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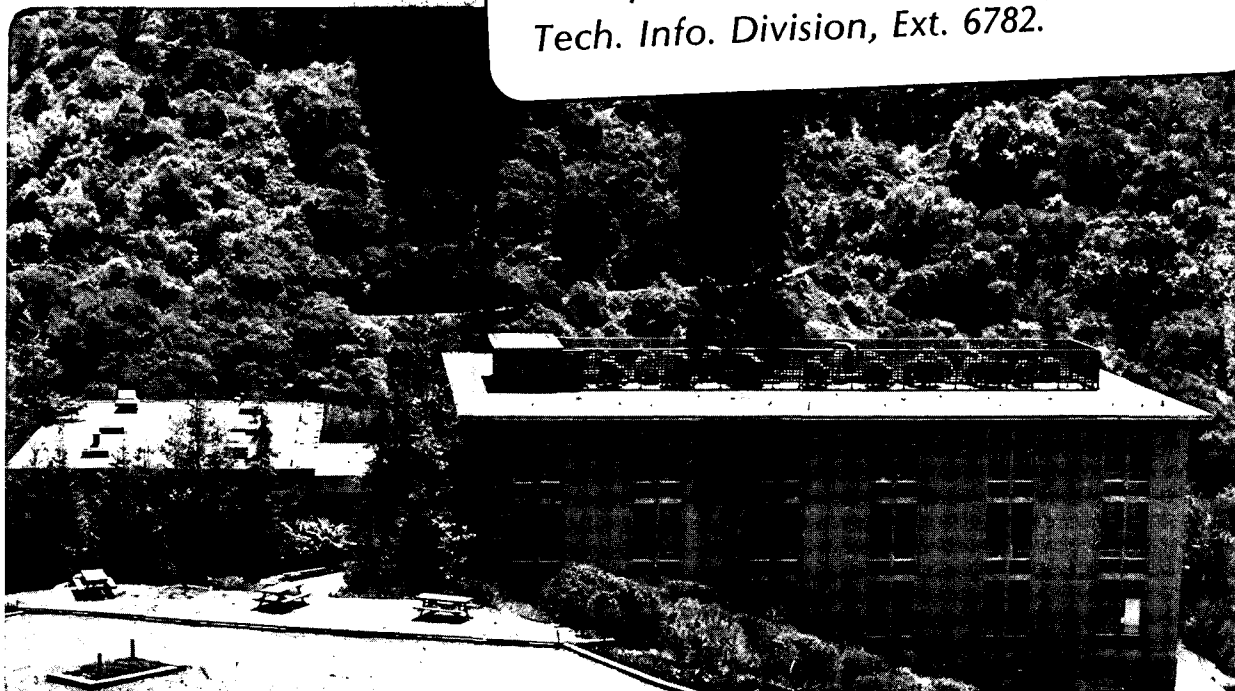
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PHASE EQUILIBRIA FOR COMPLEX FLUID MIXTURES

J.M. Prausnitz

April 1983

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PHASE EQUILIBRIA FOR COMPLEX FLUID MIXTURES

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ABSTRACT

After defining complex mixtures, attention is given to the canonical procedure used for the thermodynamics of fluid mixtures: first, we establish a suitable, idealized reference system and then we establish a perturbation (or excess function) which corrects the idealized system for real behavior. For complex mixtures containing identified components (e.g. alcohols, ketones, water) discussion is directed at possible techniques for extending to complex mixtures our conventional experience with reference systems and perturbations for simple mixtures. Possible extensions include generalization of the quasi-chemical approximation (local compositions) and superposition of chemical equilibria (association and solvation) on a "physical" equation of state.

For complex mixtures containing unidentified components (e.g. coal-derived fluids), a possible experimental method is suggested for characterization; conventional procedures can then be used to calculate phase equilibria using the concept of pseudocomponents whose properties are given by the characterization data. Finally, as an alternative to the pseudocomponent method, a brief introduction is given to phase-equilibrium calculations using continuous thermodynamics.

INTRODUCTION

During the last two or three generations, a conventional procedure has been generally adopted for quantitatively representing the properties of nonelectrolyte fluid mixtures. This procedure has been extensively used for relatively simple mixtures, i.e. for those mixtures where all components are chemically identified and where the molecules of these components are relatively symmetric with respect to shape and electronic structure. To a rough first approximation, such molecules mix in a random manner. Extension of this procedure to more difficult mixtures, however, is not immediately obvious. This work discusses some possible methods for making that extension and gives a few examples.

For our purposes here we distinguish between two classes of complex fluid mixtures:

Class I: A mixture of chemically identified nonelectrolyte components whose molecules are far from simple. In this class we include strongly polar molecules and those that form semi-stable molecular aggregates through hydrogen bonding or other "chemical" forces. In these mixtures, preferential ordering and orientation produces strong deviations from random mixing. Examples are

mixtures containing alcohols, water, organic acids, nitriles, nitro-compounds or amines in addition to common hydrocarbons and common gases such as nitrogen, carbon dioxide, ammonia, etc. These mixtures are frequently found in the petrochemical industry.

Class II: A mixture of many nonelectrolyte components that are not chemically identified. The molecules of these components are not necessarily highly complicated but little is known about their structural or electronic properties. These mixtures may have many hundreds of components and therefore it is not possible or practical to carry out a customary quantitative analysis to determine the mixture's composition.

In the physical sciences, where we try to describe quantitatively the properties of a real system, the conventional procedure is first to idealize the system, that is, to abstract from reality the primary essential features while neglecting secondary characteristics. The idealized system, often called the reference system, is described quantitatively using some idealized theory. Corrections are then added to account for differences between the real and the idealized system; these corrections are often based on semitheoretical models and in some cases these models are strictly empirical. Corrections to the reference system are often called perturbations.

An effective procedure is one that can be applied to a large class of phase behavior and that can give reliable results with a minimum of experimental effort; to achieve that effectiveness, the choice of reference system is crucial.

For a liquid mixture at temperature T , pressure P and composition x , the customary procedure is to write the Gibbs energy of mixing:

$$\Delta G(T,P,x) = \underbrace{\Delta G(T,P,x)}_{\text{Reference}} + \underbrace{\Delta G(T,P,x)}_{\text{Perturbation}} \quad (1)$$

For ΔG (Reference), we commonly use an expression derived for an ideal mixture (Raoult's Law) or for an athermal mixture of chains (Flory-Huggins). For ΔG (perturbation) we have many semi-empirical (activity-coefficient) models such as those of van Laar, Wilson, etc. In the activity-coefficient formulation, ΔG (perturbation) is often called an excess function.

