Corresponding States: I. Theoretical Development for Mixtures

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Part I of this work develops a corresponding states theory for fluid mixtures. A greater predictive capability for the thermodynamic properties of mixtures is achieved through three developments: 1. The theoretical validity of the pseudocritical method is established. 2. The theory is founded on well-defined assumptions. 3. The composition dependence of the scaling parameters (pseudocritical constants) is developed from rigorous mixing rules. Implementation of the new method is discussed in Part II.

Corresponding states correlations have proven extremely useful for the estimation of the thermodynamic properties of single component dense gases and fluids in the absence of experimental data. The three parameter formulation of the corresponding states principle by Pitzer and others (*1* to *6*) has been so successful that for engineering purposes the method is often used almost exclusively for the prediction of the thermodynamic behavior of pure nonpolar fluids when experimental data are lacking. No other predictive method has ever achieved to the same degree the combined advantages of accuracy, generality, and simplicity inherent in corresponding states theory.

Logically, therefore, physical chemists and engineers have made many attempts to extend corresponding states theory to mixtures. For example, a number of investigators (*7* to *11*) have adopted various statistical mechanical approaches to this problem. In addition, empirical or semiempirical attempts to correlate mixture properties by pseudocritical methods have been reviewed by several authors (*12* to *14*). Unfortunately several formidable difficulties confront the more fundamental statistical mechanical formulations. Among these difficulties are mathematical complexity, the need for generalized fluctuation integrals which are not readily determined experimentally, and large uncertainties in the actual intermolecular potential laws. Because of these difficulties it appears that substantial progress toward a better statistical mechanical corresponding states theory must await a much more complete understanding of molecular interactions. Because of our very incomplete knowledge of molecular behavior a macroscopic or pseudocritical approach to mixtures is adopted in this paper.

The purpose of Part I of this paper is to develop a theoretical framework for applying corresponding states theory to mixtures. The concept of pseudocritical constants or scaling parameters is clarified, and a method is developed for calculating them. These scaling parameters may be used to predict mixture thermodynamic properties, but they cannot be employed directly for the estimation of component fugacity coefficients which are of paramount importance in phase equilibrium calculations. Therefore, a method is also derived for computing partial molal properties. Part I of this paper is purely theoretical, and readers primarily interested in the practical problem of predicting vapor-liquid equilibrium may proceed immediately to Part II.

SCALING PARAMETERS

We use throughout this paper the linearized three parameter corresponding states correlation of Pitzer et al. (*2*, *3*) which for pure compounds has the form

$$\Psi = \Psi^0\left(\frac{T}{T_C}, \frac{P}{P_C}\right) + \omega\Psi^1\left(\frac{T}{T_C}, \frac{P}{P_C}\right) \qquad (1)$$

Ψ is a configurational thermodynamic property such as compressibility factor, enthalpy or entropy departure, or the logarithm of the fugacity coefficient. For the prediction of such properties the correlation requires only the availability of a critical temperature, a critical pressure, and an acentric factor for the pure compound. The correlation may be used for mixtures as well once a pseudocritical temperature and pressure and an acentric factor for the mixture are known. These scaling parameters then are defined as those parameters which correctly predict the desired thermodynamic property of a mixture when they replace T_C, P_C, and ω in Equation (1). In this case Ψ^0 and Ψ^1 are the same generalized functions used for pure gases and liquids. It is emphasized here that the pseudocritical constants are mathematical scaling parameters only, and unlike true critical constants they do not in general have any experimentally observable physical significance.

The existence of such parameters under all conditions, however, remains in question in spite of the formal definition of them in the preceding paragraph. For brevity this question is examined here only for the prediction of compressibility factors.

Examination of the Pitzer tables of compressibility factors shows that values for Z range from nearly zero for liquids at low pressures and temperatures to values much larger than one. A mixture must have a positive volume, and the compressibility factor must always be greater than zero. It is apparent, therefore, that no matter what value of Z pertains to a mixture an identical value of Z can be found in the generalized tables for pure components. For example, if a certain mixture at 60 atm. and 400°K. has a compressibility factor of 0.5, Table 1 shows several sets of coordinates (reduced pressure and reduced temperature) which correctly predict the value of Z (*2*).

