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**A FOUR-PARAMETER CORRESPONDING STATES METHOD FOR THE
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Rice University

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RICE UNIVERSITY

A FOUR-PARAMETER CORRESPONDING STATES METHOD
FOR THE PREDICTION OF
THERMODYNAMIC PROPERTIES OF
POLAR AND NONPOLAR FLUIDS

by

Wade Vincent Wilding

A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE

DOCTOR OF PHILOSOPHY

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ABSTRACT

A FOUR-PARAMETER CORRESPONDING STATES METHOD FOR THE PREDICTION OF THERMODYNAMIC PROPERTIES OF POLAR AND NONPOLAR FLUIDS

by

Wade Vincent Wilding

A four-parameter corresponding states correlation has been developed for the prediction of thermodynamic properties of nonpolar and polar fluids. The property of a fluid is given as a Taylor's series expansion about the simple fluid property at the same reduced conditions in terms of geometric and polar deviations. Three reference fluids are used to evaluate the terms of the series. The first, a simple fluid, and the second, an acentric fluid, are adopted from the Lee-Kesler three-parameter correlation. The third, a polar fluid, is water, represented by the Keenan and Keyes equation of state.

The four parameters required are the critical temperature and pressure, and two newly developed parameters which account for geometry and polarity, respectively. The geometric parameter is obtained from the radius of gyration, and the polarity parameter is derived from one liquid density point, or alternatively from the heat of vaporization (for derivative properties).

The method, in the form of an easily used computer

program, is used to obtain estimates of compressibility factors, enthalpy and entropy departure functions, and fugacity coefficients. The temperature and pressure of the fluid are specified, upon which an estimate of the desired property is calculated. The phase of the fluid may also be specified, but if unknown it is determined from a newly developed vapor-pressure correlation which is an extension to polar fluids of the Lee-Kesler nonpolar-fluid correlation. Extensive tables are also given for hand calculations.

The method has been tested on both nonpolar and polar fluids and yields results equivalent to those obtained by the Lee-Kesler three-parameter method for nonpolar fluids and better results than existing methods for polar fluids. Average errors for the compressibility factor of polar fluids for all points tested are 1.9 % for the vapor phase and 1.6 % for the liquid phase. Average errors for enthalpy departure functions are 250 J/mol for the vapor phase and 422 J/mol for the liquid phase. Preliminary mixture results indicate that the method will be effective for mixture property predictions as well.

To Julie

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CHAPTER I

INTRODUCTION

A. Setting and Relevance

Since the beginning of chemical process industries there has been a need for reliable fluid property values. An enormous amount of experimental data has been collected over the years, but the continual development of new products and processes and the unlimited number of possible combinations of conditions and mixture compositions has necessitated the use of predictive methods to obtain property values where no data exist. With the advent and continual improvement of computer technology, these predictive methods have become much more complex and reliable.

Because of the diverse uses of property values, there is a corresponding diversity in correlations used to predict them. If extremely accurate data are needed for a particular fluid, a correlation is built upon experimental data for that fluid. Such a correlation will probably be accurate over a limited range of conditions and obviously, will not have the same accuracy if applied to other fluids.

General correlations have been developed for use with many fluids, for many properties, and for wide ranges of conditions. Such correlations are unavoidably less accurate

than specific correlations, but for many engineering purposes the loss of accuracy is more than compensated for by the simplicity of a general method.

There is a continual search for improved predictive methods in terms of both improved accuracy and extended generality. The single most important basis for fluid property correlations is the corresponding states principle first introduced by van der Waals before 1900. This principle states that configurational properties are related to the critical constants in the same way for all fluids. In other words, two fluids at the same reduced temperature and reduced pressure will have the same property values. This is known as two-parameter corresponding states, with the critical temperature and critical pressure being the two required parameters.

Only the simplest of fluids (e.g. argon and krypton) obey the simple corresponding states principle. However, because of its appealing generality there have been innumerable attempts to extend the basic idea to more complicated fluids.

By adding a third parameter to the corresponding states framework, many researchers have had excellent success predicting properties for many fluids which do not obey the simple corresponding states principle. Fluids that may be effectively treated using a three-parameter method generally are composed of long chain or branched molecules, i.e. molecules that deviate from the spherical shape implicit in

the two-parameter corresponding states principle, but are still nonpolar. The third parameter is consequently a measure of the effect these size/shape deviations have on property values. The three most commonly used parameters in these methods are the critical temperature, critical pressure, and Pitzer's acentric factor.

Recently, a good deal of research has focused on extending the corresponding states principle to polar fluids with varying amounts of success. Most of the correlations developed are four-parameter methods with the fourth parameter being a polarity parameter accounting for the effect of polarity on fluid properties.

The purpose of the present work is development of a four-parameter corresponding states correlation for the prediction of equilibrium thermodynamic properties of both nonpolar and polar fluids. The final product of this work is a computer package which requires only readily available primary-property input and is easily used to obtain accurate property estimates. The generality, simplicity, and accuracy of this correlation make it a significant contribution to the scientific art of property prediction.

B. THESIS ORGANIZATION

Chapter II presents a historical overview of the corresponding states principle and of correlational methods based on this principle. Methods for both polar and nonpolar fluids are discussed.

The theoretical basis for the present work is developed in Chapter III. The result of this development is an expression in terms of three reference fluids and four corresponding states parameters which is used to estimate thermodynamic properties of both polar and nonpolar fluids.

The results of this work are presented in Chapter IV. Figures and tables comparing predictions to experimental results demonstrate the accuracy of the method. Also included are comparisons to two other corresponding states correlations.

Chapter V discusses the use of the method for the prediction of various properties and presents property tables useful for these predictions. Some special aspects of the method are treated in Chapter VI.

Chapter VII draws general conclusions about the work and suggests several topics for future study.

CHAPTER II

HISTORICAL DEVELOPMENT OF CORRESPONDING STATES TECHNIQUES

A. The Corresponding States Principle: Simple Fluids

In his doctoral dissertation of 1873, van der Waals (1) laid the foundation for the Corresponding States Principle when he introduced his equation of state:

$$\left(P + \frac{a}{V^2} \right) (V - b) = RT \quad (2.1)$$

where P = pressure

V = volume

T = temperature

R = gas constant

a, b = fluid specific constants

The constant a accounts for the reduction in pressure due to attractive forces between molecules, whereas b represents the inaccessible volume occupied by the molecules.

Applying Equation 2.1 at the critical point yields

$$\left(P_c + \frac{a}{V_c^2} \right) (V_c - b) = RT_c \quad (2.2)$$

Also at the critical point

$$\left(\frac{\partial P}{\partial V} \right)_T = 0 \quad (2.3)$$

$$\left(\frac{\partial^2 P}{\partial V^2} \right)_T = 0 \quad (2.4)$$

Differentiating Equation 2.2 with respect to volume determines the equation of state parameters, a and b , in terms of the critical constants, T_c and V_c :

$$a = \frac{9}{8} R V_c T_c \quad (2.5)$$

$$b = \frac{V_c}{3} \quad (2.6)$$

The critical compressibility factor, Z_c , can be obtained by substituting these relationships for a and b into Equation 2.2. The van der Waals equation predicts a value for Z_c of 0.375 for all fluids which is considerably higher than Z_c for most actual fluids.

Rewriting Equation 2.1 with the relationships for a and b gives

$$\left(P + \frac{9RT_c V_c}{8V^2} \right) \left(V - \frac{V_c}{3} \right) = RT \quad (2.7)$$

Using Z_c and rearranging

$$\left[Z_c \frac{P}{P_c} + \frac{9}{8} \left(\frac{V_c}{V} \right)^2 \right] \left[\frac{V}{V_c} - \frac{1}{3} \right] = \frac{T}{T_c} \quad (2.8)$$

Finally substituting ZRT/P for V and using the definitions

$$T_r = \frac{T}{T_c} \quad P_r = \frac{P}{P_c} \quad (2.9)$$

for the reduced temperature and pressure we obtain

$$Z^3 - \left(1 + \frac{Z_c P_r}{3 T_r} \right) Z^2 + \left(\frac{9}{8} \frac{P_r Z_c}{T_r} \right) Z = \frac{3}{8} \frac{P_r^2 Z_c^2}{T_r^3} \quad (2.10)$$

Since Z_c is fixed in the van der Waals formulation, Equation 2.10 represents a general correlation with two independent variables, T_r and P_r . This relation can be summarized as

$$Z = f(T_r, P_r) \quad (2.11)$$

where f is a universal function applicable to all fluids.

Equation 2.11 is valid not only for the van der Waals equation, but also for any two-parameter equation of state. The procedure that was applied to determine the van der

Waals constants in terms of the critical constants can similarly be applied to other two-parameter formulations.

The beauty of the corresponding states principle as shown by Equation 2.11 is that one function is used for all fluids. Once such a function is defined it is a simple matter to derive expressions for other properties, such as the enthalpy departure function and the heat capacity, by applying basic thermodynamic identities.

In 1939 Pitzer formalized the theory of the simple corresponding states principle from a statistical thermodynamics viewpoint. In order for a fluid to obey the simple corresponding states principle the following four requirements must be met (2,3).

- 1) The canonical ensemble partition function is assumed to be separable into independent translational, rotational, vibrational, and configurational factors. This requires molecules to have small translational and rotational energies relative to kT , where k is Boltzmann's constant. Except at very low temperatures this requirement is fulfilled. Also, molecules which exhibit hydrogen bonding or other specific interactions between individual atoms or groups of atoms within the molecule will not satisfy this requirement.
- 2) Only the configurational portion of the partition function is density dependent; all internal energy states of individual molecules are assumed to be independent of density.

- 3) Molecules exhibiting quantum effects are excluded from the simple corresponding states principle.
- 4) The total potential energy for the system may be expressed as the product of an energy parameter and a function of dimensionless separation distances between molecular centers. This potential may be written

$$U(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_n) = \epsilon f\left(\frac{r_{12}}{\sigma}, \frac{r_{13}}{\sigma}, \dots, \frac{r_{23}}{\sigma}, \frac{r_{24}}{\sigma}, \dots\right) \quad (2.12)$$

where U = the potential energy

$\vec{r}_i$ = position vector for molecule i

ϵ = energy parameter

f = universal function

r_{ij} = separation distance

σ = distance parameter

Using these assumptions an equation of state can be derived from the configurational partition function with the form

$$Z = f\left(\frac{\epsilon}{kT}, \frac{V}{N\sigma^3}\right) \quad (2.13)$$

where N is Avogadro's Number. In Equation 2.13, f is a universal function applicable to all fluids which meet the

requirements for two-parameter corresponding states.

As was done with the van der Waals equation of state, Equation 2.13 may be applied at the critical point to give

$$Z_c = f\left(\frac{\epsilon}{kT_c}, \frac{V_c}{N\sigma^3}\right) \quad (2.14)$$

Using Equations 2.3 and 2.4 one can obtain constant values for Z_c , ϵ/kT_c , and $V_c/N\sigma^3$:

$$\begin{aligned} Z_c &= a \\ \frac{\epsilon}{kT_c} &= b \\ \frac{V_c}{N\sigma^3} &= c \end{aligned} \quad (2.15)$$

The constants, a , b , and c , are universal for all fluids which obey the simple corresponding states principle.

As expressed by the fourth listed requirement, the simple corresponding states principle is applicable to any two-parameter potential function. For the Lennard-Jones potential these constants are

$$a = 0.292$$

$$b = 0.800$$

$$c = 3.14$$

Note that the value for Z_c , 0.292, is nearer actual fluid values than is the value given by the van der Waals equation.

As seen in Equation 2.15, the potential function parameters, ϵ and σ^3 are directly proportional to the

critical constants, so Equation 2.13 may be rewritten as

$$Z = f(T_r, V_r) \quad (2.16a)$$

or

$$Z = f(T_r, P_r) \quad (2.16b)$$

The same general form is thus derived from statistical thermodynamics (Equation 2.16) as from the van der Waals equation of state (Equation 2.11). The difference between the two approaches is the definition of the universal function. Equation 2.11 is based on an empirical equation of state, whereas Equation 2.16 is based upon the configurational partition function.

The accuracy obtained from a two-parameter formulation depends upon two factors: first upon the definition of the universal function, f , and second upon how well the fluid of interest conforms to the list of requirements given for the simple corresponding states principle. Only fluids with spherical molecules such as argon and krypton can be well represented by two-parameter corresponding states correlations. Such fluids are termed "simple fluids". Some other fluids which are nearly spherical, such as methane, are also quite adequately described by two-parameter correlations.

B. Three-Parameter Corresponding States: Acentric Fluids

The very attractive tenet of the corresponding states principle that one universal function with only a few required parameters is valid for all fluids has prompted many researchers to attempt extensions to more complicated fluids.

The obvious way to extend the simple corresponding states principle is by the addition of a third parameter. The earliest extensions used the critical compressibility factor, Z_c , as the third parameter. As was seen with the van der Waals equation of state, the choice of universal function in two-parameter methods fixes the value of Z_c . However, real fluid Z_c 's vary from less than 0.2 to greater than 0.3. Lydersen, Greenkorn, and Hougen (4) developed extensive tables for densities and derived thermodynamic properties based on a three-parameter formulation which may be expressed as

$$Z = f(T_r, P_r, Z_c) \quad (2.17)$$

Thus, at the same reduced temperature and pressure two fluids having the same Z_c will have the same compressibility factor. Introducing Z_c as the third parameter is intended to account for a given fluid's deviations from the two-parameter corresponding states

principle due to size-shape and polarity variations.

Augmenting the simple corresponding states principle with Z_c improves property estimation for fluids which are not well described by two-parameter methods. However, there are two drawbacks to using Z_c . First, there is a good deal of uncertainty in experimentally determined values of Z_c . This uncertainty is magnified in property predictions. Second, and more important, molecular size, shape, and polarity effect Z_c differently for different fluids, and hence it is very difficult to correlate Z_c as a function of size, shape or polarity. It is generally accepted that it is asking too much of a third parameter to account for both size-shape and polarity effects.

In independent studies Riedel (5) and Pitzer et al. (6) developed correlations for third parameters based on vapor pressure. These correlations are only applicable to nonpolar substances and represent a significant improvement over the use of Z_c .

Riedel defined a "critical parameter", α_k , as

$$\alpha_k = \left(\frac{d \ln P_{vp_r}}{d \ln T_r} \right)_{T_r=1} \quad (2.18)$$

where P_{vp_r} is the reduced vapor pressure. Pitzer defined the acentric factor, ω , as

$$\omega = -\log P_{vp_r}{}_{T_r=0.7} - 1.000 \quad (2.19)$$

Both parameters are measures of the effects of acentricity, and in fact they are linearly related to each other through the equation

$$\alpha_k = 5.811 + 4.919\omega \quad (2.20)$$

This equation demonstrates the equivalence of the two methods even though Pitzer's acentric factor is more widely used. One reason for this is that Pitzer's work was originally published in English, the language of most researchers doing correlation work, whereas Riedel's work was published in German. Another reason is that Pitzer's acentric factor goes to zero for spherical molecules, thereby automatically reverting to a two-parameter formulation for simple molecules.

As both the Pitzer and Riedel methods use tabular equations of state, many researchers have adapted analytical equations to be used with the three corresponding states parameters. One quite successful method is that of Lee and Kesler (7) published in 1975. They fit a modified Benedict-Webb-Rubin equation of state to a simple fluid (using experimental data for argon, krypton, and methane) and also to a long-chain reference fluid, n-octane. The compressibility factor of a real fluid is then obtained from the following relation:

$$Z = Z^{(0)} + \frac{\omega}{\omega^R} (Z^{(R)} - Z^{(0)}) \quad (2.21)$$

where $Z^{(0)}$ is the simple fluid compressibility factor, $Z^{(R)}$ is the reference fluid (n-octane) compressibility factor, ω is the acentric factor of the real fluid, and ω^R is 0.3978 (the acentric factor of n-octane). Defining $Z^{(1)}$ as

$$Z^{(1)} = \frac{(Z^{(R)} - Z^{(0)})}{\omega^R} \quad (2.22)$$

Equation 2.21 can be rewritten

$$Z = Z^{(0)} + \omega Z^{(1)} \quad (2.23)$$

which is the power series expansion originally proposed by Pitzer.

Having analytical equations allows simple derivation of relationships for other thermodynamic properties, and the Lee-Kesler method has proven effective for not only compressibility factors but also enthalpy and entropy departure functions, fugacity coefficients, and heat capacities. Thus, even though the Lee-Kesler method is a general correlation (useful for many properties over wide ranges of conditions) it is very accurate, largely due to the reliability of the modified BWR equation of state, and is also easily implemented because of the analytical equations.

Even though the Lee-Kesler method is intended for nonpolar fluids only, it and other three-parameter methods are commonly used for polar fluids. The reasons for this are the simplicity of methods such as the Lee-Kesler method and the dearth of accurate methods for polar fluids. Errors of 20% or more are common when three-parameter methods are applied to polar fluids.

C. Four-Parameter Corresponding States: Polar Fluids

Because three-parameter methods have proven to be inadequate for polar fluids many researchers have developed four-parameter correlations. Most of these use the three parameters of Pitzer's work adding a polarity parameter to the list.

In 1962, Eubank and Smith (8) published their work on thermodynamic properties of dilute polar gases which represents an early milestone in polar-fluid correlational efforts. They pointed out the importance of separating acentric and polar effects and used the idea of a homomorph to accomplish this separation. A homomorph is a nonpolar molecule with size and structure similar to the polar molecule of interest, but in the homomorph the polar groups have been replaced by nonpolar methyl or methylene groups. For example the homomorph for ethanol is propane, and the homomorph for acetone is 2-methylpropane.

The compressibility factor is calculated from the

following expression:

$$Z = Z_0(P_r', T_r') + \omega Z_1(P_r', T_r') + P^* Z_2(P_r, T_r) \quad (2.24)$$

The first two terms on the right-hand side are evaluated using the homomorph critical constants and acentric factor. Thus T_r' and P_r' are the reduced conditions using the homomorph T_c and P_c . The polar effects are then isolated in the third term where P^* is the polar parameter and Z_2 is a universal function similar to Z_0 and Z_1 .

The parameter P^* is given the form $c(\mu^*)^n$. Where μ^* is the reduced dipole moment calculated from the force constants of the Stockmayer potential function, ϵ/k and σ :

$$\mu^* = \mu / (\epsilon \sigma^3)^{\frac{1}{2}} \quad (2.25)$$

The reduced dipole moment alone is not a suitable fourth parameter because the location and direction of the dipole moment within a molecule have a significant influence on property values. The constant n was set equal to 5/3 for all fluids, whereas the constant c is fluid-specific and gives a measure of the effectiveness of the dipole moment due to its position and direction.

For normal alcohols and methyl fluoride, predictions of the compressibility factor were within 1.0% of experimental

data, whereas the three-parameter method of Pitzer yielded more than 3.0% error for the same data.

The method of Eubank and Smith, although representing a significant advance, has limitations. The requirement of a homomorph excludes all inorganic fluids from the correlation. Also, as with the Pitzer correlation, the universal functions Z_0 , Z_1 , and Z_2 are tabular functions. Finally, this work was limited to dilute gases where polar effects are the least important.

Stiel and coworkers have published several papers on four-parameter methods for polar fluids (9,10,11). They developed a fourth parameter χ , known as the Stiel Factor, based on the vapor pressure at $T_r=0.6$ according to the relation

$$\chi = \log P_{vp_r} \big|_{T_r=0.6} + 1.70\omega + 1.522 \quad (2.26)$$

This parameter was then used in various correlations for the prediction of thermodynamic properties. They proposed the following relationship for the compressibility factor:

$$Z = Z^{(0)} + \omega Z^{(1)} + \chi Z^{(2)} + \omega \chi Z^{(3)} + \chi^2 Z^{(4)} \quad (2.27)$$

where $Z^{(0)}$ through $Z^{(4)}$ are tabulated functions of reduced temperature and pressure and ω is Pitzer's acentric factor. $Z^{(0)}$ and $Z^{(1)}$ are taken from Pitzer's three-parameter work,

whereas $z^{(2)}$, $z^{(3)}$, and $z^{(4)}$ were fit to experimental PVT data for several polar fluids over the region of reduced temperatures from 0.8 to 1.15 and reduced pressures from 0.2 to 6.0. Predicted values of polar fluid compressibility factors reproduced the experimental values used to develop the correlation with average errors of 0.85 to 2.32%.

The work of Stiel and associates contributes significantly to the effectiveness of polar-fluid property prediction. Two limitations of the work are first, the cumbersome use of tabular deviation terms ($z^{(0)}$, $z^{(1)}$, etc.), and second, both the third and fourth parameters have acentricity and polarity combined in them. It would be theoretically more correct to have independent parameters.

In his PhD thesis of 1966, Thompson (12) developed the concept of the radius of gyration and described the method for its calculation. The radius of gyration is a measure of molecular size and shape based on the principal moments of inertia of an individual molecule. These moments are calculated from the bond lengths and bond angles of the molecule. For planar molecules

$$R_g = [(AB)^{\frac{1}{2}}/MW]^{\frac{1}{2}} \quad (2.28)$$

where R_g = radius of gyration,

AB = products of the principal moments of inertia, and

MW = molecular weight.

For three-dimensional molecules

$$R_g = [2\pi(ABC)^{\frac{1}{3}}/MW]^{\frac{1}{2}} \quad (2.29)$$

where ABC is again the product of the principal moments of inertia.

The radius of gyration was introduced as the basis for a third parameter to take the place of Pitzer's acentric factor in corresponding states correlations. As earlier noted, the acentric factor of polar fluids contains polarity effects in addition to acentric effects. In contrast, if the third parameter is based on the radius of gyration only acentric effects will be included, leaving all polarity effects for a fourth parameter. Thus the two parameters become independent, with size-shape effects isolated in the third parameter and polar effects isolated in the fourth parameter.

In their four-parameter correlations, Danner and coworkers (13,14,15,16) employed the radius of gyration as the third parameter to account for size-shape effects and developed formulae to obtain fourth parameters used to predict various properties.

In a 1974 paper Passut and Danner (13) predicted vapor pressures for associated fluids with an average error of 4 to 5% using the Frost-Kalkwarf vapor-pressure equation. The

required input data were the critical temperature and pressure, the radius of gyration, and the normal boiling point. The radius of gyration was used with the critical constants to determine the "normal fluid" contribution to the constants of the Frost-Kalkwarf equation. The normal boiling point was then used to determine the fourth parameter κ , called an "association" parameter. The results were shown to be essentially equivalent to the Halm and Stiel (9) method with the advantages of fewer required experimental data and applicability over a wider temperature range.

Lyman and Danner (14) used these same parameters in correlating liquid heat capacities of polar fluids. Their results were considerably better than those obtained using existing correlations.

Tarakad and Danner (15,16) developed a different fourth parameter based on the second virial coefficient. By dividing the second virial coefficient into a simple fluid term with two corrective terms: a size-shape and an association term, they isolated polar effects in the association term. Then ϕ , the fourth parameter, was defined as the negative of this association term at $T_r=0.6$. This method requires second virial coefficient data for polar fluids. The simple-fluid and size-shape contribution were calculated from an empirical equation in terms of the reduced temperature and the radius of gyration. Results for liquid heat capacities were shown to be essentially

equivalent to Lyman and Danner's method (13).

Bhirud (17) correlated saturated liquid densities using a four-parameter method with Pitzer's acentric factor as the third parameter and a liquid density point as the basis for the fourth parameter, ψ . Saturated liquid density estimates were obtained from the following equation:

$$\ln U = (\ln U)^0 + \omega(\ln U)^1 + \psi(\ln U)^2 \quad (2.30)$$

where U is a dimensionless volume given by

$$U = P_c V_{s1} / R T \quad (2.31)$$

and the functions $(\ln U)^0$, $(\ln U)^1$, and $(\ln U)^2$ are represented by analytical functions in Tr .

Bhirud's fourth parameter, ψ , was shown to be linearly related to Stiel's polarity factor. Tested for twenty-one substances over the reduced temperature range of 0.42 to 1.0, Bhirud's method gave an average absolute error of 1.11%

Nishiumi and Robinson (18) also developed a four-parameter method with the fourth parameter based on the second virial coefficient. They used this parameter to predict compressibility factors according to the relation

$$Z = Z^{(0)} + \omega Z^{(1)} + \psi_E (Z^{(2)} + \omega Z^{(3)}) \quad (2.32)$$

where Ψ_E is the polar parameter and $Z^{(0)}$ through $Z^{(3)}$ are tabulated functions. For reduced temperatures from 0.4 to 4.0 and reduced pressures from 0.03 to 40.0 values of the compressibility factor were estimated with average absolute deviations of 1.3% for the gaseous region and 3.3% for the liquid region.

Wu and Stiel (19) recently presented a four-parameter method for the calculation of thermodynamic properties of polar fluids which is very similar to the present work. These methods were developed independently but simultaneously. Using the Lee-Kesler three parameter method as the basis, Wu and Stiel added a third reference fluid, water, to the two reference fluids of the Lee-Kesler method and a polarity parameter, Y , which is a function of the acentric factor and the Stiel factor. Water is represented by the Keenan and Keyes equation of state (20) and thus all three reference fluids have analytical representations. The compressibility factor is calculated from the following equation:

$$Z = Z^{(0)} + \omega Z^{(1)} + Y Z^{(2)} \quad (2.33)$$

where $Z^{(0)}$ and $Z^{(1)}$ are obtained from the Lee-Kesler method and $Z^{(2)}$ is given by

$$Z^{(2)} = Z^{(w)} - (Z^{(0)} + 0.344 Z^{(1)}) \quad (2.34)$$

where $Z^{(w)}$ is the compressibility factor of water. For seven polar fluids average errors for the compressibility factor were 1.5% for the vapor and 1.3% for the liquid.

The method of Wu and Stiel is an effective method for two reasons. First, analytical equations are used to calculate the simple fluid contribution, the size-shape contribution, and the polar contribution to the overall property. With analytical equations it is simple to obtain analytical expressions for other thermodynamic properties by operating on the reference fluid equations of state with fundamental thermodynamic identities. Second, this is a general method useful for many properties over a wide range of conditions giving good results.

Because the Wu and Stiel method uses Pitzer's acentric factor as the third corresponding states parameter, there is coupling between the third and fourth parameters: both parameters contain acentric and polar effects. As will be described in the next chapter, this coupling is theoretically undesirable. Another drawback in this method is that derivative-property predictions are much less accurate than volumetric-property predictions.

The following chapters present a four-parameter correlation similar to the Wu and Stiel method, but as will be seen, the present method is superior in both theory and practice.

