that is, we obtain a cross-second virial coefficient which erroneously is linear in mole fraction. The solid lines show these calculations.

For the calculated vapor-phase solubility of methane in water, we do not see any adverse effect by this inconsistency in the mole-fraction dependence for the second virial coefficient. The cross-second virial coefficient is particularly important for the representation of the methane-rich vapor-phase properties. As shown in Figure 13, the calculated value for the mole-

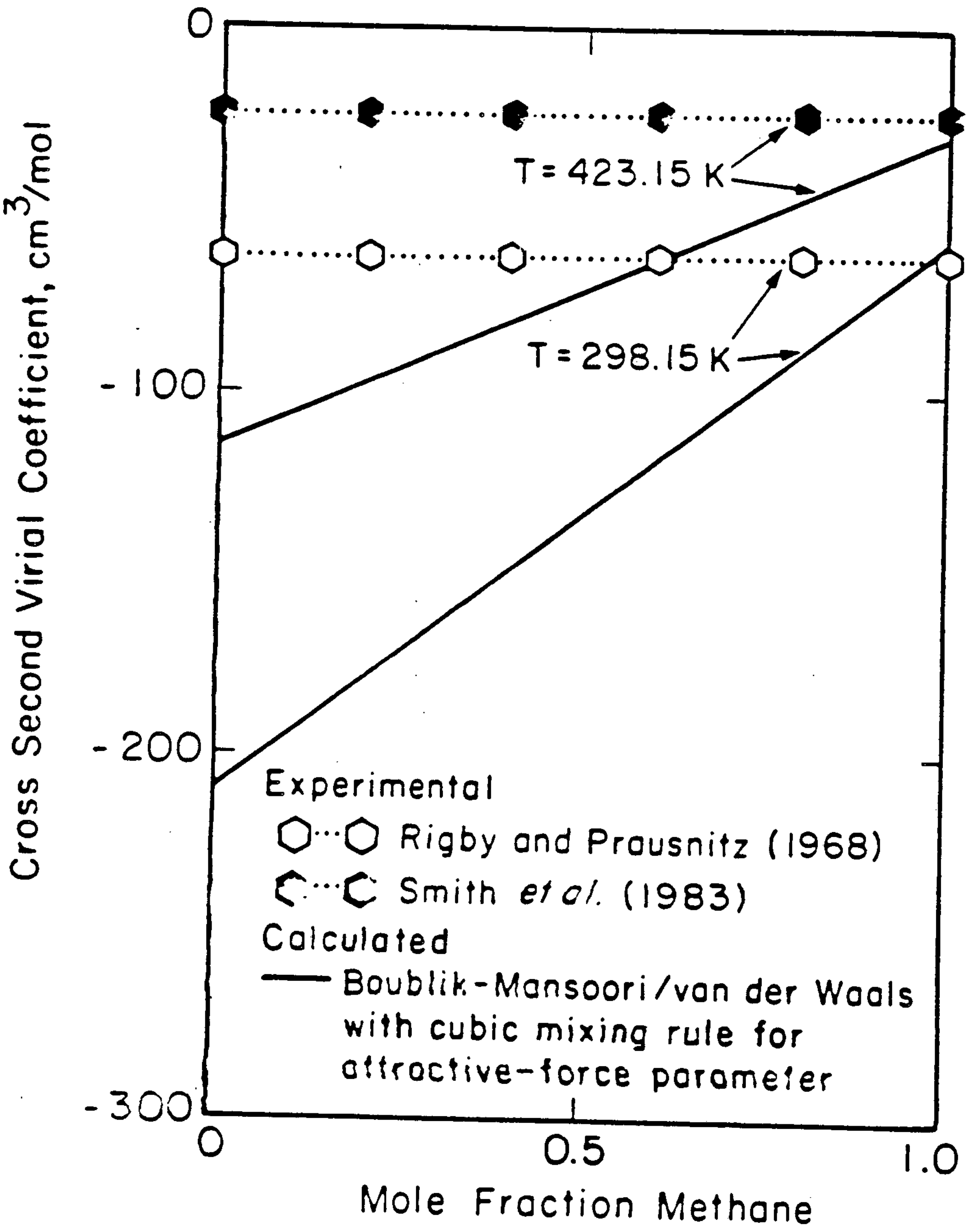

Figure 13. Calculated and Experimental Cross-Second-Virial Coefficient for the System Methane/Water (Binary Interaction Parameters $k^{df}_{CH_4,H_2O}$ and $k^{df}_{H_2O,CH_4}$ Adjusted from K-Factor Data at 680 bar).

fraction-dependent cross-second virial coefficient matches very well the experimentally observed value for B_{12} for the methane-rich end of the concentration range. The largest deviation occurs at the water-rich end of the concentration range. But the second virial coefficient is not important for liquid-phase property correlation. Therefore, the large deviation of the calculated cross-second virial coefficient from experiment at the liquid end of the concentration range is masked in some vapor-liquid-equilibrium calculations.

However, the effect of an erroneous mole-fraction dependence of the second virial coefficient can be seen in the correlation of low-pressure caloric properties. Figure 14 shows calculated and experimental (Smith and Wormald, 1984) excess enthalpies for an <u>equimolar</u> *n*-octane/water mixture at 1.013 bar as a function of temperature. Binary dense-fluid parameters $k^{df}_{n\text{-}C_8H_{18},H_2O}$ and $k^{df}_{H_2O,n\text{-}C_8H_{18}}$ have been obtained from high-pressure, liquid-liquid equilibrium data. Using the diminutive model, the calculated results show significant deviations from experiment. The calculations for the proposed model are in closer agreement with experiment. These calculations were performed for an equimolar mixture. Figure 13 shows that erroneous mole-fraction dependence for the cross-second virial coefficient gives, for an equimolar mixture, significant deviation from the experimentally observed value for B_{12}.

CONCLUSIONS

A molecular-thermodynamic framework is presented to correlate thermodynamic properties of fluids and fluid mixtures at low and high densities. The essential feature of this framework is a separation of the Helmholtz energy into low- and high-density contributions. This separation

