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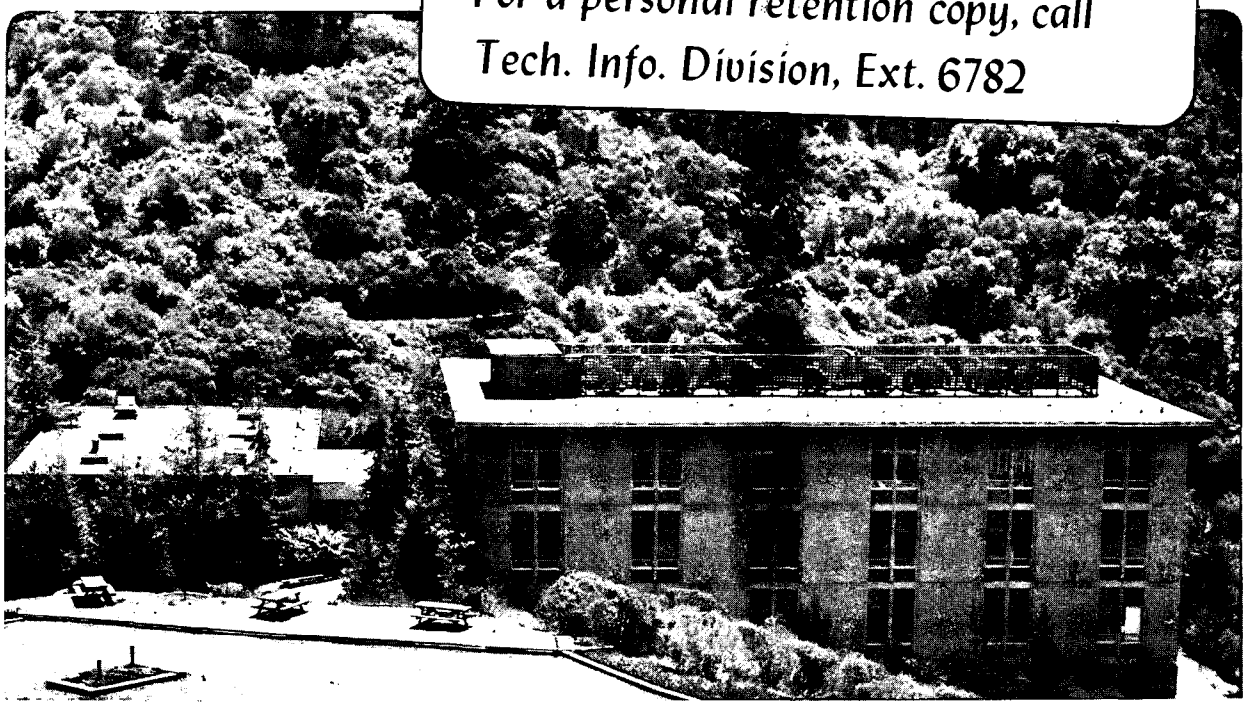

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A Local-Composition Model for Equations of State for Mixtures

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For the 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), many equations of state are available that predict vapor-liquid equilibria reasonably well. Unfortunately, however, many processes (e.g., coal gasification) involve mixtures containing highly polar components (including water and other hydrogen-bonding fluids); simple equations of state, with standard mixing rules, predict very poorly the thermodynamic properties of such systems.

This failure of simple equations of state and of simple mixing rules is due to the asymmetry of complex mixtures. There are two types of asymmetry: size/shape asymmetry and intermolecular-potential asymmetry, as indicated in Figure 1. For the former, the molecules are characterized by gross differences in their physical sizes or shapes. One species could be a small, spherical molecule and the other a long-chain polymer or a much larger globular molecule. The second type of asymmetry occurs in

mixtures of polar and nonpolar molecules. The intermolecular potential of a polar molecule can be highly orientation-dependent, such as hydrogen bonding of water, which occurs only when the molecules are aligned in a specific orientation.

The asymmetry of these mixtures leads to highly nonrandom molecular configurations in space. Instead of the traditional model of white and black billiard balls randomly positioned in space, a more complex model is required that can account for clustering of molecules into partially ordered, energetically favorable configurations.

