Conformal Solution Correlation for the Nitrogen-Oxygen-Argon System

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A correlation based on conformal solution theory has been developed for the excess properties of the nitrogen-oxygen-argon systems. A better method for calculating the conformal parameters makes possible the simultaneous correlation of the three excess properties F^E, H^E, and V^E. Each binary is characterized by a k_{12}, c_{12} set which represents corrections to the geometric and arithmetic mean combination rules. These binary constants predict the ternary data. Also, the correlation based on data at one atm. (77° and 84°K.) predicts the F^E data accurately up to the critical points (110° to 120°K.).

Conformal solution theory as developed by Longuet-Higgins (*1*) and Brown (*2*, *3*) has severe theoretical limitations. It is a random mixture theory and, if the restrictions placed by Pitzer (*4*) on the universal potential function concept are observed strictly, the theory is applicable only to spherical molecules of the same size. The restriction to spherical molecules of the same size was loosened somewhat by Longuet-Higgins when he introduced the reference substance concept and stated that the resulting equations were restricted to "mixtures of spherical molecules (not necessarily equal in size) and mixtures of nonspherical molecules of the same shape and size." Nevertheless, application of the formalism associated with the theory to mixtures of engineering interest obviously requires that certain theoretical considerations be downgraded in importance.

Despite the theoretical limitations, the conformal solution formalism offers important advantages as a starting point in the development of an improved correlation and predictive scheme for liquid mixture properties. The mathematical framework is not based on a questionable physical model such as a lattice and it is more readily usable than distribution function theory. The principle of corresponding states is invoked and the development suggests "scale-reducing" parameters which are more accurate than reduced temperature, pressure, and volume for the prediction of excess properties. The corresponding states principle is combined with a perturbation approach which permits the representation of mixture properties in terms of the thermodynamic properties of a well-defined reference substance. The resulting equations are algebraically capable of fitting empirically all types of systems and are not restricted to miscible systems. Finally, the equations contain temperature and pressure terms which may permit the correlation parameters to be temperature and pressure independent.

CORRESPONDING STATES EQUATIONS

The two major assumptions in the initial development of conformal solution theory are (1) that only the configurational part of the partition function is changed in an isothermal mixing, and (2) that the potential energy between any pair of molecules at positions *i* and *j* in a mixture can be represented by a universal function

$$u(r_{i,j}) = u^* \phi \left[\frac{r_{ij}}{r^*}\right] \tag{1}$$

which is a function of distance only. These two assumptions permit manipulation of the configurational integral to provide the following corresponding states relationship between the configurational Gibbs free energies of pure substance *a* and a reference substance *o*.

$$F'_a(T,p,N) = f_{aa} F'_o\left(\frac{T}{f_{aa}}, \frac{p h_{aa}}{f_{aa}}, N\right) - RT \ln h_{aa} \tag{2}$$

When the temperature and pressure derivatives of f_{aa} and h_{aa} are neglected, appropriate differentiations give

$$H'_a(T,p,N) = f_{aa} H'_o\left(\frac{T}{f_{aa}}, \frac{p h_{aa}}{f_{aa}}, N\right) \tag{3}$$

$$V'_a(T,p,N) = h_{aa} V'_o\left(\frac{T}{f_{aa}}, \frac{p h_{aa}}{f_{aa}}, N\right) \tag{4}$$

The scale-shifting parameters for temperature and pressure, f_{aa} and h_{aa}, are termed the *conformal parameters* and have the following theoretical definitions:

$$f_{aa} = \frac{u^*_{aa}}{u^*_{oo}} \tag{5}$$

$$h_{aa} = (g_{aa})^3 = \left(\frac{r^*_{aa}}{r^*_{oo}}\right)^3 \tag{6}$$

These definitions must be ignored in any practical application of the conformal solution formalism.

The pure component forms can be extended to mixtures by defining a pure pseudosubstance p which differs from the mixture x only by the ideal entropy of mixing; that is

$$F'_x(T,p,N_1 \cdots N_c) = F'_p(T,p) + RT \sum_a x_a \ln x_a \tag{7}$$

where $a = 1, 2, \cdots c$. Then it follows that

$$F'_p(T,p) = f_{xx} F'_o \left(\frac{T}{f_{xx}}, \frac{ph_{xx}}{f_{xx}}, N\right) - RT \ln h_{xx} \tag{8}$$

$$H'_p(T,p) = H'_x(T,p) = f_{xx} H'_o \left(\frac{T}{f_{xx}}, \frac{ph_{xx}}{f_{xx}}, N\right) \tag{9}$$

$$V'(T,p) = V'_x(T,p) = h_{xx} V'_o \left(\frac{T}{f_{xx}}, \frac{ph_{xx}}{f_{xx}}, N\right) \tag{10}$$

where f_{xx} and h_{xx} are the *mixture conformal parameters*, the scale-shifting constants necessary to make the mixture substance "correspond" with the reference substance.

TAYLOR SERIES EXPANSIONS

The *excess* Gibbs free energy can be expressed as

$$F^E = F'_p - \sum_a x_a F'_a \tag{11}$$

This equation was not used to calculate F^E because F'_p and F'_a are large numbers (say 10,000 cal./mole), while F^E falls within the 5 to 15 cal./mole range. The same difficulty arises with H^E and V^E. It is at this point that the perturbation approach becomes useful.