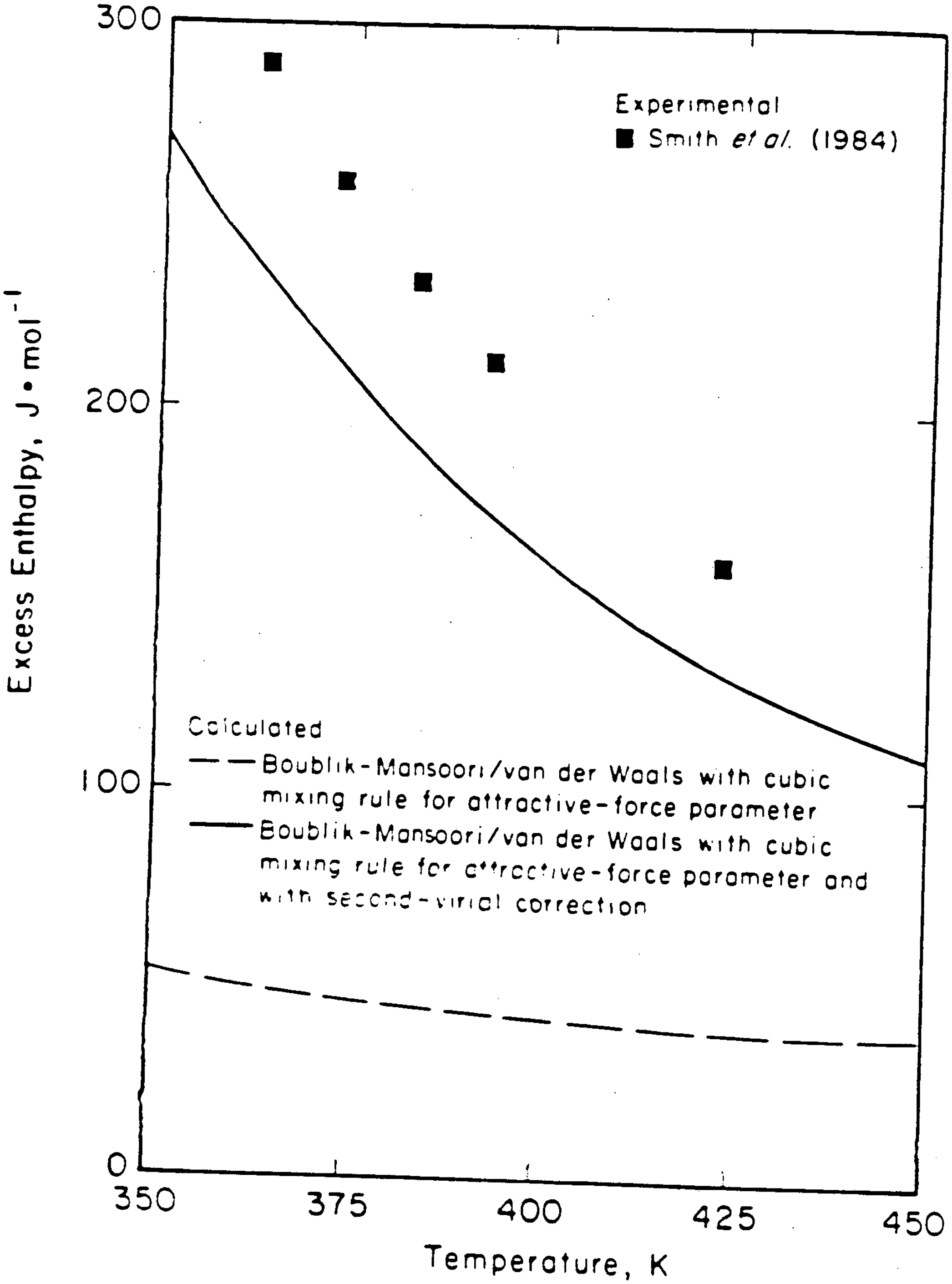

Figure 14. Calculated and Experimental Excess Enthalpy for Equimolar n-Octane/Water Mixtures at 1.013 bar (Binary Interaction Parameters $k^{df}_{n\text{-}C_8H_{18},H_2O}$ and $k^{df}_{H_2O,n\text{-}C_8H_{18}}$ Adjusted from Liquid-Liquid-Equilibrium Data).

allows accurate representation of second virial coefficients as well as high-pressure phase equilibria because it permits the use of independent mixing rules for dense-fluid equation-of-state parameters while simultaneously obeying the quadratic mole-fraction dependence for the second virial coefficient. We illustrate the proposed framework using the Boublik-Mansoori equation for the reference system and a simple van der Waals attractive term for the perturbation.

We discuss the physical significance of the second virial coefficient in correlating low-pressure phase equilibria. Erroneous mole-fraction dependence for the second virial coefficient does not necessarily produce inferior physical-property correlation; its adverse effect is often masked by the flexibility in numerical adjustment of model parameters.

ACKNOWLEDGEMENTS

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NOTATION

a	van-der-Waals Attractive-Force Parameter
$\boldsymbol{a}$	Molar Helmholtz Energy
b	van-der-Waals Covolume
B	Second Virial Coefficient

D, E, F	Parameters for the Boublik-Mansoori Expression
$\mathcal{F}$	Interpolation Function
k	Binary Interaction Parameter
m	Number of Components
P	Pressure
R	Gas Constant
T	Temperature
v	Molar Volume
x	Mole Fraction

Greek Letters:

α	Pure-Component Second-Virial-Coefficient Parameter
β	Pure-Component Second-Virial-Coefficient Parameter
ξ	Reduced Molar Density
ρ	Molar Density
τ	Closed-Packed Reduced Density
ω	Acentric Factor

Superscripts:

df	Dense Fluid
per	Perturbation
r	Residual
ref	Reference
sv	Second Virial

Subscripts:

c	Critical
i	Property of Component i

ij	Interaction between Components i and j
i,j	Interaction of Component i Infinitely Diluted in Component j.
L	Liquid
r	Reduced

APPENDIX I: Boublik-Mansoori Expression for the Molar Residual Helmholtz Energy for a Mixture of Hard Spheres.

Boublik (1970) and Mansoori *et al.* (1971), working independently and following somewhat different phenomenological arguments based, respectively, on scaled-particle theory and on Percus-Yevick theory, derived the following expression for the molar residual Helmholtz energy of a mixture of hard spheres:

$$\frac{\boldsymbol{a}^{ref}}{RT} = \frac{\frac{3DE}{F}\xi - \frac{E^3}{F^2}}{1-\xi} + \frac{\frac{E^3}{F^2}}{(1-\xi)^2} + \left(\frac{E^3}{F^2} - 1\right) \log_e(1-\xi) \qquad (I.1)$$

Reduced molar density ξ is given by Equation (13). Parameters D, E and F are given by:

$$D = \sum_{i=1}^{m} x_i b_i^{1/3} \qquad (I.2)$$

$$E = \sum_{i=1}^{m} x_i b_i^{2/3} \qquad (I.3)$$

$$F = \sum_{i=1}^{m} x_i b_i \qquad (I.4)$$

Van der Waals covolume parameter b_i is given by Equation (17).

Advantages of the Boublik-Mansoori expression versus other commonly-used reference systems are discussed elsewhere (Dimitrelis and Prausnitz, 1986).

