Perturbed Hard Chain Theory for Fluid Mixtures: Thermodynamic Properties for Mixtures in Natural Gas and Petroleum Technology

Perturbed-hard-chain theory for pure fluids, proposed previously by Beret, is modified slightly to yield better pure-component results. More important, it is extended to multicomponent mixtures.

The perturbed-hard-chain theory is a synthesis of the polymer solution theories of Flory and Prigogine and the perturbed-hard-sphere theories of Alder and Barker and Henderson. The resulting equation of state is applicable to simple as well as complex molecules (for example, heptane, naphthalene, polystyrene). It can be used to calculate both gas and liquid phase properties. Extension of perturbed-hard-chain theory to mixtures is based on a one-fluid model without, however, making the usual assumption of random mixing.

The perturbed-hard-chain theory has been applied to most fluids commonly encountered in natural-gas and petroleum refining operations. The theory gives good agreement with experiment for pure-component and fluid-mixture properties including vapor pressures, liquid densities, enthalpies, and *K* factors. Molecular parameters have been obtained for forty-five pure components and for more than sixty binary mixtures. Ternary and higher mixtures require no additional parameters.

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SCOPE

An equation of state based on perturbed-hard-chain theory is applicable to fluids containing complex as well as simple molecules and to both gas and liquid-phase properties. In this work, perturbed-hard-chain theory has been extended to mixtures by combining the recent perturbed-hard-sphere theory of Barker and Henderson with Prigogine's theory for polymer liquids. The resulting perturbed-hard-chain theory for mixtures is essentially a one-fluid theory including, however, corrections for nonrandomness. The perturbed-hard-chain theory can be used to calculate mixture properties when the components differ significantly in size, shape, or potential energy. Parameters for pure components and mixtures are given for a variety of systems. Examples comparing experimental and calculated results are shown for vapor pressures, liquid densities, second virial coefficients, *K* factors, Henry's constants, and residual enthalpies.

CONCLUSIONS AND SIGNIFICANCE

The perturbed-hard-chain theory can be used to estimate, with good accuracy, configurational thermodynamic properties of most fluids commonly encountered in petroleum refining and natural-gas processing. It is applicable to pure fluids ranging in complexity from hydrogen and methane to large hydrocarbons. The theory uses only three molecular parameters for each pure fluid.

The thermodynamic properties of binary mixtures can be calculated using pure-component parameters and one binary interaction parameter. Ternary (and higher) mixtures require no additional parameters. Mixture properties, including vapor-liquid equilibria, can be estimated for simple or highly asymmetric systems.

Since pure-component and mixture parameters for hydrocarbons correlate with carbon number, the param-

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eters reflect molecular properties. These correlations allow good prediction of molecular parameters for those systems where little or no experimental data are available.

The method described here provides a new technique for calculating thermodynamic properties at high pressures for mixtures commonly found in hydrocarbon processing. Computer programs are available.

Efficient design of separation-operation processes requires reliable thermodynamic properties of fluid mixtures. An equation of state, valid over a wide density range, provides one method for obtaining such properties.

Although the scientific literature is rich with articles describing empirical and semitheoretical equations of state, no rigorous theory of fluids exists. Empirical equations are often extremely useful but have limitations because they must be applied in the range of temperature, density, and composition where experimental data exist; when empirical equations are extrapolated into regions where no data are available, poor estimates often result. Further, since the equation-of-state parameters have little or no physical significance, it is often difficult to estimate parameters for other fluids, and especially for mixtures. Previously published semitheoretical equations often extrapolate reasonably, but they tend to be useful only for simple systems and therefore are often not useful for a variety of fluids encountered industrially.

Recently, Beret and Prausnitz (1975) proposed a new equation of state which has some radically new features. It is applicable to fluids containing complex as well as simple molecules and to calculations of both gas and liquid-phase properties.

The Beret-Prausnitz equation of state is based on perturbed-hard-chain theory. It is designed to meet the following boundary conditions:

1. At low densities, all fluids containing simple or complex molecules are described by the ideal-gas law.
2. At moderate densities, all fluids containing simple or complex molecules are described by the virial equation.
3. Fluids containing simple (argonlike) molecules are described at all fluid densities by the perturbation theories of Alder (1972) and of Barker and Henderson (1972).
4. Fluids containing complex (polymer) molecules at liquidlike densities are described by the theories of Prigogine (1957) and Flory (1970).

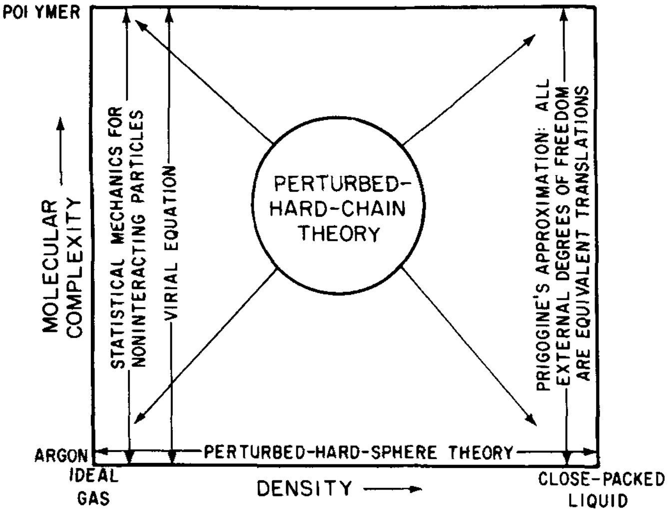

Fig. 1. Perturbed hard chain theory provides an equation of state for fluids containing simple or complex molecules, covering all fluid densities.

Figure 1 shows the domain of applicability of perturbed-hard-chain theory.

Perturbed hard chain theory meets, and reasonably interpolates between, all the boundary conditions shown in Figure 1. The theory can be used to calculate thermodynamic properties of complex as well as simple molecules and is valid at both low and high densities. In this work, the equation of state based on perturbed-hard-chain theory has been modified slightly to improve the representation of pure components and, more important, it has been extended to mixtures. The theory has been applied to, and can accurately represent, the properties of most fluids commonly encountered in natural-gas and petroleum processing.

The perturbation theories of Alder, of Barker and Henderson, and of others are modern day versions of the van der Waals equation. These theories, which are based on computer simulation studies, adequately describe the properties of simple molecules (that is, argon, methane). However, these previous theories are not valid for larger molecules (that is, heptane, benzene, polyethylene) because they do not take into account the effect of density on molecular vibrations and rotations. Only for simple molecules are vibrations and rotations (essentially) independent of density.

Prigogine's theory for fluids containing chain molecules describes the liquid-phase properties of small or large molecules but fails at low densities. Prigogine treats molecular rotations and vibrations as equivalent translations. For a chain molecule containing n atoms, there are a total of $3n$ degrees of freedom. Some of these are of such high frequency and small amplitude that they are not affected by density; these are called internal degrees of freedom. Those that are density-dependent are called external; three of these are translational degrees of freedom.

Prigogine postulated that for each molecule there are $3c$ external degrees of freedom which depend on temperature and density in the same way. For argon (or methane), $c = 1$; for more complex molecules, $c > 1$. For all molecules, $c/n \leq 1$.

The derivation of the perturbed-hard-chain theory is presented below. For pure components, the theory presented here is based on assumptions different from those originally made by Beret, but the mathematical result is the same. Empirical modifications have also been made to Beret's equation; these are discussed in Appendix A. The extension of the theory to mixtures is based on the perturbation theory of Barker and Henderson (1972). Their theory is essentially a one-fluid theory, but it eliminates the assumption of random mixing. By combining their theory with Prigogine's theory for complex molecules, the perturbed-hard-chain theory can be used to calculate mixture properties even when the components differ markedly in size, shape, or potential energy.

THEORY OF DENSE FLUIDS

Over 100 years ago, van der Waals realized that there are two corrections necessary to the ideal gas equation of state, one to account for molecular attractions and the other to account for repulsions. In addition, for polyatomic molecules, molecular rotations and vibrations also affect the equation of state, but van der Waals neglected these degrees of freedom.

The essential ideas of van der Waals can be represented by a partition function (Vera and Prausnitz, 1972); the link between bulk fluid properties and molecular properties is provided by statistical mechanics. The canonical partition function Q is related to the Helmholtz energy A and the pressure P by the simple relations

$$A = -kT \ln Q \tag{1}$$

and

$$P = kT\left(\frac{\partial \ln Q}{\partial V}\right)_{T,\ \mathrm{all}\ N_i} \tag{2}$$

For a pure fluid, the generalized van der Waals partition function is

$$Q = \frac{1}{N!}\left(\frac{V}{\Lambda^3}\right)^N (q_{\mathrm{repulsion}})^N (q_{\mathrm{attraction}})^N (q_{r,v})^N \tag{3}$$

where

$$\Lambda = \frac{h}{(2\pi mkT)^{1/2}} \tag{4}$$

For a monatomic ideal gas the last three terms are unity. For real fluids, each of the last three terms depends on temperature and density.