Table 1 shows that for each acentric factor an infinite number of sets of pseudocritical constants will predict correctly the mixture compressibility factor. Obviously then,

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Table 1. Valid Sets of Pseudocritical Parameters for a Gaseous Mixture at 400°K. and 60 Atmospheres

Z	T_R	P_R	ω	T_C, °K.	P_C, atm.
0.5	1.00	0.92	0.0	400	65.2
0.5	1.05	1.16	0.0	381	51.7
0.5	1.10	1.43	0.0	364	42.0
0.5	1.15	1.87	0.0	348	32.1
0.5	1.00	0.916	0.10	400	65.5
0.5	1.05	1.16	0.10	381	51.7
0.5	1.10	1.43	0.10	364	42.0
0.5	1.15	1.95	0.10	348	30.8

pseudocriticals do exist for mixtures under all conditions; and, in general, a unique set of these constants may be obtained only if the values of two of them are determined by some a priori rules.

ASSUMPTIONS

In this paper a corresponding states theory for mixtures is developed within the limits of the following two assumptions.

1. All pure components under consideration obey the same linearized three parameter theorem of corresponding states.
2. The scaling parameters are independent of the density of the mixture. They are definitely functions of composition and may be functions of temperature.

For nonpolar fluids the accuracy of three parameter corresponding states correlations is well established; therefore, the first assumption is a very good one. The second assumption is not strictly true, and the consequences of removing it are being studied. However, for a large number of applications the density variation of the scaling parameters is so small that the effect can be neglected entirely. In the second part of this work criteria are given which predict when the density variation may not be safely ignored.

MATHEMATICAL FORMULATION OF THE PSEUDOCRITICAL PARAMETERS

Two items of information are required for the derivation of mathematical expressions for the pseudocritical constants: A valid mixing rule and a generalized equation of state. The only theoretically rigorous mixing rules are those for the virial coefficients. For example the combining rule for the second virial coefficient is

$$B_M = \sum_{i=1}^{N}\sum_{j=1}^{N} y_i y_j B_{ij} \qquad (2)$$

Several investigators (*15, 16*) have shown that for nonpolar gases the individual second virial coefficients in Equation (2) can be correlated with generalized equations which are functions only of the reduced temperature and a shape parameter such as the acentric factor. The correlation which is used here is a special case of Equation (1).

$$B_R = \frac{B}{V_C} = B^0{}_R + B^1{}_R \qquad (3)$$

$$B^0{}_R = 0.4966 - \frac{1.1340}{T_R} - \frac{0.4759}{T_R{}^2} - \frac{0.0416}{T_R{}^3} \qquad (4)$$

$$B^1{}_R = 0.2906 + 1.4900/T_R - 1.7563/T_R{}^2 - 0.3366/T_R{}^3 - 0.0251/T_R{}^8 \qquad (5)$$

Equations (3), (4), and (5) are valid for the range of reduced temperatures from 0.5 to 3.0. The form of these equations is the same as that proposed by Pitzer and Curl (*15*) except that the constants are different because the second virial coefficient is reduced with the critical volume rather than the group (P_C/RT_C).

Cross virial coefficients B_{ij} are also calculated from Equations (4) and (5) and from interaction parameters ω_{ij}, V_{Cij}, T_{Cij}. Various methods for obtaining these parameters have been adopted by different investigators (*16* to *25*), and this problem is discussed further in Part II. Here, it is assumed that ω_{ij}, V_{Cij}, and T_{Cij} are always known.

Equations (2) through (5) provide the information necessary for the calculation of the scaling parameters; however, as explained earlier, arbitrary values should be assigned to two of the constants in order for the set of parameters to be unique. The scaling volume for the mixture is defined:

$$V_{CM} = \sum_{i=1}^{N}\sum_{j=1}^{N} y_i y_j V_{Cij} \qquad (6)$$

Equation (6) is often called the van der Waals combining rule for critical volumes. It has been used with success by a number of investigators (*20, 26* to *30*). If it is assumed that

$$V_{Cij} = 1/2\ (V_{Ci} + V_{Cj})$$

then Equation (6) can be shown to reduce to the especially simple and convenient form

$$V_{CM} = \sum_{i=1}^{N} y_i\ V_{Ci} \qquad (7)$$

For ω_M we have adopted the following relationship

$$\omega_M = \left[\sum_{i=1}^{N}\sum_{j=1}^{N} y_i\, y_j\, V_{Cij}\, \omega_{ij}\right] V_{CM}{}^{-1} \qquad (8)$$

A somewhat simpler combining rule for ω_M may be selected; however, with considerable algebraic manipulation it can be shown that Equation (8) leads to a substantial simplification of the equation for the scaling temperature.

