Perturbation Methods for Calculating Properties of Liquid Mixtures

Perturbation methods relate thermodynamic and transport properties of the system of interest (gas or liquid) to the known properties of some reference system; commonly used reference substances are hard sphere fluids and argon. Developments since 1967 are reviewed for both types of approach, with emphasis on applications to liquid mixtures of practical interest. Calculations for liquid mixtures of simple and complex molecules, gas solubility in liquids, fused salts, electrolytes, solvent extraction systems, and liquid metals are reviewed.

KEITH E. GUBBINS
Chemical Engineering Department
University of Florida
Gainesville, Florida 32601

SCOPE

Equations relating thermodynamic and transport properties of liquid mixtures to the forces between molecules are provided by statistical mechanics. These equations are solved easily for gases at low to moderate pressures (to give the virial series and the Chapman-Enskog expressions) but are difficult for dense gases and liquids. This difficulty occurs because each molecule interacts via intermolecular forces with a large number (typically 10) of neighboring molecules. Until 1967 the only methods available for liquids involved tedious numerical calculations, and the methods were only applicable to simple liquids, such as argon. As a consequence, most chemical engineering correlations for solution properties have been based either on empirical equations (for example, the Wilson equation) or on simplified models such as lattice models and regular solution theory.

Since 1967 there have been rapid advances in methods for calculating liquid properties from statistical mechanics. These methods, collectively termed perturbation methods, are relatively easy to use and can be applied to liquid mixtures of chemical engineering interest. The idea in these approaches is somewhat similar to that used in the corresponding states principle, in that properties of the liquid of interest are calculated from the known properties of some other gas or liquid (the reference system). Perturbation theory is more powerful than corresponding states, however, because the intermolecular forces between molecules in the mixture need not all be of the same type, nor need they be of the same type as those of the reference system. Thus it is possible to deal with solutions such as electrolytes containing dissolved gases or liquids, extractant phases in solvent extraction, liquid metals, fused salt mixtures, etc., where several different force laws are present simultaneously.

Three types of perturbation method are described in this review. In the first, the reference system is a fluid of hard spheres. The properties of such fluids are well understood from computer simulation studies and are available in the form of both analytic equations and tables. The second method relates the properties of a mixture of conformal substances (that is, the pure components obey a simple corresponding states law) to the properties of a pure system. The final method takes account of the effects of molecular nonsphericity and uses a simple liquid such as argon as a reference.

CONCLUSIONS AND SIGNIFICANCE

A hard sphere reference system provides equations that are highly flexible, in the sense that they can be applied to a wide variety of liquid mixtures. In the last two years excellent results have been obtained for thermodynamic properties of organic liquid mixtures, gases dissolved in mixed solvents (including electrolytes), solvent extraction systems, liquid metals, and electrolytes. This versatility occurs because the theory is not limited to any particular type of intermolecular force law. Further development of these methods can be expected in the near future. There is a strong need for more applications to liquids of complex molecules, for example, liquid metal mixtures, fused salts, electrolytes, and polymer solutions.

The conformal solution theories involve perturbation about a pure fluid reference system. They are somewhat easier to use than theories based on hard sphere fluids, but can only be used for systems in which all components interact with a single intermolecular force law. Thus they give good results for many organic liquid mixtures containing similar components, but would be difficult to apply to gases dissolved in fused salts or electrolytes, for example. They have been used to correlate thermodynamic properties of both organic liquid mixtures and fused salt mixtures.

Perturbation methods which account for the nonspherical shape of molecules have received relatively little attention, but work in progress is expected to yield useful correlations. The prediction of excess entropies, viscosities, and thermal conductivities in mixtures of polar and hydrogen-bonded liquids, for example, should be much

improved when these methods are more fully developed.

Certain physical properties have received little attention so far. Examples are transport and surface properties, although work is in progress on both of these. The rapid development of this subject over the last few years has provided a rather bewildering literature by authors of diverse backgrounds and interests. There is a need for chemical engineers to distill out of this potpourri the most useful results and to reduce them to engineering correlations for use in design.

The most significant advance in the statistical thermodynamics of liquids in the last few years has been the rapid development of perturbation theories of various types. These theories enable properties of the real system of interest to be calculated from the known properties of some reference system. Although this idea had been in existence at least from the time of van der Waals, it was first expressed in terms of modern statistical mechanics in the early 1950s. Zwanzig (1954) showed how the properties of a dense fluid could be calculated from the properties of a hypothetical fluid of hard spheres; Pople (1954) considered an expansion of the free energy of a system of nonspherical molecules about that for a system of spherical molecules (for example, argon); and Longuet-Higgins (1951) expanded the free energy of a liquid mixture about that of an ideal solution. None of these developments aroused great interest at the time because it was assumed that they would only work for very small perturbations. For example, Zwanzig's method only appeared to work for hot, dense gases, and Longuet-Higgins method (conformal solution theory) seemed to only apply to near-ideal solutions. The renewed interest in these approaches dates from about 1967 and arises mainly because of the realization that they are highly successful provided that (1) the reference is chosen carefully, and (2) the expansion is carried out in the best way. Thus Barker and Henderson (1967) were able to modify Zwanzig's method by changing the expansion procedure, and obtained excellent results even for liquids. A similar improvement has been achieved in the conformal solution theory of Longuet-Higgins by Leland, Sather, and Rowlinson (1968) by changing both the reference fluid and the expansion procedure.

In contrast to some earlier theories of liquids, the perturbation approach is not limited to simple fluids such as argon. It has already been applied to organic liquids, solutions used in solvent extraction, electrolyte solutions, fused salts, liquid metals, and polymer solutions. The theory provides a single framework for deriving both new and older approaches to a variety of problems. Conformal solution theories, for example, were previously derived by a potpourri of nonrigorous methods; now, however all of these theories can be derived in a few lines using the perturbation method, and can also be extended and improved.

This paper presents a broad review of recent developments, with emphasis on fluids of practical interest. While the physical ideas of the theory are presented, other sources should be consulted for detailed derivations. No attempt is made to compare the various ways of carrying out the expansion (the so-called "λ-expansion", "γ-expansion", "mode expansion", "variational method", etc.); these methods are similar in principle, and the λ-expansion of Barker, Henderson, and co-workers is therefore used throughout since it is the simplest and most widely used. Several reviews of the basic theory have appeared recently (Mansoori and Canfield, 1970; Stell, 1970; Barker and Henderson, 1971b; Henderson and Leonard, 1971b; Smith, 1973); the reviews by Henderson and Leonard (1971) and Smith (1973) are particularly complete. Rigby (1970) has reviewed van der Waals models.

ELEMENTS OF STATISTICAL THERMODYNAMICS

The Helmholtz free energy A of the system is conveniently separated into two parts

$$A = A' + A^c \tag{1}$$

where A^c is the configurational free energy, and is affected by the intermolecular forces; A' is the part of the free energy due to other molecular energy forms, such as molecular kinetic energy, bond vibrations, and so on. Part A' is independent of the density and is therefore the same for the real fluid or solid as for an ideal gas. Since the properties of ideal gases are well known, we need only concern ourselves with the configurational contribution A^c. This portion of A accounts for all deviations from ideal gas behavior; it is not zero for the ideal gas ($\mathcal{U} = 0$), however, but takes the value $-NkT \ln V$. Statistical mechanics gives the relation between A^c and intermolecular forces as

$$A^c = -kT \ln Z \tag{2}$$

where

$$Z(N, V, T) = \int_0^V \ldots \int_0^V e^{-\mathcal{U}/kT}\, d\mathbf{r}_1 d\mathbf{r}_2 \ldots d\mathbf{r}_N \tag{3}$$

Z is called the configuration integral, and $\mathcal{U}$ is the total potential energy due to the intermolecular forces; $d\mathbf{r}_1$ is a volume element in the fluid containing molecule one, and so on. Equation (3) assumes that the intermolecular forces, and hence $\mathcal{U}$, depend only on the positions $\mathbf{r}_1\mathbf{r}_2 \ldots \mathbf{r}_N$ of the centers of the molecules, and not, for example, on their orientation or on the vibrational state. This assumption causes some error for highly nonspherical molecules and is further discussed below. Equation (3) also requires modification for quantum fluids (notably H_2 and He at low temperature), but this restriction is unimportant in the present discussion. Equations (1) to (3) hold for pure substances or mixtures; in the case of mixtures Z depends on composition as well as N, V and T, because $\mathcal{U}$ is composition dependent. Once A^c has been evaluated from some suitable theory, other thermodynamic properties can be evaluated using the usual relationships, for example,

$$S^c = -\left(\frac{\partial A^c}{\partial T}\right)_{V,N_\alpha} \tag{4}$$

$$P^c = -\left(\frac{\partial A^c}{\partial V}\right)_{T,N_\alpha} \tag{5}$$

$$U^c = -T^2\left(\frac{\partial A^c/T}{\partial T}\right)_{V,N_\alpha} \tag{6}$$

$$\mu_\alpha{}^c = \left(\frac{\partial A^c}{\partial N_\alpha}\right)_{T,V,N_{\beta \neq \alpha}} \tag{7}$$

The potential energy $\mathcal{U}$ appearing in (3) is usually assumed to be the sum of pair potentials

$$\mathcal{U} = \frac{1}{2} \sum_{\alpha}^{r} \sum_{\beta}^{r} \sum^{N_\alpha} \sum_{i \neq j}^{N_\beta} \phi_{\alpha\beta}\,(r_{ij}) \qquad (8)$$

where $\phi_{\alpha\beta}\ (r_{ij})$ is the intermolecular potential between molecule i of component α and molecule j of component β, and the ½ factor accounts for the fact that the summations count each interaction twice. The assumption of pairwise additivity does not usually lead to errors of more than a few percent, at most, in the calculation of physical properties (Rowlinson, 1969).

Equations (2) to (7) relate thermodynamic properties to the configuration integral. An alternative, but equivalent, approach is to relate configurational properties to distribution functions. These functions give the probability that a set of molecules will be found at a particular set of relative positions at any instant. For example, the pair (or radial) distribution function $g_{\alpha\beta}(r)$ gives a measure of the probability that two molecules, one of component α and one of component β, will be found at a distance r apart. It is related to the intermolecular forces by the equation

$$g_{\alpha\beta}(r) = \frac{\rho_{\alpha\beta}(r)}{\rho_\beta} = \frac{V^2}{Z} \int_0^V \ldots \int_0^V e^{-\mathcal{U}/kT}\, dr_3 \ldots dr_N \qquad (9)$$

where $\rho_{\alpha\beta}(r)$ is the number density of β-molecules at distance r from a central α-molecule, and $\rho_\beta = N_\beta/V$ is the bulk number density of β-molecules. In the last form of Equation (9) the integrations omitted are those over the position of molecule 1 of component α and that of molecule 1 of component β. The equations relating thermodynamic properties to distribution functions are given by Kirkwood and Buff (1951), Buff and Brout (1955), O'Connell (1971), and Reed and Gubbins (1973).

