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A NEW GENERALIZED EQUATION OF STATE FOR POLAR AND NONPOLAR PURE FLUIDS

The University of Oklahoma PH.D. 1983

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THE UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

A NEW GENERALIZED EQUATION OF STATE FOR POLAR AND NONPOLAR PURE FLUIDS

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

degree of

DOCTOR OF PHILOSOPHY

BY

MAHMOUD A. MAGSOUD KHAN

Norman, Oklahoma

1983

A NEW GENERALIZED EQUATION OF STATE FOR

POLAR AND NONPOLAR PURE FLUIDS

APPROVED BY

Lloyd L. Lee

K E Starling

Carl E Locke

J M Townsend

John M. Radovich

Sherrill D Christian

DISSERTATION COMMITTEE



In The Name Of God,
Most Gracious And Most Merciful

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ABSTRACT

A new equation of state based on the concept of perturbed hard chain theory and the hard-convex body equation of state has been successfully developed for nonpolar compounds. The equation can predict the thermodynamic properties (density, enthalpy departure, and vapor pressure) of a wide range of pure fluids from small, spherical (argon-like) molecules to large structurally complex molecules. The equation employs three parameters; the shape, size and energy parameters for nonpolar compounds. For normal paraffins, the size parameter (hard-core volume) is related to the measurable Van der Waals volume given by Bondi (1968). For most other compounds, it is related to the critical volume. The shape parameter values reflect the structure and degree of acentricity of the compound of interest. The equation has been extended to polar and associating compounds by using the effective angle-averaged potential model. For polar compounds, a fourth parameter is required. The equation has been extensively tested for polar (dipolar and quadrupolar) and hydrogen-bonding compounds. The results show that the equation has promise for use for systems occuring in the natural gas, petroleum and synfuels industries.

A NEW GENERALIZED EQUATION OF STATE FOR POLAR AND NONPOLAR PURE FLUIDS

CHAPTER I

INTRODUCTION

An equation of state is a relation between pressure, density (or volume), and temperature. Most equations of state are pressure explicit, i.e., $P=f(\rho, T)$, although for many thermodynamic calculations a density explicit equation, $\rho = f(P,T)$, is preferable. Correlations of vapor liquid equilibrium data, and estimation of related thermodynamic properties can be accomplished by means of an equation of state. Thus, equations of state have obtained great importance for scientific research. A good equation of state should have the following characteristics:

1- It should be valid in a large range of densities and temperatures.

2- It should have as few adjustable parameters as

possible, and these parameters should have a physical meaning. This is desirable, as each adjustable parameter must be determined from experimental data. The values of parameters with a physical meaning can more easily be compared to values of other substances or to values obtained by independent measurements (e.g. covolumes from X-ray measurements of molecular diameters).

3- It should be applicable to a variety of chemical substances, with acceptable levels of accuracies, instead of just being limited to a certain class of fluids.

Over the years, several attempts have been made to describe the thermodynamic behavior of real fluids via equations of state. These equations of state have achieved varying degrees of success, enabling one to divide them into three separate classes. In the first class, one has the equations of state which are cubic in density. A few of the popular density-cubic equations of state are the van der Waals equation(1873), the Redlich-Kwong equation(1949), the Soave-Redlich-Kwong equation(1972), the Peng-Robinson equation(1976), and the Kumar-Starling equation(1982). This type of equations give reasonable description of the thermodynamic behavior of real fluids, with each equation

being more accurate in the chronological order of appearance in the literature. The second class of equations of state is those which are non-cubic in density and provide a good description of the thermodynamic behavior of real fluids for all fluid states. The Beattie-Bridgeman equation(1928), the Benedict-Webb-Rubin (BWR) equation(1940) and the Modified BWR equation(1973) are examples of this class of equations. The third class is the equations of state which are highly constrained for each specific fluid. Examples of this class of equations are the Keenan and Keyes equation of state for water (1969), the Goodwin equation of state for propane (1977), and the Ewers and Wagner equation of state for oxygen (1981). This class of equations give a highly accurate description of the specific real fluid behaviors.

This research presents the development of a new three parameter generalized equation of state for the accurate calculation of the thermodynamic properties (density, enthalpy departure and vapor pressure) of pure nonpolar fluids for the gaseous and liquid regions of reduced temperatures from 0.24 to 3.3 and reduced pressures to 480. This equation is of the perturbation type and is based on the empirical equation of state for argon developed by Twu

et al.(1980), but modified by employing the concepts of hard convex body (HCB) model and the hard-chain molecular theory for large, structural molecules. The constants for the temperature and density dependence of the equation of state are generalized using the experimental data for saturated hydrocarbons from ethane to normal decane. The development of the equation of state with a little review about the perturbation theory and hard convex body equations of state are discussed in chapter II. Prediction of the thermodynamic properties of different classes of fluids not used in the generalization is tested using the heavier normal paraffins, normal undecane to normal eicosane, and other types of hydrocarbons, unsaturated hydrocarbons and ring compounds. Nonhydrocarbons, hydrogen and nitrogen, were also tested. The use of the resultant equation of state has been extended to polar and associating pure fluids by applying the mean-potential model. This introduced a fourth parameter which was determined from the experimental PVT data for the fluid of interest. Results of these tests are given in chapter III. The values of the characteristic parameters for all compounds tested are also reported in chapter III.

CHAPTER II

DEVELOPMENT OF THE EQUATION OF STATE

The perturbation approach has been widely used in developing equations of state for prediction of the thermodynamic properties of anisotropic fluids. The spirit of the perturbation approach has also been employed semi empirically in the development of correlations for thermodynamic and transport properties. Pitzer (Pitzer et al., 1955; Pitzer and Curl, 1957) demonstrated that the compressibility factor and other thermodynamic properties can be adequately represented by a linear combination of two parts; the isotropic reference part and the perturbation part. Accordingly, the compressibility factor of a fluid is given by

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

where $Z^{(0)}$ is the compressibility factor of a monoatomic (spherical molecule) fluid and $Z^{(1)}$ represents the deviation of the compressibility factor of the real fluid from $Z^{(0)}$. The acentric factor, ω, is the characterization parameter

for the nonsphericity of the molecule. $Z^{(0)}$ and $Z^{(1)}$ are functions of reduced temperature and reduced pressure. Pitzer type correlations usually give a good prediction of the thermodynamic properties for normal fluids. This approach, however, has been proven inadequate when calculations are made in the critical region and for liquids at low temperatures (Lee and Kesler,1975). Since the acentric factor, ω, cannot completely reflect the molecular shape and the steric effect which become more important at high densities, the use of the the acentric factor as a characterization parameter and monoatomic fluids as reference make this approach hard to extend to large, structurally complex molecules in high density regions. One type of modification given by Lee and Kesler (1975) uses two reference systems instead of using only one reference. The Lee-Kesler correlation expresses the compressibility factor of any fluid in terms of the compressibility factor of a simple fluid, $Z^{(0)}$, and the compressibility factor of a reference fluid, $Z^{(r)}$, as follow;

$$Z = Z^{(0)} + \frac{\omega}{\omega^{(r)}} (Z^{(r)} - Z^{(0)}) \qquad (2)$$

Both $Z^{(0)}$ and $Z^{(r)}$, given by the same function form, have

been expressed by a modified BWR equation of state. Equation (2) can be applied to a wider range of compounds than equation (1). The second type of modification uses parameters other than the acentric factor to characterize the steric effect and the multipolar effect. Other characterization parameters, such as the orientation parameter, γ,(Starling et al., 1978) and the shape factor, ϕ, (Leland et al., 1962) for the steric effect and the Stiel polar factor (Reid, Prausnitz, and Sherwood, 1977) for polar effect, have been applied in the correlation of thermodynamic properties.

It is the intent of this work to use a structure parameter and a polar parameter to characterize the steric effect and polar effect, respectively. The structure parameter, α, used in this work was adopted from the recently developed hard-convex-body (HCB) equation of state given by Boublik (1981),

$$Z = 1 + \frac{y}{(1-y)} + \frac{3\alpha^* y}{(1-y)^2} + \frac{3\alpha^{*2} y^2 - \alpha^*(6\alpha^* - 5)y^3}{(1-y)^3} \qquad (3)$$

where y is the packing fraction defined as the volume occupied by the convex bodies per unit volume of the fluid.

Equation (3) reproduces spherocylinder hard convex body Monte Carlo data with values of hard-core length to breadth ratio up to 4 (or $\alpha^* = 1.8$). The structure parameter, α^*, in equation (3) is defined by

$$\alpha^* = \frac{\bar{R}\, S}{3\, \bar{V}} \tag{4}$$

where $\bar{R}$ is the radius of curvature, S is the surface area, and $\bar{V}$ is the hard-convex-body volume. For an α^* value equal to unity, equation (3) reduces to the Carnahan-Starling equation of state for hard sphere (1972). Equation (3) can be approximately represented by the hard-chain equation of state,

$$Z = 1 + \alpha^* \frac{4y - 2y^2}{(1 - y)^3} \tag{5}$$

Equation (5) gives the same compressibility factor as equation (3) in the range of $\alpha^* < 1.8$, (Figure 1). The form of equation (5) is similar to that of the hard-chain equation presented by Beret and Prausnitz (1975) except for the structure parameter, α^*. Instead of using the c-factor, the so-called degree-of-freedom parameter, equation (5) uses the structure parameter, α^*, which is defined by equation (4).

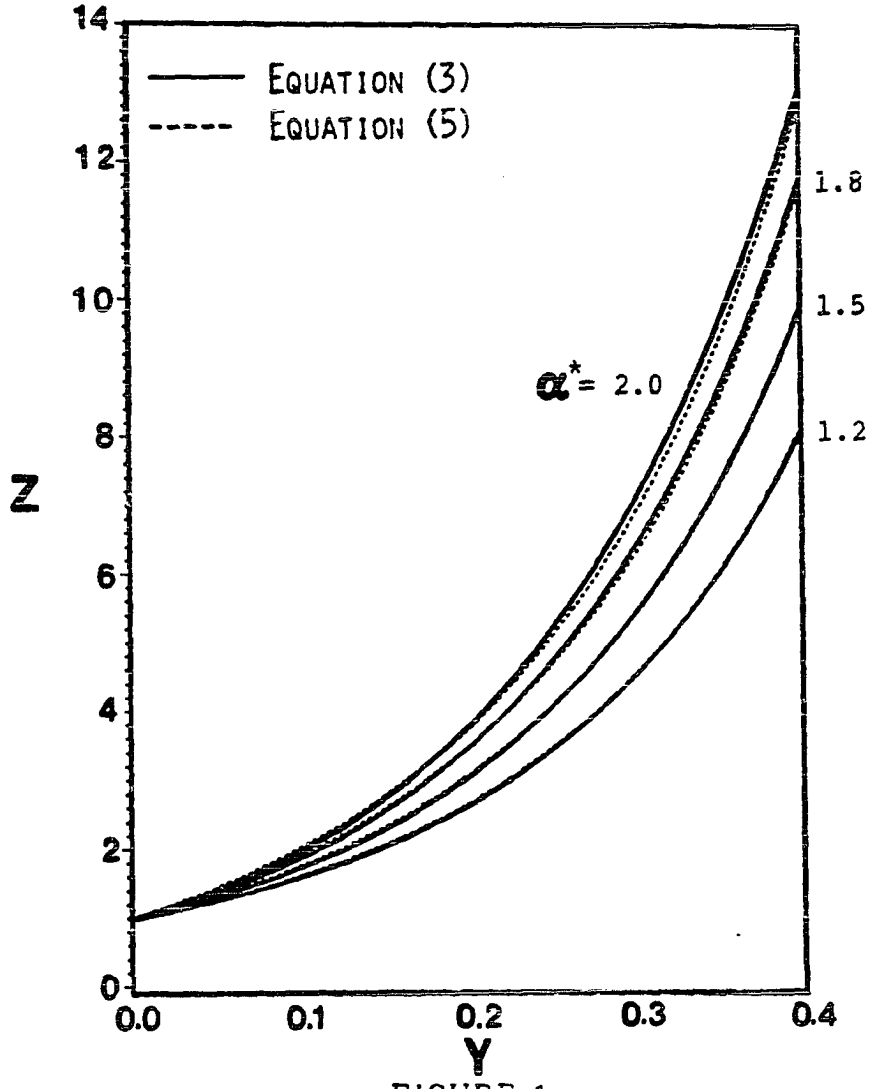


FIGURE 1.

PLOT OF Z BOUBLIK AND Z(EQN. 5) VERSUS REDUCED DENSITY FOR DIFFERENT α^* VALUES.

EQUATION OF STATE FOR NORMAL PARAFFINS:

It has been noted that equation (1) using monoatomic fluids as reference is very difficult to extend to large, complex molecules. In this work, we modeled our equation on equation (5) which accounts only for the repulsive force contribution. For soft-body, it is assumed that the equation of state can be expressed as

$$Z = 1 + \alpha (Z_{CONF.}^{(0)rep.} + Z_{CONF.}^{(0)att.}) \quad (6)$$

where $Z_{conf.}^{(0)rep.}$ and $Z_{conf.}^{(0)att.}$ are the configurational compressibility factor of the repulsive part and attractive part, respectively. Combining the repulsive and attractive parts into the total $Z_{conf.}^{(0)}$, equation (6) becomes

$$Z = 1 + \alpha Z_{CONF.}^{(0)} \quad (7)$$

where $Z_{conf.}^{(0)}$ is the configurational compressibility factor for spherical molecules. For $\alpha = 1$, equation (7) reduces to the equation of state for monoatomic fluids, i.e.,

$$Z = 1 + Z_{conf.}^{(0)} \quad (8)$$

Twu, Lee and Starling (1980) have fitted the constants in a temperature-density function chosen for equation (8) by using argon data (density and vapor pressure). This equation of state is capable of predicting the properties of simple fluids at low reduced temperatures (T_r=0.3) and high reduced pressures (P_r=132). In this work the constants of Twu-Lee-Starling correlation were modified using the molecular hard-core volume (V^*) as the reducing parameter for density, which is more realistic than using the Lennard-Jones(12-6) parameter, σ, for nonspherical molecules.