To predict phase equilibria for asymmetric mixtures, we propose 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 local-composition concept. For both the pure-component equation of state and the local-composition mixing rules, we have made compromises between statistical-mechanical rigor and engineering usefulness. The important achievement is that we have removed the common assumption that a dense fluid is a random mixture of spherically symmetric molecules.

Equation of State for Polar Fluids

For extension to polar fluids, the most popular variation on simple equations of state is to assign a purely empirical temperature dependence to the equation-of-state

parameters. This procedure increases the number of adjustable parameters and creates problems when one tries to devise a set of mixing rules with which to calculate multicomponent phase equilibria.

A more reasonable approach is to use molecular theory for estimating the effect of specific polar interactions and, thereby, to use parameters with at least some physical significance. Appropriate mixing rules can then be determined based on idealized, but theoretically tractable interactions.

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

We chose for our nonpolar, reference equation of state the Perturbed Hard Chain Theory (PHCT) of Donohue and Prausnitz (1978). The PHCT was developed from a truncated perturbation expansion in powers of reciprocal temperature for molecules with square-well potentials. If we include the effect of angle-averaged point-dipole interaction in PHCT, the Helmholtz energy of polar molecules is

$$\frac{A}{NkT} = \frac{A_0}{NkT} + \frac{A_1}{T} + \frac{A_2}{T^2} + \ldots , \qquad (1)$$

where

$$\frac{A_0}{NkT} = c\,\frac{4\left(\frac{\tau v^*}{v}\right) - 3\left(\frac{\tau v^*}{v}\right)^2}{\left(1 - \frac{\tau v^*}{v}\right)^2}$$

$$A_1 = T^* \sum_{m=1}^{5} a_{1m} \left(\frac{v^*}{v}\right)^m$$

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

The a_{nm}'s and τ are universal constants (i.e., they are the same for all substances). The 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. There is no dipole-dipole contribution to the A_1 term. The symmetry of the dipole-dipole potential guarantees that all polar contributions must cancel if each orientation is considered equally likely, as assumed in this mean-field term.

To close the expansion in reciprocal temperature, we use the discrete representation of Barker and Henderson (1976). It has been shown that this approximation gives better low-density convergence than Padé-approximant and other methods. With this method, we need only the first two perturbation terms; the rest are estimated. The

discrete representation method, applied to Equation 1, is

$$\frac{A}{NkT} = \frac{A_0}{NkT} + \frac{A_1^2}{2A_2}\left[\exp\left(\frac{2A_2}{A_1 T}\right) - 1\right] \quad . \tag{2}$$

Equation 2 is our working equation for the Helmholtz energy of polar and nonpolar pure fluids. Through standard thermodynamic relations, expressions for the pressure and for the fugacity can be easily derived.

We have used Equation 2 for several highly polar fluids (and for several nonpolar fluids with D=0). Pure-fluid parameters are obtained from experimental equilibrium properties. Figures 2 and 3 show typical agreement between experimental and calculated properties of water.

For mixtures, we must estimate binary parameters for the pure-component parameters and define a set of mixing rules. Because we have chosen parameters with some physical significance, the choices for these binary parameters are straightforward. They are

$$T^*_{ij} = \frac{\sqrt{T^*_{ii}c_{ii}T^*_{jj}c_{jj}}}{c_{ij}}(1 - k_{ij}) \tag{3}$$

$$v^*_{ij} = \left[\frac{(v^*_{ii})^{1/3} + (v^*_{jj})^{1/3}}{2}\right]^3$$

$$c_{ij} = \frac{c_{ii} + c_{jj}}{2}$$

$$D_{ij} = \sqrt{D_{ii}D_{jj}} \quad .$$

Binary parameter k_{ij} ($|k_{ij}|<1$) is obtained from limited binary experimental results.

Local-Composition Model

To calculate fluid-mixture properties with the commonly used one-fluid model, one 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 based on the random-mixing assumption--a serious flaw. Most of these 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 propose a significantly different procedure for extending an equation of state to mixtures (Whiting and Prausnitz, 1980, 1981; cf. Mollerup, 1981). Starting from the two-fluid approach (which underlies the Wilson, NRTL, UNIQUAC, and other liquid-state activity-coefficient models), we have developed a consistent mixture theory for fluids at all fluid densities. Our local-composition theory is based on reasonable approximations for the degree of nonrandomness in a fluid mixture and meets the close-packed-liquid and ideal-gas limits.

