Molecular Thermodynamics for Fluids at Low and High Densities

Part II: Phase Equilibria for Mixtures Containing Components with Large Differences in Molecular Size or Potential Energy

The molecular-thermodynamic correlation presented in Part I for pure fluids is extended to mixtures; this extension is particularly useful for mixtures of components with large differences in molecular size or potential energy. The novel feature of this correlation is a separation of the high-density and low-density contributions to the residual Helmholtz energy; this separation allows use of separate mixing rules for each density regime, guided by theoretically defined boundary conditions. Such flexibility is necessary to represent phase equilibria in highly asymmetric fluid mixtures such as water-hydrocarbon systems. Phase equilibria are correlated for a variety of binary and multicomponent mixtures, including a petroleum reservoir fluid containing carbon dioxide and including a mixture of hydrogen and coal-derived liquids.

R. L. Cotterman, J. M. Prausnitz
Materials and Molecular Research Division
Lawrence Berkeley Laboratory
and Chemical Engineering Department
University of California
Berkeley, CA 94720

Introduction

Phase equilibria for fluid mixtures are essential for efficient design and operation of chemical separation processes. Since it may be prohibitive to measure such equilibria at all conditions of interest, molecular-thermodynamic correlations are widely used to represent fluid-phase behavior over wide ranges of temperature, pressure, and composition.

Most of the successful correlations for representation of mixture phase behavior are semitheoretical in nature. One particular class of semitheoretical correlations is derived from the dense-fluid theories of Prigogine (1957) and Flory (1970). These correlations include the perturbed-hard-chain (PHC) equation (Beret and Prausnitz, 1975; Donohue and Prausnitz, 1978) and the chain-of-rotators (COR) equation (Chien et al., 1983). These equations contain physically significant molecular parameters that are obtained from pure-component thermodynamic data. Extension to mixtures is based on mixing rules to relate mixture averages to composition.

While the PHC and COR equations are derived primarily for nonpolar fluids, both have been extended to include polar fluids. Gmehling et al. (1979) superimposed a chemical dimerization theory onto the PHC equation; Vimalchand and Donohue (1985) and Vimalchand et al. (1986) extended the PHC equation to polar and quadrupolar fluids using the multipolar expansions of Gubbins and Twu (1978). Masuoka and Chao (1984) added a polar perturbation term to the COR equation.

In a manner similar to that of Vimalchand et al., this work extends the PHC theory to include both quadrupolar and dipolar fluids and their mixtures. However, the novel feature of this work is separation of high-density and low-density contributions to the residual Helmholtz energy. While this separation leads to improved correlation of pure-fluid thermodynamic properties as discussed in Part I, the main advantage of the separation follows from extension to mixtures. Separate mixing rules are selected for each density region to meet theoretically defined boundary conditions and to represent phase behavior for highly asymmetric mixtures.

As suggested by several authors (Mollerup, 1981; Whiting and Prausnitz, 1982; Wong and Johnston, 1984), density-dependent mixing rules improve the representation of phase behavior in strongly nonideal fluid mixtures. Mathias and Copeman

R. L. Cotterman is currently at W. R. Grace & Co., 7379 Route 32, Columbia, MD 21044.

(1983) apply such mixing rules to the Peng-Robinson equation. Hu et al. (1984), Luedecke and Prausnitz (1985), and Mollerup (1983) have correlated phase behavior for several binary mixtures using an equation of the van der Waals form with density-dependent mixing rules. The present work builds upon these previous developments using the PHC equation. The resulting correlation is applicable to a wide variety of mixtures containing fluids such as hydrogen, water, polymers, and coal-derived liquids, in addition to the usual hydrocarbons, nitrogen, carbon dioxide, and hydrogen sulfide.

Residual Helmholtz Energy for Mixtures

The expression for the residual Helmholtz energy presented in Part I is extended to mixtures. The molar residual Helmholtz energy for a mixture is the difference between the molar Helmholtz energy for that mixture and that for an ideal-gas mixture at the same temperature, volume, and composition

$$a^r(T, V, n_1, n_2 \ldots) = a(T, V, n_1, n_2 \ldots) - a^{IG}(T, V, n_1, n_2 \ldots) \quad (1)$$

where n_1 is the mole number of component 1, etc.

The residual Helmholtz energy is given by the sum of a reference term and two perturbation terms

$$a^r = a^{ref} + a^{sv}(1 - F) + a^{df}F \quad (2)$$

where a^{ref} is the contribution from the reference fluid and where a^{sv} and a^{df} are perturbation contributions in low-density and high-density regions, respectively. Function F provides a smooth interpolation between these two density regions.

Reference term a^{ref} includes contributions from repulsive intermolecular forces; it is calculated using a generalized form of the Carnahan-Starling equation (1972) shown by Eq. 7 of Part I. To allow for softness of the spheres, the hard-core diameter is temperature-dependent (Eq. 10, Part I), as suggested by Barker and Henderson (1967).

Separation of the perturbation term into high-density and low-density regions allows flexibility to choose separate mixing rules for each density region. Such flexibility is necessary to correlate phase behavior in highly asymmetric systems; it is this flexibility that allows us to relax the commonly used quadratic mixing rule without violating the theoretically determined composition dependence of the second virial coefficient.

The perturbation terms include contributions due to dispersion and polar and quadrupolar intermolecular forces. The low-density term a^{sv} is given by a virial expansion truncated after the second virial coefficient (Eq. 17, Part I). Generalized expressions for dispersion and polar and quadrupolar contributions were obtained from experimental second virial coefficients.

The high-density term a^{df} is given by a perturbation series in reciprocal temperature. Expressions for dispersion contributions (Eq. 16, Part I) are obtained from a generalization of computer-simulation data for Lennard-Jones molecules; polar and quadrupolar contributions follow from a multipolar expansion presented by Gubbins and Twu (1978).

Interpolation function F (Eq. 18, Part I) is chosen to meet necessary boundary conditions; it is generalized using experimental vapor pressure and density data for a large number of pure fluids.

The equation of state and the chemical potential are derived by differentiating Eq. 2 with respect to volume and mole number, respectively.

Each pure fluid is characterized by three molecular parameters v^*, $\epsilon q/k$, and c; these parameters are characteristic of soft-core volume, dispersion potential energy, and the flexibility and asymmetry of a molecule; a characteristic temperature T^* is defined by $\epsilon q/k$. (For polar fluids we also use reduced dipole moment $\tilde{\mu}$ and reduced quadrupole moment $\tilde{Q}$.) As discussed in Part I, v^* and T^* are used to define a hard-core (temperature-dependent) volume $v\dagger$. Values of parameters are determined by fitting pure-fluid vapor pressure and/or density data. For polar fluids, reduced dipole and quadrupole moments are defined by Eqs. 14 and 15 of Part I, respectively.

Reference Term

Reference term a^{ref} is calculated for mixtures by replacing pure-component parameters c and $v\dagger$ in the generalized Carnahan-Starling expression given in Eq. 7 of Part I with the composition averages $\langle c\rangle$ and $\langle v\dagger\rangle$. These averages are related to pure-component parameters using suitable mixing rules. The mixing rules are selected to meet two necessary boundary conditions: First, the expression for the entropy of mixing for an athermal mixture at high densities must reduce to the Flory-Huggins expression. Second, the composition dependence of the reference-term contribution to the second virial coefficient must be quadratic in mole fraction, as required by statistical mechanics (Prausnitz et al., 1986).

The physical significance of parameter c requires that the mixing rule for $\langle c\rangle$ be linear in mole fraction x. Since reduced volume $\tilde{v}$ is per segment, we also use a linear rule for $v\dagger$. Thus,

$$\langle c\rangle = \sum_i x_i c_i \quad (3)$$

$$\langle v\dagger\rangle = \sum_i x_i v_i\dagger \quad (4)$$

To show that Eqs. 3 and 4 meet both boundary conditions, we first consider the entropy of mixing for an athermal mixture. The expression for the entropy of mixing arising from the reference term is

$$\frac{\Delta s^{mix}}{R} = -\sum_i x_i \ln \frac{x_i v_i^{pure}}{v} + \langle c\rangle \frac{(3\tau/\tilde{v} - 4)(\tau/\tilde{v})}{(1 - \tau/\tilde{v})^2} - \sum_i x_i c_i \frac{(3\tau/\tilde{v}_i - 4)(\tau/\tilde{v}_i)}{(1 - \tau/\tilde{v}_i)^2} \quad (5)$$

where $\tau = \pi\sqrt{2}/6$; v_i^{pure} is the molar volume of pure i at the same pressure and temperature as those of the mixture, and where v is the molar volume of the mixture. $\langle c\rangle$ and $\tilde{v}$ are composition averages for parameter c and for reduced molar volume $\tilde{v} = v/\langle v\dagger\rangle$; c_i and $\tilde{v}_i$ are the corresponding pure-component quantities.

If we use Eq. 3 for $\langle c\rangle$ and if we assume that the reduced densities of all the pure components and of the mixture are equal at high pressures (close-packed density), i.e.,

$$\tilde{v} = \tilde{v}_i \quad \text{for all } i, \quad (6)$$

then Eq. 5 becomes

$$\frac{\Delta s^{mix}}{R} = -\sum_i x_i \ln (x_i v_i^{pure}/v) \tag{7}$$

which is the Flory-Huggins expression.

To show that Eqs. 3 and 4 meet the second boundary condition, we calculate the contribution to the second virial coefficient from the reference term

$$B^{ref} = \langle c \rangle \langle v\dagger \rangle (2\pi\sqrt{2}/3) \tag{8}$$

Since both $\langle c \rangle$ and $\langle v\dagger \rangle$ are linear in mole fraction, the composition dependence of B^{ref} is quadratic in mole fraction.