CHAPTER III

THEORETICAL DEVELOPMENT

A. General Correlation

Let J represent any configurational property of a fluid such as the compressibility factor, enthalpy departure function, or heat capacity. J at a given reduced temperature and pressure may be expressed as a Taylor's series expansion about the simple fluid value of J at the same reduced conditions with respect to geometrical and polar effects:

$$J = J_0 + \left(\frac{\partial J}{\partial \alpha} \right)_{T_r, P_r, \beta} (\alpha - \alpha_0) + \left(\frac{\partial J}{\partial \beta} \right)_{T_r, P_r, \alpha} (\beta - \beta_0) + \sigma(\alpha^2, \beta^2) \quad (3.1)$$

where J_0 is the simple fluid value of property J at the same T_r and P_r , α is a size-shape parameter and β is a polarity parameter. The parameters α and β are specific to the fluid of interest and are the third and fourth corresponding-states parameters. The quantity $(\alpha - \alpha_0)$ is the difference in α between the fluid of interest and the simple reference fluid. Similarly, $(\beta - \beta_0)$ is the difference in β between the fluid of interest and the simple fluid. Higher order terms of the expansion are considered negligible.

The partial derivative, $\left(\frac{\partial J}{\partial \alpha}\right)_{T_r, P_r, \beta}$, represents the change in the property J due to a change in the geometrical parameter, α , and is approximated by the linear relation

$$\left(\frac{\partial J}{\partial \alpha}\right)_{T_r, P_r, \beta} = \frac{J_1 - J_0}{\alpha_1 - \alpha_0} \Big|_{T_r, P_r, \beta} \quad (3.2)$$

which is the difference in J between an acentric (nonspherical) but nonpolar reference fluid, J_1 , and a simple fluid, J_0 , divided by the difference in α between the same fluids. Since α is defined to be zero for spherical molecules, $\alpha_0 = 0$.

The partial derivative, $\left(\frac{\partial J}{\partial \beta}\right)_{T_r, P_r, \alpha}$, represents the change in J due to a change in the polarity parameter, β , and is similarly approximated by the linear relation

$$\left(\frac{\partial J}{\partial \beta}\right)_{T_r, P_r, \alpha} = \frac{J_2 - J'_2}{\beta_2 - \beta'_2} \Big|_{T_r, P_r, \alpha} \quad (3.3)$$

which is the difference in J between a polar reference fluid, J_2 , and a hypothetical reference fluid, J'_2 , which is geometrically identical to the polar reference fluid (i.e. has the same value of α) but is nonpolar, divided by the difference in β between these same fluids. Note that as β is defined to be zero for nonpolar fluids, $\beta_0 = \beta'_2 = 0$.

Noting that subscript 0 refers to the simple reference

fluid, subscript 1 refers to the acentric reference fluid, and subscript 2 refers to the polar reference fluid, Equation 3.1 can then be rewritten as

$$J = J_0 + \alpha \left(\frac{J_1 - J_0}{\alpha_1} \right) + \beta \left(\frac{J_2 - J'_2}{\beta_2} \right) \quad (3.4)$$

Equation 3.4 may be written for any fluid provided α and β are known for that fluid. If it is written for the hypothetical fluid (whose property is given by J'_2) the following expression results:

$$J'_2 = J_0 + \alpha'_2 \left(\frac{J_1 - J_0}{\alpha_1} \right) + \beta'_2 \left(\frac{J_2 - J'_2}{\beta_2} \right) \quad (3.5)$$

But since this hypothetical fluid is nonpolar, $\beta'_2 = 0$, and the third term on the right-hand is zero. Also, since this fluid has been defined to be geometrically identical to the polar reference fluid, $\alpha'_2 = \alpha_2$. Thus an expression for J'_2 is obtained in terms of the reference fluid equations of state and reference fluid parameters:

$$J'_2 = J_0 + \alpha_2 \left(\frac{J_1 - J_0}{\alpha_1} \right) \quad (3.6)$$

With this result the final form of the correlation is given as

$$J = J_0 + \alpha \left(\frac{J_1 - J_0}{\alpha_1} \right) + \beta \left\{ \frac{J_2 - \left[J_0 + \alpha_2 \left(\frac{J_1 - J_0}{\alpha_1} \right) \right]}{\beta_2} \right\} \quad (3.7)$$

Equation 3.7 is the fundamental formula for the present work. It is seen to be the sum of three terms: a simple fluid term, a deviation term due to geometry, and a deviation term due to polarity. In order to obtain a prediction of J for a specified fluid, first the reduced temperature and pressure are calculated using the critical constants of the given fluid. Next J is calculated for each of the three reference fluids at these reduced conditions. Finally, the values of α and β for the given fluid are used in Equation 3.7 to obtain J .

Inherent in the development of Equation 3.7 are the following assumptions:

- 1) The effects of geometry and polarity are assumed to be separable and independent.
- 2) It is assumed that all deviations from simple fluid behavior can be accounted for in terms of geometry and polarity.
- 3) Second and higher order terms are assumed to be negligible in the expansion.
- 4) The linear relations of Equations 3.2 and 3.3, in terms of the three reference fluids, are assumed to accurately represent the partial derivatives of Equation 3.1.

B. Reference Fluid Equations

1. Equations of State - The three reference fluids used in this work are represented by analytical equations of state. The first two reference fluids are adopted from the Lee-Kesler three-parameter correlation and are represented by a modified Benedict-Webb-Rubin equation of state. The first reference fluid is a simple fluid and is based on experimental data of argon, krypton, and methane. The second reference fluid which is nonspherical but also nonpolar is n-octane. The equation of state developed by Lee and Kesler has been rewritten in terms of the compressibility factor and is given in Equation 3.8 with the constants to be used for the two reference fluids given in Table III.1.

$$Z = 1 + \frac{B'}{Z} + \frac{C'}{Z^2} + \frac{D'}{Z^5} + \frac{c'_4}{Z^2} \left(\beta + \frac{\gamma'}{Z^2} \right) \exp \left(-\frac{\gamma'}{Z^2} \right) \quad (3.8)$$

where $B' = B \frac{P_r}{T_r}$; $C' = C \left(\frac{P_r}{T_r} \right)^2$; $D' = D \left(\frac{P_r}{T_r} \right)^5$;

$$c'_4 = c_4 \frac{P_r^2}{T_r^5} ; \quad \gamma' = \gamma \left(\frac{P_r}{T_r} \right)^2$$

and $B = b_1 + \frac{b_2}{T_r} - \frac{b_3}{T_r^2} - \frac{b_4}{T_r^3}$ $C = c_1 - \frac{c_2}{T_r} + \frac{c_3}{T_r^3}$

$$D = d_1 + \frac{d_2}{T_r}$$

Table III.1. Constants for First and Second Reference
Fluid Equation of State

Constant	First Ref. Fluid	Second Ref. Fluid
b_1	0.1181193	0.2026579
b_2	0.265728	0.331511
b_3	0.154790	0.027655
b_4	0.030323	0.203488
c_1	0.0236744	0.0313385
c_2	0.0186984	0.0503618
c_3	0.0	0.016901
c_4	0.042724	0.041577
$d_1 \times 10^4$	0.155488	0.48736
$d_2 \times 10^4$	0.623689	0.0740336
β	0.65392	1.226
γ	0.060167	0.03754

The reduced temperature and pressure are calculated from the critical temperature and pressure of the fluid of interest. Equation 3.8 is then solved for Z_0 , the compressibility factor of the simple reference fluid, at these reduced conditions by utilizing the simple-fluid constants of Table III.1. Then Equation 3.8 is again solved, this time for Z_1 , the compressibility factor for the second reference fluid, at the same reduced conditions by utilizing the second reference fluid constants.

The third fluid, which is the polar reference fluid, was chosen to be water. The reasons for this choice are that water is highly polar, has an extensive data base, and has already been fit to an accurate equation of state: the Keenan and Keyes equation for water presented with their steam tables (20). This equation has also been written in terms of the compressibility factor and is given as

$$Z = 1 + \rho Q + \rho^2 \left(\frac{\partial Q}{\partial \rho} \right)_{\tau} \quad (3.9)$$

where ρ is the density, and

$$Q = (\tau - B_0) \sum_{j=1}^7 (\tau - B_j)^{j-2} \left[\sum_{i=1}^8 A_{ij} (\rho - C_j)^{i-1} + e^{-4.8\rho} (A_{9j} + A_{10j}\rho) \right]$$

$$B_0 = B_1 = 1.544912 \quad ; \quad B_{j>1} = 2.5$$

$$C_1 = 0.634 \quad ; \quad C_{j>1} = 1.0$$

$$\tau = 1000/T$$

and the constants A_{ij} are given in Table III.2.

2. Derived Properties - Relations for other thermodynamic properties such as the enthalpy departure function, fugacity, and heat capacity can be obtained by applying fundamental identities to the equations of state.

The change in a state variable, such as the enthalpy or internal energy, from one set of conditions to another is often required in the operation and design of process equipment. Consider for illustration purposes the change in enthalpy, ΔH , from T_1, P_1 to T_2, P_2 . The enthalpy may be expressed as a function of temperature and pressure:

$$H = f(T, P) \quad (3.10)$$

Then dH is given by

$$dH = \left(\frac{\partial H}{\partial P} \right)_T dP + \left(\frac{\partial H}{\partial T} \right)_P dT \quad (3.11)$$

This relation may be integrated to obtain an expression for the change in enthalpy:

$$\Delta H = \int_{P_1}^{P_2} \left(\frac{\partial H}{\partial P} \right)_{T_1} dP + \int_{T_1}^{T_2} \left(\frac{\partial H}{\partial T} \right)_{P_2} dT \quad (3.12)$$

Table III.2. Constants A_{ij} for Third Reference Fluid Equation of State

i	j	1	2	3	4	5	6	7
1	29.492937	-5.1985860	6.8335354	-0.1564104	-6.3972405	-3.9661401	-0.69048554	
2	-132.13917	7.7779182	-26.149751	-0.72546108	26.409282	15.453061	2.7407416	
3	274.64632	-33.301902	65.326396	-9.2734289	-47.740374	-29.142470	-5.1028070	
4	-360.93828	-16.254622	-26.181978	4.3125840	56.323130	29.568796	3.9636085	
5	342.18431	-177.31074	0	0	0	0	0	
6	-244.50042	127.48742	0	0	0	0	0	
7	155.18535	137.46153	0	0	0	0	0	
8	5.9728487	155.97836	0	0	0	0	0	
9	-410.30848	337.31180	-137.46618	6.7874983	136.87317	79.847970	13.041253	
10	-416.05860	-209.88866	-733.96848	10.401717	645.81880	399.17570	71.531353	

The difficulty arises in trying to evaluate expressions for the partial derivatives in Equation 3.12. One way to evaluate this equation is to rewrite it as

$$\Delta H = \int_{P_1}^{P^0} \left(\frac{\partial H}{\partial P} \right)_{T_1} dP + \int_{T_1}^{T_2} \left(\frac{\partial H}{\partial T} \right)_{P^0} dT + \int_{P^0}^{P_2} \left(\frac{\partial H}{\partial P} \right)_{T_2} dP \quad (3.13)$$

where P^0 is zero absolute pressure; i.e., the fluid is an ideal gas at P^0 . The partial derivative in the second term on the right-hand side, $\left(\frac{\partial H}{\partial T} \right)_{P^0}$, is the constant-pressure, ideal-gas heat capacity, C_p^0 , for which there exist accurate correlations. The first and third terms are known as departure functions and can be expressed as $(H^0 - H_{P_i})_{T_j}$. Departure functions relate a thermodynamic property at a given pressure and temperature to the ideal gas reference state at some reference pressure and at the same temperature. The relation for the change in enthalpy is rewritten as

$$\Delta H = (H^0 - H_{P_1})_{T_1} + \int_{T_1}^{T_2} C_p^0 dT - (H^0 - H_{P_2})_{T_2} \quad (3.14)$$

The two departure functions in the above equation can be calculated from an equation of state. The same is true for other departure functions and also for derivative properties.

Expressions for departure functions are obtained

through the following development. At constant temperature and composition the variation in the Gibbs energy is

$$dG = VdP \quad (3.15)$$

where V is the molar volume. Integrating at constant temperature and composition from reference pressure P° to system pressure P gives

$$G - G^\circ = \int_{P^\circ}^P VdP \quad (3.16)$$

In Equation 3.16 one limit of integration refers to the real-gas state and the other to an ideal-gas state. To facilitate the evaluation of this integral it is broken into two integrals:

$$G - G^\circ = \int_{P^\circ}^0 VdP + \int_0^P VdP \quad (3.17)$$

The second integral now deals exclusively with real-gas properties, but the first deals with ideal-gas properties and can be integrated immediately using the ideal-gas law. However, to avoid difficulty with the zero pressure limit, the term

$$\int_0^P \frac{RT}{P} dP$$

is added to and subtracted from the right-hand side. Then

integration yields

$$G - G^{\circ} = \int_0^P \left(V - \frac{RT}{P} \right) dP + RT \ln \frac{P}{P^{\circ}} \quad (3.18)$$

or

$$G - G^{\circ} = RT \int_0^P (Z - 1) d \ln P + RT \ln \frac{P}{P^{\circ}} \quad (3.19)$$

For the entropy departure function the following expression is derived:

$$\begin{aligned} S - S^{\circ} &= - \frac{\partial}{\partial T} (G - G^{\circ})_P \\ &= R \int_0^P \left[1 - Z - T \left(\frac{\partial Z}{\partial T} \right)_P \right] d \ln P - R \ln \frac{P}{P^{\circ}} \end{aligned} \quad (3.20)$$

The enthalpy departure function is given as

$$H - H^{\circ} = (G - G^{\circ}) + T(S - S^{\circ}) \quad (3.21)$$

Also the internal-energy and Helmholtz-energy departure functions can be expressed as

$$U - U^{\circ} = (G - G^{\circ}) + T(S - S^{\circ}) - RT(Z - 1) \quad (3.22)$$

$$A - A^{\circ} = (G - G^{\circ}) - RT(Z - 1) \quad (3.23)$$

The fugacity-pressure ratio may be determined from the following equation:

$$\ln \frac{f}{P} = \left(\frac{G - G^\circ}{RT} \right) - \ln \frac{P}{P^\circ} \quad (3.24)$$

Each of these relations is expressed solely in terms of pressure, temperature, and the compressibility factor. Thus if an equation of state is known, any and all of these relations can be evaluated.

Shown in Table III.3 are formulae for thermodynamic properties obtained from the reference fluid equations of state. These equations are used to obtain the reference fluid values for each property which are in turn used in Equation 3.7 to obtain the corresponding property estimate for the fluid of interest. If H^* represents the enthalpy departure function, then the enthalpy departure function is given as

$$H^* = H_0^* + \alpha \left(\frac{H_1^* - H_0^*}{\alpha_1} \right) + \beta \left\{ \frac{H_2^* - \left[H_0^* + \alpha_2 \left(\frac{H_1^* - H_0^*}{\alpha_1} \right) \right]}{\beta_2} \right\} \quad (3.25)$$

C. Development of the Third and Fourth Parameters

The third parameter, α , in Equation 3.7 represents the acentricity of the fluid molecule. It must provide an accurate measure of the combined effects of size and shape

Table III.3. Departure Function Equations

Equations for First and Second Reference Fluids

$$\frac{H^\circ - H}{RT_c} = -T_r \left[Z - 1 - \frac{b_2 + 2b_3/T_r + 3b_4/T_r^2}{T_r V_r} - \frac{c_2 - 3c_3/T_r^2}{2T_r V_r^2} + \frac{d_2}{5T_r V_r^5} + 3E \right]$$

$$\text{where } E = \frac{c_4}{2T_r^3 \gamma} \left[\beta + 1 - \left(\beta + 1 + \frac{\gamma}{V_r^2} \right) \exp \left(-\frac{\gamma}{V_r^2} \right) \right]$$

$$\frac{S^\circ - S}{R} = -\ln \frac{P^\circ}{P} - \ln Z + \frac{b_1 + b_3/T_r^2 + 2b_4/T_r^3}{V_r} + \frac{c_1 - 2c_3/T_r^3}{V_r^2} + \frac{d_1}{5V_r^5} - 2E$$

$$\ln \frac{f}{P} = Z - 1 - \ln Z + \frac{B}{V_r} + \frac{C}{2V_r^2} + \frac{D}{5V_r^5} + E$$

$$\frac{H^\circ - H}{RT_c} = -T_r \rho \tau \left(\frac{\partial Q}{\partial \tau} \right)_\rho + \rho Q + \rho^2 \left(\frac{\partial Q}{\partial \rho} \right)_\tau$$

$$\frac{S^\circ - S}{R} = -\ln Z + \rho Q - \rho \tau \left(\frac{\partial Q}{\partial \tau} \right)_\rho - \ln \frac{P^\circ}{P}$$

$$\ln \frac{f}{P} = - \left[\frac{H^\circ - H}{RT_c} \right]_{T_r} + \left[\frac{S^\circ - S}{R} \right]$$

independent of polarity. For polar fluids, Pitzer's acentric factor is a function of geometry and polarity and therefore does not qualify as a viable choice for the third parameter.

In the present work the radius of gyration was chosen to be the basis for the third parameter because it is based solely on the geometry of the molecule and gives an accurate measure of size and shape effects. Note that for nonpolar molecules Pitzer's acentric factor is similarly only a function of geometry. This fact is the basis for the definition of the third parameter, α , as a function of the radius of gyration. For a nonpolar fluid, Equation 3.7 reduces to a three-parameter correlation (since $\beta = 0$) which is identical to the Lee-Kesler method except for the use of α as opposed to ω . Thus for nonpolar fluids α and ω should be approximately equal.

For 80 nonpolar fluids the acentric factor was plotted versus the radius of gyration, R_g . (A list of these fluids is given in Appendix A.) This plot is shown in Figure III.1 along with a least squares fit of the data. The polynomial relationship between ω and R_g is given by the equation

$$\omega = -7.706 \times 10^{-4} + 0.0330 R_g + 0.01506 R_g^2 + 9.997 \times 10^{-4} R_g^3 \quad (3.26)$$

Since $\alpha = \omega$ for nonpolar fluids an explicit equation giving the third parameter, α , as a function of the radius of gyration is obtained:

Figure III.1 Acentric Factor vs. Radius of Gyration for 80 Nonpolar Fluids.

$$\alpha = -7.706 \times 10^{-4} + 0.0330 R_g + 0.01506 R_g^2 + 9.997 \times 10^{-4} R_g^3$$

(3.27)

This equation is applicable to all fluids and will represent the effects of geometry in both polar and nonpolar fluids.

Geometry effects have thus been isolated in the third parameter. The fourth parameter, β , is now left to account for all polar effects. Ideally the fourth parameter would be defined in terms of a characteristic quantity such as the dipole moment. Unfortunately, as other researchers have discovered, no such quantity adequately accounts for the effects of polarity. If the dipole moment is deep inside a molecule it will have less effect on fluid properties than if it is near the surface where it can more freely interact with neighboring molecules. Thus the location and direction of the dipole moment are important in determining its effect on property values.

After many attempts to correlate polar fluid properties with various physical parameters and groups of parameters it was concluded that the most accurate method of obtaining the fourth parameter is the use of one experimental data point. Since polarity effects are greatest in the liquid phase and density data are common, a liquid density point is used to calculate β directly. By converting the density point to a compressibility factor and solving Equation 3.7 for β , one obtains the following expression:

$$\beta = \frac{\beta_2 \left[Z - Z_0 - \alpha \left(\frac{Z_1 - Z_0}{\alpha_1} \right) \right]}{Z_2 - \left[Z_0 + \alpha_2 \left(\frac{Z_1 - Z_0}{\alpha_1} \right) \right]} \quad (3.28)$$

Once β has been obtained from Equation 3.28, it can be used in conjunction with Equation 3.7 to predict all thermodynamic properties. However, it has been found that for some fluids, especially those that hydrogen bond, that β obtained from a liquid density point yields accurate Z values but poorer enthalpy departure functions. That is, polar effects contribute differently to the enthalpy than to the volume. For the most accurate predictions it is recommended that one β , obtained from a liquid density measurement, be used in PVT estimations and a different β , obtained as described below, be used for derivative properties.

The heat of vaporization, known for most common fluids, is used to obtain this alternate value of β , denoted as β_h . If the heat of vaporization is not known it can be estimated from the normal boiling point using one of several correlations. Equation 3.29 is the Procopio and Su (21) equation which gives good estimates for polar-fluid heats of vaporization:

$$\Delta H_{vb} = 1.024 RT_c T_{br} \frac{(\ln P_c)(1 - P_c^{-1})}{1 - T_{br}} \quad (3.29)$$

where ΔH_{vb} is the heat of vaporization, T_c and P_c are the

critical constants of the fluid of interest, T_{br} is the reduced normal boiling point of the fluid of interest, and R is the gas constant. Once the heat of vaporization is determined, β_h can be calculated.

The three reference fluid enthalpy departure function equations are solved for the saturated liquid and vapor at the reduced conditions used to obtain ΔH_{vb} . Then a heat of vaporization is calculated for each reference fluid from the difference between the vapor and liquid enthalpies:

$$\Delta H_{vb_i} = H_{v_i}^* - H_{l_i}^* ; \quad i = 0, 1, 2 \quad (3.30)$$

where i indicates the reference fluid. Since the heat of vaporization is a property which can be estimated by the corresponding states formulation, the heats of vaporization for the three reference fluids are inserted into an equation similar to Equation 3.28 giving an estimate of β_h :

$$\beta_H = \frac{\beta_2 \left[\Delta H_{vb} - \Delta H_{vb0} - \alpha \left(\frac{\Delta H_{vb1} - \Delta H_{vb0}}{\alpha_1} \right) \right]}{\Delta H_{vb2} - \left[\Delta H_{vb0} + \alpha_2 \left(\frac{\Delta H_{vb1} - \Delta H_{vb0}}{\alpha_1} \right) \right]} \quad (3.31)$$

When used in the four-parameter correlation, this value of β_h gives accurate estimates of enthalpy departure functions and other derived properties and is especially useful with alcohols.

D. Mixtures

To estimate the properties of mixtures the following empirical mixing rules are recommended:

$$T_{c_m} = \frac{1}{8V_{c_m}} = \sum_i \sum_j y_i y_j (V_{c_i}^{\frac{1}{3}} + V_{c_j}^{\frac{1}{3}})^3 (T_{c_i} T_{c_j})^{\frac{1}{2}} \quad (3.32)$$

where

$$V_{c_m} = \frac{1}{8} \sum_i \sum_j y_i y_j (V_{c_i}^{\frac{1}{3}} + V_{c_j}^{\frac{1}{3}})^3 \quad (3.33)$$

$$V_{c_i} = \frac{(0.2905 - 0.085\alpha_i)RT_{c_i}}{P_{c_i}} \quad (3.34)$$

and

$$\alpha_m = \sum_i y_i \alpha_i \quad (3.35)$$

$$P_{c_m} = \frac{(0.2905 - 0.085\alpha_m)RT_{c_m}}{V_{c_m}} \quad (3.36)$$

$$\beta_m = \sum_i y_i \beta_i \quad (3.37)$$

where subscript m refers to the mixture, i and j indicate the individual components, and y_i is the mole fraction of component i .

These mixing rules have not been extensively tested,

and care should be exercised in their use. They warrent
further study in future work.

CHAPTER IV

RESULTS

A. Nonpolar Fluids

One of the theoretical bases of the four-parameter method presented in this work is the independence of the third and fourth parameters. In other words, geometric effects are isolated in the third parameter, and polar effects are isolated in the fourth parameter. The definition of the third parameter, α , in terms of the radius of gyration is the key to establishing this independence. Because the radius of gyration is a purely geometrical measure, α will be independent of polarity.

The 'goodness' of the correlation between the radius of gyration and Pitzer's acentric factor for nonpolar fluids as seen in Figure III.1 shows that the radius of gyration is an effective basis for a parameter representing geometric effects. Again, for nonpolar fluids the fourth parameter, β , is zero and Equation 3.7 becomes a three-parameter equation similar to the Lee-Kesler method with α replacing ω . Table IV.1 compares a few compressibility factor estimates for nonpolar fluids and demonstrates the equivalency of the two methods for nonpolar fluids. The importance of this is not that a new three-parameter method has been devised but that this new method uses a purely

Table IV.1 Compressibility Factors for Nonpolar Fluids

<u>Substance</u>	<u>Tr</u>	<u>Pr</u>	<u>Exptl. Z</u>	<u>Lee-Kesler</u>	<u>This Work</u>
Ethylene	1.062	0.0397	0.9887	0.9888	0.9888
	1.416	0.1986	0.9779	0.9766	0.9791
	0.531	0.0054	0.001035	0.001041	0.001042
Propane	0.947	0.0471	0.9814	0.9804	0.9803
	1.352	0.4711	0.9428	0.9430	0.9431
	0.811	0.2340	0.03590	0.03635	0.03633
Isobutane	0.931	0.1097	0.9523	0.9503	0.9499
	1.225	0.5483	0.9019	0.9026	0.9032
	0.613	0.0174	0.002931	0.002954	0.002924
2-Methyl- Butane	0.912	0.0591	0.9723	0.9712	0.9711
	1.173	1.4774	0.6533	0.6603	0.6618
	0.652	0.0288	0.004602	0.004624	0.004600
<u>Average Percent Error :</u>				0.403 %	0.354 %

geometric parameter and thus is independent of polarity.

B. Polar Fluids

With all geometric effects accounted for by the third parameter, the fourth parameter becomes a pure polarity parameter and accounts for all polar effects. In the results presented in this chapter the fourth parameter, β , is based on one liquid density datum for compressibility factor predictions and on the heat of vaporization for the enthalpy and entropy departure functions and for the fugacity-pressure ratio. The four-parameter correlation of this work has been used to predict various properties of several polar fluids. The critical constants for these fluids and the third and fourth corresponding-states parameters calculated in the correlation are given in Table IV.2.

Predictions obtained from the method of this work have been compared to literature data and also to predictions from two other corresponding states methods. The first of these is the Lee-Kesler three-parameter method which, although not intended for polar fluids, is often used because of its simplicity.

Also included in the comparison is the Wu and Stiel four-parameter method discussed in Chapter II. This method, as yet unpublished, was developed simultaneously with but independently of the method of this work. The two methods

Table IV.2 Corresponding-States Parameters for Several Polar Fluids

<u>Fluid</u>	<u>T_c(K)</u>	<u>P_c(atm)</u>	<u>α</u>	<u>β</u>	<u>β_h</u>
Ammonia	405.6	111.3	0.3775	0.7499	0.6572
Ethanol	516.2	63.0	0.1383	0.4815	1.6372
Acetone	508.1	46.4	0.1822	0.5874	0.4470
Methanol	512.6	79.9	0.0819	0.8855	1.3059
Hydrogen- Chloride	324.6	82.0	0.0104	0.4705	0.3196
Methyl- Chloride	416.3	65.9	0.0757	0.3051	0.2248
Methyl- Acetate	506.8	46.3	0.1936	0.3705	0.4160
MethylEthyl- Ketone	535.6	41.0	0.2204	0.4258	0.3689
1-Propanol	536.7	51.0	0.1818	0.3858	1.6372
2-Propanol	508.3	47.0	0.1809	0.4536	1.7128

are very similar. Both employ the same reference fluids and the same correlational framework. The major difference between the two methods is the definition of the third and fourth parameters. As earlier noted, Wu and Stiel retain Pitzer's acentric factor as the third parameter and obtain the fourth parameter from a best-fit of experimental data. However, they state that the fourth parameter may alternatively be obtained from a single volumetric datum just as is done in the method of this thesis. The results of their method used in the following comparison employ their best-fit fourth parameters and will mirror this selection.

