Conformal Solution Correlation for Simple Liquids

J. J. HOUNG and BUFORD D. SMITH

Thermodynamics Research Laboratory
Washington University, St. Louis, Missouri 63130

An application of Brown's conformal solution formalism (*1, 2*) to the simple liquids argon, nitrogen, and oxygen was described recently by Calvin and Smith (*3*). The results of that study were promising enough to justify an attempt to develop a broader correlation for mixtures of simple liquids based on the conformal solution formalism. This paper presents the initial version of such a correlation. Despite the limitations inherent in the conformal solution approach, the results are encouraging.

Insofar as this paper is concerned, the simple liquids correspond roughly to the $Z_c = 0.29$ class of Lyderson, Greenkorn, and Hougen (*4*). However, the correlation described below can include only those substances with critical temperatures between about 151.1°K. (argon) on the low end and about 305.3°K. (ethane) on the high end. This excludes the lightest gases (helium, hydrogen, and neon) and molecules like hydrogen sulfide, the hydrogen halides, carbon disulfide, etc.

The primary objective of the correlation project was the simultaneous representation of the three primary excess properties V^E, H^E, and F^E by one set of correlation constants. If this is achieved, then the prediction of F^E (and the associated quantities like activity coefficients, x-y diagrams, relative volatilities, and K values) from V^E and H^E measurements becomes feasible.

CORRELATION STRUCTURE

The conformal solution formalism utilized in this correlation project embodies three distinct concepts. The first of these is the universal potential function idea, first stated by Pitzer (*7*) and utilized by Longuet-Higgins (*8*) in his development of conformal solution theory. The universal function assumption leads to corresponding states equations which relate the properties of a pure substance a to the properties of a reference substance o.

The second major assumption is that a mixture can be treated as a pure pseudosubstance. The pseudosubstance concept permits the corresponding states equations developed for pure substances to be applied to mixtures.

Finally, it is assumed that the properties of a pure substance or a pure pseudosubstance can be accurately represented by a Taylor series expansion around a well-defined reference substance.

The working equations based on these three concepts will not be presented in detail here; they are summarized more fully in the previous paper (*3*) and are developed in detail by Houng (*6*) and by Calvin (*5*). Only enough will be included here to make clear the data reduction procedures and to provide a basis for discussion.

Corresponding States Equations

The conformal solution theory provides the following corresponding states relationship between the configurational Gibbs free energy of a pure substance a and a reference substance o.

$$F_a'(T,p) = f_{aa}F_o'\left(\frac{T}{f_{aa}}, \frac{ph_{aa}}{f_{aa}}\right) - RT\ln h_{aa} \quad (1)$$

In early applications of the theory, the conformal parameters f_{aa} and h_{aa} (the scale-shifting parameters for temperature and pressure, respectively) were always assumed to be constants and usually calculated from the critical properties. Under that assumption, differentiation of Equation (1) with respect to temperature and with respect to pressure gave the following equations for the configurational enthalpy and volume:

$$H_a'(T,p) = f_{aa}H_o'\left(\frac{T}{f_{aa}}, \frac{ph_{aa}}{f_{aa}}\right) \quad (2)$$

$$V_a'(T,p) = h_{aa}V_o'\left(\frac{T}{f_{aa}}, \frac{ph_{aa}}{h_{aa}}\right) \quad (3)$$

The corresponding states principle is not exact and the f_{aa} and h_{aa} values required to bring the configurational property surfaces together at any point vary with the temperature and pressure. The correct expressions for H_a' and V_a' obtained by differentiation of Equation (1) contain temperature and pressure derivatives, respectively, of f_{aa} and $\ln h_{aa}$. The pressure derivatives are completely negligible for the systems under consideration. As will be shown later in the results obtained with Equation (2) (which omits the temperature derivatives of f_{aa} and $\ln h_{aa}$), the temperature derivatives are almost but not quite negligible.

Pseudosubstance Concept

The pure component forms above are extended to mixtures by the definition of a pure pseudosubstance p which differs from the mixture x only by the ideal entropy change of mixing; that is

$$F_x'(T,p,N_1\ldots N_c) = F_p'(T,p) + \mathrm{RT}\sum_a x_a \ln x_a \quad (4)$$

Equations for F_p', H_p', and V_p' analogous to Equations (1) through (3) can be written with the mixture parameters f_{xx} and h_{xx} substituted for the pure component parameters f_{aa} and h_{aa}.

The f_{xx} and h_{xx} parameters characterize a hypothetical pure pseudosubstance whose thermodynamic properties are identical to those of the given mixture (at fixed T, p, x_i values), except for the ideal entropy of mixing. The necessary f_{xx} and h_{xx} values at the given mixture T, p, x_i values will be obtained by a suitable weighting of the various pure component (f_{aa}, h_{aa}) and unlike-pair (f_{ab}, h_{ab}) conformal parameters. This suitable weighting must be deduced from mixture properties.