A rigorous expression for the scaling temperature is obtained by combining Equation (8) with Equations (2) through (6).

$$B^0{}_{RM}\left(\frac{T}{T_{CM}}\right) + \omega_M\, B^1{}_{RM}\left(\frac{T}{T_{CM}}\right) V_{CM} = \sum_{i=1}^{N}\sum_{j=1}^{N} y_i\, y_j \left[B^0{}_{Rij}\left(\frac{T}{T_{Cij}}\right) + \omega_{ij}\, B^1{}_{Rij}\left(\frac{T}{T_{Cij}}\right) V_{Cij}\right] \qquad (9)$$

The calculation of the scaling temperature T_{CM} for a mixture from Equation (9) requires a trial and error solution because $B^0{}_{RM}$ and $B^1{}_{RM}$ are the same functions given by Equations (4) and (5) respectively and are polynomials involving powers of (T/T_{CM}).

The scaling pressure is calculated from the relationships

$$P_{CM} = \frac{Z_{CM}\, R\, T_{CM}}{V_{CM}} \qquad (10)$$

$$Z_{CM} = 0.291 - 0.08\, \omega_M \qquad (11)$$

For a mixture each of the individual virial coefficients B_{ij} in Equation (2) must be correctly predicted by Equations (3), (4), and (5) according to the first of two assumptions listed earlier. Whenever this assumption is correct, the relationships derived for the scaling parameters are similarly rigorous. According to the second assumption, these scaling parameters are valid for both liquid and gaseous phases at all densities.

Equation (3) however does not accurately predict virial coefficients of highly polar components; and the theory described here is less accurate for mixtures involving one or more highly polar compounds.

Part II of this work contains further details concerning the use of Equations (6), (8), and (9) for computing the thermodynamic properties of fluid mixtures.

THE CONFIGURATIONAL POTENTIAL

The primary purpose of this work is to utilize corresponding states theory for the prediction of component fugacities and of vapor-liquid equilibrium constants. Gamson and Watson (*31*) have shown that, when the composition dependence of the scaling parameters is known, component fugacities may be calculated from the following relationship:

$$\ln\left(\frac{f_i}{y_iP}\right) = \ln\left(\frac{f_M}{P}\right) - \frac{H_M{}^* - H_M}{RT_{CM}\,T}\left[\sum_{j=1}^{N} y_j\left(\frac{\partial P_{CM}}{\partial y_i} - \frac{\partial T_{CM}}{\partial y_j}\right)_{T,P}\right] - \frac{Z_M - 1}{P_{CM}}\left[\sum_{j=1}^{N} y_j\left(\frac{\partial P_{CM}}{\partial y_i} - \frac{\partial P_{CM}}{\partial y_j}\right)_{T,P}\right] + \ln\left(\frac{f_M}{P}\right)\left[\sum_{j=1}^{N} y_j\left(\frac{\partial \omega_M}{\partial y_i} - \frac{\partial \omega_M}{\partial y_j}\right)_{T,P}\right] \quad (12)$$

This approach has been used by several other investigators (*13*, *32*, *33*). Equation (12) is the preferred form to use with the variables temperature and pressure.

For our purposes, however, we prefer the variables temperature and volume. As with other statistical mechanical equations temperature and volume (or density) arise naturally as fundamental variables in the virial equation whereas pressure has little meaning on a molecular scale.

For the reasons just given and for greater mathematical simplicity volume and temperature variables are used in the derivations given here. When these variables are used, it becomes convenient to work with the Helmholtz free energy rather than the Gibb's function. It is also convenient to define a new function g called the configurational potential.