Second Virial Perturbation Term

The expression for the low-density perturbation term a^{sv} is the sum of attractive contributions to the second virial coefficient. Since the mixture second virial coefficient must be quadratic in mole fraction, the mixture expression for a^{sv} becomes

$$a^{sv} = \frac{RT}{v} \sum_i \sum_j x_i x_j (B_{ij}^{disp} + B_{ij}^{\mu\mu} + B_{ij}^{QQ}) \tag{9}$$

where B_{ij}^{disp}, $B_{ij}^{\mu\mu}$, and B_{ij}^{QQ} are attractive contributions to the second virial coefficient due to dispersion and dipolar and quadrupolar forces, respectively.

Appendices A and B of Part I give pure-component ($i = j$) expressions for each of the terms in Eq. 9. For the cross terms in Eq. 9 ($i \neq j$), we must choose combination rules to calculate cross-molecular parameters.

The cross parameters for the dispersion contributions are given by

$$c_{ij} = \tfrac{1}{2}(c_i + c_j) \tag{10}$$

$$(cv\dagger)_{ij} = \tfrac{1}{2}(c_i v_j\dagger + c_j v_i\dagger) \tag{11}$$

$$T_{ij}^* = \frac{(c_i T_i^*)^{1/2}(c_j T_j^*)^{1/2}}{c_{ij}} (1 - k_{ij}^B) \tag{12}$$

where k_{ij}^B is an adjustable binary parameter that corrects the geometric mean assumption for T_{ij}^*. Parameter k_{ij}^B is fitted to experimental second virial cross coefficients for binary mixtures.

Combination rules for the dipolar and quadrupolar contributions are given in Appendix B of this paper. No additional binary parameters are introduced.

The upper diagram in Figure 1 shows calculated and observed second virial cross coefficients for several methane-alkane binaries. Experimental values are reported by Dymond and Smith (1980). Second virial cross coefficients are calculated using Eqs. 10 to 12 with binary parameters k_{ij}^B set to zero. For these binaries, agreement between calculated and experimental cross coefficients is good without the use of any adjustable binary parameters.

The lower diagram in Figure 1 shows calculated and observed second virial cross coefficients for several water-alkane binaries. Experimental data are from Dymond and Smith (1980) and Smith et al. (1983, 1984). Calculated and experimental values

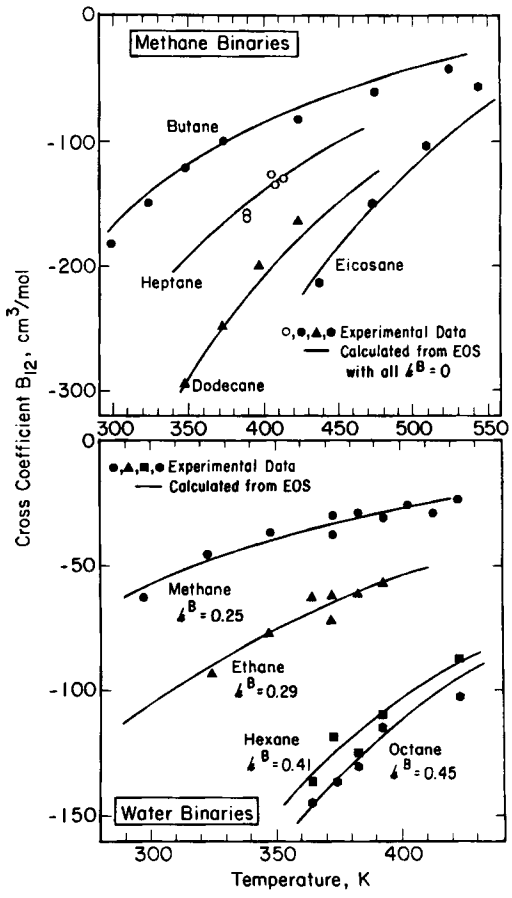

Figure 1. Second virial cross coefficients for asymmetric mixtures.

are in good agreement when one adjustable parameter is included for each binary. Fitted binary parameters are indicated in Figure 1.

Dense-Fluid Term

The dense-fluid expression a^{df} is the sum of terms representing high-density contributions due to dispersion and dipolar and quadrupolar forces. Each term is calculated using mixing rules to relate mixture composition averages to pure-component parameters. Mixing rules for the dispersion terms are similar to those of Donohue and Prausnitz (1978); mixing rules for polar terms follow the forms suggested by Gubbins and Twu (1978).

For extension to mixtures, we consider the perturbation terms due to dispersion forces, $a^{(1)}$ and $a^{(2)}$, introduced in Eq. 13 of Part I.

The composition dependence of the dispersive terms is given by the following averages

$$a^{(1)}(x) = a^{(1)}(\langle cT^* v\dagger \rangle, \langle v\dagger \rangle) \tag{13}$$

$$a^{(2)}(x) = a^{(2)}(\langle cT^{*2} v\dagger \rangle, \langle v\dagger \rangle) \tag{14}$$

where $\langle v\dagger \rangle$ is given by Eq. 4. Mixing rules for $\langle cT^* v\dagger \rangle$ and $\langle cT^{*2} v\dagger \rangle$ are composition averages over molecular segments and surface area.

As in Part I, a molecule is considered to be the sum of equi-sized segments; a molecule has r segments and an external surface area q. The soft-core volume per segment v^*_{seg} is the same for all segments; it is here set equal to 10 cm^3/mol. While this value is somewhat arbitrary, it follows from earlier work of Donohue and Prausnitz (1978); the size of each segment is approximately equal to that of a methylene group in a long-chain hydrocarbon. The soft-core volumes per mole of molecules and per mole of segments are interrelated by

$$v^* = r\sigma^3 N_{av}/\sqrt{2} = rv^*_{seg} \tag{15}$$

where N_{av} is Avogadro's number and σ is the soft-core segment diameter. The hard-core volume $v\dagger$ is defined by

$$v\dagger = rd^3 N_{av}/\sqrt{2} \tag{16}$$

where d is the hard-core diameter calculated with Eq. 10 of Part I.

The potential energy per molecule is given by $\epsilon q/k$ where ϵ is potential energy per surface area and k is Boltzmann's constant. Characteristic temperature T^* is defined by

$$T^* = \epsilon q/ck \tag{17}$$

While reduction of pure-component data yields the product $\epsilon q/k$, for correlation of mixture data it is necessary to separate that product into its two factors.

Following Donohue and Prausnitz (1978), we write a general mixing rule

$$\langle cT^{*m} v\dagger \rangle = \sum_i \sum_j x_i x_j c_i \left[\frac{\epsilon_{ij} q_i}{c_i k}\right]^m \frac{r_j d_{ij}^s N_{av}}{\sqrt{2}} \tag{18}$$

where d_{ij} is given by

$$d_{ij} = \tfrac{1}{2}(d_i + d_j) \tag{19}$$

and where ϵ_{ij} is given by

$$\epsilon_{ij} = (\epsilon_{ii}\epsilon_{jj})^{1/2}(1 - k_{ij}) \tag{20}$$

Adjustable binary parameter k_{ij} corrects the geometric-mean assumption; k_{ij} is fitted to binary phase-equilibrium data.

For alkanes, ϵ/k is chosen as 80 K. For other fluids, ϵ/k is determined using equilibrium data for a binary mixture whose second component is an alkane. Typically, the chosen value of ϵ/k is that which minimizes binary parameter k_{ij}. Table 1 lists values of ϵ/k for various hydrocarbon classes and for several other pure fluids.

For most binary mixtures, Eq. 18 is sufficient to represent phase behavior using a single adjustable parameter k_{ij}. However, for some highly asymmetric mixtures it is advantageous to introduce a second adjustable parameter into the mixing rules in Eq. 18, as shown in Appendix A. The two binary parameters, denoted $k_{1(2)}$ and $k_{2(1)}$, adjust the geometric-mean assumption for ϵ_{ij} in separate concentration regions. When component 1 is infinitely dilute in component 2, only parameter $k_{1(2)}$ applies; at the opposite limit, when component 2 is dilute in 1, only parameter $k_{2(1)}$ applies. Parameter $k_{1(2)}$ is fixed by Henry's constant $H_{1(2)}$, and parameter $k_{2(1)}$ is fixed by Henry's constant $H_{2(1)}$; these constants are defined by

$$H_{1(2)} = \lim_{x_1 \to 0} \frac{f_1}{x_1} \quad \text{and} \quad H_{2(1)} = \lim_{x_2 \to 0} \frac{f_2}{x_2} \tag{21}$$

where f is fugacity. At intermediate concentrations, both parameters are required.

Appendix A gives modified mixing rules for Eq. 18 using two adjustable parameters. When the two parameters are equal ($k_{1(2)} = k_{2(1)}$), the mixing rule in Appendix A reduces to Eq. 18.

Appendix B discusses calculation for mixtures of the perturbation terms due to polar intermolecular forces.

Table 1. Potential Energy Per Surface Area for Several Hydrocarbon Classes and Other Fluids

	ϵ/k K
Hydrocarbon Class	
n-alkanes	80
n-alkylnaphthenes	90
n-alkylaromatics	110
Other Fluids	
Ethylene	100
Hydrogen	110
Nitrogen	50
Sulfur Dioxide	80
Carbon Dioxide	80
Water	80
Ammonia	60
Acetone	80
Hydrogen Sulfide	120

Values from analysis of binary phase-equilibrium data.