Once the hypothetical pure pseudosubstance is defined via the required f_{xx} and h_{xx} values, it can be treated like any other pure component in the Taylor series expansions described below. The nonthermodynamic terms which

---

Correspondence concerning this article should be addressed to Prof. Buford D. Smith.

arise in the expansion for an actual nonrandom mixture do not appear in the pure component pseudosubstance expansion. The pseudosubstance concept is therefore an artifice which shifts the nonrandom mixture problem in conformal solution theory from the nonthermodynamic terms in Brown's mixture expansion to the weighting functions used to define the pseudosubstance. The appropriate weighting functions can be more readily deduced from mixture properties.

Taylor Series Expansions

It is assumed that the properties of any pure component a or any pure pseudosubstance p can be expressed accurately by a Taylor series expansion around a well-defined reference substance. The partial derivatives are evaluated at the reference substance and can be expressed in terms of the reference substance properties and the system temperature and pressure. The increments in the expansion are the differences between the conformal parameters of the reference substance (which are unity by definition) and the conformal parameters of the substance a or p. Substitution of the various expansions for F_a' and F_p' in

$$F^E = F_p' - \sum_a x_a F_a'$$

gives

$$F^E = F_f[(f_{xx} - 1) - \sum_a x_a(h_{aa} - 1)] \tag{5}$$

$$+ F_h[(h_{xx} - 1) - \sum_a x_a(h_{aa} - 1)]$$

$$+ \text{second order terms}$$

$$+ \text{third order terms} + \ldots$$

where

$$F_f = U_o'$$

$$F_h = pV_o - RT \text{ , etc.}$$

When the temperature and pressure derivatives of f_{aa} and h_{aa} are neglected, equations exactly analogous to Equation (5) can be written for H^E and V^E, except that

$$H_f = U_o' - T\,C'_{po} + \alpha_o pT V_o \text{ , etc.}$$

and

$$V_f = p\,V_o \beta_o - TV_o \alpha_o \text{ , etc.}$$

Third-order terms are always included in an attempt to make the neglected terms numerically smaller than the experimental error in the data being fitted.

INITIAL REDUCTION STEP FOR MIXTURE DATA

The f_{xx} and h_{xx} parameters were calculated from mixture data as a function of composition by solving the F^E and V^E expansions simultaneously at each mixture composition where F^E was known from experimental data. V^E values at the same compositions were obtained by interpolation of experimental values. Typical binary f_{xx} and h_{xx} values are shown in Figure 1.

The V^E data must be used in this calculation if accurate h_{aa} values are to be obtained, because F^E and H^E are relatively insensitive to the size parameter. Either F^E or H^E can be used for the other needed property. F^E data were used in this initial correlation work because they can be more accurately checked for consistency with the Gibbs-Duhem equation than can the H^E data.

The validity of the theory, the Taylor series expansions, the calculational procedures, etc., were all checked by using the f_{xx}, h_{xx} values obtained from a simultaneous fit of the V^E and F^E data to predict H^E data. This test was passed successfully, as will be shown later when the H^E predictions based on the final correlation are presented.

CORRELATION OF MIXTURE PARAMETERS

The f_{xx} and h_{xx} values obtained from the binary F^E and V^E data represent the effective average of the conformal parameters for the *a-a* the *b-b*, and the *a-b* molecular pairs in the binary mixture. The correlation task at this point is to find an averaging equation which best relates the experimental f_{xx} and h_{xx} values to the pure component parameters f_{aa} and h_{aa} and the unlike pair parameters f_{ab} and h_{ab}. There are many ways of averaging. Some recent papers (*9, 32, 33*) discuss this problem in terms of various models for the liquid mixture. Three averaging methods will be compared here.

Direct Average

The mixture conformal parameters can be related directly to the various pair parameters by

$$f_{xx} = \sum_a \sum_b PTP(f_{ab})\, f_{ab} \tag{6}$$

$$h_{xx} = \sum_a \sum_b PTP(h_{ab})\, h_{ab} \tag{7}$$

where $PTP(f_{ab})$ and $PTP(h_{ab})$ represent the weighting functions to be applied to the pair energy and size parameters. These functions were suggested by Wheeler (*10, 11*) as part of his definition of the pseudosubstance. He called the arbitrary weighting function a *pair-type probability*, or *PTP*, function which can be symbolically represented as follows:

$$PTP(a,b) = \frac{x_a x_b W_a W_b I(a,b)}{\sum_a \sum_b x_a x_b W_a W_b I(a,b)} \tag{8}$$

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. The *W*'s and *I*'s must be deduced from mixture properties. The correct *PTP* function is the one which gives a pseudosubstance whose free energy differs from that of the mixture as shown by Equation (4).

