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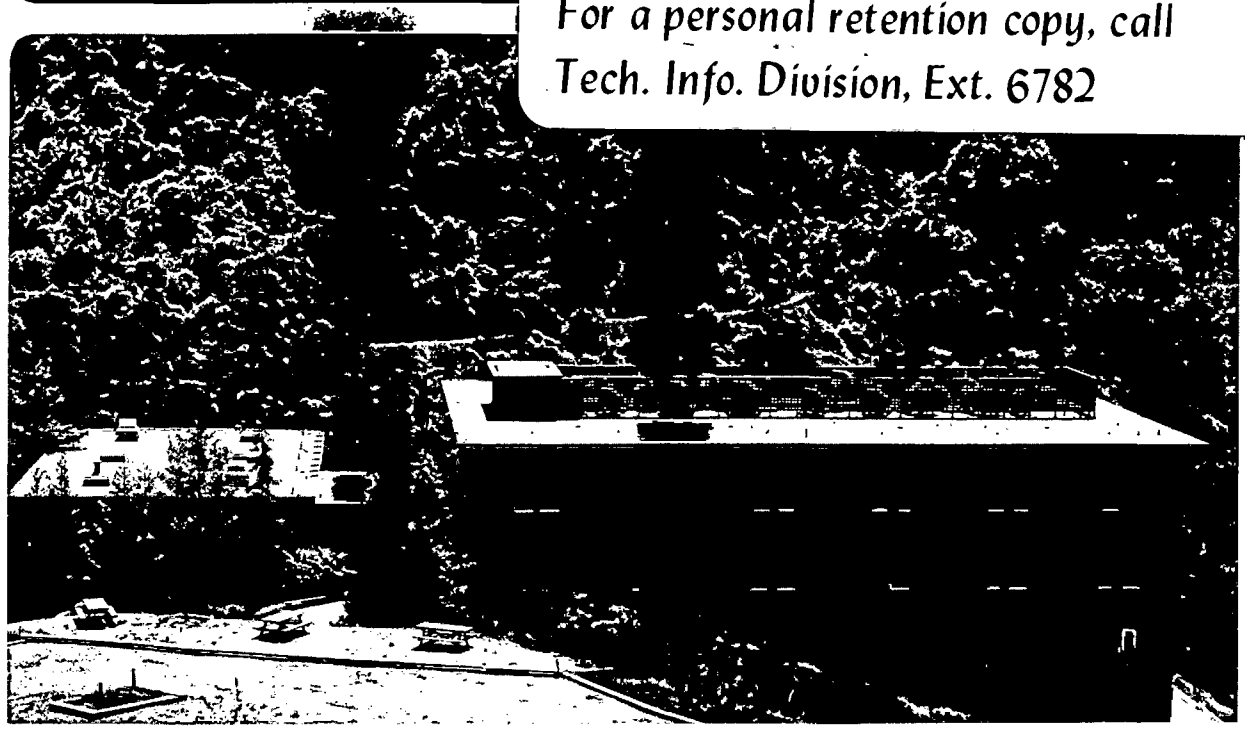

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A LOCAL-COMPOSITION EQUATION OF STATE FOR ASYMMETRIC MIXTURES

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ABSTRACT

Perturbed-hard-chain theory (PHCT) and the local-composition concept are used to obtain an equation of state for asymmetric mixtures. PHCT is extended to polar fluids by assigning a semi-theoretical temperature dependence to the energy parameter, T*, and by using Barker and Henderson's approximation for all higher-order terms in the perturbation series for the Helmholtz energy. Based on a modification of the quasi-chemical theory of Guggenheim, the local-composition model is applied to mixtures at all fluid densities. Using only one or at most two binary parameters, the equation of state can represent high-pressure vapor-liquid equilibria for several polar-nonpolar mixtures.

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For design of separation processes in the chemical industry, accurate prediction of fluid-phase equilibria is crucial. If the process design engineer does not have reliable thermodynamic subroutines for his process-simulation computer programs, he must overdesign distillation columns, extraction units, etc., to minimize the associated risk, possibly destroying the economic viability of the process.

For mixtures of simple, nonpolar fluids (such as light hydrocarbons), numerous equations of state are available that predict vapor-liquid equilibria well. However, in many industrial processes (e.g., coal gasification) it is necessary to separate mixtures containing highly polar components (including water and other hydrogen-bonding fluids) in addition to nonpolar fluids; for such mixtures, simple equations of state, with standard, one-fluid mixing rules, are often not able to represent the thermodynamic properties with sufficient accuracy for process design. The asymmetry of these mixtures produces highly nonrandom molecular configurations in space, possibly leading to formation of two liquid phases. Instead of the traditional model of white and black billiard balls randomly positioned in space, a more realistic model is required that can account for clustering of molecules into partially ordered, energetically favorable configurations.

Simple equations of state with simple mixing rules are not successful for asymmetric mixtures, that is, those where the molecules of one component are very much different from

those of the other, either with regard to molecular size or chemical nature (intermolecular potential). For such mixtures, the usual one-fluid mixing rules, quadratic in mole fracion, fail badly at liquid-like densities.

To allow for asymmetry, new empirical, one-fluid mixing rules have been suggested by a number of authors, for example, Vidal (1978) and Plöcker (1978). These rules have little theoretical foundation and violate a necessary boundary condition, viz., that the second virial coefficient of a mixture must be quadratic in mole fraction. As a result, many applications using these empirical rules hold only for phase equilibria at low or modest pressures where all significant deviations from ideality occur only in the liquid phase. For thermodynamically consistent results, and for application to high-pressure vapor-liquid equilibria, it is necessary to have a mixing rule tht is valid for both dilute and dense fluid mixtures. This is conveniently achieved through density-dependent mixing rules as discussed previously by us (Whiting and Prausnitz, 1980, 1981, 1982) and by Mollerup (1981).

An equation of state for mixtures whose molecules differ appreciably in size has been discussed by Donohue (1978) and by Liu (1980) who used perturbed-hard-chain theory (PHCT). A possible extension to mixtures containing polar molecules has been presented by Gmehling et al. (1978) who proposed to take polarity into account through a chemical (dimeriztion) hypothesis. That extension gives good

results for some polar-polar mixtures but appears to be somewhat less successful for polar-nonpolar mixtures. More important, that extension becomes computationally unwieldy for multicomponent mixtures because the number of apparent molecular species (monomers and dimers) rises quickly; for a binary polar-polar mixture, there are already five apparent species (two monomers and three dimers) and for a ternary mixture there are nine apparent species (three monomers and six dimers).

To predict phase equilibria for asymmetric mixtures, we propose here a new equation of state that can correlate pure-component thermodynamic data for polar as well as for nonpolar fluids. More important, we have established a new set of mixing rules based on the two-fluid theory and the local-composition concept. We have made compromises between statistical-mechanical rigor and engineering usefulness. The important achievement is that we have removed the common implicit assumption that the structure of a dense fluid mixture is a (van der Waals) random assembly of spherically symmetric molecules.