PERTURBATION ABOUT HARD SPHERES

General Approach

Suppose that the system of interest contains N molecules at volume V and temperature T, and consists of components $a, b, c \ldots r$ with mole fractions $x_a, x_b \ldots x_r$. The intermolecular potential in this real system is $\phi_{\alpha\beta}(r)$ for an $\alpha\beta$ pair. We wish to relate the properties of this system to those of a reference system which is also a mixture of r components at state condition $(N, V, T, x_a, x_b, \ldots x_r)$, but in which the intermolecular potentials are $\phi_{\alpha\beta}{}^{\text{ref}}(r)$. The perturbation in the potential $\phi_{\alpha\beta}{}^{p}(r)$ is just the difference $(\phi_{\alpha\beta} - \phi_{\alpha\beta}{}^{\text{ref}})$. We now introduce a potential $\phi_{\alpha\beta}(r;\lambda)$, defined by

$$\phi_{\alpha\beta}(r;\lambda) = \phi_{\alpha\beta}{}^{\text{ref}}(r) + \lambda\, \phi^{p}{}_{\alpha\beta}(r) \qquad (10)$$

When $\lambda = 1$ Equation (10) gives the potential of the real system; $\lambda = 0$ gives the potential of the reference system. The configurational Helmholtz free energy for the real system is now obtained from a Taylor series expansion of A^c about $\lambda = 0$:

$$A^c = (A^c)^{\text{ref}} + \lambda \left(\frac{\partial A^c}{\partial \lambda}\right)_{\lambda=0} + \frac{1}{2!}\lambda^2 \left(\frac{\partial^2 A^c}{\partial \lambda^2}\right)_{\lambda=0} + \ldots . \qquad (11)$$

where $(A^c)^{\text{ref}}$ is the free energy of the reference system. The first-order perturbation term $(\partial A^c/\partial\lambda)_{\lambda=0}$ is evaluated by replacing $\mathcal{U}$ in (3) by a sum of pair potentials $\phi_{\alpha\beta}(r;\lambda)$, and differentiating. From Equation (2), (3), (9), and (10), it is found that

$$\left(\frac{\partial A^c}{\partial \lambda}\right)_{\lambda=0} = 2\Pi\rho^2 V \sum_{\alpha=a}^{r} \sum_{\beta=a}^{r} x_\alpha x_\beta \int_0^\infty \phi^{p}{}_{\alpha\beta}(r)\, g_{\alpha\beta}{}^{\text{ref}}(r)\, r^2\, dr \qquad (12)$$

Putting $\lambda = 1$ to recover the real system, Equations (11) and (12) give first-order expression for the free energy:

$$A^c = (A^c)^{\text{ref}} + 2\Pi\rho^2 V \sum_{\alpha} \sum_{\beta} x_\alpha x_\beta \int_0^\infty \phi^{p}{}_{\alpha\beta}(r)\, g_{\alpha\beta}{}^{\text{ref}}(r)\, r^2\, dr + \text{second-order terms} \qquad (13)$$

Thus if the Helmholtz free energy and the radial distribution functions are known for the reference system, it is possible to estimate the free energy of the real system. Other properties of the real system can then be calculated using Equations (4) to (7). The second-order term $(\partial^2 A/\partial\lambda^2)_{\lambda=0}$, which appears in (11) has also been derived by Henderson, Barker, and Smith (1972).

The choice of reference system to be used in Equation (13) is governed by two conditions. First, the real and reference systems must be similar in some sense, so that the perturbation will not be too large. Secondly, the properties of the reference system must be known with sufficient accuracy, either from theory or experiment. The most straightforward choice is a system of hard spheres, with potential:

$$\begin{aligned} \phi_{\alpha\beta}{}^{\text{ref}} &= \infty \quad \text{for} \quad r < d_{\alpha\beta} \\ &= 0 \qquad\qquad\ \ r > d_{\alpha\beta} \end{aligned} \qquad (14)$$

The hard-sphere reference fulfills both of the above requirements well. Many properties (for example, activity coefficients, partial molal volumes) of real liquids are similar to those of hard sphere fluids (Reiss, 1965). Moreover, the properties of hard-sphere fluids are now accurately known both from theory (Carnahan and Starling, 1969; Boublik, 1970) and from computer simulation experiments (Barker and Henderson, 1971a). For a hard-sphere reference system the distribution functions depend on density but are independent of temperature. Consequently, the integral in (13) is independent of T, and it follows from (5) and (13) that for a pure fluid the equation of state takes the form

$$\frac{PV}{RT} = \left(\frac{PV}{RT}\right)^{hs} + \frac{a_1(\rho)}{T} + \frac{a_2(\rho)}{T^2} + \ldots . \qquad (15)$$

where a_1, a_2, etc. depend on density only. This equation of state is obeyed by dense fluids at high temperatures (Zwanzig, 1954).

The main difficulty with using a hard sphere reference directly in (13) is that the calculations are very sensitive to the value chosen for the hard sphere diameter. Further, the temperature-dependence of properties is poorly predicted; thus calculated heat capacities, heat and entropies of solution, etc., are inaccurate. A way of overcoming this difficulty was first suggested by Barker and Henderson (1967). They used as reference a fluid of soft spheres, consisting of molecules which interact with repulsive intermolecular forces

$$\begin{aligned} \phi_{\alpha\beta}{}^{\text{ref}}(r) &= \phi_{\alpha\beta}(r) \quad \text{for} \quad r < \sigma_{\alpha\beta} \\ &= 0 \qquad\qquad\qquad\ \ r > \sigma_{\alpha\beta} \end{aligned} \qquad (16)$$

where $\phi_{\alpha\beta}(r)$ is the potential for the real fluid. In order to find the properties of this reference fluid (subsequently referred to as the BH reference), they carried out a second expansion of the reference about a fluid mixture of hard spheres. The final equation for A^c is (Leonard, Henderson, and Barker, 1970):

$$\begin{aligned} A^c = {} & (A^c)^{hs} \\ & + 2\Pi\rho^2 V \sum_{\alpha} \sum_{\beta} x_\alpha x_\beta \int_0^\infty \phi^p{}_{\alpha\beta}(r)\, g_{\alpha\beta}{}^{hs}(r)\, r^2\, dr \\ & - 2\Pi\rho^2 V kT \sum_{\alpha \neq \beta}\sum x_\alpha x_\beta d^2{}_{\alpha\beta}\, g_{\alpha\beta}{}^{hs}(d_{\alpha\beta})\, [d_{\alpha\beta} - \delta_{\alpha\beta}] \\ & + \text{second-order terms} \qquad (17) \end{aligned}$$

In this equation superscript *hs* means the value for the hard-sphere reference system composed of components $a, b, \ldots r$ with diameters $d_a, d_b \ldots d_r$, and $\delta_{\alpha\beta}$ can be calculated from the intermolecular potential

$$\delta_{\alpha\beta} = \int_0^\infty [1 - e^{-\phi_{\alpha\beta}{}^{\text{ref}}/kT}]\, dr \qquad (18)$$

The hard sphere diameters are given by

$$d_{\alpha\alpha} = \delta_{\alpha\alpha} \qquad (19)$$

$$d_{\alpha\beta} = \frac{1}{2}[d_{\alpha\alpha} + d_{\beta\beta}] = \frac{1}{2}[\delta_{\alpha\alpha} + \delta_{\beta\beta}] \qquad (20)$$

These diameters thus depend on temperature. The last term involving $(d_{\alpha\beta} - \delta_{\alpha\beta})$ in Equation (17) arises from the expansion of the BH reference about hard spheres; it is usually negligible if the molecules in the mixture are of similar sizes, but becomes significant for mixtures of molecules of widely varying sizes.

The above expansion procedure results in good agreement with experiment for all liquid-phase properties, except in the region very near the critical. Thus, the equation of state for a pure liquid can be predicted within a few percent when the second-order perturbation term is included (Barker and Henderson, 1967), and good results are obtained for excess properties of liquid mixtures. The major reason for this good agreement arises from the fact that the radial distribution function is determined primarily by the repulsive forces between molecules for a dense fluid; the attractive forces have little effect on $g(r)$, other than in determining the density.

Leonard, Henderson, and Barker (1970) have used (17) to calculate excess properties of simple liquid mixtures. The Lennard-Jones (6, 12) potential was used for $\phi_{\alpha\beta}(r)$, with the following mixing rules for unlike pair potential parameters:

$$\epsilon_{\alpha\beta} = \zeta_{\alpha\beta}\sqrt{\epsilon_{\alpha\alpha}\,\epsilon_{\beta\beta}} \qquad (21)$$

$$\sigma_{\alpha\beta} = \frac{1}{2}(\sigma_{\alpha\alpha} + \sigma_{\beta\beta}) \qquad (22)$$

Here $\zeta_{\alpha\beta}$ depends on the $\alpha\beta$ pair and is usually slightly less than unity. The properties of the hard sphere fluid that appear in (17) were calculated using the Percus-Yevick theory. Rogers and Prausnitz (1971) have used perturbation theory with the BH reference in order to calculate high-pressure vapor-liquid equilibria for the systems argon-neopentane and methane-neopentane. Excellent agreement is obtained. The intermolecular potential used for these systems was the Kihara model, and the Percus-Yevick theory was again used for $(A^c)^{hs}$ and the $g_{\alpha\beta}{}^{hs}$. Figure 1 shows a typical result. Rajagopal, Calvin, and Reed (1972) have obtained similarly good agreement for a variety of liquids using a Mie $(n, 6)$ potential in the Barker-Henderson theory.