APPENDIX II: Second-Virial-Coefficient Correlation

For the second virial coefficient B_{ij}, we use the correlation developed by Tsonopoulos (1974):

$$B_{ij} = B_{ij}^{ref} + B_{ij}^{per} = b_{ij}^{sv} - \frac{a_{ij}^{sv}}{RT} \qquad \text{(II.1)}$$

where

$$b_{ij}^{sv} = \frac{RT_{c,ij}}{P_{c,ij}}\left(0.1445 + 0.0637\,\omega_{ij}\right) \qquad \text{(II.2)}$$

and

$$a_{ij}^{sv} = \frac{R^2 T_{c,ij}^2}{P_{c,ij}}\left(0.33 + \frac{0.1385 - 0.331\,\omega_{ij}}{T_{r,ij}} + \frac{0.0121 + 0.423\,\omega_{ij}}{T_{r,ij}^2} + \frac{0.000607 + 0.008\,\omega_{ij}}{T_{r,ij}^7}\right) + \sqrt{\frac{R^2 T_{c,i}^2}{P_{c,i}}\left(\frac{\beta_i}{T_{r,i}^7} - \frac{\alpha_i}{T_{r,i}^5}\right)\frac{R^2 T_{c,j}^2}{P_{c,j}}\left(\frac{\beta_j}{T_{r,j}^7} - \frac{\alpha_j}{T_{r,j}^5}\right)} \qquad \text{(II.3)}$$

Reduced temperatures are defined as

$$T_{r,i} = \frac{T}{T_{c,i}} \qquad \text{(II.4)}$$

$$T_{r,ij} = \frac{T}{\sqrt{T_{c,i}T_{c,j}}\,(1 - k_{ij}^{sv})} \qquad \text{(II.5)}$$

Table II.1: Binary second-virial-coefficient parameter k_{ij}^{sv}.

Binary Mixture	k_{ij}^{sv}	T, K	Reference
CO_2/H_2O	0.15	298-373	Smith and Wormald (1984)
C_3H_8/H_2O	0.38		Tsonopoulos (1979)
n-C_4H_{10}/H_2O	0.45		Tsonopoulos (1979)
C_6H_6/H_2O	0.5		Tsonopoulos (1979)
C_2H_5OH/H_2O	0		
$CH_3CHOHCH_3/H_2O$	0		
$CH_3CHOHC_2H_5/H_2O$	0		
CH_3OCH_3/H_2O	0		
CO_2/CH_3OH	0.01		Tsonopoulos (1979)
CO_2/C_2H_5OH	0.07		Tsonopoulos (1979)
$CO_2/CH_3CHOHCH_3$	0.07		Tsonopoulos (1979)
CH_4/CH_3OH	0.13	288-233	Dymond and Smith (1980)
C_3H_8/CH_3OH	0.16		Tsonopoulos (1979)
n-C_6H_{14}/CH_3OH	0.31	398-448	Zawiswa (1985)
C_3H_8/C_2H_5OH	0.2		Tsonopoulos (1979)
n-C_6H_{14}/C_2H_5OH	0.3		
C_6H_6/C_2H_5OH	0.20	333-373	Dymond and Smith (1980)

where binary parameter k_{ij}^{sv} is adjusted from experimental information on second virial coefficients for mixtures. Tsonopoulos (1979) presents correlations and values for a variety of binary mixtures. Table II.1 gives k_{ij}^{sv} values for binary mixtures investigated in this work.

Acentric factor ω for the ij-pair is given by the arithmetic-mean rule:

$$\omega_{ij} = \frac{\omega_i + \omega_j}{2} \tag{II.6}$$

Table II.2: Pure-component second-virial-coefficient parameters α_i and β_i.

Component	α_i	β_i	T, K	Reference
H_2O	-0.01921	-0.002444	293-673	Dymond and Smith(1980)
CH_3OCH_3	0.1206	0.06368	273-373	Dymond and Smith (1980)
CH_3OH	-0.06143	-0.04595	298-523	Dymond and Smith (1980)
C_2H_5OH	0.1226	0.07141	313-393	Dymond and Smith (1980)
$CH_3CHOHCH_3$	0.0505	0.03832	333-473	Dymond and Smith (1980)
$CH_3CHOHC_2H_5$	0.03869	0.02411	378-423	Dymond and Smith (1980)

Finally, the critical pressure for the ij-pair is defined using the corresponding-states relation

$$P_{c,ij} = T_{c,ij} \frac{4\left(\frac{P_{c,i} v_{c,i}}{T_{c,i}} + \frac{P_{c,j} v_{c,j}}{T_{c,j}} \right)}{\left(v_{c,i}^{1/3} + v_{c,j}^{1/3} \right)^3} \tag{I.7}$$

where v_c is the molar critical volume.

Pure-component parameters α_i and β_i [Equation (II.3)] account for hydrogen-bonding and dipolar interactions between molecules. They are obtained from experimental second virial coefficients. The last term in Equation (II.3) contributes only when both components i and j are polar; otherwise, this term is zero. Table II.2 gives values for α_i and β_i for the polar compounds investigated in this work.

APPENDIX III: Helmholtz-Energy Correction to Account for Difference in van der Waals Covolume between Low and High Densities.

The value for the van der Waals covolume parameter differs depending upon the density-range of the data used for its estimation. High-density data (e.g., dense-fluid, critical or supercritical densities) yield a lower value than second-virial-coefficient data (Prausnitz, 1985).

To circumvent this problem, we fix the covolume parameter at high densities, while adding a small correction to the Helmholtz energy [Equation (1)] to account for the different value in the low-density regime:

$$\boldsymbol{a}^{r,corr} = \rho(b^{sv} - b^{df})(1-\mathcal{F})$$

$$= \rho\{\sum_{i=1}^{m}\sum_{j=1}^{m} x_i x_j b_{ij}^{sv} - \frac{1}{4}(F+3DE))\}\ (1-\mathcal{F}) \qquad \text{(III.1)}$$

Equation (II.2) gives b_{ij}^{sv}. Parameters D, E and F are given by Equations (I.2), (I.3) and (I.4) respectively. Interpolation function $\mathcal{F}$ forces the correction function to zero at intermediate and high densities.

APPENDIX IV: Effect of Pure-Component Parameters on the Correlation of Binary Phase Equilibria near a Component's Critical Point.

Classical equations of state cannot model phase behavior in the near-critical region (see e.g. Chapela and Rowlinson, 1974). If equation-of-state parameters are obtained from fitting vapor-pressure and liquid-density data, the predicted critical temperature and pressure are too high. This is not important for most phase-equilibrium calculations. However, for fluid-phase equilibria near a component's critical point, overprediction of the critical temperature by a few degrees causes significant errors in the calculation of properties for the near-critical fluid phase.

Figure IV-1 shows the calculated and experimental (Angus *et al.*, 1976) two-phase region for carbon dioxide. Using parameters obtained from data