Equation of State for Pure Polar Fluids

For extension to polar fluids, the most popular variation on simple equations of state is to assign an empirical temperature dependence to the equation-of-state parameters (e.g., Nakamura et al., 1976; Soave, 1979). This procedure increases the number of adjustable parameters whose physical

significance is unclear.

A more fundamental approach is to follow methods discussed by Twu and Gubbins (1978), who use molecular theory for calculating the effect of polar interactions and, thereby, introduce parameters with clear physical significance. No doubt, their method will eventually be reduced to engineering practice, but, at present, we prefer to use a less rigorous but simpler model.

For many polar species, the most important term in the multipole expansion is the dipole-dipole term. Thus, we have chosen to lump all orientational contributions to pure-fluid properties into a single term based on the angle-averaged interaction between point dipoles. To this term we assign a simple temperature dependence.

For point dipoles, an effective nonpolar potential, ϕ_{ij}^{D}, can be defined by averaging the dipole-dipole potential over all possible orientations of two molecules, one of type i and one of type j. Such a procedure was first suggested by Keesom (1922), as discussed elsewhere (e.g., Prausnitz, 1969; Reed and Gubbins, 1973). The result is

$$\phi_{ij}^{D} = - \frac{\mu_i^2 \mu_j^2}{3 r^6 kT} + \ldots , \qquad (1)$$

where μ_i is the dipole moment of i, r is the distance between molecular centers, k is Boltzmann's constant, and T is the absolute temperature. The truncated terms are all of higher order in reciprocal temperature.

This idealized point dipole-point dipole potential has

the same dependence on distance of separation, r^{-6}, as does the London (1930) potential for spherically symmetric, nonpolar molecules. Thus, we define an effective potential-well-depth parameter, T*, for a polar fluid as

$$T^* = T^{*(0)} + \frac{D}{T(v^*)^2} + \ldots \qquad (2)$$

where $T^{*(0)}$ is the potential-well-depth parameter for the nonpolar part of the potential, v* is the close-packed molar volume, and where parameter D is a measure of polarity; for nonpolar fluids, D=0. As in Equation 1, all further terms contain higher powers of reciprocal temperature.

We chose for our reference equation of state the PHCT of Donohue (1978). The Helmholtz energy, A, of N moles of a pure fluid at temperature T and molar volume v is given by

$$\frac{A - A^{id}}{NRT} = \frac{A_0}{NRT} + \sum_{n=1}^{4} \frac{A_n}{T^n} \quad , \qquad (3)$$

where

$$\frac{A_0}{NRT} = c \left[\frac{4(\tau v^*/v) - 3(\tau v^*/v)^2}{(1 - \tau v^*/v)^2} \right]$$

and

$$A_n = T^{*n} \sum_{m=1}^{5} a_{nm} (v^*/v)^m \quad .$$

Here A^{id} is the Helmholtz energy in the ideal-gas state at the same temperature and molar volume. Table I gives universal constants a_{nm} and τ. Pure-component parameters T*, v*, c, and D are characteristic, respectively, of the intermolecular potential-well depth, the hard-core volume,

the number of external degrees of freedom, and the polarity of the molecule.

The PHCT was developed from a truncated perturbation expansion in powers of reciprocal temperature for molecules with square-well potentials. Thus, the form of the effective potential-well depth given in Equation 2 is appropriate for use with the PHCT. If we substitute Equation 2 into Equation 3, we obtain for the Helmholtz energy of square-well molecules containing point dipoles:

$$\frac{A - A^{id}}{NRT} = \frac{A_0}{NRT} + \frac{A_1}{T} + \frac{A_2}{T^2} + \ldots , \qquad (4)$$

where

$$A_1 = T^{*(0)} \sum_{m=1}^{5} a_{1m} (v^*/v)^m$$

$$A_2 = \sum_{m=1}^{5} \left[T^{*(0)2} a_{2m} + \frac{a_{1m} D}{c(v^*)^2} (v^*/v)^m \right] .$$

Note that there is no dipole-dipole contribution to the mean-field A_1 term.

Second, we use an approximation to take into account higher terms in the expansion of Equation 2. To close this expansion in reciprocal temperature, we use the method of Barker and Henderson (1967, 1976) who showed that their approximation gives better convergence than do Padé-approximant and other methods. Following Barker and Henderson, we need only the first two perturbation terms; the others are estimated. This method, applied to Equation 4, is

$$\frac{A - A^{id}}{NRT} = \frac{A_0}{NRT} + \frac{A_1^2}{2A_2} \exp\left[\frac{2A_2}{A_1 T} - 1\right] . \qquad (5)$$

Equation 5 is our working equation for the Helmholtz energy of pure polar or nonpolar fluids. Through standard thermodynamic relations, we can derive expressions for the pressure and for the fugacity.

We have used Equation 5 for several highly polar fluids (and for several nonpolar fluids with D=0). Pure-fluid parameters, given in Table II, are obtained from experimental equilibrium properties (vapor pressures and liquid densities). For both methanol and water, the reference energy parameter, $T^{(0)}$, is larger than would be expected for the nonpolar part of the intermolecular potential. These values, as well as the large value of the parameter c for methanol, suggest, first, that the reference system (A_0) is not entirely suitable and, second, that the simple temperature-dependence that we assign to the energy parameter T* is not sufficient to account for the strong hydrogen bonding of these fluids; thus, to obtain a good fit of the data, part of the polar contribution becomes incorporated into the reference part of the equation of state.

The pure-component surface-area parameter, q_i, also listed in Table II, is discussed below. It is used only in the calculation of mixture properties.

Figures 1 and 2 show typical agreement between experimental and calculated properties of water. Considering the simple equation used, agreement is remarkably good except in the critical region, where all analytical equations fail.

(However, see Brandani, 1981.)

Extension to Mixtures: Local-Composition Model

To calculate fluid-mixture properties with the commonly used one-fluid model, we must use a set of mixing rules to relate the characteristic parameters of the mixture to those of the pure components. Several sets of mixing rules have been proposed, but nearly all are implicitly based on a (van der Waals) random-mixing assumption. These common mixing rules are only slight variations of those proposed by van der Waals (1890), who first suggested the one-fluid mixture model almost 100 years ago.

In this work, we use a significantly different procedure for extending an equation of state to mixtures (Whiting and Prausnitz, 1980, 1981, 1982; Mollerup, 1981). Starting from the two-fluid theory (which underlies the Wilson [1964], NRTL [Renon, 1968], UNIQUAC [Maurer, 1978], and other liquid-state activity-coefficient models), we use a consistent mixture theory for fluids at all fluid densities. Our local-composition theory is based on a quasi-chemical approximation for the degree of nonrandomness in a fluid mixture; this theory meets the necessary close-packed-liquid and ideal-gas limits (Whiting and Prausnitz, 1981, 1982).