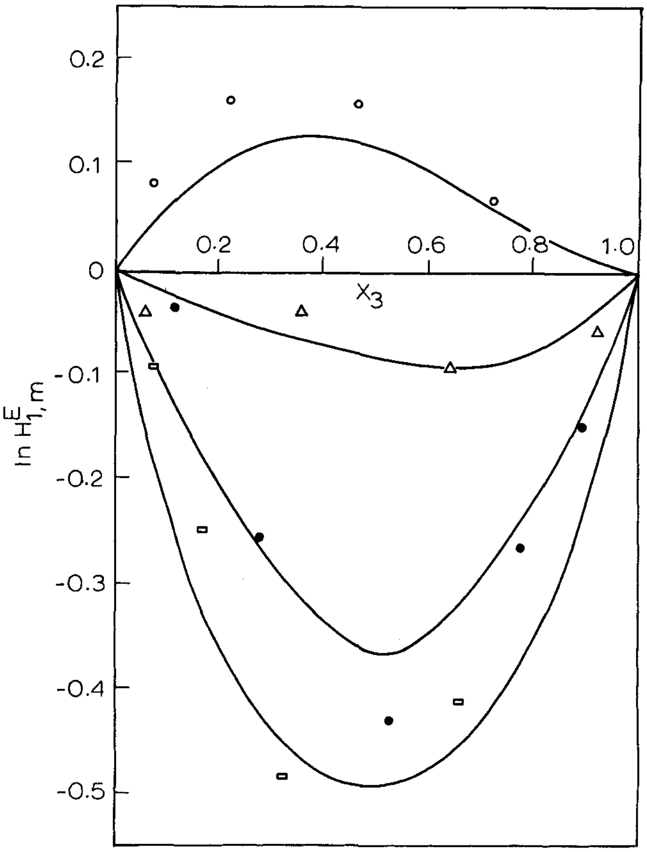

Fig. 1. Saturated vapor and liquid compositions for the methane-neopentane system at 25°C. The curve is perturbation theory (hard sphere mixture as reference) and points are experiment; $\zeta_{ab} = 0.988$. [Reproduced with permission from *Trans. Farad. Soc.*, *67*, 3474 (1971)].

A reference system slightly different from that of Barker and Henderson has been proposed by Weeks, Chandler, and Andersen (1971); it is referred to as the WCA reference. In place of Equation (16) they use

$$\begin{aligned} \phi_{\alpha\beta}{}^{\text{ref}}(r) &= \phi_{\alpha\beta}(r) + \epsilon \quad \text{for} \quad r < r^0{}_{\alpha\beta} \\ &= 0 \qquad\qquad\qquad\quad r > r^0{}_{\alpha\beta} \end{aligned} \qquad (23)$$

that is, the full repulsive region of the potential, down to the minimum of the potential well. Equation (17) still holds, but with $\phi^p{}_{\alpha\beta}$ now given by

$$\begin{aligned} \phi^p{}_{\alpha\beta}(r) &= -\epsilon \qquad\quad r < r^0{}_{\alpha\beta} \\ &= \phi_{\alpha\beta}(r) \quad r > r^0{}_{\alpha\beta} \end{aligned} \qquad (24)$$

The hard-sphere diameters, given by (18) to (20), are somewhat larger for the WCA reference system than for the BH reference, because of the new definition of $\phi_{\alpha\beta}{}^{\text{ref}}$ in (18). Use of the WCA reference system causes the perturbation series of Equation (11) to converge more rapidly at high densities (Verlet and Weis, 1972). However, this advantage is somewhat offset by the fact that the hard sphere reference system may solidify at high density because of the larger values of the reduced density ρd^3 in the case of the WCA reference. Relatively few calculations have been made so far with the WCA reference.

Van der Waals Models

While perturbation theory based on a hard sphere reference gives excellent results, the calculation of the functions $g_{\alpha\beta}{}^{hs}$ in (17) is a difficult and time-consuming task at present. However, the calculations may be greatly simplified, with only a small loss of accuracy, by assuming $g_{\alpha\beta}{}^{hs} = c$ (a constant) in the first-order perturbation term. In fact $g_{\alpha\beta}{}^{hs}$ will be a function that oscillates around unity when plotted versus r; however, replacing it by a constant in the first-order term gives good results because of cancellation of errors in evaluating the integral. This approximation leads to van der Waals models, so-called because the equation of state obtained in this way is essentially that of van der Waals. If, for example, we put $g_{\alpha\beta}{}^{\text{ref}} = c$ in (13) and apply (5) we get

$$P = P^{hs} - \frac{a_{\text{mix}}}{V^2} \tag{25}$$

where

$$a_{\text{mix}} = \sum_{\alpha} \sum_{\beta} x_\alpha \, x_\beta \, a_{\alpha\beta} \tag{26}$$

and

$$a_{\alpha\beta} = -2\Pi N^2 c \int_0^\infty \phi^p{}_{\alpha\beta}(r) \, r^2 \, dr \tag{27}$$

If, following van der Waals, we take for P^{hs} the ideal gas equation of state with V replaced by $(V - b)$, then (25) becomes

$$P = \frac{RT}{(V-b)} - \frac{a_{\text{mix}}}{V^2} \tag{28}$$

which is van der Waal's equation of state. Here b is a measure of the volume occupied by the molecules themselves.

Although Equation (28) gives only an approximate description of liquids, much of the error arises in van der Waals' approximation of P^{hs}. Better equations for P^{hs} are now available, notably those of Percus-Yevick and Carnahan-Starling (1969). When one of these results is used together with Equations (25) and (26), good results are obtained. Numerous engineering correlations for nonpolar liquid mixtures and gas solubilities have been based on these results in recent years. One of the first such applications seems to have been made by Longuet-Higgins and Widom (1964) and by Guggenheim (1965), who used Equation (25), together with the Percus-Yevick equation for P^{hs}, to predict the melting curve and other properties of liquid argon. Several authors have applied (25) to predict the excess properties of liquid mixtures. Snider and Herrington (1967) used (25) and (26) to predict excess enthalpies, entropies and volumes for ten mixtures ranging from simple mixtures such as argon-krypton to carbon tetrachloride-neopentane. Pure fluid parameters d_α and $a_{\alpha\alpha}$ were obtained from boiling-point data, and the cross-parameter a_{ab} was obtained by fitting the excess Gibbs free energy at one temperature. The results were good for the simple liquid mixtures, but somewhat poorer for the larger molecules. Subsequent workers have pointed out that it is not necessary to fit the cross-term a_{ab} to mixture data; instead, it can be estimated satisfactorily from pure-liquid values. Thus, assuming that $\phi^p{}_{\alpha\beta}$ is of the form

$$\phi^p{}_{\alpha\beta} = \epsilon_{\alpha\beta} \, f\left(\frac{\sigma_{\alpha\beta}}{r}\right)$$

where f is some arbitrary function, it follows from (27) that

$$a_{\alpha\beta} \propto \epsilon_{\alpha\beta} \, \sigma^3{}_{\alpha\beta} \tag{29}$$

Furthermore, the physical interpretation of b gives

$$b = \sum_{\alpha} x_\alpha b_\alpha \tag{30}$$

where b_α is proportional to $d_\alpha{}^3$. Using the mixing rules for $\epsilon_{\alpha\beta}$ and $\sigma_{\alpha\beta}$ given in (21) and (22) provides the mixing rule for $a_{\alpha\beta}$:

$$a_{\alpha\beta} = \zeta_{\alpha\beta}(a_{\alpha\alpha}a_{\beta\beta})^{1/2} \frac{[(b_\alpha{}^{1/3} + b_\beta{}^{1/3})/2]^3}{b_\alpha{}^{1/2} \, b_\beta{}^{1/2}} \tag{31}$$

McGlashan (1970), Marsh et al. (1970, 1971) and Miller (1971) have all obtained good results for excess properties of liquid mixtures using (31).

Equation (25) has also been widely used to predict the solubility and partial molal properties of gases dissolved in liquids. Pierotti (1963, 1965) was the first to use this method and obtained excellent results for both organic solvents and water. Good results have also been obtained along these lines by Staveley (1970), Miller (1971), de Ligny and van der Veen (1972), and Cukor and Prausnitz (1972). The last two of these papers are of particular interest since they include calculations for a large number of systems, including both nonpolar and polar solutes and solvents. Cukor and Prausnitz have given a generalized correlation for the cross-parameter a_{ab} in Equation (26) in terms of critical constants; this is the only one of the $a_{\alpha\beta}$ parameters needed to obtain the Henry constant. Equation (25) is found to give satisfactory predictions of gas solubilities but is less good for predicting partial molal enthalpies and entropies. The latter defect appears to be due to the use of a hard-core potential. A similar approach has been used to predict gas solubility in molten salts (Lee and Johnson, 1969).

An improvement over Equation (25) is obtained by putting $g_{\alpha\beta}{}^{hs} = c$ in (17), rather than in (13). In this way the finite steepness of the repulsion potential is accounted for, and this greatly improves the accuracy of predicted heats and entropies of solution. If the small term involving $(d_{\alpha\beta} - \delta_{\alpha\beta})$ in (17) is neglected, Equation (25) still holds, but P^{hs} is now for a mixture of hard spheres whose diameters are temperature-dependent and given by (18) to (20). Tiepel and Gubbins (1972a) have used this method to predict Henry constants for gases in mixed solvents; Figure 2 shows some of the results. The excess Henry constant is defined by

$$\ln H^E{}_{1,m} = \ln H_{1,m} - \sum_{j=2}^{m} x_j \ln H_{1,j} \tag{32}$$

For an ideal solution $H^E{}_{1,m} = 0$. In the calculations shown in Figure 2 the constant c was taken to be unity, and the $a_{\alpha\beta}$ were calculated from (27) by substituting for $\phi_{\alpha\beta}$. The Lennard-Jones (6, 12) model was used for nonpolar potential interactions, and an angle-averaged induced dipole term was used to represent polar interactions.