If all the *W*'s and *I*'s are 1.0, both weighting functions take on the random form used by Brown in the definition of his equivalent substance.

$$PTP(a,b) = \frac{x_a x_b}{\sum_a \sum_b x_a x_b} = x_a x_b \tag{9}$$

When Equation (9) is used in (6) and (7), the direct averages become simply

$$f_{xx} = x_1^2 f_{11} + 2x_1 x_2 f_{12} + x_2^2 f_{22} \tag{10}$$

$$h_{xx} = x_1^2 h_{11} + 2x_1 x_2 h_{12} + x_2^2 h_{22} \tag{11}$$

Leland's Equations

Leland et al. (*12*) have suggested the following averaging equations:

$$f_{xx} = (x_1^2 f_{11} h_{11} + 2x_1 x_2 f_{12} h_{12} + x_2^2 f_{22} h_{22})/h_{xx} \tag{12}$$

$$h_{xx} x_1^2 h_{11} + 2x_1 x_2 h_{12} + x_2^2 h_{22} \tag{13}$$

These equations can be obtained from Equations (6), (7), and (8) by setting all the *W*'s and $I(a,b)$'s in $PTP(h_{ab})$ and all the *W*'s in $PTP(f_{ab})$ to 1.0 and then assuming the $I(a,b)$'s in $PTP(f_{ab})$ to be h_{11}, h_{12}, and h_{22}, respectively.

Brown's Equations

Brown (*1*) derived his averaging equations by averaging the μ and ν constants in the Lennard-Jones potential equations for the *a-a*, the *b-b*, and the *a-b* interactions. When the *PTP* function is substituted for the $x_a x_b$ product used by Brown, his averaging equations are

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

and

$$h_{xx} = \left[\frac{\sum_a \sum_b PTP(\nu_{ab})\, f_{ab}\, g_{ab}{}^{n}}{\sum_a \sum_b PTP(\mu_{ab})\, f_{ab}\, g_{ab}{}^{m}}\right]^{\frac{3}{n-m}} \tag{15}$$

The use of these equations requires that the universal potential function assumed in the development of conformal solution theory must be given an analytical form; that is, m and n values must be determined. These m and n values must be the same for all components and mixtures to be covered by the correlation. The other two averaging methods described above do not require a determination of m, n values.

COMPARISON OF AVERAGING METHODS

Each of the three sets of averaging equations was used to calculate the unlike pair parameters f_{12} and h_{12} as a function of composition from the experimental binary f_{xx} and h_{xx} values. (Figure 1 is an example of binary f_{xx} and h_{xx} values.)

Two criteria were established to judge the relative merits of the various averaging methods. First, the calculated f_{12} and h_{12} values for a given binary at a specified (constant) temperature should be essentially independent of composition. Second, the f_{12} and h_{12} values finally chosen to represent the entire composition range must reproduce the original F^E and V^E data within the experimental error.

The second criterion is in a sense redundant. If the f_{12} and h_{12} are almost independent of composition, the average values chosen will be close to all of the values calculated across the composition range and will therefore closely reproduce the original fitted data. The second criterion, in effect, defines the limits on the "essentially independent of composition" phrase; if the f_{12} or h_{12} values vary too widely with composition, it will be impossible to reproduce satisfactorily the experimental data over the entire composition range with single f_{12} and h_{12} values for the binary.

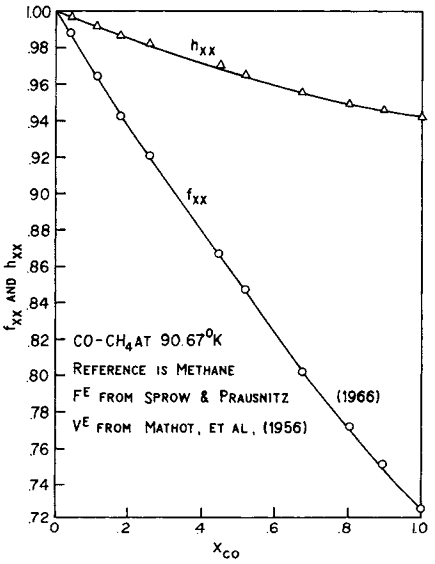

Fig. 1. Typical binary mixture conformal parameters as a function of composition.

The requirement that the unlike pair parameters be essentially independent of composition is useful in determining the best set of parameters for a given averaging method (that is, the m, n set in Brown's equation) and in comparing averaging methods. The predicted results are so powerfully influenced by the unlike pair parameters that almost any equation arising from almost any kind of theory can be made to reproduce accurately midpoint excess property values if the unlike pair parameters (or analogous constants) are fitted specifically to that data point. Only by examining the composition dependency of such parameters, and by requiring the accurate reproduction of all three excess properties, can we hope to distinguish between various alternative approaches.

The f_{12} and h_{12} values calculated as a function of composition by all three averaging methods were always constant through two digits and often through three digits for eight of the nine binaries covered in this work. Only the CH_4-CF_4 system showed deviations as large as 1 or 2%. This reflects the fact that CF_4 is a marginal member of a class based on CH_4 when the Taylor series approach is used; its f_{aa} and h_{aa} values are approximately 1.5 and 1.4, respectively, and consequently the third-order terms in the expansions are not negligible.