The form of the general correlation as given in Equation 3.7 involves three terms: a simple fluid term, a geometric deviation term, and a polar deviation term. The use of the acentric factor as the third parameter in the Wu and Stiel method causes polar effects to be included in the geometric deviation term. This term is thus made artificially large, and the polar deviation term is made artificially small.

The comparison of the three methods will demonstrate the effectiveness of four-parameter methods over three-parameter methods. As will be seen, the results of the Wu and Stiel method are similar to the results of the present work, which is not surprising based on the similarities of the two methods.

Figure IV.1 through Figure IV.35 illustrate the

accuracy of the various methods. In each figure the curves are experimental data and the individual points are predicted values. It should be remembered that the error in an estimate is measured along isobars: in plots where pressure is the ordinate the error is the horizontal distance between the predicted value and the data curve, and where pressure is the abscissa, the error is the vertical distance between the two values.

Figure IV.1 and Figure IV.2 show the saturation curve of ammonia with predictions from the Lee-Kesler method and from the method of this thesis, respectively. Both methods do well for the saturated vapor, but the Lee-Kesler method does much more poorly for the saturated liquid, overpredicting the volume by more than 20 % compared to just over 2 % for the present method.

Figure IV.3 through Figure IV.5 present ammonia saturated and superheated vapor results for the methods under consideration. All three methods do reasonably well in the vapor region which is where polar effects become less important.

Saturated and compressed liquid results for ammonia are shown in Figure IV.6 through Figure IV.8. Here the inadequacy of the three-parameter formulation is vividly demonstrated, with average deviations of over 17 %. The two four-parameter methods do comparably well, giving average errors of less than 3 %.

Enthalpy departure functions for ammonia are shown in

Figure IV.9 through Figure IV.11. Again, the four-parameter methods do considerably better than the Lee-Kesler method. Figure IV.12 through Figure IV.14 illustrate entropy departure functions for ammonia where the four-parameter methods give somewhat superior predictions to the Lee-Kesler method. Ammonia fugacity coefficients along the 400 K isotherm are given in Figures IV.15 through IV.17. In the vapor phase (pressures less than 100 bars) all three methods show excellent agreement with experimental results, but in the liquid phase the Lee-Kesler method overpredicts the fugacity coefficient by over 5 %.

Figures IV.18 through IV.20 show compressibility factors along two isotherms (473.15 K and 623.15 K) for ethanol in the dense gas phase. At the higher temperature the Wu and Stiel method gives better predictions than either the Lee-Kesler method or the method of this thesis. However, at the lower temperature the Wu and Stiel method gives poorer results than the other methods.

Predictions of enthalpy departure functions for vapor-phase ethanol are given in Figures IV.21 through IV.23. The method of this work gives predictions that are considerably better than either the Lee-Kesler or Wu and Stiel methods.

Compressibility factors of acetone in the compressed liquid region along the 508 K isotherm are shown in Figures IV.24 through IV.26. Here the Lee-Kesler method gives errors of about 15 %, the Wu and Stiel method about 1 %, and

the method of this thesis slightly over 1 %.

Figures IV.27 through IV.29 give compressibility factors of liquid methanol along two isotherms (298.12 K and 478.62 K). The Lee-Kesler method generally overpredicts the compressibility factor and yields errors of about 13 % for these data. The Wu and Stiel method gives better results with an average error of 3.5 %. The method of the present work gives excellent results with average errors of less than 1 %.

For liquid methyl chloride the four-parameter methods give good predictions of compressibility factors as shown in Figures IV.30 through IV.32. Average errors for these methods are less than 1 %. The Lee-Kesler method shows errors of more than 6 %.

In Figures IV.33 through IV.35 a pressure vs. volume plot for hydrogen chloride along the 338.15 K isotherm illustrates the effectiveness of the four-parameter methods. As for most polar fluids, the Lee-Kesler method overpredicts the specific volume. This isotherm is at $T_r = 1.04$.

The results of this work along with estimates using the Lee-Kesler and Wu and Stiel methods are summarized in Tables IV.3 through IV.5. Table IV.3 (Page 89) compares compressibility factor estimates and shows the general superiority of the four-parameter methods over the three-parameter method. The present method gives consistently better results than the Lee-Kesler method (Text continued on Page 91)

Figure IV.1 Saturation Curve of Ammonia.
Literature Data: — Lee-Kesler: $\diamond$.

Figure IV.2 Saturation Curve of Ammonia.
Literature Data: — This Method: $\odot$.

Figure IV.3 Saturated-Vapor Curve and Vapor Isotherms of Ammonia.
Literature Data: — Lee-Kesler: ◊.

Figure IV.4 Saturated-Vapor Curve and Vapor Isotherms of Ammonia.
Literature Data: — Wu and Stiel: □.

Figure IV.5 Saturated-Vapor Curve and Vapor Isotherms of Ammonia.
Literature Data: — This Method: ○.

Figure IV.6 Saturated-Liquid Curve and Liquid Isotherms of Ammonia.
 Literature Data: — Lee-Kesler: $\diamond$.

Figure IV.7 Saturated-Liquid Curve and Liquid Isotherms of Ammonia.
Literature Data: — Wu and Stiel: □.

Figure IV.8 Saturated-Liquid Curve and Liquid Isotherms of Ammonia.
Literature Data: — This Method: ○.

Figure IV.9 Enthalpy Departure Functions for Ammonia.
Literature Data: — Lee-Kesler: $\diamond$.

Figure IV.10 Enthalpy Departure Functions for Ammonia.
 Literature Data: — Wu and Stiel: $\square$.

Figure IV.11 Enthalpy Departure Functions for Ammonia.
 Literature Data: — This Method: ○.

Figure IV.12 Entropy Departure Functions for Ammonia.
Literature Data: — Lee-Kesler: $\diamond$.

Figure IV.13 Entropy Departure Functions for Ammonia.
Literature Data: — Wu and Stiel: $\square$.

Figure IV.14 Entropy Departure Functions for Ammonia.
Literature Data: — This Method: $\odot$.

Figure IV.15 Fugacity Coefficients for Ammonia
at $T=400$ K.
Literature Data: — Lee-Kesler: $\diamond$.

Figure IV.16 Fugacity Coefficients for Ammonia
at T=400 K.
Literature Data:— Wu and Stiel: $\square$.

Figure IV.17 Fugacity Coefficients for Ammonia
at T=400 K.
Literature Data: — This Method: ⊗.

Figure IV.18 Compressibility Factors of Ethanol.
Literature Data: — Lee-Kesler: $\diamond$.

Figure IV.19 Compressibility Factors of Ethanol.
Literature Data: — Wu and Stiel: $\square$.

Figure IV.20 Compressibility Factors of Ethanol.
Literature Data: — This Method: $\odot$.

Figure IV.21 Enthalpy Departure Functions of Ethanol.
Literature Data: — Lee-Kesler: $\diamond$.

Figure IV.22 Enthalpy Departure Functions of Ethanol.
Literature Data: — Wu and Stiel: $\square$.

Figure IV.23 Enthalpy Departure Functions of Ethanol.
Literature Data: — This Method: $\odot$.

Figure IV.24 Compressibility Factors of Acetone
at T=508 K
Literature Data: — Lee-Kesler: $\diamond$.

Figure IV.25 Compressibility Factors of Acetone
at T=508 K
Literature Data: — Wu and Stiel: □.

Figure IV.26 Compressibility Factors of Acetone
at T=508 K
Literature Data: — This Method: ○.

Figure IV.27 Compressibility Factors of Methanol
at $T=298.12$ K and 478.62 K
Literature Data: Lee-Kesler: ◊.

Figure IV.28 Compressibility Factors of Methanol
at $T=298.15$ K and 478.62 K
Literature Data: Wu and Stiel: □.

Figure IV.29 Compressibility Factors of Methanol
at $T=298.15$ K and 478.62 K
Literature Data: This Method: ○.

Figure IV.30 Compressibility Factors of Methyl Chloride at $T=313.15$ K
Literature Data: — Lee-Kesler: $\diamond$.

Figure IV.31 Compressibility Factors of Methyl Chloride at T=313.15 K
Literature Data: — Wu and Stiel: □.

Figure IV.32 Compressibility Factors of Methyl Chloride at T=313.15 K
Literature Data: — This Method: O.

Figure IV.33 Pressure-Volume Plot for Hydrogen Chloride at $T = 338.15 \text{ K}$
Literature Data: — Lee-Kesler: $\diamond$.

Figure IV.34 Pressure-Volume Plot for Hydrogen Chloride at $T = 338.15 \text{ K}$
Literature Data: — Wu and Stiel: $\square$.

Figure IV.35 Pressure-Volume Plot for Hydrogen Chloride at $T = 338.15 \text{ K}$
Literature Data: - - - This Method: $\odot$.

Table IV.3. Comparisons of Compressibility Factor Predictions for Several Polar Fluids

<u>Substance</u>	<u>Range</u>		<u>No. Pts.</u>	<u>Average % Error Z</u>			<u>Source</u>
	<u>Tr</u>	<u>Pr</u>		<u>This Work</u>	<u>Wu & Stiel</u>	<u>Lee- Kesler</u>	
<u>Ammonia</u>							
Liquid	0.48- 1.48	0.001- 8.87	34	2.11	2.67	17.1	(21)
Vapor	0.48- 1.48	0.001- 4.43	35	0.69	0.71	1.17	(21)
Sat. Liquid	0.50- 0.997	0.001- 0.984	17	2.24	1.73	25.7	(21)
Sat. Vapor	0.50- 0.982	0.001- 0.887	15	0.792	0.882	3.15	(21)
<u>Ethanol</u>							
Liquid	0.92- 1.21	1.30- 9.18	34	2.11	3.17	2.80	(22)
Vapor	0.53- 0.93	0.0001- 0.216	14	1.14	1.40	1.41	(23)
Sat. Liquid	0.53- 0.60	0.0001- 0.0025	8	0.16	14.3	10.0	(23)
Sat. Vapor	0.53- 0.93	0.0001- 0.497	9	1.10	1.06	1.07	(23)
<u>Acetone</u>							
Liquid	0.59- 1.06	0.021- 8.34	32	1.31	0.97	15.5	(24,25)
<u>Hydrogen- Chloride</u>							
Liquid	0.84- 1.04	0.42- 2.24	37	2.21	2.12	8.87	(26)

Table IV.3. (continued)

<u>Substance</u>	<u>Range</u>		<u>No. Pts.</u>	<u>Average % Error Z</u>			<u>Source</u>
	<u>Tr</u>	<u>Pr</u>		<u>This Work</u>	<u>Wu & Stiel</u>	<u>Lee- Kesler</u>	
<u>Methyl- Acetate</u>							
Liquid	0.50- 0.62	4.19- 12.6	12	1.34		5.94	(27)
<u>Methanol</u>							
Liquid	0.58- 0.93	0.06- 12.8	45	0.85	3.48	13.9	(28)
Vapor	0.81- 1.12	0.05- 2.55	24	4.55	2.65	7.08	(29)
<u>Methyl- Chloride</u>							
Liquid	0.75- 0.90	0.13- 4.73	25	0.68	0.51	6.55	(30)
<u>2-Propanol</u>							
Liquid	0.93- 1.13	1.45- 9.84	48	1.95	0.89	0.90	(31)
Vapor	0.73- 0.93	0.004- 0.54	62	2.21	1.88	1.82	(32)

except for saturated-liquid ethanol where the Lee-Kesler method is better by only 0.03 % and both vapor and liquid 2-propanol where the Lee-Kesler method is better by 0.39 % and 1.05 % respectively.

The method of this thesis gives better results than the Wu and Stiel methods for most points, but for some fluids the Wu and Stiel method does somewhat better. Note again that in the Wu and Stiel method the fourth parameter is a best-fit value whereas the present method uses a single data point as the basis for the fourth parameter. The Wu and Stiel method gives better results for saturated-liquid ethanol by 0.04 %, for liquid acetone by 0.33 %, for liquid hydrogen chloride by 0.19 %, for vapor methanol by 1.90 %, for liquid methyl chloride by 0.17 %, and for vapor and liquid 2-propanol by 0.33 % and 1.06 %, respectively. A composite comparison for all compressibility factor points considered gives an average error of 6.68 % for the Lee-Kesler method, 2.08 % for the Wu and Stiel method, and 1.73 % for the method of this thesis.

Results of the three methods for enthalpy departure function predictions are shown in Table IV.4. For derivative properties (including the enthalpy departure function) the present method bases the fourth parameter on the heat of vaporization. The Wu and Stiel method retains the fourth parameter used for compressibility factor predictions.

The present method does far better than the Lee-Kesler

Table IV.4. Comparisons of Enthalpy Departure Function Predictions for Several Polar Fluids

<u>Substance</u>	<u>Range</u>		<u>No. Pts.</u>	<u>Average Dev. H, J/mol</u>			<u>Source</u>
	<u>Tr</u>	<u>Pr</u>		<u>This Work</u>	<u>Wu & Stiel</u>	<u>Lee- Kesler</u>	
<u>Ammonia</u>							
Liquid	0.48- 1.48	0.001- 8.87	33	119	209	385	(21)
Vapor	0.48- 1.48	0.001- 4.43	34	68.4	66.1	149	(21)
<u>Ethanol</u>							
Vapor	0.53- 1.03	0.0001- 1.08	28	164	400	433	(23,33)
Sat. Liquid	0.53- 0.60	0.0001- 0.0025	3	764	1812	1968	(23)
Sat. Vapor	0.53- 0.60	0.0001- 0.0025	3	375	388	390	(23)
<u>Acetone</u>							
Liquid	0.78- 0.995	0.294- 1.17	3	90.3	334	737	(34)
Vapor	0.78- 1.05	0.103- 1.17	7	16.4	36	199	(34)
<u>Methanol</u>							
Vapor	0.88- 0.99	0.085- 0.85	15	433	518	676	(35)
<u>1-Propanol</u>							
Sat. Liquid	0.57- 0.90	0.0001- 0.417	7	1682	1494	3816	(36)
Vapor	0.84- 1.02	0.17- 0.77	20	260	200	195	(36)

Table IV.4. (continued)

<u>Substance</u>	<u>Range</u>		<u>No. Pts.</u>	<u>Average Dev. H, J/mol</u>			<u>Source</u>
	<u>Tr</u>	<u>Pr</u>		<u>This Work</u>	<u>Wu & Stiel</u>	<u>Lee- Kesler</u>	
<u>MethylEthyl- Ketone</u>							
Liquid	0.84- 0.94	0.33- 0.996	3	894		1479	(34)
Vapor	0.84- 1.02	0.13- 0.996	6	977		1074	(34)

method except for 2-propanol vapor where the Lee-Kesler estimates are on the average 65 J/mol better. The Wu and Stiel method does better than the method developed here for vapor-phase ammonia by 2.3 J/mol and for saturated-liquid and vapor 2-propanol by 188 J/mol and 60 J/mol, respectively. A composite comparison of enthalpy departure function predictions demonstrates the significant superiority of the present method over the other two methods. The average error is 531 J/mol for the Lee-Kesler method, 330 J/mol for the Wu and Stiel method, and 249 J/mol for the method of this thesis. Accurate enthalpy departure function estimates are more significant in the liquid phase than in the vapor phase because the values of liquid departure functions are much larger on an absolute scale. The liquid region is where the present method excels most dramatically over the other methods.

Table IV.5 shows predictions of the entropy departure function and the fugacity coefficient for ammonia. The method of this work does better than the Lee-Kesler method for both properties. The Wu and Stiel method gives slightly better results than the present method for both vapor-phase entropies and fugacity coefficients. However, the present method does considerably better in the liquid phase.

C. Determination of β_h

As discussed in the previous chapter the fourth

Table IV.5. Comparisons of Entropy Departure Function and Fugacity-Coefficient Predictions for Ammonia

<u>State</u>	<u>Range</u>		<u>Average Dev. S, J/mol K</u>				<u>Source</u>
	<u>Tr</u>	<u>Pr</u>	<u>No. Pts.</u>	<u>This Work</u>	<u>Wu & Stiel</u>	<u>Lee- Kesler</u>	
Liquid	0.48- 1.48	0.001- 8.87	33	0.382	0.717	1.27	(21)
Vapor	0.48- 1.48	0.001- 4.43	34	0.142	0.137	0.352	(21)
<u>State</u>	<u>Range</u>		<u>Average % Error ϕ</u>				<u>Source</u>
	<u>Tr</u>	<u>Pr</u>	<u>No. Pts.</u>	<u>This Work</u>	<u>Wu & Stiel</u>	<u>Lee- Kesler</u>	
Liquid	0.48- 1.48	0.001- 8.87	33	1.42	1.88	5.46	(21)
Vapor	0.48- 1.48	0.001- 4.43	34	0.73	0.72	0.76	(21)

parameter, β_h , for derivative properties can be based on the heat of vaporization directly or the heat of vaporization may be estimated from the boiling temperature by one of several correlations. It should be noted that the value of β_h is sensitive to the value of the heat of vaporization. Equation 3.29 was used to estimate the heat of vaporization for several polar fluids from which β_h was obtained. Predictions using this procedure were compared to predictions based directly upon tabular values of the heat of vaporization. Generally, the agreement was very good and predictions based upon the boiling point were within a few percent of those obtained from the heat of vaporization.

Tabulated values of heats of vaporization have been noted to vary by several percent which will translate to a several percent change in the predicted value of a property (less for the vapor phase). Thus caution should be exercised whether one is using the boiling point or the heat of vaporization as the basis for the fourth parameter. Generally, the hierarchy of preferred methods for the determination of β_h is (1) Heat of vaporization, (2) The normal boiling point, and (3) A liquid density point (i.e. use β obtained for compressibility factor calculations). The third method will give results that are near those of the first two for many polar fluids, but for alcohols it is strongly recommended that one of the first two methods be employed.

D. Mixtures

Although the purpose of this work has been the development of a method for pure fluids, it is anticipated that this method will be extended to mixtures. With this in mind a few mixture predictions were obtained using the mixing rules presented in the previous chapter. (These mixing rules are adapted from those proposed by Lee and Kesler.) These predictions are compared to literature data in Table IV.6.

These results are encouraging considering the nonideality of these mixtures. More work will need to be done to improve the mixing rules and these will have to be tested as extensively as possible.

Table IV.6 Preliminary Mixture Results (Liquids). All points are at 298.15 K and 1.00 atm.(27,28)

<u>Binary Systems</u>					
	Mole Fraction(1)	<u>Density (g/cc)</u>		% Error	
		<u>Experiment</u>	<u>This Work</u>		
Ethanol(1)-	0.4548	0.7736	0.8039	3.92	
Cyclohexane(2)	0.8639	0.7791	0.7982	2.45	
Acetone(1)-	0.2614	0.7910	0.8062	1.93	
Methanol(2)	0.6915	0.7898	0.8031	1.69	
Methylacetate(1)-	0.1480	0.7047	0.6668	-5.38	
n-Hexane(2)	0.8006	0.8818	0.8557	-2.96	
<u>Ternary Systems</u>					
	Mole Fraction		<u>Density (g/cc)</u>		% Error
	<u>(1)</u>	<u>(2)</u>	<u>Experiment</u>	<u>This Work</u>	
Acetone(1)-					
n-Hexane(2)-	0.2380	0.2110	0.7708	0.7563	-1.88
Ethanol(3)	0.4195	0.3748	0.7777	0.7292	-6.24
Methylacetate(1)-					
Cyclohexane(2)-	0.1742	0.1280	0.8061	0.8277	2.68
Ethanol(3)	0.4172	0.2931	0.8266	0.8571	3.69

CHAPTER V

USE OF THE METHOD

A. Use of Computerized Method

To obtain a property estimate for a given fluid the following general procedure is followed. As required input to the program the user supplies the critical temperature and pressure, the radius of gyration, and a liquid density datum. If derivative properties are desired, the heat of vaporization or the boiling temperature is also recommended, but not absolutely required, as input information. If neither of these properties is available then the fourth parameter obtained from the liquid density point will be used for derivative properties. The temperature and pressure at which the calculation is to be performed are also required as input data. If the phase is known it is also supplied, but if it is not the program will determine the phase. With this information the program will perform the required calculations and return predictions for the compressibility factor, the enthalpy and entropy departure functions, and the fugacity-pressure ratio.

B. Hand Calculations

The general form of the four-parameter method for any

property J may be written as

$$J = J^0 + \alpha J^1 + \beta J^2 \quad (5.1)$$

where J^0 is the simple fluid value of J , J^1 is the geometric deviation term, and J^2 is the polar deviation term. If α and β have been previously determined, a property may be estimated from a knowledge of the three different contributions. Table V.1 through Table V.24 present values of these functions for the properties considered in this work. To illustrate the use of these tables suppose an estimate for the compressibility factor of ethanol at $T_r=1.4$ and $P_r=0.6$ is desired. The parameters α and β have been previously determined: $\alpha = 0.1383$ and $\beta = 0.4815$. Using Table V.1 to obtain Z^0 , Table V.2 to obtain Z^1 , and Table V.3 to obtain Z^2 , the calculation is made as follows:

$$Z^0 = 0.9298$$

$$Z^1 = 0.0477$$

$$Z^2 = 0.0156$$

Substituting these values into Equation 5.1 written for Z :

$$Z = Z^0 + \alpha Z^1 + \beta Z^2 \quad (5.2)$$

we obtain the prediction for ethanol as $Z = 0.9441$.

It should be remembered that the values obtained from the tables must correspond to the phase of the test fluid.

The phase of the individual reference fluids is not important. The saturation line is thus drawn the same in Tables V.1 through V.12 even though the line is not the same for the three reference fluids. There exists the possibility that the phase of the test fluid may not correspond to the phase shown in the tables. To accomodate this possibility, Tables V.13 through V.24 give auxiliary values for the region where this might occur. These values are of opposite phase to those of Tables V.1 through V.12 and are obtained by extrapolating the equations of state into the two-phase region. This subject is discussed further in the following chapter.

For example suppose that an estimate for a property is needed at $T_r=0.75$ and $P_r=0.10$. If the test fluid is a vapor at these conditions then Table V.1 through Table V.12 are used, but if the test fluid is a liquid at these conditions (which is highly possible for polar fluids) then the auxiliary tables are used.

Table V.1 Compressibility Factor
 Z^0 (Simple Fluid)

Tr	Pr						
	0.01	0.05	0.10	0.20	0.40	0.60	0.80
0.30	0.0029	0.0145	0.0290	0.0579	0.1158	0.1737	0.2315
0.35	0.0026	0.0130	0.0261	0.0522	0.1043	0.1564	0.2084
0.40	0.0024	0.0119	0.0239	0.0477	0.0953	0.1429	0.1904
0.45	0.0022	0.0110	0.0221	0.0442	0.0882	0.1322	0.1762
0.50	0.0021	0.0103	0.0207	0.0413	0.0825	0.1236	0.1647
0.55	0.9804	0.0098	0.0195	0.0390	0.0778	0.1166	0.1553
0.60	0.9849	0.0093	0.0186	0.0371	0.0741	0.1109	0.1476
0.65	0.9881	0.9377	0.0178	0.0356	0.0710	0.1063	0.1415
0.70	0.9904	0.9504	0.8958	0.0344	0.0687	0.1027	0.1366
0.75	0.9922	0.9598	0.9165	0.0336	0.0670	0.1001	0.1330
0.80	0.9935	0.9669	0.9319	0.8539	0.0661	0.0985	0.1307
0.85	0.9946	0.9725	0.9436	0.8810	0.0661	0.0983	0.1301
0.90	0.9954	0.9768	0.9528	0.9015	0.7800	0.1006	0.1321
0.93	0.9959	0.9790	0.9573	0.9115	0.8059	0.6635	0.1359
0.95	0.9961	0.9803	0.9600	0.9174	0.8206	0.6967	0.1410
0.97	0.9963	0.9815	0.9625	0.9227	0.8338	0.7240	0.5580
0.98	0.9965	0.9821	0.9637	0.9253	0.8398	0.7360	0.5887
0.99	0.9966	0.9826	0.9648	0.9277	0.8455	0.7471	0.6138
1.00	0.9967	0.9832	0.9659	0.9300	0.8509	0.7574	0.6353
1.01	0.9968	0.9837	0.9669	0.9322	0.8561	0.7671	0.6542
1.02	0.9969	0.9842	0.9679	0.9343	0.8610	0.7761	0.6710
1.05	0.9971	0.9855	0.9707	0.9401	0.8743	0.8002	0.7130
1.10	0.9975	0.9874	0.9747	0.9485	0.8930	0.8323	0.7649
1.15	0.9978	0.9891	0.9780	0.9554	0.9081	0.8576	0.8032
1.20	0.9981	0.9904	0.9808	0.9611	0.9205	0.8779	0.8330
1.30	0.9985	0.9926	0.9852	0.9702	0.9396	0.9083	0.8764
1.40	0.9988	0.9942	0.9884	0.9768	0.9534	0.9298	0.9062
1.50	0.9991	0.9954	0.9909	0.9818	0.9636	0.9456	0.9278
1.60	0.9993	0.9964	0.9928	0.9856	0.9714	0.9575	0.9439
1.70	0.9994	0.9971	0.9943	0.9886	0.9775	0.9667	0.9563
1.80	0.9995	0.9977	0.9955	0.9910	0.9823	0.9739	0.9659
1.90	0.9996	0.9982	0.9964	0.9929	0.9861	0.9796	0.9735
2.00	0.9997	0.9986	0.9972	0.9944	0.9892	0.9842	0.9796
2.20	0.9998	0.9992	0.9983	0.9967	0.9937	0.9910	0.9886
2.40	0.9999	0.9996	0.9991	0.9983	0.9969	0.9957	0.9948
2.60	1.0000	0.9998	0.9997	0.9994	0.9991	0.9990	0.9990
2.80	1.0000	1.0000	1.0001	1.0002	1.0007	1.0013	1.0021
3.00	1.0000	1.0002	1.0004	1.0008	1.0018	1.0030	1.0043
3.50	1.0001	1.0004	1.0008	1.0017	1.0035	1.0055	1.0075
4.00	1.0001	1.0005	1.0010	1.0021	1.0043	1.0066	1.0090