More generally, - for fluids that may be either gaseous or liquid at volume V , the customary procedure is to write for Helmholtz energy A

$$\underline{A}(T,V,x) = \underbrace{\underline{A}(T,V,x)}_{\text{Reference}} + \underbrace{\underline{A}(T,V,x)}_{\text{Perturbation}} \quad (2)$$

For A (Reference) we commonly use an expression assumed to hold for a mixture of non-attracting convex bodies, usually spheres, such as the expression of Carnahan and Starling or some simplified version of that expression. For A (Perturbation), many suggestions have been made; the most common is the mean-field approximation of van der Waals.

From Equations (1) or (2) we can calculate the chemical potential of any component in the mixture. Therefore, either of these equations is sufficient for calculating phase-equilibria and other thermodynamic properties.

If we want to apply this conventional procedure to complex mixtures of Class I, we must first ask: what shall we use as our reference system? Having answered that primary question, we can then decide on a suitable model for the perturbation.

One possible answer is to say that we will use the same reference system as that to which we are accustomed from our experience with relatively simple mixtures. For example, for complex liquid mixtures, we can use the ideal mixture (Raoult's Law) as our reference and express the perturbations by some simplified model for nonrandom mixing such as that given by the NRTL equation. Alternatively, we can use Staverman's modification of the athermal Flory-Huggins model for the reference and then express the perturbation with the residual part of the UNIQUAC equation. This procedure has provided some success but it is limited to liquid mixtures of subcritical components.

For hydrogen-bonded systems, we might use a chemical hypothesis by postulating the existence of dimers, trimers, etc. including, perhaps, solvated aggregates (complexes) consisting of chemically different molecules. In this case, we use for our reference system an ideal, athermal solution (either in the sense of Raoult or in the sense of Flory-Huggins) containing not the apparent, but the true species in the mixture; the concentrations of these true species are determined by chemical equilibrium constants and by material balances. When this "chemical" reference system is used, the perturbation is usually small. These "chemical" theories of liquid solutions have been applied with success to a variety of mixtures, especially to liquid mixtures of alcohols and hydrocarbons. However, when applied to Equation (1), these "chemical" theories are also limited to liquid mixtures of subcritical components.

To represent the properties of complex mixtures (Class I) that may contain also supercritical components, we must use Equation (2). Again the same question arises: What shall we use for our reference system?

In recent years there has been progress in applying Equation (2) to complex mixtures. First, suppose we use for such mixtures the familiar reference system, viz. some "hard-sphere" form such as the Carnahan-Starling expression or one of its variations (including, perhaps, the original van der Waals "hard-sphere" expression). In that event, we must include in the perturbation term the effect of orientation, clustering or segregation, i.e. nonrandom mixing. One way to do so is to use in the perturbation the concept of local compositions that has been successful for describing complex liquid mixtures. This procedure must take into account the effect of density, with the following boundary conditions:

At low density, \underline{A} (perturbation) \rightarrow an expression for random mixing.

At high density, \underline{A} (perturbation) \rightarrow an expression for nonrandom mixing.

Another way of stating these boundary conditions is to say that at low densities the expression must give a second virial coefficient that is quadratic in mole fraction while at high densities it must give an expression for the excess Gibbs energy similar to that given by the Wilson or NRTL equations.

Suggestions for calculating \underline{A} (perturbation) as a function of composition have been offered by several authors, notably by Vidal and co-workers, by Mollerup and by Whiting. To illustrate, consider the recent work of Dimitrelis and Topliss who use the simple equation of state:

$$z = \frac{Pv}{RT} = z \text{ (Carnahan-Starling)} - \frac{a\rho}{RT} \quad (3)$$

where, for a pure component, van der Waals "constant" a is an arbitrary function of temperature. Here $\rho = 1/v$ is the molar density.

For the molar perturbation energy U^P , Dimitrelis and Topliss use a generalized van Laar expression of the form

$$U^P = N_{Av} [q_1 x_1 x_{21} (\epsilon_{21} - \epsilon_{21}^0) + q_2 x_2 x_{12} (\epsilon_{12} - \epsilon_{12}^0)] \quad (4)$$

where N_{Av} is Avogadro's number, and q_1 is a size parameter (external surface area of molecule 1). For pure component 1, characteristic energy ϵ_{11} is related to a_{11} through

$$\epsilon_{11} = \frac{-\rho}{N_{Av} q_1} \left(\frac{\partial a_{11} / T}{\partial 1 / T} \right). \quad (5)$$

There is a similar relation for ϵ_{22} .

Note that ϵ_{ij} is a segment-segment energy that depends on temperature (through the effect of temperature on a_{ij}) and is proportional to density.

In Equation (4),

$$\epsilon_{12} = \epsilon_{21} = -(\epsilon_{11} \epsilon_{22})^{1/2} v_{12} \quad (6)$$

and

$$\epsilon_{12}^{\circ} = \epsilon_{21}^{\circ} = (1/2) (\epsilon_{11} + \epsilon_{22}) \quad (7)$$

where v_{12} (an adjustable binary parameter) is dimensionless and of order unity.

The local mole fractions x_{21} and x_{11} are given by a generalization from Guggenheim's quasi-chemical theory:

$$\frac{x_{21}}{x_{11}} = \frac{x_2}{x_1} S_{21} \exp - \left[\frac{(\epsilon_{21} - \epsilon_{21}^{\circ})}{kT} \right] \quad (8)$$

where $x_{21} + x_{11} = 1$ and S_{21} is a density-dependent entropy term which has the properties

$$S_{21} \rightarrow 1 \text{ as } \rho \rightarrow 0 \quad (9)^{\dagger}$$

$$S_{21} \rightarrow r_{21} \text{ as } \rho \rightarrow \text{liquid-like}$$

where r_{21} is a characteristic entropic constant. Similar relations hold for S_{12} : at low densities, $S_{12} \rightarrow 1$ and at liquid-like densities, $S_{12} \rightarrow r_{12} = r_{21}^{-1}$. Dimitrelis and Topliss use an exponential switching function for the density dependence of S_{21} and S_{12} .

The molar perturbation Helmholtz energy \underline{A}^P is calculated by integrating the last term of Equation (3) with respect to density, giving

$$\frac{\underline{A}^P}{RT} = \frac{-(x_1 a_{11} + x_2 a_{22})\rho}{RT} + \frac{\underline{A}^E}{RT} \quad (10)$$

The excess Helmholtz energy \underline{A}^E is obtained by integrating Equation (4) with respect to temperature (Gibbs-Helmholtz equation) giving

$$\begin{aligned} \frac{\underline{A}^E}{RT} = & x_1 q_1 \ln \left(x_1 + x_2 S_{21} \exp \frac{-(\epsilon_{21} - \epsilon_{21}^{\circ})}{kT} \right) \\ & + x_2 q_2 \ln \left(x_2 + x_1 S_{12} \exp \frac{-(\epsilon_{12} - \epsilon_{12}^{\circ})}{kT} \right) \end{aligned} \quad (11)$$

In form (but not in detail), Equation (11) is similar to Wilson's equation. An important feature of Equation (11) is that if $\epsilon_{12} = \epsilon_{21}$ is given by the arithmetic mean of ϵ_{11} and ϵ_{22} , the mixture is athermal.