We are particularly concerned with nonrandomness that occurs even in mixtures of nearly equal-sized molecules whenever their intermolecular potentials are significantly different. We assume that this nonrandomness exists, to

some extent, at all non-zero densities.

First, following van der Waals, we separate the Helmholtz energy into an ideal-gas, a repulsive (hard-chain), and an attractive part:

$$A = A^{id} + A^{rep} + A^{attr} \quad . \tag{6}$$

The repulsive Helmholtz energy of the mixture is calculated using either the one-fluid model or a "rigorous" equation of state for mixtures of molecules having purely repulsive potentials (e.g., the equation of state for a hard-sphere mixture of Mansoori et al. [1972] or the hard-convex-body equation of Boublik [1975]). For the calculations reported below, we have used the one-fluid model rather than a "rigorous" hard-sphere-mixture equation because we have found that, for binary hard-sphere mixtures, the entropy of mixing calculated with the equation of Mansoori et al. is essentially identical to that calculated with the one-fluid equation (Whiting and Prausnitz, 1982). Further, the one-fluid equation offers more flexibility; while the equation of Mansoori et al. requires additivity of diameters for unlike spheres, the one-fluid model allows, when necessary, introduction of a binary parameter l_{ij} to account for nonadditivity. The one-fluid mixing rules we use for the repulsive contribution are

$$v^*_M = \sum_{i=1}^{m} \sum_{j=1}^{m} x_i x_j v^*_{ij} \tag{7}$$

$$c_M = \sum_{i=1}^{m} x_i c_{ii} \quad , \tag{8}$$

where

$$v^*_{ij} = \left[\frac{v^{*1/3}_{ii} + v^{*1/3}_{ii}}{2}\right]^3 (1 - l_{ij}) \quad . \tag{9}$$

Here x_i is the mole fraction of component i, subscript M denotes mixture, and m is the number of components.

Although much of the structure of the fluid is determined by the repulsive part of the intermolecular potentials (cf. Chandler, 1978), we seek to include the effects of the attractive potential on the nonrandomness of the mixture.

For a binary mixture, we consider two representative regions in the fluid, as suggested by Maurer (1978) and as indicated in Figure 3. One region centers around a type-1 molecule, and the other centers around a type-2 molecule. The local compositions in these two regions are different. As suggested by quasi-chemical theory (Guggenheim, 1935, 1952), and following Wilson (1964), we approximate these local compositions using Boltzmann factors with energies characteristic of the like and unlike two-body interactions:

$$\frac{x_{ji}}{x_{ii}} = \frac{x_j}{x_i} \frac{\exp(-\alpha E_{ji}/RT)}{\exp(-\alpha E_{ii}/RT)} \tag{10}$$

$$x_{ji} + x_{ii} = 1 \quad , \tag{11}$$

where i=1 or 2 and α is a universal constant here set equal to 0.5. This somewhat arbitrary value for α is a compromise between Guggenheim's quasi-chemical theory for lattices

(where α is about 1/5) and the Wilson model for local compositions (where α is 1). (See Whiting and Prausnitz, 1982.) Equation 10 indicates that the local mole fraction (x_{ji}) of j molecules around an i molecule is proportional to the total mole fraction of j molecules and proportional to the Boltzmann factor of αE_{ji}, where E_{ji} is characteristic of the attractive ji interaction. In previous models (see, e.g., Maurer, 1978), this energy was taken to be $z\varepsilon/2$, where z is the coordination number and ε is the energy between two nearest-neighbor molecules. For liquids, this lattice-theory simplification may be reasonable, but, for lower densities, we know that the product $z\varepsilon$ is a strong function of density and a weak function of temperature. For any equation of state of the van der Waals type, we can calculate E_{ji} as a function of density and temperature: it is the molar attractive Helmholtz energy of a fluid whose molecules interact with a ji-type intermolecular potential.

The total attractive internal energy, U^{attr}, of a binary fluid mixture is the sum of contributions from both types of regions:

$$U^{attr} = N_1(x_{21}u_{21}+x_{11}u_{11}) + N_2(x_{12}u_{12}+x_{22}u_{22}) \quad , \quad (12)$$

where u_{ji} is the molar internal energy of a fluid of molecules interacting with a ji-type intermolecular potential.

By combining Equations 10-12 and recognizing (from the Gibbs-Helmholtz relation) the following relationship between the characteristic Helmholtz energy E_{ji} and the attractive

internal energy u_{ji}:

$$\left[\frac{\partial(E_{ji}/T)}{\partial(1/T)}\right]_v = u_{ji} \quad , \tag{13}$$

we obtain

$$\frac{\Pi^{attr}}{N} = \sum_{i=1}^{2} x_i \frac{\sum_{j=1}^{2} x_j \left[\frac{\partial(E_{ji}/T)}{\partial(1/T)}\right]_v \exp(-\alpha E_{ji}/RT)}{\sum_{j=1}^{2} x_j \exp(-\alpha E_{ji}/RT)} \quad , \tag{14}$$

where $N=N_1+N_2$. Using the Gibbs-Helmholtz relation, we substitute Equation 14 to obtain the attractive contribution to the Helmholtz energy:

$$\frac{A^{attr}}{N} = T \int_0^{1/T} \frac{\Pi^{attr}}{N} \, d(1/T)$$

$$= \frac{-RT}{\alpha} \sum_{i=1}^{2} x_i \ln \sum_{j=1}^{2} x_j \exp(-\alpha E_{ji}/RT) \quad , \tag{15}$$

where the lower limit of integration is at infinite temperature. At this limit, there is no attractive contribution to the Helmholtz energy.

The attractive contribution to the equation of state is obtained by differentiating Equation 15 with respect to volume:

$$p^{attr} = -\left[\frac{\partial A^{attr}/N}{\partial v}\right]_{T,x}$$

$$= \frac{-\sum_{i=1}^{2} \sum_{j=1}^{2} x_i x_j \left[\frac{\partial E_{ji}}{\partial v}\right]_T \exp(-\alpha E_{ji}/RT)}{\sum_{j=1}^{2} x_j \exp(-\alpha E_{ji}/RT)} \quad . \tag{16}$$

This procedure can be applied to any generalized van der Waals equation of state.

To calculate E_{ji} and u_{ji} from an equation of state, we need to specify those parameters which characterize the ji interaction. They are

$$T^{*(0)}_{ji} = 2\left[\frac{T^{*(0)}_{ii}c_{ii}T^{*(0)}_{ij}c_{ij}}{(c_{ii}+c_{jj})^2}\right]^{0.5}(1-k_{ji}) \qquad (17)$$

$$D_{ji} = (D_{ii}D_{jj})^{0.5} \quad . \qquad (18)$$

The parameter v^*_{ji} is given by Equation 9, as it was for the athermal (reference) system. Binary parameter k_{ji} ($|k_{ji}|<1$) is obtained from limited, binary experimental results.