Van der Waals suggested that

$$q_{\mathrm{repulsion}} = \frac{V_f}{V} \tag{5}$$

and

$$q_{\mathrm{attraction}} = \exp\left(\frac{-\phi}{2kT}\right) \tag{6}$$

where the free volume V_f is the volume available to the center of mass of a single molecule as it moves about the system holding the positions of all other molecules fixed, and where $\phi/2$ is the intermolecular potential energy of one molecule due to the presence of all other molecules.

The attractive partition function is a Boltzmann factor whose argument is the ratio of the attractive potential energy to the kinetic energy. Polyatomic molecules have kinetic energy arising from translational, rotational, and vibrational degrees of freedom. For a polyatomic molecule with n atoms, there are a total of $3n$ degrees of freedom. In classical statistical mechanics, neglecting quantum effects, each degree of freedom contributes $\frac{1}{2}kT$ to the molecule's total kinetic energy. However, many vibrations are of such small amplitude and high frequency that at normal fluid densities they do not affect intermolecular interactions; therefore, they do not contribute to the equation of state. The parameter c is defined by saying that the remaining $3c$ degrees of freedom are those that affect intermolecular interactions, and therefore the kinetic energy associated with these degrees of freedom appears in the Boltzmann factor.

The potential energy is proportional to E, the depth of the intermolecular potential well. For polyatomic molecules, it is customary to write E as ϵq, where ϵ is the energy per unit area and q is the external surface area of the molecule.[*] Therefore, in Equation (6), the Boltzmann factor $\phi/2kT$ for a polyatomic molecule is proportional to $\epsilon q/ckT$. For a monomer ($q = c = 1$), this reduces to the familiar ϵ/kT.

The final term in the partition function accounts for molecular rotations and vibrations. For a polyatomic molecule with a total of $3n$ degrees of freedom, many are functions of temperature but not of density. These affect only the ideal-gas properties and are not considered here.

Some rotational and vibrational degrees of freedom are dependent on density as well as on temperature. Factoring the rotational and vibrational partition function into external (density-dependent) and internal (density independent) terms, we write

$$(q_{r,v}) = (q_{r,v})_{\mathrm{ext}}(q_{r,v})_{\mathrm{int}} \tag{7}$$

The central problem is how $(q_{r,v})_{\mathrm{ext}}$ varies with temperature and volume. Following Prigogine, we assume that contributions to the partition function from rotational and vibrational motions may be calculated as contributions from equivalent translational motions. Quantitatively, we assume that the nonidealities in the equation of state (that is, attractions and repulsions) that are caused by external molecular rotational and vibrational motions are equivalent to the nonidealities caused by translational motions. Each translational degree of freedom contributes

$$\left[\frac{V_f}{V}\exp\frac{-\phi}{2kT}\right]^{1/3} \tag{8}$$

to the nonideal part of the equation of state. Treating the external rotational and vibrational motions similarly, we get

$$(q_{r,v})_{\mathrm{ext}} = \left[\frac{V_f}{V}\exp\frac{-\phi}{2kT}\right]^{\frac{3(c-1)}{3}} \tag{9}$$

Therefore, the partition function for a polyatomic pure fluid is

$$Q = \frac{1}{N!}\left(\frac{V}{\Lambda^3}\right)^N \left[\frac{V_f}{V}\exp\frac{-\phi}{2kT}\right]^{Nc} f(T) \tag{10}$$

This result is equivalent to that given by Beret and Prausnitz (1975). However, the physical significance of Equation (9) is somewhat different.

The expressions for V_f/V and ϕ given by Beret and Prausnitz have been used with some minor modifications as discussed in Appendix A.

To account for molecular repulsions, the free volume expression of Carnahan and Starling (1972) gives

$$\ln\frac{V_f}{V} = \frac{3\left(\frac{\tau}{\tilde{v}}\right)^2 - 4\left(\frac{\tau}{\tilde{v}}\right)}{\left(1 - \frac{\tau}{\tilde{v}}\right)^2} \tag{11}$$

with

$$\tau = \frac{\pi\sqrt{2}}{6} = 0.7405 \tag{12}$$

To account for molecular attractions, the molecular dynamics (computer simulation) results of Alder describe molecules which interact with a square-well intermolecular potential. For monatomic molecules ($c = 1$), Alder gives the constants A_{nm} for the equation

$$\frac{\phi}{2kT} = \sum_{n,m} \frac{A_{nm}}{\tilde{T}^n \tilde{v}^m} \tag{13}$$

For chain molecules

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[*] This q is not to be confused with the q appearing in the partition function, Equations (3), (5), (6), (7), and (9). Unfortunately, the conventional literature uses q both for molecular partition function and for molecular surface area.

$$\tilde{T} = \frac{ckT}{\epsilon q} \tag{14}$$

and

$$\tilde{v} = \frac{v}{v^*} = \frac{v\sqrt{2}}{Nr\sigma^3} \tag{15}$$

The configurational Helmholtz energy is given by

$$\frac{A_{conf}}{NkT} = \ln V + c \left\{ \frac{3\left(\frac{\tau}{\tilde{v}}\right)^2 - 4\left(\frac{\tau}{\tilde{v}}\right)}{\left(1 - \frac{\tau}{\tilde{v}}\right)^2} + \sum_{n,m} \frac{A_{nm}}{\tilde{T}^n \tilde{v}^m} \right\} \tag{16}$$

All other configurational thermodynamic properties of pure fluids can be derived from Equation (16).

Mixtures

For a mixture containing N_i molecules of component i, the generalized van der Waals partition function [Equation (3)] is

$$Q = \frac{V^N}{\underset{i}{\pi}[N_i! \Lambda_i^{3N_i}]} \left[\frac{V_f}{V} \exp \frac{-\phi}{2kT}\right]^N [q_{r,v}]^N \tag{17}$$

where

$$N = \sum_i N_i \tag{18}$$

The functions Λ_i depend only on temperature and on pure-component properties. However, V_f, ϕ, and $q_{r,v}$ depend on the properties of the fluid mixture.

Just as the pure-component partition function must meet the theoretical boundary conditions discussed in the introduction, there are three theoretical conditions imposed on the mixture partition function.

1. At moderate densities, the virial equation is valid for all pure and mixed gases. The statistical mechanical derivation for mixtures requires no arbitrary assumptions; it shows that B_M, the second virial coefficient of any mixture, has a quadratic dependence on the mole fraction x

$$B_M = \sum_{i,j} x_i x_j B_{ij} \tag{19}$$

where for a given ij pair, B_{ij} depends only on temperature.

2. For molecules with significantly different intermolecular potential energies, molecular clustering becomes important. The low-density approximation and the random-mixing approximation both break down. Theoretical corrections for mixture nonrandomness have been made for spherical molecules; they are discussed below.

3. Mixture properties for systems containing both small and large molecules (monomers and polymers) must be calculated using some sort of surface or volume fraction. Mole fractions cannot be used.

It is convenient to break complex molecules into segments. Each segment has a hard core diameter σ, and there are r segments per molecule. Lattice theory shows that for mixtures of similar chain molecules (such as hexadecane dissolved in eicosane), the hard core volume of the mixture is

$$(v^*)_M \sim (r\sigma^3)_M = \sigma^3 \sum_j x_j r_j \tag{20}$$

If Equation (20) is used with Equations (11), (15), and (17), then, setting $\phi = 0$, the athermal combinatorial entropy of mixing can be calculated; as expected, at liquid densities the result is identical to the Flory-Huggins entropy of mixing for athermal mixtures of chain molecules.

To calculate the intermolecular potential energy ϕ, lattice theory gives

$$(\epsilon q)_M = \epsilon \sum_i x_i q_i \tag{21}$$

The product of these two equations can be generalized to

$$(\epsilon q r \sigma^3)_M = \sum_{i,j} x_i x_j \epsilon_{ij} q_i r_j \sigma^3_{ji} \tag{22}$$

Equation (22) is the basis of the mixing rules used in the perturbed-hard-chain theory. Details are given elsewhere (Donohue and Prausnitz, 1977).