Parameters q_i are obtained from pure-component structural data, as given, for example in Bondi's tables.

[†]In Guggenheim's theory $S_{21} = S_{12} = 1$ for all densities.

There are two adjustable binary parameters: one is a characteristic energy (v_{12}) and the other is a characteristic entropy (r_{12}). These are, in principle, orthogonal parameters. The second one, r_{12} , reflects orientational effects due to differences in molecular size and asymmetry of intermolecular forces.

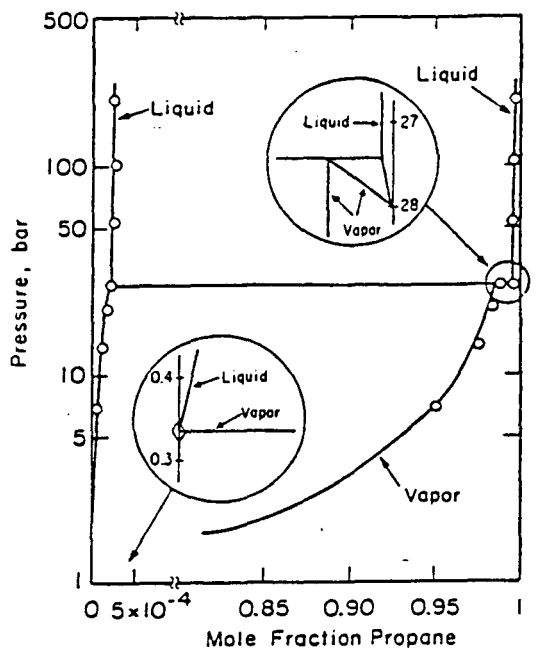
Equation (4) is similar to van Laar's equation if the exponential in Equation (8) is omitted and if S_{21} is replaced by the constant r_{21} . For relatively simple mixtures, $r_{21} = q_2/q_1$. In that event, the entropic constant r_{21} is determined only by differences in molecular size.

Dimitrelis and Topliss applied their theory to vapor-liquid-liquid equilibria for propane(1) - water(2). Figure 1 presents a phase diagram at 344.26K which agrees well with the experimental data at Kobayashi and Katz. The two adjustable binary parameters ($v_{12} = 1.098$ and $r_{12} = 2.60$) are physically reasonable because ϵ_{12} refers to a segment-segment (not molecule-molecule) interaction as indicated by parameter q in the denominator of Equation (5). Parameter r_{12} is close to what one might expect from the molecular-size ratio of propane and water.

Figure 2 shows liquid-liquid equilibria for the same system for a large temperature range using the same (temperature-independent) parameters v_{12} and r_{12} . Agreement with experiment is surprisingly good but could be improved if a small temperature dependence were given to these binary parameters.

The method developed by Dimitrelis and Topliss is shown here only as an illustration. It is likely that other methods, using a similar procedure, could produce better results. Further, in its present state, the method of Dimitrelis and Topliss suffers from a slight inconsistency since thermodynamics requires that the entropic terms S_{12} and S_{21} vary with temperature in a manner consistent with Equation (5). While we are free to assign any convenient density dependence to S_{12} and S_{21} , we are required to assign temperature dependencies to S_{12} and S_{21} which are related to that for ϵ as given by the Gibbs-Helmholtz equation. In the approximation described here, S_{12} and S_{21} are considered independent of temperature.

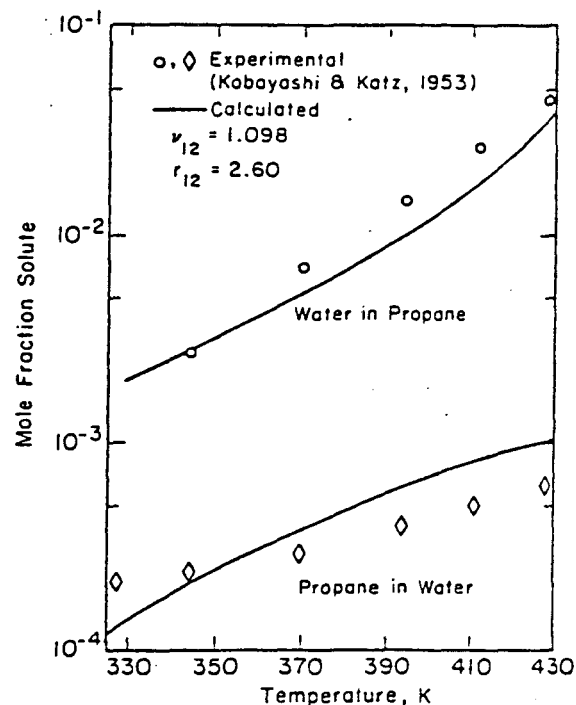
In principle, however, the method proposed by Dimitrelis and Topliss, suffers from a more serious deficiency: it concerns itself only with the perturbation term. For the reference term (Carnahan-Starling), they used a simple one-fluid approximation wherein $b(\text{mixture}) = x_1 b_1 + x_2 b_2$. Computer-simulation calculations by Shing and Gubbins have clearly shown that a one-fluid approximation is poor for mixtures containing molecules of different size, particularly in the dilute region. However, it may be that this deficiency is, in part, cancelled by the entropic contribution of the perturbation; even if $\epsilon_{12} = \epsilon_{12}^0$, \underline{A}^E does not vanish unless, in addition, $S_{12} = S_{21}$.



PHASE DIAGRAM FOR PROPANE (1)-
WATER (2) AT 344.26 K

○ Experimental (Kobayashi & Katz, 1953)
— Calculated
 $v_{12} = 1.098$, $r_{12} = 2.60$

Fig. 1



LIQUID-LIQUID EQUILIBRIA FOR
PROPANE (1)-WATER (2) AT
103.4 BAR

Fig. 2

HELMHOLTZ ENERGY A FOR A "CHEMICAL" SYSTEM

An alternate way to describe both liquid and gaseous complex mixtures is provided by introducing the well-known chemical hypothesis into an expression for Helmholtz energy A. This hypothesis profoundly affects A for the reference system. It has also an effect on the perturbation contribution but the major effect is on the reference system which now is an assembly of "true", rather than "apparent" molecules. The chemical hypothesis assumes that strong forces of attraction lead to new chemically-bonded species. Following recent work of Hu, Azevedo and Lüdecke, we assume that in a mixture of components A and B, there exist chemical equilibria of the form



where A_1 is a monomer, A_2 is a dimer, etc. Each of these chemical equilibria is characterized by a chemical equilibrium constant which depends on temperature but, for simplicity, is assumed to be independent of i .