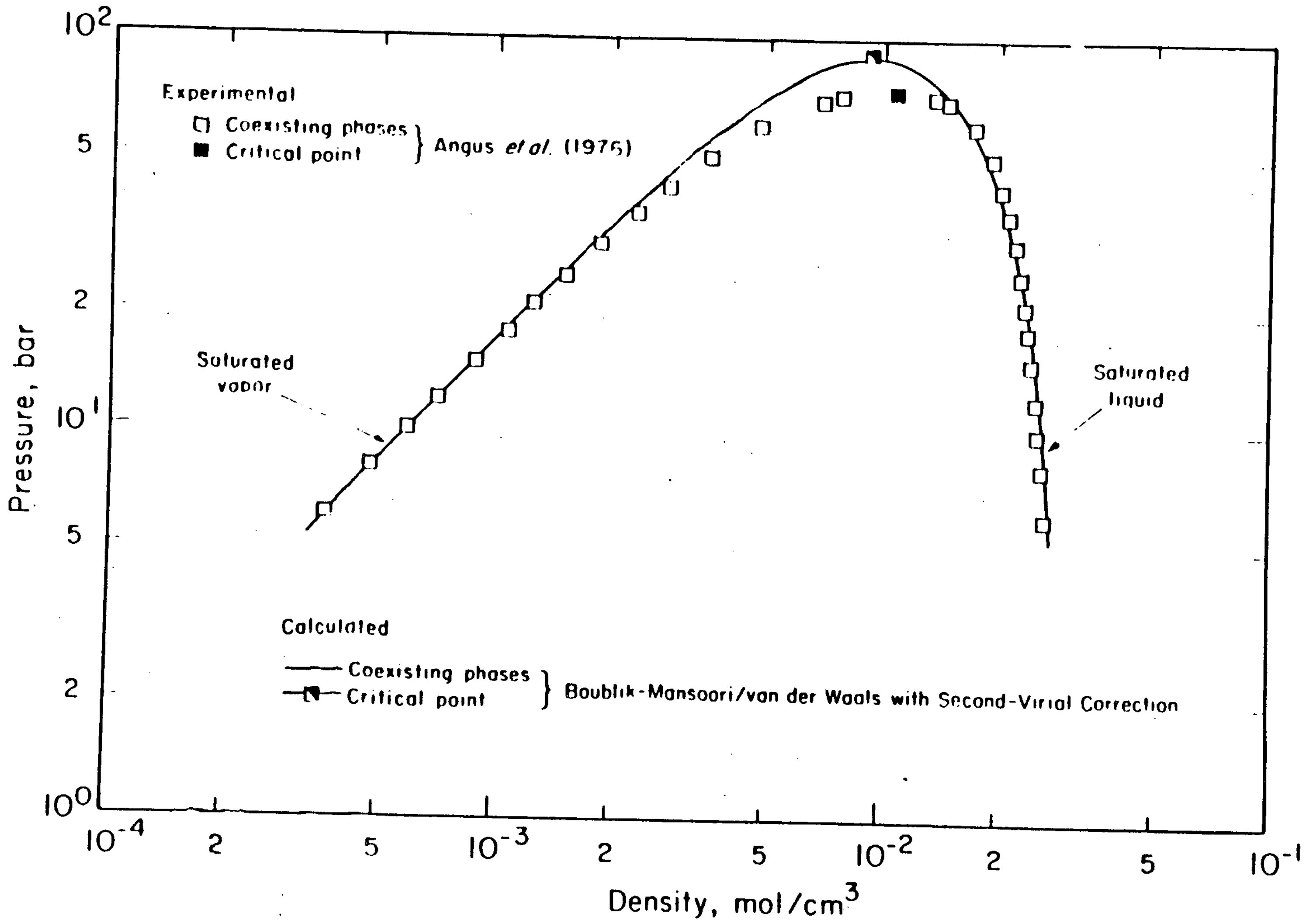

Figure IV-1. Calculated and Experimental Two-Phase Region for Carbon Dioxide reduction far from the critical region, the model overpredicts the critical point. Thus, separation of the Helmholtz energy into low-density and high-density contributions [Equation (2)] does not improve property correlation near critical points.

To demonstrate the negative effect of overprediction, we present near-critical calculations for the ethylene/naphthalene system. Figure IV-2 shows calculated and experimental (Eckert *et al.*, 1986) infinite-dilution partial molar volumes for naphthalene in ethylene at 298.15 K. The critical point of ethylene is 282.4 K and 50.4 bar.

Using ethylene parameters obtained far from its critical region, the model (dashed curve) behaves as if, at 298.15, it is significantly closer to the critical point than it should be. Therefore, the partial molar volume exhibits a significantly larger divergence than experimentally observed (There is a singularity in the partial molar volume at the critical point).

We can empirically circumvent this problem by adjusting the equation-of-state parameters for the near-critical component. To determine these parameters, we give higher weight to pure-component vapor-pressure data in the near-critical region and we require the calculated critical isotherm to go through the critical point at the experimentally observed critical pressure and temperature. The calculation of the critical volume and the liquid volume are then in significant error (of the order of 20%). However, these shortcomings do not affect correlation of mixture-derivative properties such as partial molar properties. The solid line in Figure IV-2 shows calculated results using parameters as described above. The correlation of the experimentally

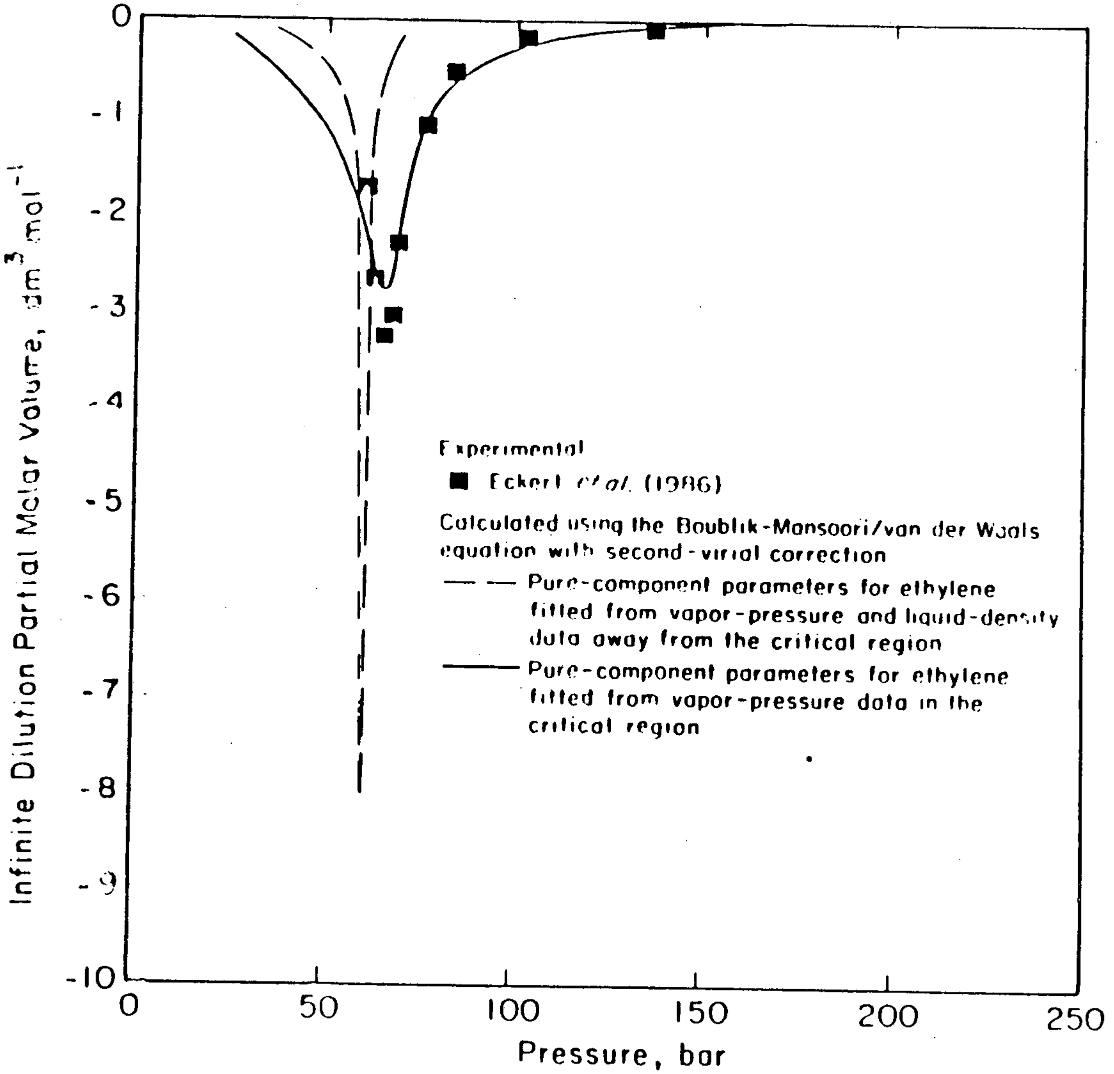

Figure IV-2. Partial Molar Volume of Naphthalene Infinitely Dilute in Supercritical Ethylene at 298.15 K.