Extension to Multicomponent Mixtures of Large and Small Molecules

We extend the local-composition model to multicomponent mixtures by considering m different types of regions in the fluid, where m is the number of components. Each region contains a molecule of type i at its center (i=1,2,...,m). Thus, whereas we speak of a two-fluid model for binary mixtures, we speak of a three-fluid model for ternary mixtures and, in general, an m-fluid model for multicomponent mixtures containing m components.

To extend our model to mixtures of large and small molecules, we assume that each molecule has an external surface area equal to q_i; only this area is available for

intermolecular attraction. (The parameter q_i is calculated with the method of Bondi [1968], and, thus, requires no binary experimental data.) The parameter q_i is arbitrarily normalized as in UNIQUAC (Abrams, 1975), such that q_i is unity for one $-CH_2-$ unit in a long-chain normal hydrocarbon. If we designate the average attractive Helmholtz energy per unit surface area of a ji interaction as η_{ji}, the attractive internal energy of the fluid is

$$\frac{U^{attr}}{N} = \sum_{i=1}^{m} x_i \sum_{j=1}^{m} x_{ji} q_i \left[\frac{\partial(\eta_{ji}/T)}{\partial(1/T)}\right]_{v,x} , \qquad (19)$$

where x_{ji} is the local mole fraction of type j molecules in a type i region. These local compositions are given by Equations 10 and 11, where the characteristic energy, E_{ji}, is now equal to $q_i \eta_{ji}$.

For a multicomponent mixture of large and small molecules, the attractive contribution to the pressure, p^{attr}, is

$$p^{attr} = \frac{-\sum_{i=1}^{m}\sum_{j=1}^{m} x_i x_j q_i \left[\frac{\partial \eta_{ji}}{\partial v}\right]_T \exp\left[\frac{-\alpha q_i \eta_{ji}}{RT}\right]}{\sum_{j=1}^{m} x_j \exp\left[\frac{-\alpha q_i \eta_{ji}}{RT}\right]} , \qquad (20)$$

where, for the equation of state given by Equation 5,

$$\eta_{ij} = \frac{RTA_1^2 v^*_{ii}}{(q_i q_j)^{0.5} 2A_2 v^*_{ij}} \exp\left[\frac{2A_2}{A_1 T} - 1\right] . \qquad (21)$$

Parameters in the equation of state are given by Equations 9, 17, and 18.

At zero density (also at infinite temperature), our

local-composition model reduces to the random-mixing model, as all local mole fractions become identical to the respective overall mole fractions.

In our model, the second virial coefficient of the mixture has the proper quadratic mole-fraction dependence. Our model also has a reasonable high-density limit; in that limit, our local-composition model, when applied to the van der Waals equation, gives an expression similar to the Wilson equation for liquid-state activity coefficients.

Results

To illustrate application, we have reduced high-pressure vapor-liquid equilibria for five, strongly asymmetric binary systems. Table III gives values of the binary parameter k_{ij} for these mixtures.

Figures 4-10 show good agreement between experiment and calculation. For vapor-liquid equilibria of the hydrogen sulfide-water system (Figures 4 and 5), we obtain a good fit at both 38 and 171°C using our equation of state and the local-composition mixing rules with one temperature-dependent binary parameter. By contrast, Evelein et al. (1976) found that the same data at any one temperature could be fit with the Soave-Redlich-Kwong (1972) equation and the standard one-fluid mixing rules only by the addition of a second binary parameter and by correcting the energy parameter a in the equation of state for water at each temperature.

Figure 7 shows our fit of the vapor-liquid equilibria for ethane-water at 300°C. Unlike the other systems studied, this system is not well represented with our method if only one binary parameter is used. To fit the compositions of both phases, we included binary parameter l_{ij} for the nonadditivity of molecular diameters (Equation 9). This second parameter helps to correct for deficiencies of our reference system, the hard-chain fluid as described by one-fluid theory. Improvement of this reference system is needed. Whiting and Prausnitz (1982) have indicated a possible way to include corrections to the hard-chain entropy of mixing.

Conclusion

The work reported here increases our ability to calculate high-pressure vapor-liquid equilibria for asymmetric systems, especially for those containing one or more polar components. Improvements have been made in both the pure-component equation of state (to account for orientation-dependent intermolecular potentials) and in the mixing rules (to account for density-dependent nonrandomness).

Acknowledgment

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Nomenclature

a_{nm} = universal constants given in Table I

A = total Helmholtz energy

c = one-third the number of effective external degrees of freedom per molecule

D = polarity parameter in the equation of state

E_{ij} = molar attractive energy of ij interactions

k = Boltzmann's constant

k_{ij} = binary parameter for the energy parameter

l_{ij} = binary parameter for the size parameter

N = total number of moles

N_i = number of moles of component i

P = pressure

q_i = surface-area parameter for component i

r = distance of separation between two molecules

R = ideal-gas constant

T = absolute temperature

T^* = total energy parameter in the equation of state

$T^{*(0)}$ = reference energy parameter in the equation of state

u_{ij} = internal energy (per mole) of an ij interaction

U = total internal energy

v = molar volume

v^* = molecular size parameter in the equation of state

x_i = mole fraction of component i

x_{ij} = local mole fraction of component i in the neighborhood of a type j molecule

α = nonrandomness parameter (equal to 0.5 in this work)

ε = nearest-neighbor energy in quasi-chemical theory

η_{ij} = attractive Helmholtz energy per unit surface area for an ij interaction

μ_i = dipole moment for an i molecule

ϕ^D_{ij} = intermolecular potential between two point dipoles, one of type i and one of type j

τ = universal constant, given in Table I

Subscripts

M = mixture

ij = the interaction between an i molecule and a j molecule

Superscripts

attr = attractive contribution

id = ideal gas contribution

rep = repulsive contribution

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Table I. Universal Constants for Perturbed-Hard-Chain Theory

n\m	1	2	3	4	5
1	-7.04677	-7.22636	-3.16538	14.34352	-1.26227
2	-3.56999	11.35209	-10.85375	-3.6131	7.34334

$$\tau = \frac{\pi}{(18)^{0.5}} = 0.7405$$

Table II. Pure-Component Parameters

Component	$T^{(0)}$ (K)	v^* (cm^3/mol)	c	D(dm^6K^2/mol^2)	q	Data Ref.
CH_4	150.9	20.18	1.0	0	1.16	2
CH_3OH	329.2	20.12	2.34	3.00	1.43	1,6
C_2H_6	231.8	28.40	1.18	0	1.70	5
CO_2	205.5	17.52	1.62	1.01	1.12	4
H_2O	440.4	11.17	1.74	4.17	1.40	3
H_2S	276.5	18.81	1.24	0.315	1.68	7
NH_3	289.0	12.81	1.54	0.694	1.28	4

Data References:

1. Ambrose, D.; Sprake, C. H. S. J. Chem. Thermodynamics 1970, 2, 631.
2. Angus, S.; Armstrong, B.; de Reuck, K. M. "International Thermodynamic Tables of the Fluid State. 5: Methane"; Pergamon Press: Oxford, 1978.
3. Bain, R. W. "NEL Steam Tables 1964"; Her Majesty's Stationery Office: Edinburgh, 1964.
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5. Goodwin, R. D.; Roder, H. M.; Straty, G. C. Nat. Bur. Stand. (U.S.) Technical Note 1976, No. 684.
6. Kay, W. B.;Donham, W. E. Chem. Eng. Sci. 1955, 4, 1.
7. Reamer, H. H.; Sage, B. H.; Lacey, W. N. Ind. Eng. Chem. 1950, 42, 140.