At constant temperature

$$dA = -RT\ d(\ln g) \quad (13)$$

$$\lim_{P\to 0}\quad g = V \quad (14)$$

From the definition the following result is obtained by integration of Equation (13) at constant temperature and composition between the limits V_θ equal to infinity and V_θ equal to V.

$$\ln(g/V) = \int_{\infty}^{V} \frac{Z-1}{V_\theta}\,dV_\theta \quad (15)$$

The name configuration potential reflects the fact that it is directly related to the configurational integral of statistical mechanics. The new function has dimensions of molar volume and is designated as a potential in the sense of being a type of driving force.

The function g may be incorporated in the framework of a three parameter corresponding states correlation, and according to Equation (1)

$$\ln(g/V) = \ln(g/V)^0 + \omega \ln(g/V)^1 \quad (16)$$

$$\ln(g/V)^0 = \int_{\infty}^{V_R} \frac{(Z^0-1)}{V_{R\theta}}\,dV_{R\theta} \quad (17)$$

$$\ln(g/V)^1 = \int_{\infty}^{V_R} \frac{Z^1}{V_{R\theta}}\,dV_{R\theta} \quad (18)$$

For practical calculations the configuration potential must be related to the fugacity coefficients. For pure components this relationship is readily established by standard thermodynamic methods as outlined in Appendix I.

$$\ln\left(\frac{Zf}{P}\right) = -\ln(g/V) + Z - 1 \quad (19)$$

The development of corresponding states theory for mixtures also requires a relationship between component fugacities and the configuration potential, and this derivation follows next.

The Helmholtz free energy is defined in differential form for an open, multicomponent system

$$d(nA_M) = -nS_M dT - P d(nV_M) + \mu_i dn_i + \mu_j dn_j + \ldots\ldots\ldots\ldots\ldots \quad (20)$$

In Equation (20) the symbols A, S, and V all represent molar thermodynamic properties of the mixture, that is, they are intensive rather than extensive properties. With the aid of Equation (20) it may be shown that

$$\left[\frac{\partial(nA_M)}{\partial n_i}\right]_{\substack{T,V_M,\\ n_j,n_k,\ldots}} = \mu_i - PV_M, \quad (21)$$

Similarly for an ideal gaseous mixture

$$\left[\frac{\partial(nA_M{}^*)}{\partial n_i}\right]_{\substack{T,V_M,\\ n_j,n_k,\ldots}} = \mu_i{}^* - RT \quad (22)$$

At isothermal conditions the difference between the chemical potentials of a real and an ideal gas both at the same temperature and molar volume is given by the fugacity coefficient.

$$\mu_i - \mu_i{}^* = RT\ln\left(\frac{Z_M f_i}{y_iP}\right) \quad (23)$$

As explained in Appendix I, the compressibility factor enters into this expression because the real and ideal gaseous mixtures are being compared at equal temperatures and molar volumes rather than at equal pressures.

Equations (21), (22), and (23) are combined to give:

$$\left[\frac{\partial(nA_M - nA_M{}^*)}{\partial n_i}\right]_{\substack{T,V_M,\\ n_j,n_k,\ldots}} = RT\ln\left(\frac{Z_M f_i}{y_iP}\right) + RT(1 - Z_M) \quad (24)$$

An alternative expression for the partial derivative in Equation (24) is obtained by mathematical methods discussed in detail in the literature (*34*).

$$\left[\frac{\partial(nA_M - nA_M{}^*)}{\partial n_i}\right]_{\substack{T,V_M,n_j,\\ n_k,\ldots}} = (A_M - A_M{}^*)$$

$$+\sum_{j=1}^{N} y_j \left\{ \left[\frac{\partial(A_M - A_M^*)}{\partial y_i} \right]_{\substack{T,V_M,\text{all } y_k \\ k\neq i}} - \left[\frac{\partial(A_M - A_M^*)}{\partial y_j} \right]_{\substack{T,V_M,\text{all } y_k \\ k\neq j}} \right\} \quad (25)$$

On the right hand side of Equation (25) derivatives are taken with respect to one mole fraction holding all others constant. This convention is mathematically correct and convenient although it is a physical impossibility because all mole fractions must sum to one.