Table IV.1: Pure-component parameters $a_i^{(0)}$, $a_i^{(1)}$, $b_i^{(0)}$ and $b_i^{(1)}$ adjusted from vapor-pressure data in the near-critical region.

Component	$a_i^{(0)}$	$a_i^{(1)}$	$b_i^{(0)}$	$b_i^{(1)}$	Reference
C_3H_8	0.7185	0.5079	0.2314	0.3188	Goodwin and Haynes (1982)
n-C_4H_{10}	0.7119	0.4971	0.2204	0.2602	Haynes and Goodwin (1982)
CH_3OCH_3	0.7767	0.8985	0.2464	0.7505	Boublik *et al.* (1984)
CO_2	0.9235	0.9474	0.2840	0.6295	Angus *et al.* (1976)

observed behavior is now much better. Table IV.1 gives adjusted pure-component parameters for fluids of interest here.

APPENDIX V: Phase-Equilibrium Correlation for Strongly-Associating Mixtures such as Alcohol/Hydrocarbon.

Mixtures of molecules which exhibit strong hydrogen-bonding or association forces are characterized by the presence of large liquid-liquid immiscibility regions. When these regions are near vapor-liquid two-phase regimes in the pressure-temperature phase space, as is the case for hydrocarbon/alcohol mixtures, correlation of fluid-phase behavior is particularly difficult.

Figure V-1 shows the pressure/temperature diagram for the propane/methanol system. It exhibits a large liquid-liquid immiscibility gap extending from a few bars above the vapor pressure for propane up to very high pressures.

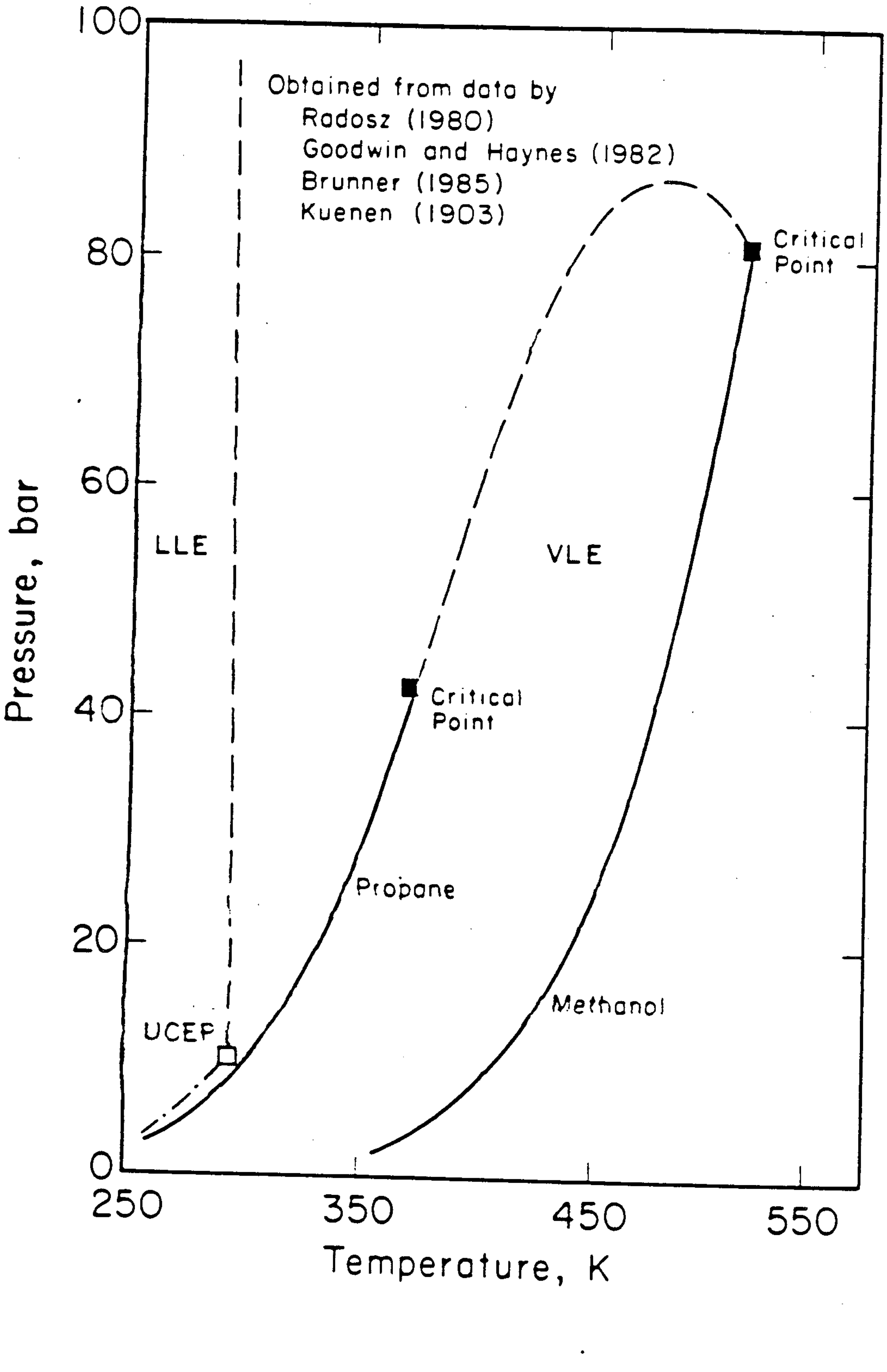

Figure V-1. Pressure-Temperature Diagram for Propane/Methanol.