Table III. Binary Parameters

System	T(°C)	k_{12}	l_{12}	Data Ref.
CH_4/H_2O	150‡300	0.10	-	4
C_2H_6/H_2O	250	0.26	0.03	1
CO_2/CH_3OH	25	0.16	-	2
H_2S/H_2O	38	0.205	-	3
	171	0.17	-	3
CH_4/NH_3	25	0.136	-	5

Data References:

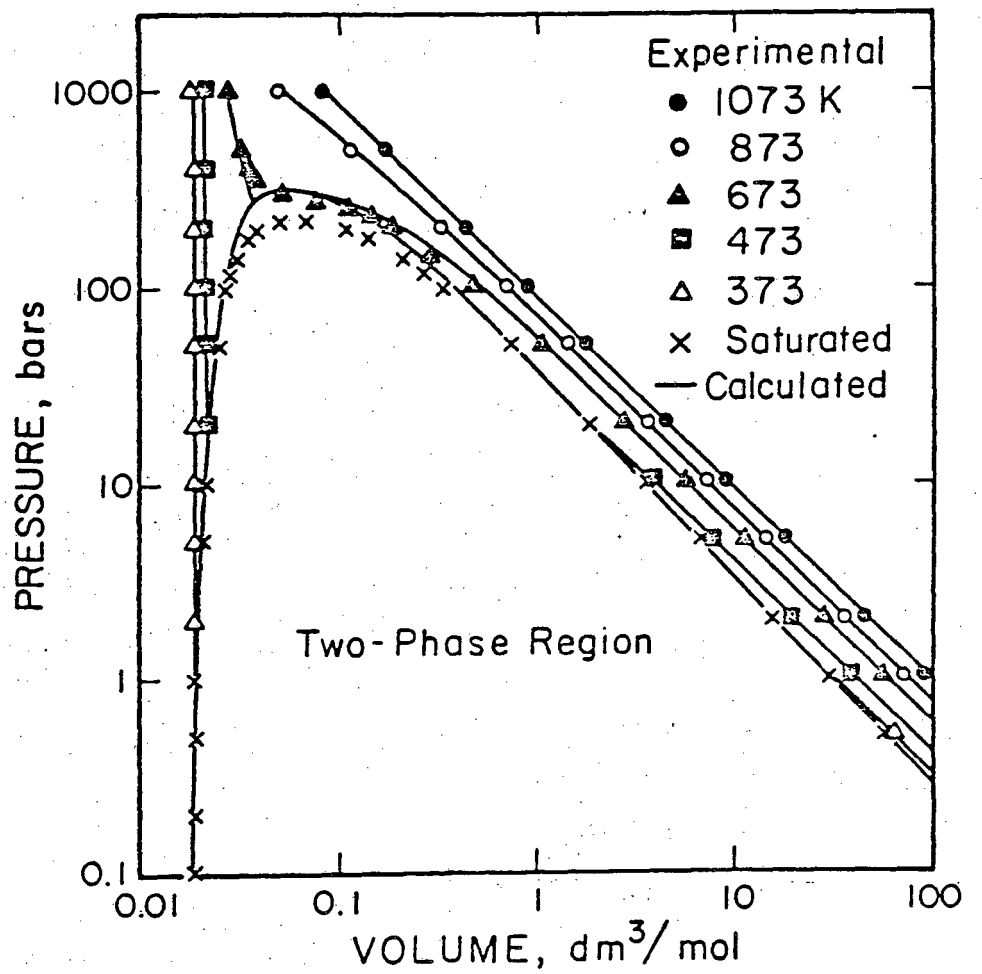
1. Danneil, A.; Tödheide, K.; Franck, E. U. Chem.-Ing.-Tech. 1967, 39, 816.

2. Ohgaki, K.; Katayama, T. J. Chem. Eng. Data 1976, 21, 53.

3. Selleck, F. T.; Carmichael, L. T.; Sage, B. H. Ind. Eng. Chem. 1952, 44, 2219.

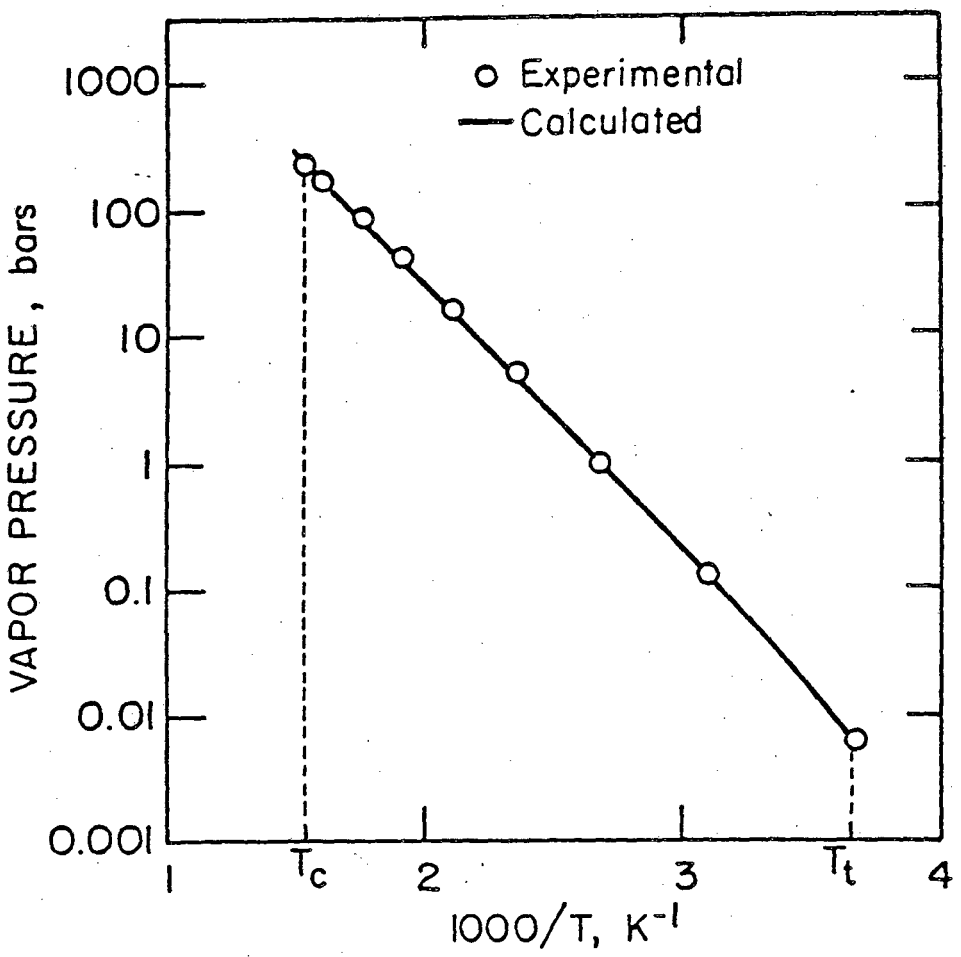
4. Sultanov, R. G.; Skripka, V. G.; Namiot, A. Yu. Gazov. Promysh. 1971, 16 (4), 6; Ibid. 1972, 17 (5), 6.