All of the above calculations are based on the approximation $g^{\text{ref}} = c$, which leads to van der Waals equation. As pointed out by Vera and Prausnitz (1972), however, it is possible to obtain other empirical equations of state by modifying the assumed form for g^{ref}. They base their method on a simplified partition function, and show the forms that this function must have to yield 7 commonly used equations of state. A closely analogous procedure is possible starting from Equation (13). For example, substituting

$$g^{\text{ref}} = \frac{c}{T} \quad \text{and} \quad P^{\text{ref}} = \frac{RT}{V-b} \tag{33}$$

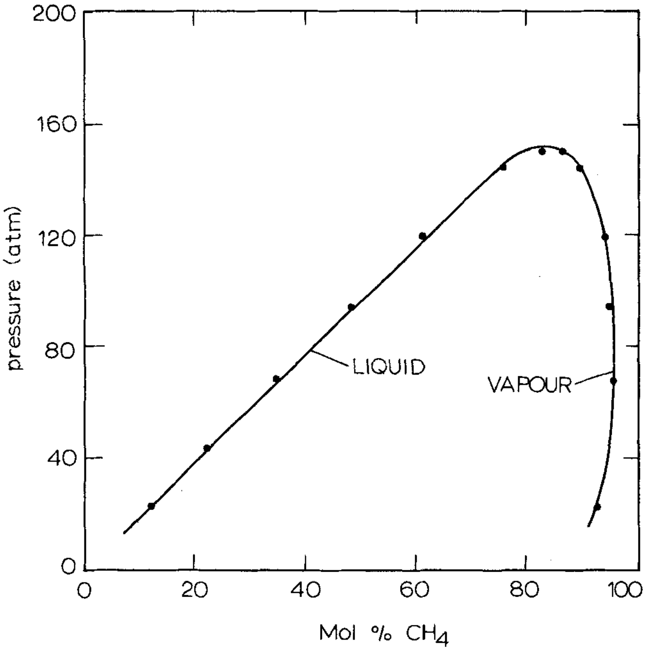

Fig. 2. Deviations of Henry's constants from ideal solution behavior for argon in binary solvents, 25°C. Solid lines are predicted from equations (25) to (27), with $c = 1$ and temperature-dependent hard sphere diameters given by (19). Points are experiment: O $H_2O(2)$-ethylene glycol (3); △, $H_2O(2)$-MeOH(3); •, $H_2O(2)$-EtOH (3); □, $H_2O(2)$-*p*-dioxane (3). [Reproduced with permission from *Can. J. Chem. Eng.*, 50, 365 (1972a)].

in (13) gives the Berthelot equation of state

$$\left(P+\frac{a}{TV^2}\right)(V-b)=RT \tag{34}$$

Similarly, if we put

$$g^{\text{ref}}=\frac{cV}{bT^{1/2}}\ln\left(\frac{V+b}{V}\right) \quad \text{and} \quad P^{\text{ref}}=\frac{RT}{V-b} \tag{35}$$

in (13), the Redlich-Kwong equation of state is obtained

$$\left(P+\frac{a}{T^{1/2}V(V+b)}\right)(V-b)=RT \tag{36}$$

In these equations a is given by (26) and (27). The above procedure is useful as a basis for deriving mixing rules for equation of state parameters. The success of the van der Waals models, using improved equations for P^{hs}, has led Vera and Prausnitz (1972) to suggest that the Redlich-Kwong and other equations of state might be improved in a similar fashion. This idea has recently been used by Carnahan and Starling (1972) to develop an improved Redlich-Kwong equation.

Salt Effects in Phase Equilibria

When a salt is added to an aqueous phase containing a dissolved nonelectrolyte, the solubility of the nonelectrolyte may either decrease (salting-out) or increase (salting-in), depending on the system. Such salt effects can bring about large shifts in the distribution of nonelectro-

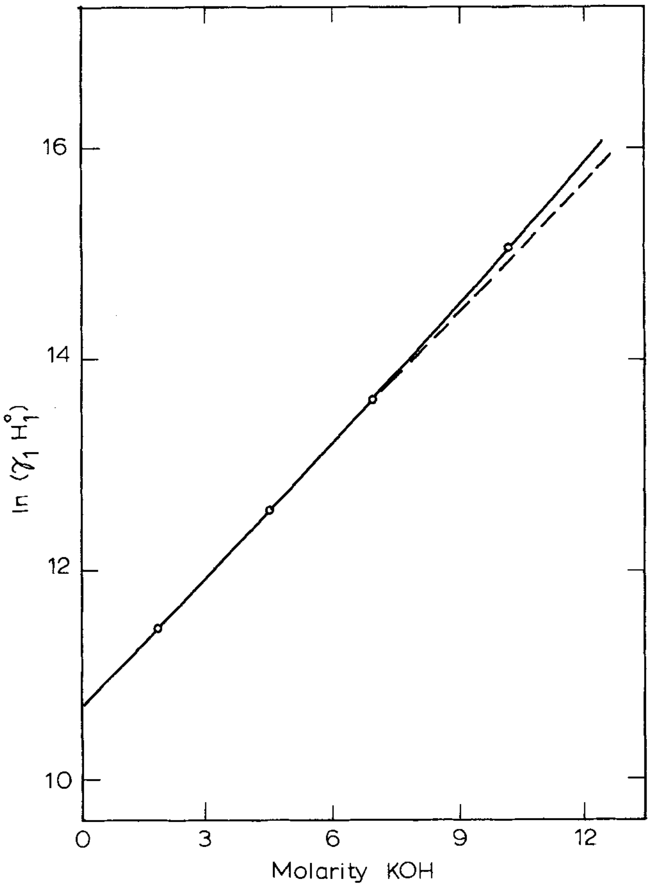

Fig. 3. Activity coefficients of oxygen dissolved in KOH solutions at 25°C. Points are experiment, and dashed line is calculation based on Equation (25). H°_1 is the Henry constant of oxygen in pure water. [Reproduced with permission from *Ind. Eng. Chem. Fundamentals*, 12, 18 (1973)].

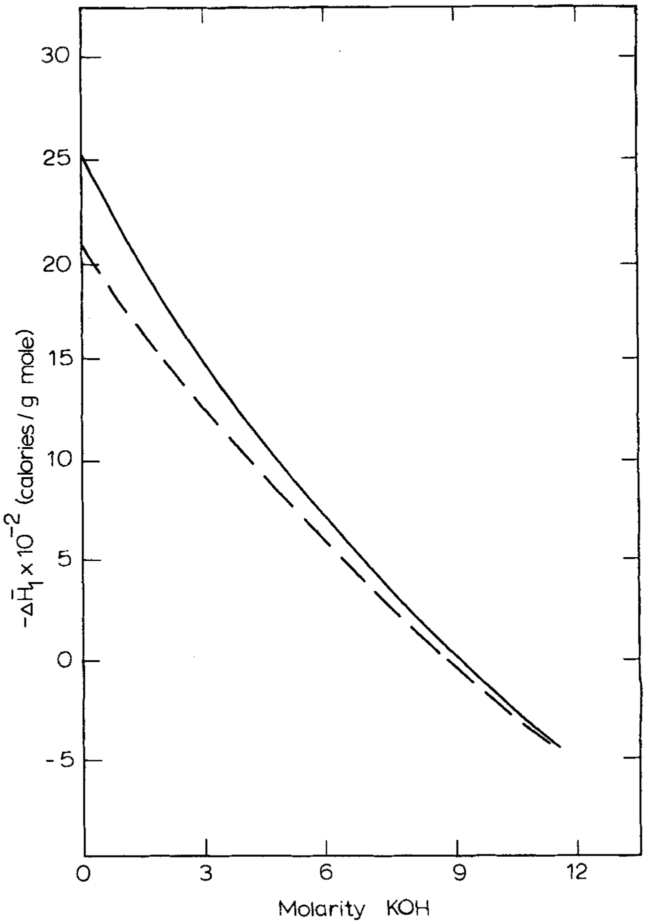

Fig. 4. Partial molal heats of solution for oxygen in KOH solution, 25°C. Solid and dashed lines are experiment and theory, respectively. [Reproduced with permission from *Ind. Eng. Chem. Fundametals*, 12, 18 (1973)].

lyte between phases and find practical applications in stagewise separation processes and in pollution abatement.

Theories of the van der Waals type described above have been used to predict the effect of salts on activity coefficients and partial molal properties of nonelectrolytes. Earlier attempts of this type (Shoor and Gubbins, 1969; Masterton and Lee, 1970; Wilcox and Schrier, 1971) were based on Equation (25), and were similar to the approach of Pierotti. Somewhat better results are obtained (Tiepel and Gubbins, 1972b, 1973), particularly for heats of solution, if the theory is based on (17), with $g_{\alpha\beta}{}^{hs} = 1$. This gives (25), with temperature-dependent hard-sphere diameters given by (19). Tiepel and Gubbins (1973) have also extended the van der Waals model to second-order, by putting $g_{\alpha\beta}{}^{hs} = 1$ in the second-order perturbation term; this yields a significant overall improvement in the results.

This last method gives good results for all properties (activity coefficients, partial molal enthalpies, entropies, and volumes) of salting-out systems, even at high salt concentrations. Some results are shown in Figures 3 and 4. These calculations use the Carnahan-Starling (1969) equation for P^{hs}. The nonpolar part of the intermolecular potential is taken to be the Lennard-Jones (6, 12) model, and induced electrostatic interactions are also accounted for. For salting-in systems (for example, hydrocarbons in tetraalkylammonium salt solutions) the theory is less successful, apparently because association forces are involved between the nonelectrolyte and the ions.

Solvent Extraction Systems

Tiepel and Gubbins (1971) applied Equation (25) to the prediction of thermodynamic properties in solvent extraction systems and to the problem of solvent selection. Some of the results are shown in Table 1 and in Figure 5. Table 1 also includes values predicted by the regular solution theory, which has been extensively used for solvent extraction systems. Perturbation theory is capable of dealing with a wider variety of systems than regular solution theory. The principal defect of regular solution theory is the assumption that the entropy of mixing is ideal; this approximation leads to significant errors for many solvent extraction systems. No such approximation is necessary in perturbation theory.

Electrolyte Solutions

Perturbation methods, using a hard sphere fluid reference, have recently been applied to electrolyte solutions.

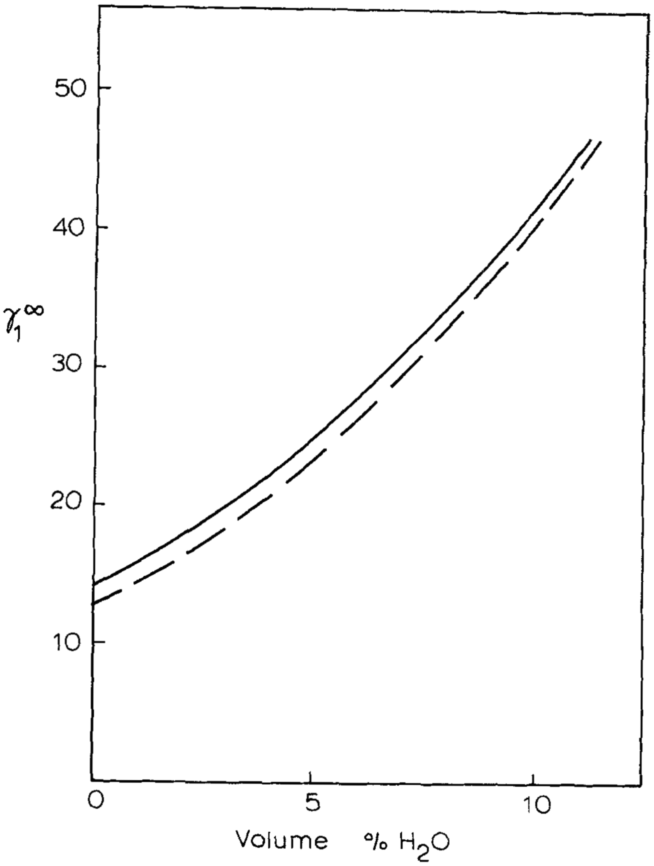

Fig. 5. Infinite dilution activity coefficients for pentane in a mixed solvent of methyl cellosolve and water at 25°C. Solid line is experiment, dashed line is theory. [Reproduced with permission from *Proc. Intern. Solv. Extrn. Conf.*, P. 25, The Hague (1971)].