A possible advantage of the "chemical" hypothesis is that the Helmholtz energy of the reference system now takes into account repulsive forces of the "true" molecules; the number and identity of these "true" molecules depend

strongly on temperature and density. The perturbation Helmholtz energy takes into account only physical forces of attraction between the "true" molecules.

To calculate phase equilibria, we use well-known general relations for the chemical potential μ :

$$\text{for component A, } \mu_A = \mu_{A_1} \quad (15)$$

$$\text{for component B, } \mu_B = \mu_{B_1} \quad (16)$$

A chemical hypothesis was used many years ago to represent thermodynamic properties of liquid mixtures or of moderately dense gases (second virial coefficients) but only recently has this hypothesis been applied toward an equation of state for fluids at low and high densities (Heidemann; Wenzel and co-workers; Gmehling and Liu). A systematic general treatment has now been provided by Hu, Azevedo and Lüdecke who used a Carnahan-Starling expression for the repulsive contribution and a simple van der Waals expression for the contribution of (physical) forces of attraction. Through reasonable but well-chosen simplifying assumptions, Hu and co-workers have very much simplified the complicated algebra to obtain a tractable analytical method which requires no numerical integrations and which is applicable to multicomponent as well as binary mixtures. In this treatment, the maximum degree of polymerization can be arbitrarily set anywhere from 2 to infinity. It is advantageous to use infinity since, in that event, the algebra is simplified because material balances are replaced by easily-summed geometric series.

The chemical potential μ_{A_1} has the form

$$\mu_{A_1} = \mu_{A_1}^{\text{ref}} \left[\left(\frac{n_T}{n_0} \right), \xi, T, \left(\frac{n_{A_1}}{n_0} \right) \right] + \mu_{A_1}^p \left[\left(\frac{n_T}{n_0} \right), \xi, T, \frac{\hat{a}}{b} \right] \quad (17)$$

$$\text{where reduced density } \xi = \frac{n_T \hat{b}}{V} = \frac{n_0}{V} \left(x_A b_{A_1} + x_B b_{B_1} \right),$$

a_1 and b refer to van der Waals constants and

$$\frac{\hat{a}}{b} = \frac{x_A^2 a_{A_1} + x_B^2 a_{B_1} + 2x_A x_B \sqrt{a_{A_1} a_{B_1}}}{x_A b_{A_1} + x_B b_{B_1}} \quad (18)$$

Here n_T is the total number of true moles and x is the (apparent) mole fraction. The ratio n_T/n_0 is found from ξ , T and the chemical equilibrium constants.

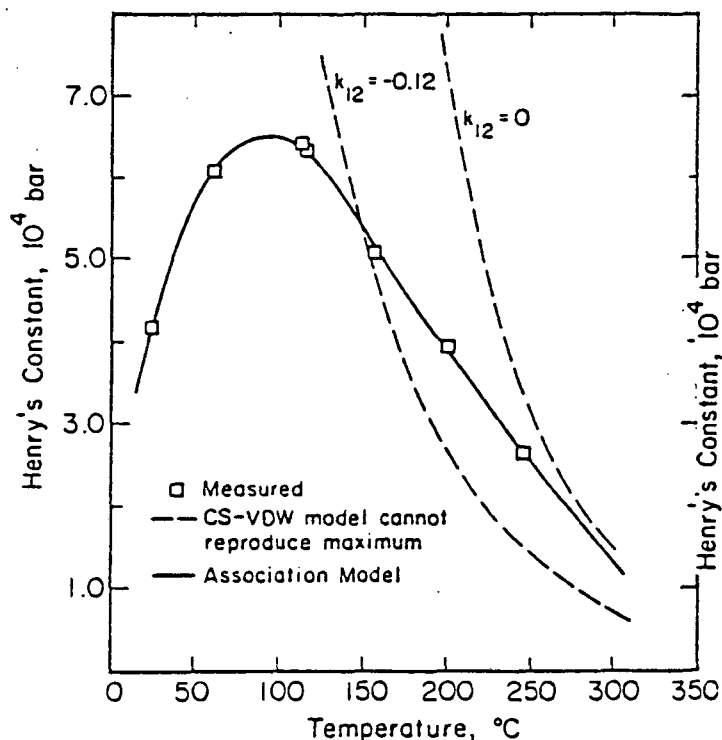
The most sensitive test of any theory is to apply it to the dilute region. Therefore, Hu and co-workers used their method to calculate Henry's constants for nonpolar solutes in water. First, it was necessary to obtain equation-of-state parameters for pure water and, as so often happens, it was found that several sets of physically reasonable parameters could equally well represent the properties of gaseous and liquid water over a wide temperature range. To obtain a unique set, Hu used experimental data for Henry's constant of methane in water, arbitrarily setting the usual binary parameter $k_{12} = 0$.

[Here k_{12} is defined in the usual way: $a_{12} = (a_{11}a_{22})^{1/2}(1-k_{12})$, where van der Waals parameter a_{11} is for the attractive forces in pure methane and parameter a_{22} is for the "physical" attractive forces between water monomers; the strong "chemical" forces between water molecules are reflected in the chemical equilibrium constant for association.]

Figure 3 shows Henry's constants for methane in water over a wide temperature range. It is particularly gratifying that the calculated results correctly reproduce the maximum. When a simple equation of state (without chemical effects) is used with customary mixing rules, it is not possible to reproduce the experimentally observed maximum.

Figures 4 and 5 show Henry's constants for other gases in water. The indicated values of k_{12} are reasonable when we recall that they are relative to the arbitrarily chosen $k_{12} = 0$ for methane.