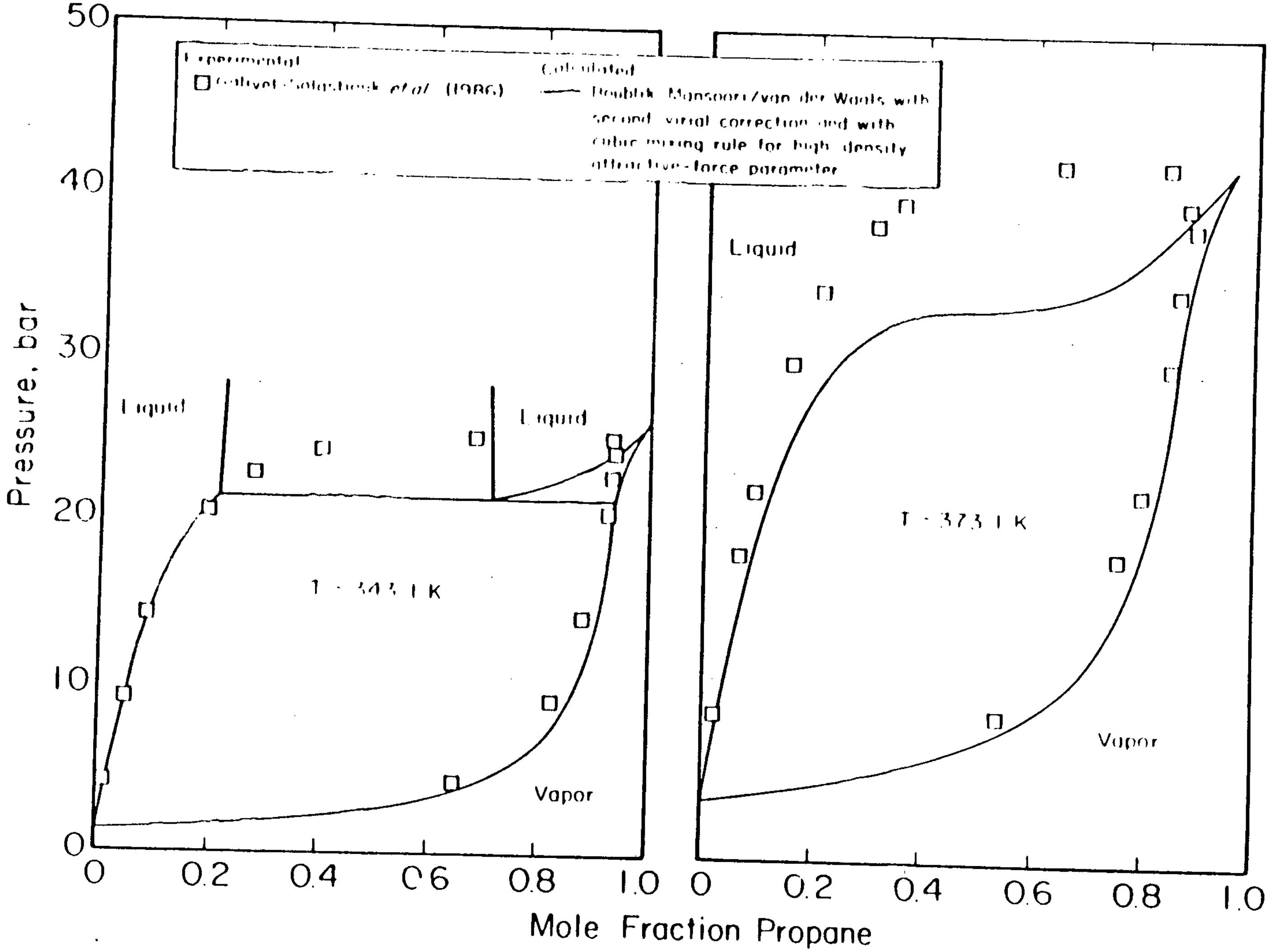

Figure V-2. Calculated and Experimental Phase Equilibria for Propane/Methanol (Calculations *Erroneously* Predict Liquid-Liquid Equilibria).

When equations of state are used to correlate isobaric liquid-liquid equilibria they tend to overpredict dramatically the upper solution temperature. As a result, the liquid-liquid critical locus penetrates the vapor-liquid two-phase region leading to erroneous three-phase predictions. Figure V-2 shows such an example, again for the propane/methanol system. The model predicts at 20 bar and 343 K a liquid-liquid equilibrium while the observed upper solution temperature for this pressure is at approximately 290 K. The effect of the overprediction of the liquid-liquid critical locus can be still seen in the calculations for the 373-K isotherm.

Recently, de Pablo and Prausnitz (1988) proposed a semi-theoretical correction to the excess Gibbs energy to correct for such a deficiency in liquid-liquid-equilibrium calculations. Incorporation of a similar correction within an equation-of-state framework may be advantageous for simultaneous correlation of liquid-liquid and vapor-liquid equilibria.

LITERATURE CITED

Adachi, Y. and Sugie, H., 1986, A New Mixing Rule-Modified Conventional Mixing Rule. *Fluid Phase Equilibria*, **26**, 103-118.

Boublik, T, 1970. Hard-Sphere Equation of State. *Journal of Chemical Physics*, **53**, 471-472.

Chapela, G.A. and Rowlinson, J.S., 1974, Accurate Representation of Thermodynamic Properties near the Critical Point. *Journal of the Chemical Society, Faraday Transactions I*, **70**, 584-593.

Cotterman, R. L., Schwarz, B. J. and Prausnitz, J. M., 1986, Molecular Thermodynamics for Fluids at Low and High Densities. *AIChE Journal*, **32**, 1787-1812.

de Pablo, J.J. and Prausnitz, J.M., 1988, Thermodynamics of Liquid-Liquid Equilibria Including the Critical Region. *AIChE Journal*, **31**, 1595-1606.

Dimitrelis, D. and Prausnitz, J. M., 1982, Thermodynamic Properties of Strongly Nonideal Fluid Mixtures from an Extended Quasi-Chemical Theory. *Lawrence Berkeley Laboratory Report 15256*, University of California, Berkeley, California.

Dimitrelis, D. and Prausnitz, J. M., 1986, Comparison of Two Hard-Sphere Reference Systems for Perturbation Theories for Mixtures. *Fluid Phase Equilibria*, **31**, 1-21.

Eckert, C. A., Ziger, D. H., Johnston, K. P. and Kim, S., 1986, Solute Partial Molar Volumes in Supercritical Fluids. *Journal of Physical Chemistry*, **90**, 2738-2746.

Huron, M.-J. and Vidal, J., 1979, New Mixing Rules in Simple Equations of State for Representing Vapour-Liquid Equilibria of Strongly Nonideal Mixtures. *Fluid Phase Equilibria*, **3**, 255-271.

Kohler, F. and Haar, L., 1981, A New Representation for Thermodynamic Properties of a Fluid. *Journal of Chemical Physics*, **75**, 388-394.

Larsen, E.R. and Prausnitz, J.M., 1984, High-Pressure Phase Equilibria for the Water/Methane System. *AIChE Journal*, **30**, 732-738.

Lüdecke, D. and Prausnitz, J.M., 1985, Phase Equilibria for Strongly Nonideal Mixtures from an Equation of State with Density-Dependent Mixing Rules. *Fluid Phase Equilibria*, **22**, 1-19.

Mansoori, G.A., Carnahan, N.F., Starling, K.E. and Leland, T.W., 1971. Equilibrium Thermodynamic Properties of the Mixture of Hard Spheres. *Journal of Chemical Physics*, **54**, 1523-1525.

Mathias, P.M. and Copeman, T.W., 1983, Extension of the Peng-Robinson Equation of State to Complex Mixtures: Evaluation of the Various Forms of the Local Composition Concept. *Fluid Phase Equilibria*, **13**, 91-108.