Prigogine's theory for polymer mixtures (which is based on lattice theory) can be written in terms of Equation (22). For small molecules, this equation reduces to the familiar van der Waals mixing rule

$$a_M = \sum_{i,j} x_i x_j a_{ij} \tag{23}$$

Equations (23) follows because of the special properties of the critical point. Van der Waals shows that

$$a \sim T_c v_c \tag{24}$$

For small molecules $T_c \sim \epsilon q$ and $v_c \sim r\sigma^3$. Substitution in Equation (23) gives Equation (22).

Expansion of Helmholtz Energy in Powers of Reciprocal Temperature

The compressibility factor z can be expanded in reciprocal volume to yield the theoretically significant virial equation of state

$$z = 1 + \frac{B}{v} + \frac{C}{v^2} + \ldots \tag{25}$$

where $B, C, \ldots$ are virial coefficients.

Similarly, expanding z in reciprocal temperature yields perturbation theory

$$z = z^{(0)} + \frac{z^{(1)}}{T} + \frac{z^{(2)}}{T^2} + \ldots \tag{26}$$

or, equivalently, for the Helmholtz energy

$$A = A^{(0)} + \frac{A^{(1)}}{T} + \frac{A^{(2)}}{T^2} + \ldots \tag{27}$$

Just as the statistical mechanical derivation for Equation (25) (see, for example, Hill, 1960) yields the exact composition dependence of the virial coefficients, the derivation of Equation (27) gives the composition dependence of each perturbation term.*

The first term $A^{(0)}$ in the perturbation expansion [Equation (27)] accounts for molecular repulsions, and the remaining terms correct for molecular attractions. The first attractive term $A^{(1)}$ is often called the mean-field term, and perturbation expansions truncated after this term are called mean-field theories. Mean-field theories assume that molecules are randomly positioned in space. The higher-order terms $A^{(2)}$, etc., correct for nonrandom-

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* It follows from Equation (1) that deriving mixing rules for each term in the perturbation expansion of the Helmholtz energy is equivalent to deriving mixing rules to be used in the partition function of the mixture [Equation (17)].

ness by accounting for clusters of molecules. Including the higher-order terms allows for density and composition fluctuations.

Chen, Henderson, and Barker (1969) derive the perturbation expansion for multicomponent mixtures of spherical molecules in terms of integrals which include the hard sphere radial distribution function g^0 and the two-body intermolecular potential energy Γ. Since each integral has a different composition dependence, exact relations can be derived for fluid-mixture properties by evaluating these integrals. However, Chen's result is not directly useful because it contains a number of terms which are unknown. Further, Chen's equations require a number of numerical integrations for each mixture. Henderson (1974) has simplified Chen's result by considering mixtures where the molecules are the same size. With this assumption, Henderson obtains

$$\frac{A^{(1)}}{NkT} = \frac{1}{2}\frac{Nd^3}{V} I \Sigma x_i x_j \frac{E_{ij}}{k} \qquad (28)$$

$$\begin{aligned}\frac{A^{(2)}}{NkT} = &-\frac{1}{4}\frac{Nd^3}{V} J_1 \Sigma x_i x_j \frac{E_{ij}{}^2}{k^2} \\ &-\frac{1}{2}\left(\frac{Nd^3}{V}\right)^2 J_2 \Sigma x_i x_j x_k \frac{E_{ij}E_{jk}}{k^2} \\ &-\frac{1}{8}\left(\frac{Nd^3}{V}\right)^3 J_3 \Sigma x_i x_j x_k x_l \frac{E_{ij}E_{kl}}{k^2}\end{aligned} \qquad (29)$$

with

$$I = \int \Gamma'(12) g^0(12) d\underline{r}_2' \qquad (30)$$

$$J_1 = \int (\Gamma'(12))^2 g^0(12) d\underline{r}_2' \qquad (31)$$

$$J_2 = \int \Gamma'(12)\Gamma'(23)(g^0(123) - g^0(12)g^0(23)) d\underline{r}_2' d\underline{r}_3' \qquad (32)$$

where $dr_i' = 4\pi(r/d)^2 d(r/d)$, Γ' $(= \Gamma - \Gamma^0/E)$ is the reduced perturbation potential and d is the hard-core diameter per molecule. The integral J_3 is a complicated term involving $g^0(1234)$ and need not be specified. The integrals I and J_1 have been evaluated by numerical methods; however, the integral J_2 is not known because $g^0(123)$ is not known accurately at all densities. The superposition approximation proposed by Kirkwood (1935) is valid at low densities and gives

$$g^0(123) = g^0(12)g^0(23)g^0(13) \qquad (33)$$

Then

$$J_2 = \int \Gamma'(12)\Gamma'(23)(g^0(12)g^0(13)g^0(23) - g^0(12)g^0(23)) \underline{d\underline{r}_2' d\underline{r}_3'} \qquad (34)$$

Integral J_2 has been evaluated by Smith et al. (1970) and has been fitted to a polynomial in density. The integral J_3 cannot be evaluated accurately using the superposition approximation, but the function

$$F_2(\tilde{\rho}) = -\frac{1}{4}\frac{Nd^3}{V}\left[J_1 + 2\frac{Nd^3}{V}J_2 + \frac{1}{2}\left(\frac{Nd^3}{V}\right)^2 J_3\right] \qquad (35)$$

has been evaluated independently as a function of reduced density ($\tilde{\rho} = v^*/v$), and therefore J_3 can be found by difference.

Equations similar to Equations (28) and (29) can be derived for the higher-order perturbations. Unfortunately, they are not useful because they require the unknown behavior of the higher-order distribution functions $g^0(12345)$, etc. However, a good approximation can be made for the higher-order terms by writing them in a form similar to Equation (35) and neglecting corrections to nonrandomness which are third and higher order in composition and density. This is discussed in Appendix B.

The advantage of the procedure outlined above is that it eliminates the customary approximation that the mixture is completely random, an approximation implicit in essentially all previously proposed one-fluid theories. To illustrate the effect of the nonrandomness corrections, Figure 2 shows $A^{(2)}/NkT$ vs. reduced density for a binary, equimolar mixture of spherical molecules having the same size but different potential energies. In this binary mixture, the molecules of the first component are hard spheres (no attraction), and the molecules of the second component follow a square-well potential. The rigorous result is marked perturbation theory. Shown are the rigorous results calculated by Henderson (1974), the result that would be obtained if the random-mixing approximation had been used, and the result obtained for pure, square-well molecules. The large difference between the two top lines in Figure 2 demonstrates that for this hypothetical system, the random-mixing approximation is seriously in error for the second-order perturbation term. Nonrandomness corrections are also important in the third- and fourth-order terms, but because both of these terms are about one order of magnitude smaller than the second-order term, their effect on mixture properties is small.

These nonrandomness corrections can be combined with the mixing rule derived from lattice theory [Equation (22)] to yield the Helmholtz energy for mixtures containing polyatomic molecules. The complicated result is given in Appendix B. For a more detailed discussion of the derivation, see Donohue and Prausnitz (1977).

In addition to differences in energy of attraction, nonrandomness can also be caused by differences in the size or shape of the mixture's components. However, Henderson and Davison (1967) have shown that for spherical molecules even a large difference in molecular size does not lead to significant mixture nonrandomness or phase separation. For mixtures of nonspherical molecules, nonrandomness can arise because of changes in

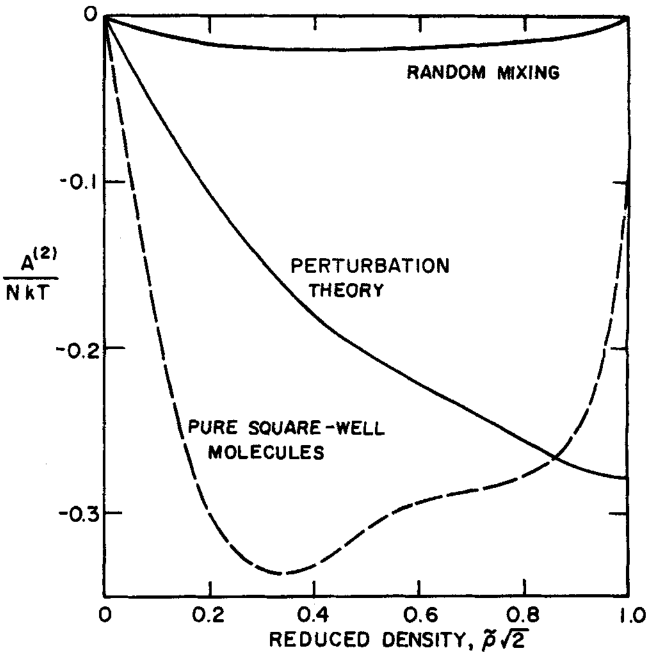

Fig. 2. Second-order term in perturbation theory for an equimolar mixture of square-well and hard-sphere molecules, $A^{(2)}/RT$.