TABLE 1. INFINITE DILUTION ACTIVITY COEFFICIENTS IN THE EXTRACT PHASE, 25°C
(TIEPEL AND GUBBINS, 1971)

Solute (1)	Solvent (2)	$(\gamma_1{}^{E,\infty})_{\text{theory}}$	$(\gamma_1{}^{E,\infty})_{\text{exptl}}$	$(\gamma_1{}^{E,\infty})_{RS}$†
Pentane	Methanol	28.8	27.0	151.0
Hexane	Methanol	24.6	27.0	242.0
Heptane	Aniline	26.8	23.1	29.3
Benzene	Aniline	1.4	2.2	3.8
Hexane	Nitrobenzene	6.7	7.0	10.2
Benzene	Nitrobenzene	1.2	1.2	2.2
Cyclohexane	Ethylene glycol	432.0	316.0	451.0
Hexane	Ethylene glycol	618.0	625.0	2,346.0
Pentane	Dimethyl sulphoxide	55.2	61.3	49.1
Cyclohexane	Dimethyl sulphoxide	54.5	40.6	28.2
Benzene	Acetophenone	1.2	1.2	1.5
Pentane	Acetophenone	5.4	5.4	4.8
Isoprene	Acetophenone	3.8	2.1	2.7
Pentane	Methyl Cellosolve	12.7	14.5	—
Hexane	Methyl Cellosolve	14.1	16.0	—
1-Pentene	Methyl Cellosolve	13.6	8.6	—
Pentane	Acetone	5.7	5.3	4.3
Hexane	Acetone	6.9	6.5	4.7
1-Pentene	Acetone	5.8	3.2	4.0

† Calculated from regular solution theory correlation of Weimer and Prausnitz (1965). This theory is not applicable to hydrogen-bonded systems.

The approaches used so far treat the system as one containing ions immersed in a dielectric medium. Thus ion-solvent and solvent-solvent interactions are not explicitly accounted for. Instead, a dielectric constant is included in the ion-ion potential model to take solvent interactions into account approximately. Thus the ion-ion potential is

$$\phi_{\alpha\beta}(r) = \phi^*{}_{\alpha\beta}(r) + \frac{z_\alpha z_\beta e^2}{Dr} \tag{37}$$

where $\phi^*{}_{\alpha\beta}$ is the short range nonpolar interaction. The model studied most extensively is the primitive model of electrolytes, which takes $\phi^*{}_{\alpha\beta}$ to be a hard sphere potential

$$\begin{aligned} \phi^*{}_{\alpha\beta}(r) &= \infty \qquad r < d_{\alpha\beta} \\ &= 0 \qquad r > d_{\alpha\beta} \end{aligned} \tag{38}$$

This model differs from that used in the older Debye-Hückel theory in that the ions are assigned hard cores; Equations (37) and (38) reduce to the Debye-Hückel form when $d_{\alpha\beta} = 0$.

Rasaiah and Stell (1970) and Anderson et al. (1971, 1972) have calculated thermodynamic properties of electrolytes by assuming the primitive model and perturbing about the hard sphere potential as reference. The expansion procedure used by Anderson et al. differs somewhat from that described in this paper and is called the mode expansion. Unfortunately these calculations do not yet seem to have been compared directly with experiment. They have, however, been compared with Monte Carlo computer simulations of an electrolyte solution. These comparisons indicate that the theory works well for concentrations up to 2 molar, the upper limit of the Monte Carlo results. Thus the results provide a considerable improvement over Debye-Hückel theory. A method that is closely related to the mode expansion of Anderson et al. has been developed by Waisman and Lebowitz (1972) and is called the mean spherical approximation; the equations are somewhat simpler than those of the mode expansion and still give good results.

Direct comparisons of these methods with experimental data should appear in the near future. These theories can probably be further improved by the use of more realistic models for the short-range potential and by accounting for solvent interactions.

Liquid Metals

Liquid metals consist of metallic ions immersed in a bath of conduction electrons, and the situation is complicated by the various potential interactions and the introduction of quantum effects when treating the electrons. However, a simple and successful model of liquid metals is the pseudopotential method, in which classical statistical mechanics is used and the total potential energy is taken to be a sum of effective pair potentials between ions. Such effective pair potentials include electron-screening effects as well as the direct ion-ion interaction. Several models have been proposed for these effective potentials (March, 1968).

Perturbation calculations of liquid-metal properties have been carried out by Smith and Jena (1971), Jones (1971), and Edwards and Jarzynski (1972). All of these calculations used hard spheres as the reference. Table 2 shows the results of Jones for liquid sodium. Good agreement is obtained for a wide variety of properties.

TABLE 2. THERMODYNAMIC DERIVATIVES FOR LIQUID SODIUM AT THE MELTING POINT*

	Property	Theory	Experiment
$1/K_T$	(k bar)	50.5	53.8
C_p	(cal/mole. K)	7.87	7.61
ρ_m	(g/cm^3)	0.905	0.9265
c	(cm/sec)	2.533×10^5	2.531×10^5
α	(K^{-1})	2.98×10^{-4}	2.44×10^{-4}
C_p/C_v		1.1503	1.103
$\partial c/\partial T$	(cm/sec. K)	-65	-52

* Reproduced with permission from H. D. Jones, *J. Chem. Phys.*, **55**, 2640 (1971).

Surface Properties

Toxvaerd (1971, 1972) has applied the Barker-Henderson theory to surface properties of liquids. He develops an equation for the surface free energy which is the analogue of Equation (17) and uses it to calculate the surface tension of liquid argon. Excellent results are obtained, as shown in Figure 6. Plesner, Platz, and Christiansen (1968) have also calculated surface properties using a van der Waals model, which is the analogue of Equation (25). Again, their calculations are only for simple liquids and their mixtures. These methods should also be applicable to liquids composed of more complex molecules, provided a suitable intermolecular potential is used.

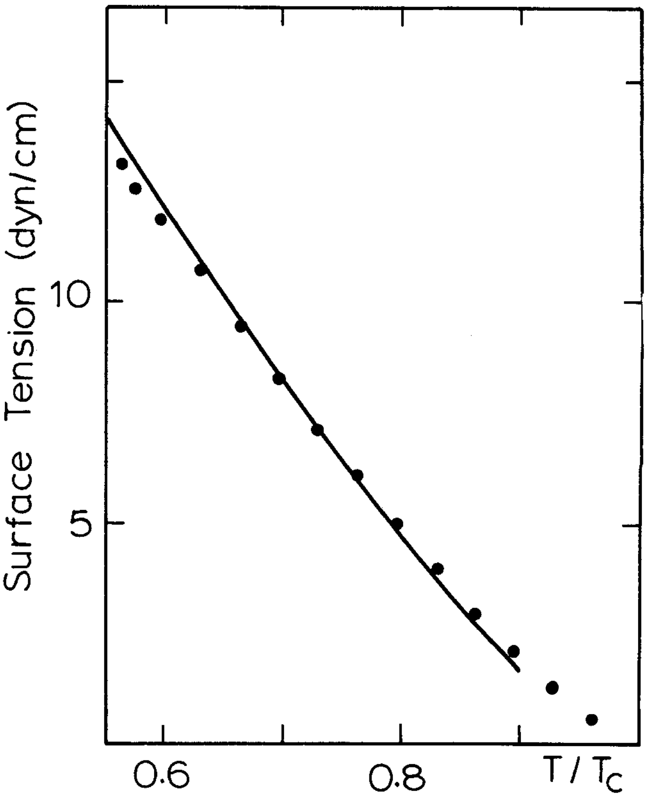

Fig. 6. Surface tension of liquid argon. The line is the Barker-Henderson theory, using the Lennard-Jones 6,12 potential and Percus-Yevick theory for hard sphere properties. Points are experiment. [Reproduced with permission from *J. Chem. Phys.*, **55**, 3116 (1971)].

PERTURBATION ABOUT A PURE CONFORMAL FLUID

General Approach

The perturbation theory using a reference of hard spheres is highly flexible, in the sense that essentially no restrictions are placed on the form of the pair potential.

This approach can therefore be applied to mixtures in which different types of intermolecular potentials exist between different components; examples are gases dissolved in electrolyte solutions, mixtures of polar and nonpolar liquids, and liquid metal mixtures.