Michel, S., Hooper, H.H. and Prausnitz, J.M., 1989, Mutual Solubilities of Water and Hydrocarbons from an Equation of State. Need for an Unconventional Mixing Rule. *Fluid Phase Equilibria*, **44**.(in press).

Mollerup, J., 1983, Correlation of Thermodynamic Properties of Mixtures Using a Random-Mixture Reference State. *Fluid Phase Equilibria*, **15**, 189-207.

Panagiotopoulos, A. Z. and Reid. R. C., 1986, New Mixing Rule for Cubic Equations of State for Highly Polar, Asymmetric Systems. In *Equations of State: Theories and Applications*. Edited by K. C. Chao and R. L. Robinson, Jr. American Chemical Society Symposium Series, Vol. 300. American Chemical Society, Washington, D.C.

Peng, D.-Y. and Robinson, D. B., 1980, Two- and Three-Phase Equilibrium Calculations for Coal Gasification and Related Processes. In *Thermodynamics of Aqueous Systems with Industrial Applications*. Edited by S. A. Newman. American Chemical Society Symposium Series, Vol. 133. American Chemical Society, Washington, D.C.

Prausnitz, J. M., 1983, Phase Equilibria for Complex Fluid Mixtures. *Fluid Phase Equilibria*, **14**, 1-18.

Prausnitz, J. M., 1985, Equations of State from van der Waals Theory: The Legacy of Otto Redlich. *Fluid Phase Equilibria*, **24**, 63-76.

Rowlinson, J.S. and Swinton, F.L., 1982, *Liquids and Liquid Mixtures*, Butterworths, London.

Sandler, S.I., 1985, The Generalized van der Waals Partition Function. I. Basic Theory. *Fluid Phase Equilibria*, **19**, 233-257.

Stryjek, R. and Vera, J. H., 1986, PRSV - An Improved Peng-Robinson Equation of State with New Mixing Rules for Strongly Nonideal Mixtures. *The Canadian Journal of Chemical Engineering*, **64**, 334-340.

Topliss, R.J., Dimitrelis, D. and Prausnitz, J.M., 1988, Computational Aspects of a Non-cubic Equation of State for Phase-Equilibrium Calculations. Effect of Density-Dependent Mixing Rules. *Computers and Chemical Engineering*, **12**, 483-489.

Tsonopoulos, C., 1974, An Empirical Correlation of Second Virial Coefficients. *AIChE Journal*, **20**, 263-272.

Tsonopoulos, C., 1979, Second Virial Cross-Coefficients: Correlation and Prediction of k_{ij}. In *Equations of State in Engineering and Research*, Edited by K. C. Chao and R. L. Robinson, Jr. Advances in Chemistry Series, No. 182. American Chemical Society, Washington, D.C.

Wilson, G. M., 1972, Equations of State Analogies to Excess Free Energy of Mixing Equations. Contribution No. 29. Center for Thermochemical Studies and Department of Chemical Engineering, Brigham Young University. Provo, Utah.

Wogatzki, H., 1988, Doctoral Dissertation, Technische Universität Berlin.

DATA REFERENCES

Altsybeeva, A.I., Belousov, V.P., Ovtrakht, N.V. and Morachevskii, A.G., 1964, Phase Equilibria and the Thermodynamic Properties of the System *sec*-Butyl Alcohol-Water. *Zhurnal Fizicheskoi Khimii*, **38**, 1242-1247.

Ambrose, D. and Sprake, C.H.S., 1970, Thermodynamic Properties of Organic Oxygen Compounds. XXV. Vapour Pressures and Normal Boiling Temperatures of Aliphatic Alcohols. *Journal of Chemical Thermodynamics*, **2**, 631-645.

Ambrose, D., Sprake, C.H.S. and Townsend, R., 1975, Thermodynamic Properties of Organic Oxygen Compounds. XXXVII. Vapour Pressures of Methanol, Ethanol, Pentan-1-ol, and Octan-1-ol from the Normal Boiling Temperature to the Critical Temperature. *Journal of Chemical Thermodynamics*, **7**, 185-190.

Angus, S, Armstrong, B., and de Reuck, K.M., 1976, *International Thermodynamic Tables of the Fluid State. Volume 3: Carbon Dioxide.* Pergamon Press, Oxford.

Angus, S., Armstrong, B. and de Reuck, K.M., 1978, *International Thermodynamic Tables of the Fluid State. Volume 5: Methane.* Pergamon Press, Oxford.

Bain, R.W., 1964, *Steam Tables 1964*. Her Majesty's Stationery Office, Edinburgh.

Boublik, T., Fried, V. and Hala, E., 1984, *The Vapour Pressures of Pure Substances.* Elsevier, Amsterdam.

Brown, I. and Smith, F., 1954, Liquid-Vapor Equilibria. IV. The System Ethanol-Benzene at 45 °C. *Australian Journal of Chemistry*, **7**, 264-268.

Brunner, E., 1985, Fluid Mixtures at High Pressures: II. Phase Separation and Critical Phenomena of (Ethane + an *n*-Alkanol) and of (Ethene + Methanol) and (Propane + Methanol). *Journal of Chemical Thermodynamics*, **17**, 871-885.

Dymond, J.H. and Smith, E.B., 1980, *The Virial Coefficients of Pure Gases and Mixtures.* Oxford University Press, Oxford.

Galivel-Solastiouk, F., Laugier, S. and Richon, D., 1986, Vapor-Liquid Equilibrium Data for the Propane-Methanol and Propane-Methanol-Carbon Dioxide System. *Fluid Phase Equilibria*, **28**, 73-85.

Gomez-Nieto, M. and Thodos, G., 1978, Vapor-Liquid Equilibrium Measurements for the Propane-Ethanol System at Elevated Pressures. *AIChE Journal*, **24**, 672-678.

Goodwin, R.D., Roder, H.M. and Straty, G.C., 1976, *Thermophysical Propoerties of Ethane from 90 to 600 K at Pressures to 700 bar.* NBS Technical Note 684, Washington, D.C.

Goodwin, R.D. and Haynes, W.M., 1982, *Thermophysical Properties of Propane from 85 to 700 K at Pressures to 70 MPa.* NBS Monograph 170, Washington, D.C.

Gupta, S.K., Leslie, R.D. and King, A.D., Jr., 1973, Solubility of Alcohols in Compressed Gases. A Comparison of Vapor-Phase Interactions of Alcohols and Homomorphic Compounds with Various Gases: I. Ethanol in Compressed Helium, Hydrogen, Argon, Methane, Ethylene, Ethane, Carbon Dioxide and Nitrous Oxide. *The Journal of Physical Chemistry,* **77**, 2011-2015.

Haynes, W.M. and Goodwin, R.D., 1982, *Thermophysical Properties of Butane from 135 to 700 K at Pressures to 70 MPa.* NBS Monograph 169, Washington, D.C.