At isothermal conditions and at constant composition

$$A_M - A_M^* = -RT \ln \left(\frac{g_M}{V_M} \right) \quad (26)$$

and Equations (24), (25), and (26) are combined to give the desired result:

$$\ln \left(\frac{f_i}{y_i P} \right) = \ln \left(\frac{f_M}{P} \right) - \sum_{j=1}^{N} y_j \left[\frac{\partial \ln \left(\frac{g_M}{V_M} \right)}{\partial y_i} - \frac{\partial \ln \left(\frac{g_M}{V_M} \right)}{\partial y_j} \right]_{T,V_M} \quad (27)$$

In both Equations (19) and (24) to (26) the partial derivatives are taken with temperature and volume constant and with all mole fractions constant except one. Evaluation of these partial derivatives in terms of the scaling parameters represents the final step in the theoretical development in Part I of this paper.

The configuration potential is a function of the reduced volume, reduced temperature, and the acentric factor. The derivative $(\partial \ln(g_M/V_M)/\partial y)$ is related to the scaling parameters through the chain rule for differentiation

$$\left[\frac{\partial \ln(g_M/V_M)}{\partial y_i} \right]_{\substack{T,\, V_M,\, \text{all } y_j \\ j\neq i}} = \left[\frac{\partial \ln(g_M/V_M)}{\partial T_{RM}} \right]_{V_{RM},\omega_M} \left[\frac{\partial T_{RM}}{\partial y_i} \right]_{\substack{T,\, V_M,\, \text{all } y_j \\ j\neq i}} + \left[\frac{\partial \ln(g_M/V_M)}{\partial V_{RM}} \right]_{T_{RM},\omega_M} \left[\frac{\partial V_{RM}}{\partial y_i} \right]_{\substack{T,\, V_M,\, \text{all } j \\ j\neq i}} + \left[\frac{\partial \ln(g_M/V_M)}{\partial \omega_M} \right]_{T_{RM},V_{RM}} \left[\frac{\partial \omega_M}{\partial y_i} \right]_{\substack{T,\, V_M,\, \text{all } y_j \\ j\neq i}} \quad (28)$$

The derivatives in Equation (28) which involve $\ln(g_M/V_M)$ are related to the following thermodynamic functions.

$$\left[\frac{\partial \ln(g_M/V_M)}{\partial T_{RM}} \right]_{V_{RM},\omega_M} = -\left[\frac{U_M^* - U_M}{RT\, T_{RM}} \right] \quad (29)$$

$$\left[\frac{\partial \ln(g_M/V_M)}{\partial V_{RM}} \right]_{T_{RM},\omega_M} = \left[\frac{Z_M - 1}{V_{RM}} \right] \quad (30)$$

$$\left[\frac{\partial \ln(g_M/V_M)}{\partial \omega_M} \right]_{T_{RM},V_{RM}} = \ln(g_M/V_M)^1 \quad (31)$$

The following identities are also required in order to obtain the final result.

$$\frac{\partial T_{RM}}{\partial y_i} = -\frac{T}{(T_{CM})^2} \left(\frac{\partial T_{CM}}{\partial y_i} \right) \quad (32)$$

$$\frac{\partial V_{RM}}{\partial y_i} = -\frac{V_M}{(V_{CM})^2} \left(\frac{\partial V_{CM}}{\partial y_i} \right) \quad (33)$$

Substitution of Equations (29) through (33) into Equations (28) and (27) yields the desired result.

$$\ln \left(\frac{f_i}{y_i P} \right) = \ln \left(\frac{f_M}{P} \right) - \frac{U_M^* - U_M}{RT\, T_{CM}} \left[\sum_{j=1}^{N} y_j \left(\frac{\partial T_{CM}}{\partial y_i} - \frac{\partial T_{CM}}{\partial y_j} \right)_{T,V} \right] + \frac{Z_M - 1}{V_{CM}} \left[\sum_{j=1}^{N} y_j \left(\frac{\partial V_{CM}}{\partial y_i} - \frac{\partial V_{CM}}{\partial y_j} \right)_{T,V} \right] - \ln(g_M/V_M)^1 \left[\sum_{j=1}^{N} y_j \left(\frac{\partial \omega_M}{\partial y_j} - \frac{\partial \omega_M}{\partial y_i} \right)_{T,V} \right] \quad (34)$$