Interpolation Function

Function F is calculated for mixtures by replacing pure-fluid parameters with a composition average

$$F = 1 - \exp\left[-6\frac{\langle T^*(\epsilon q/k)^{total} v\dagger\rangle}{T^2 v}\right] \tag{22}$$

where $(\epsilon q/k)^{total}$ is the sum of the dispersion, dipolar, and quadrupolar contributions to the potential energy (Eq. 19, Part I). The mixing rule used here is determined empirically by examining phase equilibria for a large number of binary mixtures

$$\langle T^*(\epsilon q/k)^{total} v\dagger\rangle = \sum_i \sum_j x_i x_j \cdot \left(\frac{T_i^* + T_j^*}{2}\right)\left\{\frac{[(\epsilon q/k)_i^{total} v_i\dagger + (\epsilon q/k)_j^{total} v_j\dagger]}{2}\right\} \tag{23}$$

This mixing rule for interpolation function F uses only pure-component parameters; no adjustable binary parameters are introduced.

Data Reduction

To calculate phase equilibria for fluid mixtures, it is necessary to fit adjustable binary parameters to experimental data for

binary mixtures. In the correlation presented here, the resulting equation of state has one, two, or three adjustable parameters depending upon the complexity of the mixture. These parameters can be determined independently using experimental second virial cross coefficients and Henry's constants. However, for many binary mixtures of interest, reliable virial coefficients and Henry's constants are not available. Therefore, we have developed procedures to obtain binary parameters from various types of phase-equilibrium data that may be available for a particular mixture. The most common types of data include pressure-temperature-composition (P-T-x-y) data for equilibrium phases, bubble-point (P-T-x) data, or dew-point (P-T-y) data.

Our regression method is based on the maximum-likelihood technique described by Anderson et al. (1979). The maximum-likelihood technique accounts for experimental uncertainties in both independent and dependent variables. The following estimates of experimental uncertainties are used for correlation of mixture data; temperatures ±0.1 K; pressures ±1.0%; vapor phase and liquid phase mole fractions ±0.01; and Henry's constants ±3.0%.

The maximum-likelihood method determines optimal values of adjustable parameters and estimates of standard deviations. Since these parameters may not be unique and since they depend on the specified objective function, we must be concerned with the sensitivity of phase-equilibrium calculations to fitted values. Such sensitivity comparisons depend on the region of the phase diagram as well as on the specific system studied; however, we can give some generalizations based on our correlation experience from this work.

Phase-equilibrium calculations are not sensitive to the value of adjustable parameter k^B; its value is usually determined by fitting cross-virial coefficients. We find it is generally sufficient to estimate k^B within ±0.10 without significant effects on calculated phase equilibria.

Phase equilibria for most binary mixtures are adequately represented with a single adjustable dense-fluid parameter. For many mixtures, this parameter may vary ±0.01 without significant effect; however, calculated results are often sensitive to larger deviations. For binary mixtures where two adjustable, dense-fluid parameters are used, such as water-hydrocarbon mixtures, calculated results are usually sensitive to fitted parameters; parameters should be known to within ±0.005 for favorable comparison to experimental results.

At dilute concentrations, small changes in calculated mole fractions may result in large changes in calculated K factors. Such sensitivity differences in calculated quantities should be taken into account when evaluating goodness of fit of experimental data. Finally, calculations in the critical region are more sensitive to estimated parameters than are other regions of the phase diagram; experimental data near the critical point are excluded when determining optimal values of fitted parameters.

Asymmetric Binary Mixtures

To illustrate, Figure 2 shows calculated and observed vapor-liquid equilibria for the system hydrogen-hexane. Experimental phase equilibria of Nichols et al. (1957) are correlated using a single binary parameter for the dense fluid. The second virial parameter k^B is set to zero.

Figure 3 shows calculated and observed phase equilibria for the system nitrogen-ammonia. Nitrogen and ammonia have similar molecular sizes but have large differences in potential energy. Nitrogen has a weak quadrupole moment; ammonia has a strong dipole moment. The phase equilibria for this mixture are correlated using two binary parameters; one for the second virial cross coefficient and another for the dense-fluid region. The second virial binary parameter k^B is fitted to experimental second virial cross coefficients reported by Lee et al. (1970). The dense-fluid parameter k_{ij} is correlated to vapor-liquid equilibrium data from Reamer and Sage (1959).

Figure 4 presents vapor-liquid equilibria for the system carbon dioxide-ethane at 250 K. (At this temperature, both pure

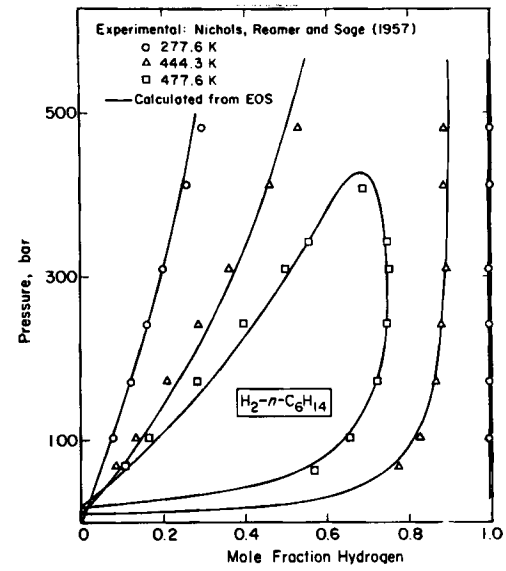

Figure 2. Vapor-liquid equilibria for the system hydrogen-*n*-hexane.
Binary parameters: $k^B = 0$; $k_{12} = 0.065$

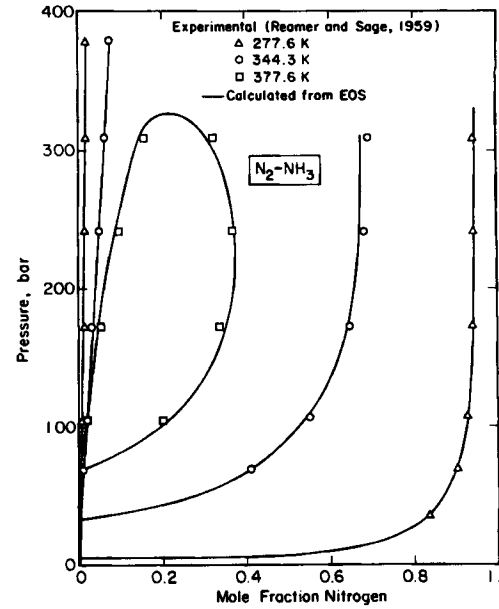

Figure 3. Vapor-liquid equilibria for the system nitrogen-ammonia.
Binary parameters: $k^B = 0.21$; $k_{12} = 0.0256$.

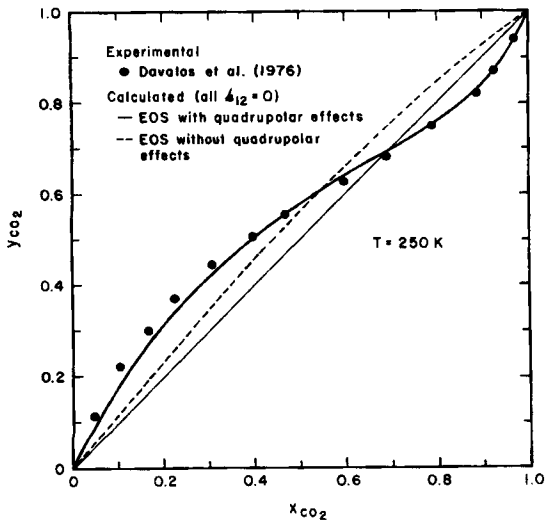

Figure 4. Equation-of-state results with and without quadrupolar effects for the system carbon dioxide-ethane.

All binary parameters set to zero.

components are subcritical.) Figure 4 shows experimental data (solid points) on a y-x diagram; this system has an azeotrope near $x_{co_2} = 0.7$. For this binary mixture, the quadrupole moment of carbon dioxide has an important qualitative effect on calculated results. Following Vimalchand and Donohue (1985), we present calculations with and without quadrupolar effects, setting all binary parameters to zero. If we ignore the quadrupole moment of carbon dioxide (dashed line), the equation of state does not predict an azeotrope. Including the quadrupole moment (heavy curved line), an azeotrope is predicted with good agreement between calculated and observed results.

Table 2 summarizes typical correlation results for several binary systems. Average deviations in K factors are reported for both components. A comprehensive tabulation of binary results and data references is deposited as supplementary material.

Aqueous Binary Mixtures

Water-hydrocarbon binaries represent an important class of asymmetric mixtures because such mixtures are of interest in many chemical and petroleum processes. However, strong polar

Table 2. Typical Agreement between Calculated and Experimental K Factors for Some Illustrative Binary Systems

System		Temp.	Press.	Avg. % Dev.	
1	2	K	bar	K_1	K_2
Hydrogen	Methane	116–172	34–275	7.72	5.16
Hydrogen	Decane	462–583	19–255	3.24	4.74
Methane	Tetralin	462–665	20–253	3.20	5.01
Methane	Water	311–573	27–980	5.90	3.23
Hydrogen sulfide	Pentane	278–444	1–69	4.93	7.41
Hydrogen sulfide	Propylcyclohexane	311–478	2–116	4.01	9.67
Carbon dioxide	Toluene	311–477	3–153	3.36	5.48
Carbon dioxide	Hexadecane	463–664	20–51	8.48	10.43
Nitrogen	Ammonia	278–378	34–310	5.88	3.48
Nitrogen	Benzene	348–398	62–307	1.31	5.99

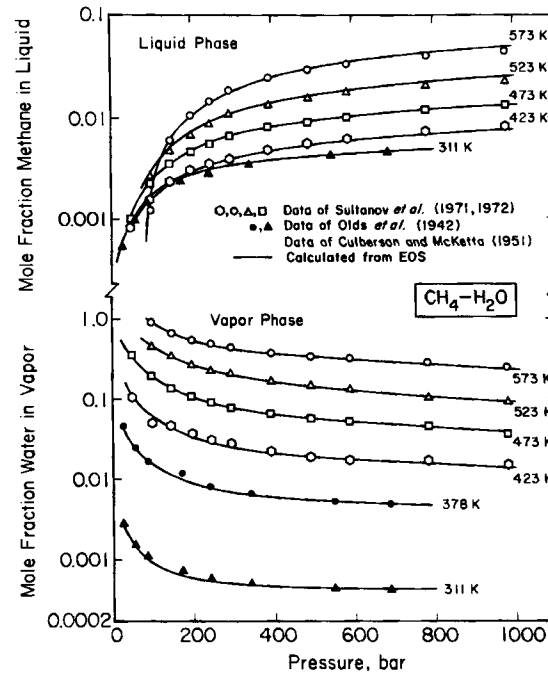

Figure 5. Vapor-liquid equilibria for the system methane-water.