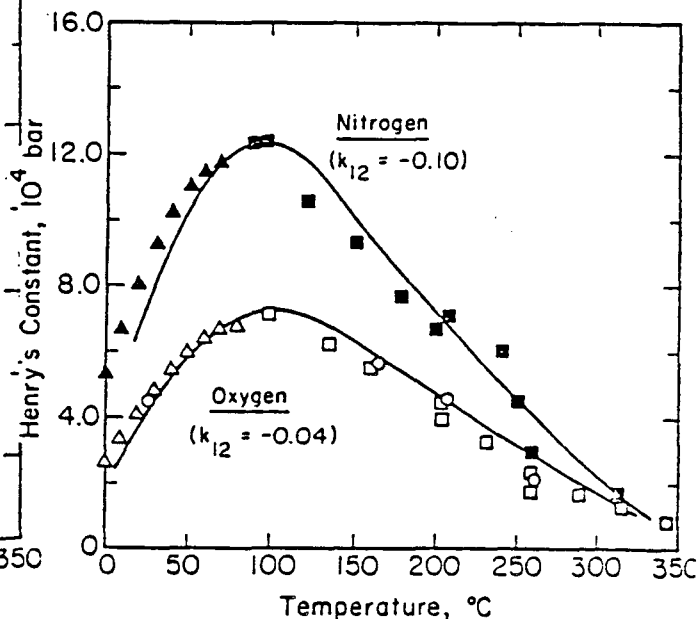
Figure 5 indicates a small but significant displacement for the largest solute, xenon. Such displacement is even more pronounced for hydrogen (whose molecules are much smaller than those of water) and for benzene (whose molecules are much larger than those of water), as indicated in Figure 6. These results suggest that the chemical method, while offering improvement over strictly "physical" theories, does not allow us to escape from the fundamental problem: What reference system shall we use for mixtures of molecules that differ appreciably in size? Hu and co-workers took into account formation of dimers, trimers, etc. but they retained the one-fluid approximation for the repulsive term. The computer-simulation studies of Shing and Gubbins suggest that this approximation is untenable, especially for Henry's constants, even though the strong orientation forces in water (association) were included in the reference system.



HENRY'S CONSTANT FOR METHANE IN WATER

Methane is used as a probe to determine the chemical equilibrium constant for water. (k_{12} is arbitrarily set equal to zero.)

Figure 3

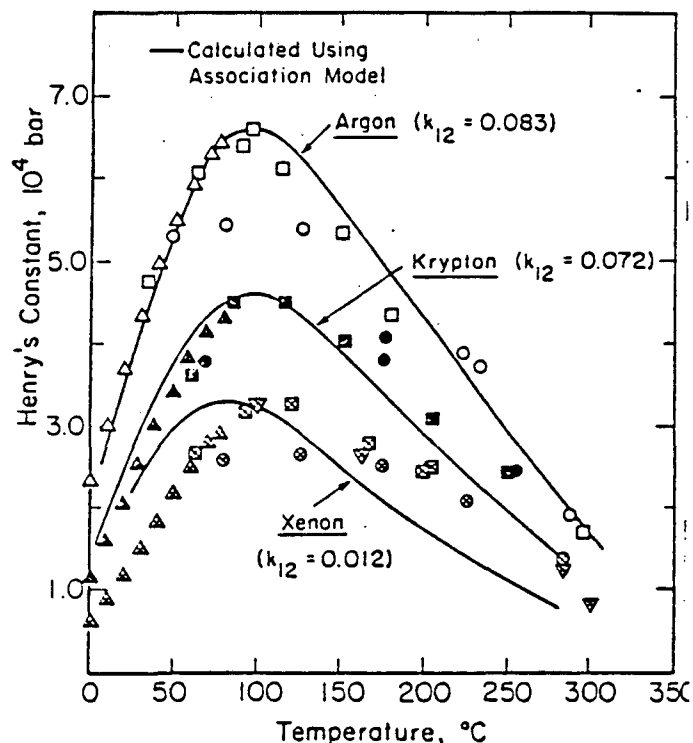


HENRY'S CONSTANTS FOR TWO GASES IN WATER

Figure 4

For complex mixtures of Class I, it is relatively easy to introduce ad hoc phenomenological modifications into the perturbation term; no doubt, many will be suggested in the next few years. What is more difficult—but ultimately more important—is to establish a good reference system for such mixtures. The chemical method provides a possible route provided that judicious simplifying assumptions are adopted to reduce the tedious algebra. However, the central problem—mixtures containing molecules of different size—remains.

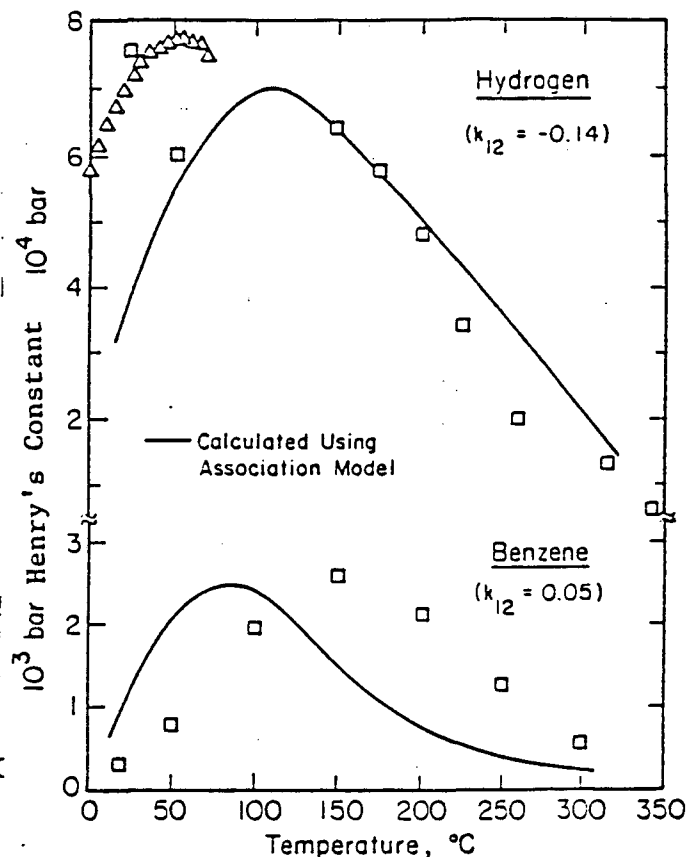
The only theoretically significant analytical method for mixtures of different-sized, non-attracting molecules is that given by Mansoori (who generalized the Carnahan-Starling equation to mixtures) and its extension to mixtures of convex non-spherical molecules by Boublik and by Naumann. Unfortunately, these methods require tedious algebra, although it is still small compared to that in the Chandler-Anderson-Weeks theory. For engineering purposes, our first need is to establish a mathematically simple expression which can approximate the properties of a mixture containing non-attracting molecules of different size and shape over the entire range of fluid densities. Our second need is to devise a theoretically sound method for incorporating size effects in the perturbation term.



HENRY'S CONSTANTS FOR THREE NOBLE GASES IN WATER

Note systematic horizontal displacement for xenon where solute-solvent size difference is largest.