5. Zeininger, H. Chem.-Ing.-Tech. 1973, 45, 1067.



PRESSURE-VOLUME DIAGRAM FOR WATER

Figure 1.

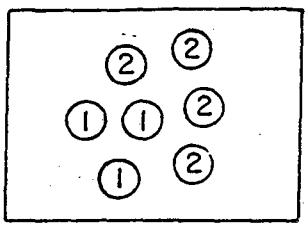


VAPOR PRESSURE FOR WATER

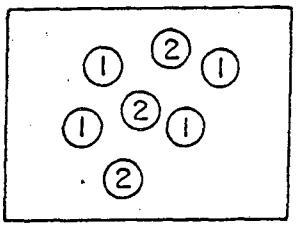
XBL 797-6615

Figure 2.

TWO-FLUID THEORY FOR A BINARY MIXTURE



TYPE-1 REGION



TYPE-2 REGION

$$u^{(1)} = x_{21}u_{21} + x_{11}u_{11}$$

$$u^{(2)} = x_{12}u_{12} + x_{22}u_{22}$$

FOR THE MIXTURE:

$$\frac{U^{attr.}}{N} = x_1 u^{(1)} + x_2 u^{(2)}$$

$u^{(i)}$ = molar attractive internal energy of hypothetical fluid i
i = 1 or 2

x_i = mole fraction of component i

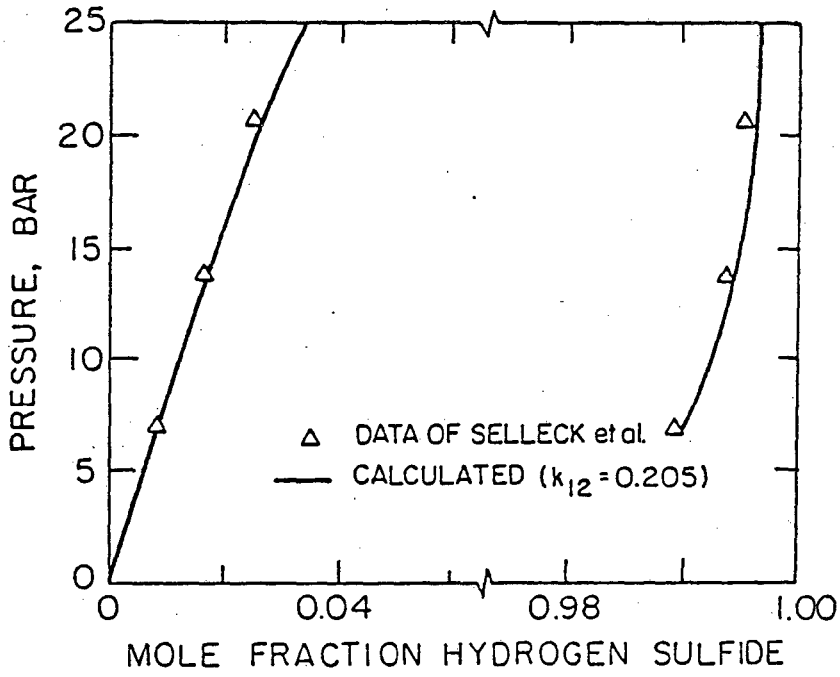
x_{ij} = local mole fraction of component i about a central molecule j

u_{ij} = attractive internal energy per mole for a hypothetical fluid where all molecules interact according to an ij potential

N = total number of moles

XBL 22-5144

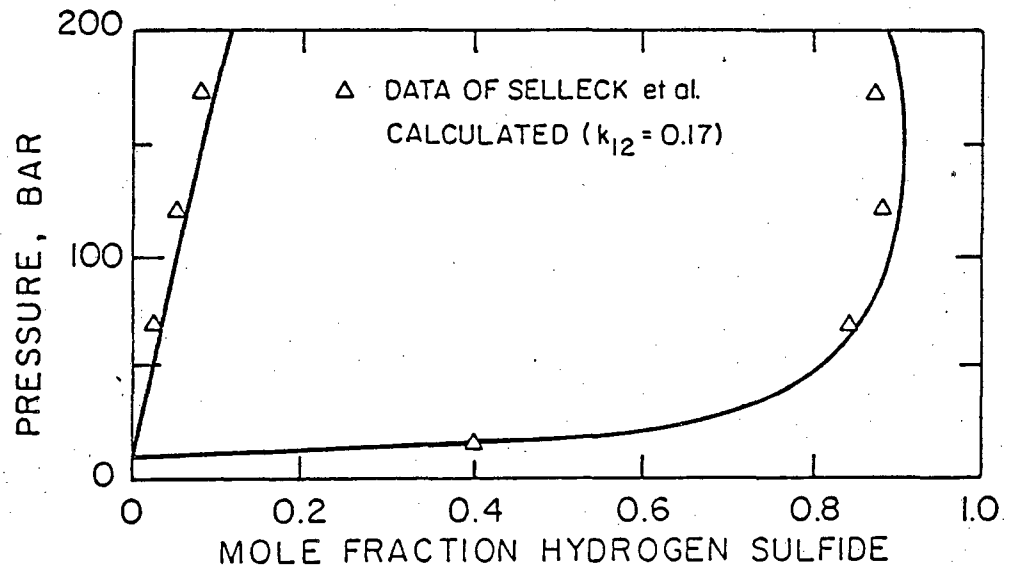
Figure 3.