At high densities, the compressibility factor is sensitive to molecular shape and the deviation of equation (7) with real values increases with density for complex molecules. Therefore, a perturbation term, $Z^{(p)}_{conf.}$ was added. The final equation of state is

$$Z = 1 + \alpha Z^{(0)}_{CONF.} + (\alpha - 1) Z^{(p)}_{CONF.} \qquad (9)$$

The configurational compressibility factors of both the isotropic fluid, $Z^{(0)}_{conf.}$, and the perturbation contribution, $Z^{(p)}_{conf.}$, have been represented herein by the Strobridge form,

$$Z_{CONF.} = \left(A_1 + \frac{A_2}{T^*} + \frac{A_3}{T^{*2}} + \frac{A_4}{T^{*3}} + \frac{A_5}{T^{*5}} \right) \rho^* + \left(A_6 + \frac{A_7}{T^*} \right) \rho^{*2} + A_8 \rho^{*3} + \left(\frac{A_9}{T^{*3}} + \frac{A_{10}}{T^{*4}} + \frac{A_{11}}{T^{*5}} \right) \rho^{*2} \exp(-A_{16} \rho^{*2}) + \left(\frac{A_{12}}{T^{*3}} + \frac{A_{13}}{T^{*4}} + \frac{A_{14}}{T^{*5}} \right) \rho^{*4} \exp(-A_{16} \rho^{*2}) + \frac{A_{15}}{T^{*5}} \rho^{*5} \qquad (10)$$

Where $\rho^* = \rho V^*$ and $T^* = kT/\epsilon$

ϵ/k and V^* are the characteristic energy parameter and characteristic volume, respectively.

From thermodynamics, e.g. Balzhiser et al. (1972), the enthalpy departure is related to the equation of state by the following equation:

$$\frac{H - H^o}{RT} = Z - 1 - \int_0^\rho T \left[\frac{\partial Z}{\partial T}\right]_\rho \frac{\partial \rho}{\rho} \qquad (11)$$

and the entropy departure is related to the equation of state by:

$$\frac{S - S^o}{R} = -\ln(\rho RT) - \int_0^\rho \left[(Z-1) + T \left[\frac{\partial Z}{\partial T}\right]_\rho\right] \frac{\partial \rho}{\rho} \qquad (12)$$

When equation (9) is used, the expression for enthalpy departure has the form,

$$\frac{H-H^{o}}{RT} = (Z-1) + \left(\frac{A_2}{T^*} + \frac{2A_3}{T^{*2}} + \frac{3A_4}{T^{*3}} + \frac{5A_5}{T^{*5}}\right)\rho^* + 0.5\,\frac{A_7}{T^*}\,\rho^{*2} + \frac{1}{2A_{16}}\left(\frac{3A_9}{T^{*3}} + \frac{4A_{10}}{T^{*4}} + \frac{5A_{11}}{T^{*5}}\right)\left[1 - \exp(-A_{16}\rho^{*2})\right] + \frac{1}{2A_{16}^2}\left(\frac{3A_{12}}{T^{*3}} + \frac{4A_{13}}{T^{*4}} + \frac{5A_{14}}{T^{*5}}\right)\left[1 - (1 + A_{16}\rho^{*2})\exp(-A_{16}\rho^{*2})\right] + \frac{1}{5}\,\frac{A_{15}}{T^*}\,\rho^{*5} \tag{13}$$

and for entropy departure,

$$\frac{S-S^{o}}{R} = -\ln(\rho RT) - \left(A_1 - \frac{A_3}{T^{*2}} - \frac{2A_4}{T^{*3}} - \frac{4A_5}{T^{*5}}\right)\rho^* - \tfrac{1}{2}A_6\rho^{*2} + 1/3A_8\rho^{*3} + \frac{1}{2A_{16}}\left[\frac{2A_9}{T^{*3}} + \frac{3A_{10}}{T^{*4}} + \frac{4A_{11}}{T^{*5}}\right]\left[1 - \exp(-A_{16}\rho^{*2})\right] + \frac{1}{2A_{16}^2}\left[\frac{2A_{12}}{T^{*3}} + \frac{3A_{13}}{T^{*4}} + \frac{4A_{14}}{T^{*5}}\right]\left[1 - (1 + A_{16}\rho^{*2})\exp(-A_{16}\rho^{*2})\right] \tag{14}$$

where H^o, S^o are the ideal gas enthalpy and entropy at the same temperature of the fluid and unit pressure.

Corresponding to equation (9), all constants appearing in equations (10),(13), and (14), have been separated into two parts; isotropic and perturbation parts,

$$A_i = B_i^{(0)} + (\alpha - 1) B_i^{(p)} , \qquad i = 1,16 \tag{15}$$

where $B_i^{(0)}$ is the constant for $Z_{conf.}^{(0)}$ and $B_i^{(p)}$ is the constant for $Z_{conf.}^{(p)}$. The constants for $Z_{conf.}^{(0)}$ are converted from the Twu-Lee-Starling correlation(1980) and the constants for $Z_{conf.}^{(p)}$ are determined from the thermodynamic property data including vapor pressure, density, and enthalpy departure of normal paraffins (ethane to normal decane) with the parameters (ϵ/k , α, and V^*) fixed as linear functions of carbon number. The numerical values of the constants, $B_i^{(0)}$ and $B_i^{(p)}$, used in equation (9) are given in Table 2.1. The behavior of the universal functions $Z_{conf.}^{(0)}$ and $Z_{conf.}^{(p)}$ is shown in Figures 2 and 3. for different isotherms. It can be seen that $Z_{conf.}^{(p)}$ contributes only in the high density region ($\rho^* > 0.3$) where the fluid properties become more sensitive to differences of molecular shape. For larger molecules, the reduced density range increases and also the α-value. Therefore, the

Table 2.1

Universal constants $B_i^{(0)}$ and $B_i^{(p)}$ to be used in equation (9)

i	$B_i^{(0)}$	$B_i^{(p)}$
1	2.5023740	0.52182
2	-7.2696120	-0.73780
3	-4.5309120	-2.56040
4	-1.5257331	-5.25270
5	0.3796055	-0.12000
6	5.3624275	-3.37530
7	-2.8683227	17.10530
8	15.2886580	-19.27400
9	20.9891320	79.29000
10	24.7384980	6.84750
11	-36.2897450	15.57000
12	-207.7690100	-104.00000
13	1152.7599000	-435.80400
14	246.4964200	149.09100
15	229.8994200	850.00000
16	31.6711280	0.0

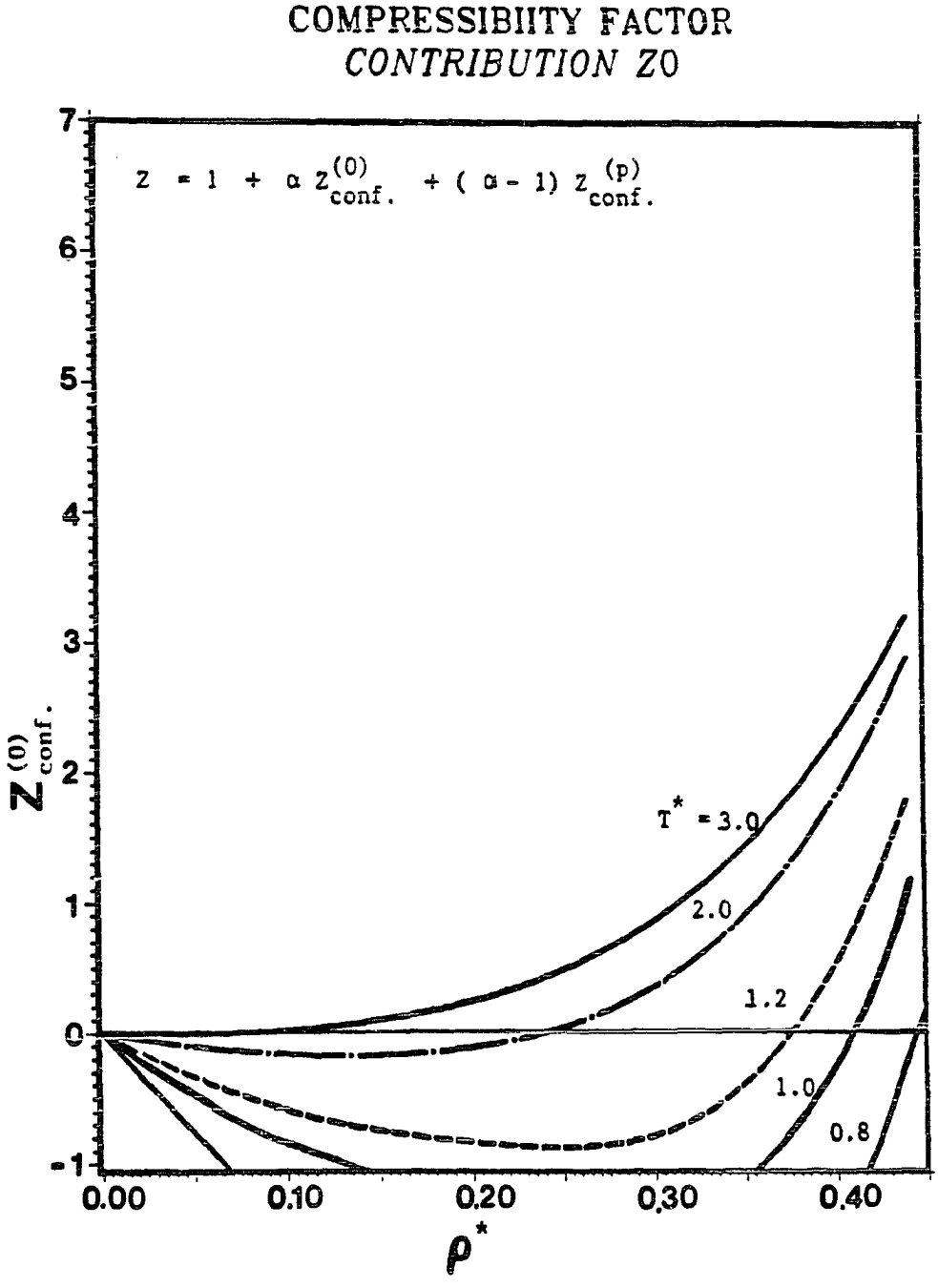


FIGURE 2.
PLOT OF Z0 AS A FUNCTION OF
REDUCED DENSITY AND REDUCED TEMPERATURE

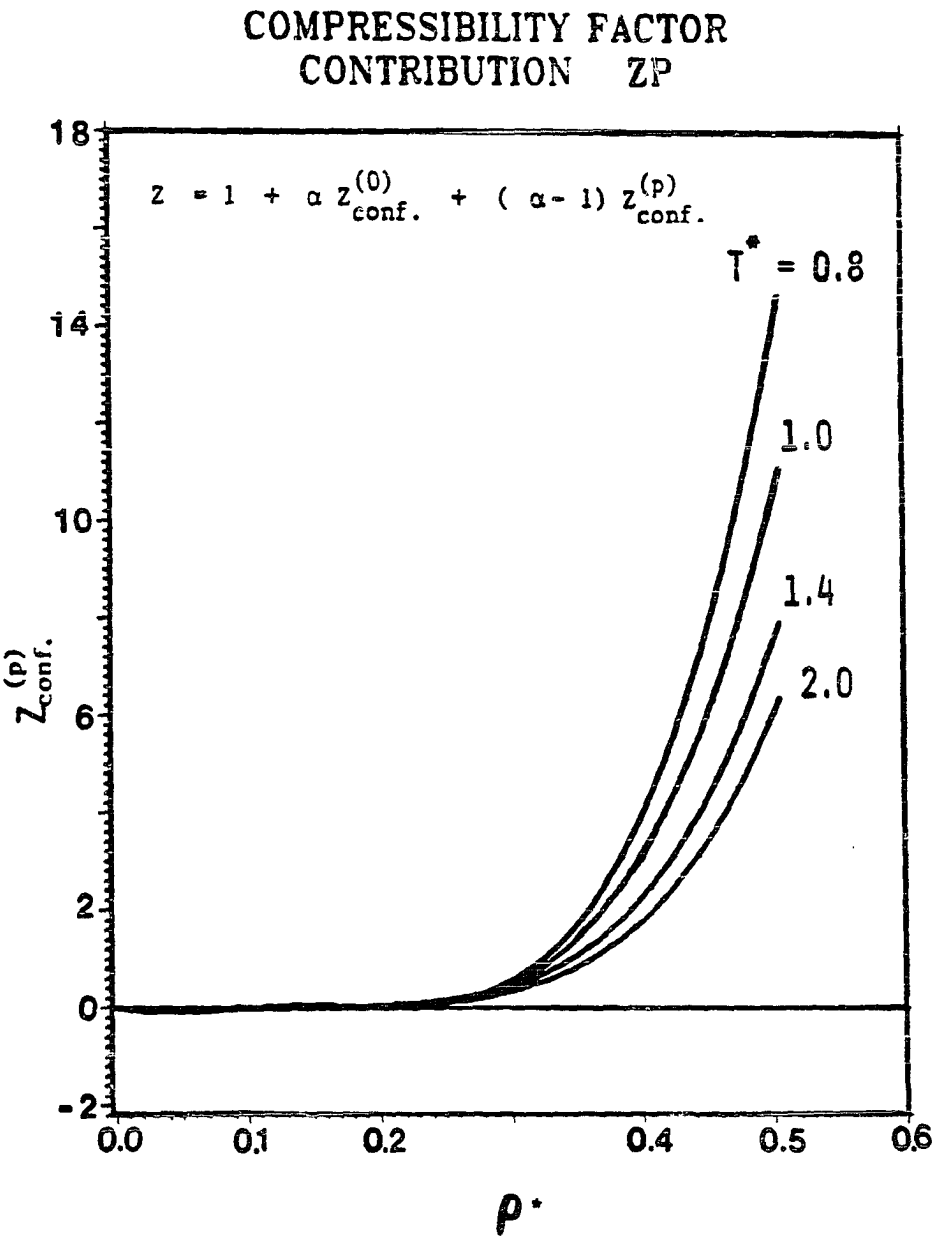


FIGURE 3
PLOT OF ZP AS A FUNCTION OF REDUCED DENSITY AND TEMPERATURE

$Z_{conf.}^{(p)}$ term becomes more important for larger and more complicated molecules.