The m, n values in Brown's equations, Equations (14) and (15), which gave the least variation in the f_{12} and h_{12}, were 3,4. The usual Lennard-Jones exponents of 6,12 were not competitive. Some justification for an n value of 3.0 has been provided by the work of Leland et al. (*32*, *33*). Also, there is always the possibility that the physically unrealistic 3,4 values may actually give a good analytical representation of that small portion of the potential curve of interest for liquids at low pressures. Nevertheless, the m, n values in Brown's equations were regarded as just adjustable parameters in this correlation work and the 3,4 values were the ones which satisfied the fitting criteria. Any set below 4,6 worked almost equally well.

For each of the three averaging methods, a straight line was fitted to each set of binary f_{12} and h_{12} values and the midpoint value was designated as the unlike pair parameter value for that binary. These average binary f_{12} and h_{21} values were then used to recalculate the F^E and V^E data originally fitted. The root-mean-squared deviations (RMSD's) between the calculated and the experimental values for each binary were calculated for the nine binaries and summed for each averaging method. The F^E summations were 10.15, 9.54, and 10.26 for the direct-average, Leland, and Brown equations, respectively. The analogous values for V^E were 0.210, 0.210, and 0.220. (Disproportionate shares of these RMSD values were contributed by the CH_4-CF_4 binary.) The slightly poorer performance of Brown's equations at this point was balanced by a slightly better performance later in the predictions of ternary data. Consequently, for the simple liquids under consideration, there seems to be no basis other than convenience for the selection of one averaging method as best. Brown's equations are inherently less convenient than the other two methods investigated.

COMBINATION RULES

The unlike pair parameters obtained in the previous section can be related to the pure component parameters via combination rules. None of the theoretically based rules (*13* to *16*) tried could reproduce the required f_{12} values within the 0.2% accuracy required. The simple means—arithmetic, geometric, and harmonic—were tried and, surprisingly, the harmonic mean performed slightly