Fig. 5



EFFECT OF MOLECULAR SIZE ON HENRY'S CONSTANT IN WATER

Calculated Henry's Constants obtained by adjusting k_{12} to give experimental maximum. Note required shift to left for (small) hydrogen, to right for (large) benzene. This suggests a systematic error in the the calculated entropy of mixing.

Fig. 6

Class II: Characterization

We now turn attention to the second class of complex mixtures, i.e. those where the molecules are not identified. In chemical engineering practice, such mixtures commonly appear in the technology of heavy fossil fuels. To describe the thermodynamic properties of such mixtures, we must first perform an approximate chemical analysis to determine at least partial information concerning the nature and concentrations of the molecules present. This approximate analysis is called characterization.

Gibson, Alexander and Chough have recently described a possible technique for characterization which is intermediate between the simplistic methods introduced fifty years ago (e.g. Watson characterization factor) and the highly sophisticated methods of modern analytical chemistry: the complex mixture is first fractionated by distillation in a spinning-band column operating at low pressure and high reflux. Typically, eight or ten fractions are obtained. When a fraction is removed, the temperature and pressure are noted, giving one vapor-pressure datum.

Each fraction is characterized by measuring: the number-average molecular weight (cryoscopy); ratios of carbon, hydrogen, nitrogen, sulfur and oxygen, (elemental analysis); aromaticity (proton-nuclear-magnetic resonance); and, for fractions with high hetero-atomicity, concentrations of hydroxyl, primary amine and secondary amine groups (infra-red spectroscopy). These characterization data for each fraction are then used to calculate constants in some equation of state. Each fraction is considered to be a pseudocomponent. Vapor-liquid equilibria are then calculated in the usual way.

To illustrate, characterization data have been used to calculate constants in a modification of the Soave-Redlich-Kwong equation of state:

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)} \quad (19)$$

where

$$a(T) = a^{(1)} [1 + a^{(2)}(1 - T/T^*)^n]^2 \quad (20)$$

$$T^* = (0.2027)a^{(1)}/Rb$$

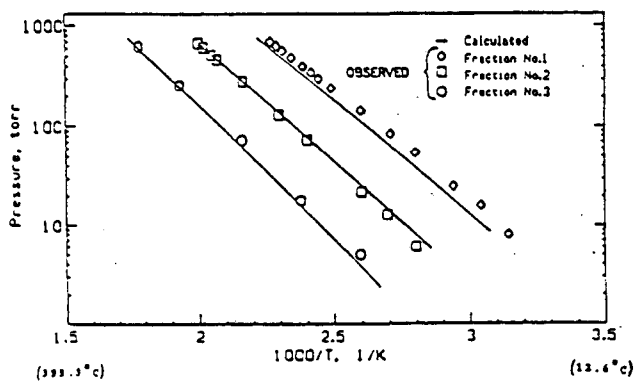
For pure fluids, Soave uses $n = 0.5$. Constants b , $a^{(1)}$ and $a^{(2)}$ are known for model compounds whose characterization data are also known by inspection. Therefore, using model-compound data for calibration, correlating equations were obtained relating these constants to characterization data: these are of the form

$$\begin{aligned} b &= b(\text{MW}, \text{FA}, \text{HA}) \\ a^{(1)} &= a^{(1)}(\text{MW}, \text{FA}, \text{HA}) \\ a^{(2)} &= a^{(2)}(\text{MW}, \text{FA}, \text{HA}) \end{aligned} \quad (21)$$

where MW = molecular weight, FA = fraction aromaticity and HA = hetero-atomicity. Exponent n is then determined by matching the single experimental vapor-pressure datum to the vapor pressure calculated from the equation of state.

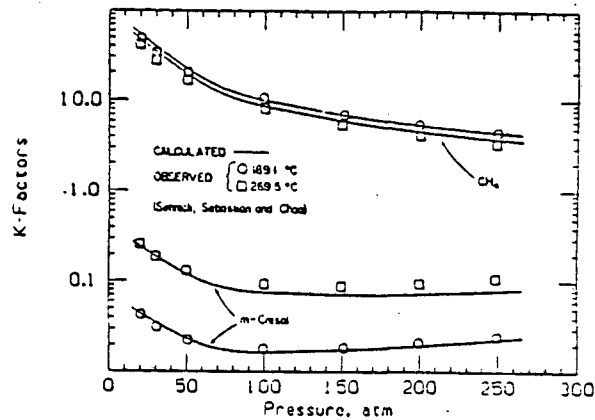
For light components (e.g. methane or carbon dioxide), all constants are found as specified by Soave.

For three fractions obtained from Belridge Crude, Figure 7 compares calculated and observed vapor pressures. Calculations were performed with Equation (19) using constants obtained from characterization data. While agreement is generally good, it is clear that there is a systematic deviation for Fraction 1, probably because the vapor-pressure datum from the spinning-band column was not obtained at the same conditions as those prevailing in the vapor-pressure measurements; since each fraction is itself a narrow-boiling mixture, there is no unique vapor pressure at a fixed temperature because, for a mixture, bubble point and dew point are not identical. The characterization



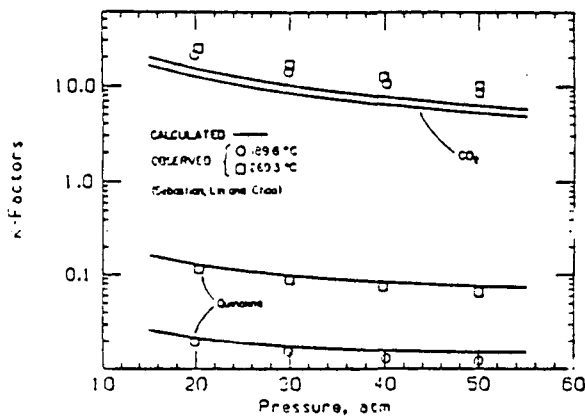
Calculated and Observed Vapor Pressures for Belridge Crude Oil Fractions (Parameter n from Datum at 760 torr).

Fig. 7



Predicted K-Factors for CH₄ + m-Cresol. Calculations with Generalized Parameters from Characterization Data with $k_{12} = 0$.