Pr							
1.00	1.20	1.50	2.00	3.00	5.00	7.00	10.0
0.2892	0.3470	0.4335	0.5775	0.8648	1.4366	2.0048	2.8507
0.2604	0.3123	0.3901	0.5195	0.7775	1.2902	1.7987	2.5539
0.2379	0.2853	0.3563	0.4744	0.7095	1.1758	1.6373	2.3211
0.2200	0.2638	0.3294	0.4384	0.6551	1.0841	1.5077	2.1338
0.2056	0.2465	0.3077	0.4092	0.6110	1.0094	1.4017	1.9801
0.1939	0.2323	0.2899	0.3853	0.5747	0.9475	1.3137	1.8520
0.1842	0.2207	0.2753	0.3657	0.5446	0.8959	1.2398	1.7440
0.1765	0.2113	0.2634	0.3495	0.5197	0.8526	1.1773	1.6519
0.1703	0.2038	0.2538	0.3364	0.4991	0.8161	1.1241	1.5729
0.1656	0.1981	0.2464	0.3260	0.4823	0.7854	1.0787	1.5047
0.1626	0.1942	0.2411	0.3182	0.4690	0.7598	1.0400	1.4456
0.1614	0.1924	0.2382	0.3132	0.4591	0.7388	1.0071	1.3943
0.1630	0.1935	0.2383	0.3114	0.4527	0.7220	0.9793	1.3496
0.1664	0.1963	0.2405	0.3122	0.4507	0.7138	0.9648	1.3257
0.1705	0.1998	0.2432	0.3138	0.4501	0.7092	0.9561	1.3108
0.1779	0.2055	0.2474	0.3164	0.4504	0.7052	0.9480	1.2968
0.1844	0.2097	0.2503	0.3182	0.4508	0.7035	0.9442	1.2901
0.1959	0.2154	0.2538	0.3204	0.4514	0.7018	0.9406	1.2835
0.2918	0.2237	0.2583	0.3229	0.4522	0.7004	0.9372	1.2772
0.4648	0.2370	0.2640	0.3260	0.4533	0.6991	0.9339	1.2710
0.5146	0.2629	0.2715	0.3297	0.4547	0.6980	0.9307	1.2650
0.6026	0.4437	0.3131	0.3452	0.4604	0.6956	0.9222	1.2481
0.6880	0.5984	0.4580	0.3953	0.4770	0.6950	0.9110	1.2232
0.7443	0.6803	0.5798	0.4760	0.5042	0.6987	0.9033	1.2021
0.7858	0.7363	0.6605	0.5605	0.5425	0.7069	0.8990	1.1844
0.8438	0.8111	0.7624	0.6908	0.6344	0.7358	0.8998	1.1580
0.8827	0.8595	0.8256	0.7753	0.7202	0.7761	0.9112	1.1419
0.9103	0.8933	0.8689	0.8328	0.7887	0.8200	0.9297	1.1339
0.9308	0.9180	0.9000	0.8738	0.8410	0.8617	0.9518	1.1320
0.9463	0.9367	0.9234	0.9043	0.8809	0.8984	0.9745	1.1343
0.9583	0.9511	0.9413	0.9275	0.9118	0.9297	0.9961	1.1391
0.9678	0.9624	0.9552	0.9456	0.9359	0.9557	1.0157	1.1452
0.9754	0.9715	0.9664	0.9599	0.9550	0.9772	1.0328	1.1516
0.9865	0.9847	0.9826	0.9806	0.9827	1.0094	1.0600	1.1635
0.9941	0.9936	0.9935	0.9945	1.0011	1.0313	1.0793	1.1728
0.9993	0.9998	1.0010	1.0040	1.0137	1.0463	1.0926	1.1792
1.0031	1.0042	1.0063	1.0106	1.0223	1.0565	1.1016	1.1830
1.0057	1.0074	1.0101	1.0153	1.0284	1.0635	1.1075	1.1848
1.0097	1.0120	1.0156	1.0221	1.0368	1.0723	1.1138	1.1834
1.0115	1.0140	1.0179	1.0249	1.0401	1.0747	1.1136	1.1773

Table V.2 Compressibility Factor
 Z^1 (Geometric Deviation)

Tr	Pr						
	0.01	0.05	0.10	0.20	0.40	0.60	0.80
0.30	-0.0008	-0.0040	-0.0081	-0.0161	-0.0323	-0.0484	-0.0645
0.35	-0.0009	-0.0046	-0.0093	-0.0185	-0.0370	-0.0554	-0.0738
0.40	-0.0010	-0.0048	-0.0095	-0.0190	-0.0380	-0.0570	-0.0758
0.45	-0.0009	-0.0047	-0.0094	-0.0187	-0.0374	-0.0560	-0.0745
0.50	-0.0009	-0.0045	-0.0090	-0.0181	-0.0360	-0.0539	-0.0716
0.55	-0.0298	-0.0043	-0.0086	-0.0172	-0.0343	-0.0513	-0.0682
0.60	-0.0203	-0.0041	-0.0082	-0.0164	-0.0326	-0.0487	-0.0646
0.65	-0.0137	-0.0680	-0.0078	-0.0156	-0.0309	-0.0461	-0.0611
0.70	-0.0093	-0.0502	-0.0948	-0.0148	-0.0294	-0.0438	-0.0579
0.75	-0.0064	-0.0339	-0.0734	-0.0143	-0.0282	-0.0417	-0.0550
0.80	-0.0044	-0.0228	-0.0487	-0.1097	-0.0272	-0.0401	-0.0526
0.85	-0.0029	-0.0152	-0.0319	-0.0715	-0.0268	-0.0391	-0.0509
0.90	-0.0019	-0.0099	-0.0205	-0.0442	-0.1118	-0.0396	-0.0503
0.93	-0.0015	-0.0075	-0.0154	-0.0326	-0.0763	-0.1592	-0.0514
0.95	-0.0012	-0.0062	-0.0126	-0.0262	-0.0589	-0.1110	-0.0540
0.97	-0.0010	-0.0050	-0.0101	-0.0208	-0.0450	-0.0770	-0.1623
0.98	-0.0009	-0.0044	-0.0090	-0.0184	-0.0390	-0.0641	-0.1100
0.99	-0.0008	-0.0039	-0.0079	-0.0161	-0.0335	-0.0531	-0.0796
1.00	-0.0007	-0.0034	-0.0069	-0.0140	-0.0285	-0.0435	-0.0588
1.01	-0.0006	-0.0030	-0.0060	-0.0120	-0.0240	-0.0351	-0.0429
1.02	-0.0005	-0.0026	-0.0051	-0.0102	-0.0198	-0.0277	-0.0303
1.05	-0.0003	-0.0015	-0.0029	-0.0054	-0.0092	-0.0097	-0.0032
1.10	0.0000	0.0000	0.0001	0.0007	0.0038	0.0106	0.0236
1.15	0.0002	0.0011	0.0023	0.0052	0.0127	0.0237	0.0396
1.20	0.0004	0.0019	0.0040	0.0084	0.0190	0.0326	0.0499
1.30	0.0006	0.0030	0.0061	0.0125	0.0267	0.0429	0.0612
1.40	0.0007	0.0036	0.0072	0.0147	0.0306	0.0477	0.0661
1.50	0.0008	0.0039	0.0078	0.0158	0.0323	0.0497	0.0677
1.60	0.0008	0.0040	0.0080	0.0162	0.0330	0.0501	0.0677
1.70	0.0008	0.0040	0.0081	0.0163	0.0329	0.0497	0.0667
1.80	0.0008	0.0040	0.0081	0.0162	0.0325	0.0488	0.0652
1.90	0.0008	0.0040	0.0079	0.0159	0.0318	0.0477	0.0635
2.00	0.0008	0.0039	0.0078	0.0155	0.0310	0.0464	0.0617
2.20	0.0007	0.0037	0.0074	0.0147	0.0293	0.0437	0.0580
2.40	0.0007	0.0035	0.0070	0.0139	0.0276	0.0411	0.0544
2.60	0.0007	0.0033	0.0066	0.0131	0.0260	0.0387	0.0512
2.80	0.0006	0.0031	0.0062	0.0124	0.0245	0.0365	0.0483
3.00	0.0006	0.0029	0.0059	0.0117	0.0232	0.0345	0.0456
3.50	0.0005	0.0026	0.0052	0.0103	0.0204	0.0303	0.0401
4.00	0.0005	0.0023	0.0046	0.0091	0.0182	0.0270	0.0357

Pr							
1.00	1.20	1.50	2.00	3.00	5.00	7.00	10.0
-0.0806	-0.0966	-0.1207	-0.1608	-0.2407	-0.3996	-0.5572	-0.7915
-0.0921	-0.1105	-0.1379	-0.1834	-0.2738	-0.4523	-0.6279	-0.8863
-0.0946	-0.1134	-0.1414	-0.1879	-0.2799	-0.4603	-0.6365	-0.8936
-0.0929	-0.1113	-0.1387	-0.1840	-0.2734	-0.4475	-0.6162	-0.8606
-0.0893	-0.1069	-0.1330	-0.1762	-0.2611	-0.4253	-0.5831	-0.8099
-0.0849	-0.1015	-0.1263	-0.1669	-0.2465	-0.3991	-0.5446	-0.7521
-0.0803	-0.0960	-0.1192	-0.1572	-0.2312	-0.3718	-0.5047	-0.6929
-0.0759	-0.0906	-0.1123	-0.1476	-0.2160	-0.3447	-0.4653	-0.6346
-0.0718	-0.0855	-0.1057	-0.1385	-0.2013	-0.3184	-0.4270	-0.5785
-0.0681	-0.0808	-0.0996	-0.1298	-0.1872	-0.2929	-0.3901	-0.5250
-0.0648	-0.0767	-0.0940	-0.1217	-0.1736	-0.2682	-0.3545	-0.4740
-0.0622	-0.0731	-0.0888	-0.1138	-0.1602	-0.2439	-0.3201	-0.4254
-0.0604	-0.0701	-0.0840	-0.1059	-0.1463	-0.2195	-0.2862	-0.3788
-0.0602	-0.0687	-0.0810	-0.1007	-0.1374	-0.2045	-0.2661	-0.3516
-0.0607	-0.0678	-0.0788	-0.0967	-0.1310	-0.1943	-0.2526	-0.3339
-0.0623	-0.0669	-0.0759	-0.0921	-0.1240	-0.1837	-0.2391	-0.3163
-0.0641	-0.0661	-0.0740	-0.0893	-0.1202	-0.1783	-0.2322	-0.3075
-0.0680	-0.0646	-0.0715	-0.0861	-0.1162	-0.1728	-0.2254	-0.2989
-0.0789	-0.0609	-0.0678	-0.0824	-0.1118	-0.1672	-0.2185	-0.2902
-0.0223	-0.0473	-0.0621	-0.0778	-0.1072	-0.1615	-0.2116	-0.2816
-0.0062	0.0227	-0.0524	-0.0722	-0.1021	-0.1556	-0.2047	-0.2731
0.0220	0.1059	0.0451	-0.0432	-0.0838	-0.1370	-0.1835	-0.2476
0.0476	0.0897	0.1630	0.0698	-0.0373	-0.1021	-0.1469	-0.2056
0.0625	0.0943	0.1548	0.1667	0.0332	-0.0611	-0.1084	-0.1642
0.0719	0.0991	0.1477	0.1990	0.1095	-0.0141	-0.0678	-0.1231
0.0819	0.1048	0.1420	0.1991	0.2079	0.0875	0.0176	-0.0423
0.0857	0.1063	0.1383	0.1894	0.2397	0.1737	0.1008	0.0350
0.0864	0.1055	0.1345	0.1806	0.2433	0.2309	0.1717	0.1058
0.0855	0.1035	0.1303	0.1729	0.2381	0.2631	0.2255	0.1673
0.0838	0.1008	0.1259	0.1658	0.2305	0.2788	0.2628	0.2179
0.0816	0.0978	0.1216	0.1593	0.2224	0.2846	0.2871	0.2576
0.0792	0.0947	0.1173	0.1532	0.2144	0.2848	0.3017	0.2876
0.0767	0.0916	0.1133	0.1476	0.2069	0.2820	0.3097	0.3096
0.0719	0.0857	0.1057	0.1374	0.1932	0.2720	0.3135	0.3355
0.0675	0.0803	0.0989	0.1285	0.1812	0.2602	0.3089	0.3459
0.0634	0.0754	0.0929	0.1207	0.1706	0.2484	0.3009	0.3475
0.0598	0.0711	0.0876	0.1138	0.1613	0.2372	0.2915	0.3443
0.0565	0.0672	0.0828	0.1076	0.1529	0.2268	0.2817	0.3385
0.0497	0.0591	0.0728	0.0949	0.1356	0.2042	0.2584	0.3194
0.0443	0.0527	0.0651	0.0849	0.1219	0.1857	0.2378	0.2994

Table V.3 Compressibility Factor
 Z^2 (Polar Deviation)

Tr	Pr						
	0.01	0.05	0.10	0.20	0.40	0.60	0.80
0.30	-0.0007	-0.0035	-0.0070	-0.0139	-0.0278	-0.0416	-0.0554
0.35	-0.0005	-0.0025	-0.0051	-0.0102	-0.0205	-0.0310	-0.0418
0.40	-0.0005	-0.0026	-0.0053	-0.0106	-0.0214	-0.0322	-0.0432
0.45	-0.0006	-0.0028	-0.0056	-0.0112	-0.0224	-0.0338	-0.0451
0.50	-0.0006	-0.0028	-0.0056	-0.0113	-0.0226	-0.0340	-0.0454
0.55	-0.0226	-0.0028	-0.0056	-0.0112	-0.0224	-0.0336	-0.0449
0.60	-0.0133	-0.0028	-0.0055	-0.0110	-0.0220	-0.0330	-0.0440
0.65	-0.0076	-0.0441	-0.0054	-0.0108	-0.0216	-0.0324	-0.0431
0.70	-0.0044	-0.0284	-0.0616	-0.0106	-0.0211	-0.0317	-0.0421
0.75	-0.0026	-0.0158	-0.0411	-0.0104	-0.0207	-0.0310	-0.0412
0.80	-0.0015	-0.0089	-0.0219	-0.0649	-0.0204	-0.0304	-0.0404
0.85	-0.0009	-0.0049	-0.0117	-0.0326	-0.0202	-0.0300	-0.0398
0.90	-0.0004	-0.0025	-0.0059	-0.0157	-0.0568	-0.0300	-0.0394
0.93	-0.0003	-0.0016	-0.0037	-0.0097	-0.0324	-0.0949	-0.0396
0.95	-0.0002	-0.0010	-0.0025	-0.0068	-0.0222	-0.0558	-0.0403
0.97	-0.0001	-0.0006	-0.0015	-0.0044	-0.0147	-0.0340	-0.0945
0.98	-0.0001	-0.0004	-0.0011	-0.0034	-0.0117	-0.0265	-0.0581
0.99	0.0000	-0.0002	-0.0007	-0.0025	-0.0091	-0.0204	-0.0396
1.00	0.0000	-0.0001	-0.0004	-0.0017	-0.0068	-0.0154	-0.0276
1.01	0.0000	0.0001	-0.0001	-0.0010	-0.0048	-0.0112	-0.0189
1.02	0.0001	0.0002	0.0002	-0.0003	-0.0031	-0.0076	-0.0123
1.05	0.0001	0.0005	0.0009	0.0014	0.0011	0.0003	0.0007
1.10	0.0002	0.0009	0.0018	0.0032	0.0056	0.0080	0.0116
1.15	0.0002	0.0012	0.0023	0.0043	0.0082	0.0121	0.0169
1.20	0.0003	0.0013	0.0026	0.0050	0.0097	0.0144	0.0196
1.30	0.0003	0.0014	0.0028	0.0055	0.0107	0.0160	0.0214
1.40	0.0003	0.0014	0.0027	0.0053	0.0105	0.0156	0.0207
1.50	0.0002	0.0012	0.0025	0.0049	0.0097	0.0144	0.0190
1.60	0.0002	0.0011	0.0022	0.0044	0.0086	0.0128	0.0168
1.70	0.0002	0.0010	0.0019	0.0038	0.0075	0.0111	0.0145
1.80	0.0002	0.0008	0.0017	0.0033	0.0065	0.0095	0.0123
1.90	0.0001	0.0007	0.0014	0.0029	0.0056	0.0081	0.0105
2.00	0.0001	0.0006	0.0013	0.0025	0.0048	0.0069	0.0089
2.20	0.0001	0.0005	0.0010	0.0020	0.0037	0.0053	0.0066
2.40	0.0001	0.0005	0.0009	0.0017	0.0032	0.0045	0.0056
2.60	0.0001	0.0004	0.0009	0.0017	0.0031	0.0044	0.0054
2.80	0.0001	0.0005	0.0009	0.0018	0.0033	0.0047	0.0058
3.00	0.0001	0.0005	0.0010	0.0019	0.0037	0.0053	0.0067
3.50	0.0001	0.0006	0.0013	0.0025	0.0050	0.0073	0.0095
4.00	0.0002	0.0008	0.0016	0.0032	0.0063	0.0094	0.0125

Pr							
1.00	1.20	1.50	2.00	3.00	5.00	7.00	10.0
-0.0692	-0.0829	-0.1034	-0.1375	-0.2051	-0.3378	-0.4676	-0.6569
-0.0530	-0.0656	-0.0883	-0.1207	-0.1843	-0.3109	-0.4361	-0.6208
-0.0543	-0.0655	-0.0825	-0.1114	-0.1711	-0.2955	-0.4226	-0.6135
-0.0566	-0.0680	-0.0854	-0.1145	-0.1735	-0.2947	-0.4194	-0.6111
-0.0568	-0.0682	-0.0854	-0.1142	-0.1722	-0.2898	-0.4097	-0.5939
-0.0561	-0.0673	-0.0842	-0.1124	-0.1688	-0.2823	-0.3967	-0.5701
-0.0550	-0.0660	-0.0825	-0.1099	-0.1646	-0.2738	-0.3827	-0.5458
-0.0538	-0.0645	-0.0805	-0.1071	-0.1600	-0.2647	-0.3684	-0.5220
-0.0526	-0.0629	-0.0785	-0.1042	-0.1552	-0.2555	-0.3541	-0.4991
-0.0513	-0.0614	-0.0765	-0.1014	-0.1505	-0.2465	-0.3402	-0.4772
-0.0503	-0.0601	-0.0746	-0.0987	-0.1459	-0.2377	-0.3269	-0.4566
-0.0493	-0.0588	-0.0729	-0.0961	-0.1414	-0.2293	-0.3144	-0.4374
-0.0487	-0.0578	-0.0713	-0.0934	-0.1368	-0.2209	-0.3023	-0.4197
-0.0485	-0.0572	-0.0703	-0.0917	-0.1338	-0.2158	-0.2953	-0.4096
-0.0486	-0.0570	-0.0695	-0.0904	-0.1316	-0.2123	-0.2906	-0.4030
-0.0492	-0.0568	-0.0688	-0.0890	-0.1293	-0.2086	-0.2858	-0.3966
-0.0500	-0.0568	-0.0683	-0.0882	-0.1280	-0.2067	-0.2834	-0.3934
-0.0519	-0.0568	-0.0678	-0.0873	-0.1267	-0.2048	-0.2810	-0.3903
-0.0581	-0.0568	-0.0672	-0.0863	-0.1253	-0.2028	-0.2786	-0.3872
-0.0180	-0.0557	-0.0664	-0.0852	-0.1238	-0.2008	-0.2761	-0.3841
-0.0082	-0.0434	-0.0650	-0.0839	-0.1222	-0.1987	-0.2736	-0.3810
0.0071	0.0317	-0.0431	-0.0779	-0.1167	-0.1920	-0.2660	-0.3718
0.0184	0.0305	0.0412	-0.0443	-0.1036	-0.1795	-0.2524	-0.3566
0.0234	0.0321	0.0459	0.0140	-0.0814	-0.1649	-0.2377	-0.3411
0.0258	0.0330	0.0442	0.0404	-0.0490	-0.1481	-0.2220	-0.3254
0.0270	0.0327	0.0409	0.0476	0.0065	-0.1076	-0.1883	-0.2933
0.0257	0.0306	0.0372	0.0442	0.0286	-0.0663	-0.1527	-0.2614
0.0234	0.0276	0.0331	0.0393	0.0335	-0.0355	-0.1180	-0.2305
0.0206	0.0241	0.0287	0.0340	0.0320	-0.0168	-0.0883	-0.2005
0.0177	0.0206	0.0244	0.0287	0.0281	-0.0069	-0.0657	-0.1719
0.0150	0.0174	0.0204	0.0238	0.0235	-0.0023	-0.0498	-0.1459
0.0126	0.0145	0.0169	0.0194	0.0191	-0.0007	-0.0389	-0.1234
0.0106	0.0121	0.0139	0.0158	0.0151	-0.0006	-0.0314	-0.1047
0.0078	0.0087	0.0098	0.0107	0.0096	-0.0012	-0.0220	-0.0766
0.0065	0.0072	0.0079	0.0084	0.0074	-0.0002	-0.0148	-0.0561
0.0063	0.0069	0.0077	0.0084	0.0081	0.0034	-0.0068	-0.0387
0.0068	0.0077	0.0088	0.0100	0.0111	0.0096	0.0029	-0.0219
0.0079	0.0091	0.0106	0.0127	0.0156	0.0176	0.0144	-0.0044
0.0117	0.0138	0.0168	0.0215	0.0299	0.0421	0.0480	0.0427
0.0156	0.0186	0.0232	0.0305	0.0442	0.0669	0.0822	0.0902

Table V.4 Enthalpy Departure Function
 $[(H^\circ - H)/RT_c]^0$ (Simple Fluid)

Tr	Pr						
	0.01	0.05	0.10	0.20	0.40	0.60	0.80
0.30	6.046	6.043	6.040	6.034	6.022	6.011	5.999
0.35	5.907	5.904	5.901	5.895	5.882	5.870	5.858
0.40	5.763	5.761	5.757	5.751	5.738	5.726	5.713
0.45	5.615	5.612	5.609	5.603	5.590	5.577	5.564
0.50	5.465	5.462	5.459	5.453	5.440	5.427	5.414
0.55	0.032	5.312	5.309	5.303	5.290	5.277	5.265
0.60	0.027	5.162	5.159	5.153	5.141	5.129	5.116
0.65	0.023	0.118	5.008	5.002	4.991	4.980	4.968
0.70	0.020	0.101	0.213	4.848	4.839	4.828	4.818
0.75	0.017	0.088	0.183	4.687	4.679	4.672	4.664
0.80	0.015	0.078	0.160	0.345	4.507	4.504	4.499
0.85	0.014	0.069	0.141	0.300	4.308	4.313	4.316
0.90	0.012	0.062	0.126	0.264	0.596	4.074	4.094
0.93	0.011	0.058	0.118	0.246	0.545	0.960	3.920
0.95	0.011	0.056	0.113	0.235	0.516	0.885	3.763
0.97	0.011	0.054	0.109	0.225	0.490	0.824	1.356
0.98	0.010	0.053	0.107	0.221	0.478	0.797	1.273
0.99	0.010	0.052	0.105	0.216	0.466	0.773	1.206
1.00	0.010	0.051	0.103	0.212	0.455	0.750	1.151
1.01	0.010	0.050	0.101	0.208	0.445	0.728	1.102
1.02	0.010	0.049	0.099	0.203	0.434	0.708	1.060
1.05	0.009	0.046	0.094	0.192	0.407	0.654	0.955
1.10	0.008	0.042	0.086	0.175	0.367	0.581	0.827
1.15	0.008	0.039	0.079	0.160	0.334	0.523	0.732
1.20	0.007	0.036	0.073	0.148	0.305	0.474	0.657
1.30	0.006	0.031	0.063	0.127	0.259	0.399	0.545
1.40	0.005	0.027	0.055	0.110	0.224	0.341	0.463
1.50	0.005	0.024	0.048	0.097	0.196	0.297	0.400
1.60	0.004	0.021	0.043	0.086	0.173	0.261	0.350
1.70	0.004	0.019	0.038	0.076	0.153	0.231	0.309
1.80	0.003	0.017	0.034	0.068	0.137	0.206	0.275
1.90	0.003	0.015	0.031	0.062	0.123	0.185	0.246
2.00	0.003	0.014	0.028	0.056	0.111	0.167	0.222
2.20	0.002	0.012	0.023	0.046	0.092	0.137	0.182
2.40	0.002	0.010	0.019	0.038	0.076	0.114	0.150
2.60	0.002	0.008	0.016	0.032	0.064	0.095	0.125
2.80	0.001	0.007	0.014	0.027	0.054	0.080	0.105
3.00	0.001	0.006	0.011	0.023	0.045	0.067	0.088
3.50	0.001	0.004	0.007	0.015	0.029	0.043	0.056
4.00	0.000	0.002	0.005	0.009	0.017	0.026	0.033

Pr							
1.00	1.20	1.50	2.00	3.00	5.00	7.00	10.0
5.987	5.975	5.957	5.927	5.868	5.748	5.628	5.446
5.845	5.833	5.814	5.783	5.721	5.595	5.469	5.278
5.700	5.687	5.668	5.636	5.572	5.442	5.311	5.113
5.551	5.538	5.519	5.486	5.420	5.288	5.154	4.950
5.401	5.388	5.369	5.336	5.270	5.135	4.999	4.791
5.252	5.239	5.220	5.187	5.121	4.986	4.849	4.638
5.104	5.091	5.073	5.041	4.976	4.842	4.704	4.492
4.956	4.945	4.927	4.896	4.833	4.702	4.565	4.353
4.808	4.797	4.781	4.752	4.693	4.566	4.432	4.221
4.655	4.646	4.632	4.607	4.554	4.434	4.303	4.095
4.494	4.488	4.478	4.459	4.413	4.303	4.178	3.974
4.316	4.316	4.312	4.302	4.269	4.173	4.056	3.857
4.108	4.118	4.127	4.132	4.119	4.043	3.935	3.744
3.953	3.976	4.000	4.020	4.024	3.963	3.863	3.678
3.825	3.865	3.904	3.939	3.958	3.910	3.815	3.634
3.658	3.732	3.796	3.853	3.890	3.856	3.767	3.591
3.544	3.652	3.736	3.806	3.854	3.829	3.743	3.569
3.376	3.558	3.670	3.758	3.818	3.801	3.719	3.548
2.574	3.441	3.598	3.706	3.782	3.774	3.695	3.526
1.796	3.283	3.516	3.652	3.744	3.746	3.671	3.505
1.627	3.039	3.422	3.595	3.705	3.718	3.647	3.484
1.359	2.034	3.030	3.398	3.583	3.632	3.575	3.420
1.120	1.487	2.203	2.965	3.353	3.484	3.453	3.315
0.968	1.239	1.719	2.479	3.091	3.329	3.329	3.211
0.857	1.076	1.443	2.079	2.807	3.166	3.202	3.107
0.698	0.860	1.116	1.560	2.274	2.825	2.942	2.899
0.588	0.716	0.915	1.253	1.857	2.486	2.679	2.692
0.505	0.611	0.774	1.046	1.549	2.175	2.421	2.486
0.440	0.531	0.667	0.894	1.318	1.904	2.177	2.285
0.387	0.466	0.583	0.777	1.139	1.672	1.953	2.091
0.344	0.413	0.515	0.683	0.996	1.476	1.751	1.908
0.307	0.368	0.458	0.606	0.880	1.309	1.571	1.736
0.276	0.330	0.411	0.541	0.782	1.167	1.411	1.577
0.226	0.269	0.334	0.437	0.629	0.937	1.143	1.295
0.187	0.222	0.275	0.359	0.513	0.761	0.929	1.058
0.155	0.185	0.228	0.297	0.422	0.621	0.756	0.858
0.130	0.154	0.190	0.246	0.348	0.508	0.614	0.689
0.109	0.129	0.159	0.205	0.288	0.415	0.495	0.545
0.069	0.081	0.099	0.127	0.174	0.239	0.270	0.264
0.041	0.048	0.058	0.072	0.095	0.116	0.110	0.061