The approach described in this section is less flexible and is usually called corresponding states theory or conformal solution theory. For many liquid mixtures, however, it gives results that are as good as the hard sphere perturbation theory; in such cases it is easier to do the calculations using conformal solution theory. The basic assumption is that all pair potential interactions in the fluid are of the same functional form (that is, they are conformal). The potential is usually taken to be of the type

$$\phi_{\alpha\beta}(r) = \epsilon_{\alpha\beta} f\left(\frac{r}{\sigma_{\alpha\beta}}\right) \qquad (39)$$

although it is possible to extend this to include 3 or more potential parameters. In (39) f is the same function for all component pairs. It follows from (39) that the pure components obey the simple two-parameter corresponding states law. To obtain the solution properties, the Helmholtz (or Gibbs) free energy is expanded in a Taylor series about the free energy of an ideal solution. The ideal solution consists of a mixture of components, all of which have the same intermolecular potential; this potential is of the form (39), with parameters (of as yet unspecified values) ϵ_x and σ_x. Various ways of carrying out such an expansion are possible. One procedure would be to write, by analogy with (10),

$$\phi_{\alpha\beta}(r; \lambda) = \phi_x(r) + \lambda\, \phi^p{}_{\alpha\beta}(r)$$

where ϕ_x is the potential for the reference fluid; the expansion can then be carried out in powers of λ as before. However, a more versatile procedure is to use $\epsilon_{\alpha\beta}$ and $\sigma_{\alpha\beta}$ as expansion parameters. The most straightforward method is to expand A^c in powers of $(\epsilon_{\alpha\beta} - \epsilon_x)$ and $(\sigma_{\alpha\beta} - \sigma_x)$. Such a series turns out to have poor convergence properties, however. Various combinations of ϵ and σ have been suggested, but the optimum choice of expansion parameters appears to be $\epsilon_{\alpha\beta}\, \sigma^3{}_{\alpha\beta}$ and $\sigma^3{}_{\alpha\beta}$ in place of $\epsilon_{\alpha\beta}$ and $\sigma_{\alpha\beta}$. Expanding the Helmholtz free energy A for the mixture about the ideal solution value using these expansion parameters gives (Smith, 1972)*

$$A^c = A_x{}^c + \sum_\alpha \sum_\beta \left(\frac{\partial A^c}{\partial \epsilon_{\alpha\beta}\sigma^3{}_{\alpha\beta}}\right)_x (\epsilon_{\alpha\beta}\sigma^3{}_{\alpha\beta} - \epsilon_x\sigma_x{}^3)$$
$$+ \sum_\alpha \sum_\beta \left(\frac{\partial A^c}{\partial \sigma^3{}_{\alpha\beta}}\right)_x (\sigma^3{}_{\alpha\beta} - \sigma_x{}^3)$$
$$+ \text{second order terms} \qquad (40)$$

In this equation $A_x{}^c$ is the configurational free energy for the ideal solution. Because the parameters ϵ_x and σ_x are the same for all components in this solution, $U(\mathbf{r}_1 \ldots \mathbf{r}_N)$ is independent of the composition and of the way in which components are assigned to the positions. Therefore, it follows from (2) and (3) that $A_x{}^c$ is just the configurational free energy of a pure fluid with parameters ϵ_x and σ_x. The differential terms in (40) can be found by differentiating Equation (2). When this is done (41) takes the form

$$A^c = A_x{}^c + R_a \sum_\alpha \sum_\beta x_\alpha x_\beta\, (\epsilon_{\alpha\beta}\sigma^3{}_{\alpha\beta} - \epsilon_x\sigma_x{}^3)$$
$$+ R_b \sum_\alpha \sum_\beta x_\alpha x_\beta\, (\sigma^3{}_{\alpha\beta} - \sigma_x{}^3)$$
$$+ \text{second order terms} \qquad (41)$$

The terms R_a and R_b involve integrals over $g_x(r)$. However, their form does not concern us, since we shall now choose ϵ_x and σ_x to make the first-order terms in (41) vanish

$$\epsilon_x\sigma_x{}^3 = \sum_\alpha \sum_\beta x_\alpha x_\beta\, \epsilon_{\alpha\beta}\, \sigma^3{}_{\alpha\beta} \qquad (42)$$

$$\sigma_x{}^3 = \sum_\alpha \sum_\beta x_\alpha x_\beta\, \sigma^3{}_{\alpha\beta} \qquad (43)$$

The reference system is therefore a (hypothetical) pure fluid (more precisely an ideal solution) with composition-dependent potential parameters given by (42) and (43). If the second- and higher-order terms in (41) can be neglected,

$$A^c = A_x{}^c \qquad (44)$$

The free energy of the pure fluid is most readily calculated by putting (2) and (3) in dimensionless form. This gives

$$A_x{}^c = \epsilon_x F(P\sigma_x{}^3/\epsilon_x, kT/\epsilon_x) - 3NkT \ln \sigma_x \qquad (45)$$

where F is a universal function of reduced pressure and temperature and is determined from pure-fluid data. The final equation for the excess Helmholtz free energy of the mixture is

$$A^E(P, T) = \epsilon_x F(P\sigma_x{}^3/\epsilon_x, kT/\epsilon_x)$$
$$- \sum_\alpha x_\alpha \epsilon_{\alpha\alpha}\, F(P\sigma^3{}_{\alpha\alpha}/\epsilon_{\alpha\alpha}, kT/\epsilon_{\alpha\alpha})$$
$$- 3NkT \sum_\alpha x_\alpha \ln(\sigma_x/\sigma_{\alpha\alpha}) \qquad (46)$$

Equations (42) to (44) comprise the so-called "van der Waals 1" theory of Leland, Rowlinson, and Sather (1968). The reason for this name can be seen from Equations (25) to (29). Combining (26) and (29) gives the mixing rule of Equation (42), while b in (28) is proportional to the hard-sphere volume, that is, d^3. The above derivation of the van der Waals 1 theory differs from that originally used by Leland et al. and is due to Smith (1972). It has the advantage that it can be extended to second order if desired. In fact Smith has made such an extension and has presented calculations for hard spheres.

Although the van der Waals 1 theory apparently is the most successful of the conformal solution theories, several other similar approaches have been presented. These are reviewed by Henderson and Leonard (1971b) and can be derived using the above method by choosing suitable expansion parameters and performing an expansion similar to (40). For example, the random mixture theory (Prigogine et al., 1956) for the Lennard-Jones (6, 12) potential is obtained by using $\epsilon_{\alpha\beta}\, \sigma^6{}_{\alpha\beta}$ and $\epsilon_{\alpha\beta}\, \sigma_{\alpha\beta}{}^{12}$ as expansion parameters. Other conformal solution theories are discussed by Smith (1972) within the framework of perturbation theory.

If (39) is taken to be the form of the pair potential, an equivalent treatment to the above is to replace potential parameters using critical constants. If (39) holds, then

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* Some authors, including Smith (1972), include the combinatorial term $(\prod_\alpha N_\alpha!)^{-1}$ as a multiplying factor in their definition of the configuration integral Z, whereas others include this term in the kinetic part of the partition function as is done here. Thus the configurational part of the free energy differs for these two definitions, although the total free energy is the same. Thus Smith includes a term $NkT \sum_\alpha x_\alpha \ln x_\alpha$ in Equation (40), which is the free energy of mixing for an ideal solution and arises from the combinatorial term. This ideal mixing term cancels out when excess properties are calculated.

$$T_c = c_1 \epsilon \quad \text{and} \quad V_c = c_2 \sigma^3 \tag{47}$$

where c_1 and c_2 are constants. The unlike pair parameters are given to good approximation by (21) and (22). Using these equations in (42) and (43) give the van der Waals 1 mixing rules in terms of critical constants

$$T_c^x = \frac{\sum\limits_{\alpha} \sum\limits_{\beta} x_\alpha x_\beta \, \zeta_{\alpha\beta} \, (T_c^\alpha T_c^\beta)^{1/2} \, (V_c^{\alpha 1/3} + V_c^{\beta 1/3})^3}{\sum\limits_{\alpha} \sum\limits_{\beta} x_\alpha x_\beta \, (V_c^{\alpha 1/3} + V_c^{\beta 1/3})^3} \tag{48}$$

$$V_c^x = \frac{1}{8} \sum_{\alpha} \sum_{\beta} x_\alpha x_\beta \, (V_c^{\alpha 1/3} + V_c^{\beta 1/3})^3 \tag{49}$$

Minor variations on the above conformal solution approach include the n-fluid theories, and the use of one of the pure components of the mixture as the reference. The n-fluid theories use as a reference a suitable (usually a mole fraction) average of the properties of n hypothetical pure fluids. Thus the van der Waals 2 theory involves the use of two pure reference fluids (Leland et al., 1969). Although the 1- and 2-fluid theories give similar results on comparison with experiment, comparisons with computer simulation results show that the 1-fluid theory converges faster, at least when truncated at the first-order term (Henderson and Leonard, 1971b). Since the 1-fluid theory is also easier to use, it is preferable to the multifluid theories. The other modification, the use of one of the mixture components as reference, requires the calculation of the first-order terms in (41). This is not particularly difficult since the first-order terms can be related to thermodynamic functions of the pure reference fluid.

Organic Liquid Mixtures

For simple liquid mixtures, Equations (42) to (44) work well. Potential parameters are usually obtained from (21) and (22), with the binary $\zeta_{\alpha\beta}$ factors determined either from second virial coefficient data or from liquid excess property data. Comparisons with experiment are given by Henderson and Leonard (1971b). Watson and Rowlinson (1969) obtained good agreement with experiment for bubble-point calculations for the argon-nitrogen-oxygen system. For liquids composed of more complex molecules, several empirical extensions of conformal solution theory have appeared. Leland and coworkers (Fisher and Leland, 1970) have extended the theory to hydrocarbon mixtures by using shape factors to describe molecular nonsphericity. Ellis and Chao (1972) have made empirical modifications to the original Longuet-Higgins (1951) form of conformal solution theory and have calculated relative volatilities of 15 binary organic liquid systems, including such systems as ethyl benzene/o-xylene. They have also carried out similar calculations for a multicomponent system, some of which are shown in Table 3. In a series of papers by Smith and co-workers, the most recent of which are those of Yuan, Palmer, and Smith (1972) and Palmer, Yuan, and Smith (1972), engineering correlations are developed by introducing empirical modifications into conformal solution theory. These correlations give good results for excess Gibbs free energy, volume, and enthalpy for binary and ternary mixtures of hydrocarbons up to C_7; a typical result is shown in Figure 7. The van der Waals 1 theory has also been used by Swinton (1970) to predict properties of sour gas mixtures.

TABLE 3. PHASE EQUILIBRIA† IN THE SYSTEM PROPANE/ PROPYLENE/PROPADIENE/PROPYNE AT 140°F, 344 LB./SQ.IN.ABS.*

i	x	y	$(\alpha_{i,1})_{\text{calc}}$	$(\alpha_{i,1})_{\text{expt}}$	% Deviation
Propylene	0.4690	0.4907	1.1057	1.0958	−0.9
Propadiene	0.0100	0.0095	0.9873	0.9929	0.6
Propyne	0.0100	0.0099	1.0350	1.0347	0.0

* Reproduced with permission from J. A. Ellis and K.-C. Chao, *AIChE J.*, 18, 70 (1972).

† $\alpha_{i,1}$ = relative volatility of i with respect to propane.