Hemmaplardh, B. and King, A.D., Jr., 1972, Solubility of Methanol in Compressed Nitrogen, Argon, Methane, Ethylene, Ethane, Carbon Dioxide, and Nitrous Oxide. Evidence for Association of Carbon Dioxide with Methanol in the Gas Phase. *The Journal of Physical Chemistry,* **76**, 2170-2175.

Hölscher, I.F., Schneider, G.M. and Ott, J.B., 1986, Liquid-Liquid Phase Equilibria of Binary Mixtures of Methanol with Hexane, Nonane and Decane at Pressures to 150 MPa. *Fluid Phase Equilibria,* **27**, 153-169.

Hong, J.H., Jett, M.D., Malone, P.V. and Kobayashi, R., 1986, The Measurement and Interpretation of the Solubility of a Normal Fluid in a Hydrogen Bonding Solvent: The Methane-Methanol System. GRI Report 86/0154, Gas Research Institute, Chicago, Illinois.

Institute of Gas Technology, 1978, *Coal Conversion Systems Technical Data Book*, Department of Energy, Washington, D.C.

Kell, G.S. and McLaurin, G.E., 1969, Virial Coefficients of Methanol from 150 to 300 °C and Polymerization in the Vapor. *The Journal of Chemical Physics,* **51**, 4345-4352.

Kobayashi, R. and Katz, D.L., 1953, Vapor-Liquid Equilibria for Binary Hydrocarbon-Water Systems. *Industrial and Engineering Chemistry*, **45**, 440-451.

Kudchadker, A.P. and Eubank, P.T., 1970, Second Virial Coefficient of Methanol. *Journal of Chemical and Engineering Data*, **15**, 7-9.

Kuenen, J.P., 1903, On the Mutual Solubility of Liquids-II. *Philosophical Magazine and Journal of Science, Sixth Series*, **6**, 637-653.

Lazalde-Crabtree, H., Breedveld, G.J.F. and Prausnitz, J.M., 1980, Solvent Losses in Gas Adsorption. Solubility of Methanol in Compressed Natural and Synthetic Gases. *AIChE Journal*, **26**, 462-470.

Lo, H.Y. and Stiel, L.I., 1969, The PVT Behavior of Ethyl Alcohol at Elevated Pressures and Temperatures. *Industrial and Engineering Chemistry Fundamentals*, **8**, 713-718.

Machado, J.R.S. and Streett, W.B., 1983, Equation of State and Thermodynamic Properties of Liquid Methanol from 298 to 489 K and Pressures to 1040 bar. *Journal of Chemical and Engineering Data*, **28**, 218-223.

Mertl, I., 1972, Liquid-Vapour Equilibrium. IL. Phase Equilibria in the Ternary System Ethyl Acetate-Ethanol-Water. *Collection of Czechoslovakian Chemical Communications*, **37**, 366-374.

Moriyoshi, T., Kaneshina, S., Aihara, K. and Yabumoto, K., 1975, Mutual Solubility of 2-Butanol+Water Under High Pressure. *Journal of Chemical Thermodynamics*, **7**, 537-545.

Ohgaki, K. and Katayama, T., 1976, Isothermal Vapor-Liquid Equilibrium Data for Binary Systems Containing Carbon Dioxide at High Pressures: Methanol-Carbon Dioxide, *n*-Hexane-Carbon Dioxide, and Benzene-Carbon Dioxide Systems. *Journal of Chemical and Engineering Data*, **21**, 53-55.

Olds, R.H., Sage, B.H. and Lacey, W.N., 1942, Phase Equilibria in Hydrocarbon Systems: Composition of the Dew-Point Gas of the Methane-Water System. *Industrial and Engineering Chemistry*, **34**, 1223-1227.

Panagiotopoulos, A.Z., 1986, *High-Pressure Phase Equilibria: Experimental and Monte Carlo Simulation Studies*. Doctoral Dissertation, Massachusetts Institute of Technology, Cambridge.

Pozo, M.E. and Streett, W.B., 1984, Fluid Phase Equilibria for the System Dimethyl Ether/Water from 50 to 220 ^{o}C and Pressures to 50.9 MPa. *Journal of Chemical and Engineering Data*, **29**, 324-329.

Raal, D.J., Code, R.K. and Best, D.A., 1972, Examination of Ethanol-*n*-Heptane, Methanol-*n*-Hexane Systems Using New Vapor-Liquid Equilibrium Still. *Journal of Chemical and Engineering Data*, **17**, 211-216.

Rigby, M. and Prausnitz, J.M., 1968, Solubility of Water in Compressed Nitrogen, Argon, and Methane. *The Journal of Physical Chemistry*, **72**, 330-334.

Radosz, M., 1980, Thermodynamic Properties of Aliphatic Alcohols in the State of Saturation. Chemical Engineering Laboratory, Technical University of Norway, Trondheim.

Radosz, M., 1986, Vapor-Liquid Equilibrium for 2-Propanol and Carbon Dioxide. *Journal of Chemical and Engineering Data*, **31**, 43-45.

Reamer, H.H., Sage, B.H. and Lacey, W.N., 1952, Phase Equilibria in Hydrocarbon Systems. *n*-Butane-Water System in the Two-Phase Region. *Industrial and Engineering Chemistry*, **44**, 609-615.

Sada, E. and Morisue, T., 1975, Isothermal Vapor-Liquid Equilibrium Data of Isopropanol-Water System. *Journal of Chemical Engineering of Japan*, **8**, 191-195.

Smith, G., Sellars, A., Yerlett, T.K. and Wormald, C.J., 1983, The Excess Enthalpy of (Water + Hydrogen) Vapour and (Water + Methane) Vapour. *Journal of Chemical Thermodynamics*, **15**, 29-35.

Smith, G.R. and Wormald, C.J., 1984, The Excess Molar Enthalpies of $\{xH_2O+(1-x)CO\}$ (g) and $\{xH_2O+(1-x)CO_2\}$ (g). *Journal of Chemical Thermodynamics*, **16**, 543-550.

Smith, V.C. and Robinson, R.L., Jr., 1970, Vapor-Liquid Equilibria at 25 °C in the Binary Mixtures Formed by Hexane, Benzene and Ethanol. *Journal of Chemical and Engineering Data*, **15**, 391-395.

Tsonopoulos, C. and Wilson, G.M., 1983, High-Temperature Mutual Solubilities of Hydrocarbons and Water. Part I: Benzene, Cyclohexane and *n*-Hexane. *AIChE Journal*, **29**, 990-999.

Vargaftik, N.B., 1975, *Tables on the Thermophysical Properties of Liquids and Gases*. Wiley, New York.

Wiebe, R., 1941, The Binary System Carbon Dioxide-Water Under Pressure. *Chemical Reviews*, **29**, 475-481.

Yuan, K.S., Ho, J.C.K., Keshpande, A.K. and Lu, B.C.-Y., 1963, Vapor-Liquid Equilibria. *Journal of Chemical and Engineering Data,* **8**, 549-559.

Zawisza, A., 1985, High-Pressure Liquid-Vapour Equilibria, Critical State, and $p(V_m,T,x)$ to 448.15 K and 4.053 MPa for $\{xC_6H_{14}+(1-x)CH_3OH\}$. *Journal of Chemical Thermodynamics,* **17**, 941-947.

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