EQUATION OF STATE FOR MULTIPOLAR AND ASSOCIATING FLUIDS:

According to the treatment of Pople(1954), the pair potential for polar fluids is divided into two parts; a reference potential Uo which is spherical and therefore a function only of interparticle distance, r_{ij}, and a perturbation potential U_1, which is a function of the angular variables, ω_i and ω_j,

$$U(r_{ij}, \omega_i, \omega_j) = Uo(r_{ij}) + \lambda U_1(r_{ij}; \omega_i, \omega_j) \tag{16}$$

where λ is a perturbation parameter. The Stockmayer pair potential is

$$Uo(r_{ij}) = 4\epsilon \left(\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6} \right) \tag{17}$$

$$U_1(r_{ij}; \omega_i, \omega_j) = \frac{\mu_i \mu_j}{r_{ij}^3} \left(\sin\theta_i \sin\theta_j \cos\phi_{ij} - 2\cos\theta_i \cos\theta_j\right) \tag{18}$$

and $\lambda = 1$

The perturbation expansion of the Helmholtz free energy, A, with respect to the parameter λ, for the potential of equation(16) can be written (for $\lambda = 1$) as:

$$A = A_o + A_2 + A_3 + \text{-------} \tag{19}$$

The first-order term, A_1, disappears because the reference potential U_o is defined as the angular average of the total potential U (i.e, the angular average of U is zero). A_o is the free energy of isotropic fluids. The expressions for A_2 and A_3 involve the state variables, intermolecular potential parameters, and certain integrals, J and K, for the reference fluid. Details of the derivation of the equations for these terms, as well as expressions for other thermodynamic properties are given by Twu (1976). As an example the J-integral is given as

$$J^{(n)} = \int_0^\infty dr^* \, r^{*-(n-2)} g^{(0)}(r^*) \tag{20}$$

Where J is the two-body pure fluid integral, r^* is the reduced intermolecular separation, $g(0)$ is the pair

correlation function for the reference system, and $-(n-2)$ is the power of the distance in the multipolar potential. The J and K integrals for the Lennard-Jones(12-6) reference have been evaluated by Gubbins and coworkers (Twu et al., 1976; Gray et al.,1978; Gubbins and Twu(1978); Nicolas et al.,1979). With these integrals correlated as functions of reduced temperature and reduced density, the perturbation theory has been successfully applied to real fluids of moderate polarity and molecules of simple structure. Another problem for the perturbation theory is that the series of the perturbation expansion converges slowly as the dipole moment increases. The application of Pade resummation suggested by Stell, Rasaiah and Narang (1972) can help the series (19) converge faster. However, for highly polar fluids, if a simple reference model is used, the perturbation terms become greater than the reference term which makes the series divergent. Therefore, unless a more sophisticated reference term is used, perturbation theory still cannot be easily applied to highly polar compounds ($\mu^{*} \gg 1$).

For practical purposes, this work employs the mean-potential model, instead of the statistical mechanical

perturbation theory, to approach this problem. The orientation-averaged pair potential for polar molecules is given (Reed and Gubbins,1973) as:

$$U^{ave.} = 4\epsilon \left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right) - \frac{1}{r^6}\left(\frac{\mu_a^2 \mu_b^2}{3kT} + \mu_a^2 \alpha_b + \mu_b^2 \alpha_a\right) \qquad (21)$$

The potential can be written in the following form by combining the terms of r^{-6}, as

$$U^{ave.} = 4\epsilon' \left(\left(\frac{\sigma'}{r}\right)^{12} - \left(\frac{\sigma'}{r}\right)^{6} \right) \qquad (22)$$

where

$$\epsilon' = \left(1 + \frac{\mu_a^2 \mu_b^2}{6kT\varepsilon(\sigma)^6} + \text{---------} \right) \qquad (23a)$$

$$(\sigma')^6 = \sigma^6 / \left(1 + \frac{\mu_a^2 \mu_b^2}{12kT\varepsilon(\sigma)^6} + \text{-------} \right) \qquad (23b)$$

Where μ_i is the dipole moment, and $\alpha_{a,b}$ is the dipole polarizability. Since the hard-core volume, V^* was used

instead of σ^3, the relationship of equation (23b) is not applicable in this work. The relationship of (23a) for the energy parameter was employed in equation (9). For many polar species, one of the most important terms in the multipole expansion is the dipole-dipole term. Thus it was chosen to lump all orientational contributions to pure-fluid properties into a single term based on the angle-averaged interaction between point dipoles. To this term, a simple temperature dependence was assigned. Thus the energy parameter, ϵ/k, was changed to ϵ'/k, which is a function of temperature plus another parameter, κ, as

$$\frac{\epsilon'}{k} = \frac{\epsilon}{k} + \frac{\kappa}{T\,(U^*)^2} \qquad (24)$$

where κ is used to characterize the multipolar and association effects. The form of the polar term is such that its value drops with increasing temperatures in accordance with theoretical and experimental evidence.

When equations (13) and (14) were derived for nonpolar fluids, they involved the derivative of the compressibility factor with respect to temperature (see equations 11 and 12). From the definition of T^*, one can easily prove that

$$T \left(\frac{\partial Z}{\partial T} \right) = T^* \left(\frac{\partial Z}{\partial T^*} \right) \tag{25}$$

This relation holds true as long as T is nondimensionlaized to T^* by dividing it by a constant. In the case of nonpolar fluids, this constant is equal to ϵ/k, the energy parameter which is constant for a given fluid. Equation (24), however, indicates that ϵ/k for polar fluids is a function of temperature. This has been taken care of by using the relation

$$T \left(\frac{\partial Z}{\partial T} \right)_\rho = T \left(\frac{\partial Z}{\partial T^*} \right)_\rho \left(\frac{\partial T^*}{\partial T} \right)_\rho \tag{26}$$

which when the expression for polar compounds is used changes to

$$T \left(\frac{\partial Z}{\partial T} \right) = \left(1 + \frac{K}{T^* \, (\varepsilon/k)^2 \, (V^*)^2} \right) T^* \left(\frac{\partial Z}{\partial T^*} \right) \tag{27}$$

Equation (27) above reduces to (25) for nonpolar fluids since $K = 0$.

CHAPTER III

APPLICATION OF THE GENERALIZED EQUATION OF STATE TO PURE COMPOUNDS

The new generalized correlation is applied to a wide variety of compounds including hydrocarbon, nonhydrocarbon, halogenated hydrocarbon, ring compounds, hydrogen, nitrogen, carbon dioxide, ethers, acetone, alcohols, ammonia and water. Tables 3.1 and 3.2 list the compounds used in the application and their data source(s).

In order to calculate the thermodynamic properties of a compound (e.g. density, enthalpy departure, etc. ...) at a given temperature and pressure, the density has to be determined. The density is calculated implicitly by solving equation (9). The density search technique used in this work is described by Goin (1978). Other thermodynamic properties can be calculated using the obtained density in the expressions derived by classical thermodynamic relations (e.g. equations (11) and (12) of chapter II). To calculate the vapor pressure for a compound at a given temperature, one calculates the fugacity of the compound in the vapor phase and the fugacity in the liquid phase at an assumed initial pressure. Since the fugacities in both phases are equal at the vapor pressure, the initial pressure can be

Table 3.1
Hydrocarbons and other nonpolar, or weakly polar compounds data sources.

Compound	Property	No. of points	Data reference(s)
Methane	P	128	Matthews(1946), Prydz and Goodwin(1972)
	den.	41	Van Itterbeck et al.(1963), Douslin et al.(1964), Vennix(1967)
	$H-H^{o}$	38	Jones(1963), Yesavage(1968)
Ethane	P	46	API-44(1953), Canjar and Manning(1967)
	den.	49	Sage and Lacey(1950), API-44(1953), Canjar and Manning(1967)
	$H-H^{o}$	98	Sage and Lacey(1950), Starling et al. (1978).
Propane	P	59	API-44(1953), Canjar and Manning(1967)
	den.	41	Sage and Lacey(1950), API-44(1953), Huang et al.(1967)
	den.	70	Goodwin(1977)
	den.	145	Thomas and Harrison (1982)
	$H-H^{o}$	39	Yesavage(1968), Kwok et al.(1971)
n-Butane	P	38	API-44(1953), Canjar and Manning(1967)
	den.	40	Sage and Lacey(1950), API-44(1953)
	$H-H^{o}$	39	Sage and Lacey(1950)
n-Pentane	P	50	API-44(1953), Canjar and Manning(1967)
	den.	41	Sage and Lacey(1950), API-44(1953)
	$H-H^{o}$	39	Sage and Lacey(1950)

Table 3.1, (continued)

Compound	Property	No. of points	Data reference(s)
n-Hexane	P	53	API-44(1953), Canjar and Manning(1967)
	den.	41	API-44(1953), Stewart et al.(1954)
n-Heptane	P	44	Kay(1938), API-44(1953),
	den.	41	Stuart et al.(1950), API-44(1953)
	$H-H^{\circ}$	17	Gilland and Parekh(1942)
n-Octane	P	64	Young(1900), Mundel(1913), API-44(1953)
	den.	54	Felsing and Watson(1942), API-44(1953)
	$H-H^{\circ}$	62	Lenoir et al.(1968)
n-Nonane	P	21	API-44(1953)
	den.	75	Vargaftik(1975)
n-Decane	P	24	API-44(1953)
	den.	32	Sage and Lacey(1950)
n-Undecane to n-Eicosane	P	164	Vargaftik(1975)
	den.	157	Vargaftik(1975)
Isobutane	P	64	Dana et al.(1926), Sage and Lacey(1938), Aston et al.(1940), Wackher et al.(1945), Beattie et al.(1949), Connolly(1962), Zwolinski and Wilhoit(1971)
	den.	321	Sage and Lacey(1938), Morris et al.(1940), Sage and Lacey(1950), Rossini et al.(1953), Canjar and Manning(1967), Waxman et al.(1978)
	$H-H^{\circ}$	24	Beattie et al.(1950), Canjar and Manning(1967)

Table 3.1, (continued)

Compound	Property	No. of points	Data reference(s)
Isopentane	P	72	Aston and Shumann(1942), Rossini et al.(1953)
	den.	128	Rossini et al.(1953), Silberberg et al.(1959), Douslin et al.(1964)
Ethylene	P	35	Tickner and Lossing(1951), Rossini et al.(1953), Canjar and Manning(1967)
	den.	41	Michels et al.(1953), Rossini et al.(1953), Canjar and Manning(1967)
	$H-H^{o}$	38	Canjar and Manning(1967)
Propylene	P	28	Tickner and Lossing(1951), Rossini et al.(1953), Canjar and Manning(1967)
	den.	61	Farrington and Sage(1949), Michels et al.(1953), Rossini et al.(1953), Canjar and Manning(1967)
Cyclohexane	P	43	Vargaftik(1975), Reid et al(1977), API-44(1978)
	den.	26	Vargaftik(1975), Reid et al.(1977), API-44(1978)
Benzene	P	36	Vargaftik(1975)
	den.	60	Chao (1978)
o-Xylene	P	41	Vargaftik(1975)
	den.	59	Vargaftik(1975)

Table 3.2 (continued)

Compound	Property	No. of points	Data reference(s)
Toluene	P	33	Vargaftic (1975)
	denl.	13	Vargaftic (1975)
Dichloro-	P	40	ASHRAE (1969)
difluoro	den.	189	ASHRAE (1969)
methane	$H-H^{o}$	40	ASHRAE (1969)
Argon	P	64	Clark et al.(1951) Michels et al.(1958)
	den.	1423	Michels and Wijker (1949), Michels et al.(1958), Van Itterbeek et al.(1960), Van Itterbeek et al.(1963), Van Itterbeek et al.(1964), Street and Staveley (1968), Van Witzenburgh et al.(1968), Crawford and Daniels (1969), Goldman and Scrase (1969), Terry et al.(1969)

Table 3.2
Multipolar and associating compounds data sources.