We assume that gross nonrandomness occurs even in mixtures of nearly equal-sized molecules if their intermolecular potentials are vastly different. Further, we assume that this nonrandomness exists, to some extent, at all non-zero densities.

First, we separate the Helmholtz energy into an ideal-gas, a repulsive (hard-sphere), and an attractive

part:

$$A = A^{id} + A^{rep} + A^{attr} \quad . \tag{4}$$

For molecules of nearly equal size, the repulsive Helmholtz energy is calculated with the one-fluid model because the unperturbed state (the hard-sphere fluid) is assumed random, i.e., all nonrandomness is caused by the attractive forces.

For a binary mixture, we consider two representative regions in the fluid, as indicated in Figure 4. 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), we approximate these local compositions using Boltzmann factors with energies characteristic of the like and unlike two-body interactions:

$$\frac{x_{ji}}{x_{ii}} = \frac{x_j}{x_i} \frac{\exp(-u_{ji}/kT)}{\exp(-u_{ii}/kT)} \tag{5}$$

$$x_{ji} + x_{ii} = 1 \quad , \tag{6}$$

where i=1 or 2. Equation 5 indicates that the local composition (x_{ji}) of j molecules around an i molecule is proportional to the total number of j molecules (required to satisfy the mass balance) and proportional to the Boltzmann factor of an energy, u_{ji}, characteristic of the attractive ji interaction. In previous models, this energy was taken to be zw/2, where z is the coordination number and w is the energy between two nearest-neighbor molecules. For

liquids, this lattice-theory simplification may be reasonable, but, for lower densities, we know that z and w are functions of temperature and density. For any equation of state of the van der Waals type, we can calculate this characteristic energy as a function of density and temperature: it is merely the attractive internal energy of a system of molecules interacting with a ji-type intermolecular potential.

The total attractive internal energy, U^{attr}, of the fluid mixture is the sum of all contributions from molecular pairs:

$$U^{attr} = N_1 (x_{21}u_{21} + x_{11}u_{11}) + N_2 (x_{12}u_{12} + x_{22}u_{22}) \quad . \qquad (7)$$

Equation 7 can be integrated with respect to temperature to calculate the attractive Helmholtz energy of the mixture and, then, differentiated with respect to density to produce a mixture equation of state. This procedure can be applied to any generalized van der Waals equation of state.

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.

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. If we designate the average attraction per unit surface area of a ji interaction as

e_{ji}, the attractive energy of the fluid is

$$\frac{U^{attr}}{N} = \sum_{i=1}^{m} x_i \sum_{j=1}^{m} x_{ji} q_i e_{ji} \quad , \tag{8}$$

where x_{ji} is the local composition of type j molecules in a type i region.

The result for the attractive contribution to the pressure of a multicomponent mixture of large and small molecules is

$$p^{attr} = \frac{1}{v}\sum_{i=1}^{m} x_i \left\{ q_i e_{ii} + \frac{\sum_{j=1}^{m} q_i x_j (e_{ji}-e_{ii}) \exp\left[\frac{-q_i(e_{ji}-e_{ii})}{kT}\right]}{\sum_{j=1}^{m} x_j \exp\left[\frac{-q_i(e_{ji}-e_{ii})}{kT}\right]} \right\} . \tag{9}$$

At zero density (as well as at infinite temperature), our local-composition model reduces to the random-mixing model, as all local compositions become identical to the respective overall compositions. In our work, the second virial coefficient of the mixture has the proper quadratic mole-fraction dependence. The model also has a reasonable high-density limit, in that the infinite-pressure limit of the local-composion model for the van der Waals equation gives the Wilson equation for liquid-state activity coefficients.

Figures 5-8 show good agreement between experiment and calculations performed with the local-composition model for some typical binary vapor-liquid equilibria. In these calculations, we used the equation of state given by

Equation 2.