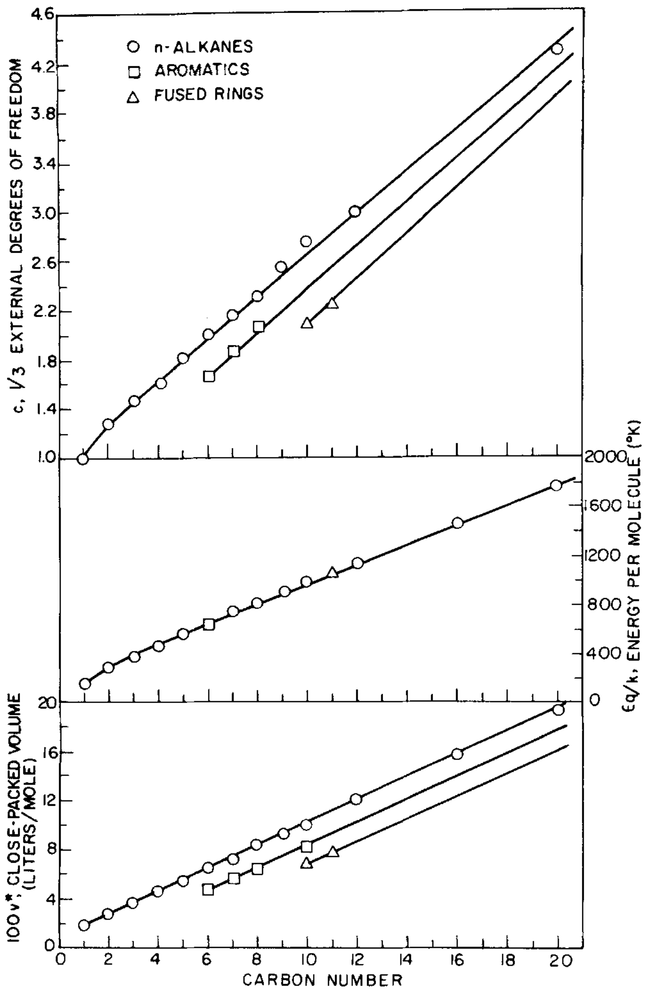

Fig. 3. Pure component parameters for hydrocarbons.

liquid structure on mixing, as shown by Tancrède et al. (1977) and by Heintz and Lichtenthaler (1977). The variation of c, the external degrees of freedom of the mixture, with composition tends at least in part to account for this effect.

Results

The perturbed-hard-chain theory has been applied to a wide variety of pure and mixed fluids of interest in the natural-gas and petroleum refining industries. Pure-component and mixture configurational properties can be calculated using parameters which are independent of temperature, density, and composition. Parameters were fitted to available experimental data and then correlated to insure the reliability of the data and the data reduction.

Pure-component parameters have been obtained for forty five common fluids; they are given elsewhere (Donohue and Prausnitz, 1977). Included are normal and branched alkanes to C_{30}, aromatics, fused-ring hydrocarbons, and light inorganic gases. There are a total of seven parameters (T^*, v^*, c, ϵ, q, r, σ) for each pure component, but only five of these are independent because of the relations $T^* = \epsilon q/ck$ and $v^* = Nr\sigma^3/\sqrt{2}$. Three of the parameters (T^*, v^*, and c) are necessary to calculate pure-component properties, and these were determined from experimental vapor-pressure and liquid-density data. The other two parameters are determined by correlating parameters for a large number of similar fluids.[*]

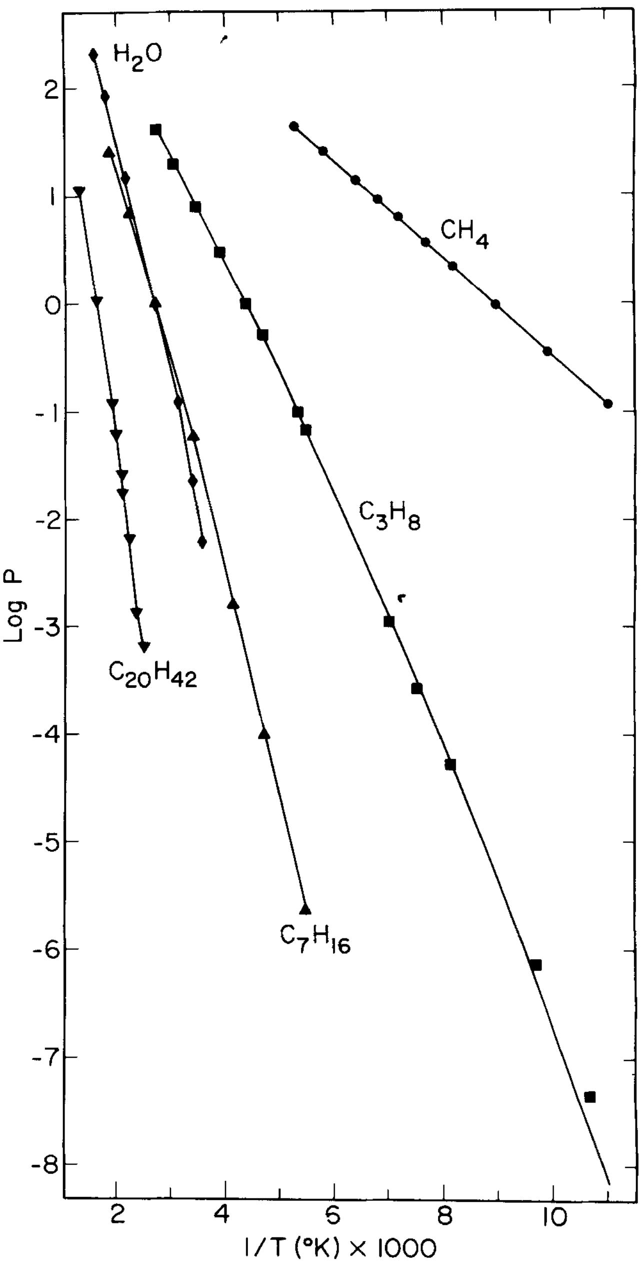

Fig. 4. Vapor pressures on *n*-alkanes and water from their triple points to their critical points.

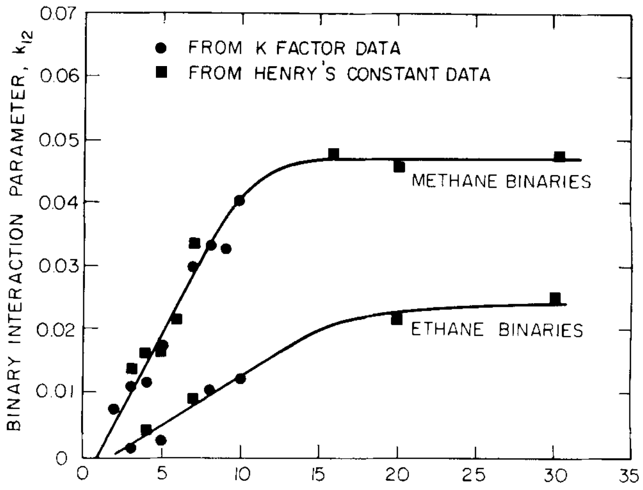

Fig. 5. Binary interaction parameters for methane and ethane with alkanes.

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[*] ϵ was determined from the slope of $\epsilon q/k$ in Figure 3, and σ was determined from the slope of v^* in Figure 3.