Both F'_p and F'_a are expressed as Taylor series expansions around F'_o with respect to the conformal parameters. The partial derivatives in both expansions are evaluated at the reference substance and are therefore identical. Substitution of the expansions in Equation (11) gives the following working equation for F^E:

$$\begin{aligned}
F^E &= F_f \left[(f_{xx}-1) - \sum_a x_a(f_{aa}-1)\right] \\
&+ F_h \left[(h_{xx}-1) - \sum_a x_a(h_{aa}-1)\right] \\
&+ \frac{1}{2} F_{ff} \left[(f_{xx}-1)^2 - \sum_a x_a(f_{aa}-1)^2\right] \\
&+ F_{hf} \left[(f_{xx}-1)(h_{xx}-1) - \sum_a x_a(f_{aa}-1)(h_{aa}-1)\right] \\
&+ \frac{1}{2} F_{hh} \left[(h_{xx}-1)^2 - \sum_a x_a(h_{aa}-1)^2\right] \\
&+ \frac{1}{6} F_{fff} \left[(f_{xx}-1)^3 - \sum_a x_a(f_{aa}-1)^3\right] \\
&+ \frac{1}{2} F_{ffh} \left[(f_{xx}-1)^2(h_{xx}-1) - \sum_a x_a(f_{aa}-1)^2(h_{aa}-1)\right] \\
&+ \frac{1}{2} F_{fhh} \left[(f_{xx}-1)(h_{xx}-1)^2 - \sum_a x_a(f_{aa}-1)(h_{aa}-1)^2\right] \\
&+ \frac{1}{6} F_{hhh} \left[(h_{xx}-1)^3 - \sum_a x_a(h_{aa}-1)^3\right] + \cdots
\end{aligned} \tag{12}$$

where $F_f = (\partial F'_p/\partial f_{xx})$, $F_h = (\partial F'_p/\partial h_{xx})$, etc.

Differentiation of Equation (8) and evaluation of the derivatives at the reference substance provide the following relationships:

$$F_f = U'_o$$

$$F_h = pV_o - RT$$

$$F_{ff} = -TC'_{po} - p^2V_o\beta_o + 2pTV_o\alpha_o$$

$$F_{fh} = -pTV_o\alpha_o + p^2V_o\beta_o$$

$$F_{hh} = RT - p^2V_o\beta_o$$

$$\begin{aligned}
F_{fff} &= 2TC'_{po} + T^2\left(\frac{\partial C'_{po}}{\partial T}\right) - 3pT^2\left(\frac{\partial^2 V_o}{\partial T^2}\right) \\
&+ 3p^2\beta_o V_o - 6pT\alpha_o V_o - 3p^2T\left(\frac{\partial^2 V_o}{\partial p \partial T}\right) \\
&- p^3\left(\frac{\partial^2 V_o}{\partial p^2}\right)
\end{aligned}$$

$$\begin{aligned}
F_{ffh} &= 2\alpha_o pTV_o + pT^2\left(\frac{\partial^2 V_o}{\partial T^2}\right) + 2p^2T\left(\frac{\partial^2 V_o}{\partial p \partial T}\right) \\
&- 2p^2V_o\beta_o + p^3\left(\frac{\partial^2 V_o}{\partial p^2}\right)
\end{aligned}$$

$$F_{fhh} = p^2V_o\beta_o - p^2T\left(\frac{\partial^2 V_o}{\partial p \partial T}\right) - p^3\left(\frac{\partial^2 V_o}{\partial p^2}\right)$$

$$F_{hhh} = p^3\left(\frac{\partial^2 V_o}{\partial p^2}\right) - 2RT$$

The third-order terms in the F^E equation are often necessary to ensure that the neglected terms are numerically smaller than the experimental error in the data to be fitted.

The working equations for H^E and V^E are analogous to Equation (12) but the partial derivatives are, of course, different combinations of thermodynamic properties. For example

$$H_f = U'_o - TC'_{po} + \alpha_o pTV_o$$

and

$$V_f = pV_o\beta_o - TV_o\alpha_o$$

A complete listing of these relationships, plus the activity coefficient equation obtained from Equation (12), is given by Calvin (5).

PURE COMPONENT CONFORMAL PARAMETERS

The pure component energy and size conformal parameters f_{aa} and h_{aa} are the two most important parameters in the theory. They must provide a measure of the difference between the substance a and the reference substance o. (The conformal parameters of substance o are both 1.0.) They must be known quite accurately if the expansions are to give accurate values of the excess properties.

Values calculated from Equations (5) and (6) using u^* and r^* values determined by fitting the Lennard-Jones 6, 12 equation to gas data give F^E predictions which can be in error by several orders of magnitude.

The usual procedure in previous work has been to calculate f_{aa} and h_{aa} from the critical properties. This gives values which are approximately correct but which are not sufficiently accurate to predict the excess properties well. The principle of corresponding states is not exact and it is not reasonable to expect that scale-shifting parameters obtained from the pVT surfaces will be accurate for the configurational free energy and enthalpy surfaces. Also, the inexactness of the corresponding states principle makes it unlikely that one set of scale-shifting constants will be accurate over wide temperature ranges; that is, we must expect the conformal parameters to be slightly temperature dependent.

When the critical point properties failed to provide adequate f_{aa} and h_{aa} values, the triple point properties were tried because the triple points were closer to the system conditions. The calculated excess property values were still unsatisfactory.

Satisfactory f_{aa} and h_{aa} values were finally obtained by simultaneous solution of Equations (3) and (4). The configurational properties needed were calculated as described by Rowlinson (6). The results are shown in the bottom half of Table 1. Values calculated by the previous methods are also shown in Table 1 for comparison.