Conclusion

The work reported here increases our ability to calculate high-pressure vapor-liquid equilibria for asymmetric systems, especially those containing one or more polar components.

Acknowledgment

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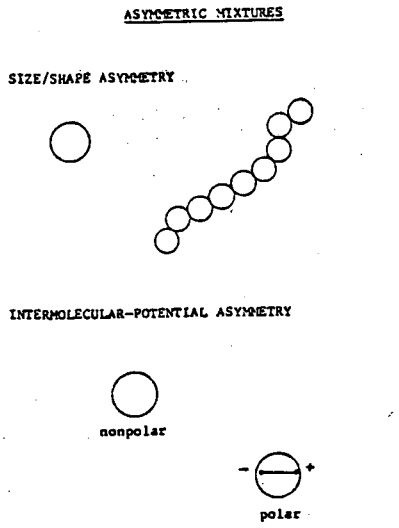

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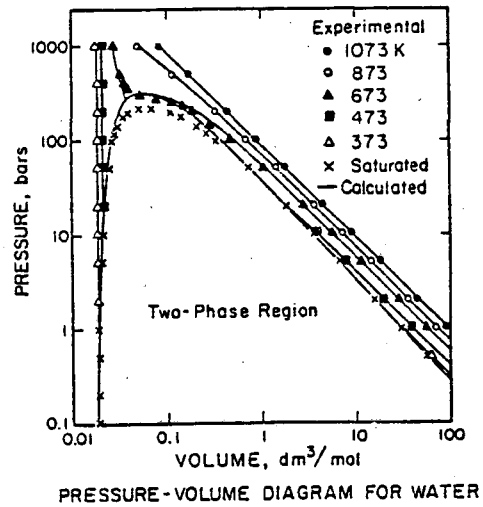

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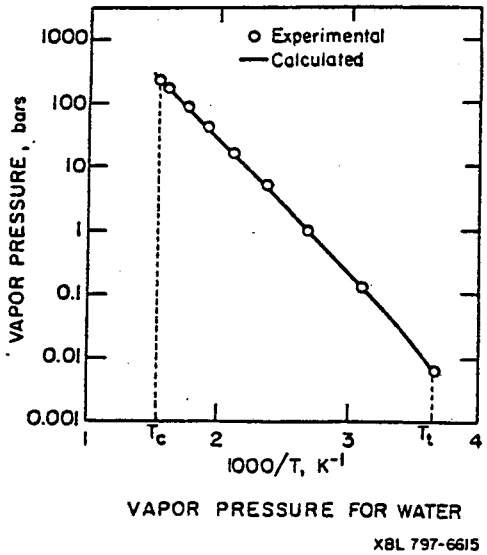

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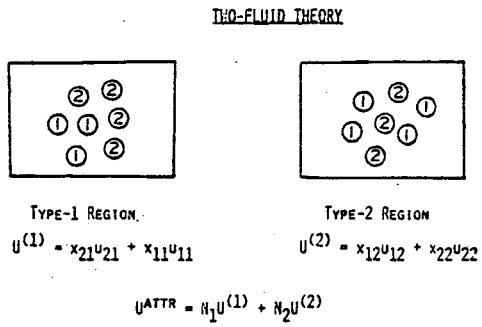
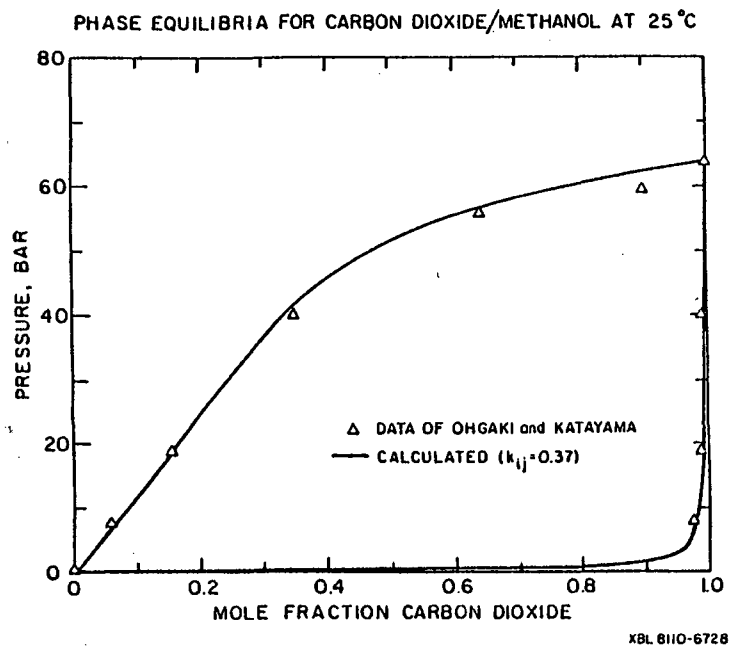