PHASE EQUILIBRIA FOR HYDROGEN SULFIDE/WATER AT 38 °C

XBL 822-5145

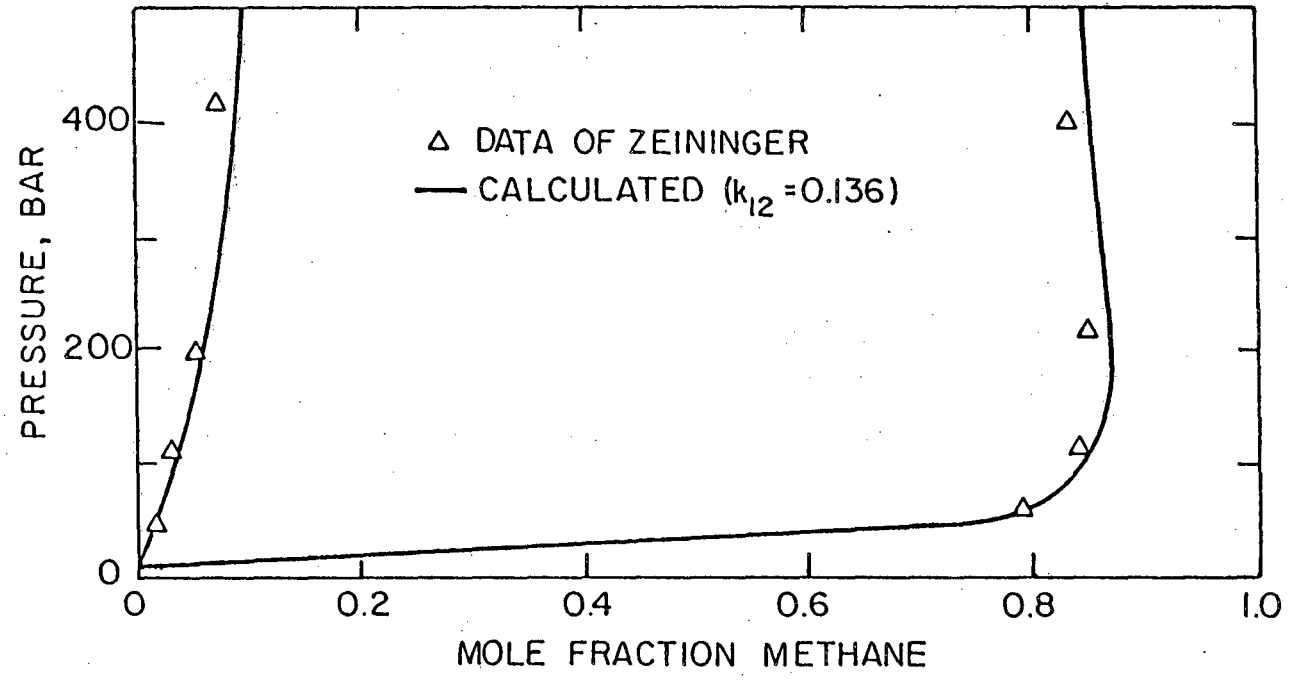
Figure 4.



PHASE EQUILIBRIA FOR HYDROGEN SULFIDE/WATER AT 171 °C

X8L 822-5146

Figure 5.



PHASE EQUILIBRIA FOR METHANE/AMMONIA AT 25°C

XBL821-5096

Figure 6.

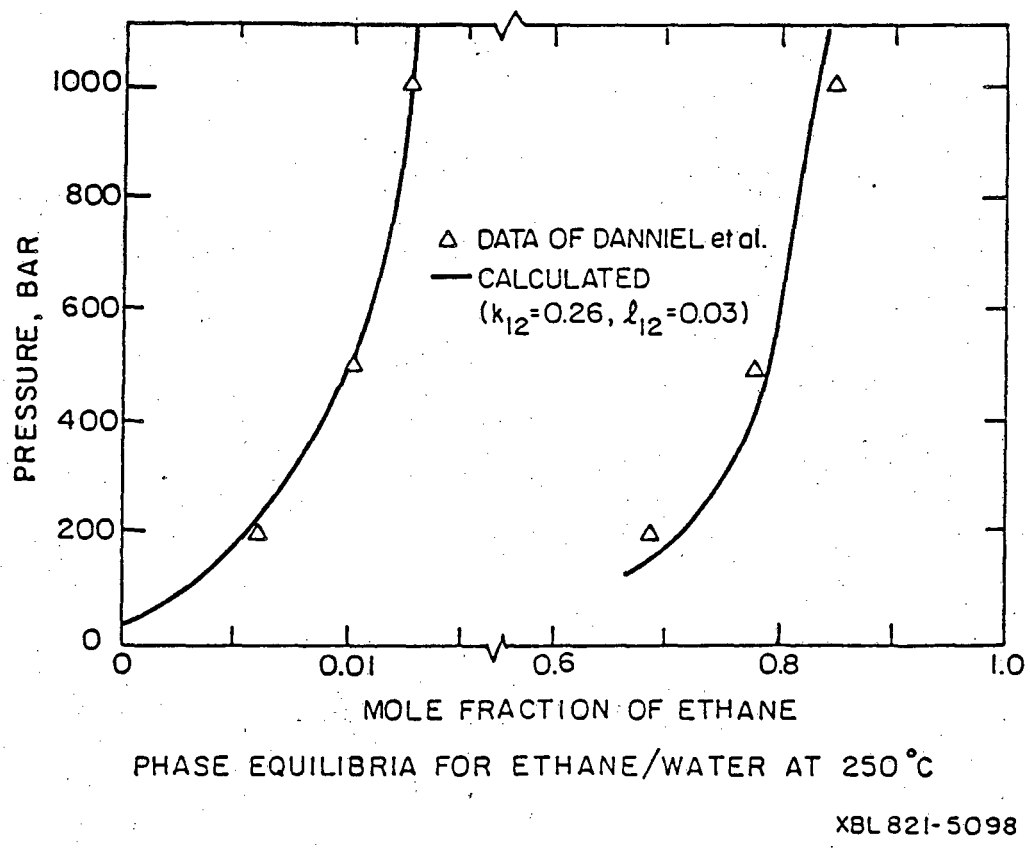
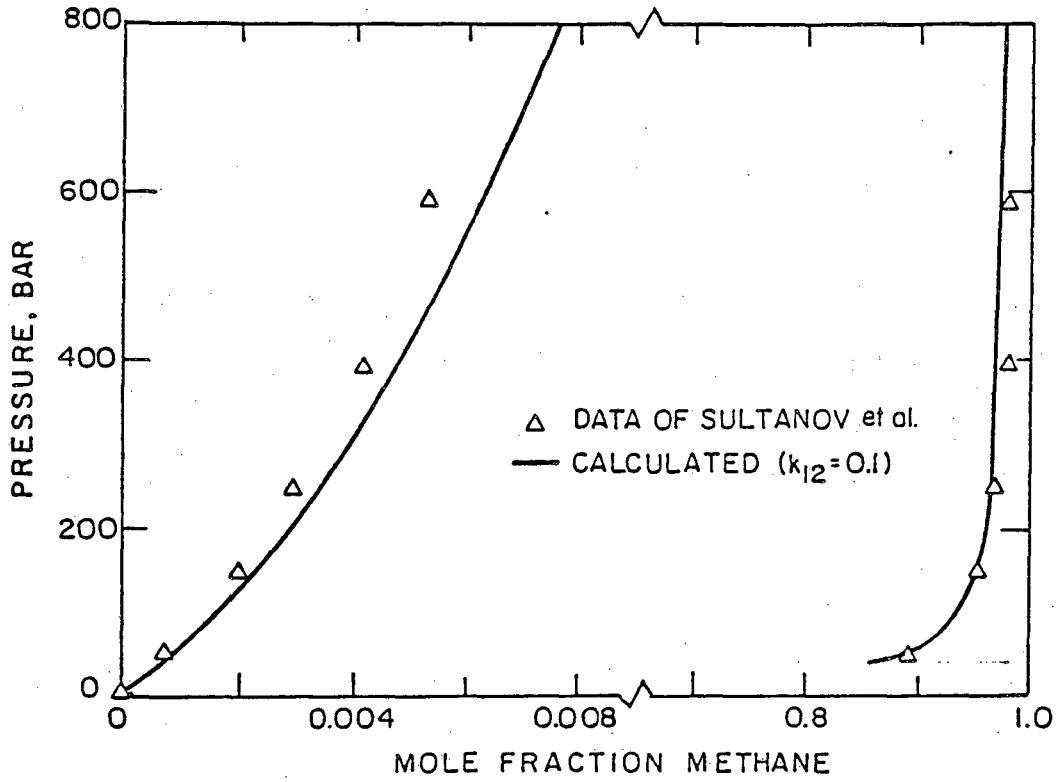