Table 1. Recommended Binary Interaction Parameters $k_{12} \times 100$

	C_1H_4	C_2H_6	C_3H_8	C_4H_{10}	N_2	CO_2	H_2S	H_2	CO
C_1H_4	0				1.8	6.0	8.5	1.7	0.8
C_2H_6	0.5	0			3.9	5.0	6.0	3.5	2.0
C_3H_8	1.0	0.17	0		4.6	4.3	5.9	5.2	3.0
C_4H_{10}	1.45	0.32	0.12	0	4.7	3.6	5.8	7.0	3.5
C_5H_{12}	1.82	0.48	0.24	0.08	4.8	3.6	5.8	7.5	3.8
C_6H_{14}	2.40	0.64	0.36	0.16	4.8	3.6	5.7	7.5	4.0
C_7H_{16}	2.87	0.80	0.48	0.24	4.8	3.6	5.7	7.5	4.0
C_8H_{18}	3.34	0.95	0.60	0.32	4.8	3.6	5.6	7.5	4.0
C_9H_{20}	3.77	1.12	0.72	0.40	4.8	3.6	5.6	7.5	4.0
$C_{10}H_{22}$	4.07	1.27	0.84	0.48	4.8	3.6	5.5	7.5	4.0
$C_{12}H_{26}$	4.48	1.58	0.94	0.63	4.8	3.6	5.5	7.5	4.0
$C_{16}H_{34}$	4.70	2.10	1.0	0.75	4.8	3.6	5.5	7.5	4.0
$C_{20}H_{42}$	4.70	2.30	1.0	0.75	4.8	3.6	5.5	7.5	4.0
$C_{30}H_{62}$	4.75	2.40	1.0	0.75	4.8	3.6	5.5	7.5	4.0

For binary mixtures containing large hydrocarbons, such as a mixture of pentane and heptane, k_{ij} is zero. For mixtures of light gases and aromatics of carbon number n use k_{ij} for a binary mixture of that light gas and alkanes with carbon number $n + 2$.

Figure 3 shows the variation of molecular parameters with carbon number. Where there are few or no experimental data, Figure 3 may be used to estimate the required parameters. The linear behavior indicated in Figure 3 suggests that these parameters relate to molecular properties and are not merely adjustable constants.

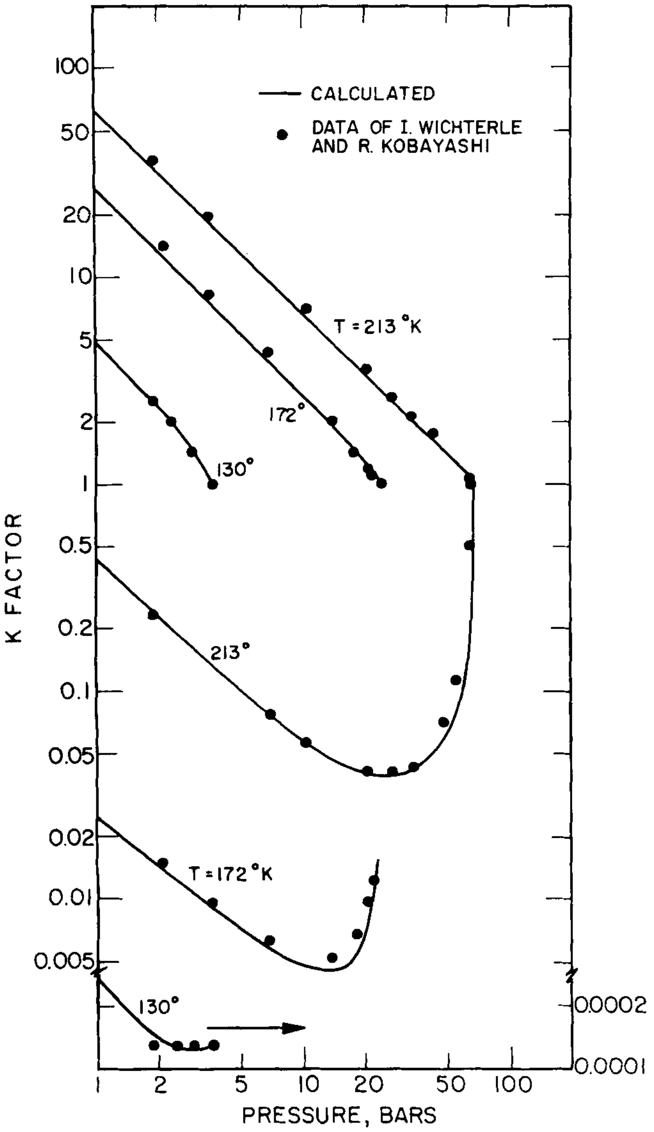

Fig. 6. K factors for methane-propane ($k_{ij} = 0.011$).

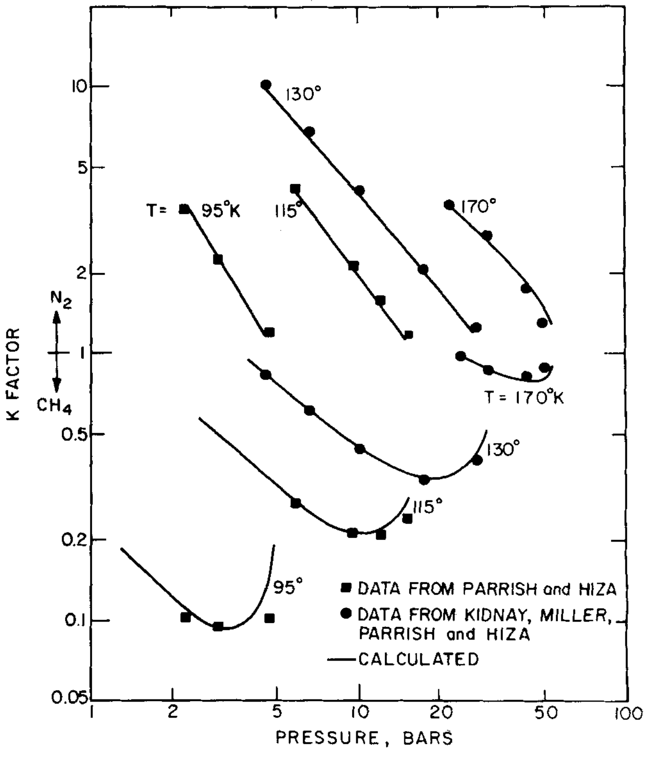

Fig. 7. K factors for methane-nitrogen ($k_{ij} = 0.017$).

For pure fluids, agreement between calculated and experimental properties is good, often within experimental uncertainty. Vapor pressures and liquid densities are represented with less than 3% average error, with few exceptions. To illustrate, Figure 4 shows vapor pressures from the triple point to the critical point for some normal alkanes and water. Liquid densities, second virial coefficients, and residual enthalpies can also be calculated with similar accuracy using the same pure-component parameters.

Fluid-mixture properties can be calculated using the pure-component parameters and one binary interaction parameter k_{ij} defined by

$$\epsilon_{ij} = (\epsilon_{ii}\epsilon_{jj})^{1/2}(1 - k_{ij}) \qquad (36)$$

Experimental K-factor and Henry's-constant data have been used to determine interaction parameters for over sixty binary mixtures. These include mixtures containing alkanes to C_{30}, aromatics, and light inorganic gases such

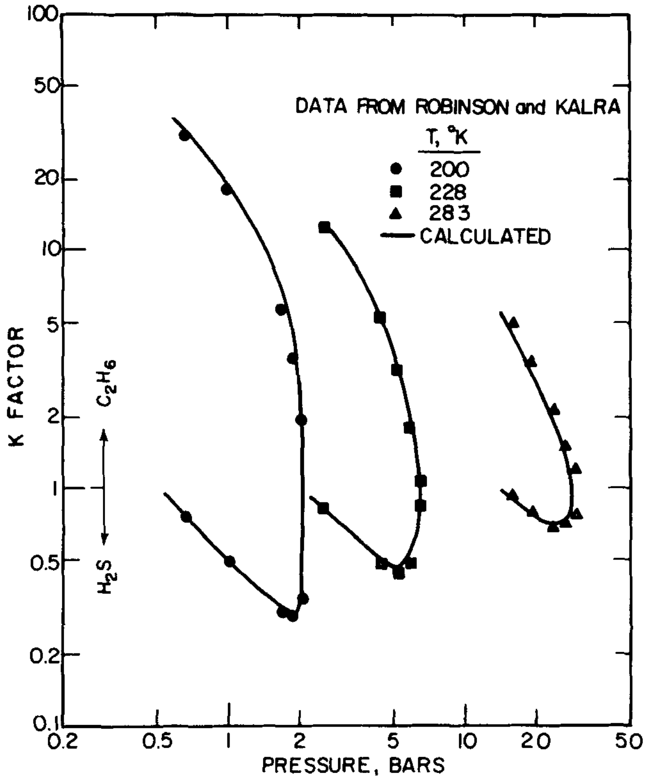

Fig. 8. K factors for ethane-hydrogen sulfide (k_{ij} = 0.055).

as carbon dioxide, hydrogen sulfide, and nitrogen. (Aqueous mixtures, however, are not considered here.) The parameters and the temperature and pressure ranges of the experimental data are given elsewhere (Donohue, 1977). Figure 5 shows the interaction parameters k_{ij} determined for binary systems of methane and ethane with normal and branched alkanes. Figure 5 can also be used to interpolate (and extrapolate) parameters for mixtures where no experimental data are available. Table 1 gives recommended values of the binary interaction parameters for a number of systems. These were determined by smoothing the results (as in Figure 5) obtained from a number of binary mixtures.