Compound	Property	No. of points	Data reference(s)
Nitrogen	P	17	Friedman, A.S.(1950)
	den.	41	Canjar and Manning(1967) Streett and Staveley(1968)
	$H-H^{\circ}$	87	Mage et al. (1963)
Hydrogen	P	24	Vargaftik(1975)
	den.	180	Vargaftik(1975)
Carbon Dioxide	P	18	Canjar and Manning(1967)
	den.	41	Din (1961)
	$H-H^{\circ}$	39	Din (1961)
Sulfur Dioxide	P	20	Kang et al.(1961)
	den.	309	Kang et al.(1961)
Hydrogen Sulfide	P	24	West(1948), Kay and Rambosek (1953)
	den.	41	Reamer and Sage(1950), Lewis and Fredericks(1968)
Hydrogen Chloride	P	14	Frank et al.(1962), Thomas(1962)
	den.	150	Frank et al.(1962), Thomas(1962)
Methyl Fluoride	P	28	ASHRAE (1969)
	den.	107	ASHRAE (1969)
Difluoro-monochloro methane	P	16	ASHRAE (1969)
	den.	17	ASHRAE (1969)
Dichloro-monofluoro methane	P	51	ASHRAE (1969)
	den.	300	ASHRAE (1969)

Table 3.2, (continued)

Compound	Property	No. of points	Data reference(s)
Methyl Ethyl Ether	P	18	Int. crit. tables(1926)
	denl	17	Int. crit. tables(1926)
	denv	18	Int. crit. tables(1926)
Dimethyl Ether	P	17	Int. crit. tables(1926)
	denl	18	Int. crit. tables(1926)
	denv	19	Int. crit. tables(1926)
Diethyl Ether	P	26	Int. crit. tables(1926)
	denl	23	Int. crit. tables(1926)
	denv	23	Int. crit. tables(1926)
Acetone	P	30	Int. crit. tables(1926)
	denl	24	Int. crit. tables(1926)
	denv	24	Int. crit. tables(1926)
Ammonia	P	172	Garnjost(1974), Haar and Gallagher(1977)
	den.	307	Garnjost(1974), Haar and Gallagher(1977)
Aniline	P	45	Kudchadker(1982)
	denl	35	Kudchadker(1982)
Methanol	P	33	Young(1910)
	den.	232	Ramsey and Young(1887), Young(1910)
Ethanol	P	42	Young(1910)
	den.	289	Ramsey and Young(1887), Young(1910)
Propanol	P	54	Kemme and Kreps(1969), Ambrose and Townsend(1963), Ambrose and Sparke(1970)
	den.	38	Int. crit. tables(1926)

Table 3.2 (continued)

Compound	Property	No. of points	Data reference(s)
Phenol	P	15	Kudchadker et al.(1977)
	den.	15	Kudchadker et al.(1977)
2,4-Xylenol	P	32	Kudchadker et al.(1978)
	denl.	5	Kudchadker et al.(1978)
Water	P	66	Obsorne et al.(1939)
	density	385	Keyes and Smith(1934), Keyes et al.(1936), Obsorne et al.(1939), Kennedy(1957), Holser and Kennedy(1958), Kell and Whalley(1965), Keenan et al.(1969)
	$H-H^{\circ}$	256	Callendar and Egerton(1960), Keenan et al.(1969)

* P = vapor pressure, den. = density,

denl. = liquid density, denv. = vapor density,

$H-H^{\circ}$=enthalpy departure

adjusted until the equality of the vapor phase fugacity and liquid phase fugacity is obtained. This final obtained pressure is the desired vapor pressure.

The characterization parameters for the compounds tested are not measurable properties and are therefore determined from reduction of experimental vapor pressure, enthalpy departure, and density data whenever available. The inclusion of more than one property in the test of the applicability of the equation of state is important because in order for the generalized equation to be used effectively in process design, it must be capable of predicting accurate vapor pressures, densities, and other derived properties for process-stream fluids. The temperature dependence of the equation can be critically tested with the use of enthalpy data because the entahlpy expression, equation (11), contains the temperature derivative of the compressibility factor, Z. Furthermore, if only one property, e.g. density, is used in determining the parameters, an excellent fit could be obtained but the resulting parameters might have one or two disadvantages. The first one is when these parameters are applied to another property, e.g. vapor pressure, the equation prediction accuracy might be

drastically deteriorated. This is because the effect of the value of each parameter on a given property is not the same as on another. The second drawback is that the values obtained might not be systematic with values obtained for another compound of the same class and hence, the generalization of the equation of state becomes even tougher. These phenomena were notably observed during the development of the equation. A discussion on the values of the characterization parameters and their effect on the accuracy of the thermodynamic property predictions is presented in chapter IV.

APPLICATION OF THE EQUATION OF STATE TO NORMAL PARAFFINS:

The characterization parameters determined for normal paraffins are summerized in Table 3.3 . The prediction results are presented in Table 3.4. Satisfactory prediction accuracy was achieved for all compounds studied, especially for methane. For propane, three density predictions are reported. The data of Thomas and Harrison (1982), was obtained after the constants of the equation of state were determined. Hence, for density predictions, these 145 data

Table 3.3
Values of parameters for use with equation (9).

Compound	ε/k Deg. R	V^* cu.ft./lbmole	α	κ +
Methane	270.804	0.25905	1.03331	0.0
Ethane	390.331	0.33585	1.40973	0.0
Propane	449.770	0.42520	1.64696	0.0
n-Butane	501.850	0.51454	1.81894	0.0
n-Pentane	534.200	0.60388	2.05819	0.0
n-Hexane	556.517	0.69323	2.30282	0.0
n-Heptane	573.681	0.78257	2.55143	0.0
n-Octane	596.236	0.87191	2.72312	0.0
n-Nonane	602.405	0.96126	3.02846	0.0
n-Decane	619.610	1.05060	3.19038	0.0
n-Undecane	624.770	1.13994	3.47422	0.0
n-Dodecane	629.927	1.22928	3.73635	0.0
n-Tridecane	639.020	1.31863	3.95480	0.0
n-Tetradecane	645.526	1.40797	4.17842	0.0
n-Pentadecane	650.269	1.49732	4.41929	0.0
n-Hexadecane	655.182	1.58666	4.64994	0.0
n-Heptadecane	660.173	1.67600	4.87238	0.0
n-Octadecane	664.333	1.76534	5.09688	0.0
n-Nonadecane	665.679	1.85469	5.37682	0.0
n-Eicosane	666.379	1.94403	5.68279	0.0

Table 3.3
Values of parameters for use with equation (9).

Compound	ε/k Deg. R	V^* cu.ft./lbmole	α	K^+
Isobutane	486.253	0.526474	1.76444	0.0
Isopentane	533.891	0.613940	1.93374	0.0
Ethylene	368.844	0.290322	1.35634	0.0
Propylene	448.552	0.385617	1.60734	0.0
Cyclohexane	642.239	0.611280	1.91294	0.0
Benzene	669.312	0.506596	1.82792	0.0
o-Xylene	690.612	0.698227	2.31868	0.0
Toluene	658.809	0.610572	2.16520	0.0
Dichloro-difluoromethane	459.703	0.441159	1.75124	0.0
Hydrogen	56.0699	0.129691	1.01372	-7.3172
Argon	215.634	0.199450	1.00000	0.0
Nitrogen	168.969	0.210863	1.22598	0.0
Carbon Dioxide	358.899	0.209042	1.36653	930.242
Sulfur Dioxide	499.896	0.248729	1.77884	737.352
Hydrogen Sulfide	498.486	0.254407	1.02500	1590.420
Hydrogen Chloride	426.049	0.226240	1.01000	1421.630
Methyl Fluoride	351.61	0.292249	1.66562	720.803
Difluoro-mono chloromethane	451.387	0.376581	1.27521	4534.430

$^+$in units of $(^oR\ ft.^3/lbmole)^2$

Table 3.3 , (continued)
Values of parameters for use with equation (9).

Compound	ε/k Deg. R	V^* cu.ft./lbmole	α	κ +
Dichloro-mono fluoromethane	529.761	0.392497	1.85043	168.985
Methylethylether	505.499	0.444777	1.76410	2877.160
Dimethylether	480.569	0.402000	1.33792	5113.510
Diethylether	523.728	0.546213	2.09362	1369.090
Acetone	599.138	0.448461	1.62079	8145.340
Ammonia	492.043	0.153614	1.65667	257.410
Aniline	767.357	0.549676	2.05710	14413.400
Methanol	525.791	0.267275	2.11110	4235.920
Ethanol	476.325	0.333049	2.15632	10992.000
Propanol	506.038	0.404247	2.47944	12032.800
Phenol	703.892	0.520417	2.32465	16426.500
2,4-xylenol	739.692	0.805434	1.77258	96141.70
Water	789.390	0.108835	1.83760	185.84

+in units of $(^{o}R\ ft.^3/lbmole)^2$

Table 3.4

Prediction of thermodynamic properties for noromal paraffins.

Fluid	Prop.	No. of Data Points	Temperature Range, °R	Pressure Range, Psia	A.A.D. % Eq.(9)
Methane	P	128	163.5-342.0	1.774-655.7	0.41
	den.	40	206.2-1122.	129.7-606.5	0.54
	H-H°	38	209.7-509.7	450.0-2000.	0.51
Ethane	P	46	249.7-549.7	0.489-709.80	0.65
	den.	49	219.7-769.7	14.70-9000.0	1.98
	H-H°	98	299.7-769.7	200.0-3000.0	1.65
Propane	P	59	211.4-665.9	0.0002-617.5	1.09
	den.*	145	536.7-806.7	147.6-5372.8	1.78
	den.**	70	162.0-1080.	15.24-10624.	1.44
	den.	41	209.7-986.7	14.70-3910.0	1.55
	H-H°	39	209.7-709.7	500.0-2000.0	0.97
n-Butane	P	38	364.7-765.3	.3420-550.70	0.89
	den.	40	259.7-889.7	14.70-7000.0	1.32
	H-H°	39	559.7-889.7	200.0-5000.0	0.74
n-Pentane	P	50	323.3-845.6	.00299-489.5	1.38
	den.	41	259.7-919.7	14.700-10000.	1.98
	H-H°	39	559.7-919.7	200.00-10000.	1.60
n-Hexane	P	53	395.8-914.2	0.0200-439.7	1.01
	den.	41	319.7-799.7	14.700-3977.	2.14
n-Heptane	P	44	346.9-956.9	.00014-350.0	1.97
	den.	41	369.7-919.7	14.700-3082.	1.61
	H-H°	17	971.9-1166.	78.800-2363.	0.89
n-Octane	P	64	389.9-1020.	.00033-350.0	1.72
	den.	54	389.7-969.7	14.700-239.0	2.58
	H-H°	62	534.7-1060.	200.00-1400.	1.38

* Thomas and Harrison Experimental Data (1982).
** Generated Goodwin Data (1977).

Table 3.4 (continued)

Fluid	Prop.	No. of Data Points	Temperature Range, ^{o}R	Pressure Range, Psia	A.A.D.% Eq. (9)
n-Nonane	P	21	426.3-814.7	.00048-29.65	1.66
	den.	75	455.7-1032.	.00226-72518.	2.89
n-Decane	P	24	438.3-859.7	.00022-30.00	2.05
	den.	32	559.7-919.7	200.00-6000.	1.60
n-Undecane	P	19	624.7-899.7	0.182-29.600	0.55
n-Dodecane	P	22	581.7-1187.	0.016-363.52	3.24
	den.	17	581.7-869.7	0.016-12.626	1.04
n-Tridecane	P	19	617.7-1219.	0.0242-249.5	2.36
	den.	17	617.7-905.7	0.0242-12.93	0.93
n-Tetradecane	P	16	707.7-1251.	0.180-235.00	2.42
	den.	14	707.7-941.7	0.180-13.540	0.78
n-Pentadecane	P	14	743.7-995.7	0.2384-17.91	0.59
	den.	14	743.7-977.7	0.2384-14.44	1.03
n-Hexadecane	P	10	833.7-995.7	1.003-12.659	0.81
	den.	9	833.7-977.7	1.003-10.094	1.31
n-Heptadecane	P	16	779.7-1050.	0.181-17.106	0.73
	den.	13	779.7-995.7	0.181-8.8910	1.03
n-Octadecane	P	15	815.7-1068.	0.254-15.468	0.77
	den.	13	815.7-1032.	0.254-10.090	1.13
n-Nonadecane	P	16	833.7-1104.	0.236-17.332	0.79
	den.	12	833.7-1032.	0.2357-7.367	1.55
n-Eicosane	P	17	851.7-1395.	0.222-161.57	2.96
	den.	48	671.7-1032.	725.2-72518.	4.08

** P=vapor pressure, den. =density,

$H-H^{o}$ = enthalpy departure, Btu/lb.

points were calculated using the parameters obtained from the other experimental data. The generated data from Goodwin equation of state for propane was also tested to see how good the equation is when the data includes higher ranges of temperatures and pressures than those used for determining the characterization parameters. For the twenty compounds applied (methane to normal eicosane), the average absolute relative deviation (AARD%) for vapor pressure and density predictions are 1.23 % and 1.58 % respectively. For enthalpy departure the average absolute difference is 1.24 Btu/lb.

APPLICATION OF THE EQUATION OF STATE TO OTHER NONPOLAR OR WEAKLY POLAR COMPOUNDS:

For an equation of state to achieve widespread use in research and industry its ability to predict the thermodynamic properties of a wide range of fluids is essential. A number of compounds representing different classes of fluids not used in the determination of the equation of state constants were applied. Branch-chain hydrocarbons, unsaturated hydrocarbons, ring compounds. halogenated hydrocarbons, and nonhydrocarbon fluids were

tested. Table 3.3 gives the values of the parameters for each fluid used and Table 3.5 gives the results of the tests along with the number of data points and temperature and pressure ranges. The AARD% for vapor pressure and density for all twelve fluids are 1.00 % and 0.68 % respectively. For enthalpy departure, the average absolute difference is 0.49 Btu/lb. From these results, it can be seen that the new equation performs quite well for fluids not used in the generalization. A typical point by point calculation for enthalpy departure for dichloro-difluoro methane is presented in Table A.1

Table 3.5

Prediction of thermodynamic properties for nonpolar compounds.