Liquid-phase isotherm at 378 K not shown for clarity.
Binary parameters listed in Table 3.

effects in aqueous mixtures make the phase equilibria of these systems difficult to correlate.

Two adjustable binary parameters are used in the dense-fluid region to represent both water-rich and hydrocarbon-rich composition regions. To obtain good representation, the binary parameter for the water-rich end must be temperature-dependent.

Figure 5 shows calculated and experimental phase equilibria for the system methane-water. Experimental data for this system (Olds et al., 1942; Culberson and McKetta, 1951; Sultanov et al., 1971, 1972) cover wide ranges of temperature and pressure. Observed and calculated vapor-liquid equilibria are in excellent agreement using the binary parameters listed in Table 3.

Figures 6 and 7 show vapor-liquid and liquid-liquid equilibria for the system propane-water. Experimental and calculated results are shown at three temperatures. Figure 6 shows the solubility of water in the propane-rich phase. Below 370 K, there is a three-phase (vapor-liquid-liquid) region, indicated by dashed lines. At the lowest temperature shown (327.6 K), there

Table 3. Binary Parameters for Two Water(1)-Hydrocarbon(2) Binary Mixtures

Binary Parameter	Component 2	
	Methane	Propane
k^{B*}	0.250	0.330
$k_{1(2)}$	0.3722	0.3657
$k_{2(1)}$	$0.1759-49{,}050/T^{2**}$	$0.1186-41{,}890/T^{2**}$

*From second-virial-coefficient data
**T in K

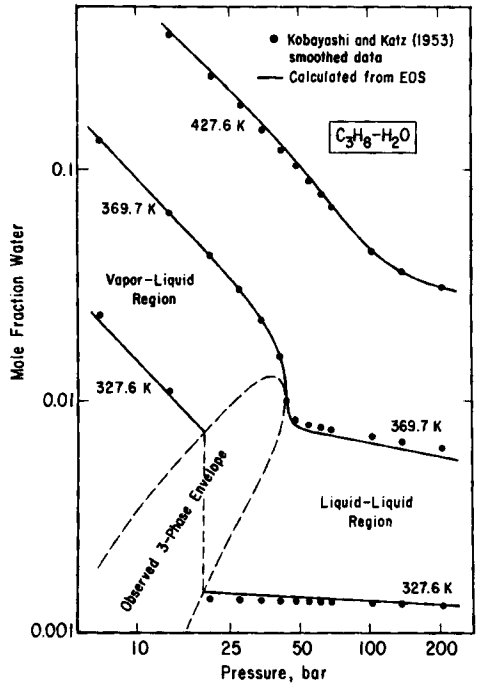

Figure 6. Phase equilibria for the system propane-water at three temperatures.
Solubility of water in propane.
Binary parameters listed in Table 3.

is a transition from vapor-liquid to liquid-liquid equilibria near 20 bar (2 MPa). The middle isotherm (369.7 K) passes through a three-phase critical point. The highest temperature (427.6 K) is beyond the liquid-liquid region; only vapor-liquid equilibria are observed.

For this difficult-to-fit binary system, calculated and experimental phase equilibria are in good agreement. Binary parameters are listed in Table 3. The virial parameter k^B is interpolated between the values listed in Figure 1; this interpolated value based on second virial cross coefficients is in excellent agreement with k^B correlated to dense-fluid data.

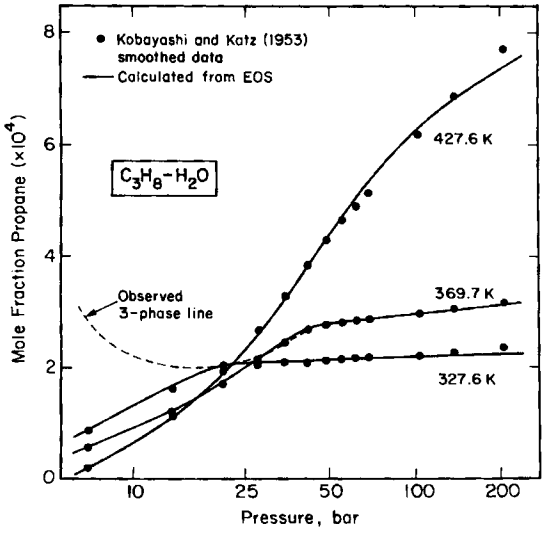

Figure 7. Phase equilibria for the system propane-water at three temperatures.
Solubility of propane in water.
Binary parameters listed in Table 3.

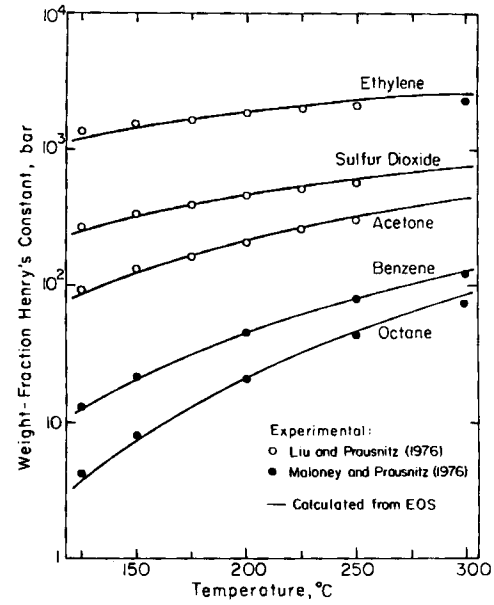

Figure 8. Weight-fraction Henry's constants for solutes in low-density polyethylene.
Binary parameters listed in Table 4.

Henry's Constants for Solutes in Polyethylene

The correlation presented here is useful for calculating phase behavior for mixtures containing high-molecular-weight fluids. To illustrate, the solubilities of several low-molecular-weight solutes in low-density polyethylene are calculated using binary parameters fitted to experimental Henry's constants reported by Liu and Prausnitz (1976) and Maloney and Prausnitz (1976).

Figure 8 shows typical agreement between calculated and observed results. Pure-component parameters for polyethylene are given in Part I. Fitted binary parameters (for the dense fluid) are reported in Table 4.

Ternary Mixtures

Phase equilibria are calculated for a ternary mixture using only pure-component and binary data. First, experimental and calculated phase-equilibrium results are presented for two binary systems, methane-tetralin and hydrogen-tetralin. Then, phase equilibria are calculated for the ternary system methane-hydrogen-tetralin.

Figure 9 shows K factors as functions of temperature and

Table 4. Binary Parameters for Five Solutes in Polyethylene

Solute	$100k_{12}$
Ethylene	0.05
Sulfur dioxide	5.38
Acetone	2.69
Benzene	1.94
Octane	0.00

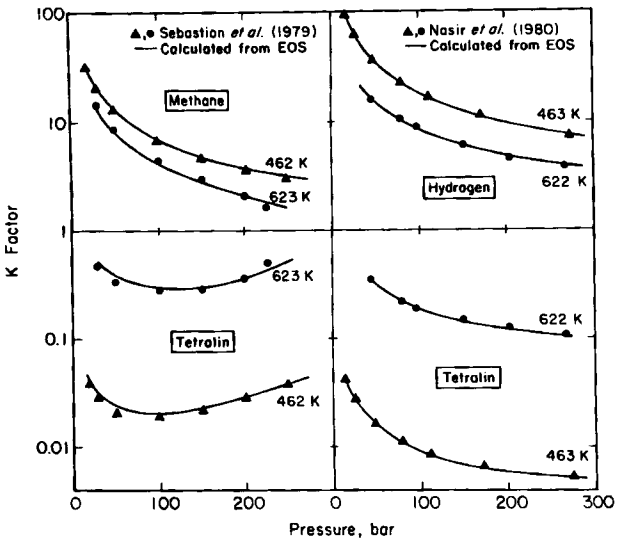

Figure 9. *K* factors for methane(1)-tetralin(3) and hydrogen(2)-tetralin(3).

Binary parameters: all $k^B = 0$; $k_{13} = 0.0461$; $k_{23} = 0.0133$

pressure for the systems methane-tetralin and hydrogen-tetralin. For each binary, one adjustable binary parameter is obtained from data reduction; second virial parameters k^B are set to zero. For the hydrogen-tetralin system, calculated and observed K factors are in good agreement. However, for the methane-tetralin system at 623 K, the correlation overpredicts the apparent critical pressure.

Calculated and experimental vapor-liquid equilibria for the system methane-hydrogen (not shown) are in good agreement using a single binary parameter $k_{12} = 0.1431$. (Temperatures corresponding to the vapor-liquid region for methane-hydrogen are significantly below those shown in Figure 9 for the tetralin binaries.)