Smoothing the k_{ij} determined from a number of binary mixtures helps to identify inaccurate data and eliminate uncertainties in the k_{ij} introduced when the experimental data are over a limited temperature or pressure range. In all cases, the variation of k_{ij} with carbon number is similar to that shown in Figure 5. The k_{ij} parameters vary linearly at low carbon numbers and then level off and become constant, as expected for mixtures containing *n*-alkanes. As the carbon number of the second component increases, the difference between the molecules increases, and, as a consequence, k_{ij} increases also. However, there comes a point where the methane (or ethane) molecule can no longer distinguish between molecules of different chain lengths. This happens because it can only interact with a limited number of segments (—CH_2— groups) at one time. This number, called the coordination number, is between six and twelve for liquids. Figure 5 indicates that parameter k_{ij} levels off at approximately the coordination number, in further support of the theory.

Figures 6 to 12 and Table 2 compare calculated and experimental results for a number of typical binary systems; shown are *K* factors, Henry's constants, and residual enthalpies. These systems are representative of mixtures commonly encountered in natural-gas and petroleum processing.

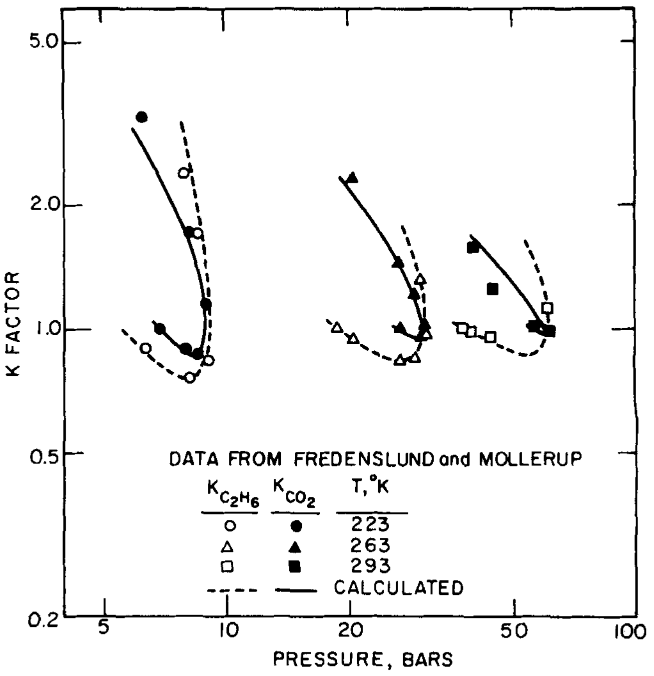

Fig. 9. K factors for ethane-carbon dioxide (k_{ij} = 0.047).

Figure 12 shows Henry's constants for a number of gases in hexadecane. The accuracy of these results is remarkable because Henry's constant provides an extremely stringent test of the theory. Errors in the mixing rules are exponentially magnified in Henry's constant. The accuracy of Henry's constants over such a wide temperature range is a consequence of the higher-order terms in perturbation theory.

The results shown in Figures 6 to 12 are typical. Calculations are in good agreement with the experiment. Table 3 lists average errors in *K* factors for some binary mixtures. Although the errors in Table 3 appear high, the comparison is between raw experimental data and calculated results. For most of these systems, the deviations would be much less if the comparison had been made to smoothed data.

Table 2 gives a comparison between calculated and experimental residual enthalpies; these enthalpies were calculated using parameters determined from *K*-factor data. The enthalpies are included to illustrate that the perturbed-hard-chain theory can be used to calculate several configurational thermodynamic properties using only one set of parameters.

Thermodynamic properties of multicomponent mixtures can be calculated using only single-component and binary parameters. No ternary (or higher) parameters are required.

TABLE 2. RESIDUAL ENTHALPIES FOR METHANE-NITROGEN

(56.6 mole % CH_4; 43.4 mole % N_2)

T, °K	P, bars	$-\Delta H$, Btu/lb expt.	 calc.	
100	17	138	139	(L)
	138	134	134	(L)
144	17	44	39	(L + V)
	138	112	114	(L)
172	17	12	12	(V)
	138	95	99	(L)

$\Delta H = H(T, P, z) - H(T, z)_{\text{ideal gas}}$

x = composition

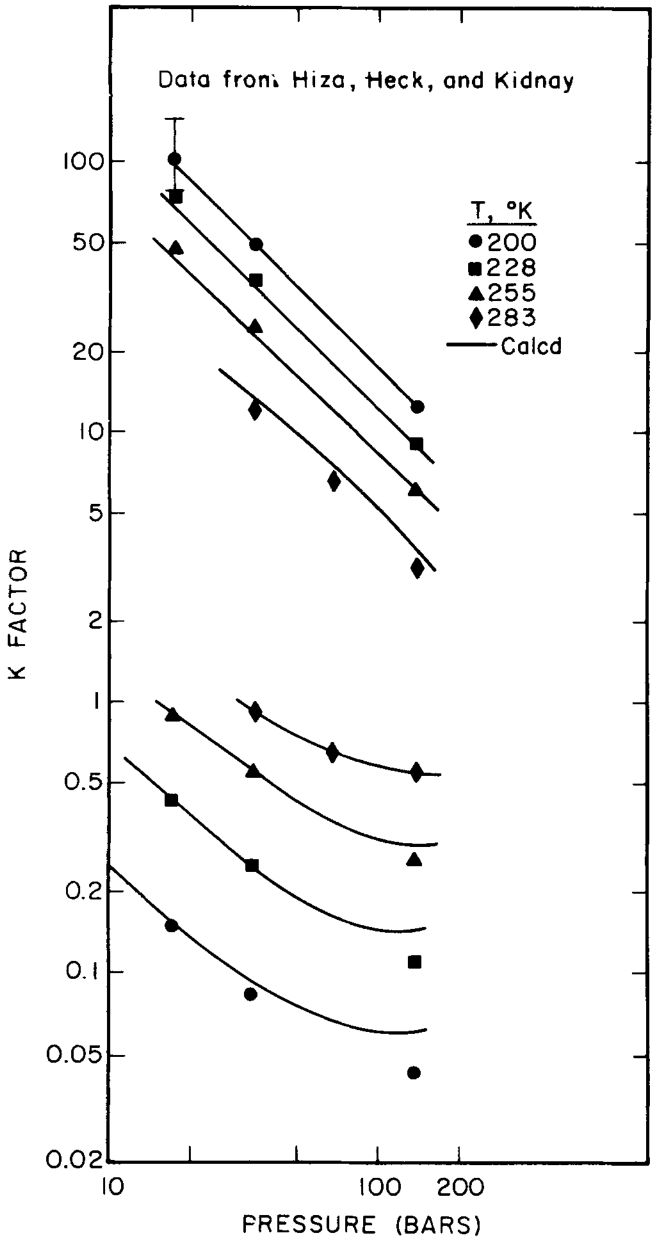

Fig. 10. *K* factors for ethane-hydrogen ($k_{ij} = 0.04$). Data from Hiza, Heck & Kidney.

Table 3. Typical Errors in Calculated K Factors for Binary Systems

System	T, °K	P, bars	Avg. % error K_1	Avg. % error K_2
Methane/propane	130-283	1.9-82.8	1.8	6.0
Methane/heptane	244-478	6.9-120.7	4.3	23.1*
Hydrogen/methane	103-117	0.9-1.0	7.6	28.4*
Hydrogen/ethane	144-283	0.8-1.0	15.4	4.4*
Methane/carbon dioxide	200-272	14.8-76.4	7.7	6.5
Propane/carbon dioxide	233-273	3.4-27.6	2.7	7.1
Methane/hydrogen sulfide	277-344	13.8-131.0	6.5	3.8
Ethane/hydrogen sulfide	200-283	0.7-29.1	5.5	2.5
Nitrogen/methane	95-170	2.3-49.0	4.0	1.7
Nitrogen/hexane	311-444	17.2-344.7	6.1	18.9*

* For these systems, the liquid phase mole fraction x_1 and the vapor phase mole fraction y_2 are extremely small. Under these conditions, slight errors in the composition are magnified in the *K* factors.