Table V.5 Enthalpy Departure Function
 $[(H^\circ - H)/RT_c]^1$ (Geometric Deviation)

Tr	Pr						
	0.01	0.05	0.10	0.20	0.40	0.60	0.80
0.30	11.101	11.100	11.098	11.095	11.088	11.081	11.074
0.35	10.652	10.651	10.651	10.649	10.646	10.643	10.640
0.40	10.120	10.120	10.120	10.120	10.120	10.120	10.120
0.45	9.513	9.514	9.514	9.515	9.518	9.520	9.522
0.50	8.867	8.868	8.869	8.871	8.875	8.879	8.883
0.55	0.079	8.213	8.214	8.216	8.222	8.227	8.232
0.60	0.059	7.568	7.570	7.573	7.579	7.585	7.592
0.65	0.045	0.240	6.949	6.952	6.959	6.966	6.973
0.70	0.034	0.184	0.393	6.360	6.366	6.373	6.381
0.75	0.027	0.142	0.305	5.796	5.803	5.809	5.816
0.80	0.021	0.110	0.234	0.533	5.266	5.271	5.277
0.85	0.017	0.087	0.182	0.401	4.753	4.754	4.758
0.90	0.014	0.070	0.144	0.308	0.751	4.254	4.248
0.93	0.012	0.061	0.126	0.265	0.612	1.218	3.941
0.95	0.011	0.056	0.115	0.241	0.542	0.994	3.737
0.97	0.010	0.052	0.105	0.219	0.483	0.837	1.607
0.98	0.010	0.050	0.101	0.209	0.457	0.776	1.324
0.99	0.009	0.048	0.097	0.200	0.433	0.722	1.154
1.00	0.009	0.046	0.093	0.191	0.410	0.675	1.034
1.01	0.009	0.044	0.089	0.183	0.389	0.632	0.940
1.02	0.008	0.042	0.085	0.175	0.370	0.594	0.863
1.05	0.007	0.037	0.075	0.153	0.318	0.498	0.691
1.10	0.006	0.030	0.061	0.123	0.251	0.381	0.507
1.15	0.005	0.025	0.050	0.099	0.199	0.296	0.385
1.20	0.004	0.020	0.040	0.080	0.158	0.232	0.297
1.30	0.003	0.013	0.026	0.052	0.100	0.142	0.177
1.40	0.002	0.008	0.016	0.032	0.060	0.083	0.100
1.50	0.001	0.005	0.009	0.018	0.032	0.042	0.048
1.60	0.000	0.002	0.004	0.007	0.012	0.013	0.011
1.70	0.000	0.000	0.000	0.000	-0.003	-0.009	-0.017
1.80	0.000	-0.001	-0.003	-0.006	-0.015	-0.025	-0.037
1.90	-0.001	-0.003	-0.005	-0.011	-0.023	-0.037	-0.053
2.00	-0.001	-0.004	-0.007	-0.015	-0.030	-0.047	-0.065
2.20	-0.001	-0.005	-0.010	-0.020	-0.040	-0.062	-0.083
2.40	-0.001	-0.006	-0.012	-0.023	-0.047	-0.071	-0.095
2.60	-0.001	-0.006	-0.013	-0.026	-0.052	-0.078	-0.104
2.80	-0.001	-0.007	-0.014	-0.027	-0.055	-0.082	-0.110
3.00	-0.001	-0.007	-0.014	-0.029	-0.058	-0.086	-0.114
3.50	-0.002	-0.008	-0.016	-0.031	-0.062	-0.092	-0.122
4.00	-0.002	-0.008	-0.016	-0.032	-0.064	-0.096	-0.127

Pr							
1.00	1.20	1.50	2.00	3.00	5.00	7.00	10.0
11.067	11.061	11.051	11.034	11.001	10.936	10.873	10.782
10.637	10.634	10.630	10.623	10.610	10.584	10.561	10.529
10.120	10.120	10.120	10.121	10.122	10.127	10.135	10.150
9.525	9.527	9.531	9.537	9.550	9.579	9.611	9.663
8.887	8.891	8.897	8.908	8.931	8.979	9.030	9.111
8.238	8.243	8.252	8.266	8.296	8.359	8.426	8.531
7.598	7.605	7.615	7.632	7.668	7.744	7.825	7.950
6.980	6.987	6.999	7.018	7.059	7.147	7.239	7.383
6.388	6.396	6.408	6.430	6.475	6.573	6.677	6.837
5.824	5.832	5.845	5.868	5.918	6.027	6.141	6.317
5.285	5.292	5.306	5.330	5.384	5.506	5.632	5.824
4.763	4.771	4.784	4.810	4.871	5.008	5.149	5.358
4.249	4.255	4.268	4.298	4.371	4.530	4.688	4.916
3.934	3.937	3.951	3.987	4.073	4.251	4.422	4.662
3.713	3.713	3.730	3.773	3.873	4.068	4.248	4.498
3.471	3.467	3.492	3.551	3.670	3.886	4.077	4.336
3.332	3.327	3.363	3.434	3.568	3.795	3.992	4.257
3.164	3.164	3.222	3.313	3.464	3.705	3.908	4.178
2.382	2.952	3.065	3.186	3.358	3.615	3.825	4.100
1.375	2.595	2.880	3.051	3.251	3.525	3.743	4.023
1.180	1.723	2.650	2.906	3.142	3.435	3.660	3.947
0.877	0.878	1.496	2.381	2.800	3.167	3.418	3.722
0.617	0.673	0.617	1.261	2.167	2.720	3.023	3.362
0.459	0.503	0.487	0.604	1.497	2.275	2.641	3.019
0.349	0.381	0.381	0.361	0.934	1.840	2.273	2.692
0.203	0.218	0.218	0.178	0.300	1.066	1.592	2.086
0.111	0.115	0.108	0.070	0.044	0.504	1.012	1.547
0.049	0.046	0.032	-0.008	-0.078	0.142	0.556	1.080
0.005	-0.004	-0.023	-0.065	-0.151	-0.082	0.217	0.689
-0.027	-0.040	-0.063	-0.109	-0.202	-0.223	-0.028	0.369
-0.051	-0.067	-0.094	-0.143	-0.241	-0.317	-0.203	0.112
-0.070	-0.088	-0.117	-0.169	-0.271	-0.381	-0.330	-0.092
-0.085	-0.105	-0.136	-0.190	-0.295	-0.428	-0.424	-0.255
-0.106	-0.128	-0.163	-0.221	-0.331	-0.493	-0.551	-0.489
-0.120	-0.144	-0.181	-0.242	-0.357	-0.535	-0.631	-0.645
-0.130	-0.156	-0.194	-0.257	-0.376	-0.567	-0.687	-0.754
-0.137	-0.164	-0.204	-0.269	-0.391	-0.591	-0.729	-0.836
-0.142	-0.170	-0.211	-0.278	-0.403	-0.611	-0.763	-0.899
-0.152	-0.181	-0.224	-0.294	-0.425	-0.650	-0.827	-1.015
-0.158	-0.188	-0.233	-0.306	-0.442	-0.680	-0.874	-1.097

Table V.6 Enthalpy Departure Function
 $[(H^\circ - H)/RT_c]^2$ (Polar Deviation)

Tr	Pr						
	0.01	0.05	0.10	0.20	0.40	0.60	0.80
0.30	5.178	5.179	5.179	5.180	5.182	5.184	5.185
0.35	2.619	2.619	2.619	2.621	2.623	2.626	2.631
0.40	2.658	2.657	2.656	2.655	2.652	2.650	2.647
0.45	2.559	2.558	2.558	2.558	2.557	2.556	2.555
0.50	2.462	2.462	2.462	2.462	2.462	2.463	2.463
0.55	0.084	2.366	2.366	2.367	2.368	2.369	2.370
0.60	0.053	2.268	2.269	2.270	2.271	2.273	2.274
0.65	0.034	0.214	2.168	2.169	2.171	2.173	2.175
0.70	0.022	0.134	0.344	2.064	2.066	2.069	2.071
0.75	0.015	0.086	0.212	1.956	1.958	1.960	1.962
0.80	0.010	0.057	0.133	0.377	1.845	1.847	1.849
0.85	0.007	0.040	0.088	0.224	1.728	1.728	1.730
0.90	0.005	0.028	0.061	0.143	0.432	1.602	1.601
0.93	0.004	0.023	0.049	0.112	0.305	0.762	1.518
0.95	0.004	0.020	0.043	0.096	0.249	0.531	1.463
0.97	0.003	0.018	0.037	0.083	0.206	0.403	0.921
0.98	0.003	0.017	0.035	0.077	0.188	0.356	0.688
0.99	0.003	0.016	0.033	0.071	0.172	0.318	0.564
1.00	0.003	0.015	0.030	0.066	0.157	0.285	0.479
1.01	0.003	0.014	0.028	0.062	0.145	0.257	0.415
1.02	0.002	0.013	0.027	0.057	0.133	0.232	0.364
1.05	0.002	0.010	0.022	0.046	0.104	0.175	0.258
1.10	0.001	0.007	0.015	0.032	0.069	0.112	0.157
1.15	0.001	0.005	0.010	0.021	0.045	0.072	0.098
1.20	0.001	0.003	0.006	0.013	0.027	0.043	0.058
1.30	0.000	0.000	0.000	0.001	0.003	0.005	0.007
1.40	0.000	-0.002	-0.004	-0.007	-0.013	-0.019	-0.025
1.50	-0.001	-0.003	-0.006	-0.012	-0.023	-0.034	-0.046
1.60	-0.001	-0.004	-0.007	-0.014	-0.029	-0.043	-0.058
1.70	-0.001	-0.004	-0.008	-0.015	-0.031	-0.047	-0.063
1.80	-0.001	-0.004	-0.008	-0.015	-0.031	-0.047	-0.064
1.90	-0.001	-0.004	-0.007	-0.014	-0.029	-0.045	-0.060
2.00	-0.001	-0.003	-0.006	-0.013	-0.026	-0.040	-0.054
2.20	0.000	-0.002	-0.004	-0.009	-0.018	-0.027	-0.037
2.40	0.000	-0.001	-0.002	-0.004	-0.008	-0.012	-0.016
2.60	0.000	0.000	0.000	0.001	0.002	0.003	0.004
2.80	0.000	0.001	0.002	0.005	0.010	0.016	0.023
3.00	0.000	0.002	0.004	0.009	0.018	0.028	0.039
3.50	0.001	0.004	0.007	0.015	0.031	0.049	0.067
4.00	0.001	0.004	0.009	0.018	0.038	0.059	0.081

Pr							
1.00	1.20	1.50	2.00	3.00	5.00	7.00	10.0
5.187	5.189	5.191	5.196	5.204	5.220	5.236	5.259
2.638	2.655	2.725	2.762	2.800	2.842	2.867	2.890
2.645	2.642	2.639	2.634	2.628	2.624	2.626	2.627
2.554	2.553	2.552	2.551	2.550	2.552	2.558	2.570
2.463	2.463	2.464	2.466	2.469	2.480	2.496	2.525
2.371	2.372	2.374	2.377	2.384	2.402	2.424	2.464
2.276	2.278	2.280	2.285	2.295	2.319	2.346	2.394
2.177	2.179	2.182	2.188	2.201	2.230	2.263	2.319
2.073	2.076	2.080	2.087	2.101	2.135	2.173	2.236
1.965	1.968	1.972	1.979	1.996	2.034	2.076	2.145
1.852	1.854	1.859	1.867	1.885	1.927	1.972	2.046
1.732	1.735	1.739	1.748	1.768	1.815	1.864	1.942
1.602	1.604	1.609	1.619	1.644	1.697	1.752	1.835
1.516	1.518	1.523	1.534	1.563	1.624	1.683	1.769
1.456	1.455	1.460	1.474	1.506	1.573	1.636	1.725
1.392	1.388	1.393	1.409	1.447	1.521	1.588	1.680
1.359	1.351	1.357	1.375	1.416	1.494	1.563	1.657
1.327	1.311	1.318	1.339	1.384	1.467	1.539	1.635
1.186	1.265	1.276	1.302	1.352	1.440	1.514	1.612
0.655	1.198	1.230	1.262	1.318	1.412	1.489	1.589
0.533	1.016	1.175	1.220	1.284	1.383	1.464	1.567
0.345	0.371	0.857	1.073	1.174	1.295	1.387	1.497
0.198	0.220	0.233	0.673	0.965	1.141	1.253	1.380
0.119	0.132	0.128	0.259	0.714	0.978	1.115	1.260
0.069	0.075	0.071	0.090	0.447	0.811	0.974	1.138
0.007	0.004	-0.005	-0.022	0.084	0.478	0.697	0.898
-0.032	-0.040	-0.055	-0.080	-0.073	0.193	0.439	0.672
-0.057	-0.070	-0.089	-0.120	-0.152	-0.011	0.213	0.472
-0.072	-0.087	-0.110	-0.146	-0.197	-0.141	0.034	0.298
-0.079	-0.096	-0.120	-0.159	-0.220	-0.218	-0.094	0.156
-0.080	-0.097	-0.122	-0.161	-0.225	-0.256	-0.172	0.050
-0.076	-0.092	-0.116	-0.154	-0.216	-0.262	-0.208	-0.018
-0.068	-0.083	-0.104	-0.138	-0.196	-0.246	-0.210	-0.048
-0.046	-0.056	-0.070	-0.093	-0.131	-0.163	-0.137	-0.009
-0.020	-0.024	-0.030	-0.039	-0.049	-0.042	0.001	0.126
0.006	0.007	0.011	0.017	0.036	0.093	0.169	0.317
0.029	0.036	0.048	0.069	0.116	0.225	0.341	0.530
0.050	0.062	0.081	0.114	0.187	0.344	0.502	0.741
0.086	0.106	0.138	0.193	0.311	0.560	0.808	1.169
0.104	0.127	0.165	0.230	0.369	0.664	0.963	1.406

Table V.7 Entropy Departure Function
 $[(S^\circ - S)/R]^0$ (Simple Fluid)

Tr	Pr						
	0.01	0.05	0.10	0.20	0.40	0.60	0.80
0.30	11.613	10.008	9.319	8.635	7.961	7.574	7.304
0.35	11.185	9.579	8.890	8.205	7.529	7.140	6.869
0.40	10.802	9.196	8.506	7.821	7.144	6.755	6.483
0.45	10.453	8.847	8.158	7.472	6.795	6.405	6.132
0.50	10.137	8.531	7.842	7.156	6.479	6.089	5.816
0.55	0.038	8.245	7.555	6.870	6.193	5.803	5.531
0.60	0.029	7.983	7.294	6.610	5.933	5.544	5.273
0.65	0.023	0.122	7.052	6.368	5.694	5.306	5.036
0.70	0.018	0.096	0.206	6.140	5.467	5.082	4.814
0.75	0.015	0.078	0.164	5.917	5.248	4.866	4.600
0.80	0.013	0.064	0.134	0.294	5.026	4.649	4.388
0.85	0.011	0.054	0.111	0.239	4.785	4.418	4.166
0.90	0.009	0.046	0.094	0.199	0.463	4.145	3.912
0.93	0.008	0.042	0.085	0.179	0.408	0.750	3.723
0.95	0.008	0.039	0.080	0.168	0.377	0.671	3.556
0.97	0.007	0.037	0.075	0.157	0.350	0.607	1.056
0.98	0.007	0.036	0.073	0.153	0.337	0.580	0.971
0.99	0.007	0.035	0.071	0.148	0.326	0.555	0.903
1.00	0.007	0.034	0.069	0.144	0.315	0.532	0.847
1.01	0.007	0.033	0.067	0.139	0.304	0.510	0.799
1.02	0.006	0.032	0.065	0.135	0.294	0.491	0.757
1.05	0.006	0.030	0.060	0.124	0.267	0.439	0.656
1.10	0.005	0.026	0.053	0.108	0.230	0.371	0.537
1.15	0.005	0.023	0.047	0.096	0.201	0.319	0.452
1.20	0.004	0.021	0.042	0.085	0.177	0.277	0.389
1.30	0.003	0.017	0.033	0.068	0.140	0.217	0.298
1.40	0.003	0.014	0.027	0.056	0.114	0.174	0.237
1.50	0.002	0.011	0.023	0.046	0.094	0.143	0.194
1.60	0.002	0.010	0.019	0.039	0.079	0.120	0.162
1.70	0.002	0.008	0.017	0.033	0.067	0.102	0.137
1.80	0.001	0.007	0.014	0.029	0.058	0.088	0.117
1.90	0.001	0.006	0.013	0.025	0.051	0.076	0.102
2.00	0.001	0.006	0.011	0.022	0.044	0.067	0.089
2.20	0.001	0.004	0.009	0.018	0.035	0.053	0.070
2.40	0.001	0.004	0.007	0.014	0.028	0.042	0.056
2.60	0.001	0.003	0.006	0.012	0.023	0.035	0.046
2.80	0.000	0.002	0.005	0.010	0.020	0.029	0.039
3.00	0.000	0.002	0.004	0.008	0.017	0.025	0.033
3.50	0.000	0.001	0.003	0.006	0.012	0.017	0.023
4.00	0.000	0.001	0.002	0.004	0.009	0.013	0.017

Pr							
1.00	1.20	1.50	2.00	3.00	5.00	7.00	10.0
7.099	6.935	6.740	6.497	6.182	5.847	5.683	5.578
6.663	6.497	6.299	6.052	5.728	5.376	5.194	5.060
6.275	6.109	5.909	5.660	5.330	4.967	4.772	4.619
5.924	5.757	5.557	5.306	4.974	4.603	4.401	4.234
5.608	5.441	5.240	4.989	4.656	4.282	4.074	3.899
5.324	5.157	4.956	4.706	4.373	3.998	3.788	3.607
5.066	4.900	4.700	4.451	4.120	3.747	3.537	3.353
4.830	4.665	4.467	4.220	3.892	3.523	3.315	3.131
4.610	4.446	4.250	4.007	3.684	3.322	3.117	2.935
4.399	4.238	4.046	3.807	3.491	3.138	2.939	2.761
4.191	4.034	3.846	3.615	3.310	2.970	2.777	2.605
3.976	3.825	3.646	3.425	3.135	2.812	2.629	2.463
3.738	3.599	3.434	3.231	2.963	2.663	2.491	2.334
3.569	3.444	3.295	3.108	2.860	2.577	2.412	2.262
3.433	3.326	3.193	3.023	2.790	2.520	2.361	2.215
3.259	3.188	3.081	2.932	2.719	2.463	2.312	2.170
3.142	3.106	3.019	2.884	2.682	2.436	2.287	2.148
2.972	3.010	2.953	2.835	2.646	2.408	2.263	2.126
2.167	2.893	2.879	2.784	2.609	2.380	2.239	2.105
1.391	2.736	2.798	2.730	2.571	2.352	2.215	2.083
1.225	2.495	2.706	2.673	2.533	2.325	2.191	2.062
0.965	1.523	2.328	2.483	2.415	2.242	2.121	2.001
0.742	1.012	1.557	2.081	2.202	2.104	2.007	1.903
0.607	0.790	1.126	1.649	1.968	1.966	1.897	1.810
0.512	0.651	0.890	1.308	1.727	1.827	1.789	1.722
0.385	0.478	0.628	0.891	1.299	1.554	1.581	1.556
0.303	0.372	0.478	0.663	0.990	1.303	1.386	1.402
0.246	0.299	0.381	0.520	0.777	1.088	1.208	1.260
0.204	0.247	0.312	0.421	0.628	0.913	1.050	1.130
0.172	0.208	0.261	0.350	0.519	0.773	0.915	1.013
0.147	0.177	0.222	0.296	0.438	0.661	0.799	0.908
0.127	0.153	0.191	0.255	0.375	0.570	0.702	0.815
0.111	0.134	0.167	0.221	0.325	0.497	0.620	0.733
0.087	0.105	0.130	0.172	0.251	0.388	0.492	0.599
0.070	0.084	0.104	0.138	0.201	0.311	0.399	0.496
0.058	0.069	0.086	0.113	0.164	0.255	0.329	0.416
0.048	0.058	0.072	0.094	0.137	0.213	0.277	0.353
0.041	0.049	0.061	0.080	0.116	0.181	0.236	0.303
0.029	0.034	0.042	0.056	0.081	0.126	0.166	0.216
0.021	0.025	0.031	0.041	0.059	0.093	0.123	0.162

Table V.8 Entropy Departure Function
 $[(S^\circ - S)/R]^1$ (Geometric Deviation)

Tr	Pr						
	0.01	0.05	0.10	0.20	0.40	0.60	0.80
0.30	16.790	16.783	16.773	16.753	16.714	16.675	16.637
0.35	15.408	15.402	15.395	15.382	15.355	15.328	15.301
0.40	13.989	13.985	13.980	13.971	13.951	13.932	13.914
0.45	12.562	12.559	12.556	12.549	12.535	12.521	12.508
0.50	11.201	11.198	11.196	11.191	11.181	11.171	11.161
0.55	0.113	9.949	9.947	9.943	9.936	9.928	9.921
0.60	0.078	8.828	8.827	8.823	8.817	8.811	8.806
0.65	0.055	0.297	7.832	7.829	7.824	7.819	7.815
0.70	0.040	0.215	0.460	6.951	6.946	6.941	6.937
0.75	0.029	0.156	0.339	6.173	6.167	6.162	6.158
0.80	0.022	0.116	0.246	0.568	5.474	5.467	5.462
0.85	0.017	0.088	0.183	0.408	4.853	4.841	4.832
0.90	0.013	0.068	0.140	0.301	0.744	4.269	4.250
0.93	0.011	0.058	0.120	0.254	0.593	1.200	3.914
0.95	0.010	0.053	0.109	0.228	0.517	0.961	3.697
0.97	0.010	0.048	0.099	0.206	0.456	0.797	1.561
0.98	0.009	0.046	0.094	0.196	0.429	0.734	1.270
0.99	0.009	0.044	0.090	0.186	0.405	0.680	1.098
1.00	0.008	0.042	0.086	0.177	0.382	0.632	0.977
1.01	0.008	0.040	0.082	0.169	0.361	0.590	0.883
1.02	0.008	0.039	0.078	0.161	0.342	0.552	0.807
1.05	0.007	0.034	0.069	0.140	0.292	0.460	0.642
1.10	0.005	0.028	0.055	0.112	0.229	0.350	0.470
1.15	0.005	0.023	0.045	0.091	0.183	0.275	0.361
1.20	0.004	0.019	0.037	0.075	0.149	0.220	0.286
1.30	0.003	0.013	0.026	0.052	0.102	0.148	0.190
1.40	0.002	0.010	0.019	0.037	0.072	0.104	0.133
1.50	0.001	0.007	0.014	0.027	0.053	0.076	0.097
1.60	0.001	0.005	0.011	0.021	0.040	0.057	0.073
1.70	0.001	0.004	0.008	0.016	0.031	0.044	0.056
1.80	0.001	0.003	0.006	0.013	0.024	0.035	0.044
1.90	0.001	0.003	0.005	0.010	0.019	0.028	0.036
2.00	0.000	0.002	0.004	0.008	0.016	0.023	0.029
2.20	0.000	0.001	0.003	0.006	0.011	0.016	0.021
2.40	0.000	0.001	0.002	0.004	0.008	0.012	0.015
2.60	0.000	0.001	0.002	0.003	0.006	0.009	0.012
2.80	0.000	0.001	0.001	0.003	0.005	0.008	0.010
3.00	0.000	0.001	0.001	0.002	0.004	0.006	0.008
3.50	0.000	0.000	0.001	0.001	0.003	0.004	0.006
4.00	0.000	0.000	0.001	0.001	0.002	0.003	0.005

Pr							
1.00	1.20	1.50	2.00	3.00	5.00	7.00	10.0
16.598	16.559	16.501	16.405	16.214	15.838	15.469	14.927
15.274	15.248	15.208	15.142	15.012	14.757	14.511	14.154
13.895	13.876	13.848	13.803	13.713	13.540	13.376	13.144
12.494	12.481	12.461	12.429	12.367	12.251	12.144	11.998
11.151	11.142	11.128	11.105	11.063	10.986	10.920	10.836
9.914	9.907	9.897	9.881	9.853	9.806	9.770	9.732
8.800	8.795	8.788	8.777	8.759	8.735	8.723	8.720
7.810	7.807	7.801	7.794	7.784	7.778	7.785	7.811
6.933	6.930	6.926	6.922	6.919	6.928	6.952	7.002
6.155	6.152	6.149	6.146	6.149	6.174	6.213	6.285
5.458	5.455	5.452	5.452	5.461	5.501	5.555	5.648
4.826	4.822	4.820	4.822	4.839	4.898	4.969	5.083
4.238	4.232	4.230	4.236	4.267	4.351	4.442	4.578
3.893	3.885	3.883	3.896	3.941	4.046	4.151	4.300
3.658	3.647	3.648	3.669	3.728	3.851	3.966	4.125
3.406	3.391	3.401	3.437	3.517	3.661	3.788	3.957
3.264	3.247	3.268	3.318	3.412	3.569	3.701	3.875
3.093	3.082	3.126	3.195	3.306	3.477	3.616	3.795
2.311	2.868	2.967	3.067	3.200	3.387	3.532	3.717
1.306	2.513	2.784	2.933	3.094	3.297	3.450	3.640
1.113	1.655	2.557	2.790	2.986	3.209	3.369	3.565
0.820	0.831	1.443	2.283	2.655	2.949	3.134	3.348
0.577	0.640	0.618	1.241	2.067	2.534	2.767	3.013
0.437	0.489	0.502	0.654	1.471	2.138	2.428	2.708
0.343	0.385	0.412	0.447	0.991	1.767	2.115	2.430
0.226	0.254	0.282	0.300	0.481	1.147	1.569	1.944
0.158	0.178	0.200	0.220	0.290	0.730	1.138	1.544
0.115	0.130	0.147	0.166	0.206	0.479	0.823	1.222
0.086	0.098	0.112	0.129	0.159	0.334	0.604	0.969
0.067	0.076	0.087	0.102	0.127	0.248	0.456	0.775
0.053	0.060	0.070	0.083	0.105	0.195	0.355	0.628
0.043	0.049	0.057	0.069	0.089	0.160	0.286	0.518
0.035	0.040	0.048	0.058	0.077	0.136	0.238	0.434
0.025	0.029	0.035	0.043	0.060	0.105	0.178	0.322
0.019	0.022	0.027	0.034	0.048	0.086	0.142	0.254
0.015	0.018	0.021	0.028	0.041	0.074	0.120	0.210
0.012	0.014	0.018	0.023	0.035	0.065	0.104	0.180
0.010	0.012	0.015	0.020	0.031	0.058	0.093	0.158
0.007	0.009	0.011	0.015	0.024	0.046	0.073	0.122
0.006	0.007	0.009	0.012	0.020	0.038	0.060	0.100

Table V.9 Entropy Departure Function
 $[(S^\circ - S)/R]^2$ (Polar Deviation)