Phase equilibria for the ternary system hydrogen-methane-tetralin are calculated at 462 K. Figure 10 shows calculated and experimental results at three pressures. K factors for each component are plotted as functions of overall methane mole fraction on a tetralin-free basis. The left and right sections in Figure 10 give K factors for methane and hydrogen in the ternary mixture. These K factors are nearly independent of the relative amount of methane. However, in the center section the K factor of tetralin depends strongly on the methane content, as noted previously by Gray et al. (1983).

At the lowest pressure, 51 bar (5.1 MPa), tetralin shows little preference for either methane or hydrogen. At higher pressures (101 and 253 bar; 10.1 and 25.3 MPa) the tetralin K factor is much larger in methane-rich mixtures than in hydrogen-rich mixtures, indicating that, as expected from second virial coefficient correlations, the vapor-phase solubility of tetralin is larger in dense methane than in dense hydrogen.

Equilibria in a Reservoir Fluid

Equations of state are commonly used to calculate phase equilibria for reservoir fluid mixtures as needed for simulation of miscible-gas processes. Carbon dioxide is commonly used for reservoir injection; phase equilibria of carbon dioxide-rich mixtures are therefore of industrial importance.

Two examples are presented here for carbon dioxide-hydrocarbon mixtures. In the first example, binary parameters are correlated using solubility data for carbon dioxide in several heavy-hydrocarbon solvents (Gasem and Robinson, 1985). In the second example, phase equilibria are calculated for a 12-component synthetic oil mixture containing a significant

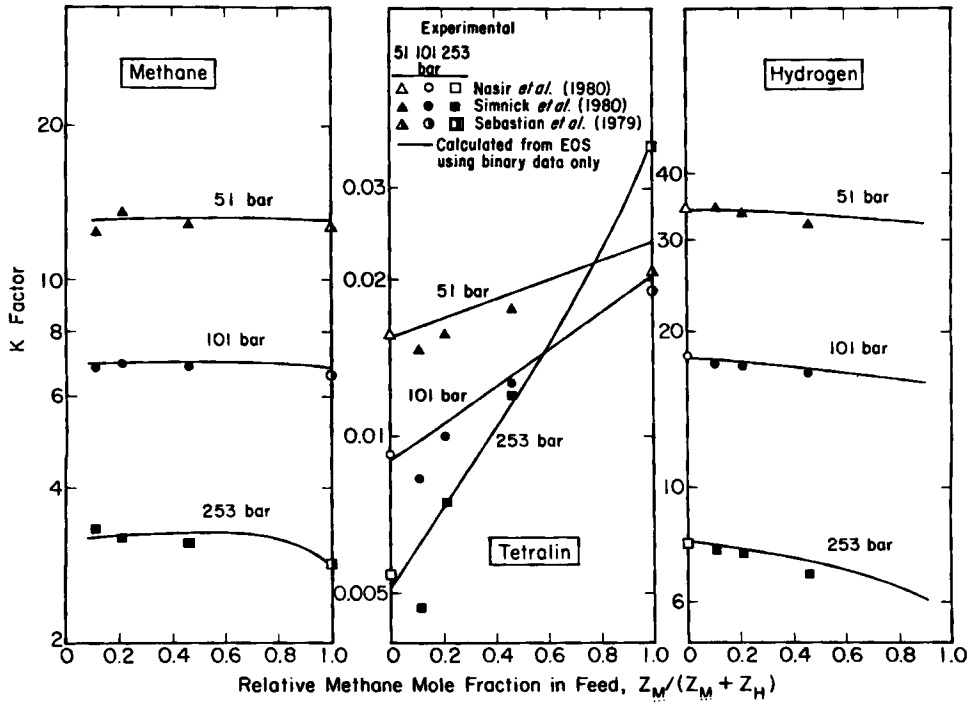

Figure 10. Equilibrium flash calculations for the system hydrogen(1)-methane(2)-tetralin(3) at 462 K.

amount of carbon dioxide. Such systems are valuable for testing correlation methods without introducing uncertainties due to incomplete characterization of real-oil mixtures.

Figure 11 shows calculated and experimental solubilities of carbon dioxide in four high-boiling alkane solvents at 100°C. Similar results are obtained at 50 and 150°C. One (high-density) adjustable binary parameter is used for each solvent. Table 5 lists generalized dense-fluid binary parameters k_{ij}. Since quadrupolar effects for carbon dioxide are explicitly taken into account, second virial parameters k^B are set to zero for carbon dioxide-hydrocarbon binaries.

Figure 12 shows calculated and experimental phase equilibria for a 12-component synthetic-oil mixture at 322 K. Experimental flash data are reported by Turek et al. (1984). The feed composition of the oil is given in Table 6; the overall mole fraction of carbon dioxide is 70 mol %.

Calculated and experimental results are in good agreement from low pressures to the mixture bubble point [experimental, 115.1 bar; calculated, 114.9 bar (11.51 and 11.49 MPa)]. Calculated K factors for tetradecane are somewhat below experimental values; however, vapor-phase mole fractions for tetradecane are extremely small and perhaps subject to some experimental uncertainty.

The results in Figure 12 are calculated from flash calculations using the feed composition given in Table 6. Adjustable parameters for all binaries are given in Table 5. For all binaries, virial parameter k^B is set to zero.

Comparisons at other overall carbon dioxide concentrations give similar good results except near mixture critical conditions.

Hydrogen Solubility in Coal-Derived Liquids

The final example shows a correlation for the solubility of hydrogen in a middle distillate from the solvent-refined-coal-II (SRC-II) process at several temperatures and pressures. Experimental data are reported by Harrison et al. (1985). The coal-derived liquid is considered to be a mixture of two pseudocomponents. One pseudocomponent corresponds to a saturated hydrocarbon and another corresponds to an aromatic hydrocarbon. To calculate hydrogen solubility in a mixture of these two pseudocomponents, three simplifying assumptions are necessary to determine pure-component parameters, relative amounts of each pseudocomponent, and binary parameters.

First, pure-fluid parameters are estimated for each pseudocomponent using the generalized correlations presented in Appendix C of Part I. The alkane correlation is used for the

Table 5. Binary Parameters for Several Binary Systems

	$100k_{12}$						
Component	CH_4	C_2H_6	C_3H_8	N_2	H_2S	CO_2	H_2
n-Alkanes							
CH_4	—	1.0	1.7	3.0	3.5	3.0	15.0
C_2H_6	1.0	—	0.2	4.0	4.0	3.5	12.0
C_3H_8	1.7	0.2	—	5.0	4.5	4.0	10.0
C_4H_{10}	2.2	0.5	0.1	5.5	4.7	4.4	8.5
C_5H_{12}	2.7	0.7	0.2	5.5	5.0	4.6	7.5
C_6H_{14}	3.0	0.8	0.3	5.5	5.2	4.8	6.5
C_7H_{16}	3.3	0.9	0.4	5.5	5.4	5.0	6.0
C_8H_{18}	3.6	1.0	0.5	5.5	5.6	5.2	6.0
$C_{10}H_{22}$	4.0	1.2	0.5	5.5	5.8	5.4	6.0
$C_{16}H_{34}$	4.8	1.2	0.5	5.5	6.0	5.9	6.0
$C_{20}H_{42}$	5.0	1.2	0.5	5.5	6.0	6.0	6.0
$C_{30}H_{62}$	5.0	1.2	0.5	5.5	6.0	6.0	6.0
n-Alkylcyclohexanes	3.0	1.5	0.7	9.0	3.0	3.0	0.0
n-Alkylbenzenes	4.0	2.0	1.5	9.5	0.0	4.0	4.5

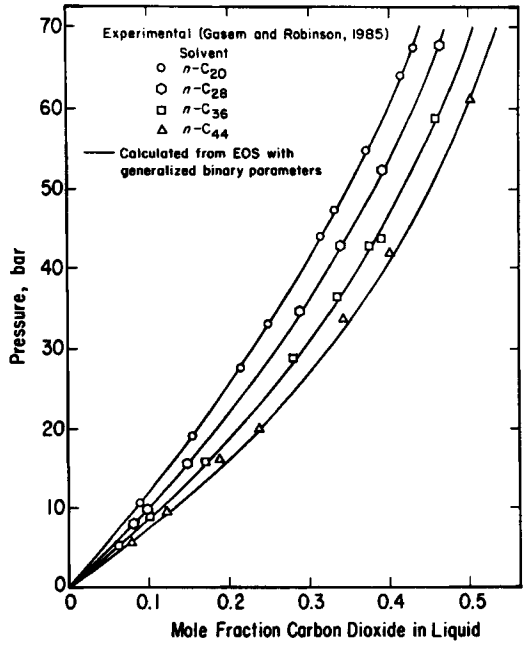

Figure 11. Solubility of carbon dioxide in high-boiling normal paraffins at 100°C.
Similar results are obtained at 50 and 150°C.
Calculated using binary parameters from Table 5.

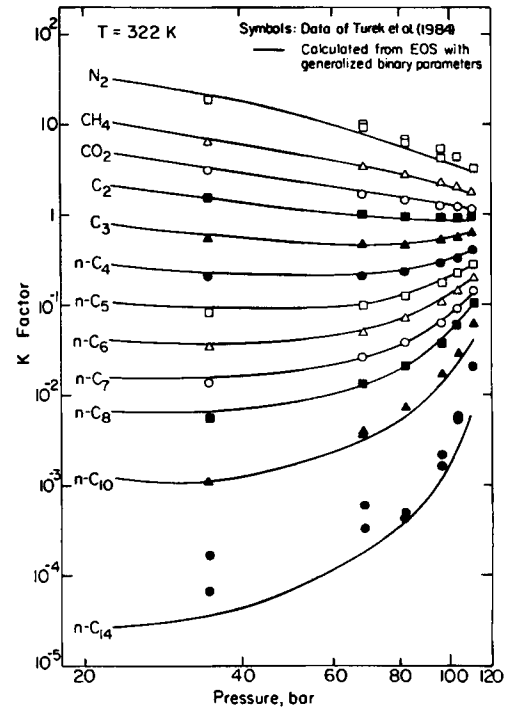

Figure 12. *K* factors for 12-component synthetic oil with 70 mol % carbon dioxide.
Calculated using binary parameters from Table 5.