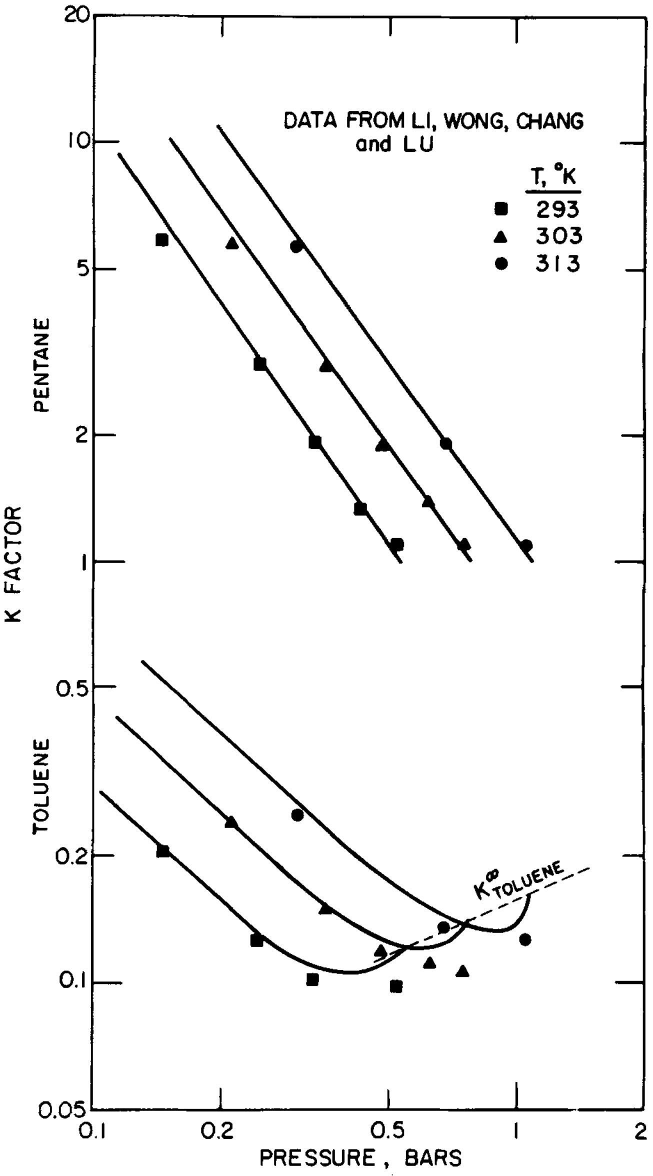

Fig. 11. *K* factors for pentane-toluene ($k_{ij} = 0.01$).

Table 4. Universal Constants A_{nm} Used in Perturbation Expansion

	A_{nm}* n			
m	1	2	3	4
1	−7.0346	−3.5173	−1.1724	−0.29311
2	−7.2736	11.15	7.15	−1.32
3	−1.252	−10.69	−31.3	32.9
4	6.03	−3.5977	63.1073	−94.2481
5	6.8	7.4318	−40.6084	73.3867
6	1.7	0.0	0.0	0.0

* The universal constants A_{nm} presented here are not in any way unique. Although these constants accurately represent the properties of all systems studied here, it may be possible to improve the representation for other classes of molecules (for example, polymers) by adjusting these constants slightly.

In summary, single-component and binary parameters have been obtained by fitting experimental data. Correlation allows prediction of parameters for other systems where no experimental data are available. The perturbed-hard-chain theory can accurately represent the properties

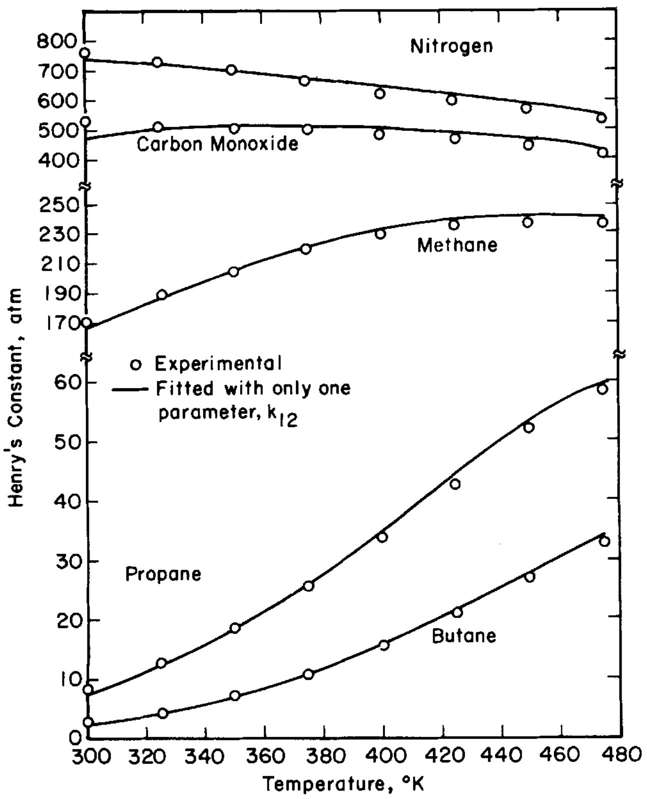

Fig. 12. Henry's constants in hexadecane.

of most mixtures commonly encountered in petroleum refining and natural-gas processing, including those mixtures where the components differ greatly in size, shape, or potential energy. Pertinent computer programs are in preparation by Gas Processors' Association, 1812 First Place, Tulsa, Oklahoma 74103.

ACKNOWLEDGMENT

The authors are indebted to the Gas Processors' Association and the American Gas Association for financial support and to the Computer Centers at the University of California, Berkeley, and Lawrence Berkeley Laboratory for the use of their facilities. We also want to thank Enrique Bazúa, Bal Kaul, David Liu, D. Henderson, and B. J. Alder for helpful discussions.

NOTATION

A = Helmholtz energy
$A^{(n)}$ = n^{th} order perturbation in Helmholtz energy
A_{nm} = constants used in Equation 13
a = van der Waals' constant
B = second virial coefficient
C_J = constants used in Equation B4
c = one third the number of external degrees of freedom
d = hard-core diameter per molecule
E = depth of intermolecular potential energy well
F_2 = function defined by Equation 35
$f(T)$ = a function of temperature
g = radial distribution function
H = enthalpy
h = Plank's constant
I = integral involving radial distribution function and intermolecular potential energy
J_1, J_2, J_3 = integrals involving radial distribution function and intermolecular potential energy
k = Boltzmann's constant
k_{ij} = binary potential-energy interaction parameter
m = mass per molecule
N = total number of molecules
N_i = number of molecules of species i
n = number of atoms per molecule
n = carbon number
P = pressure
Q = canonical partition function
q = canonical partition function per molecule
q = molecular surface area
r = number of segments per molecule
r' = integration coordinate
T = temperature
T^* = characteristic potential-energy parameter
$\tilde{T}$ = reduced temperature
T_c = critical temperature
V = total volume
V_f = free volume
v_c = vertical volume
v = molar volume
$\tilde{v}$ = reduced volume
v^* = close-packed volume per mole
x = composition
z = compressibility factor

Greek Letters

Γ = intermolecular potential energy between two molecules
Γ' = reduced perturbation potential
ϵ = intermolecular potential energy per unit area
Λ = de Broglie wavelength
τ = constant equal to 0.7405
$\tilde{\rho}$ = reduced density
σ = hard-core diameter per segment
ϕ = intermolecular potential energy of one molecule in the presence of all other molecules

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APPENDIX A: MODIFICATIONS TO THE PURE COMPONENT PARTITION FUNCTION

Although the theory proposed by Beret gives good representation of pure component liquid properties, predicted second virial coefficients were only fair. Further, Beret's partition function showed systematic deviations from experimental measurements at very low temperatures and very high densities. Two minor modifications have therefore been made to reduce these inadequacies.

The first, which improves agreement between calculated and experimental second virial coefficients, is achieved by adding an empirical term to the Helmholtz energy:

$$A_{\text{Total}} = A_{\text{Beret}} + A_{SV} \qquad (\text{A1})$$

$$\frac{A_{SV}}{NkT} = \frac{1.7\left(3.65 - \dfrac{q}{c}\right)\left(\dfrac{q}{c} - 1.45\right)^4}{\tilde{T}\,4\,\tilde{v}\,(1 + 10/\tilde{v}\,)^4} \qquad (\text{A2})$$

As shown by Kaul (1977), the dependence of A_{SV} on molecular complexity was determined from pure component and cross second virial coefficients for normal alkanes. The temperature dependence was determined from data available for *n*-heptane. The volume dependence was adjusted to ensure a reasonable third virial coefficient and to make the correction negligible at high densities.