Fluid	Prop.	No. of Data Points	Temperature Range, ^{o}R	Pressure Range, Psia	A.A.D. % Eq.(9)
Isobutane	P	64	334.7-734.1	0.183-526.6	0.72
	$H-H^{o}$	24	559.7-939.7	250.0-3000.	0.95
	den.	321	349.7-1032.	14.70-5000.	1.53
Isopentane	P	72	314.65-829.	.0036-490.4	0.99
	den.	128	400.16-852.	.3034-2674.	1.81
Ethylene	P	35	239.67-510.	0.885-742.1	0.63
	$H-H^{o}$	38	339.67-720.	100.0-2000.	0.75
	den.	41	209.67-720.	14.69-2000.	0.99
Propylene	P	28	264.47-657.	0.039-670.3	1.37
	den.	61	409.68-910.	16.19-2939.	1.36
Cyclo-Hexane	P	43	509.7-930.	0.918-371.0	0.56
	den.	26	519.7-960.	1.212-461.9	1.60
Benzene	P	36	504.7-996.	0.760-636.9	1.23
	den.	60	923.7-1104.	375.3-867.4	1.59
o-Xylene	P	41	473.7-1137.	0.011-552.3	0.56
	den.	59	536.7-986.7	14.50-5800.	1.13
Toluene	P	33	491.7-1060.	0.130-547.4	1.73
	den.	13	491.7-689.7	0.130-547.4	0.91
Dichloro-difluoro methane	P	40	307.7-689.7	0.140-577.0	0.58
	$H-H^{o}$	40	307.7-689.7	0.140-577.0	0.31
	den.	189	307.7-919.7	0.140-440.0	1.03
Argon	P	64	150.8-271.4	9.863-709.3	0.20
	den.	1423	154.1-761.9	12.04-93723.	0.26

APPLICATION OF THE EQUATION OF STATE TO MULTIPOLAR AND ASSOCIATING COMPOUNDS:

A fundamental approach to extend the application of an equation of state to polar fluids is to follow methods discussed by Twu and Gubbins (1978), as mentioned in the previous chapter, who use molecular theory for calculating the effect of polar interactions and, thereby, introduce parameters with clear physical significance. No doubt, their method will eventually be reduced to engineering practice but at the present it is preferred to use a less rigorous but simple model. Theory is pushed to its practical limits but to get better accuracy some empiricism is needed. The newly introduced parameter, κ , defined in equation (24) was initially intended to correlate with the dipole moment and/or other measurable properties. However to achieve this one needs to test several compounds of each class of fluids with enough data to cover all practical ranges in order to be able to observe a particular trend for the correlation. Furthermore, such correlation could have been done, in theory, if this parameter was to describe polar effects only. However, there are other factors to be taken into consideration for fluids other than nonpolar (e.g.

association, quadrupole, quantum effects, etc.).

The characterization parameters determined for polar and associating fluids used in this work are listed in Table 3.4. The prediction results along along with the temperature and pressure ranges for the data used are reported in Tables 3.6 and 3.7. For the twenty compounds tested, the AARD% for vapor pressure and density are 2.17 % and 2.25 % respectively. A typical point by point calculation for vapor pressure is shown in Table A.2 for ammonia.

Table 3.6
Prediction of thermodynamic properties of multipolar compounds.

Fluid	Prop.	No. of Data Points	Temperature Range, °R	Pressure Range, Psia	A.A.D. % Eq.(9)
Nitrogen	P	17	150.6-224.2	29.06-454.41	0.60
	$H-H^0$	87	159.7-509.7	200.0-2500.0	0.34
	den.	41	139.3-699.7	14.69-8936.4	0.30
Hydrogen	P	24	25.2-59.81	1.081-190.9	5.20
	den.	180	720.0-1440.	14.50-3626.	0.44
Carbon Dioxide	P	18	389.8-547.7	75.15-1070.	0.43
	$H-H^0$	39	437.7-743.7	441.0-4410.	1.72
	den.	41	437.7-743.7	220.5-4410.	0.67

Table 3.7
Prediction of thermodynamic properties of polar and associative compounds.

Fluid	Prop.	No. of Data Points	Temperature Range, °R	Pressure Range, Psia	A.A.D. % Eq. (9)
Sulfur-Dioxide	P	20	581.7-775.2	124.7-1143.7	0.29
	den.	309	509.7-941.7	7.35-4630.5	0.83
Hydrogen-Sulfide	P	24	383.27-672.4	14.69-1306.0	0.66
	den.	41	499.67-799.7	100.0-2000.0	0.46
Hydrogen-Chloride	P	14	491.7-581.7	378.3-1163.9	0.22
	den.	157	491.67-1212.	370.0-29554.	3.67
Methyl-Fluoride	P	28	269.7-538.3	0.620-701.4	1.74
	den.	107	269.7-899.7	0.620-400.0	0.58
Difluoro-monochloro methane	P	16	455.7-664.7	35.62-723.2	0.69
	den.	17	319.7-859.7	0.450-497.3	3.84
Dichloro-monofluoro methane	P	51	383.7-812.5	0.367-812.5	0.51
	den.	300	491.7-851.7	14.50-2901.	0.57
Methyl-ethyl-ether	P	18	505.0-788.0	14.70-638.0	1.28
	den.	35	505.0-788.0	14.70-638.0	7.82
Dimethyl-ether	P	19	449.0-720.0	14.70-764.0	0.53
	den.	37	449.0-720.0	14.70-764.0	4.82
Diethyl-ether	P	26	474.0-841.0	2.170-523.0	0.43
	den.	46	492.0-841.0	3.580-523.0	3.82
Acetone	P	30	506.0-915.0	1.930-691.0	1.80
	den.	48	492.0-915.0	14.70-691.0	7.56

Table 3.7, (continued)

Fluid	Prop.	No. of Data Points	Temperature Range, °R	Pressure Range, Psia	A.A.D. % This Work
Ammonia	P	172	398.6-726.5	5.350-1592.0	0.86
	den.	307	428.0-1077.	12.71-11816.	2.93
Aniline	P	45	491.7-1259.	0.0014-770.15	3.33
	den.	35	491.7-1248.	0.0014-725.19	3.30
Methanol	P	33	473.7-922.8	0.299-1143.7	7.00
	den.	232	491.7-923.7	0.572-1135.9	4.48
Ethanol	P	42	527.0-925.1	0.831-891.7	5.16
	den.	289	491.7-1122.	0.237-10000.	3.84
Propanol	P	54	526.4-966.1	0.284-749.8	3.86
	den.	38	635.7-959.7	7.27-698.12	2.49
Phenol	P	15	581.7-1248.	0.047-884.5	3.24
	den.	15	581.7-1248.	0.047-884.5	2.19
2,4-Xylenol	P	32	545.7-1266.	0.020-594.5	5.11
	den.	5	545.7-617.7	0.020-0.051	0.81
Water	P	66	492.0-1160.	0.089-3090.	2.70
	$H-H^0$	256	510.0-2860.	0.666-15721.	10.30
	den.	385	492.0-2860.	0.089-20305.	2.81

** P = vapor pressure, den.= density,

$H-H^0$= enthalpy departure, Btu/lb.

SOME PROPERTIES OF THE PARAMETERS:

Equation (9) requires three parameters, V^* , α , and ϵ/k , for each pure nonpolar compound and one more parameter, κ , for polar compounds. All these parameters are obtained from reduction of experimental data. The values of V^* for normal paraffins are fixed as a linear function of carbon number, i.e.,

$$V^* = 0.157167 + 0.0893432(\text{Carbon Number}) \qquad (28)$$

This increase with each additional CH2 group, or carbon, is of the same nature as that of the critical volume,Vc, (see Figure 4). Since the equation was to be applied to other classes of compounds, the idea of relating the V^* to CH2 group was changed to relating it with the critical volume, which is a measurable quantity that is a characteristic of each compound. The characteristic volume parameter also increases linearly with the critical volume. The equation for this linear relation is

$$V^* = 0.10537 + 0.098222(Vc) \qquad (29)$$

Where Vc is in $ft^3/lbmole$. Figure 5 is a plot of the characteristic volume versus the critical volume for normal