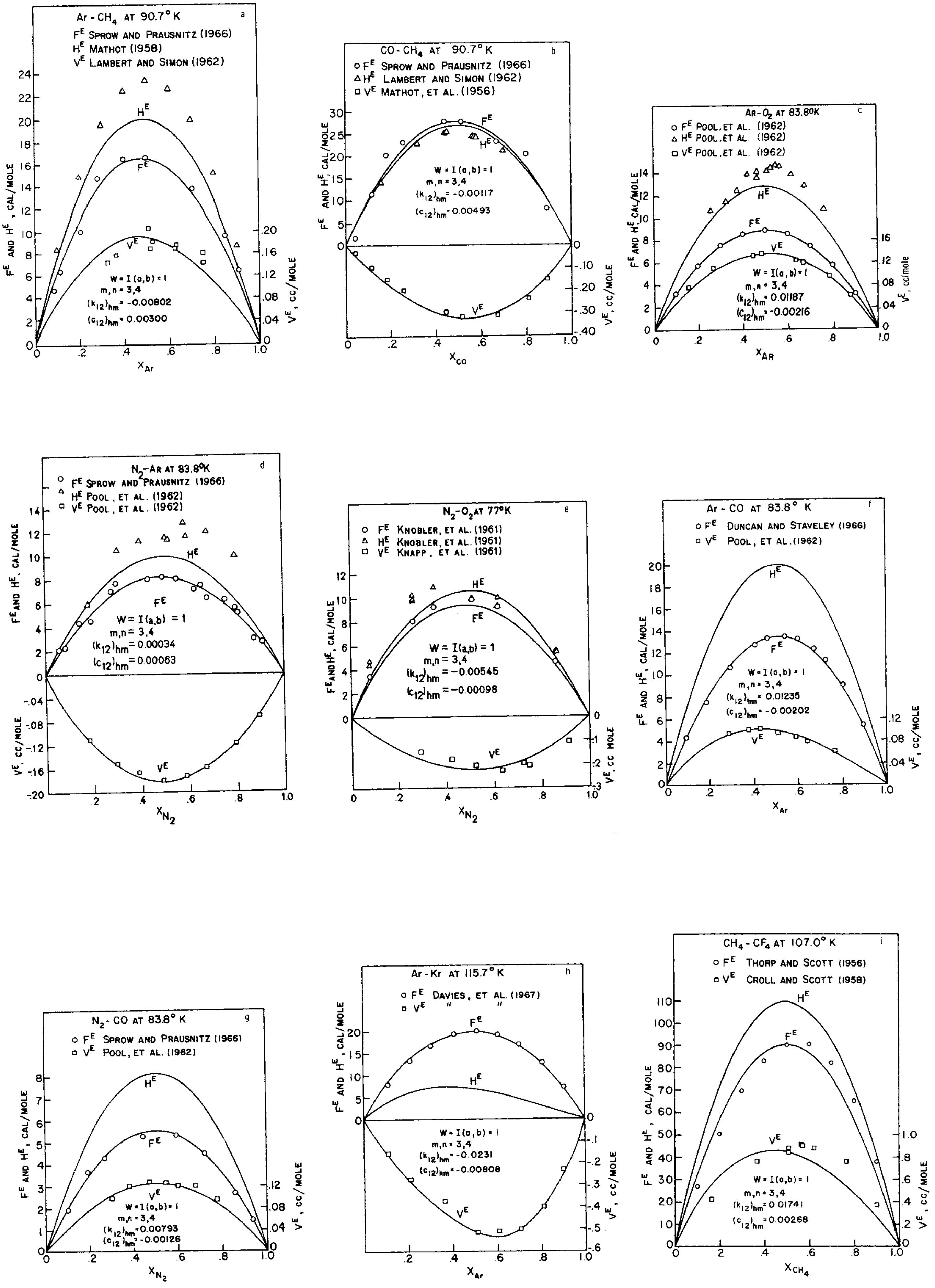

Fig. 2. Reproduction of the fitted F^E and V^E data and prediction of the H^E data for nine binaries using the correlation constants in Table 1.

better for both the energy and size parameters than either of the other two. It was finally decided to represent the unlike pair parameters by empirically corrected harmonic means:

$$f_{12} = (1 - k_{12}) \frac{2f_{11} f_{22}}{f_{11} + f_{22}} \tag{16}$$

$$(h_{12})^{1/3} = g_{12} = (1 - c_{12}) \frac{2g_{11}\, g_{22}}{g_{11} + g_{22}} \tag{17}$$

where the binary correction constants, k_{12} and c_{12}, are determined from mixture data.

FINAL DATA REDUCTION STEPS

The initial data reduction steps reduced the isothermal binary F^E and V^E data to binary f_{xx} and h_{xx} values tabulated versus composition.

The final data reduction begins with the selection of an averaging procedure. (For this presentation, Brown's method will be used.) Equations (14) and (15) were used to calculate f_{12} and h_{12} as functions of composition from the f_{xx} and h_{xx} values using different m, n sets. The $m, n = 3, 4$ set was found to give the least variation in the f_{12} and h_{12} values across the composition range. The average f_{12} and h_{12} values were then converted to the binary constants k_{12} and c_{12} via Equations (16) and (17).

Obviously, the average f_{12}, h_{12} set for a given binary would serve as well for the binary constants as the k_{12}, c_{12} set. The conversion to the k_{12}, c_{12} values was done in the hope that some order could be discerned in the way the various binaries deviated from some mean formula. Unfortunately, there has been no success as yet in the correlation of the deviation constants with pure component properties.

CORRELATION CONSTANTS

Correlation constants for the nine binaries fitted are listed in Table 1. The values shown are based on Brown's equations with $m, n = 3, 4$. Numbers of similar magnitude were obtained with the other averaging methods. Each data reduction path (averaging method, combination rules, etc.) gives different k_{12}, c_{12} values. Consequently, agreement of these values with analogous values obtained from other kinds of experimental data (for example, virial coefficient data) is probably more fortuitous than meaningful.

The constants in Table 1 along with the pure component f_{aa}, h_{aa} values [calculated from Equations (2) and (3)] and the reference substance properties can be used to predict mixture properties. The k_{12}, c_{12} values are used in Equations (16) and (17) to give f_{12} and h_{12} values, which along with the m, n values, predict the f_{xx} and h_{xx} values as a function of composition via Equations (14) and (15). The f_{xx}, h_{xx} values, the f_{aa}, h_{aa} values, and the reference substance properties then permit F^E, V^E, and H^E to be calculated with the Taylor series expansions.

TABLE 1. CORRELATION CONSTANTS BASED ON BROWN'S EQUATIONS WITH $m,n = 3,4$ AND ALL W's AND I's $= 1.0$

System	T, °K.	Binary constants k_{12}	c_{12}
Ar-Kr	115.7	−0.02310	0.00808
Ar-N_2	83.8	0.00034	0.00063
Ar-O_2	83.8	0.01187	−0.00216
Ar-CO	83.8	0.01235	−0.00202
Ar-CH_4	90.7	−0.00802	0.00300
N_2-O_2	77.0	−0.00545	−0.00098
N_2-CO	83.8	0.00793	−0.00126
CO-CH_4	90.7	−0.00117	0.00493
CH_4-CF_4	107.0	0.01741	0.00268

The correlation has been tested by making four kinds of predictions. First, the F^E and V^E data for the nine fitted binaries were reproduced to demonstrate the effectiveness of the formalism as a correlation scheme. Second, the H^E data available at the correlation temperature for five of the nine binaries were predicted; this is a true prediction because the H^E data were not involved in any way in the correlation. Third, F^E data available at other temperatures were predicted. Fourth, the two available sets of ternary data were predicted.

The first and second predictions will be presented simultaneously because they both will be at the original correlation temperatures. The third and fourth predictions will be discussed separately.

PREDICTIONS AT CORRELATION TEMPERATURES

Figure 2 shows how well the binary k_{12}, c_{12} constants reproduce the fitted F^E and V^E data. Figure 2*a* through 2*e* also show how well the H^E data at the correlation temperatures can be predicted; the predicted H^E curves are also shown in Figures 2*f* through 2*i* but no experimental H^E data are available for those four binaries.