The second modification concerns the perturbation expansion given in Equation (7). Alder et al. (1972) give coefficients to calculate the first four perturbation terms:

$$\frac{A^{(n)}}{NkT} = \sum_m \frac{A_{nm}T^{*n}}{\tilde{v}^{\,m}} \quad \text{for} \quad n = 1, 2, 3, 4 \qquad (\text{A3})$$

For a monatomic fluid, the attractive Helmholtz energy is the sum of the perturbation terms

$$\frac{A_{\text{attractive}}}{NkT} = c \sum_{n,m} \frac{A_{nm}}{\tilde{T}^{\,n}\,\tilde{v}^{\,m}} \qquad (\text{A4})$$

The constants A_{nm} form a matrix which allows the equation to be easily programed onto an electronic computer.

Alder's original matrix contained thirty-six terms (4 × 9) with twelve zero elements. We have reduced this matrix to twenty-four terms (4 × 6) with three zero elements. Since the computation time is proportional to the number of elements in the matrix (including zeros), we have decreased computing time for the perturbation expansion by approximately one third. More important, we significantly improved the representation for vapor pressures, liquid densities, and enthalpies for essentially all fluids of interest here.

In fitting these universal constants, we were guided by the molecular dynamics results of Alder, but we made modifications in those terms in which there was a large uncertainty. The perturbation expansion was fitted to vapor pressure and liquid density data for methane, holding constant the first-order perturbation terms and those terms which comprise the lower virial coefficients.

Table 4 gives the new A_{nm} constants. These constants are universal in the sense that they are used for all fluids. They are not, however, in any way unique. They give an accurate representation of the systems studied here, but it may be possible to improve the representation for other types of systems (for example, polymers, polar molecules) by adjusting these constants further.

With these new constants, the fit for methane and essentially all other fluids is significantly improved. For methane, the average error in vapor pressure is reduced from 1 to 0.2%. Excluding the critical region, average errors are less than 3% for both vapor pressures and liquid densities for most pure components.

APPENDIX B: COMPOSITION DEPENDENCE OF THE HELMHOLTZ ENERGY

The composition dependence of the attractive terms in the perturbation expansion is found by combining the mixing rule derived from lattice theory [Equation (22)] with Henderson's nonrandomness corrections for spherical molecules. From the definition of $T^*(\equiv \epsilon q/ck)$, Equation (22) can be rewritten

$$<cT^*v^*> = \sum_i \sum_j x_i x_j \frac{\epsilon_{ij} q_i}{k} \frac{r_j \sigma_{ji}^3}{\sqrt{2}} \qquad (\text{B1})$$

where $<>$ denotes a mixture property. In the form given by Equation (A3), the first-order perturbation [Equation (28)] becomes

$$\frac{A^{(1)}}{NkT} = \sum_m \frac{A_{1m}<cT^*v^*><v^*>^{m-1}}{v^m} \qquad (\text{B2})$$

where

$$<v^*> = \Sigma x_i v_j^* = \Sigma x_i r_i \sigma_{ii}^3/\sqrt{2} \qquad (\text{B3})$$

as given by Equation (20).

While the first-order term in the perturbation expansion has a simple quadratic composition dependence, the higher-order terms cannot be described using only one mixing rule. The second-order perturbation requires three mixing rules even for mixtures of spherical molecules having the same diameter. After algebraic rearrangement and simplification of the summations, Equations (29), (34), and (35) can be put in the form of Equation (A3). The result is that

$$\begin{aligned}\frac{A^{(2)}}{NkT} = {} & \sum_m \frac{A_{2m}<cT^*v^*><T^*>^{(2)}<v^*>^{m-1}}{mv} \\ & + \sum_m \frac{A_{1m}}{2v^m}[<cT^{*2}v^*> \\ & \qquad - <cT^*v^*><T^*>^{(2)}]<v^*>^{m-1} \\ & + \sum_m \frac{(C_J)_m}{V^{m+1}}[<cT^*v^*><T^*>_L \\ & \qquad - <cT^*v^*><T^*>^{(2)}]<v^*>^m \end{aligned} \qquad (\text{B4})$$

where

$$<T^*>^{(2)} = \frac{\sum_i \sum_j x_i x_j q_i \dfrac{\epsilon_{ij} q_i}{c_i k} r_j \sigma_{ji}^3}{\sum_i \sum_j x_i x_j q_i r_j \sigma_{ji}^3} \tag{B5}$$

$$<T^*>_L = \frac{\sum_i x_i q_i \dfrac{\epsilon_{ii} q_i}{c_i k}}{\sum_i x_i q_i} \tag{B6}$$

and the constants $(C_J)_m$ have been fitted to the J_2 integral [Equation (34)] evaluated by Smith et al. (1970). Equation (B2) and the first term in Equation (B4) give the random mixing result. The second and third terms in Equation (B4) correct the random mixing approximation for clusters of two and three molecules, respectively.

The third- and fourth-order terms have been derived, they are of a form similar to Equations (28) and (29). These are not useful, however, because they require the higher-order distribution functions $g^0(1234)$, etc., which are unknown. A good approximation can be made for these terms by writing them in the form of Equation (B4) and including only the correction for clusters of two molecules. This provides the dominant correction for mixture nonrandomness. The result is

$$\begin{aligned}\frac{A^{(3)}}{NkT} = {} & \sum_m \frac{A_{3m}}{v^m} <cT^*v^*><T^*>^{(2)}<T^*>^{(3)}<v^*>^{m-1} \\ & + \sum_m \frac{A_{2m}}{3v^m} [<cT^{*3}v^*> \\ & - <cT^*v^*><T^*>^{(2)}<T^*>^{(3)}]<v^*>^{m-1}\end{aligned} \tag{B7}$$

$$\begin{aligned}\frac{A^{(4)}}{NkT} = {} & \sum_m \frac{A_{4m}}{v^m} <cT^*v^*><T^*>^{(2)}<T^*>^{(3)} \\ & <T^*>^{(4)}<v^*>^{m-1} \\ & + \sum_m \frac{A_{3m}}{4v^m} [<cT^{*4}v^*> \\ & - <cT^*v^*><T^*>^{(2)}<T^*>^{(3)}<T^*>^{(4)}]<v^*>^{m-1}\end{aligned} \tag{B8}$$

where

$$<cT^{*n}v^*> = \sum_i \sum_j x_i x_j c_i \left[\frac{\epsilon_{ij} q_i}{c_i k}\right]^n \frac{r_j \sigma_{ji}^3}{\sqrt{2}} \tag{B9}$$

$$<T^*>^{(3)} = \frac{\sum_i \sum_j x_i x_j q_i \dfrac{q_i}{c} \dfrac{\epsilon_{ij} q_i}{c_i k} r_j \sigma_{ji}^3}{\sum_i \sum_j x_i x_j q_i \dfrac{q_i}{c_i} r_j \sigma_{ji}^3} \tag{B10}$$

$$<T^*>^{(4)} = \frac{\sum_i \sum_j x_i x_j q_i \left[\dfrac{q_i}{c_i}\right]^2 \dfrac{\epsilon_{ij} q_i}{c_i k} r_j \sigma_{ji}^3}{\sum_i \sum_j x_i x_j q_i \left[\dfrac{q_i}{c_i}\right]^2 r_j \sigma_{ji}^3} \tag{B11}$$

These complex equations allow calculation of mixture properties when the molecules differ in size, shape or intermolecular potential energy.

For athermal solutions, the perturbed-hard-chain theory yields the Flory-Huggins combinatorial entropy of mixing for chain molecules, while for mixtures of spherical molecules of the same size, perturbed-hard-chain theory becomes essentially equivalent to Guggenheim's quasichemical approximation. Perturbed-hard-chain theory, in effect, interpolates between these two well-established theories of mixtures.

Manuscript received August 1, 1977; revision received February 20, and accepted March 6, 1978.

Selective Copper Recovery with Two Types of Liquid Membranes

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Copper can be selectively separated and concentrated by diffusion across liquid membranes. These membranes are effective either as thin films supported by porous polymer sheets or as liquid microcapsules or liquid surfactant membranes.

SCOPE

This paper shows how two different liquid membranes can selectively separate and concentrate copper or nickel ions. In other words, it demonstrates how copper or nickel can be removed from a dilute solution and concentrated in a more acidic solution. As such, the work is another effort in this laboratory aimed at making mass transfer fast and selective.

These membranes contain liquid ion exchangers which function as the mobile carriers so often postulated in biophysics (Stein, 1967). These carriers react with the solutes of interest and diffuse with them across the membrane. The criteria which these carriers must fulfill to be effective are described elsewhere (Cussler and Evans, 1974; Schultz et al., 1974).

This paper directly compares two different membrane geometries capable of effecting these separations. In the

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