Figure 4.



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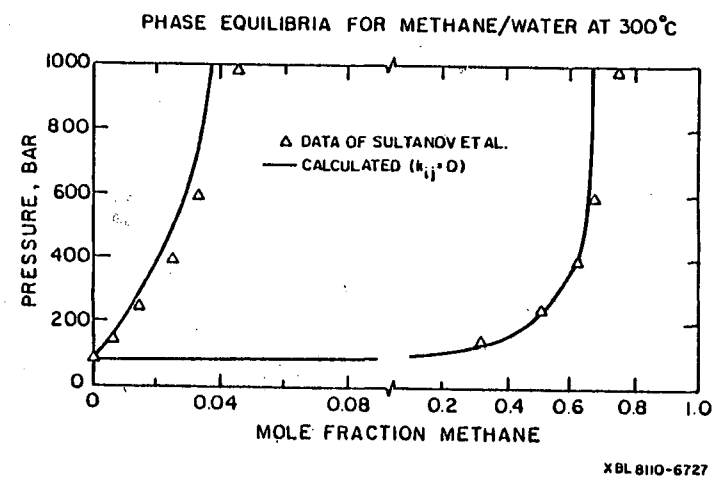

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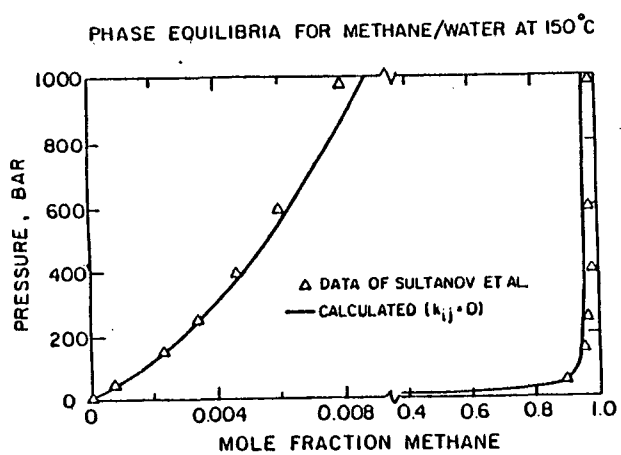

Figure 7.

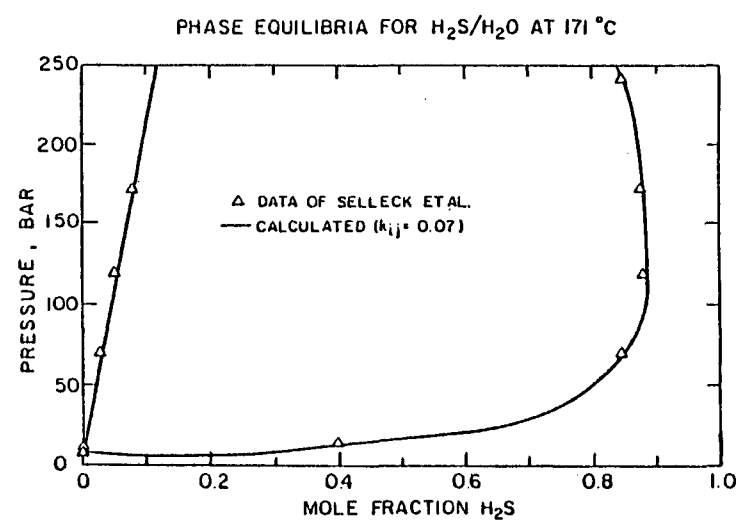

Figure 8.

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