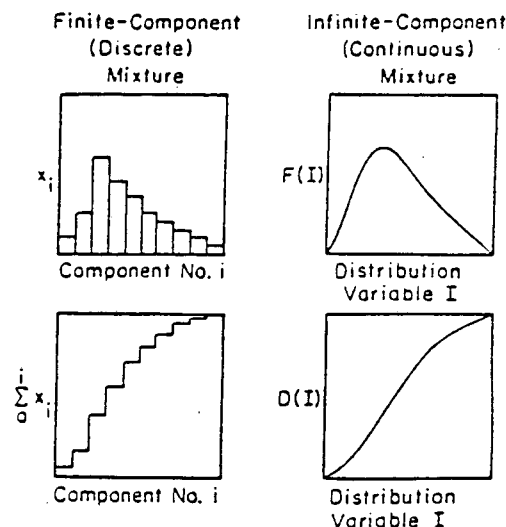
Fig. 8



Predicted K-Factors for CO₂ + Quinoline. Calculations with Generalized Parameters from Characterization Data with $k_{12} = 0$.

Fig. 9

DISCRETE AND CONTINUOUS COMPOSITION FOR A MULTICOMPONENT MIXTURE



$\sum_{\text{all } i} x_i = 1.0$ $D(I=\infty) = \int_0^{\infty} F(I)dI = 1.0$

x = Mole Fraction F = Distribution Function
 I is a characterizing quantity, e.g., molecular weight.

Fig. 10

procedure, therefore, is in need of some refinement or, more precisely, we must more carefully define what we mean by the vapor pressure of a fraction, as discussed elsewhere.

We do not as yet have any experimental data for K-factors in mixtures of characterized fractions with common gases but we can calculate such K-factors using Equation (19) with constants obtained from characterization data and the usual mixing rules; here the K-factor is defined in the usual way as the ratio of mole fractions in the two phases. To illustrate, Figure 8 shows K-factors for methane-metacresol and Figure 9 shows K-factors for carbon dioxide-quinoline. The important point here is that constants for the heavy components were obtained not from critical data and acentric factors, but from characterization data. For our present illustrative purposes, the usual binary parameter k_{12} was set equal to zero. It is evident that for carbon dioxide-quinoline, a small positive value for k_{12} would bring the calculated results into essential agreement with experiment. Figs. 8 and 9 suggest that if fractions are properly characterized, they can be treated as pseudocomponents in conventional phase-equilibrium calculations based on an equation of state.

Class II: Continuous Thermodynamics

While the finite-pseudo-component method provides a useful technique for calculating phase equilibria in a complex mixture, an alternate technique is provided by infinite-component, continuous thermodynamics. In finite-component (discrete) thermodynamics, the composition of the mixture is given by mole fractions. In infinite-component (continuous) thermodynamics, the composition of the mixture is given by a distribution function of some continuous variable chosen to characterize the mixture. Fig. 10 illustrates the correspondence between discrete and continuous thermodynamics.

Let I stand for the characterizing variable and let $F(I)$ stand for the distribution of that variable. For example, I could be the normal boiling point τ . As shown by Rätzsch and Kehlen, for a mixture with an infinite number of components, we can reformulate Raoult's Law at temperature T and total pressure P

$$F^V(\tau) P = F^L(\tau) p^{\text{sat}}(T, \tau) \quad (22)$$

where F^V is the distribution in the vapor phase and F^L is the distribution in the liquid phase. The pure-component vapor pressure p^{sat} is given by the simple form

$$p^{\text{sat}}(T, \tau) = P_0 \exp [A(1 - \tau/T)] \quad (23)$$

where P_0 is 1 atm and A is a constant.

At temperature T , the total pressure P is the sum of all the partial pressures

$$P = \int_{\text{all } \tau} F^L(\tau) p^{\text{sat}}(T, \tau) d\tau \quad (24)$$

Suppose we choose a normal distribution for $F^L(\tau)$ with mean θ_L and variance σ_L^2 . It can then be shown that the vapor-phase distribution $F^V(\tau)$ is also normal with mean

$$\theta_V = \theta_L - \sigma_L^2 A/T \quad (25)$$

The vapor-phase variance σ_V^2 is the same as the liquid-phase variance σ_L^2 .

More generally, as indicated by Morrison and Kincaid, we can apply an equation of state to calculate phase equilibria using continuous thermodynamics. Instead of writing for chemical potential μ :

$$\mu_i^V = \mu_i^L \quad \text{for every component } i, \quad (26)$$

we write

$$\mu^V(I) = \mu^L(I) \quad \text{for every } I. \quad (27)$$

Omitting those ideal-gas contributions which depend only on temperature, the chemical potential in phase L is found from

$$\mu^L(I) = \int_{V^L}^{\infty} \left[\left(\frac{\partial P}{\partial n_T F(I)} \right)_{T, V, I} - \frac{RT}{V} dV \right] - RT \ln \frac{V^L}{RT n_T F(I)} \quad (28)$$

where n_T = total number of moles (conveniently set equal to unity). A similar relation is used for vapor phase V .

To illustrate the application of continuous thermodynamics, Cotterman used the Redlich-Kwong equation of state coupled with molecular weight MW for variable I . Using experimental data for paraffins, Cotterman found that RK constants $a^{1/2}$ and b are nearly linear functions of MW .

To describe the distribution of MW , Cotterman used a gamma density function

$$F(I) = \frac{I^{\alpha-1}}{\beta^{\alpha} \Gamma(\alpha)} \exp(-I/\beta) \quad (29)$$

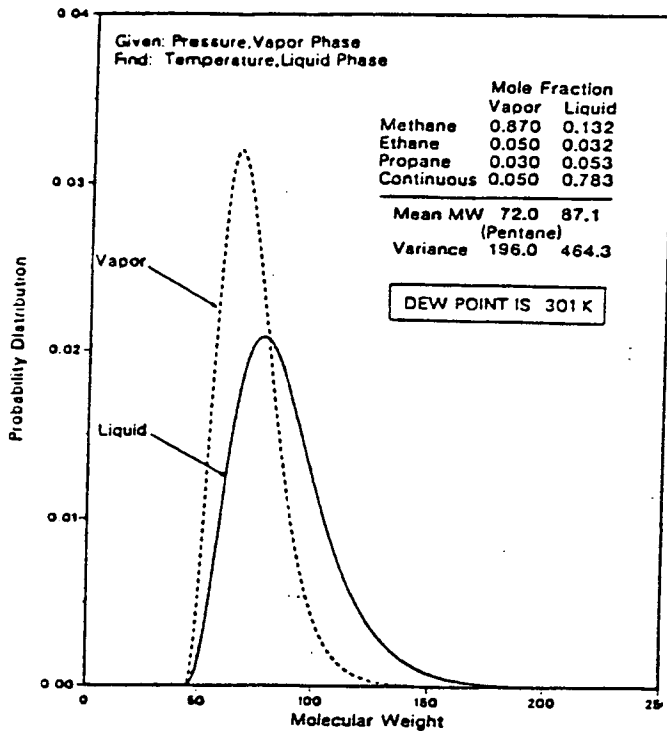
where Γ is the gamma function. For this distribution, the mean θ is given by $\theta = \alpha\beta$ and the variance is $\sigma^2 = \alpha\beta^2$.