TABLE 1. PURE COMPONENT CONFORMAL PARAMETERS FOR NITROGEN AND OXYGEN WITH ARGON AS THE REFERENCE

	N_2		O_2	
Method of calculation	f_{aa}	h_{aa}	f_{aa}	h_{aa}
Gas viscosity	0.7379	1.2491	0.9113	1.0132
Second virial coefficient	0.7934	1.2810	0.9808	1.1622
Critical point	0.8343	1.1954	1.0216	0.9866
Triple point	0.7538	1.1436	0.6485	0.8660
Conformal equations:				
T, °K.				
75	0.8692	1.1952	1.0622	0.9651
80	0.8682	1.1991	1.0549	0.9728
85	0.8690	1.2003	1.0490	0.9772
90	0.8742	1.2019	1.0451	0.9787
95	0.8815	1.2034	1.0400	0.9766

MIXTURE CONFORMAL PARAMETERS

Each liquid mixture of composition x_1, x_2, $\cdots$ is considered to be a pseudo-pure substance with unique energy and size conformal parameters f_{xx} and h_{xx}. These mixture parameters vary with composition (and temperature) and the pure component values f_{aa} and h_{aa} are the limiting values.

Any two of the three excess properties F^E, H^E, and V^E (if known as a function of composition at the same temperature) can be used to calculate f_{xx} and h_{xx} at any given composition. This is done by solving the two series expansions simultaneously using the known reference substance properties and the f_{aa} and h_{aa} values calculated previously. However, only V^E is strongly dependent upon h_{xx} and should always be one of the pair chosen. For the basic correlation work, F^E is preferable to H^E because it can be easily checked for thermodynamic consistency.

The calculated f_{xx} and h_{xx} versus x curves are illustrated in Figure 1 for the N_2-Ar binary. The curves for the three binaries are all concave upward except for the h_{xx} curve for Ar-O_2 system, which is the only one of the three that exhibits positive V^E values. Of course, none of the curves deviates widely from linearity in these almost ideal systems.

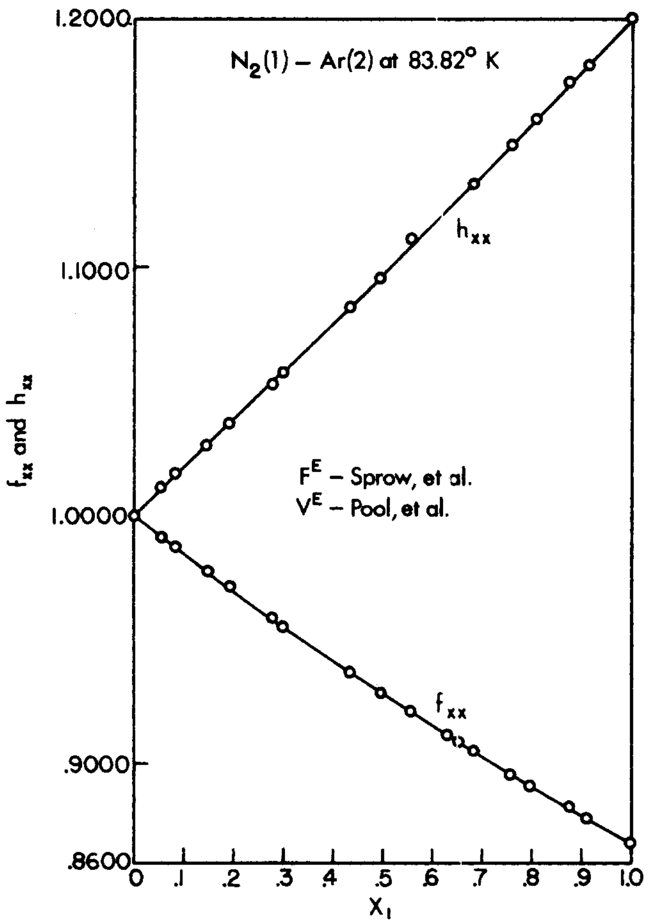

Fig. 1. The f_{xx} and h_{xx} curves for the N_2-Ar binary based on the F^E (7) and V^E (8) data.

PREDICTION OF H^E (OR F^E)

At this point in the correlation, the F^E and V^E data for each binary have been reduced to f_{xx} and h_{xx} values. The validity of the entire procedure can be checked at this point by using these f_{xx} and h_{xx} values to predict the unused H^E data. The points requiring validation are the correctness of Equations (2) to (4) and (8) to (10) as corresponding states relationships for the configurational properties; the use of Equations (3) and (4) to calculate the f_{aa} and h_{aa} values; and the adequacy of the Taylor series approximations of the configurational properties.

The agreement between predicted and experimental H^E values was very good, indicating the relationships assumed are valid for the systems under consideration. Evidence of this agreement is given later in the paper when the final correlation is presented.

It should be noted that at this point no analytical form has been assumed for the universal potential function, Equation (1), which was assumed in the derivation of Equation (2). Without doing so, it has been possible to produce graphical correlations of f_{xx} and h_{xx} versus x from two excess properties and predict the third. This means that F^E (activity coefficients, K values, x-y diagrams) can be predicted from heat and volume of mixing (H^E and V^E) data. The accuracy of these predictions is indicated below with the final correlation.