Table 6. Overall Feed Composition for 12-Component Synthetic Oil

Component	Mol %
Carbon dioxide	69.520
Nitrogen	0.456
Methane	10.130
Ethane	0.851
Propane	1.195
Butane	1.798
Pentane	1.305
Hexane	0.966
Heptane	1.482
Octane	1.505
Decane	9.196
Tetradecane	1.596

saturated component; the fused-ring correlation is used for the aromatic component. These correlations require the molecular weight of each component. Molecular weights for both pseudocomponents are estimated using the boiling-point characterization for the SRC-II middle distillate presented by Brinkman and Bowden (1982). The molecular weight of the alkane pseudocomponent is 183.3, that of the fused-ring pseudocomponent is 134.8.

Second, the relative amount of each pseudocomponent is estimated from the average molecular weight of the coal-derived liquid. Harrison et al. (1985) report an average molecular weight of 146.1 determined by mass spectrometry. Since the pseudocomponents have different molecular weights, the fraction of each is determined by matching the overall experimental molecular weight. On a hydrogen-free basis, the mole fractions of the alkane and the fused-ring pseudocomponents are 0.767 and 0.233, respectively.

Finally, binary parameters are estimated for binary pairs. Since the liquid-phase mole fraction of hydrogen is small, only one binary parameter is used for each hydrogen-hydrocarbon pair; virial parameters k^B and the hydrocarbon-hydrocarbon parameter are set to zero. The hydrogen-alkane binary parameter is estimated from Table 5 ($k_{12} = 0.06$). The molecular weight of the aromatic corresponds roughly to that for tetralin. Therefore, the hydrogen-tetralin parameter used in Figure 9 is also used here ($k_{12} = 0.0133$).

Figure 13 shows calculated (dashed lines) and experimental (symbols) solubilities for hydrogen in the SRC-II middle distillate. Agreement is good considering the simplifying assumptions that are required for performing calculations for this complex mixture.

Agreement between calculated and experimental results can be improved by correcting for decomposition and hydrogenation reactions. Harrison et al. (1985) correct their experimental results for the presence of volatile reaction products. The authors report an overall 5% increase in the molecular weight of the coal-derived liquid following solubility measurements. (This increase in molecular weight results from the conversion of aromatics to saturates in the presence of hydrogen at high temperatures.) Assuming that this increase is a linear function of temperature, the relative amounts of each pseudocomponent are adjusted accordingly. As a result, the mole fraction of the alkane rises, leading to increased solubilities of hydrogen. The increased solubility is indicated by the solid lines in Figure 13.

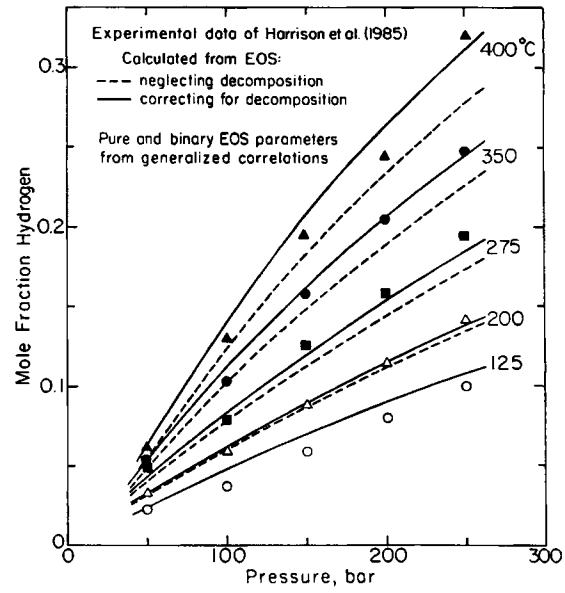

Figure 13. Solubility of hydrogen in a middle distillate from the solvent-refined-coal-II process.

This example illustrates the applicability of our correlation to provide quantitative estimates of hydrogen solubilities in complex mixtures. Further improvement requires more detailed experimental characterization of the complex hydrocarbon mixtures. Experimental procedures for such characterization are the subject of current research at Berkeley.

Conclusion

The correlation presented here uses an extended perturbed-hard-chain theory to calculate phase equilibria in mixtures. The extension takes into consideration the effect of hard-core softness as well as effects arising from dipole and quadrupole moments. More important, the extension considers separately contributions to the residual Helmholtz energy from low-density and high-density regions. This separation makes it easy to use density-dependent mixing rules: one mixing rule is used for the low-density region and another mixing rule is used for the high-density region. While the low-density mixing rule is always quadratic in mole fraction, the high-density mixing rule is arbitrary, dictated by the kind of mixture under consideration. For the high-density region, a quadratic mixing rule is satisfactory for most ordinary mixtures while a cubic mixing rule is necessary for those mixtures (e.g., water-hydrocarbons) where there is much deviation from randomness.

The correlation given here is entirely analytic, requiring no numerical integrations. It is therefore suitable for computer-aided process design. Computer programs are available upon request.

While the correlation presented here is applicable to a wide variety of fluid mixtures encountered in chemical technology, it has one significant limitation: it is not able to supply consistently reliable results in the critical region. That limitation is not peculiar to this correlation; it unfortunately prevails in all correlations used in contemporary chemical engineering.

For significant advance in chemical engineering thermodynamics, our first priority should not be to refine further existing equations of state in the high-density and low-density regions.

Instead, primary attention should now be given to establishing a useful, engineering-oriented equation of state that is reliable for correlating the phase behavior of pure fluids and mixtures in the critical region as well as in regions remote from critical.

Acknowledgment

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy. Additional support was provided by the National Science Foundation, the Gas Research Institute, the Fannie and John Hertz Foundation, the American Petroleum Institute, Texaco, Inc., and Chevron Research Company. The authors are grateful to Marc Donohue, Shaqing Pan, and Dimitrios Dimitrelis for helpful discussions.

Notation

a = molar Helmholtz energy
$a^{(m)}$ = binary combination of molecular parameters $cT^{*m}v\dagger$
$A^{(m)}$ = ternary combination of molecular parameters $cT^{*m}v\dagger$
B = second virial coefficient
c = shape and flexibility parameter
d = hard-core (temperature-dependent) diameter
f = fugacity
F = interpolation function
$H_{i(j)}$ = Henry's constant of solute i in solvent j
J = integral of two-body radial distribution function
K = integral of three-body radial distribution function
k = Boltzmann's constant
k^B = second virial adjustable binary parameter
k_{ij} = dense-fluid adjustable binary parameter
$\tilde{k}_{ij}$ = average dense-fluid adjustable binary parameter
n = number of moles
P = absolute pressure
q = external molecular surface area
Q = molecular quadrupole moment
$\tilde{Q}$ = reduced quadrupole moment in low-density region
$\hat{Q}$ = reduced quadrupole moment in high-density region
r = number of segments per molecule
R = gas constant
Δs^{mix} = entropy of mixing
T = absolute temperature
$\tilde{T}$ = reduced temperature, $\tilde{T} = T/T^*$
$\hat{T}$ = characteristic temperature for high-density polar perturbation terms
T^* = characteristic temperature, $T^* = \epsilon q/ck$
v = molar volume
$\tilde{v}$ = reduced volume, $\tilde{v} = v/v\dagger$
$\hat{v}$ = characteristic volume for high-density polar perturbation terms
v^* = soft-core molar-volume parameter
v^*_{seg} = soft-core segment-volume parameter
$v\dagger$ = hard-core molar-volume parameter
v^{pure} = pure-component molar volume
V = total volume
x = mole fraction

Greek letters

μ = molecular dipole moment
$\tilde{\mu}$ = reduced dipole moment in low-density region
$\hat{\mu}$ = reduced dipole moment in high-density region
ϵ = potential energy per unit surface area
σ = soft-core diameter
τ = hard-sphere packing factor (0.7405)

Superscripts and subscripts

df = dense-fluid contribution
$disp$ = dispersive contribution
IG = ideal-gas contribution
i, j, k = component i, j, or k
ij = interaction between components i and j
ijk = interaction between components i, j, and k
m = integer in dense-fluid mixing rule
QQ = quadrupolar contribution
r = residual property
ref = reference term
sv = second virial contribution
$\mu\mu$ = dipolar contribution
μQ = dipolar-quadrupolar contribution

Appendix A. Modified Dense-Fluid Mixing Rules for Highly Asymmetric Mixtures

This appendix describes a modification of the generalized mixing rule given in Eq. 18 for the nonpolar perturbation terms $a^{(1)}$ and $a^{(2)}$. This modification is useful for representing phase behavior for mixtures containing components with very large differences in potential energy. Two adjustable binary parameters are introduced, allowing flexibility to correlate separately the dilute region of each component in a binary mixture.

The two adjustable parameters $k_{1(2)}$ and $k_{2(1)}$ adjust the geometric-mean assumption for ϵ_{ij} in the two Henry's constant limits, Eq. 21. When the two parameters are equal to one another, the modified mixing rule reduces to Eq. 18.

The modified mixing rule is cubic in mole fraction

$$\langle cT^{*m}v\dagger\rangle = \sum_i \sum_j \sum_k x_i x_j x_k A^{(m)}_{ijk} \tag{A1}$$

where $A^{(m)}$ represents a particular combination of molecular parameters. The order of the subscripts on $A^{(m)}$ is important for selecting the correct sequence of parameters.