The derivation of Equation (34) is analogous to that of Equation (12), which has been described in considerable detail elsewhere (*31* to *33*, *35*). The use of Equation (34) in lieu of the widely used Equation (12) is essential to the theoretical development presented. The conversion of constant pressure derivatives to constant volume derivatives in Equation (12) leads to extremely complicated expressions, whereas the use of Equation (12) without regard to whether pressure or volume is constant leads to results which are inconsistent. For example after much mathematical manipulation it can be shown that incorrect expressions are obtained for component fugacities at low densities for which only second virial coefficients need be considered. Equation (34), of course, does lead to the correct equations, which is an important consideration because the corresponding states method in this work is based upon the theory of second virial coefficients. At high pressures numerical calculations show that, compared to Equation (12), Equation (34) produces an improvement by a factor of three for some systems in the accuracy of predicted thermodynamic properties.

For the calculation of component fugacity coefficients with Equation (34) the derivatives of the scaling parameters with respect to composition are evaluated from Equations (6), (8), and (9). The scaling parameters are also used to calculate $\ln(f_M/P)$, Z_M, and $\frac{U_M^* - U_M}{RT_{CM}}$ for the mixture from the appropriate generalized tables. As explained in Part II the function $\ln(g_M/V_M)^1$ is also approximated from the generalized tables for other properties.

CONCLUSION

Four salient features listed below represent important aspects of the theoretical development. First, a precise definition is given for the scaling parameters which in turn makes an existence proof possible. This important step shifts emphasis away from questions concerning the validity of the pseudocritical method. Since scaling parameters do exist under all conditions, emphasis can be placed on developing methods for finding them. Second, the extension of corresponding states theory to mixtures is founded on well-defined assumptions. These assumptions are clearly subject to debate, but once accepted the theoretical development proceeds rigorously. Third, the composition dependence of the scaling parameters is established from rigorous mixing rules for the second virial coefficient. Fourth, consistent with the statistical mechanical mixing rules, derivatives of the scaling parameters are taken at constant temperature and at constant volume rather than constant pressure. A new function, a configuration potential, is defined in order to simplify the mathematical derivations.

The formal development of theory is completed; implementation and testing of Equation (34) is discussed in Part II.

ACKNOWLEDGMENT

This work has been supported in part by NSF grant GK-4471.

NOTATION

A = Helmholtz free energy
B = second virial coefficient
f = fugacity
g = configuration potential
H = molar enthalpy
n = number of moles
P = pressure
R = universal gas constant
S = molar entropy
T = temperature
U = molar internal energy
V = molar volume
y = mole fraction
Z = compressibility factor
ω = acentric factor
Ψ = any configurational thermodynamic property
μ = chemical potential

Subscripts

c = critical property
i, j, k = components i, j, k respectively
M = mixture property
CM = scaling parameter (pseudocritical constant)
θ = variable of integration

Superscripts

0 = property of a simple fluid, for example, argon, krypton, xenon
1 = deviation function for acentric fluids
$*$ = ideal gas property at temperature and pressure of interest

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APPENDIX I. THE RELATIONSHIP BETWEEN THE FUGACITY AND THE CONFIGURATION POTENTIAL

The derivation of the relationship between the fugacity and the configuration potential stems from the following equation

$$G = A + PV \tag{A1}$$

where for a real gas

$$PV = ZRT \tag{A2}$$

Substitution of Equation (A1) into (A2) gives

$$G = A + ZRT \tag{A3}$$

and for an ideal gas

$$G^* = A^* + RT \tag{A4}$$

Subtraction of Equation (A4) from (A3) yields

$$G - G^* = A - A^* + RT\ (Z - 1) \tag{A5}$$

The following identities are readily proven from the definitions of the fugacity and the configuration potential respectively.

$$G - G^* = RT\ \ln(f/f^*) \tag{A6}$$

$$A - A^* = -RT\ \ln(g/g^*) \tag{A7}$$

where f^* and g^* are respectively the fugacity and the configuration potential of an ideal gas at the same temperature and molar volume as the real gas. It is emphasized that the comparison of real and ideal gas properties is made at equal molar volumes rather than at equal pressures.