Tr	Pr						
	0.01	0.05	0.10	0.20	0.40	0.60	0.80
0.30	11.296	11.294	11.292	11.288	11.280	11.272	11.263
0.35	3.215	3.214	3.213	3.211	3.208	3.207	3.209
0.40	3.329	3.326	3.321	3.312	3.295	3.278	3.260
0.45	3.096	3.093	3.090	3.083	3.070	3.056	3.043
0.50	2.892	2.890	2.887	2.882	2.871	2.860	2.849
0.55	0.128	2.708	2.705	2.700	2.691	2.681	2.672
0.60	0.076	2.537	2.535	2.531	2.522	2.514	2.506
0.65	0.045	0.283	2.374	2.370	2.362	2.354	2.347
0.70	0.027	0.168	0.426	2.215	2.207	2.200	2.193
0.75	0.017	0.101	0.250	2.065	2.058	2.050	2.043
0.80	0.011	0.064	0.149	0.425	1.912	1.904	1.897
0.85	0.008	0.042	0.094	0.240	1.770	1.761	1.752
0.90	0.005	0.029	0.062	0.147	0.447	1.616	1.605
0.93	0.004	0.023	0.050	0.113	0.308	0.767	1.514
0.95	0.004	0.020	0.043	0.096	0.248	0.531	1.456
0.97	0.003	0.018	0.037	0.082	0.203	0.397	0.909
0.98	0.003	0.017	0.035	0.076	0.185	0.350	0.677
0.99	0.003	0.016	0.032	0.070	0.168	0.310	0.550
1.00	0.003	0.015	0.030	0.065	0.154	0.277	0.465
1.01	0.003	0.014	0.028	0.061	0.141	0.249	0.401
1.02	0.002	0.013	0.026	0.057	0.130	0.225	0.352
1.05	0.002	0.011	0.022	0.046	0.102	0.170	0.249
1.10	0.001	0.008	0.016	0.032	0.070	0.111	0.155
1.15	0.001	0.005	0.011	0.023	0.048	0.075	0.102
1.20	0.001	0.004	0.008	0.016	0.033	0.051	0.068
1.30	0.000	0.001	0.003	0.006	0.013	0.020	0.027
1.40	0.000	0.000	0.000	0.000	0.001	0.002	0.003
1.50	0.000	-0.001	-0.002	-0.003	-0.006	-0.008	-0.011
1.60	0.000	-0.001	-0.002	-0.005	-0.009	-0.014	-0.019
1.70	0.000	-0.001	-0.003	-0.005	-0.011	-0.016	-0.022
1.80	0.000	-0.001	-0.003	-0.005	-0.011	-0.016	-0.022
1.90	0.000	-0.001	-0.002	-0.005	-0.010	-0.015	-0.021
2.00	0.000	-0.001	-0.002	-0.004	-0.008	-0.013	-0.017
2.20	0.000	0.000	-0.001	-0.002	-0.004	-0.006	-0.009
2.40	0.000	0.000	0.000	0.000	0.000	0.000	0.000
2.60	0.000	0.001	0.001	0.002	0.004	0.006	0.008
2.80	0.000	0.001	0.002	0.004	0.007	0.011	0.015
3.00	0.000	0.001	0.002	0.005	0.010	0.015	0.020
3.50	0.000	0.002	0.003	0.007	0.014	0.021	0.029
4.00	0.000	0.002	0.004	0.008	0.016	0.024	0.033

Pr							
1.00	1.20	1.50	2.00	3.00	5.00	7.00	10.0
11.255	11.247	11.235	11.215	11.174	11.092	11.011	10.888
3.219	3.258	3.439	3.517	3.565	3.560	3.506	3.385
3.243	3.227	3.202	3.162	3.090	2.965	2.850	2.670
3.030	3.017	2.997	2.966	2.906	2.794	2.689	2.535
2.839	2.828	2.812	2.787	2.737	2.643	2.557	2.440
2.663	2.654	2.640	2.618	2.575	2.494	2.421	2.322
2.497	2.489	2.477	2.457	2.420	2.349	2.285	2.202
2.339	2.332	2.321	2.303	2.269	2.208	2.153	2.081
2.186	2.179	2.169	2.152	2.122	2.067	2.019	1.958
2.036	2.029	2.020	2.004	1.976	1.927	1.885	1.832
1.890	1.883	1.874	1.859	1.833	1.789	1.752	1.705
1.745	1.738	1.729	1.715	1.692	1.653	1.620	1.579
1.596	1.589	1.580	1.568	1.549	1.519	1.492	1.457
1.503	1.495	1.486	1.475	1.461	1.438	1.417	1.385
1.438	1.428	1.419	1.411	1.401	1.385	1.366	1.338
1.372	1.358	1.349	1.343	1.339	1.330	1.317	1.291
1.338	1.321	1.312	1.308	1.307	1.303	1.292	1.268
1.306	1.280	1.273	1.272	1.275	1.275	1.267	1.245
1.164	1.233	1.231	1.234	1.242	1.248	1.242	1.222
0.634	1.167	1.185	1.195	1.209	1.220	1.217	1.200
0.514	0.988	1.131	1.154	1.175	1.192	1.192	1.177
0.332	0.361	0.824	1.011	1.069	1.107	1.118	1.110
0.195	0.220	0.240	0.640	0.874	0.963	0.993	1.001
0.125	0.141	0.146	0.272	0.652	0.819	0.870	0.894
0.082	0.093	0.098	0.127	0.424	0.676	0.750	0.791
0.032	0.036	0.037	0.037	0.132	0.410	0.529	0.598
0.003	0.003	0.000	-0.006	0.015	0.198	0.338	0.431
-0.014	-0.018	-0.024	-0.034	-0.039	0.057	0.181	0.292
-0.024	-0.029	-0.037	-0.051	-0.068	-0.027	0.065	0.181
-0.028	-0.034	-0.044	-0.059	-0.082	-0.074	-0.012	0.094
-0.029	-0.035	-0.044	-0.060	-0.086	-0.095	-0.057	0.033
-0.026	-0.032	-0.041	-0.056	-0.081	-0.099	-0.077	-0.004
-0.022	-0.028	-0.035	-0.048	-0.071	-0.091	-0.077	-0.019
-0.012	-0.015	-0.019	-0.027	-0.040	-0.051	-0.043	-0.001
-0.001	-0.001	-0.002	-0.003	-0.004	0.001	0.017	0.058
0.010	0.012	0.014	0.019	0.030	0.055	0.084	0.134
0.019	0.022	0.028	0.039	0.060	0.104	0.148	0.213
0.026	0.031	0.040	0.054	0.084	0.145	0.204	0.286
0.037	0.045	0.057	0.079	0.123	0.212	0.298	0.418
0.042	0.051	0.065	0.089	0.138	0.240	0.340	0.482

Table V.10 Fugacity-Pressure Ratio
 $[\ln(f/P)]^0$ (Simple Fluid)

Tr	Pr						
	0.01	0.05	0.10	0.20	0.40	0.60	0.80
0.30	-8.538	-10.136	-10.815	-11.479	-12.114	-12.462	-12.692
0.35	-5.691	-7.290	-7.970	-8.637	-9.278	-9.631	-9.867
0.40	-3.606	-5.206	-5.887	-6.556	-7.202	-7.559	-7.800
0.45	-2.025	-3.625	-4.307	-4.978	-5.627	-5.989	-6.232
0.50	-0.793	-2.394	-3.077	-3.749	-4.401	-4.766	-5.012
0.55	-0.019	-1.414	-2.098	-2.771	-3.425	-3.792	-4.041
0.60	-0.015	-0.620	-1.304	-1.979	-2.635	-3.003	-3.254
0.65	-0.012	-0.061	-0.652	-1.327	-1.985	-2.355	-2.607
0.70	-0.010	-0.049	-0.099	-0.786	-1.445	-1.816	-2.069
0.75	-0.008	-0.040	-0.080	-0.332	-0.991	-1.363	-1.618
0.80	-0.006	-0.033	-0.066	-0.137	-0.608	-0.981	-1.236
0.85	-0.005	-0.027	-0.055	-0.113	-0.284	-0.656	-0.911
0.90	-0.005	-0.023	-0.046	-0.095	-0.198	-0.382	-0.636
0.93	-0.004	-0.021	-0.042	-0.085	-0.178	-0.282	-0.492
0.95	-0.004	-0.020	-0.039	-0.080	-0.166	-0.261	-0.405
0.97	-0.004	-0.018	-0.037	-0.075	-0.155	-0.242	-0.342
0.98	-0.004	-0.018	-0.036	-0.073	-0.150	-0.234	-0.328
0.99	-0.003	-0.017	-0.035	-0.070	-0.145	-0.226	-0.315
1.00	-0.003	-0.017	-0.034	-0.068	-0.140	-0.218	-0.303
1.01	-0.003	-0.016	-0.033	-0.066	-0.136	-0.211	-0.292
1.02	-0.003	-0.016	-0.032	-0.064	-0.132	-0.204	-0.282
1.05	-0.003	-0.014	-0.029	-0.059	-0.120	-0.185	-0.254
1.10	-0.002	-0.013	-0.025	-0.051	-0.103	-0.158	-0.215
1.15	-0.002	-0.011	-0.022	-0.044	-0.089	-0.136	-0.184
1.20	-0.002	-0.010	-0.019	-0.038	-0.078	-0.118	-0.159
1.30	-0.001	-0.007	-0.015	-0.030	-0.060	-0.090	-0.121
1.40	-0.001	-0.006	-0.012	-0.023	-0.046	-0.070	-0.093
1.50	-0.001	-0.005	-0.009	-0.018	-0.036	-0.055	-0.073
1.60	-0.001	-0.004	-0.007	-0.014	-0.029	-0.043	-0.057
1.70	-0.001	-0.003	-0.006	-0.011	-0.023	-0.034	-0.045
1.80	0.000	-0.002	-0.005	-0.009	-0.018	-0.027	-0.035
1.90	0.000	-0.002	-0.004	-0.007	-0.014	-0.021	-0.028
2.00	0.000	-0.001	-0.003	-0.006	-0.011	-0.016	-0.022
2.20	0.000	-0.001	-0.002	-0.003	-0.007	-0.010	-0.013
2.40	0.000	0.000	-0.001	-0.002	-0.003	-0.005	-0.006
2.60	0.000	0.000	0.000	-0.001	-0.001	-0.002	-0.002
2.80	0.000	0.000	0.000	0.000	0.000	0.001	0.001
3.00	0.000	0.000	0.000	0.001	0.002	0.003	0.004
3.50	0.000	0.000	0.001	0.002	0.003	0.005	0.007
4.00	0.000	0.001	0.001	0.002	0.004	0.006	0.009

Pr							
1.00	1.20	1.50	2.00	3.00	5.00	7.00	10.0
-12.857	-12.981	-13.118	-13.261	-13.378	-13.313	-13.076	-12.576
-10.038	-10.168	-10.313	-10.471	-10.617	-10.611	-10.432	-10.020
-7.975	-8.110	-8.262	-8.431	-8.599	-8.638	-8.506	-8.164
-6.412	-6.550	-6.707	-6.885	-7.072	-7.147	-7.052	-6.765
-5.194	-5.335	-5.497	-5.682	-5.883	-5.989	-5.923	-5.682
-4.225	-4.369	-4.534	-4.725	-4.938	-5.068	-5.028	-4.825
-3.440	-3.586	-3.754	-3.950	-4.173	-4.323	-4.304	-4.133
-2.795	-2.942	-3.113	-3.313	-3.544	-3.711	-3.709	-3.566
-2.258	-2.407	-2.579	-2.782	-3.021	-3.202	-3.215	-3.095
-1.808	-1.957	-2.131	-2.336	-2.580	-2.773	-2.799	-2.699
-1.426	-1.576	-1.751	-1.959	-2.206	-2.409	-2.445	-2.362
-1.102	-1.252	-1.427	-1.636	-1.887	-2.097	-2.142	-2.074
-0.826	-0.976	-1.151	-1.360	-1.613	-1.829	-1.881	-1.826
-0.682	-0.831	-1.006	-1.214	-1.467	-1.685	-1.741	-1.693
-0.594	-0.742	-0.916	-1.124	-1.376	-1.596	-1.655	-1.610
-0.512	-0.660	-0.833	-1.040	-1.291	-1.512	-1.572	-1.532
-0.474	-0.621	-0.793	-0.999	-1.251	-1.471	-1.533	-1.494
-0.439	-0.584	-0.755	-0.960	-1.211	-1.432	-1.494	-1.457
-0.406	-0.548	-0.718	-0.923	-1.173	-1.394	-1.457	-1.422
-0.387	-0.515	-0.683	-0.886	-1.135	-1.357	-1.420	-1.387
-0.370	-0.484	-0.649	-0.851	-1.099	-1.320	-1.385	-1.353
-0.329	-0.414	-0.558	-0.753	-0.997	-1.217	-1.284	-1.256
-0.276	-0.340	-0.446	-0.615	-0.847	-1.063	-1.131	-1.110
-0.235	-0.287	-0.369	-0.507	-0.719	-0.929	-0.997	-0.981
-0.202	-0.245	-0.312	-0.425	-0.612	-0.811	-0.879	-0.867
-0.152	-0.183	-0.231	-0.309	-0.450	-0.619	-0.682	-0.674
-0.117	-0.140	-0.175	-0.232	-0.336	-0.472	-0.527	-0.521
-0.091	-0.109	-0.135	-0.178	-0.255	-0.361	-0.406	-0.397
-0.071	-0.085	-0.105	-0.137	-0.196	-0.277	-0.310	-0.298
-0.056	-0.066	-0.082	-0.107	-0.151	-0.211	-0.234	-0.217
-0.044	-0.052	-0.064	-0.083	-0.116	-0.159	-0.174	-0.152
-0.034	-0.041	-0.050	-0.064	-0.089	-0.119	-0.125	-0.099
-0.027	-0.032	-0.038	-0.049	-0.067	-0.086	-0.086	-0.055
-0.015	-0.018	-0.022	-0.027	-0.035	-0.038	-0.028	0.010
-0.007	-0.009	-0.010	-0.012	-0.013	-0.006	0.011	0.055
-0.002	-0.002	-0.002	-0.001	0.002	0.016	0.038	0.086
0.002	0.003	0.004	0.006	0.012	0.031	0.057	0.107
0.005	0.006	0.008	0.011	0.020	0.042	0.070	0.121
0.009	0.011	0.014	0.019	0.031	0.058	0.089	0.141
0.011	0.013	0.017	0.023	0.036	0.064	0.095	0.146

Table V.11 Fugacity-Pressure Ratio
 $[\ln(f/P)]^1$ (Geometric Deviation)

Tr	Pr						
	0.01	0.05	0.10	0.20	0.40	0.60	0.80
0.30	-20.214	-20.217	-20.221	-20.229	-20.245	-20.261	-20.278
0.35	-15.026	-15.030	-15.035	-15.044	-15.063	-15.081	-15.099
0.40	-11.310	-11.314	-11.319	-11.328	-11.348	-11.367	-11.385
0.45	-8.579	-8.583	-8.587	-8.597	-8.615	-8.634	-8.653
0.50	-6.534	-6.537	-6.542	-6.551	-6.569	-6.587	-6.605
0.55	-0.031	-4.983	-4.987	-4.996	-5.013	-5.030	-5.047
0.60	-0.020	-3.786	-3.790	-3.798	-3.815	-3.831	-3.847
0.65	-0.014	-0.072	-2.859	-2.866	-2.882	-2.897	-2.913
0.70	-0.009	-0.048	-0.102	-2.134	-2.149	-2.164	-2.178
0.75	-0.006	-0.033	-0.068	-1.555	-1.569	-1.583	-1.597
0.80	-0.004	-0.022	-0.046	-0.099	-1.108	-1.121	-1.135
0.85	-0.003	-0.015	-0.030	-0.064	-0.739	-0.753	-0.765
0.90	-0.002	-0.010	-0.020	-0.041	-0.090	-0.458	-0.471
0.93	-0.001	-0.007	-0.015	-0.031	-0.066	-0.110	-0.324
0.95	-0.001	-0.006	-0.012	-0.025	-0.053	-0.085	-0.237
0.97	-0.001	-0.005	-0.010	-0.020	-0.042	-0.066	-0.096
0.98	-0.001	-0.004	-0.009	-0.018	-0.037	-0.057	-0.081
0.99	-0.001	-0.004	-0.008	-0.016	-0.032	-0.049	-0.068
1.00	-0.001	-0.003	-0.007	-0.014	-0.028	-0.042	-0.057
1.01	-0.001	-0.003	-0.006	-0.012	-0.024	-0.036	-0.047
1.02	-0.001	-0.003	-0.005	-0.010	-0.020	-0.030	-0.039
1.05	0.000	-0.001	-0.003	-0.006	-0.011	-0.015	-0.017
1.10	0.000	0.000	0.000	0.000	0.002	0.004	0.009
1.15	0.000	0.001	0.002	0.005	0.010	0.017	0.026
1.20	0.000	0.002	0.004	0.008	0.017	0.027	0.039
1.30	0.001	0.003	0.006	0.012	0.025	0.039	0.054
1.40	0.001	0.004	0.007	0.014	0.029	0.045	0.061
1.50	0.001	0.004	0.008	0.016	0.032	0.048	0.065
1.60	0.001	0.004	0.008	0.016	0.032	0.049	0.066
1.70	0.001	0.004	0.008	0.016	0.033	0.049	0.066
1.80	0.001	0.004	0.008	0.016	0.032	0.049	0.065
1.90	0.001	0.004	0.008	0.016	0.032	0.048	0.064
2.00	0.001	0.004	0.008	0.016	0.031	0.047	0.062
2.20	0.001	0.004	0.007	0.015	0.029	0.044	0.059
2.40	0.001	0.003	0.007	0.014	0.028	0.042	0.055
2.60	0.001	0.003	0.007	0.013	0.026	0.039	0.052
2.80	0.001	0.003	0.006	0.012	0.025	0.037	0.049
3.00	0.001	0.003	0.006	0.012	0.023	0.035	0.046
3.50	0.001	0.003	0.005	0.010	0.021	0.031	0.041
4.00	0.000	0.002	0.005	0.009	0.018	0.027	0.036

Pr							
1.00	1.20	1.50	2.00	3.00	5.00	7.00	10.0
-20.294	-20.310	-20.334	-20.374	-20.455	-20.615	-20.774	-21.012
-15.118	-15.136	-15.164	-15.210	-15.301	-15.483	-15.663	-15.931
-11.404	-11.423	-11.452	-11.499	-11.592	-11.778	-11.961	-12.231
-8.671	-8.690	-8.718	-8.764	-8.855	-9.036	-9.214	-9.475
-6.623	-6.641	-6.667	-6.711	-6.799	-6.971	-7.139	-7.386
-5.064	-5.081	-5.106	-5.148	-5.231	-5.393	-5.551	-5.780
-3.863	-3.879	-3.903	-3.943	-4.020	-4.172	-4.318	-4.530
-2.928	-2.943	-2.966	-3.003	-3.076	-3.216	-3.352	-3.547
-2.193	-2.207	-2.228	-2.263	-2.331	-2.462	-2.587	-2.765
-1.611	-1.624	-1.644	-1.677	-1.741	-1.862	-1.976	-2.138
-1.148	-1.161	-1.180	-1.210	-1.270	-1.381	-1.485	-1.632
-0.778	-0.790	-0.808	-0.837	-0.892	-0.994	-1.088	-1.221
-0.483	-0.495	-0.512	-0.539	-0.590	-0.682	-0.767	-0.885
-0.336	-0.348	-0.365	-0.391	-0.439	-0.525	-0.604	-0.713
-0.250	-0.261	-0.278	-0.303	-0.349	-0.431	-0.505	-0.609
-0.172	-0.183	-0.199	-0.223	-0.267	-0.344	-0.415	-0.513
-0.136	-0.148	-0.163	-0.187	-0.229	-0.304	-0.373	-0.468
-0.102	-0.114	-0.129	-0.152	-0.193	-0.265	-0.332	-0.425
-0.072	-0.083	-0.098	-0.119	-0.158	-0.228	-0.293	-0.383
-0.056	-0.056	-0.068	-0.088	-0.125	-0.193	-0.255	-0.343
-0.044	-0.034	-0.041	-0.059	-0.094	-0.159	-0.219	-0.304
-0.015	-0.005	0.018	0.015	-0.011	-0.067	-0.120	-0.197
0.016	0.028	0.057	0.094	0.097	0.061	0.019	-0.043
0.037	0.052	0.079	0.129	0.170	0.160	0.131	0.083
0.052	0.067	0.095	0.146	0.213	0.234	0.220	0.186
0.069	0.086	0.114	0.163	0.250	0.327	0.344	0.340
0.078	0.095	0.123	0.170	0.259	0.370	0.416	0.440
0.082	0.099	0.126	0.171	0.258	0.385	0.453	0.502
0.083	0.100	0.126	0.169	0.253	0.386	0.469	0.539
0.082	0.099	0.124	0.166	0.246	0.380	0.472	0.558
0.081	0.097	0.122	0.162	0.239	0.371	0.468	0.566
0.079	0.095	0.119	0.158	0.232	0.361	0.460	0.566
0.077	0.093	0.115	0.153	0.224	0.350	0.450	0.562
0.073	0.087	0.109	0.143	0.210	0.329	0.428	0.544
0.069	0.082	0.102	0.135	0.197	0.309	0.405	0.523
0.065	0.077	0.096	0.127	0.185	0.292	0.384	0.500
0.061	0.073	0.091	0.119	0.175	0.276	0.365	0.479
0.058	0.069	0.086	0.113	0.165	0.262	0.347	0.458
0.051	0.061	0.075	0.099	0.146	0.232	0.309	0.412
0.045	0.054	0.067	0.089	0.130	0.208	0.279	0.375

Table V.12 Fugacity-Pressure Ratio
 $[\ln(f/P)]^2$ (Polar Deviation)

Tr	Pr						
	0.01	0.05	0.10	0.20	0.40	0.60	0.80
0.30	-5.966	-5.969	-5.972	-5.979	-5.993	-6.007	-6.021
0.35	-4.266	-4.268	-4.271	-4.276	-4.286	-4.297	-4.307
0.40	-3.315	-3.317	-3.320	-3.325	-3.336	-3.347	-3.357
0.45	-2.590	-2.592	-2.595	-2.600	-2.612	-2.623	-2.634
0.50	-2.032	-2.034	-2.037	-2.042	-2.054	-2.065	-2.076
0.55	-0.024	-1.595	-1.597	-1.603	-1.614	-1.625	-1.637
0.60	-0.013	-1.243	-1.246	-1.252	-1.263	-1.274	-1.285
0.65	-0.007	-0.046	-0.961	-0.967	-0.978	-0.988	-0.999
0.70	-0.004	-0.024	-0.065	-0.734	-0.745	-0.755	-0.766
0.75	-0.003	-0.014	-0.032	-0.542	-0.553	-0.563	-0.574
0.80	-0.001	-0.008	-0.018	-0.046	-0.394	-0.404	-0.415
0.85	-0.001	-0.005	-0.010	-0.024	-0.263	-0.273	-0.283
0.90	0.000	-0.002	-0.005	-0.012	-0.033	-0.164	-0.174
0.93	0.000	-0.001	-0.003	-0.007	-0.020	-0.052	-0.118
0.95	0.000	-0.001	-0.002	-0.005	-0.014	-0.028	-0.084
0.97	0.000	-0.001	-0.001	-0.003	-0.009	-0.018	-0.040
0.98	0.000	0.000	-0.001	-0.002	-0.007	-0.014	-0.025
0.99	0.000	0.000	0.000	-0.001	-0.005	-0.011	-0.019
1.00	0.000	0.000	0.000	-0.001	-0.003	-0.008	-0.014
1.01	0.000	0.000	0.000	0.000	-0.002	-0.005	-0.009
1.02	0.000	0.000	0.000	0.000	-0.001	-0.003	-0.005
1.05	0.000	0.001	0.001	0.002	0.003	0.003	0.003
1.10	0.000	0.001	0.002	0.004	0.007	0.009	0.012
1.15	0.000	0.001	0.002	0.005	0.009	0.013	0.017
1.20	0.000	0.001	0.003	0.005	0.010	0.015	0.020
1.30	0.000	0.001	0.003	0.006	0.011	0.016	0.022
1.40	0.000	0.001	0.003	0.005	0.011	0.016	0.021
1.50	0.000	0.001	0.002	0.005	0.010	0.015	0.019
1.60	0.000	0.001	0.002	0.004	0.009	0.013	0.017
1.70	0.000	0.001	0.002	0.004	0.008	0.011	0.015
1.80	0.000	0.001	0.002	0.003	0.007	0.010	0.013
1.90	0.000	0.001	0.001	0.003	0.006	0.008	0.011
2.00	0.000	0.001	0.001	0.003	0.005	0.007	0.010
2.20	0.000	0.001	0.001	0.002	0.004	0.006	0.008
2.40	0.000	0.000	0.001	0.002	0.003	0.005	0.006
2.60	0.000	0.000	0.001	0.002	0.003	0.005	0.006
2.80	0.000	0.000	0.001	0.002	0.004	0.005	0.007
3.00	0.000	0.001	0.001	0.002	0.004	0.006	0.007
3.50	0.000	0.001	0.001	0.003	0.005	0.008	0.010
4.00	0.000	0.001	0.002	0.003	0.006	0.009	0.013