The correlation reproduces the fitted data well, with the exception of the CH_4-CF_4 system. As mentioned previously, methane is not a good reference substance for this binary; the f_{aa} and h_{aa} values for CF_4 are approximately 1.5 and 1.4 and the third-order terms in the Taylor series expansions are not negligible.

The predicted H^E values are within 15% but are generally low. Some of the discrepancies could, of course, be due to inaccurate experimental data but it is more likely that the differences arise because of the omission of the temperature derivatives in Equation (2) and in the Taylor series expansion for H^E.

The predicted H^E values obtained in this work with methane as a reference agreed almost exactly with those obtained by Calvin (3, 5) with argon as the reference substance. This comparison illustrates the fact that any member of a class can be used as the reference if its physical properties are known accurately, and it gives f_{aa} and h_{aa} values for all the other class members close enough to unity to make the Taylor series expansions convergent.

PREDICTION OF F^E AT OTHER TEMPERATURES

Wilson, Silverberg, and Zellner (28) have provided vapor-liquid equilibrium data at various pressures for the Ar-N_2, Ar-O_2, and N_2-O_2 binaries. Din (29) has reported similar data for the N_2-O_2 binary. The accuracy with which the correlation constants in Table 1 predict those and other available F^E data for the Ar-N_2-O_2 binaries is shown in Figure 3. In each binary, the correlation constants were determined at the temperature of the point at the left end of the predicted line.

The Din and the Wilson et al. data in Figure 3*a* agree well at the higher temperatures with each other and with the predicted line. Also, the slope of the predicted curve on a F^E/T versus $1/T$ plot is approximately 14 cal./mole, which is close to but slightly higher than the probable experimental H^E value at the midpoint in Figure 2*e*. Consequently, it is believed that the high temperature data and the predictions shown in Figure 3*a* are fairly accurate.

In Figures 3*b* and 3*c* the predicted F^E line falls well above the experimental points at the highest temperatures. (This is also true of some of the points at the lower temperatures.) However, the slopes of the predicted lines agree quite well with the H^E data. The predicted Ar-O_2 values in Figure 3c have a slope of approximately 14 cal./mole on a F^E/T versus $1/T$ plot, and this value agrees closely to the midpoint H^E value in Figure 2c at 83.8°K. The slope of the Ar-N_2 line on the F^E/T versus $1/T$ plot is only 9.5 compared to a Figure 2*d* midpoint value of about 11.5 cal./mole, but a slope of 11.5 would still leave the predicted line above the experimental F^E values at 105° and 109°K.

PREDICTIONS OF TERNARY DATA

Another minimal requirement for a good working correlation is the prediction of multicomponent mixture properties from binary constants. Two sets of ternary phase equilibrium data are available for the group of components represented in Table 1. One set is the ternary Ar-N_2-O_2 data at 1,000 mm. Hg reported by Weishaupt (*30*). These data are of doubtful accuracy; about half the points were discarded because they gave activity coefficients less than 1.0. The prediction of the remaining points differed little from that shown by Calvin (3) and need not be shown again in this paper.

The other set of available ternary data is for the Ar(1)-N_2(2)-CH_4(3) system at 90.7°K. (*31*). Comparison of the predicted and experimental F^E values is made in Figure 4. The binary k and c values (corrections to the harmonic means) used are shown on Figure 4. The k_{12} and c_{12} values for the Ar(1)-N_2(2) binary are from F^E and V^E data at 83.82°K. Since no V^E data were available for the N_2(2)-CH_4(3) binary, it was necessary to assume that c_{23} was equal to the c value listed in Table 1 for the CO-CH_4 binary. (This assumption was justified by noting that nitrogen and carbon monoxide have very similar liquid molar volumes.) The k_{23} value in Figure 4 was then obtained from the F^E data available at 90.67°K. for the N_2-CH_4 binary using the assumed c_{23} value. Despite these necessary assumptions the prediction appears to be good. The points in Figure 4 scatter somewhat but they fall along both sides of the 45-deg. line with a root-mean-squared deviation of 2.9 cal./mole. The comparable number was 3.9 when the direct average equations, Equations (10) and (11), were used.