CORRELATION OF f_{xx} AND h_{xx}

Further progress toward a general predictive scheme requires correlations for f_{xx} and h_{xx} in terms of the known pure component conformal parameters f_{aa} and h_{aa}. This is essentially an averaging procedure and the various methods which have been proposed have been summarized by Rowlinson (*9*). The results to be presented here are based upon Brown's equations as modified by Wheeler and Smith (*10*)

$$f_{xx} = \frac{\left[\sum_a \sum_b PTP(\mu_{ab}) f_{ab}\, g_{ab}^{m}\right]^{\frac{n}{n-m}}}{\left[\sum_a \sum_b PTP(\nu_{ab}) f_{ab}\, g_{ab}^{n}\right]^{\frac{m}{n-m}}} \tag{13}$$

and

$$h_{xx} = \left[\frac{\sum_a \sum_b PTP(\nu_{ab}) f_{ab}\, g_{ab}^{n}}{\sum_a \sum_b PTP(\mu_{ab}) f_{ab}\, g_{ab}^{m}}\right]^{\frac{3}{n-m}} \tag{14}$$

These equations represent mixture averages over the μ and ν constants

$$\mu_{xx} = \sum_a \sum_b PTP(\mu_{ab})\, \mu_{ab} \tag{15}$$

$$\nu_{xx} = \sum_a \sum_b PTP(\nu_{ab})\, \nu_{ab} \tag{16}$$

in the Lennard-Jones equations for the various pairs in the mixture

$$u_{ab}(r_{ij}) = -\frac{\mu_{ab}}{r_{ij}^{m}} + \frac{\nu_{ab}}{r_{ij}^{n}} \tag{17}$$

The $PTP(\mu_{ab})$ and $PTP(\nu_{ab})$ are *pair-type-probability* functions which permit weighting of the individual pairs as necessary to secure agreement between prediction and experiment (*10*). The *PTP* function can be represented symbolically as

$$PTP(a, b) = \frac{x_a x_b W_a W_b I(a, b)}{\sum_a \sum_b x_a x_b W_a W_b I(a, b)} \tag{18}$$

The W_a and W_b are factors which give numerical representation of the size and shape effects of species *a* and *b*. The $I(a, b)$ function weights a molecular pair according to the strength of its specific interaction. When the *W*'s and *I*'s are all 1.0, the weighting function reduces to the random mixing form, $x_a x_b$.

As denoted in Equations (15) and (16), the repulsion and attraction terms in the potential equation can be weighted separately. No advantage of doing so has been evident in the work so far.

It should be noted that the use of Brown's averaging equations does assume an analytical form for the universal potential function, the Lennard-Jones equation. Other averaging techniques which avoid the use of any specific potential equation work as well for these simple systems. Since many of the other averaging methods are special forms of the Brown equations, the approach used in this work has been to use Brown's equations with *m* and *n* as parameters to be deduced from mixture data according to criteria described below.

MODIFIED LORENTZ-BERTHELOT RULES

The use of any averaging method, such as Equations (13) and (14), presumes some combination rule for calculating the unlike pair conformal parameters, f_{ab} and g_{ab}, from the f_{aa}'s and g_{aa}'s.

The values for F^E, H^E, and V^E obtained from the expansions are extremely sensitive to the f_{ab} and g_{ab} values used. It was discovered early in the work that all three excess properties cannot be simultaneously correlated for even one binary when the unmodified Lorentz-Berthelot rules are used. Various other general combining rules also failed. It was finally decided to adopt the following currently popular empirical modifications of the Lorentz-Berthelot equations.

$$f_{12} = (1 - k_{12})(f_{11} f_{22})^{1/2} \tag{19}$$

$$(h_{12})^{1/3} = g_{12} = (1 - c_{12})\left(\frac{g_{11} + g_{22}}{2}\right) \tag{20}$$

An alternative to Equation (19)

$$f_{12} = (f_{11} f_{22})^{t} \tag{21}$$

was also used. The k_{12} and c_{12} values are always very small, whereas *t* must vary appreciably from 0.5 to have the same effect as the small k_{12} value.

FINAL CORRELATION

The first data reduction step in the overall correlation work reduced the excess property data to f_{xx} and h_{xx} values. The second data reduction step reduces the f_{xx} and h_{xx} values to k_{12}, c_{12} (or t_{12}, c_{12}) pairs for each binary. There are as many possible paths for this second step as there are possible averaging methods. Results for only one path, the one utilizing Brown's equations, will be presented here.

The criteria used to judge the relative effectiveness of the various averaging methods tried, and to determine the best parameter values for any given averaging method, are as follows. First, the method must provide a final set of correlation constants which reproduces the original F^E, H^E, and V^E data within experimental error. Second, the k_{12} (or t_{12}) and c_{12} values resulting from the second data reduction step must be *independent of composition*. The second criterion was usually the controlling one.

The usual *m*, *n* set of 6, 12 for the Lennard-Jones equation fails badly on both criteria when Brown's equations are used. Any *m* below 4 will work reasonably well but the set which best satisfies both criteria appears to be in the region of 3, 4. The 3, 4 gave slightly better results than 3, 6 and other sets with lower *m* values.

No obvious improvement was realized when non-unity values were used for the *W*'s and *I*'s in Equation (18). The random weighting function, $PTP(a, b) = x_a x_b$, appears sufficient for these molecules despite the facts that the molecular volume for nitrogen is about 1.2 times that for argon and oxygen, and that there is evidence that oxygen molecules exhibit specific interactions. It should be noted, however, that the numerical effect on the predicted excess property values due to small changes in the *W* and *I* values is small compared to the effect of changes in the combination rules or in the *m*, *n* values. Variations in any one of the latter completely overshadows any effect of the *W* and *I* factors in these almost ideal systems.

Table 2 lists the corrections to the Lorentz-Berthelot rules resulting from $m, n = 3, 4$. This table also presents a set of correlation constants for the nitrogen-oxygen-argon system. With $m, n = 3, 4$ and all the *W*'s and *I*'s set equal to 1.0, the absolute variation in f_{12} from $x_1 = 0$ to $x_1 = 1.0$ was

0.0003 for N_2-O_2, 0.0030 for N_2-Ar, and 0.0005 for Ar-O_2. The h_{12} parameter was equally constant. This permitted the k_{12} and c_{12} values calculated from the midpoint f_{12} and h_{12} values to represent accurately the experimental data over the entire composition range.