This distribution has the properties

$$F(0) = 0 \text{ and } F(\infty) = 0 \quad (30)$$

$$\int_0^{\infty} F(I) dI = 1 \quad (31)$$

PHASE EQUILIBRIA IN A
SEMI-CONTINUOUS REDLICH-KWONG FLUID
Dew-Point Calculation at 20 atm



PHASE EQUILIBRIA IN A
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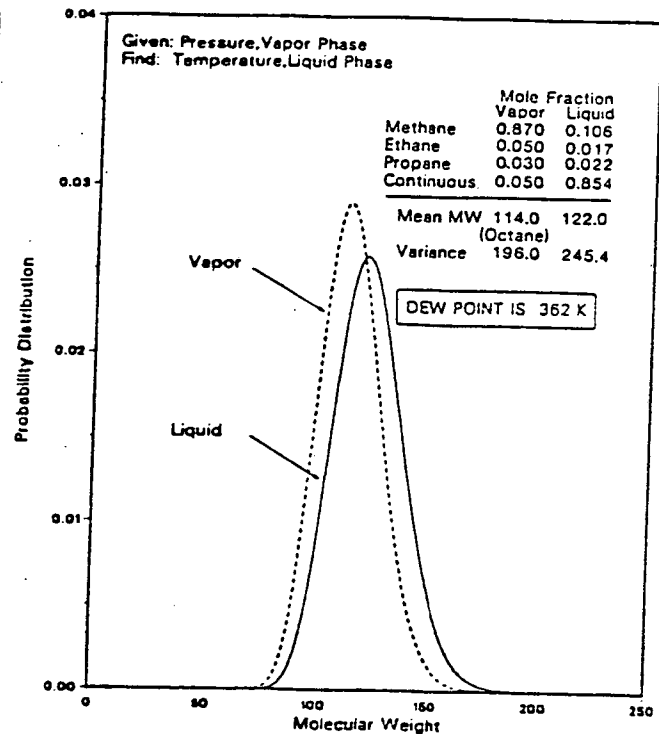


Fig. 11

It is also possible to use this function for a semi-continuous case wherein all species up to some molecular weight γ are treated as discrete components and all heavier components are treated in a continuous manner. In that event, the distribution function is

$$F(I) = \frac{(I-\gamma)^{\alpha-1}}{\beta^{\alpha}\Gamma(\alpha)} \exp\left(-\frac{I-\gamma}{\beta}\right) \quad (32)$$

Dew-point calculations have been performed for the case where a vapor at 20 atm contains methane (87 mole %), ethane (5%), propane (3%) and 5% "heavies". If we assume that the mean molecular weight of the "heavies" is 72 (pentane), and the variance is 196, the calculated dew point is 301 K. However, if we assume that the mean molecular weight of the heavies is 114 (octane), and the variance is again 196, the calculated dew point is appreciably higher, 362 K. Figs. 11 and 12 give some details for these calculations, including the (given) distribution of "heavies" in the vapor and the calculated distribution of "heavies" in the equilibrium liquid.

CONCLUSIONS

To discuss the properties of complex systems we must first be clear about the definition of "complex". If we define complex in the sense of Class I, our main problem is to decide first, on a suitable reference system and second, on a suitable perturbation, consistent with our choice of reference system. Current efforts are directed toward application of equations of state, using either density-dependent mixing rules or else chemical equilibria superimposed on the usual physical nonidealities of mixtures. Both procedures introduce new adjustable parameters but, through reasonable simplifying assumptions, the number of these new parameters can be minimized.

If we define complex in the sense of Class II, our main problem is first, to devise useful experimental methods for characterizing the mixture and second, to decide on a procedure for calculating thermodynamic properties as a function of experimental characterization data. One procedure is provided by the pseudocomponent method; another is provided by continuous thermodynamics. Both procedures require calibration with experimental data for model compounds.

While the methods for complex mixtures outlined here are, in principle, straight-forward extensions of methods that have been used for many years, we require more practical experience with these extended methods before they can be used in chemical industry in a routine way. It is likely that this experience will be forthcoming in the next few years.

However, for complex mixtures, we should not be satisfied with mere extension of existing methods for simple mixtures. The history of science has repeatedly shown that when new problems arise, extensions of methods previously used for simple problems have only limited success; to make significant progress, new methods must be established. Perhaps the best example is provided by the state of affairs in physics at the end of the nineteenth century when classical methods failed to do justice to newly discovered phenomena. It was not until a radically new method (quantum theory) was developed, that these new phenomena could be properly described.

Complex fluid mixtures are not new phenomena but it may be that their proper description will require radically new models. Hopefully, some of our more imaginative colleagues will attempt to establish such models. For these colleagues, I call attention to a profound sentence written about 100 years ago:

"The principal object of theoretical research in any department of knowledge is to find that point of view from which the subject appears in its greatest simplicity."

That sentence was written by Josiah Willard Gibbs.

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LITERATURE CITED

- Boublik and Lu, J. Phys. Chem. 82 2801 (1978).
Cotterman and Prausnitz, work in progress.
Dimitrelis, Topliss and Prausnitz, work in progress. See Dimitrelis and Prausnitz, paper presented at Annual Meeting of AIChE, Los Angeles (1982).
Gibson, Alexander, Chough and Prausnitz, submitted to IEC Proc. Des. & Dev. Quarterly.
Gmehling, Liu and Prausnitz, Chem. Eng. Sci. 34 951 (1979).
Heidemann and Prausnitz, Proc. Nat. Acad. Sci. 73 1773 (1976).
Hu, Azevedo, Lüdecke and Prausnitz, work in progress.
Mansoori, Carnahan, Starling and Leland, J. Chem. Phys. 54 1523 (1971).
Mollerup, Fluid Phase Equilibria 7 121 (1981).
Morrison, Kincaid and Gualtieri, J. Chem. Phys. 77 521 (1982).
Naumann, Chen and Leland, Ber. Bunsenges. 85 1029 (1981).
Rätzsch and Kehlen, Proc. 6th Int. Conf. on Thermo., Merseburg (GDR) p. 41 (1980).
Shing and Gubbins, Dissertation of K. Shing, Cornell Univ. (1982) and Mol. Physics, in press.
Wenzel, Moorwood and Baumgartner, Fluid Phase Equilibria 9 22 (1982).
Vidal and Huron, Fluid Phase Equilibria 3 255 (1979).
Whiting and Prausnitz, Fluid Phase Equilibria 9 119 (1982).

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