Pr							
1.00	1.20	1.50	2.00	3.00	5.00	7.00	10.0
-6.035	-6.049	-6.069	-6.104	-6.172	-6.308	-6.443	-6.642
-4.317	-4.328	-4.345	-4.375	-4.436	-4.560	-4.684	-4.871
-3.368	-3.379	-3.395	-3.423	-3.479	-3.596	-3.715	-3.898
-2.645	-2.657	-2.674	-2.702	-2.760	-2.877	-2.996	-3.177
-2.088	-2.099	-2.116	-2.145	-2.202	-2.317	-2.434	-2.611
-1.648	-1.659	-1.676	-1.704	-1.760	-1.873	-1.986	-2.157
-1.296	-1.307	-1.323	-1.351	-1.406	-1.515	-1.625	-1.788
-1.010	-1.021	-1.037	-1.064	-1.117	-1.223	-1.329	-1.486
-0.776	-0.787	-0.802	-0.829	-0.881	-0.983	-1.085	-1.236
-0.584	-0.594	-0.609	-0.635	-0.685	-0.785	-0.882	-1.027
-0.425	-0.435	-0.450	-0.474	-0.523	-0.619	-0.714	-0.852
-0.293	-0.303	-0.317	-0.341	-0.389	-0.482	-0.573	-0.706
-0.184	-0.193	-0.208	-0.231	-0.277	-0.367	-0.454	-0.582
-0.128	-0.137	-0.152	-0.175	-0.220	-0.307	-0.393	-0.517
-0.094	-0.104	-0.118	-0.141	-0.185	-0.271	-0.355	-0.478
-0.063	-0.073	-0.087	-0.109	-0.153	-0.238	-0.320	-0.441
-0.049	-0.058	-0.072	-0.095	-0.138	-0.222	-0.304	-0.423
-0.035	-0.045	-0.058	-0.081	-0.124	-0.207	-0.288	-0.406
-0.022	-0.032	-0.045	-0.067	-0.110	-0.192	-0.272	-0.390
-0.014	-0.019	-0.033	-0.055	-0.096	-0.178	-0.257	-0.374
-0.008	-0.008	-0.021	-0.043	-0.084	-0.164	-0.243	-0.359
0.004	0.007	0.008	-0.010	-0.049	-0.127	-0.203	-0.316
0.015	0.020	0.028	0.028	-0.003	-0.074	-0.146	-0.254
0.021	0.026	0.035	0.046	0.031	-0.032	-0.099	-0.201
0.025	0.030	0.039	0.052	0.052	0.001	-0.061	-0.158
0.027	0.032	0.041	0.054	0.067	0.042	-0.007	-0.092
0.026	0.031	0.039	0.051	0.067	0.060	0.024	-0.049
0.024	0.029	0.036	0.046	0.062	0.064	0.039	-0.022
0.021	0.025	0.031	0.040	0.054	0.061	0.044	-0.006
0.019	0.022	0.027	0.035	0.047	0.054	0.043	0.002
0.016	0.019	0.023	0.029	0.039	0.047	0.039	0.006
0.014	0.016	0.020	0.025	0.033	0.039	0.033	0.006
0.012	0.014	0.017	0.021	0.027	0.032	0.028	0.005
0.009	0.011	0.013	0.016	0.020	0.023	0.019	0.003
0.008	0.009	0.011	0.013	0.016	0.019	0.017	0.005
0.008	0.009	0.010	0.013	0.016	0.019	0.019	0.012
0.008	0.009	0.011	0.014	0.018	0.024	0.026	0.024
0.009	0.011	0.013	0.016	0.022	0.031	0.036	0.039
0.012	0.015	0.018	0.024	0.034	0.052	0.068	0.084
0.016	0.019	0.023	0.031	0.046	0.074	0.099	0.131

Table V.13 Compressibility Factor (Auxiliary Values)
 Z^0 (Simple Fluid)

Tr	Pr						
	0.01	0.05	0.10	0.20	0.40	0.60	0.80
0.45	0.9648	0.8241					
0.50	0.9741	0.8699					
0.55	0.0020	0.9000	0.7995				
0.60	0.0019	0.9211	0.8405				
0.65	0.0018	0.0089	0.8707	0.7367			
0.70	0.0017	0.0086	0.0172	0.7805	0.5498		
0.75	0.0018	0.0085	0.0169	0.8181	0.6122		
0.80	0.0020	0.0086	0.0168	0.0332	0.6659	0.4746	
0.85	0.0027	0.0092	0.0174	0.0336	0.7222	0.5346	
0.90	0.0058	0.0123	0.0203	0.0364	0.0685	0.6040	0.4034
0.93	0.0125	0.0187	0.0265	0.0422	0.0735	0.1047	0.4439
0.95		0.0308	0.0382	0.0529	0.0822	0.1116	0.4853
0.97			0.0762	0.0872	0.1092	0.1312	0.1532
0.98				0.1438	0.1527	0.1615	0.1703
0.99					0.3275	0.2800	0.2324

Table V.14 Compressibility Factor (Auxiliary Values)
 Z^1 (Geometric Deviation)

Tr	Pr						
	0.01	0.05	0.10	0.20	0.40	0.60	0.80
0.45	-0.0740	-0.3696					
0.50	-0.0457	-0.2270					
0.55	-0.0009	-0.1438	-0.2864				
0.60	-0.0008	-0.0949	-0.1857				
0.65	-0.0008	-0.0039	-0.1262	-0.2424			
0.70	-0.0008	-0.0038	-0.0075	-0.1685	-0.3160		
0.75	-0.0009	-0.0037	-0.0072	-0.1298	-0.2203		
0.80	-0.0013	-0.0040	-0.0073	-0.0139	-0.1682	-0.2185	
0.85	-0.0027	-0.0052	-0.0082	-0.0144	-0.1503	-0.1692	
0.90	-0.0077	-0.0099	-0.0125	-0.0179	-0.0286	-0.1580	-0.1464
0.93	-0.0176	-0.0193	-0.0214	-0.0256	-0.0340	-0.0424	-0.1418
0.95		-0.0363	-0.0374	-0.0397	-0.0444	-0.0490	-0.1532
0.97			-0.0893	-0.0857	-0.0786	-0.0714	-0.0643
0.98				-0.1628	-0.1361	-0.1095	-0.0828
0.99					-0.3809	-0.2715	-0.1621

Table V.15 Compressibility Factor Z^2 (Polar Deviation) (Auxiliary Values)

Tr	Pr						
	0.01	0.05	0.10	0.20	0.40	0.60	0.80
0.45	-0.0710	-0.3547					
0.50	-0.0396	-0.1978					
0.55	-0.0006	-0.1117	-0.2229				
0.60	-0.0006	-0.0671	-0.1334				
0.65	-0.0005	-0.0027	-0.0871	-0.1728			
0.70	-0.0005	-0.0027	-0.0053	-0.1217	-0.2420		
0.75	-0.0006	-0.0026	-0.0052	-0.0905	-0.1805		
0.80	-0.0007	-0.0027	-0.0052	-0.0103	-0.1385	-0.2090	
0.85	-0.0012	-0.0031	-0.0055	-0.0104	-0.1060	-0.1629	
0.90	-0.0026	-0.0044	-0.0068	-0.0114	-0.0206	-0.1244	-0.1720
0.93	-0.0051	-0.0068	-0.0090	-0.0134	-0.0220	-0.0307	-0.1457
0.95		-0.0108	-0.0128	-0.0167	-0.0246	-0.0324	-0.1275
0.97			-0.0234	-0.0263	-0.0320	-0.0376	-0.0433
0.98				-0.0410	-0.0433	-0.0455	-0.0478
0.99					-0.0893	-0.0769	-0.0645

Table V.16 Enthalpy Departure Function (Auxiliary Values)
 $[(H^\circ - H)/RT_c]^0$ (Simple Fluid)

Tr	Pr						
	0.01	0.05	0.10	0.20	0.40	0.60	0.80
0.45	0.048	0.265					
0.50	0.039	0.207					
0.55	5.315	0.168	0.360				
0.60	5.163	0.140	0.297				
0.65	5.000	5.011	0.250	0.555			
0.70	4.799	4.852	4.853	0.471	1.160		
0.75	4.487	4.668	4.686	0.403	0.973		
0.80	3.940	4.415	4.483	4.508	0.832	1.531	
0.85	3.154	3.991	4.179	4.277	0.708	1.306	
0.90	2.107	3.258	3.628	3.891	4.037	1.100	1.908
0.93	1.496	2.584	3.072	3.472	3.762	3.869	1.726
0.95		1.989	2.517	3.027	3.455	3.654	1.573
0.97			1.752	2.285	2.895	3.251	3.505
0.98				1.727	2.373	2.853	3.249
0.99					1.442	1.999	2.654

Table V.17 Enthalpy Departure Function (Auxiliary Values)
 $[(H^\circ - H)/RT_c]^1$ (Geometric Deviation)

Tr	Pr						
	0.01	0.05	0.10	0.20	0.40	0.60	0.80
0.45	0.159	1.099					
0.50	0.110	0.672					
0.55	8.212	0.451	1.107				
0.60	7.572	0.321	0.734				
0.65	6.977	6.948	0.522	1.315			
0.70	6.485	6.364	6.356	0.915	2.879		
0.75	6.199	5.848	5.803	0.683	1.857		
0.80	6.156	5.442	5.323	5.266	1.323	2.728	
0.85	5.760	5.186	4.951	4.809	1.013	1.910	
0.90	4.774	4.840	4.669	4.456	4.294	1.441	2.476
0.93	3.101	4.409	4.393	4.270	4.077	3.974	2.090
0.95		3.782	4.094	4.096	3.957	3.825	1.884
0.97			3.238	3.774	3.833	3.723	3.571
0.98				3.253	3.734	3.703	3.536
0.99					3.237	3.675	3.616

Table V.18 Enthalpy Departure Function (Auxiliary Values)
 $[(H^\circ - H)/RT_c]^2$ (Polar Deviation)

Tr	Pr						
	0.01	0.05	0.10	0.20	0.40	0.60	0.80
0.45	0.176	1.102					
0.50	0.129	0.990					
0.55	2.366	0.592	2.012				
0.60	2.270	0.351	1.036				
0.65	2.179	2.168	0.581	2.276			
0.70	2.115	2.066	2.063	1.162	7.778		
0.75	2.130	1.974	1.959	0.646	3.280		
0.80	2.267	1.916	1.864	1.845	1.602	5.451	
0.85	2.422	1.915	1.802	1.744	0.835	2.553	
0.90	2.000	1.908	1.765	1.663	1.611	1.229	3.239
0.93	0.477	1.711	1.693	1.609	1.546	1.527	2.102
0.95		1.021	1.437	1.524	1.497	1.479	1.493
0.97			0.527	1.111	1.386	1.423	1.423
0.98				0.530	1.159	1.355	1.400
0.99					0.497	1.020	1.330

Table V.19 Entropy Departure Function (Auxiliary Values)
 $[(S^\circ - S)/R]^0$ (Simple Fluid)

Tr	Pr						
	0.01	0.05	0.10	0.20	0.40	0.60	0.80
0.45	0.071	0.397					
0.50	0.051	0.277					
0.55	9.851	0.204	0.442				
0.60	9.586	0.156	0.333				
0.65	9.327	7.741	0.260	0.584			
0.70	9.034	7.506	6.823	0.462	1.157		
0.75	8.623	7.254	6.593	0.370	0.917		
0.80	7.983	6.933	6.332	5.687	0.742	1.390	
0.85	7.117	6.442	5.971	5.408	0.592	1.135	
0.90	5.789	5.635	5.360	4.972	4.475	0.904	1.634
0.93	4.690	4.842	4.745	4.518	4.176	3.922	1.442
0.95		4.030	4.087	4.028	3.848	3.692	1.282
0.97			3.011	3.151	3.246	3.271	3.288
0.98				2.389	2.659	2.852	3.025
0.99					1.507	1.920	2.413

Table V.20 Entropy Departure Function (Auxiliary Values)
 $[(S^\circ - S)/R]^1$ (Geometric Deviation)

Tr	Pr						
	0.01	0.05	0.10	0.20	0.40	0.60	0.80
0.45	0.275	1.916					
0.50	0.172	1.058					
0.55	9.951	0.648	1.596				
0.60	8.837	0.425	0.977				
0.65	7.883	7.834	0.648	1.631			
0.70	7.142	6.968	6.954	1.069	3.319		
0.75	6.705	6.252	6.190	0.758	2.050		
0.80	6.520	5.716	5.566	5.489	1.404	2.864	
0.85	5.994	5.367	5.102	4.932	1.041	1.951	
0.90	5.403	4.973	4.761	4.520	4.327	1.439	2.458
0.93	4.311	4.687	4.513	4.321	4.089	3.962	2.056
0.95		4.348	4.346	4.182	3.965	3.805	1.845
0.97			3.878	4.035	3.877	3.704	3.523
0.98				3.764	3.862	3.704	3.488
0.99					3.629	3.778	3.585

Table V.21 Entropy Departure Function (Auxiliary Values)
 $[(S^\circ - S)/R]^2$ (Polar Deviation)

Tr	Pr						
	0.01	0.05	0.10	0.20	0.40	0.60	0.80
0.45	0.300	1.081					
0.50	0.212	1.492					
0.55	2.709	0.868	2.804				
0.60	2.542	0.489	1.394				
0.65	2.397	2.376	0.748	2.783			
0.70	2.304	2.226	2.219	1.371	7.903		
0.75	2.325	2.104	2.074	0.743	3.372		
0.80	2.515	2.041	1.962	1.923	1.641	4.414	
0.85	2.893	2.083	1.913	1.813	0.869	2.271	
0.90	3.022	2.276	1.976	1.775	1.645	1.176	2.193
0.93	1.696	2.394	2.108	1.823	1.617	1.534	1.683
0.95		1.945	2.097	1.903	1.641	1.510	1.321
0.97			1.449	1.779	1.717	1.548	1.414
0.98				1.345	1.665	1.603	1.439
0.99					1.149	1.483	1.528

Table V.22 Fugacity-Pressure Ratio (Auxiliary Values)
 $[\ln(f/P)]^0$ (Simple Fluid)

Tr	Pr						
	0.01	0.05	0.10	0.20	0.40	0.60	0.80
0.45	-0.035	-0.191					
0.50	-0.026	-0.136					
0.55	0.187	-0.101	-0.213				
0.60	0.982	-0.077	-0.161				
0.65	1.634	0.032	-0.125	-0.270			
0.70	2.178	0.574	-0.110	-0.210	-0.501		
0.75	2.640	1.029	0.345	-0.168	-0.380		
0.80	3.058	1.415	0.728	0.052	-0.299	-0.523	
0.85	3.406	1.747	1.054	0.376	-0.241	-0.402	
0.90	3.447	2.015	1.329	0.649	-0.010	-0.319	-0.486
0.93	3.081	2.064	1.442	0.785	0.131	-0.239	-0.413
0.95		1.936	1.437	0.842	0.212	-0.154	-0.374
0.97			1.205	0.794	0.261	-0.081	-0.326
0.98				0.627	0.237	-0.059	-0.291
0.99					0.051	-0.099	-0.268

Table V.23 Fugacity-Pressure Ratio (Auxiliary Values)
 $[\ln(f/P)]^1$ (Geometric Deviation)

Tr	Pr						
	0.01	0.05	0.10	0.20	0.40	0.60	0.80
0.45	-0.078	-0.526					
0.50	-0.048	-0.286					
0.55	-4.979	-0.172	-0.417				
0.60	-3.783	-0.109	-0.247				
0.65	-2.852	-2.855	-0.156	-0.392			
0.70	-2.122	-2.123	-2.127	-0.238	-0.794		
0.75	-1.561	-1.545	-1.548	-0.152	-0.426		
0.80	-1.174	-1.087	-1.088	-1.094	-0.250	-0.546	
0.85	-0.782	-0.735	-0.722	-0.726	-0.150	-0.296	
0.90	0.099	-0.405	-0.427	-0.431	-0.444	-0.162	-0.293
0.93	0.977	-0.054	-0.211	-0.271	-0.295	-0.311	-0.191
0.95		0.367	0.037	-0.130	-0.200	-0.222	-0.138
0.97			0.539	0.144	-0.074	-0.135	-0.158
0.98				0.445	0.052	-0.075	-0.120
0.99					0.360	0.066	-0.068

Table V.24 Fugacity-Pressure Ratio (Auxiliary Values)
 $[\ln(f/P)]^2$ (Polar Deviation)

Tr	Pr						
	0.01	0.05	0.10	0.20	0.40	0.60	0.80
0.45	-0.090	-1.369					
0.50	-0.047	-0.489					
0.55	-1.592	-0.208	-0.854				
0.60	-1.241	-0.096	-0.333				
0.65	-0.955	-0.959	-0.146	-0.719			
0.70	-0.718	-0.726	-0.729	-0.289	-3.209		
0.75	-0.515	-0.528	-0.537	-0.118	-1.001		
0.80	-0.319	-0.353	-0.369	-0.384	-0.361	-2.399	
0.85	0.044	-0.171	-0.206	-0.239	-0.114	-0.733	
0.90	0.800	0.156	0.015	-0.073	-0.145	-0.189	-1.406
0.93	1.183	0.555	0.287	0.092	-0.045	-0.108	-0.577
0.95		0.871	0.585	0.299	0.065	-0.047	-0.251
0.97			0.906	0.633	0.288	0.081	-0.053
0.98				0.804	0.482	0.220	0.010
0.99					0.647	0.453	0.184

CHAPTER VI

DISCUSSION OF METHOD

A. The Computer Program

One aspect that contributes to the value and importance of any predictive method is its simplicity from the point of view of the user. The computer code for the method of this work is written to require the least amount of input information and only minimal understanding of the theory. Figure VI.1 presents a flow diagram for the computer program. The purpose of this figure is to give a general idea of program organization and does not present details of the program logic.

Appendix B contains the computer code for the Commodore 64 computer. A version has also been written for the IBM PC and another has been written in fortran.

B. Special Considerations

1. Reference Fluid Equations - When using reference fluids a problem arises from the fact that the saturation curves of these fluids are not superimposable. This means that at given reduced conditions one reference fluid may be a liquid and another a vapor.

It is thus important to know the phase of the fluid for

Figure VI.1 Flow Diagram of Computer Program.

Figure VI.1 (continued)

Figure VI.1 (continued)

which the calculations are being done. If the phase is unknown it is determined by the program using the following vapor-pressure correlation. Lee and Kesler (7) developed a vapor-pressure correlation for their three-parameter method. This correlation consists of a vapor-pressure equation for each of the two reference fluids which are used in the same series expansion as for other properties. A similar vapor-pressure equation has been developed for the third reference fluid, water. This equation and the two Lee-Kesler equations have been combined in the general correlation of Equation 3.7 to give a four-parameter correlation for the vapor-pressure. The three reference fluid vapor-pressure equations are shown below where subscript 0 refers to the first reference fluid, subscript 1 to the second, and subscript 2 to the third. It should be noted that it is the natural logarithm of the vapor-pressure that obeys the principle of corresponding states.

$$\ln(P_{vp_r})_0 = 5.92714 - \frac{6.09648}{T_r} - 1.28862 \ln T_r + 0.169347 T_r^6 \quad (6.1)$$

$$\ln(P_{vp_r})_1 = 11.99431 - \frac{12.33697}{T_r} - 6.647821 \ln T_r + 0.342696 T_r^6 \quad (6.2)$$

$$\ln(P_{vp_r})_2 = 9.76059 - \frac{10.05808}{T_r} - 4.15481 \ln T_r + 0.298975 T_r^6 \quad (6.3)$$

where P_{vp_r} is the reduced vapor pressure and T_r the reduced temperature.

By substituting these relations into Equation 3.7 a value for the logarithm of the vapor-pressure is obtained. Exponentiation yields a prediction of the vapor-pressure for the fluid of interest. Note that the value of the fourth parameter used for derivative properties is used in this vapor-pressure correlation because of the close relation of the vapor pressure to the heat of vaporization through the Clausius-Claapeyron equation.

If the vapor pressure obtained from this equation is greater than the given pressure then the fluid is a vapor; if the vapor pressure is less than the given pressure then the fluid is a liquid.

The phase of the fluid is then used to obtain the appropriate roots to the reference fluid equations of state. As a simplified illustration of this situation consider Figure VI.2 which is a pressure-volume plot of the same isotherm for two reference fluids. For simplicity, the saturation curve in the figure will represent the two-phase region for both fluids. Let the conditions of the calculation be the reduced temperature of the reference fluid isotherms shown, reduced pressure equal to 0.67 (shown as the dashed line), and the test fluid is a liquid. At these conditions the first reference fluid is a liquid, but the second is a vapor. Of course the liquid root of the first reference fluid is the desired value for that fluid. A liquid-like root is desired for the second fluid as well, and this is obtained by linearly extrapolating into the

Figure VI.2 Simplified Plot of the Same Isotherm for Two Reference Fluids.

two-phase region to the point V'_r . A similar procedure would be followed if the test fluid were a vapor.

2. Initial Estimate for Iterative Solution to Equations of State - Because of the implicit nature of the reference fluid equations of state they are solved iteratively. A modified Newton-Raphson method with emphasis on good initial estimates is employed. In the vapor region and dense fluid region above $T_r=1.00$ the Peng-Robinson (39) cubic equation of state provides the initial estimate.

In the liquid region ($Pr < 1.00$) the Gunn-Yamada (40) method for predicting saturated liquid volumes is used as the basis for an initial estimate. First, the compressibility factor at the given reduced temperature and the saturation pressure for the specific reference fluid is determined. This compressibility factor is then multiplied by the ratio of the given reduced pressure to the reduced saturation pressure. This is equivalent to assuming the liquid is incompressible. This new compressibility factor is then used as the initial estimate for the equation of state iterations.

In the compressed liquid region ($Pr > 1.00$ and $T_r < 1.00$) the procedures just presented for the vapor and liquid are both performed and the smaller value is used as the initial estimate. This assures a safe estimate which is guaranteed to converge to the desired root.

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

A four-parameter corresponding states correlation for the prediction of thermodynamic properties of nonpolar and polar fluids has been developed. The four parameters are the critical temperature and pressure, a geometric parameter, α , and a polarity parameter, β . The third parameter, α , is obtained from the radius of gyration, which is readily available for common fluids. The fourth parameter, β , is obtained from a single liquid density point. This value of β can be used for all properties, but for derivative properties better results are obtained if β is obtained from the heat of vaporization or alternatively from the normal boiling point.

To obtain a property estimate for any fluid, the critical constants, radius of gyration, and a liquid density point and/or the heat of vaporization or normal boiling point are given as input. Then the temperature and pressure are input along with the phase if it is known. If the phase is unknown it is determined from the vapor-pressure correlation included in the computer code.

The method has been used to predict properties of several polar fluids. These results have been compared to the Lee-Kesler (7) three-parameter method and the four-parameter method of Wu and Stiel (19). The method of

this thesis is shown to be equivalent to the Lee-Kesler method for nonpolar fluids and far superior for polar fluids. The present method is also shown to be generally superior to the Wu and Stiel method.

Average errors for the compressibility factor for all fluids tested are 1.9 % for the vapor phase and 1.6 % for the liquid phase. For enthalpy departure functions the average error is 250 J/mol for the vapor phase and 422 J/mol for the liquid phase.

The method is designed to be as simple to use as possible. The computer program is written with easy-to-follow directions so that no experience or understanding of the theory is required. Also included are extensive tables for hand calculations.

Although not the main objective of this study, mixtures were briefly considered and mixture rules were included. The preliminary results indicate that effective predictions for mixtures can be obtained using the framework of the correlation.

The following items are recommended for future consideration.

1. Perhaps the most important extension of the present work will be its application to mixtures. The mixing rules suggested should be tested further and most probably modified. The preliminary results for mixtures are encouraging and suggest that accurate predictions will be obtainable from this method.

2. The third corresponding states parameter is neatly based upon the radius of gyration: a specific characteristic of a molecule's geometry. It would be advantageous to establish a similar method for the fourth parameter. Although efforts to do so have as yet been fruitless, further study could yield useful results.
3. Water was selected as the third reference fluid because of the existence of the accurate Keenan and Keyes equation of state. Interesting and useful results may result if a different fluid were used as the third reference fluid. An alcohol, such as ethanol, would be a logical choice.

APPENDICES

APPENDIX A

Radii of Gyration and Acentric Factors of
Eighty Nonpolar Fluids Used in Third-Parameter Correlation

Radii of Gyration and Acentric Factors for 80 Nonpolar Fluids

<u>FLUID</u>	<u>RADIUS OF GYRATION</u>	<u>ACENTRIC FACTOR</u>
zero	0.0000	0.000
argon	0.000	-0.004
nitrogen	0.5471	0.040
oxygen	0.6037	0.021
methane	1.1234	0.008
ethene	1.5382	0.085
ethane	1.8314	0.098
propene	2.2283	0.148
propane	2.4255	0.152
trans-2-butene	2.7123	0.214
1-butene	2.7458	0.187
1,2-butadiene	2.7497	0.255
cis-2-butene	2.7765	0.202
2-methylpropene	2.8281	0.190
n-butane	2.8885	0.193
2-methylpropane	2.8962	0.176
benzene	3.0037	0.212
2,2-dimethylpropane	3.1530	0.197
1-pentene	3.1956	0.245
2-methyl-1-butene	3.2239	0.232
2-methyl-2-butene	3.2301	0.285
cyclohexane	3.2605	0.213
cis-2-pentene	3.2763	0.240
trans-2-pentene	3.2826	0.237
2-methylbutane	3.3130	0.227
n-pentane	3.3850	0.251
methylbenzene	3.4431	0.257
2,2-dimethylbutane	3.4846	0.231
2,3-dimethylbutane	3.5209	0.247
1-hexene	3.6472	0.285
3-methylpentane	3.6797	0.275
2,2,3-trimethylbutane	3.6960	0.251
trans-2-hexene	3.6964	0.242
methylcyclohexane	3.7467	0.233
1,2-dimethylbenzene	3.7889	0.314
3,3-dimethylpentane	3.7952	0.270
1,4-dimethylbenzene	3.7962	0.324
2-methylpentane	3.8090	0.279
n-hexane	3.8120	0.296
ethylbenzene	3.8211	0.301

1,3-dimethylbenzene	3.8966	0.331
2,3-dimethylpentane	3.9210	0.299
2,4-dimethylpentane	3.9634	0.306
2,2-dimethylpentane	4.0001	0.289
2,3,3-trimethylpentane	4.0859	0.290
1-heptene	4.0971	0.358
3-methylhexane	4.1454	0.324
2,2,3,3-tetramethylpentane	4.1556	0.279
2,2,3-trimethylpentane	4.1618	0.297
2,2,4-trimethylpentane	4.1714	0.303
isopropylbenzene	4.1870	0.335
2,3,4-trimethylpentane	4.2052	0.317
n-heptane	4.2665	0.351
2-methylhexane	4.2779	0.330
3,3-dimethylhexane	4.3197	0.321
2,4-dimethylhexane	4.3463	0.343
3,4-dimethylhexane	4.4000	0.338
2,3-dimethylhexane	4.4084	0.346
2,2-dimethylhexane	4.4956	0.338
1-octene	4.5342	0.386
4-methylheptane	4.5581	0.369
3-methylheptane	4.5932	0.369
2,5-dimethylhexane	4.5932	0.352
n-octane	4.6804	0.394
2-methylheptane	4.7401	0.378
1-nonene	4.9687	0.430
n-nonane	5.1263	0.444
1-decene	5.4017	0.491
n-decane	5.5390	0.490
1-undecene	5.8389	0.518
n-undecane	5.9867	0.535
1-dodecene	6.2966	0.558
n-dodecane	6.4321	0.562
1-tridecene	6.7514	0.598
1-tetradecene	7.2244	0.644
n-tetradecane	7.3578	0.679
1-pentadecene	7.6969	0.682
n-pentadecane	7.8387	0.706
1-hexadecene	8.1872	0.721
n-hexadecane	8.3180	0.742