1000
800
600
400
200
0
PRESSURE, BAR
0
0.01
0.6
0.8
1.0
MOLE FRACTION OF ETHANE
△ DATA OF DANNIEL et al.
— CALCULATED
(k_{12}=0.26, ℓ_{12}=0.03)
PHASE EQUILIBRIA FOR ETHANE/WATER AT 250 °C
XBL 821-5098

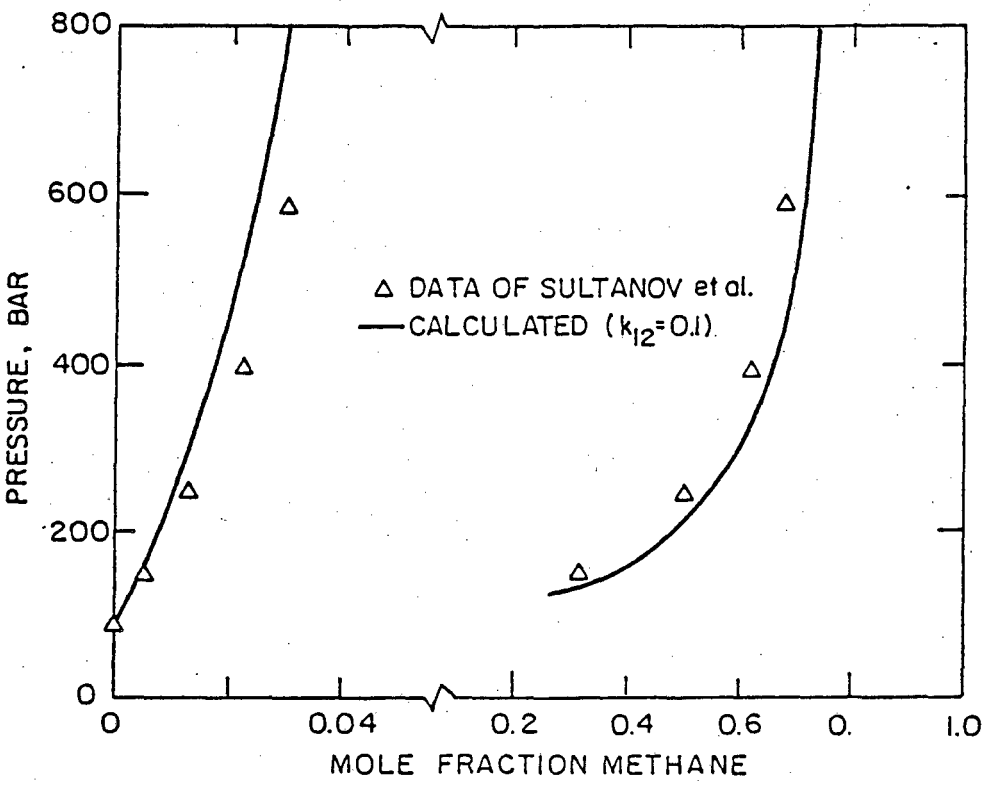
Figure 7.



PHASE EQUILIBRIA FOR METHANE/WATER AT 150 °C

XBL821-5097

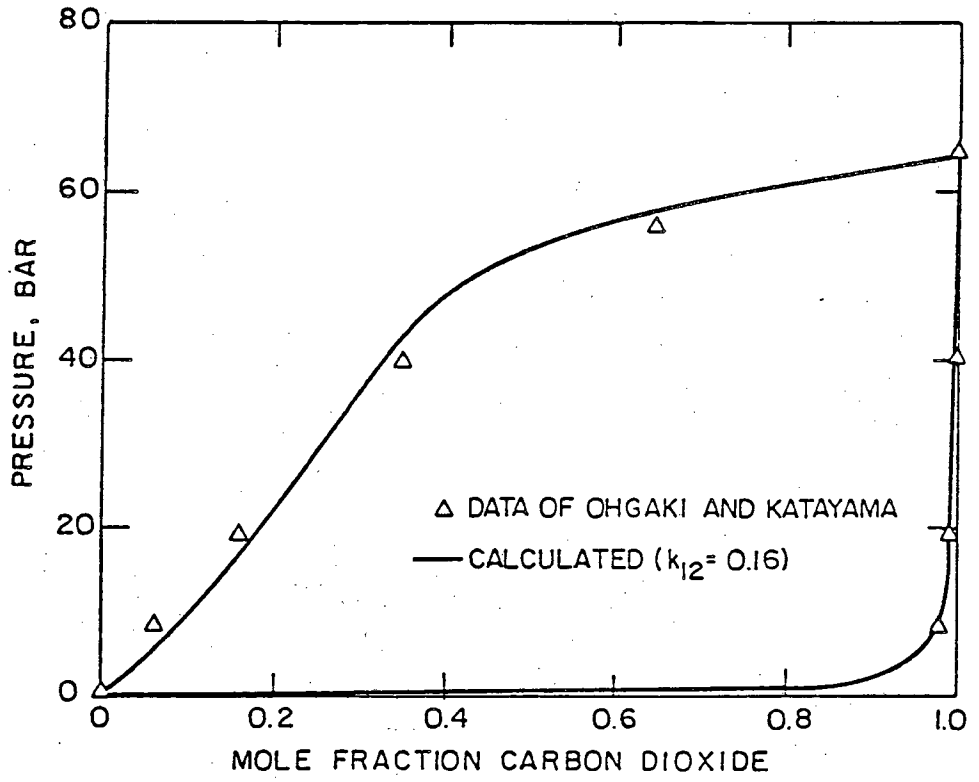
Figure 8.



PHASE EQUILIBRIA FOR METHANE/WATER AT 300 °C

XBL 821-5099

Figure 9.



PHASE EQUILIBRIA FOR CARBON DIOXIDE/METHANOL AT 25 °C

XBL 821-5095

Figure 10.

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