The accuracy with which the excess property data is reproduced by the Table 2 constants is illustrated in Figures 2, 3, and 4. These figures also serve as evidence that the H^E data are accurately predicted by constants derived from F^E and V^E data. The F^E data are equally well predicted when the correlation is based on H^E and V^E data.

TABLE 2. CORRELATION CONSTANTS

	$m, n = 3, 4$; all W's and I's = 1.0		
	Correction factors for Equations (19) and (21)		Correction factor for Equation (20)
Binary	t_{12}	k_{12}	c_{12}
Ar-O_2	0.1985	0.0148	−0.0018
N_2-O_2	0.4801	−0.0017	−0.0019
N_2-Ar	0.5413	0.0047	0.0008

TERNARY PREDICTIONS

A minimal requirement for any predictive scheme is that it be able to predict ternary data from constants derived solely from binary data. Only one set of ternary vapor-liquid equilibria data is available for the N_2-O_2-Ar system, that of Weishaupt (*14*). These ternary data were not checked for thermodynamic consistency because they obviously would fail the test. About half of the points were arbitrarily discarded because they gave activity coefficients less than 1.0. The bias in the discarded points undoubtedly exists in the retained points and one would expect the F^E values calculated from the experimental data to be low. In view of this bias in the data, the prediction of the remaining ternary F^E points illustrated in Figure 5 is satisfactory.

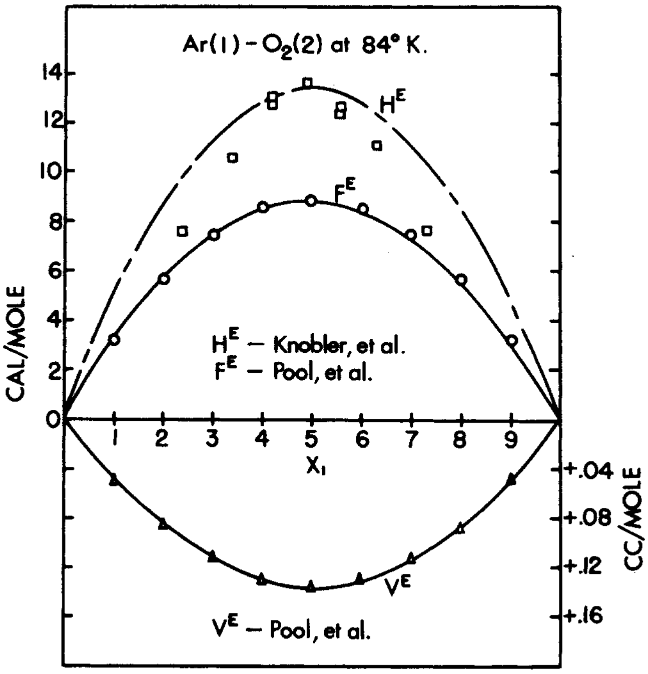

Fig. 2. Predicted curves for Ar-O_2 based on k_{12} and c_{12} constants from midpoint F^E and V^E values at 84°K. The points represent the experimental H^E (*11*), F^E (*8*), and V^E (*8*) data.

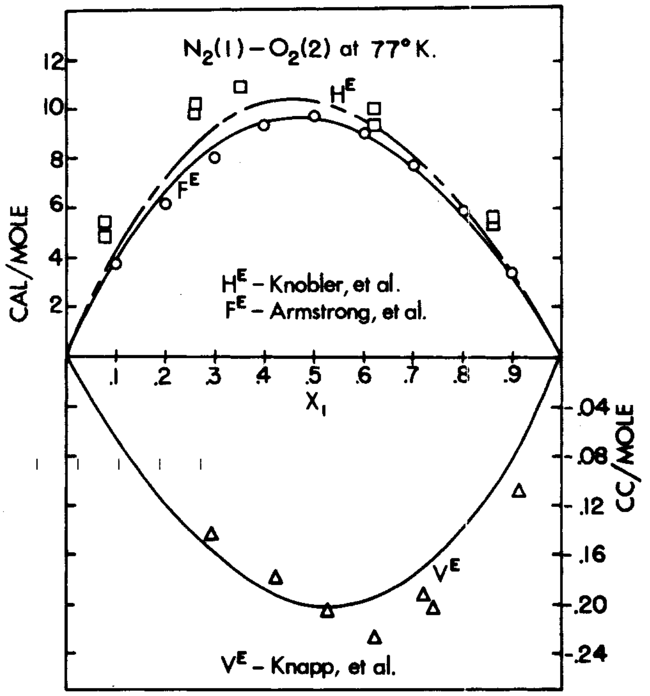

Fig. 3. Predicted curves for N_2-O_2 based on k_{12} and c_{12} constants from midpoint F^E and V^E values at 77°K. The points represent the experimental H^E (*11*), F^E (*12*), and V^E (*13*) data.