APPENDIX B

Program Listing for the Commodore 64

```

10 REM PURE.1J
20 R=82.057
30 DEF FNVOL(X)=X*TR/PR
40 DEF FNALPHA(Z)=-7.7062E-4+0.0330285*Z+0.015056*Z^2-9.9966E-4*Z^3
60 DEF FNCOMPRS(X)=PR*X/TR
70 A1=0:A2=.3978:A3=.006053:T3=647.286:P3=218.0135:MOL=18.015
80 ROC=MOLW*P3/R/T3
150 DIM P(2,12),A(10,7)
160 FORJ=1TO2:FORI=1TO12:READ P(J,I):NEXT I,J
170 FORJ=1TO7:FORI=1TO10:READ A(I,J):NEXT I,J
180 B(0)=1000/T3:B(1)=B(0):C(1)=.634
190 FORJ=2TO7:B(J)=2.5:C(J)=1:NEXT J
200 REM
220 OPEN4,4,4
260 PRINT"NAME":INPUT NA$
270 PRINT"MOL WT":INPUT MW
360 PRINT"TC(K)":INPUT TC
370 PRINT"PC(ATM)":INPUT PC
380 PRINT"RADIUS OF GYRATION(ANG)":INPUT RG
390 PRINT"[P]OLAR OR [N]ONPOLAR:"
400 GET NP$:IFNP$=""THEN400
405 IFNP$="N"GOTO450
410 IFNP$="P"THEN420
415 GOTO390
420 PRINT"LIQ DENSITY (G/CC)":INPUT LD
430 PRINT"T DENSITY (K)":INPUT TD
435 PRINT"P DENSITY (ATM)":INPUT PD
436 PRINT"HOW DO YOU WANT HB CALCULATED? (HV,TB,LD)":INPUT HB$
437 IF HB$<>"HV"ANDHB$<>"TB"ANDHB$<>"LD"GOTO 436
438 IF HB$="LD" GOTO 450
440 PRINT "NORM BOILING PT (K)":INPUT TB
441 IF HB$="TB" GOTO 450
445 PRINT"HV (J/MOL)":INPUT HV
450 PRINT#4,"NAME: ";NA$
455 PRINT#4,"MOLWT: ";MW
460 PRINT#4,"TC(K): ";TC;"PC(ATM): ";PC
470 PRINT#4,"RG(A): ";RG
475 ALPHA=FNALPHA(RG)
480 IF NP$="N" GOTO 560
490 PRINT#4,"LIQ DENS(G/CC): ";LD;"T DENS(K): ";TD;"P DENS(ATM) ";PD
491 IF HB$="LD" GOTO 500
492 PRINT#4,"TB(K): ";TB
493 IF HB$<>"HV" GOTO 500:PRINT#4,"HV (J/MOL): ";HV
495 PRINT#4,"HV: ";HV
500 TR=TD/TC:VO=MW/LD:ZL=VO*PD/R/TD:P=PD:PR=PD/PC:KQ=1
505 PH$="L":GOTO 620
510 BETA=(ZL-Z1-AL*Z2)/Z3
511 IF HB$="LD" THEN HB=BE:GOTO550
515 TR=TB/TC:P=1.0:PR=1/PC
516 IF HB$="TB" GOTO 520
517 HV=HV/8.314/TC:KQ=2:GOTO525
520 HV=1.024*8.314*TC*TR*LOG(PC)*(1-1/PC)/(1-TR)
521 PRINT#4,"HV CALCULATED FROM TB: ";HV:HV=HV/TC/8.314:KQ=2
525 PH$="V":GOTO 620

```

```

530 Q1=H1:Q2=H2:Q3=H3:KQ=3
535 PH$="L":GOTO 620
540 G1=H1:G2=H2:G3=H3
545 HBETA=(HV-((Q1-G1)+AL*(Q2-G2)))/(Q3-G3)
550 PRINT#4,"ALPHA=";ALPHA;"BETA RATIO=";BETA;"HBETA RATIO=";HBETA
555 KQ=0
560 IF NP$="P" THEN GOTO 562
561 PRINT#4,"ALPHA=";ALPHA
562 PRINT#4
563 REM***** INPUT RUN CONDITIONS *****
570 PRINT"INPUT T(K), P(ATM), AND PHASE(V,L,U):":INPUT T,P,PH$
590 TR=T/TC:PR=P/PC
600 PRINT"TR=";TR:PRINT"PR=";PR:PRINT"PHASE=";PH$
610 PRINT#4,"T(K)=";T;"P(ATM)=";P:PRINT#4,"TR=";TR;"PR=";PR;"PHASE=";PH$
620 PF=PR:GOSUB 4000
630 PRINT#4
670 REM
690 REM ITERATIONS ON REFERENCE FLUID EOS'S
700 IFNP$="N"THENNR=2
710 IFNP$="P"THENNR=3
720 TAU=1000/T3/TR
730 FOR I=1TONR
740 PRINT"REFERENCE FLUID ";I
750 REM LINES 750-1115 CONTROL WHICH EOS IS BEING SOLVED
755 PR=PF
760 IF I<>1 THEN GOTO 880
765 IF JO<>1 THEN GOTO 815
770 FOR IN=1TO2
775 IF IN=1 THEN PR=V3
780 IF IN=2 THEN PR=V3+0.001*V3
782 IF IN=2 AND TR>0.99 THEN PR=V3+0.0001*V3
785 IF IN=1 THEN GOSUB 5000
790 GOSUB 2000
795 O(IN)=Z
800 NEXT IN
805 IF TR<=.99 THEN Z=(PF-V3)*(O(2)-O(1))/(.001*V3)+O(1)
807 IF TR>.99 THEN Z=(PF-V3)*(O(2)-O(1))/(.0001*V3)+O(1)
810 Z(1)=Z:GOTO 1120
815 IF JO<>2 THEN GOTO 865
820 FOR IN=1 TO 2
825 IF IN=1 THEN PR=V3
830 IF IN=2 THEN PR=V3-.001*V3
832 IF IN=2 AND TR>0.99 THEN PR=V3-0.0001*V3
835 IF IN=1 THEN GOSUB 3000
840 GOSUB 2000
845 O(IN)=Z
850 NEXT IN
855 IF TR<=.99 THEN Z=(PF-V3)*(O(2)-O(1))/(.001*V3)+O(1)
857 IF TR>.99 THEN Z=(PF-V3)*(O(2)-O(1))/(.0001*V3)+O(1)
860 Z(1)=Z:GOTO 1120
865 IF PF<=1.0 AND PH$="L" THEN PR=V3:GOSUB 3000:GOTO 867
866 GOTO 869
867 Z=Z*PF/PR:PR=PF:GOSUB 2000
868 Z(1)=Z:GOTO 1120
869 GOSUB 5000
871 GOSUB 2000

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875 Z(1)=Z:GOTO 1120
880 IF I<>2 THEN GOTO 1000
885 IF J1<>1 THEN GOTO 935
890 FOR IN=1 TO 2
895 IF IN=1 THEN PR=V4
900 IF IN=2 THEN PR=0.001*V4+V4
902 IF IN=2 AND TR>.99 THEN PR=0.0001*V4+V4
905 IF IN=1 THEN GOSUB 5000
910 GOSUB 2000
915 O(IN)=Z
920 NEXT IN
925 IF TR<=.99 THEN Z=(PF-V4)*(O(2)-O(1))/(.001*V4)+O(1)
927 IF TR>.99 THEN Z=(PF-V4)*(O(2)-O(1))/(.0001*V4)+O(1)
930 Z(2)=Z:GOTO 1120
935 IF J1<>2 THEN GOTO 985
940 FOR IN=1 TO 2
945 IF IN=1 THEN PR=V4
950 IF IN=2 THEN PR=V4-.001*V4
952 IF IN=2 AND TR>.99 THEN PR=V4-.0001*V4
955 IF IN=1 THEN GOSUB 3000
960 GOSUB 2000
965 O(IN)=Z
970 NEXT IN
975 IF TR<=.99 THEN Z=(PF-V4)*(O(2)-O(1))/(-.001*V4)+O(1)
977 IF TR>.99 THEN Z=(PF-V4)*(O(2)-O(1))/(-.0001*V4)+O(1)
980 Z(2)=Z:GOTO 1120
985 IF PF<=1.0 AND PH$="L" THEN PR=V4:GOSUB 3000:GOTO 987
986 GOTO 989
987 Z=Z*PF/PR:PR=PF:GOSUB 2000
988 Z(2)=Z:GOTO 1120
989 GOSUB 5000
990 GOSUB 2000
995 Z(2)=Z:GOTO 1120
1000 IF I<>3 THEN GOTO 1140
1005 IF J2<>1 THEN GOTO 1055
1010 IN=1:PR=V5:GOSUB 5000
1015 GOSUB 2000:O(1)=Z
1020 IN=2:PR=.001*V5+V5
1023 IF TR>.99 THEN PR=.0001*V5+V5
1030 GOSUB 2000
1035 O(2)=Z
1045 IF TR<=.99 THEN Z=(PF-V5)*(O(2)-O(1))/(.001*V5)+O(1)
1047 IF TR>.99 THEN Z=(PF-V5)*(O(2)-O(1))/(.0001*V5)+O(1)
1050 Z(3)=Z:GOTO 1120
1055 IF J2<>2 THEN GOTO 1105
1060 IN=1:PR=V5
1065 GOSUB 3000
1070 GOSUB 2000:O(1)=Z
1075 IN=2:PR=V5-.001*V5
1077 IF TR>.99 THEN PR=V5-.0001*V5
1080 GOSUB 2000
1085 O(2)=Z
1095 IF TR<=.99 THEN Z=(PF-V5)*(O(2)-O(1))/(-.001*V5)+O(1)
1097 IF TR>.99 THEN Z=(PF-V5)*(O(2)-O(1))/(-.0001*V5)+O(1)
1100 Z(3)=Z:GOTO 1120
1105 IF PF<=1.0 AND PH$="L" THEN PR=V5:GOSUB 3000:GOTO 1107
1106 GOTO 1109

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1107 Z=Z*PF/PR:PR=PF:GOSUB 2000
1108 Z(3)=Z:GOTO 1120
1109 GOSUB 5000
1110 GOSUB 2000
1115 Z(3)=Z
1120 REM Z HAS BEEN CALCULATED
1125 PR=PF:P=PR*PC
1127 IF I=3 THEN RHO=PR*ROC/TR/Z
1130 VR=FVOL(Z)
1135 GOSUB 1440
1140 NEXT I
1145 REM DEVIATION FUNCTIONS
1150 Z1=Z(1):Z2=(Z(2)-Z(1))/A2:Z3=Z(3)-(Z(1)+A3*Z2):IFKQ=1THEN510
1160 PRINT"DEVIATION FUNCTIONS: Z1=";Z1;"Z2=";Z2;"Z3=";Z3
1165 PRINT#4,"DEVIATION FUNCTIONS: Z1=";Z1;"Z2=";Z2;"Z3=";Z3
1170 H1=H(1):H2=(H(2)-H(1))/A2:H3=H(3)-(H(1)+A3*H2):IFKQ=2THEN530
1175 IFKQ=3THEN540
1180 IFNP$="N"THENH=H1+ALPHA*H2
1182 IFNP$="P"THENH=H1+ALPHA*H2+HBETA*H3
1183 PRINT#4,"1183 H";H
1185 PRINT"H1=";H1;"H2=";H2;"H3=";H3:H=H*8.314*TC
1187 PRINT#4,"H1=";H1;"H2=";H2;"H3=";H3
1188 PRINT#4,"1188 H";H
1190 S1=S(1):S2=(S(2)-S(1))/A2:S3=S(3)-(S(1)+S2*A3)
1195 IFNP$="N"THENS=S1+ALPHA*S2
1197 IFNP$="P"THENS=S1+S2*ALPHA+S3*HBETA
1200 S=S*8.314
1210 PRINT"S1=";S1;"S2=";S2;"S3=";S3
1220 PRINT#4,"S1=";S1;"S2=";S2;"S3=";S3
1240 REM
1260 PRINT"T=";T;"K P=";P;"ATM"
1270 IFNP$="N"THENZ=Z1+ALPHA*Z2
1272 IFNP$="P"THENZ=Z1+ALPHA*Z2+BETA*Z3
1280 PRINT"Z=";Z
1285 G(1)=H1/TR-S1:G(2)=H2/TR-S2:G(3)=H3/TR-S3
1286 PRINT#4,"PHI=";G(1);G(2);G(3)
1290 Q1=H/8.314/T:Q2=S/8.314
1310 PHI=EXP(Q1-Q2)
1320 V=Z*R*T/P
1322 VG=V/MW
1325 PRINT"V=";V;"CC/MOL"
1330 PRINT"H=";H/1000;"KJ/MOL"
1340 PRINT"S=";S;"J/MOL K"
1350 PRINT"PHI=";PHI
1355 PRINT#4,"Z=";Z
1360 PRINT#4,"V=";V;"CC/MOL"
1362 PRINT#4,"VG=";VG;"CC/G"
1365 PRINT#4,"H=";H/1000;"KJ/MOL"
1370 PRINT#4,"S=";S;"J/MOL K"
1375 PRINT#4,"PHI=";PHI
1380 PRINT#4
1410 CLOSE4
1430 END
1440 REM DEPARTURE FUNCTIONS
1450 ON I GOTO 1460,1460,1540
1460 ARG=P(I,12)/VR^2

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1470 E=P(I,8)*(P(I,11)+1-(P(I,11)+1+ARG)*EXP(-ARG))/(2*TR^3*P(I,12))
1480 EE=Z-1-(P(I,2)+2*P(I,3)/TR+3*P(I,4)/TR^2)/TR/VR
1490 EE=EE-(P(I,6)-3*P(I,7)/TR^2)/(2*TR*VR^2)+P(I,10)/(5*TR*VR^5)
1500 H(I)=-(-TR*(EE+3*E))
1510 EE=(P(I,1)+P(I,3)/TR^2+2*P(I,4)/TR^3)/VR+P(I,9)/(5*VR^5)
1515 EE=EE+(P(I,5)-2*P(I,7)/TR^3)/(2*VR^2)
1520 S(I)=LOG(Z)-EE+2*E
1530 RETURN
1540 TW=T3*TR
1550 DT=0
1551 FOR J=2 TO 7
1552 S1=0:S2=0:S3=0
1553 TX=RHO-1:IF J=1 THEN TX=RHO-0.634
1554 FOR II=1 TO 8
1555 S1=S1+A(II,J)*TX^(II-1)
1556 NEXT II
1557 EW=EXP(-4.8*RHO)
1558 S1=S1+EW*(A(9,J)+A(10,J)*RHO)
1559 TY=TAU-B(0)
1560 TX=(TAU-2.5)^(J-3)
1561 TZ=(TAU-2.5)
1562 DT=DT+S1*TX*(TZ+(J-2)*TY)
1563 NEXT J
1600 H(3)=(RHO*TAU*DT+RHO*Q+RHO*RHO*DQ)*TR
1610 S(3)=LOG(Z(3))-RHO*Q+RHO*TAU*DT
1630 RETURN
2000 REM EQUATIONS OF STATE ITERATIONS
2010 ITER=0
2020 ITER=ITER+1
2030 ON I GOTO 2380,2380,2520
2380 REM MBWR EOS
2390 BB=(PR/TR)*(P(I,1)-P(I,2)/TR-P(I,3)/TR^2-P(I,4)/TR^3)
2400 CB=(PR/TR)^2*(P(I,5)-P(I,6)/TR+P(I,7)/TR^3)
2410 DB=(PR/TR)^5*(P(I,9)+P(I,10)/TR)
2430 GA=(PR/TR)^2*P(I,12)
2440 C4=PR^2/TR^5*P(I,8)
2450 BA=P(I,11)
2460 F=PR*(1/Z+BB/Z/Z+CB/(Z^3)+DB/(Z^6)+C4/(Z^3)*(BA+GA/Z/Z)*EXP(-GA/Z/Z)-1)
2470 F1=-((1/Z/Z+2*BB/(Z^3)+3*CB/(Z^4)+6*DB/(Z^7))
2480 F2=C4*EXP(-GA/Z/Z)*(1/(Z^8)*(2*BA*GA*Z*Z+2*GA*GA-3*BA*Z^4-5*GA*Z*Z))
2490 FP=PR*(F1+F2)
2500 GOTO 2720
2520 REM NEWTON-RAPHSON FOR 3RD REFERENCE FLUID
2600 RHO=PR*ROC/(TR*Z)
2610 FOR J=1 TO 7
2611 S1=0:S2=0:S3=0
2615 TX=RHO-1:IF J=1 THEN TX=RHO-0.634
2620 FOR II=1 TO 8
2640 S1=S1+A(II,J)*TX^(II-1)
2641 IF II<2 GOTO 2646
2642 S2=S2+A(II,J)*TX^(II-2)*(II-1)
2643 IF II<3 GOTO 2646
2644 S3=S3+A(II,J)*TX^(II-3)*(II-2)*(II-1)
2646 NEXT II
2647 EW=EXP(-4.8*RHO)
2648 S1=S1+EW*(A(9,J)+A(10,J)*RHO)
2649 S2=S2+EW*(A(10,J)-4.8*(A(9,J)+A(10,J)*RHO))

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2650 S3=S3+EW*4.8*(4.8*A(9,J)+A(10,J)*(4.8*RHO-2))
2657 TY=TAU-B(0)
2658 TG=(TAU-2.5)^(J-2)
2660 IF J=1 THEN Q=S1:DQ=S2:G=S3:GOTO 2670
2662 Q=Q+S1*TY*TG
2664 DQ=DQ+S2*TY*TG
2666 G=G+S3*TY*TG
2670 NEXT J
2672 ZQ=1+RHO*Q+RHO*RHO*DQ
2690 F=RHO*R/MOL*TR*T3*ZQ-PR*P3
2710 FP=R/MOL*TR*T3*(ZQ+RHO*(Q+RHO*(3*DQ+RHO*G)))
2720 DUF=F/FP:EPS=ABS(DUF):Z=Z-DUF:RD=RHO:RHO=RHO-DUF
2721 IF I<3 GOTO 2724
2722 IF ABS(DUF)/RD>.1 THEN RHO=RD-.1*DUF
2723 Z=PR*ROC/RHO/TR:GOTO 2725
2724 ZT=Z+DUF:IF ABS(DUF)/ZT>.1 THEN Z=ZT-.1*DUF
2725 PRINT ITER;"Z=";Z
2730 IF ITER>100 THEN PRINT#4,"NO CONVERGENCE-ABORTED":GOTO1410
2735 IF I<3 GOTO 2745
2740 IF EPS>.00001*RHO THEN 2020
2741 GOTO 2760
2745 IF EPS>.00001*Z THEN 2020
2760 RETURN
3000 REM INITIAL ESTIMATE FOR SAT'D LIQUID
3005 REM THIS ROUTINE USES THE GUNN AND YAMADA METHOD FOR SAT'D LIQ VOLUMES
3006 REM ALSO USED FOR LIQUIDS BELOW PR=1.0
3010 IF TR>.86GOTO3030
3020 VV=.33593-.33953*TR+1.51941*TR*TR-2.02512*TR^3+1.11422*TR^4:GOTO 3070
3030 IF TR>=1.0GOTO 3050
3040 VV=1+.56457*SQR(1-TR)*LOG(1-TR)-.50879*(1-TR)-.91534*(1-TR)^2:GOTO3070
3050 IF TR=1.00 THEN VV=1.0:GOTO3070
3060 IF TR>1.00 THEN PRINT"TR>1.00 IN SAT'D LIQUID INIT ESTIMATE":END
3070 IF I=1 THEN Z=PR/TR*.29076*VV:RETURN
3080 IF I=2THENZ=PR/TR*.26328*VV*(1-.3978*(.29607-.09045*TR-.04842*TR^2)):RETURN
3090 IF I=3THENZ=PR/TR*.21469*VV*(1-.344*(.29607-.09045*TR-.04842*TR^2)):RETURN
3100 PRINT"I <> 1, 2, OR 3":END
4000 REM PHASE CALCULATIONS
4002 J0=0:J1=0:J2=0
4005 IF PR>1.0 OR TR>=1.0 THEN GOTO 4320
4010 V0=5.92714-6.09648/TR-1.28862*LOG(TR)+0.169347*TR^6
4020 V1=11.99431-12.33697/TR-6.647821*LOG(TR)+.3426963*TR^6
4030 V2=9.76059-10.05808/TR-4.15481*LOG(TR)+.298975*TR^6
4070 IF PH$="L" OR PH$="V" THENGOTO4150
4080 REM CALCULATE PHASE FOR UNKNOWN
4090 VF=V0+A1/A2*(V1-V0)+HB*(V2-(V0+A3/A2*(V1-V0)))
4100 VF=EXP(VF)
4110 REM: COMPARE PRESSURES
4120 CH=VF-PR
4130 IFCH>0THENPH$="V":PRINT#4,"CALCULATED PHASE: ";PH$
4140 IFCH<0THENPH$="L":PRINT#4,"CALCULATED PHASE: ";PH$
4150 REM NOW WE KNOW THE PHASE AND FIND WHICH IF ANY REF'S ARE IN 2-PHASE
4152 V3=EXP(V0)
4154 V4=EXP(V1)
4156 V5=EXP(V2)
4160 IF PH$="L" THEN GOTO 4240
4165 REM VAPOR: COMPARE REFERENCE VAPOR PRESSURES TO GIVEN PRESSURE

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4170 IF V3>PR THEN GOTO 4190
4180 IF V3<=PR THEN J0=1
4190 IF V4>PR THEN GOTO 4210
4200 IF V4<=PR THEN J1=1
4210 IF V5>PR THEN GOTO 4230
4220 IF V5<=PR THEN J2=1
4230 RETURN
4240 REM LIQUID: COMPARE REFERENCE VAPOR PRESSURES TO GIVEN PRESSURE
4250 IF V3<PR THEN GOTO 4270
4260 IF V3>=PR THEN J0=2
4270 IF V4<PR THEN GOTO 4290
4280 IF V4>=PR THEN J1=2
4290 IF V5<PR THEN GOTO 4310
4300 IF V5>=PR THEN J2=2
4310 RETURN
4320 IF TR>=1.0 THEN PH$="V":RETURN
4330 IF TR<1.0 THEN PH$="L":RETURN
5000 REM PENG-ROBINSON EOS FOR CALCULATING INITIAL ESTIMATES
5010 REM USED FOR ALL VAPOR INITIAL ESTIMATES AND LIQUID ESTIMATES ABOVE PR=1
5020 REM FOR LIQUIDS BELOW PR=1 THE GUNN-YAMADA METHOD IS EMPLOYED
5190 T(1)=184.0:PP(1)=54.00:T(2)=568.8:PP(2)=24.5:T(3)=647.3:PP(3)=217.6
5200 A7=.45724*R*R*T(I)*T(I)/PP(I)
5210 BQ(I)=.07780*R*T(I)/PP(I)
5400 TT=TR*T(I):P=PR*PP(I)
5410 ON I GOTO 5430,5440,5450
5430 A=A7*(1+0.37464*(1-SQR(TR)))^2*P/R/R/TT/TT:GOTO 5460
5440 A=A7*(1+0.94039*(1-SQR(TR)))^2*P/R/R/TT/TT:GOTO 5460
5450 A=A7*(1+0.87324*(1-SQR(TR)))^2*P/R/R/TT/TT
5460 B=BQ(I)*P/R/TT
5470 C1=1-B
5480 C2=A-3*B*B-2*B
5490 C3=A*B-B*B-B^3
5500 I1=-C1:I4=I1/3:I2=C2:I3=-C3:LA=I2-I1*I4:TZ=2.0*I4*I4-I2*I4+I3
5510 I5=TZ/2.0:K5=LA/3.0:K6=K5*K5*K5:I6=I5*I5:EQ=K6+I6
5520 IF EQ<0.0 GOTO 5650
5530 IF EQ>0.0 GOTO 5580
5540 M1=0.0:G1=SQR(-K5)
5550 IF TZ<=0.0 GOTO 5570
5560 ZZ(1)=-2.0*G1-I4:ZZ(2)=G1-I4:ZZ(3)=ZZ(2):GOTO 5710
5570 ZZ(1)=2.0*G1-I4:ZZ(2)=-G1-I4:ZZ(3)=ZZ(2):GOTO 5710
5580 M1=1.0:E1=SQR(EQ):TU=-I5:RU=TU+E1:SC=TU-E1:SR=1.000:SZ=1.000
5590 IF RU>0.0 GOTO 5610
5600 SR=-1.0
5610 IF SC>0.0 GOTO 5630
5620 SZ=-1.0
5630 R1=SR*(SR*RU)^.3333:SQ=SZ*(SZ*SC)^.3333
5640 ZZ(1)=R1+SQ-I4:ZZ(2)=-(R1+SQ)/2.0-I4:ZZ(3)=0.86602540*(R1-SQ):GOTO 5710
5650 M1=-1.0:Q1=I6/K6:R2=SQR(-Q1)
5660 IF TZ<0.0 GOTO 5680
5665 IF SQR(1.0-R2*R2)=0 THEN EQ=0:GOTO 5540
5670 PI=(1.5707963+ATN(R2/SQR(1.0-R2*R2)))/3.0:GOTO 5690
5680 PI=ATN(SQR(1.0-R2*R2)/R2)/3.0
5690 FT=2.0*SQR(-K5):ZZ(1)=FT*COS(PI)-I4:ZZ(2)=FT*COS(PI+2.0943951)-I4
5700 ZZ(3)=FT*COS(PI+4.1887902)-I4
5710 REM CONTINUE
5730 IF M1=0 THEN Z=ZZ(1):RETURN
5740 IF M1=1 THEN Z=ZZ(1):IF PF>=1 AND TR<1 THEN GOTO 5900

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5745 IF M1=1 THEN RETURN
5750 IF M1=-1.0 AND PH$="L" THEN GOTO 5790
5760 REM M1=-1.0 AND PH$="V"
5770 Z=ZZ(1): IF ZZ(2)>Z THEN Z=ZZ(2)
5780 IF ZZ(3)>Z THEN Z=ZZ(3)
5785 RETURN
5790 REM M1=-1.0 AND PH$="L"
5800 Z=ZZ(1): IF ZZ(2)<Z THEN Z=ZZ(2)
5810 IF ZZ(3)<Z THEN Z=ZZ(3)
5815 RETURN
5900 REM COMPARE PENG-ROB ROOT TO GUNN-YAM ROOT AND TAKE SMALLER FOR PR>=1.TR<1
5910 GOSUB 3000
5920 IF ZZ(1)<Z THEN Z=ZZ(1)
5930 RETURN
6160 DATA .1181193,.265728,.15479,.030323,.0236744,.0186984,0,.042724
6170 DATA 1.55488E-5,6.23689E-5,.65392,.060167
6180 DATA .2026579,.331511,.027655,.203488,.0313385,.0503618,.016901
6190 DATA .041577,4.8736E-5,7.40336E-6,1.226,.03754
6200 DATA 29.492937,-132.13917,274.64632,-360.93828,342.18431,-244.50042
6205 DATA 155.18535,5.9728487,-410.30848,-416.0586
6210 DATA -5.198586,7.7779182,-33.301902,-16.254622,-177.31074,127.48742
6215 DATA 137.46153,155.97836,337.3118,-209.88866
6220 DATA 6.8335354,-26.149751,65.326396,-26.181978,0,0,0,0,-137.46618
6225 DATA -733.96848
6230 DATA -.1564104,-.72546108,-9.2734289,4.312584,0,0,0,0,6.7874983,10.401717
6240 DATA -6.3972405,26.409282,-47.740374,56.32313,0,0,0,0,136.87317,645.8188
6250 DATA -3.9661401,15.453061,-29.142470,29.568796,0,0,0,0,79.84797,399.1757
6260 DATA -.69048554,2.7407416,-5.102807,3.9636085,0,0,0,0,13.041253,71.531353
READY.
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