For the two simplest cases, when $i = j = k$,

$$A^{(m)}_{iii} = c_i \left[\frac{\epsilon_{ii} q_i}{c_i k}\right]^m \frac{r_i d^3_{ii} N_{av}}{\sqrt{2}} \tag{A2}$$

and when $i \neq j \neq k$,

$$A^{(m)}_{ijk} = \tfrac{1}{2}\, a^{(m)}_{ij}(1 - \hat{k}_{ij}) + \tfrac{1}{2}\, a^{(m)}_{jk}(1 - \hat{k}_{jk}) \tag{A3}$$

where $\hat{k}_{ij}$ is an average of the two binary parameters

$$\hat{k}_{ij} = \tfrac{1}{2}\,(k_{i(j)} + k_{j(i)}) \tag{A4}$$

and where $a^{(m)}_{ij}$ represents the parameter combination

$$a^{(m)}_{ij} = c_i \left[\frac{(\epsilon_{ii}\epsilon_{jj})^{1/2} q_i}{c_i k}\right]^m \frac{r_j d^3_{ij} N_{av}}{\sqrt{2}} \tag{A5}$$

The order of the subscripts in Eq. A5 is important since $a^{(m)}_{ij} \neq a^{(m)}_{ji}$.

For the $A^{(m)}_{ijk}$ terms that have two identical subscripts, individual terms are defined such that only $k_{1(2)}$ contributes to $H_{1(2)}$ and only $k_{2(1)}$ contributes to $H_{2(1)}$. The following expressions are chosen to meet these conditions:

$$A^{(m)}_{iij} = \tfrac{1}{2}\,[a^{(m)}_{ii} + a^{(m)}_{ij}(1 - k_{j(i)})] \tag{A6a}$$

$$A^{(m)}_{iji} = \tfrac{1}{2}\,[a^{(m)}_{ij} + a^{(m)}_{ji}](1 - k_{j(i)}) \tag{A6b}$$

$$A^{(m)}_{jii} = \tfrac{1}{2}\,[a^{(m)}_{ii} + a^{(m)}_{ji}(1 - k_{j(i)})] \tag{A6c}$$

where all a_{ij} are defined by Eq. A5.

Appendix B. Expressions for Polar Contributions to Attractive Perturbation Terms in Mixtures

Appendix B of Part I gives expressions for multipolar contributions to low-density and high-density perturbation terms. This appendix extends those expressions to mixtures. The composition dependence of the low-density term is chosen to meet the boundary condition that the second virial coefficient is quadratic in mole fraction; the composition dependence of the high-density term follows from the forms suggested by Gubbins and Twu (1978). The high-density expressions presented here differ slightly from those presented earlier by Vimalchand and Donohue (1985).

Low-density contributions

Equation 9 gives the expression for the low-density perturbation term due to polar and nonpolar contributions; Eqs. 10–12 give cross parameters as needed for B_{ij}^{disp}. To calculate B_{ij}^{QQ} and $B_{ij}^{\mu\mu}$ from the expressions given in Appendix B of Part I, cross parameters are needed for reduced dipole and quadrupole moments; these are

$$\tilde{\mu}_{ij}^2 = \frac{\mu_i\mu_j}{c_{ij}T_{ij}^* v_{ij}^*}\left(\frac{N_{av}}{k\sqrt{2}}\right) \tag{B1}$$

$$\tilde{Q}_{ij}^2 = \frac{Q_iQ_j}{c_{ij}T_{ij}^* v_{ij}^{*5/3}}\, k\left(\frac{N_{av}}{\sqrt{2}}\right)^{5/3} \tag{B2}$$

where the cross soft-core volume is defined

$$v_{ij}^* = \left[\frac{(v_i^*)^{1/3} + (v_j^*)^{1/3}}{2}\right]^3 \tag{B3}$$

The product cv^* is defined in a manner analogous to that for the nonpolar expression

$$(cv^*)_{ij} = \tfrac{1}{2}\,(c_iv_j^* + c_jv_i^*) \tag{B4}$$

These cross parameters are substituted directly into the expressions for pure fluids given in Part I. No adjustable binary parameters are introduced.

High-density contributions

Expressions for the high-density polar contributions in pure fluids are extended to mixtures using forms given by Gubbins and Twu (1978). These forms are derived from two-body and three-body radial distribution functions. Hence, two-body mixing rules are quadratic mole fraction averages over pure-component parameters and three-body mixing rules are cubic mole fraction averages over pure-component parameters.

To simplify the mixture expressions, we define characteristic parameters for both two-body and three-body interactions. The two-body characteristic parameters are defined by

$$\hat{T}_{ij} = \frac{(\epsilon_{ii}\epsilon_{jj})^{1/2}q_i}{c_ik} \tag{B5}$$

$$\hat{v}_{ij} = r_j\left(\frac{\sigma_i + \sigma_j}{2}\right)^3 N_{av}/\sqrt{2} \tag{B6}$$

Two-body dipole and quadrupole moments are defined by

$$\hat{\mu}_{ij}^2 = \frac{\mu_i\mu_j}{c_i\hat{T}_{ij}\hat{v}_{ij}}\left(\frac{N_{av}}{k\sqrt{2}}\right) \tag{B7}$$

$$\hat{Q}_{ij}^2 = \frac{Q_iQ_j}{c_i\hat{T}_{ij}\hat{v}_{ij}^{5/3}}\, k\left(\frac{N_{av}}{\sqrt{2}}\right)^{5/3} \tag{B8}$$

$$(\hat{\mu}\hat{Q})_{ij} = \frac{\tfrac{1}{2}\,(\mu_iQ_j + \mu_jQ_i)}{c_i\hat{T}_{ij}\hat{v}_{ij}^{4/3}}\, k\left(\frac{N_{av}}{\sqrt{2}}\right)^{4/3} \tag{B9}$$

These two-body expressions are used to define characteristic parameters for three-body interactions:

$$\hat{T}_{ijk} = (\hat{T}_{ij}\hat{T}_{ki}\hat{T}_{jk})^{1/3} \tag{B10}$$

$$\hat{v}_{ijk} = (\hat{v}_{ij}\hat{v}_{jk})^{1/2} \tag{B11}$$

$$\hat{\mu}_{ijk} = (\hat{\mu}_{ij}\hat{\mu}_{ki}\hat{\mu}_{jk})^{1/3} \tag{B12}$$

$$\hat{Q}_{ijk} = (\hat{Q}_{ij}\hat{Q}_{ki}\hat{Q}_{jk})^{1/3} \tag{B13}$$

The order of subscripts is important in Eqs. B5 to B13 since $\hat{T}_{ij} \neq \hat{T}_{ji}$ and $\hat{v}_{ij} \neq \hat{v}_{ji}$.

As discussed in Appendix B of Part I, the perturbation expansions for contributions due to dipolar and quadrupolar intermolecular forces are replaced by Padé approximants. For a mixture, the expression for dipole-dipole interactions is

$$a^{\mu\mu} = a_{\mu\mu}^{(2)}\left[1 - \frac{a_{\mu\mu}^{(3)}}{a_{\mu\mu}^{(2)}}\right]^{-1} \tag{B14}$$

where

$$\frac{a_{\mu\mu}^{(2)}}{RT} = -\frac{2.9619}{T^2v}\sum_i\sum_j x_ix_jc_i\hat{T}_{ij}^2\hat{v}_{ij}\hat{\mu}_{ij}^4 J^{\mu\mu}\left(\frac{T}{\hat{T}_{ij}}, \frac{v}{\hat{v}_{ij}}\right) \tag{B15}$$

$$\frac{a_{\mu\mu}^{(3)}}{RT} = \frac{43.596}{T^3v^2}\sum_i\sum_j\sum_k x_ix_jx_kc_i \cdot \hat{T}_{ijk}^3\hat{v}_{ijk}^2\hat{\mu}_{ijk}^6 K^{\mu\mu\mu}\left(\frac{T}{\hat{T}_{ijk}}, \frac{v}{\hat{v}_{ijk}}\right) \tag{B16}$$

where J and K are integrals of two-body and three-body radial distribution functions. Expressions for these integrals are given by Gubbins and Twu (1978) and are included in supplementary material for Part I.

For a mixture, the expression for quadrupole-quadrupole interactions is

$$a^{QQ} = a_{QQ}^{(2)}\left[1 - \frac{a_{QQ}^{(3)}}{a_{QQ}^{(2)}}\right]^{-1} \tag{B17}$$

where

$$\frac{a_{QQ}^{(2)}}{RT} = -\frac{12.440}{T^2v}\sum_i\sum_j x_ix_jc_i\hat{T}_{ij}^2\hat{v}_{ij}\hat{Q}_{ij}^4 J^{QQ}\left(\frac{T}{\hat{T}_{ij}}, \frac{v}{\hat{v}_{ij}}\right) \tag{B18}$$

$$\frac{a^{(3)}_{QQ}}{RT} = \frac{2.6113}{T^3v}\sum_i\sum_j x_i x_j c_i \hat{T}^3_{ij}\hat{v}_{ij}\hat{Q}^6_{ij} J^{QQQ}\left(\frac{T}{\hat{T}_{ij}}, \frac{v}{\hat{v}_{ij}}\right) + \frac{77.716}{T^3v^2}\sum_i\sum_j\sum_k x_i x_j x_k c_i \hat{T}^3_{ijk}\hat{v}^2_{ijk}\hat{Q}^6_{ijk} K^{QQQ} \cdot \left(\frac{T}{\hat{T}_{ijk}}, \frac{v}{\hat{v}_{ijk}}\right) \quad \text{(B19)}$$

Dipole-quadrupole contributions are expressed using only the second-order term

$$\frac{a^{\mu Q}}{RT} = -\frac{8.8858}{T^2v}\sum_i\sum_j x_i x_j c_i \hat{T}^2_{ij}\hat{v}_{ij}(\hat{\mu}\hat{Q})^2_{ij} J^{\mu Q}\left(\frac{T}{\hat{T}_{ij}}, \frac{v}{\hat{v}_{ij}}\right) \quad \text{(B20)}$$

For use here, constants reported by Gubbins and Twu for the above integrals must be multiplied by $\sqrt{2}$ wherever reduced density appears; thus follows since reduced density in this work is based on a close-packed molecular volume.