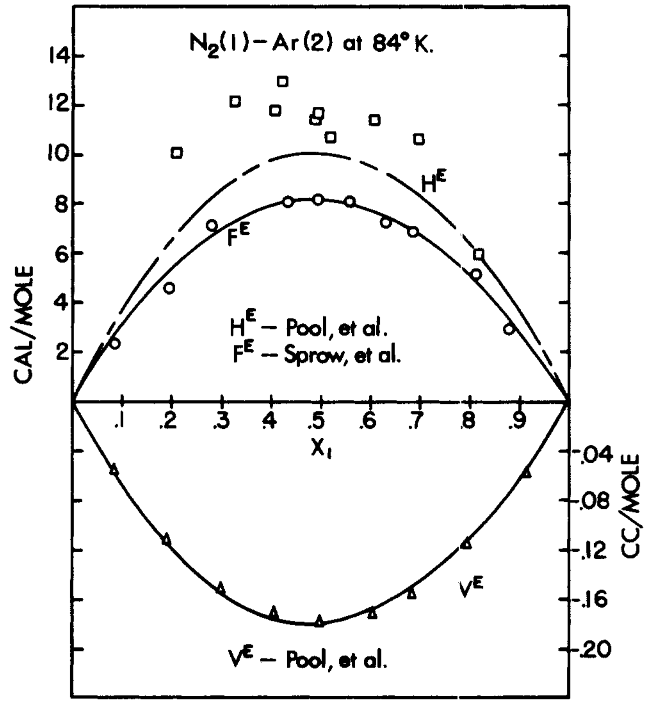

Fig. 4. Predicted curves for N_2-Ar based on k_{12} and c_{12} constants from midpoint F^E and V^E values at 84°K. The points represent the experimental H^E (*8*), F^E (*7*), and V^E (*8*) data.

PREDICTION OF HIGHER PRESSURE DATA

One of the major attractions of the conformal solution theory formalism is the appearance of temperature and pressure in the Taylor series coefficients. This, plus the fact that the pure component conformal parameters f_{aa} and h_{aa} are calculated and tabulated a priori as functions of temperature, may make the equations effective for data extrapola-

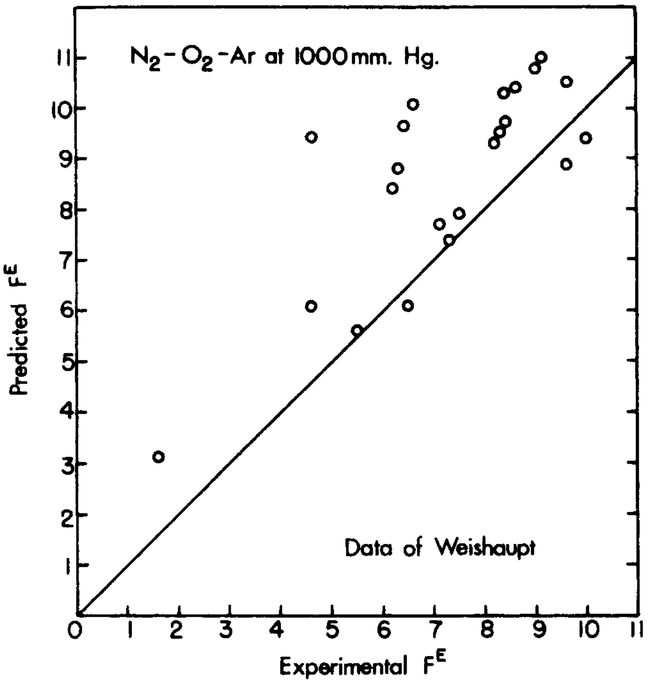

Fig. 5. Comparison of predicted ternary points with Weishaupt's data (*14*). F^E is in cal./mole.

tion. Fortunately, Wilson et al. (*15*) have provided data to check this capability for the N_2-O_2-Ar systems. The check can be made only up to about 10 atm. because the correlation requires both species to be below their critical points.

The calculation of F^E values from the *x-y-t-p* data at higher pressures is arbitrary because the results depend upon the equation of state used to correct for the gas-phase nonideality. The relative importance of the gas-phase and the liquid-phase nonideality corrections is illustrated in Figure 6. Curve 1 is the prediction based on Raoult's law. Curve 2 assumes ideal gases but utilizes activity coefficients predicted with the constants in Table 2. Curve 3 utilizes these same activity coefficients plus the Redlich-Kwong equation of state to provide the fugacity coefficients in the equation

$$\ln \gamma_i = \frac{y_i p}{x_i p_i^*} - \frac{V_i^L (p - p_i^*)}{RT} + \ln \bar{\phi}_{i,p} - \ln \phi_{i,p*} \qquad (22)$$

It can be seen that at 10 atm. the gas-phase corrections are already as important as the liquid-phase correction.

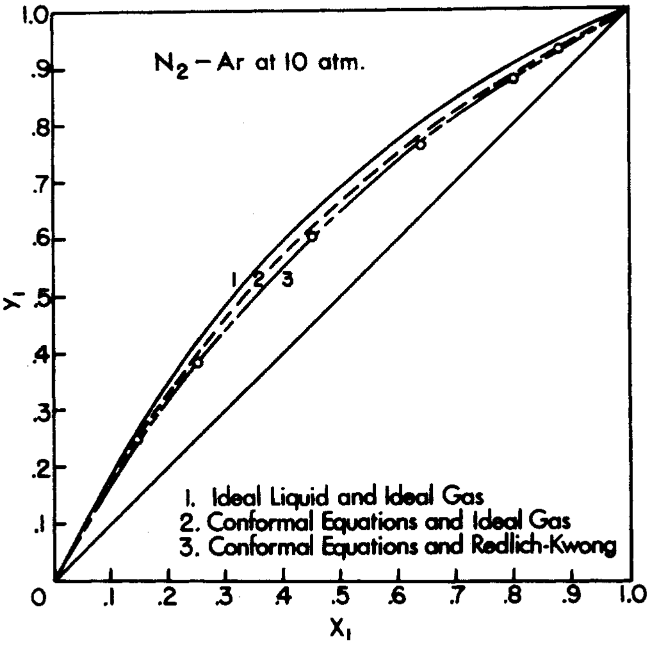

Fig. 6. Relative importance of the gas-phase and liquid-phase nonideality corrections. The points are the experimental data of Wilson et al. (*15*).