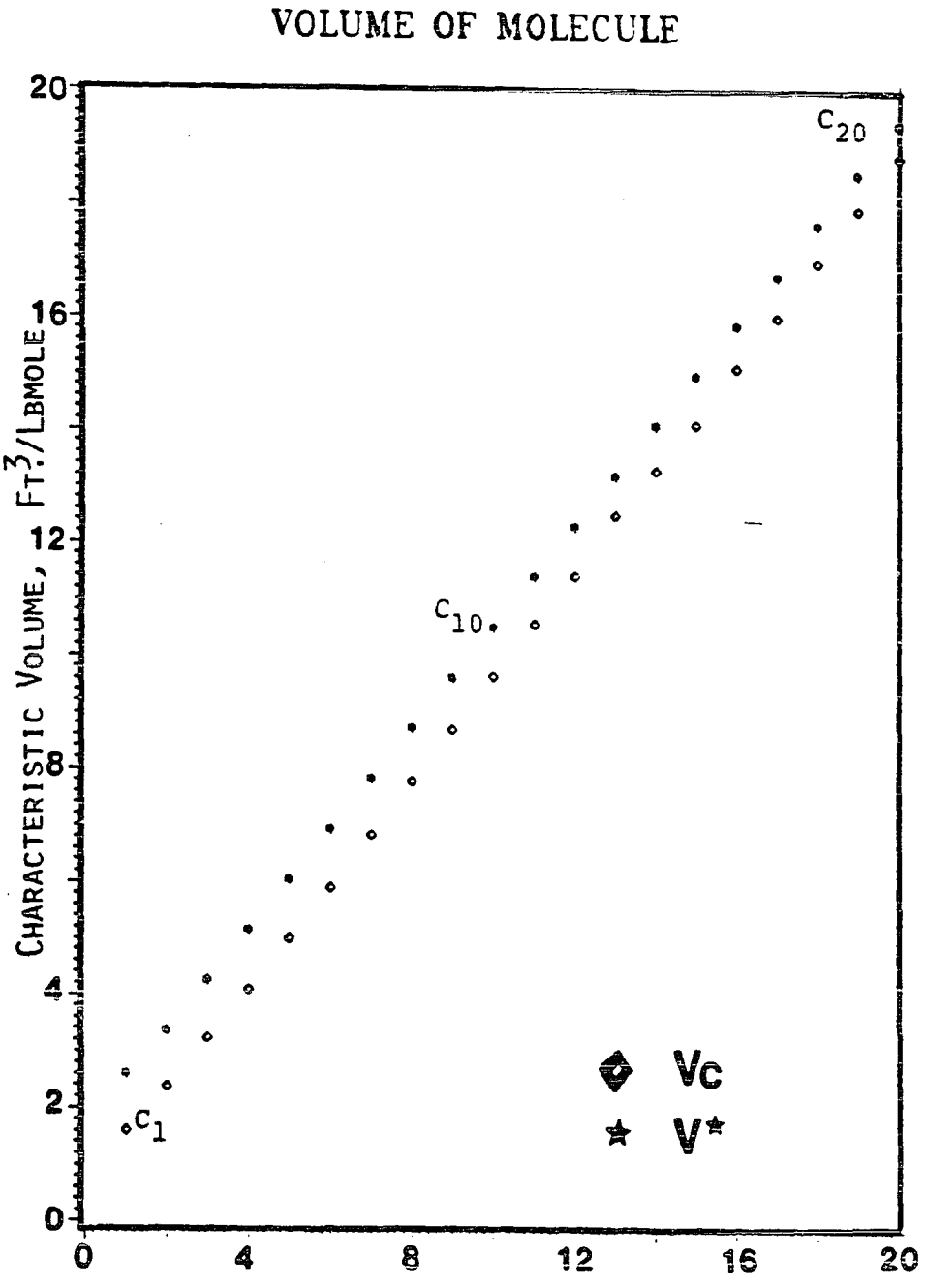


FIGURE 4
PLOT OF V AND CRITICAL VOLUME VERSUS CARBON NUMBER*

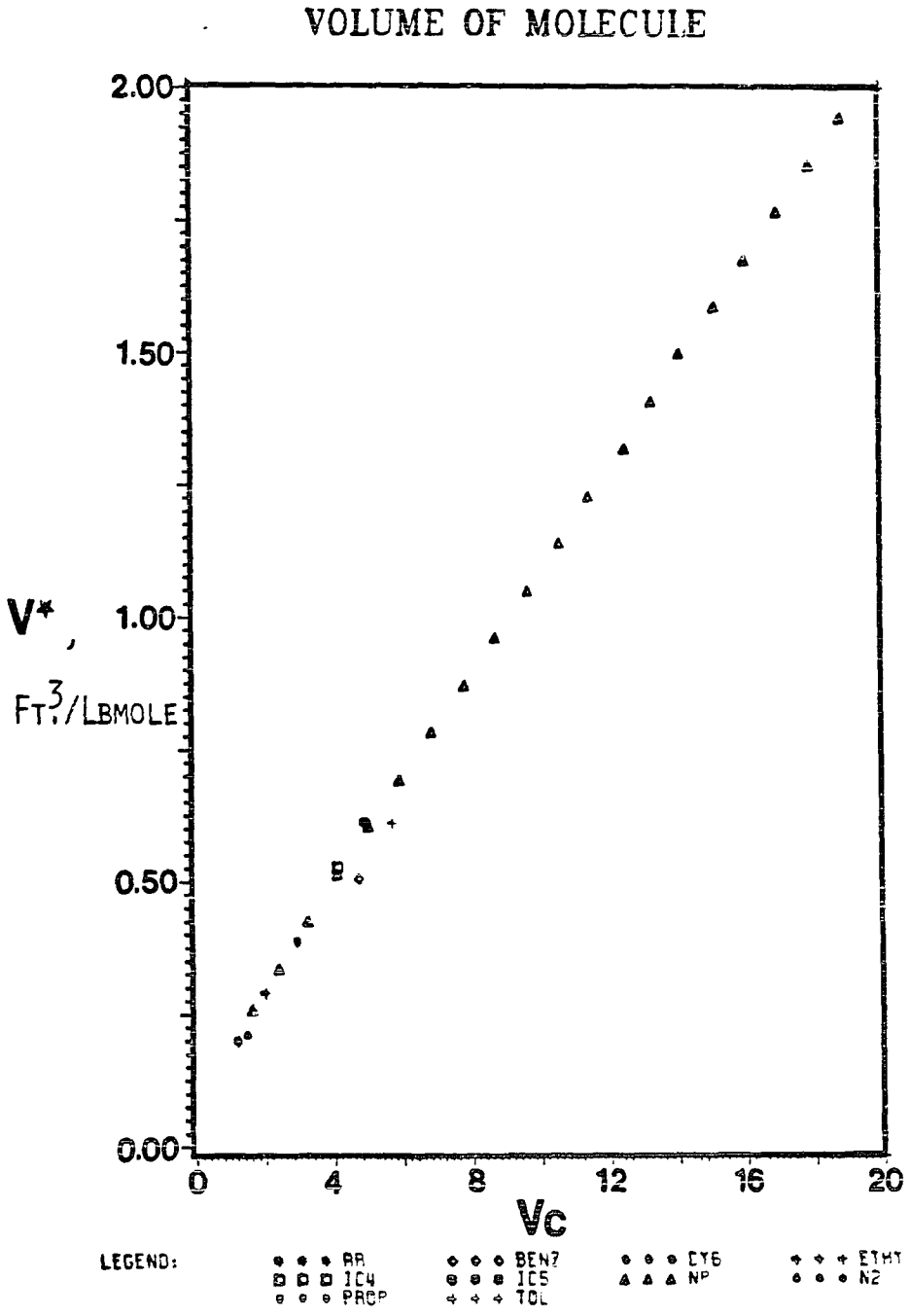


FIG. 5: PLOT OF V* VS. CRITICAL VOLUME

paraffins and a few other classes of compounds. The molecular volume parameter values are related to the van der Waals close-packing volume, which can be calculated using the group contribution method given by Bondi (1968). Figure 6 shows the relation of V^* with the calculated van der Waals volume. Equation 29 can be used as a starting estimate for the volume parameter and this reduces the number of parameters for the equation of state by one. To illustrate this further, compounds other than normal paraffins were used and the property prediction is of reasonable accuracy with a very few exceptions. Appendix B lists the values of the parameters used for the compounds tested along with the results of these tests. The structure parameter (α) is unity for spherical molecules (e.g. argon) and greater than unity for structural molecules. For normal paraffins, its value increases linearly with carbon number as illustrated by Figure 7. For branch-chain and unsaturated compounds, its value is smaller than that of same carbon number normal paraffins (e.g., ethane>ethylene, propane> propylene, n-butane>iso-butane, and n-pentane>iso-pentane). Figure 8 is a plot of ϵ/k versus critical temperature for normal paraffins and a few nonpolar compounds. A higher critical temperature gives a higher energy parameter but the

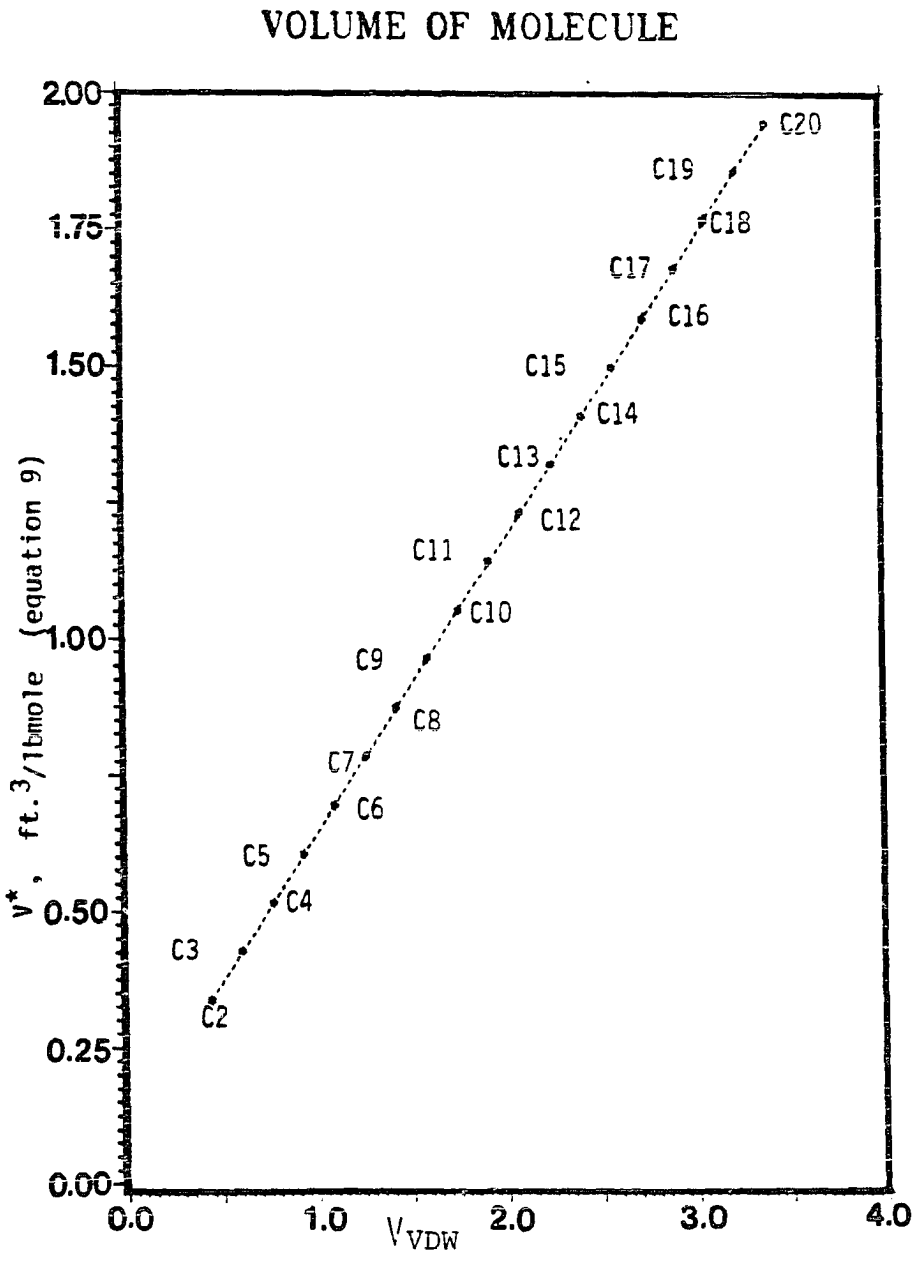


FIG. 6 : PLOT OF V* VS. VAN DER WAALS VOLUME FOR NORMAL PARAFFINS.

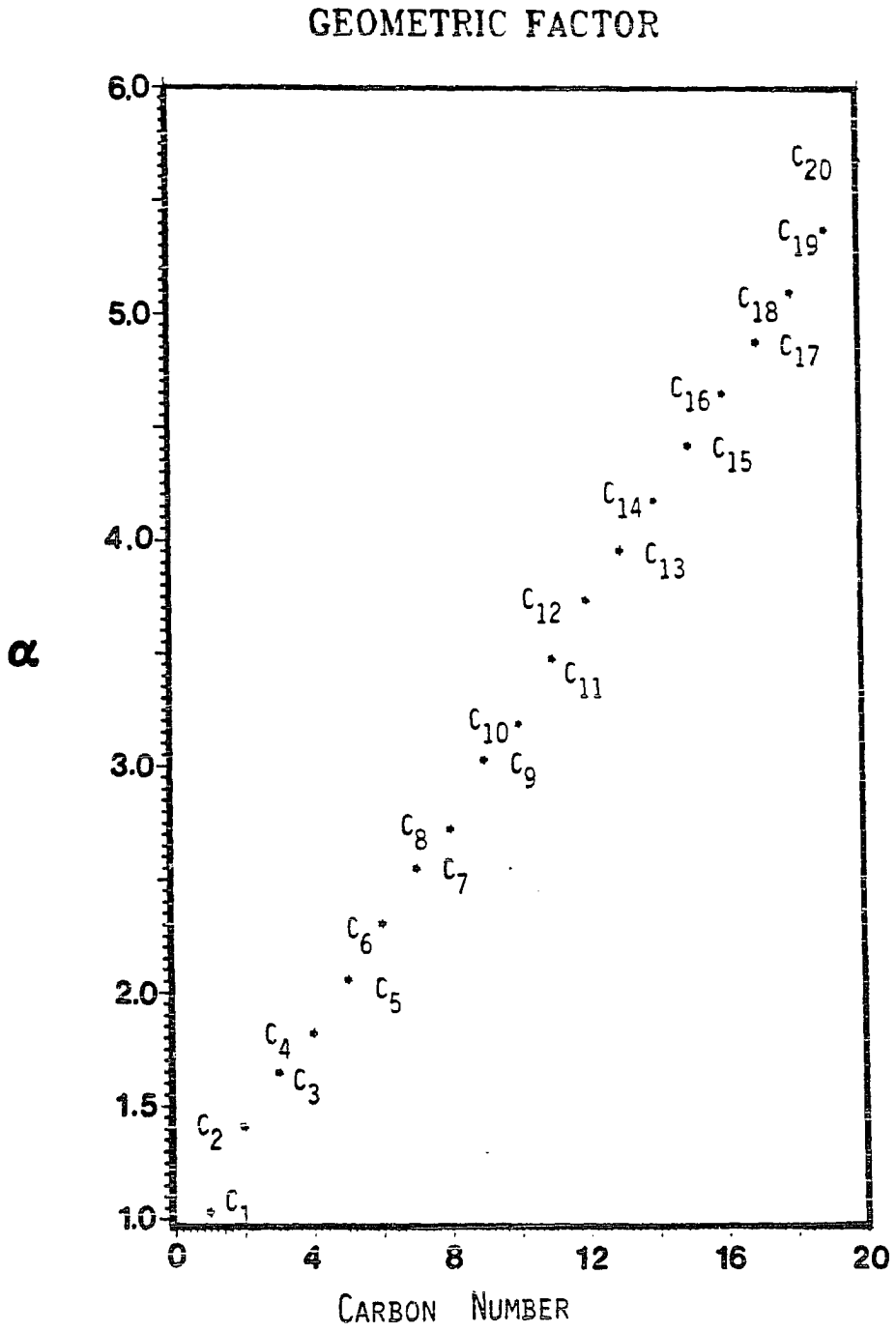


FIGURE 7

PLOT OF α FOR NORMAL PARAFFINS

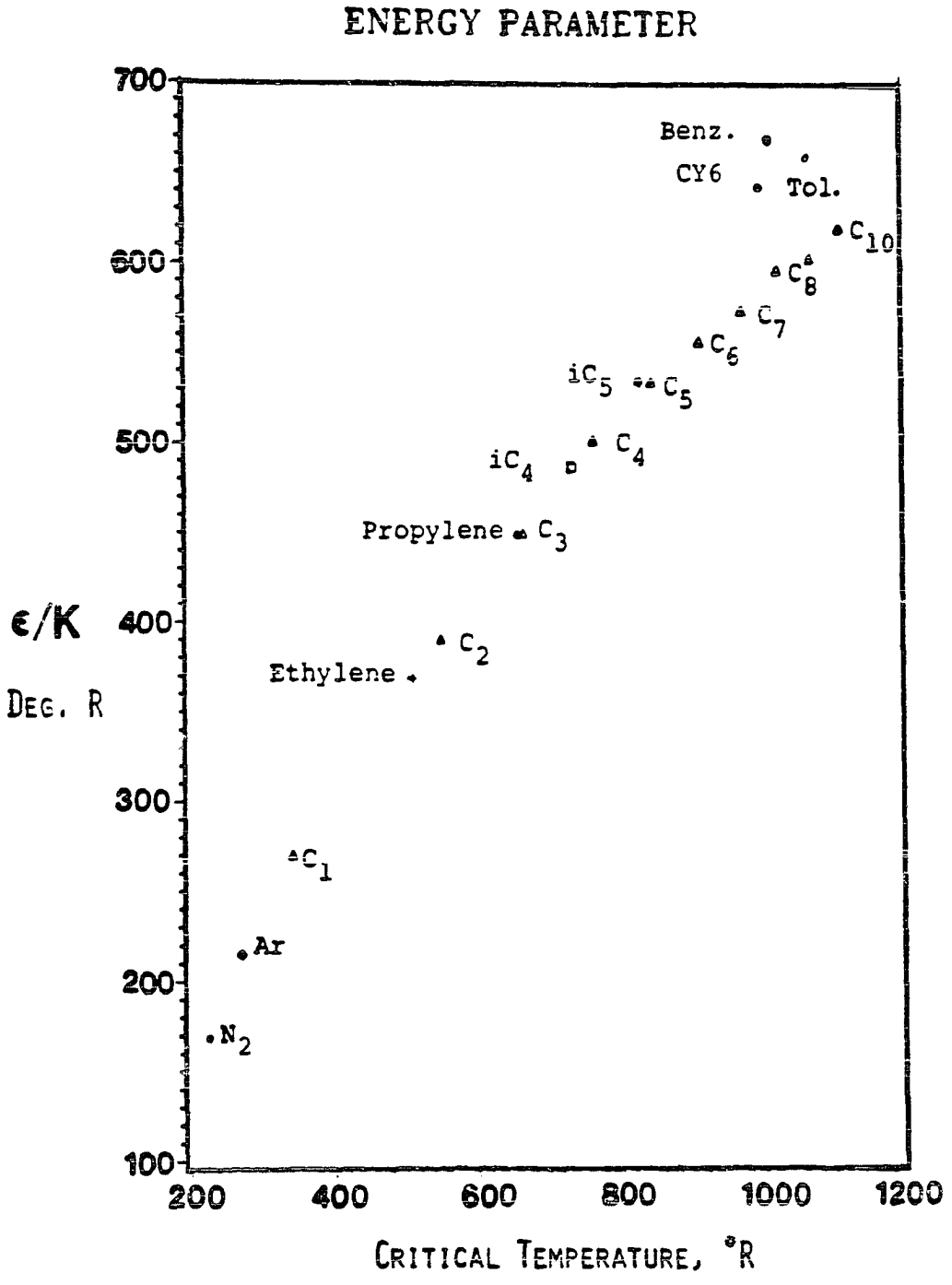


FIGURE 8
PLOT OF €/K
VERSUS CRITICAL TEMPERATURE

increase is more for ring compounds. All these plots show that these characterization parameters relate somewhat to molecular properties and are not merely random constants.