Literature cited

Anderson, T. F., D. S. Abrams, and E. A. Grens II, "Evaluation of Parameters for Nonlinear Thermodynamic Models," *AIChE J.*, **24,** 20 (1978).

Barker, J. A., and D. Henderson, "Perturbation Theory and Equation of State for Fluids. II: A Successful Theory of Liquids," *J. Chem. Phys.*, **47,** 4714 (1967).

Beret, S., and J. M. Prausnitz, "Perturbed-Hard-Chain Theory: An Equation of State for Fluids Containing Small of Large Molecules," *AIChE J.*, **21,** 1123 (1975).

Brinkman, D. W., and J. N. Bowden, "Stability of Some Coal and Tar Sands Syncrude Fractions," *Fuel*, **61,** 1141 (1982).

Carnahan, N. F., and K. E. Starling, "Intermolecular Repulsions and the Equation of State for Fluids," *AIChE J.*, **18,** 1184 (1972).

Chien, C. H., R. A. Greenkorn, and K. C. Chao, "Chain-of-Rotators Equation of State," *AIChE J.*, **29,** 560 (1983).

Culberson, O. L., and J. J. McKetta, "Phase Equilibria in Hydrocarbon-Water Systems," *Pet. Trans. AIME*, **192,** 223 (1951).

Davalos, J., W. R. Anderson, R. E. Phelps, and A. J. Kidnay, "Liquid-Vapor Equilibria at 250.00 K for Systems Containing Methane, Ethane, and Carbon Dioxide," *J. Chem. Eng. Data*, **21,** 81 (1976).

Donohue, M. D., and J. M. Prausnitz, "Perturbed-Hard-Chain Theory for Fluid Mixtures: Thermodynamic Properties for Mixtures in Natural Gas and Petroleum Technology." *AIChE J.*, **24,** 849 (1978).

Dymond, J. H., and E. B. Smith, *The Virial Coefficients of Pure Gases and Mixtures: A Critical Compilation*, Clarendon Press, Oxford (1980).

Flory, P. J., "Thermodynamics of Polymer Solutions," *Disc. Faraday Soc.*, **49,** 7 (1970).

Gasem, K. A. M., and R. L. Robinson, Jr., "Solubilities of Carbon Dioxide in Heavy Normal Paraffins ($C_{20} - C_{44}$) at Pressures to 9.6 MPa and Temperatures from 323 to 423 K," *J. Chem. Eng. Data*, **30,** 53 (1985).

Gmehling, J., D. D. Liu, and J. M. Prausnitz, "High-Pressure Vapor-Liquid Equilibria for Mixtures Containing One or More Polar Components," *Chem. Eng. Sci.*, **34,** 951 (1979).

Gray, R. D., J. L. Heidman, S. C. Hwang, and C. Tsonopoulos, "Industrial Applications of Cubic Equations of State for VLE Calculations, with Emphasis on H_2 Systems," *Fluid Phase Equil.*, **13,** 59 (1983).

Gubbins, K. E., and C. H. Twu, "Thermodynamics of Polyatomic Fluid Mixtures. I: Theory," *Chem. Eng. Sci.*, **33,** 863 (1978).

Harrison, R. H., S. E. Scheppele, G. P. Sturm, and P. L. Grizzle, "Solubility of Hydrogen in Well-defined Coal Liquids," *J. Chem. Eng. Data*, **30,** 183 (1985).

Hu, Y., D. Luedecke, and J. M. Prausnitz, "Molecular Thermodynamics of Fluid Mixtures Containing Molecules Differing in Size and Potential Energy," *Fluid Phase Equil.*, **17,** 217 (1984).

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

Lee, C. S., J. P. O'Connell, C. D. Myrat, and J. M. Prausnitz, "Intermolecular Forces in Gaseous Ammonia and in Ammonia-Nonpolar Gas Mixtures," *Can. J. Chem.*, **48,** 2993 (1970).

Liu, D. D., and J. M. Prausnitz, "Solubilities of Gases and Volatile Liquids in Polyethylene and in Ethylene-Vinyl Acetate Copolymers in the Region 125-225°C," *Ind. Eng. Chem. Fundam.*, **15,** 330 (1976).

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

Maloney, D. P., and J. M. Prausnitz, "Solubilities of Ethylene and Other Organic Solutes in Liquid, Low-Density Polyethylene in the Region 124° to 300°C," *AIChE J.*, **22,** 74 (1976).

Masouka, H., and K. C. Chao, "Chain-of-Rotators Equation of State. II. Polar Fluids," *Ind. Eng. Chem., Fundamentals*, **23,** 24 (1984).

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

Mollerup, J., "A Note on Excess Gibbs Energy Models, Equations of State, and the Local Composition Concept," *Fluid Phase Equil.*, **7,** 121 (1981).

———, "Correlation of Thermodynamic Properties of Mixtures Using a Random-Mixture Reference State," *Fluid Phase Equil.*, **15,** 189 (1983).

Nasir, P., R. J. Martin, and R. Kobayashi, "A Novel Apparatus for the Measurement of the Phase and Volumetric Behavior at High Temperatures and Pressures and Its Application to Study VLE in the Hydrogen-Tetralin System," *Fluid Phase Equil.*, **5,** 279 (1980).

Nichols, W. B., H. H. Reamer, and B. H. Sage, "Volumetric and Phase Behavior in the Hydrogen–*n*-Hexane System," *AIChE J.*, **3,** 262 (1957).

Olds, R. H., B. H. Sage, and W. N. Lacey, "Phase Equilibria in Hydrocarbon Systems," *Ind. Eng. Chem.*, **34,** 1223 (1942).

Prausnitz, J. M., R. N. Lichtenthaler, and E. G. de Azevedo, *Molecular Thermodynamics of Fluid-Phase Equilibria*, 2nd ed., Prentice-Hall, Englewood Cliffs, NJ (1986).

Prigogine, I., *The Molecular Theory of Solutions*, Interscience, New York (1957).

Reamer, H. H., and B. H. Sage, "Phase Behavior in the Nitrogen-Ammonia System," *J. Chem. Eng. Data*, **4,** 303 (1959).

Sebastian, H. M., J. J. Simnick, N. M. Lin, and K. C. Chao, "Gas-Liquid Equilibrium in Binary Mixtures of Methane with Tetralin. Diphenylmethane and 1-Methylnaphthalene," *J. Chem. Eng. Data*, **24,** 149 (1979)

Simnick, J. J., H. M. Sebastian, H. M. Lin, and K. C. Chao, "Vapor-Liquid Phase Equilibria in the Ternary System Hydrogen + Methane + Tetralin," *J. Chem. Eng. Data*, **25,** 147 (1980).

Smith, G., A. Sellars, T. K. Yerlett, and C. J. Wormald, "The Excess Enthalpy of (Water + Hydrogen) Vapor and (Water + Methane) Vapor," *J. Chem. Thermody.*, **15,** 29 (1983).

Smith, G. R., M. J. Fahy, and C. J. Wormald, "The Excess Molar Enthalpy of $\{xH_2O+(1-x)C_nH_{2n+2}\}(g)$ for n = 5, 6, 7, and 8," *J. Chem. Thermody.*, **16,** 825 (1984).

Sultanov, R. G., V. G. Skripka, and A. Yu. Namiot, "Moisture Content of Methane at High Temperatures and Pressures," (in Russian), *Gazov. Prom.*, **16,** 6 (1971).

———, "Solubility of Methane in Water at High Temperatures and Pressures," (in Russian), *Gazov. Prom.*, **17,** 6 (1972).

Turek, E. A., R. S. Metcalfe, L. Yarborough, and R. L. Robinson, Jr., "Phase Equilibria in CO_2-Multicomponent Hydrocarbon Systems: Experimental Data and an Improved Prediction Technique," *Soc. Pet. Eng. J.*, **24,** 308 (1984).

Vimalchand, P., and M. D. Donohue, "Thermodynamics of Quadrupolar Molecules: The Perturbed-Anisotropic-Chain Theory," *Ind. Eng. Chem. Fundam.*, **24,** 246 (1985).

Vimalchand, P., M. D. Donohue, and I. C. Celmins, "Thermodynamics of Multipolar Molecules: The Perturbed-Anisotropic-Chain Theory," *Equations of State: Theories and Applications*, K. C. Chao and R. L. Robinson, eds., Amer. Chem. Soc., Washington, *DC (1986).*

Whiting, W. B., and J. M. Prausnitz, "Equations of State for Strongly Nonideal Fluid Mixtures: Application of Local Compositions toward

Density-Dependent Mixing Rules," *Fluid Phase Equil.*, **9**, 119 (1982).
Wong, J. M., and K. P. Johnston, "Thermodynamic Models for Nonrandom and Strongly Nonideal Liquid Mixtures," *Ind. Eng. Chem. Fundam.*, **23**, 320 (1984).

Manuscript received Nov. 26, 1985, and revision received Apr. 29, 1986.

See NAPS document no. 04421 for 12 pages of supplementary material. Order from NAPS c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance in U.S. funds only $7.75 for photocopies or $4.00 for microfiche. Outside the U.S. and Canada, add postage of $4.50 for the first 20 pages and $1.00 for each of 10 pages of material thereafter, $1.50 for microfiche postage.