Four equations of state were tried: the virial equation truncated after the second coefficient (*SV*), the virial equation truncated after the third coefficient (*TV*), the Redlich-Kwong (*RK*) equation, and the Benedict-Webb-Rubin (*BWR*) equation. The use of the third virial coefficients was feasible because Wilson et al. (*15*) provided values for both the second and third coefficients. The *RK* equation requires only the critical constants T_c and p_c plus the acentric factor. *BWR* constants for argon were obtained from Zudkevitch and Kaufmann (*16*); the values of Stotler and Benedict (*17*) were used for nitrogen. The constants for oxygen were not available in the literature when this work was done so they were estimated from the argon values via corresponding states relationships (*5*). Oxygen values were published later by Cooper and Goldfrank (*18*) but the calculations were not repeated with their values because the *RK* equation seemed to give adequate results.

That equation of state which made the *x-y-t-p* data appear most consistent with the Gibbs-Duhem equation was used in each pressure range. A ln (γ_1/γ_2) versus x_1 plot was prepared for each binary with each of the four equations of state and the ratio of the smaller to the larger area calculated. The equation of state giving the area ratio closest to 1.0 was deemed best at that pressure. The results are summarized in Table 3. Each number represents the average of the area ratios of the three binaries. The third virial (*TV*) equation works well, as expected, over the entire range covered. The second virial (*SV*) equation is slightly better than the *RK* equation at low pressures but worse above 4 atm. The *BWR* equation is not competitive, possibly because of inaccuracies in the estimated oxygen constants.

The data at 4, 6, 8, and 10 atm. for the N_2-Ar and Ar-O_2 binaries were predicted accurately by the constants listed in Table 2. This means that activity coefficients were predicted accurately at temperatures up to 114°K. for N_2-Ar and 120°K. for Ar-O_2 from constants obtained by fitting data at 84°K. Figure 6 illustrates the prediction at 10 atm. for N_2-Ar; Figure 7 does the same for the Ar-O_2 binary in terms of the activity coefficients.

The comparison of the predicted and experimental values at higher pressures is not so good for the N_2-O_2 binary as shown by Figure 8. However, the validity of the experimental data can be questioned in this case. Comparison of Figure 8 with Figure 3 shows that the experimental values of F^E have remained about constant even though the temperature has increased from 77° to 118°K. The N_2-O_2 binary has a positive heat of mixing and the F^E values should decrease with temperature at about the same rate as in the case of the other two binaries which have midpoint F^E values around 5 cal./mole at 10 atm.

TABLE 3. AVERAGE AREA RATIOS FOR ALL THREE BINARIES

Equation of state	Pressure, atm. 1	2	4	6	8	10
RK	0.87	0.89	0.93	0.91	0.98	0.95
TV	0.90	0.97	0.95	0.85	0.93	0.95
SV	0.89	0.90	0.89	0.78	0.75	0.70
BWR	0.83	0.87	0.80	0.79	0.82	0.71

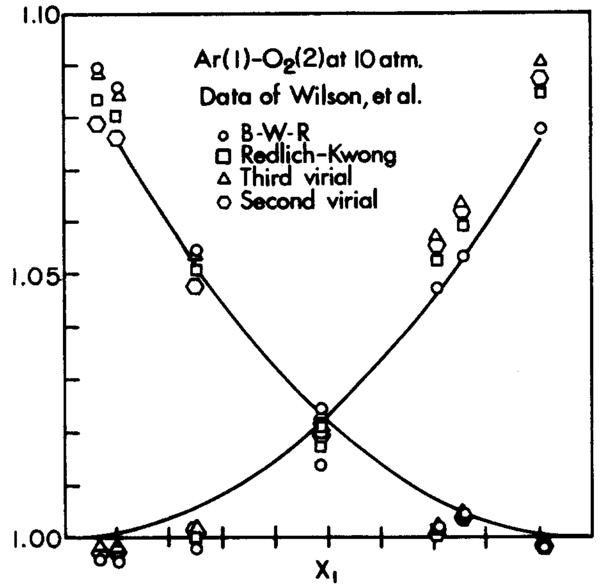

Fig. 7. The curves represent predicted activity coefficients for the Ar-O_2 binary at 10 atm. The points represent the experimental points of Wilson et al. (*15*) calculated with the various equations of state.

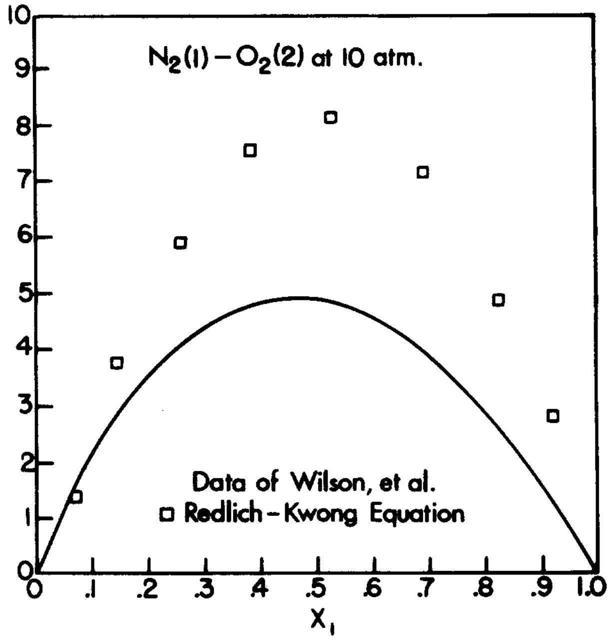

Fig. 8. Predicted (curve) and experimental values (points) of F^E for the N_2-O_2 binary at 10 atm. (*15*). The Redlich-Kwong equation was used.