CHAPTER IV

DISCUSSION OF RESULTS

Equation (9) has been applied to fifty one pure compounds of interest in natural-gas, synthetic fuels and petroleum operations. These compounds represent different groups; polar and nonpolar, hydrocarbon and nonhydrocarbon, straight-chain and non-straight chain. A wide range of data has been used to test the equation of state; e.g., the highest pressure is up to 72,518 psia for n-nonane and n-eicosane, and the lowest temperature is about 25 R for hydrogen. The average absolute deviations of predicted density, vapor pressure and enthalpy departure for all fifty one compounds are listed in Tables 3.3, 5 and 6. To provide further perspective of the accuracy achieved by the new correlation, property calculations were made using the PHC equation of state developed by Donohue and Prausnitz (1978). The parameters used for the PHC equation were taken from GPA research report prepared by the same authors (1977). The values of the PHC parameters used are reported in Table C.1. The comparison results of the two equations are presented in Table 4.1. The overall prediction by the new correlation is of better accuracy, overall, for all the twenty six

Table 4.1
Comparison of thermodynamic property predictions for nonpolar compounds.

Fluid	Property	No. of Data Points	A.A.D. %	
			This Work	PHC
Methane	P	128	0.41	0.35
	den.	40	0.54	1.37
	H-H°	38	0.51	2.88
Ethane	P	46	0.65	0.98
	den.	49	1.98	1.92
	H-H°	98	1.65	3.77
Propane	P	59	1.09	3.13
	den.*	145	1.78	4.76
	den.**	70	1.44	2.71
	den.	41	1.55	2.70
	H-H°	39	0.97	3.84
n-Butane	P	38	0.89	0.90
	den.	40	1.32	0.97
	H-H	39	0.74	5.39
n-Pentane	P	50	1.38	2.65
	den.	41	1.98	3.16
	H-H°	39	1.60	6.04
n-Hexane	P	53	1.01	2.38
	den.	41	2.14	0.76
n-Heptane	P	44	1.97	4.99
	den.	41	1.61	1.46
	H-H°	17	0.89	3.51
n-Octane	P	64	1.72	6.18
	den.	54	2.58	2.53
	H-H°	62	1.38	5.28
n-Nonane	P	21	1.66	7.64
	den.	75	2.89	1.76
n-Decane	P	24	2.05	6.01
	den.	32	1.60	1.30

* Thomas and Harrison data (1982)

** Goodwin generated data (1977)

Table 4.1, (continued)

Fluid	Property	No. of Data Points	A.A.D. %	
			This Work	PHC
n-Dodecane	P	22	3.24	5.10
	den.	17	1.04	1.51
n-Hexadecane	P	10	0.81	4.30
	den.	9	1.31	3.34
n-Eicosane	P	17	2.96	2.29
	den.	48	4.08	4.47
Isobutane	P	64	0.72	1.54
	$H-H^o$	24	0.95	4.26
	den.	321	1.53	4.65
Isopentane	P	72	0.99	2.23
	den.	128	1.81	8.53
Ethylene	P	35	0.63	1.17
	$H-H^o$	38	0.75	2.83
	den.	41	0.99	3.19
Propylene	P	28	1.37	27.88
	den.	61	1.36	3.52
Cyclohexane	P	43	0.56	1.14
	den.	26	1.60	1.68
Benzene	P	36	1.23	1.73
	den.	60	1.59	12.39
Toluene	P	33	1.73	0.46
	den.	13	0.91	1.53
Nitrogen	P	17	0.60	0.12
	$H-H^o$	87	0.34	1.05
	den.	41	0.30	1.35

** P = vapor pressure, den.= density,

$H-H^o$ = enthalpy departure, Btu/lb

Table 4.1, (continued)
Comparison of thermodynamic property predictions for polar and associative compounds.

Fluid	Property	No. of Data Points	A.A.D. %	
			This Work	PHC
Carbon Dioxide	P	18	0.43	0.26
	$H-H^{\circ}$	39	1.72	4.45
	den.	41	0.67	2.60
Sulfur-Dioxide	P	20	0.29	1.72
	den.	309	0.83	4.24
Hydrogen-Sulfide	P	24	0.66	2.12
	den.	41	0.46	0.43
Ammonia	P	172	0.86	1.20
	den.	307	2.93	5.11
Water	P	66	2.83	5.97
	$H-H^{\circ}$	256	10.44	17.38
	den.	385	2.79	6.02

** P = vapor pressure, den. = density,

$H-H^{\circ}$ = enthalpy departure, Btu/lb

compounds used in the comparison, although the vapor pressure prediction for methane, ethane, toluene, nitrogen and carbon dioxide are not. However, for these same compounds, the deviation in the density predictions by the new correlation is less than half of that obtained by the PHC equation. Furthermore, equation (9) can be applied to a wider class of compounds such as phenol, acetone, and alcohols. Figure 9 is a plot of calculated vapor pressure compared with observed values for eight polar compounds. The accuracy of equation (9) for vapor pressure prediction will be of benefit for VLE calculations in multicomponent systems. The calculated second virial coefficient from equation (9) for propane is more accurate than popular cubic equations of state, especially in the low temperature region (Figure 10). Figure 11 is a plot of the calculated second virial coefficient compared with the smoothed experimental values (Dymond and Smith,1980) for nine nonpolar compounds. The fit for nitrogen, methane, propane and normal hexane is very good for all temperature ranges. For n-butane, n-pentane, benzene and n-octane, the experimental values of the second virial coefficients are more negative than the calculated ones in the low temperature regions. The same observation is noted for polar compounds as illustrated by

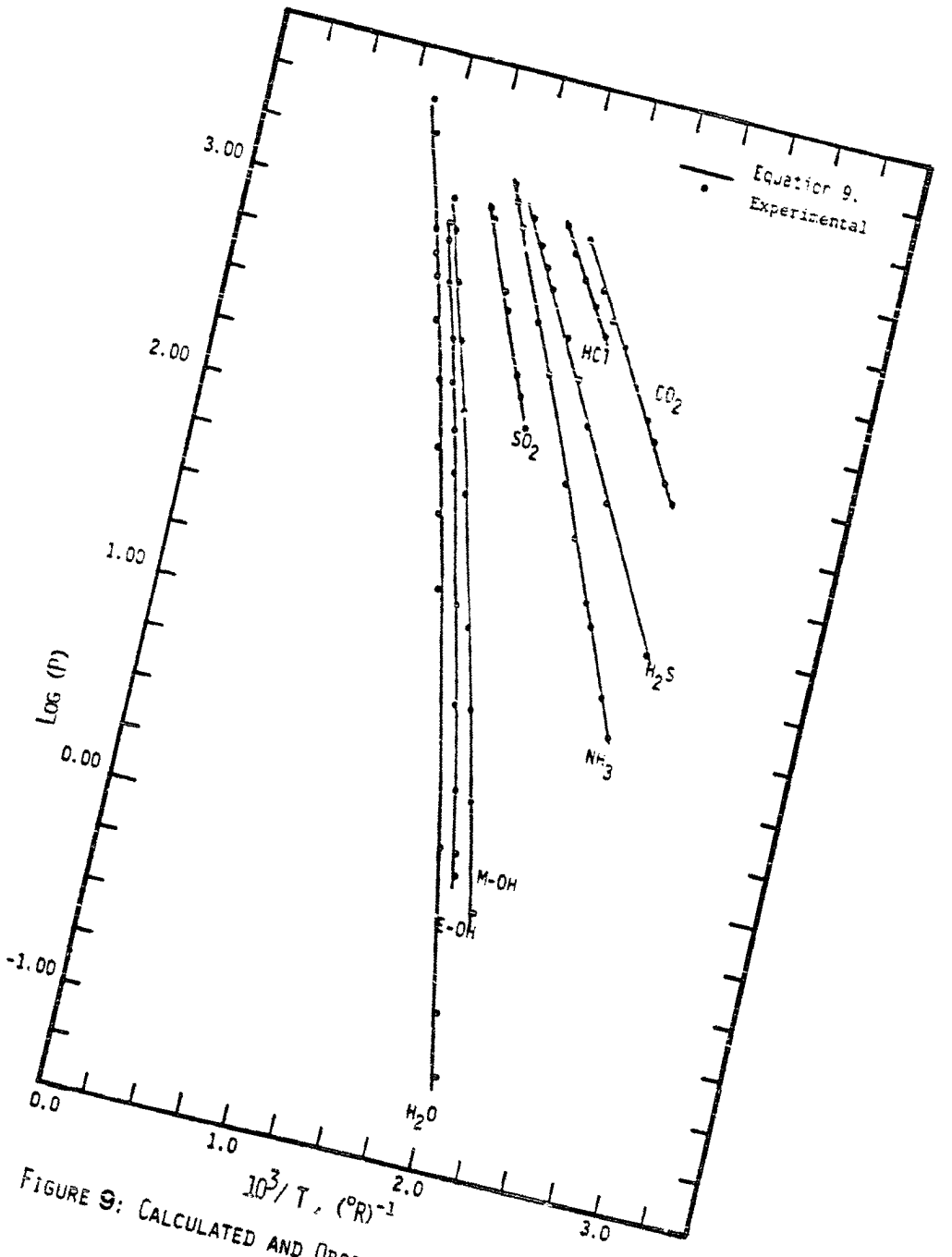


FIGURE 9: CALCULATED AND OBSERVED VAPOR PRESSURES

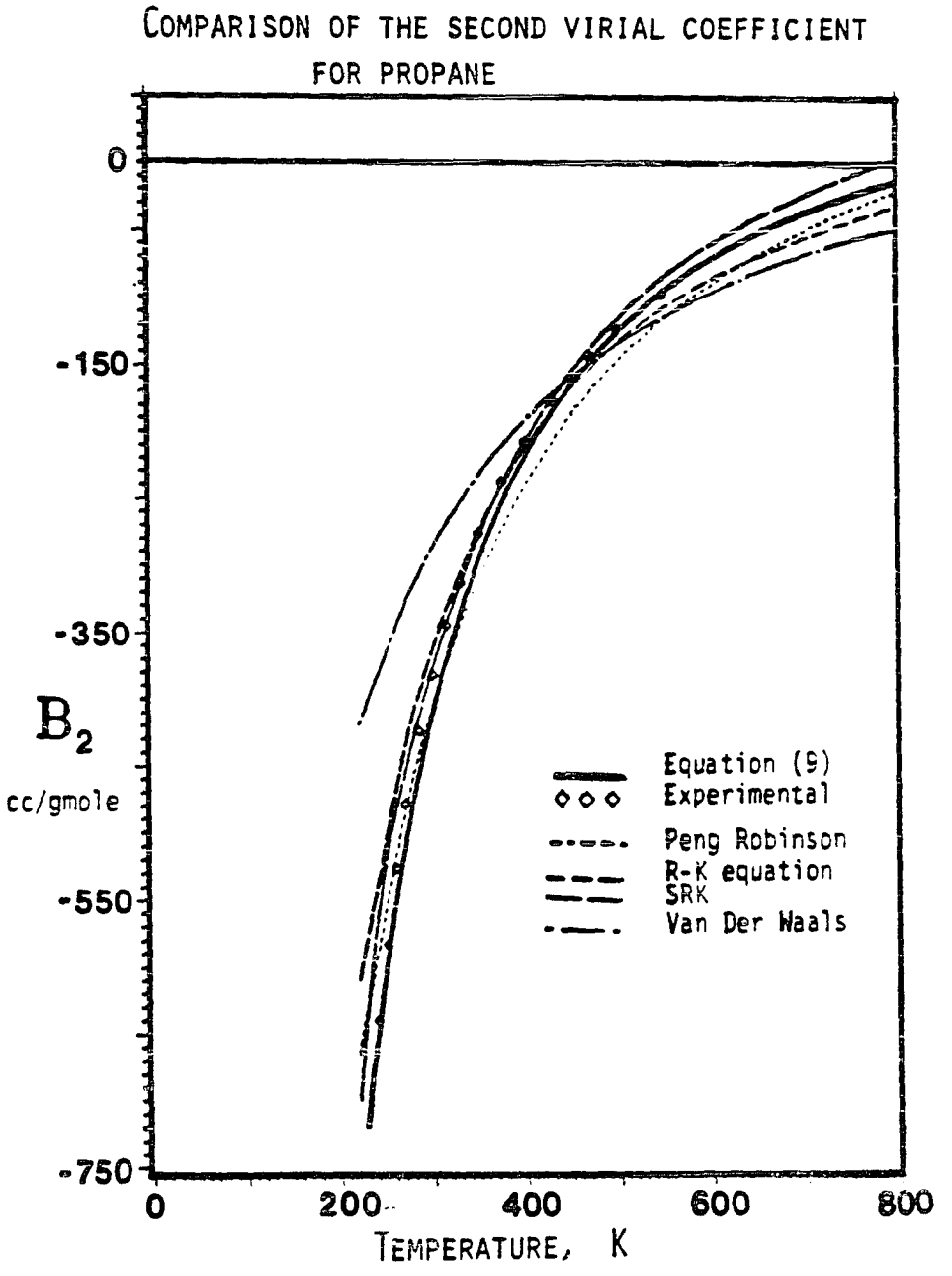

COMPARISON OF THE SECOND VIRIAL COEFFICIENT
FOR PROPANE
0
-150
-350
-550
-750
B_2
cc/gmole
0
200
400
600
800
TEMPERATURE, K
Equation (9)
Experimental
Peng Robinson
R-K equation
SRK
Van Der Waals