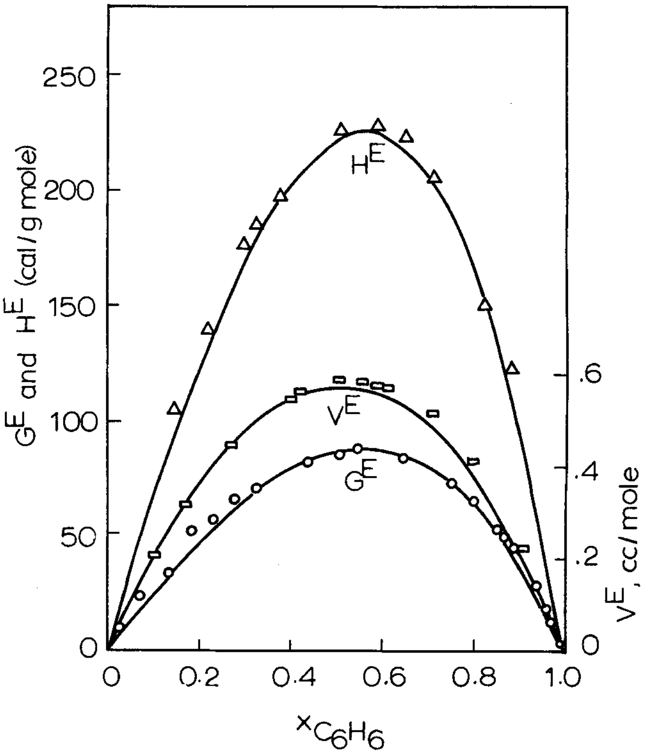

Fig. 7. Excess properties for benzene/*n*-heptane mixtures at 20°C. Points are experiment and lines are the correlation of Yuan *et al.* The calculated values are based on benzene as the reference. [Reproduced with permission from *Ind. Eng. Chem. Fundamentals,* 11, 387 (1972)].

For liquid mixtures containing complex molecules (Patterson, 1969; Flory, 1970), including polymers, Prigogine's (1957) corresponding states theory for r-mers has been successfully used (Hermsen and Prausnitz, 1966; Fredenslund and Sather, 1969; Winnick and Prausnitz, 1971; Winnick, 1972, 1973; Bonner, Bellemans, and Prausnitz, 1973). This theory introduces a third parameter c, which measures the number of degrees of freedom that are affected by density; in long-chain molecules these include translation, overall rotation, flexible bending modes, and free internal rotations. The potential energy of interaction between two monomer groups on different molecules is usually assumed to be of the form (39). The theory can be extended to mixtures by the conformal solution concepts outlined above. Thus Hermsen and Prausnitz (1966) used the random mixture version of conformal solutions to predict excess enthalpies and free energies of mixtures of paraffinic, olefinic, naphthenic and aromatic hydrocarbons up to C_{12}. More recently, Winnick and Prausnitz (1971) used Scott's 2-fluid theory to extend Prigogine's model to mixtures of complex nonpolar liquids, including such liquids as eicosane, octamethylcyclotetrasiloxane, and perfluorobenzene. They obtain good agreement for excess free energies, but predictions were poorer for excess enthalpies and entropies (Table 4). Winnick

TABLE 4. EQUIMOLAR EXCESS PROPERTIES FOR BINARY LIQUID MIXTURES[*]

System	T, °K	G^E, cal/mole Calc.	G^E, cal/mole Expt.	H^E, cal/mole Calc.	H^E, cal/mole Expt.	V^E, cc/mole Calc.	V^E, cc/mole Expt.
CCl_4/benzene	298	19.6	19.5	32.0	27.5	0.11	—
	313	18.9	19.0	32.1	—	0.13	—
	343	17.6	17.9	32.7	—	0.19	0.10
n-hexane *n*-hexadecane	293	−15.9	−15.6	17.4	31.0	3.4	−0.48
	313	−18.2	−18.2	16.8	15.3	3.7	—
	333	−20.4	−20.0	17.3	(2.4)	3.9	—
C_6F_6/cyclohexane	303	191.0	192.0	287.0	370.0	1.2	—
	323	181.0	181.0	282.0	353.0	1.4	(2.5)
	343	172.0	171.0	278.0	334.0	1.7	—
OMCTS[†]/benzene	298	28.4	27.7	191.0	178.0	−3.3	−0.006
	333	9.3	10.2	192.0	—	−2.6	−0.04

[*] Reproduced with permission from J. Winnick and J. M. Prausnitz, *Chem. Eng. J.*, **2**, 241 (1971).
[†] Octamethylcyclotetrasiloxane.

(1972, 1973) has extended these results to include polar fluids, by incorporating a canonically pre-averaged dipole-dipole potential interaction; good results are obtained for all excess properties except the entropy, for which predicted values are too high. Bonner et al. (1973) have recently presented preliminary calculations for vapor-liquid coexistence curves of long-chain n-alkanes.

Fused Salt Mixtures

Reiss, Katz, and Kleppa (1962) developed a conformal solution theory for fused salt mixtures and used it to predict heats of mixing for binary mixtures. They assumed that the coulomb interaction creates a locally ordered structure in which a positive ion is surrounded by negative ions and vice versa. They therefore neglected short-range interactions between ions of like sign and wrote

$$\phi_{\alpha\beta}(r) = \frac{z_\alpha z_\beta e^2}{Dr} \quad \text{(like sign)} \tag{50}$$

For ions of opposite sign the short range interaction was approximated by a hard-sphere potential,

$$\begin{aligned} \phi_{\alpha\beta}(r) &= \infty \qquad r \leqq \lambda \\ &= \frac{z_\alpha z_\beta}{Dr} \qquad r > \lambda \quad \text{(opposite sign)} \end{aligned} \tag{51}$$

where $\lambda = d_+ + d_-$ is the sum of the ionic radii. This theory gives good results provided that the ions do not differ greatly in size. An improvement in this theory has been given by Luks and Davis (1967), who use a potential more realistic than (50) and (51).

NONSPHERICAL MOLECULES

The approaches outlined above (with the exception of Prigogine's r-mer model) assume that the potential is independent of molecular orientation, that is, that the molecules are effectively spherical. However, molecular nonsphericity is known to have a significant effect on thermodynamic and transport properties. Perturbation theory can be applied to such fluids by writing the pair potential in the form

$$\phi(r_{12}\,\omega_1\,\omega_2;\,\lambda) = \phi^{\text{ref}}(r_{12}) + \lambda\phi^p\,(r_{12}\,\omega_1\,\omega_2) \tag{52}$$

where ω_i represents the angles necessary to specify the orientation of molecule i. Here ϕ^{ref} is a potential for spherical, nonpolar molecules, for example, the Lennard-Jones (6, 12), while the perturbation ϕ^p is the part due to anisotropic intermolecular forces; thus ϕ^p may include dipolar, quadrupolar, or higher multipolar interactions, and also anisotropic overlap and dispersion forces. The perturbation in the free energy due to ϕ^p is obtained by expanding A^c about $(A^c)^{\text{ref}}$, that is, about $\lambda = 0$, in the same way as in Equation (11). The explicit relationships obtained are given by Pople (1954), Rowlinson (1969), and Stell et al. (1972). A closely related expansion for molecules with noncentral hard cores has been given by Bellemans (1968). Rigby (1972) has presented a van der Waals model for molecules with nonspherical hard cores.

These theories provide a rigorous basis for the homomorph concept, frequently used by engineers (for example, Weimer and Prausnitz, 1965). Knowing the properties of the corresponding fluid of spherical molecules (the homomorph), it is possible to calculate the properties of the fluid of nonspherical molecules. Thus the experimentally known properties of argon, for example, can be used to calculate properties of more complex fluids such as carbon dioxide, benzene, etc. Some preliminary calculations along these lines have been made by Ananth et al. (Ananth, 1972; Gubbins and Gray, 1972; Ananth, Gubbins, and Gray, 1973). Excellent results were obtained for all thermodynamic properties of the fluids tested (N_2, O_2, CH_4, CO_2, CCl_4). It was found that the heat capacity and entropy calculations were particularly sensitive to anisotropic forces. More extensive calculations along these lines will probably appear in the near future.

For isothermal compressibilities, partial molal volumes, and the concentration derivatives of chemical potentials in mixtures, perturbation theory gives simple results (Ananth, 1972). These properties are related in a particularly direct way to the molecular distribution functions (Kirkwood and Buff, 1951; O'Connell, 1971), and the first-order perturbation term vanishes. Thus for isothermal compressibility one obtains

$$\rho K_T RT = (\rho K_T RT)^{\text{ref}} + \text{second-order terms} \tag{53}$$

where the reference is a fluid of spherical molecules (argon). Thus the isothermal compressibility for complex molecular fluids should obey the same corresponding-states relation as that for argon. Brelvi and O'Connell (1972) have used this idea to correlate liquid compressibilities; they find that for liquids ρKRT is almost independent of temperature (Figure 8). They obtain similarly good results for partial molal volumes.

TRANSPORT PROPERTIES

Conformal solution theory can be applied to viscosity, thermal conductivity, and self-diffusion in mixtures. Having decided on the expansion parameters to be used, the

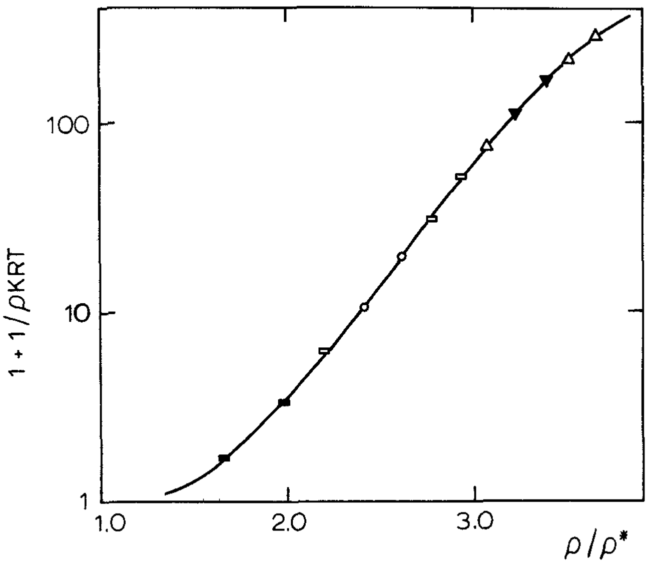

Fig. 8. Generalized correlation of liquid compressibilities based on Equation (53); ρ is a characteristic density. Points are: ■ = Ar, ○ = methanol, □ = isopentane, △ = *n*-decane, ▼ = *n*-hexadecane. [Reproduced with permission from *AIChE J.*, 18, 1239 (1972)].