The results indicate that the m, n, k_{12} (or t_{12}), and c_{12} constants in Table 2 can be considered to be temperature independent over the range (less than 40°C.) covered by these predictions.

ULTIMATE PREDICTIVE SCHEME

It has been shown for these simple molecules that once the k_{12} and c_{12} constants have been determined from mixture data for each binary, the correlating equations can predict ternary data from binary constants only and can predict activity coefficients over a temperature range of about 40°C. A true predictive scheme, however, would require no mixture data on a new mixture; that is, the k_{12} and c_{12} constants would have to be deduced solely from the pure component characteristics of the species making up the new mixture.

Table 4. Deviation from Geometric Mean

Binary	This work	Eckert et al. (*19*) (cell theory)	Virial coefficients (6, 12 potential)
N_2-O_2	−0.0017	−0.0015	−0.0010
N_2-Ar	0.0047	0.0032	0.0037
Ar-O_2	0.0148	0.0120	0.0042

There is some evidence that the k_{12} and c_{12} values resulting from the arbitrary data reduction steps have some significance beyond empirical data-fitting constants. Table 4 shows that k_{12} values obtained from three different sources are amazingly similar. The conformal solution equations and the cell theory formulation used by Eckert et al. (*19*) represent two entirely different data reduction schemes for liquid-state data and they both give k_{12} values similar to those obtained when the 6, 12 Lennard-Jones equation is applied to virial coefficient data for gases.

Even if the k_{12} and c_{12} values do have some natural significance, it must still be demonstrated that the unlike pair interaction can be characterized in terms of the properties and/or structure of the interacting molecules. It may be that the unlike pair interaction is a "mixture" property which cannot be deduced from the individual molecules. If such is the case, the task becomes simply the definition of the most convenient kind of mixture data to be taken to provide k_{12} and c_{12} values for each binary to be included in the corresponding states class defined by an m, n set.

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NOTATION

c_{12} = correction to arithmetic mean combination rule
C'_p = configurational heat capacity
f_{aa} = energy conformal parameter for the aa pair
f_{ab} = energy conformal parameter for the ab pair
f_{xx} = energy conformal parameter for the mixture
F' = configurational Gibbs free energy
F^E = excess Gibbs free energy
F_f, F_h, etc. = partial derivatives of F'
g_{aa} = distance conformal parameter for the aa pair
g_{ab} = distance conformal parameter for the ab pair
g_{xx} = distance conformal parameter for the mixture
h_{aa} = size conformal parameter for the aa pair
h_{ab} = size conformal parameter for the ab pair
h_{xx} = size conformal parameter of mixture
H' = configurational enthalpy
H^E = excess enthalpy
H_f, H_h, etc. = partial derivatives of H'
$I(a, b)$ = specific interaction factor for the ab pair
k_{12} = correction to geometric mean combination rule
m = exponent of attractive term in intermolecular potential function
n = exponent of repulsive term in intermolecular potential function
N = number of molecules
p = pressure
p^* = vapor pressure
$PTP(a, b)$ = pair type probability weighting function for the ab pair
r_{ij} = distance between positions i and j
r^* = distance parameter in pair potential
R = gas constant

t = correction to geometric mean combination rule
T = absolute temperature
u = intermolecular potential energy
u^* = energy parameter in pair potential
U_x = potential energy of mixture
V' = configurational volume; same as V^L
V^E = excess volume
V^L = liquid molar volume
V_f, V_h, etc. = partial derivatives of V'
W_a = size and shape factor for molecule a
x = liquid mole fraction
y = vapor mole fraction

Greek Letters

α = thermal expansion coefficient
β = isothermal compressibility
γ = activity coefficient
μ = coefficient of attractive term in intermolecular potential function
ν = coefficient of repulsive term in intermolecular potential function
ϕ = universal function of distance r_{ij}
$\overline{\phi}_{i,p}$ = fugacity coefficient of species i in a gas mixture at T and p
$\phi_{i,p*}$ = fugacity coefficient of pure species i at T and its vapor pressure

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Peak-Time Method for Measuring Thermal Diffusivity of Small Solid Specimens

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A simple test method is developed for determining the thermal diffusivity of solids and granular materials by measuring the time at which the peak on a temperature-time record occurs. It allows the use of small easily prepared specimens and specimens of irregular shape (for example, stones). The tests can be performed at room temperature as well as at high temperatures, and can be repeated in short time intervals.

The principal difficulties of measuring the thermal diffusivity of solids are associated with specimen preparation. Very often a specimen has to be machined or ground to a certain shape, and for solids of considerable hardness this operation may be extremely time-consuming and costly. The difficulties are further increased by the fact that it is often next to impossible to find a piece of the solid sufficiently large to serve as a specimen.

This latter problem is especially acute with some concrete aggregates that are often unavailable in sizes larger than about 1½ in. As the thermal conductivity of aggregates is known to be the primary factor in the conductivity of concrete (*1*, *2*), inability to determine this property seriously hinders the design of concrete mixtures in applications where thermal characteristics are of principal importance.

The method to be described for measuring thermal diffusivity of solids is notable for its simplicity with regard to both specimen preparation and the performance of the test. It is especially suitable for nonmetallic materials, and can be carried out on very small specimens.

THEORY

It will be shown that a method developed earlier (*3*) for the measurement of thermal diffusivity, using idealized semi-infinite solids, can be extended to include the use of