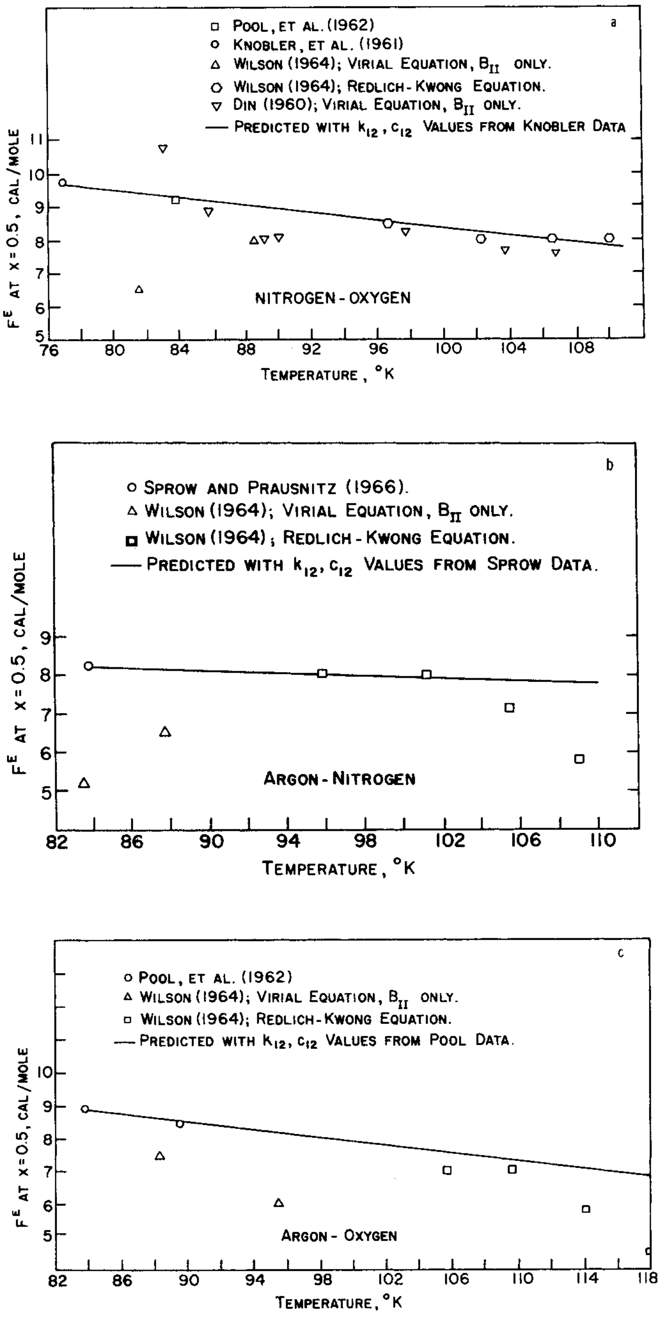

Fig. 3. Prediction of F^E for three binaries up to the critical temperature with correlation constants obtained at a single temperature.

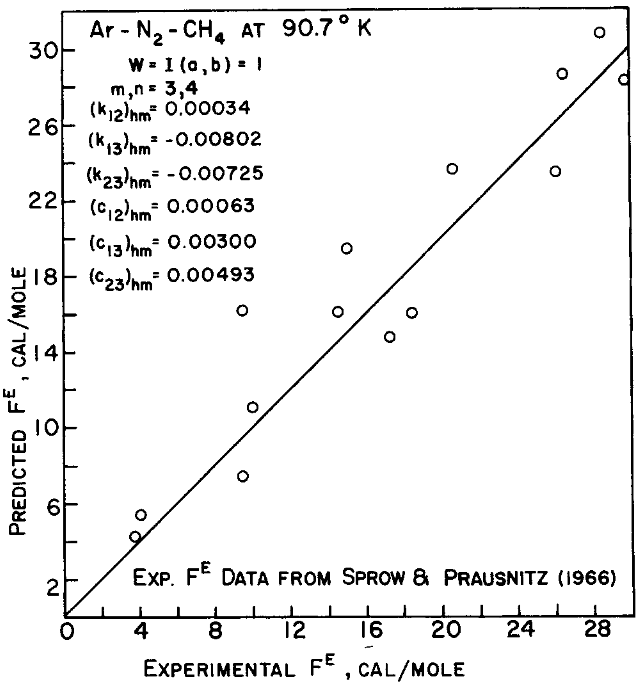

Fig. 4. Predicted vs. experimental F^E values for the Ar-N_2-CH_4 ternary system at 90.7°K.

CONCLUSIONS

The conformal solution formalism appears to provide a suitable mathematical framework for a good correlation and prediction scheme for a class of simple fluids ranging from argon to ethane. In its present form, the correlation does not relate the Gibbs excess free energy and the excess enthalpy exactly; the H^E values predicted from F^E and V^E measurements are usually 1 or 2 cal./mole too low. Presumably this discrepancy is due to the omission of the temperature derivatives. These derivatives will be included in the final correlation.

Despite this apparent discrepancy, the determination of a pair of constants for each binary from F^E and V^E or H^E

and V^E measurements at a single temperature permits what appear to be reasonably accurate predictions of F^E up to the critical temperature. The binary constants are probably not completely temperature independent but, for the simple molecules studied, they evidently can be assumed to be constant over a 30° or 40°C. range.

The correlation appears to be capable of predicting ternary data from binary constants. However, the data available to check this capability for the simple fluids are limited and involve only positive-deviation systems.

All three averaging methods used to relate the mixture parameters to the pure component parameters worked about equally well. The simplicity of the direct-average and Leland's equations gives those methods an inherent advantage over Brown's equations; also they avoid the use of a pseudopotential equation.

The results obtained for the simple fluids justify the development of a final, working correlation for this class. The major problem yet to be solved is the calculation of the pure component conformal parameters with the temperature derivatives included but without requiring an inordinate amount of pure component property data. Another question to be resolved is the exact temperature dependence of the binary constants. Finally, there seems to be no reason why the correlation framework developed for the simple fluids from the conformal solution theory cannot be extended empirically to more complicated molecules.