transport property is expanded in the same way as the free energy in Equation (40). Transport properties are affected by the molecular masses m_α as well as $\sigma_{\alpha\beta}$ and $\epsilon_{\alpha\beta}$. Therefore it is necessary to expand in the mass as well as in the potential parameters; the reference fluid thus has parameters ϵ_x, σ_x and m_x. As for thermodynamic properties, the main problem lies in determining the best expansion parameters to give good convergence. Brunet and Doan (1970) have obtained good results by assuming the random mixture rules for ϵ_x and σ_x, and an ad hoc mixture rule for m_x. Mo and Gubbins (1973) have examined the time correlation function expressions for viscosity and thermal conductivity in the Enskog approximation, and find these expressions to be of the form

$$\eta = \sum_\alpha \sum_\beta x_\alpha x_\beta G_\eta \left(\sigma^3{}_{\alpha\beta};\ \epsilon_{\alpha\beta}\,\sigma^3{}_{\alpha\beta};\ (\mu_{\alpha\beta}\,\epsilon_{\alpha\beta})^{1/2}/\sigma_{\alpha\beta}{}^2\right) \tag{54}$$

$$\kappa = \sum_\alpha \sum_\beta x_\alpha x_\beta G_\kappa \left(\sigma^3{}_{\alpha\beta};\ \epsilon_{\alpha\beta}\,\sigma^3{}_{\alpha\beta};\ \left(\frac{\epsilon_{\alpha\beta}}{\mu_{\alpha\beta}}\right)^{1/2} \frac{1}{\sigma^2{}_{\alpha\beta}}\right) \tag{55}$$

where G_η and G_κ are functions of the groups shown. Accordingly, these groups are used as expansion parameters. Annulling the first-order terms yields $\eta = \eta_x$ and $\kappa = \kappa_x$, with ϵ_x and σ_x given by the van der Waals 1 mixing rules (42) and (43). The mixing rules for the reduced mass μ_x differ for viscosity and thermal conductivity:

Viscosity:

$$\frac{(\mu_x\,\epsilon_x)^{1/2}}{\sigma_x{}^2} = \sum_\alpha \sum_\beta x_\alpha x_\beta \frac{(\mu_{\alpha\beta}\,\epsilon_{\alpha\beta})^{1/2}}{\sigma^2{}_{\alpha\beta}} \tag{56}$$

Thermal
Conductivity:

$$\left(\frac{\epsilon_x}{\mu_x}\right)^{1/2} \frac{1}{\sigma_x{}^2} = \sum_\alpha \sum_\beta x_\alpha x_\beta \left(\frac{\epsilon_{\alpha\beta}}{\mu_{\alpha\beta}}\right)^{1/2} \frac{1}{\sigma^2{}_{\alpha\beta}} \tag{57}$$

These equations give good results for mixtures of simple liquids and are substantially superior to the square-well theory (Rice, Boon, and Davis, 1968). For mixtures of more complex molecules, the above theory may be modified by introducing a third parameter, as in the corresponding states approach of Tham and Gubbins (1970). An example of the results is shown in Figure 9. Doan and Brunet (1972) have also extended the conformal solution theory to mixtures of high molecular weight *n*-paraffins, based on Prigogine's (1957) model for *r*-mers.

The conformal solution approach is not immediately applicable to isothermal concentration diffusion because such diffusion does not occur in pure fluids. Perturbation about hard-sphere fluids would be of more general application than the conformal solution approach; although the formal equations are available (Harris, 1971; Gubbins, 1973), no calculations have appeared so far.

CONCLUSION

The two most successful methods at present involve expansion about hard spheres and expansion about a pure fluid (conformal solution theory), respectively. These two methods give similar results for conformal mixtures; the advantage of using a hard-sphere reference is that nonconformal mixtures can be treated. An inconvenience in using the hard-sphere reference is the time-consuming calculation of the reference distribution functions. However, this difficulty should be partly overcome by the recent development of faster methods for calculating these functions (Grundke and Henderson, 1972).

Most of the papers published from 1967 to date have been concerned with the underlying theory and the method of carrying out the expansion. Much work remains to be done in applying the theory to systems of practical interest. Calculations of surface and transport properties for systems of complex molecules, for mixtures of nonspherical and polar molecules, and for liquid-metal mixtures are needed. The mode expansion approach to electrolyte solutions seems to have considerable promise and is not restricted to the highly simplified primitive model; what is needed is a civilized model that takes into account the solvent interactions (Stokes, 1972). Finally, several obvious applications await development, for example, the properties of water and of other liquids with association forces.

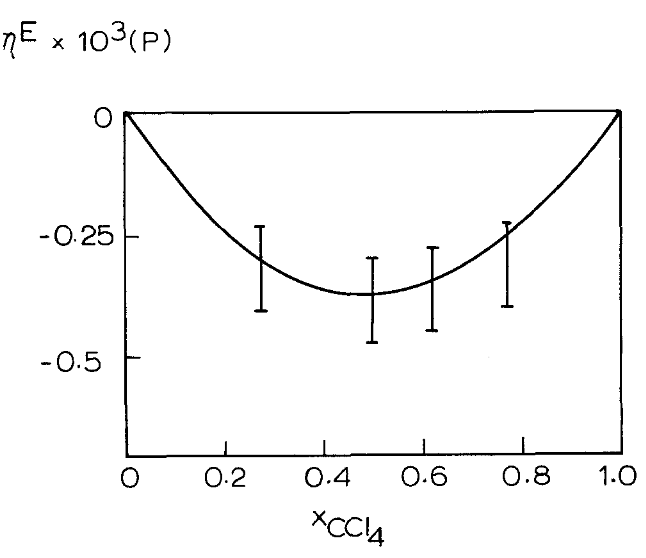

Fig. 9. Excess viscosity for liquid mixtures of carbon tetrachloride and cyclohexane at 25°C. The line is the conformal solution theory of Mo and Gubbins (1973) with ξ_{ab} = 0.980, and points are experiment.

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NOTATION

a = constant in van der Waals equation
A = Helmholtz free energy
A^c = configurational part of A
A_x = Helmholtz free energy for pure hypothetical reference fluid
b = constant in van der Waals equation
c = velocity of sound in the liquid; constant in van der Waals models; Prigogine parameter
C_p = constant pressure heat capacity
C_v = constant volume heat capacity
$d_{\alpha\alpha}$ = hard sphere diameter for component α
D = dielectric constant for electrolyte solution
e = electronic charge
$g_{\alpha\beta}$ = radial distribution function for an α-β pair
G^E = excess Gibbs free energy
H^E = excess enthalpy
$H_{1,j}$ = Henry constant for component 1 in pure solvent j
$H_{1,m}$ = Henry constant for component 1 in mixed solvent
k = Boltzmann constant
K_T = isothermal compressibility
m_α = molecular mass for component α
N = total number of molecules in system
N_α = number of molecules of component α in system
P = pressure
r = number of components in mixture
$\mathbf{r}_i$ = vector locating center of molecule i
$r^0{}_{\alpha\alpha}$ = intermolecular separation at potential minimum for component α
R = gas constant
S = entropy
T = absolute temperature
T_c = critical temperature
U = internal energy
$\mathcal{U}$ = total potential energy due to intermolecular forces
V = volume of system
V_c = critical volume
V^E = excess volume
x = mole fraction of component α
z_α = charge on ion of type α
Z = configuration integral

Greek Letters

α = thermal expansion coefficient
$\alpha_{i,1}$ = relative volatility of i with respect to component 1
$\gamma^{E,\infty}$ = infinite dilution activity coefficient in the extract phase
$\delta_{\alpha\beta}$ = function defined by Equation (18)
$\epsilon_{\alpha\alpha}$ = energy parameter in pair potential for component α
$\zeta_{\alpha\beta}$ = parameter in mixing rule for $\epsilon_{\alpha\beta}$, defined by Equation (21)
η = viscosity
κ = thermal conductivity
λ = perturbation parameter
λ = sum of ionic radii, Equation (51)
μ_α = chemical potential per molecule of component α
$\mu_{\alpha\beta}$ = reduced mass = $(1/m_\alpha + 1/m_\beta)^{-1}$
ρ_m = mass density
ρ_α = number density of component $\alpha = N_\alpha/V$
$\sigma_{\alpha\alpha}$ = intermolecular separation at which $\phi_{\alpha\alpha} = 0$
$\phi_{\alpha\beta}$ = intermolecular pair potential between a molecule of component α and a molecule of component β
ω_i = set of angles giving the orientation of molecule i

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THE AUTHOR

The author was born in England and educated at the University of London. He received his Ph.D. in 1962 and then joined the University of Florida where he is now Professor of Chemical Engineering. His research interest centers around the understanding of molecular transport processes in liquid mixtures. He spent the 1970-1971 academic year on sabbatical leave at Imperial College, London. During the past few summers he has migrated northwards to the University of Guelph, Canada, where he has been a visiting professor of Physics. He has recently co-authored a book called *Applied Statistical Mechanics*.

Diffusion in High Viscosity Liquids

The diffusion coefficients D of n-hexane and of naphthalene in a series of hydrocarbon liquids with viscosities μ from $5 \cdot 10^{-4}$ to 5 kg m^{-1} sec^{-1} (0.5 to 5000 centipoise) have been measured at 25°C with a one Savart plate wavefront-shearing interferometer. This apparatus allows direct determinations at effectively infinite dilution. The values obtained suggest that for a small solute diffusing in a large solvent

$$D\mu^{2/3} = \text{constant}$$

a result consistent with earlier studies. The exponent of 2/3 may be rationalized on the basis of the Eyring rate theory.

TIMOTHY G. HISS
and E. L. CUSSLER

Department of Chemical Engineering
Carnegie-Mellon University
Pittsburgh, Pennsylvania 15213

SCOPE

This paper explores the relation between diffusion and viscosity for a small solute diffusing in a high viscosity liquid. The liquid viscosity varies about 10,000 times. The best known relation of this type is the Stokes-Einstein equation, which involves a rigid sphere moving in a continuum, that is, a large solute molecule diffusing in a solvent of relatively small molecules. This work represents the other limiting case of a small solute molecule diffusing in a solvent of relatively large molecules.

This work is not concerned with diffusion in high polymers or gels, but with diffusion in liquids. In both high polymers and gels, viscosity is greatly affected by long range entanglements, while diffusion is controlled by short range interactions (Komiyama and Fuoss, 1972; Wasan et