Substitution of Equations (A6) and (A7) into (A5) gives after simplification

$$\ln(f/f^*) = -\ln(g/g^*) + Z - 1 \qquad \text{(A8)}$$

From the definition it can be shown that g^* is equal to the volume. The fugacity of an ideal gas f^* is simply the pressure. It must be noted however that an ideal gas and a nonideal gas at the same temperature and molar volume cannot have the same pressure. This fact leads to the following relationship

$$f^* = P^* = P/Z \qquad \text{(A9)}$$

Substitution for f^* and g^* in Equation (A8) gives the desired result.

$$\ln(Zf/P) = -\ln(g/V) + Z - 1 \qquad \text{(A10)}$$

Manuscript received March 30, 1971; revision received August 11, 1971; paper accepted August 16, 1971.

II. Prediction of Component Fugacities and Related Properties of Mixtures

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A computer program based on the theory of Part I is developed for calculating equilibrium ratios and related thermodynamic properties of mixtures, and a variety of data are used to test the method. For the carbon dioxide-*n*-butane system both liquid and gaseous compressibility factors are predicted with an average absolute deviation from experimental values of 1.3% for a wide range of conditions. A maximum deviation of 5.4% occurs in the critical region. Derivative properties such as component fugacities and equilibrium ratios show somewhat larger deviations as expected. For the same system average deviations are 2.7% for carbon dioxide fugacities, 2.6% for *n*-butane fugacities, and 3.3% for carbon dioxide and *n*-butane equilibrium ratios. Average deviation for predicted equilibrium ratios for eight binary systems and 574 data points is 4.6%. Equilibrium ratios for two ternary systems are also predicted accurately. The major advantage of the method, however, is the small or negligible amount of experimental mixture data required. The method has not been tested below a mixture reduced temperature of 0.8, the lower limit of the Pitzer tables. Without density corrections to the scaling parameters best results are obtained if all binary pairs in a mixture fall within range $0.25 < V_{Cj}\, T_{Cj}/V_{Ci}\, T_{Ci} < 4.0$.

In Part I a method founded on the principle of corresponding states is developed for predicting component fugacities and related thermodynamic properties of dense fluid mixtures. An accurate method for calculating the fugacity of a component is especially important for the prediction of phase equilibria. Equation (35) defines the criterion for equilibrium between a gaseous and a liquid phase involving any number of components.

$$f_{iG} = f_{iL} \qquad (35)$$

In a multicomponent mixture, a separate relationship, each of the same form as Equation (35), is obeyed by each component. The problem of predicting vapor-liquid equilibria, therefore, is resolved into one of predicting the temperature, pressure, and composition dependence of the component fugacities. Such predictions are possible through the use of Equation (34).

DERIVATIVES OF THE SCALING PARAMETERS

Equation (34) requires the derivatives of the scaling parameters with respect to composition. These derivatives for the scaling volume and the mixture acentric factor are readily derived from Equations (6) and (8)

$$\left(\frac{\partial V_{CM}}{\partial y_i}\right)_{\substack{\text{all } y_j \\ j\neq i}} = 2\sum_{j=1}^{N} y_j\, V_{Cij} \qquad (36)$$

$$\left(\frac{\partial \omega_M}{\partial y_i}\right)_{\substack{\text{all } y_j \\ j\neq i}} = \frac{2}{V_{CM}}\sum_{j=1}^{N} y_j\,(\omega_{ij} - \omega_M)\, V_{Cij} \qquad (37)$$

As with Equation (25) the composition derivatives are taken with the temperature, the molal volume, and all but one mole fraction being held constant. The derivative of the scaling temperature is obtained from Equation (9).

$$V_{CM}\frac{\partial B_{RM}}{\partial T_{RM}}\left(\frac{\partial T_{RM}}{\partial y_i}\right)_{\substack{T,\text{ all } y_j \\ j\neq i}} + V_{CM}\, B^1{}_{RM}\left(\frac{\partial \omega_M}{\partial y_i}\right)_{\substack{\text{all } y_j \\ j\neq i}} + B_{RM}\left(\frac{\partial V_{CM}}{\partial y_i}\right)_{\substack{\text{all } y_j \\ j\neq i}} = 2\sum_{j=1}^{N} y_j\, B_{Rij}\, V_{Cij} \qquad (38)$$

The desired relationship is obtained after substitution of Equation (32) into (38) and after further rearrangement:

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