ACKNOWLEDGMENT

This research was made possible by support from the National Science Foundation through Grant GK-1971, by support from industrial funds in the Thermodynamics Research Laboratory, and by the services rendered by the Washington University Computing Facilities.

NOTATION

c_{12} = correction to harmonic mean combination rule
C_p' = configurational heat capacity at constant pressure
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 = g_{aa}^3
h_{ab} = size conformal parameter for the *ab* pair = g_{ab}^3
h_{xx} = size conformal parameter of mixture = g_{xx}^3
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 harmonic 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
$PTP(a, b)$ = pair-type probability weighting function for the *ab* pair
r_{ij} = distance between positions i and j
R = gas constant
RMSD = root-mean-squared deviation
T = absolute temperature
u = intermolecular potential energy
U' = configurational internal energy
V' = configurational volume. Same as V
V^E = excess volume
V = 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

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

LITERATURE CITED

1. Brown, W. B., *Phil. Trans. Roy. Soc.* (*London*), **250A**, 175 (1957).
2. ———, *Proc. Roy. Soc.*, **240A**, 561 (1957).
3. Calvin, W. J., and B. D. Smith, *AIChE J.*, **17**, 191 (1971).
4. Hougen, O. A., K. M. Watson, and R. A. Ragatz, "Chemical Process Principles," Pt. II, p. 573, Wiley, New York (1959).
5. Calvin, W. J., D.Sc. dissertation, Washington Univ., St. Louis, Mo. (1969).
6. Houng, J. J., D.Sc. dissertation, Washington Univ., St. Louis, Mo. (1969).
7. Pitzer, K. S., *J. Chem. Phys.*, 7, 583 (1939).
8. Longuet-Higgins, H. C., *Proc. Roy. Soc.*, **205A**, 247 (1951).
9. Fredenslund, A., and G. A. Sather, *Ind. Eng. Chem. Fundamentals*, **8**, 718 (1969).
10. Wheeler, J. D., Ph.D. dissertation, Purdue Univ., Lafayette, Ind. (1964).
11. ———, and B. D. Smith, *AIChE J.*, **13**, 303 (1967).
12. Leland, T. W., P. S. Chappelear, and B. W. Gamson, *ibid.*, **8**, 482 (1962).
13. Hudson, G. H., and J. C. McCoubrey, *Trans. Faraday Soc.*, **56**, 761 (1960).
14. Mathot, V. D. J., *Discussions Faraday Soc.*, **15**, 114 (1953).
15. Muller, A., *Proc. Roy. Soc.*, **154A**, 624 (1936).
16. Fender, B. E. F., and G. D. Halsey, Jr., *J. Chem. Phys.*, **36**, 1881 (1962).
17. Sprow, F. B., and J. M. Prausnitz, *AIChE J.*, **12**, 780 (1966).
18. Mathot, V., *Nuovo Cimento Suppl.*, **9**, Ser. 10, 356 (1958).
19. Lambert, M., and M. Simon, *Physica*, **28**, 1191 (1962).
20. Mathot, V., L. A. K. Stavely, J. A. Young, and N. G. Parsonage, *Trans. Faraday Soc.*, **52**, 1488 (1956).
21. Pool, R. A. H., G. Saville, T. M. Herrington, B. D. C. Shields, and L. A. K. Stavely, *ibid.*, **58**, 1692 (1962).
22. Knobler, C. M., J. M. Van Heijningen, J. J. M. Beenakker, *Physica*, **27**, 296 (1961).
23. Knapp, H. F. P., M. Knoester, and J. J. M. Beenakker, *ibid.*, **27**, 309 (1961).
24. Duncan, A. G., and L. A. K. Stavely, *Trans. Faraday Soc.*, **62**, 548 (1966).
25. Davies, R. H., A. G. Duncan, G. Saville, and L. A. K. Stavely, *ibid.*, **63**, 855 (1967).
26. Thorp, N., and R. L. Scott, *J. Phys. Chem.*, **60**, 670 (1956).
27. Croll, I. M., and R. L. Scott, *ibid.*, **62**, 954 (1958).
28. Wilson, G. M., P. M. Silverberg, and M. G. Zellner, *Techn. Document Rept. No. APL TDR 64-64* (Apr. 1964).
29. Din, F., *Trans. Farday Soc.*, **56**, 668 (1960).
30. Weishaupt, J., *Angew. Chem.*, **B20**, 321 (1948).
31. Sprow, F. B., and J. M. Prausnitz, *Cryogenics*, **6**, 338 (1966).
32. Leland, T. W., J. S. Rowlinson, and G. A. Sather, *Trans. Faraday Soc.*, **64**, 1447 (1968).
33. —————, and I. D. Watson, *ibid.*, **65**, 2034 (1969).

Manuscript received February 3, 1970; revision received June 9, 1970; paper accepted June 15, 1970.