FIGURE 10

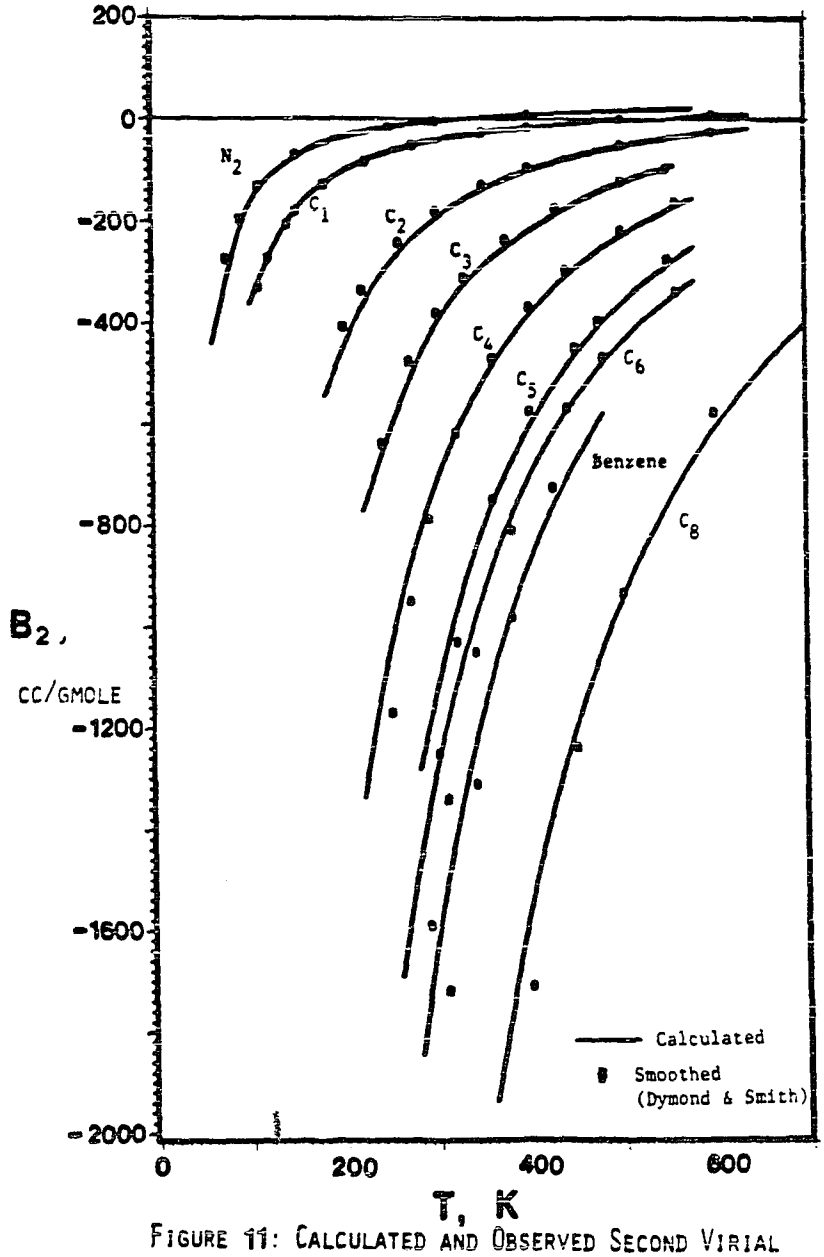


FIGURE 11: CALCULATED AND OBSERVED SECOND VIRIAL

Figure 12 for sulfur dioxide, ammonia, and hydrogen chloride. Tsonopoulos (1974) presented an empirical correlation of the second virial coefficients and his results have the same general trend. Tsonopoulos noted that for low reduced densities, or ρ_r < 0.25, the effect of vapor-phase imperfection can be reliably calculated using only the second virial coefficient. Since the second virial coefficient predictions are more accurate in the higher temperature regions, the developed equation of state, equation (9), is expected to be of high reliability in the vapor phase and so is the case. Figure 13 compares the prediction of density values for propane by equation (9) and by the PHC equation. It shows that the density of propane is better predicted by equation 9 as opposed to those predicted by the PHC equation both in the high and low density regions. For intermediate values of density, the prediction is about the same. In the critical region, equation (9) predictions for the thermodynamic properties are fairly accurate (6-7 % for density). Figure 14 shows the percent deviation of the vapor pressure predictions for methane using two different data sources where the more recent one covers a higher range. The maximum deviation occurs at the lowest temperature, 90 K, and is only 2.0 %.

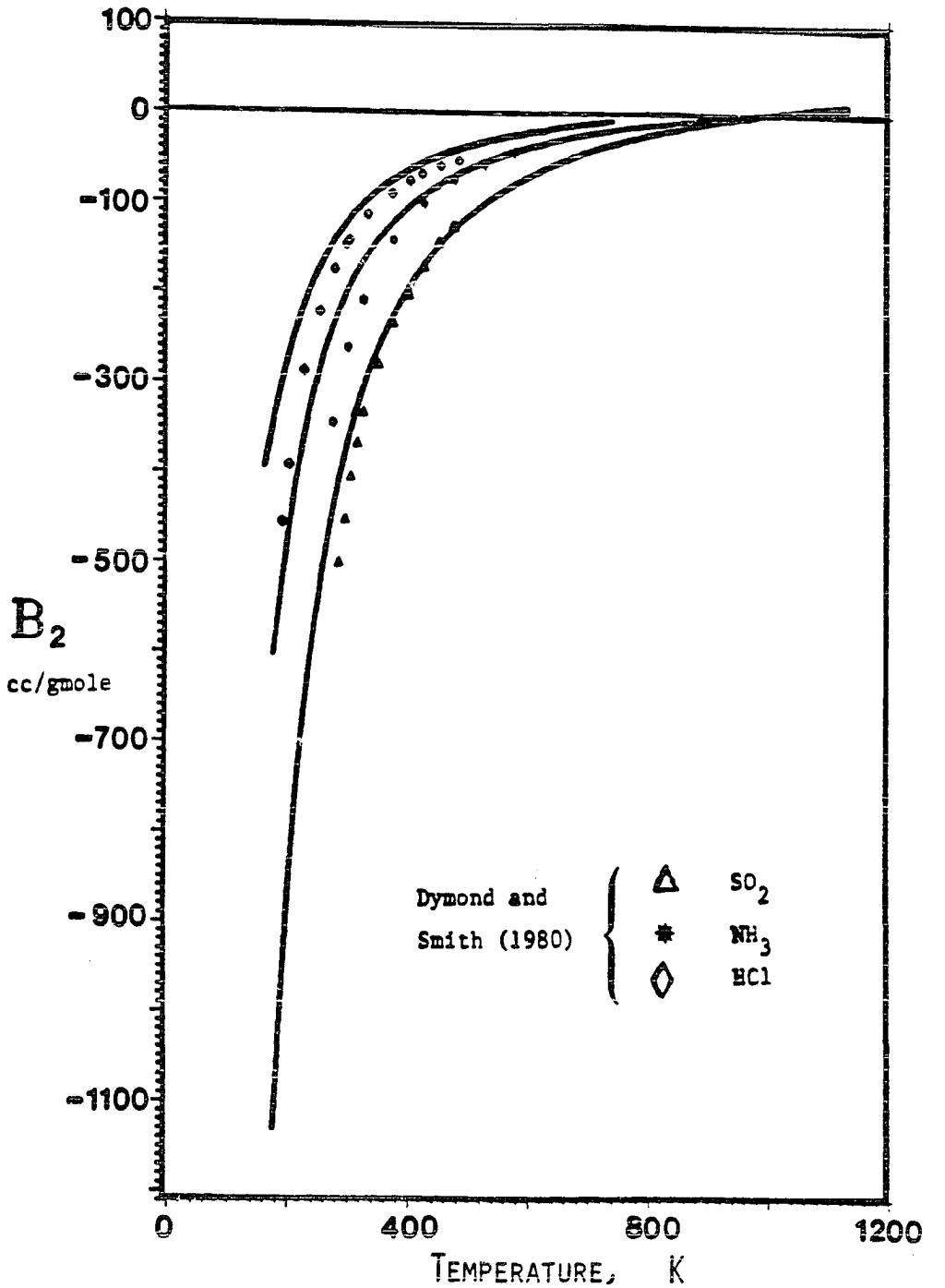


FIGURE 12

CALCULATED AND OBSERVED SECOND VIRIAL COEFFICENTS

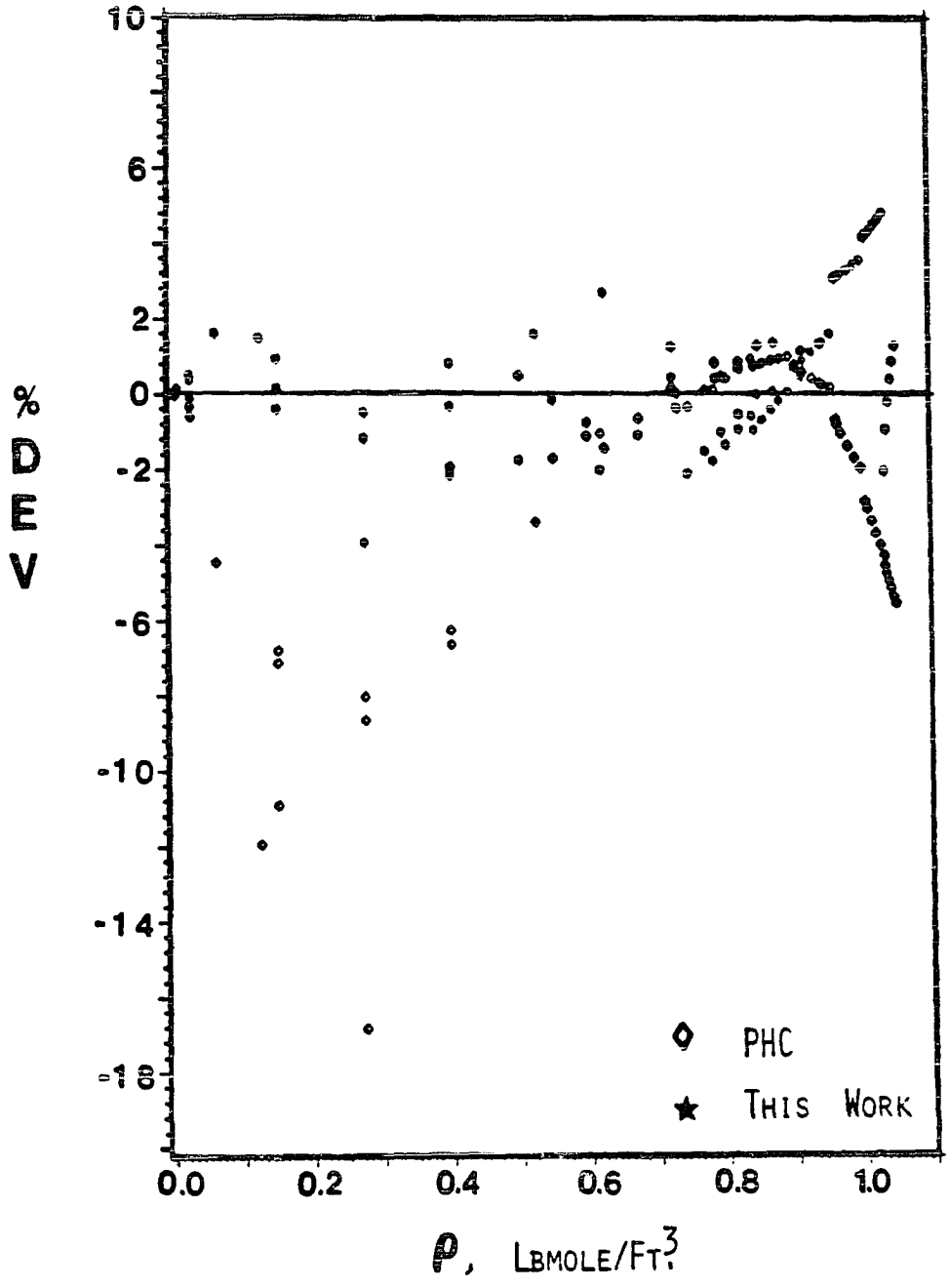


FIGURE 13 : PLOT OF THE % DEVIATION VS DENSITY FOR PROPANE

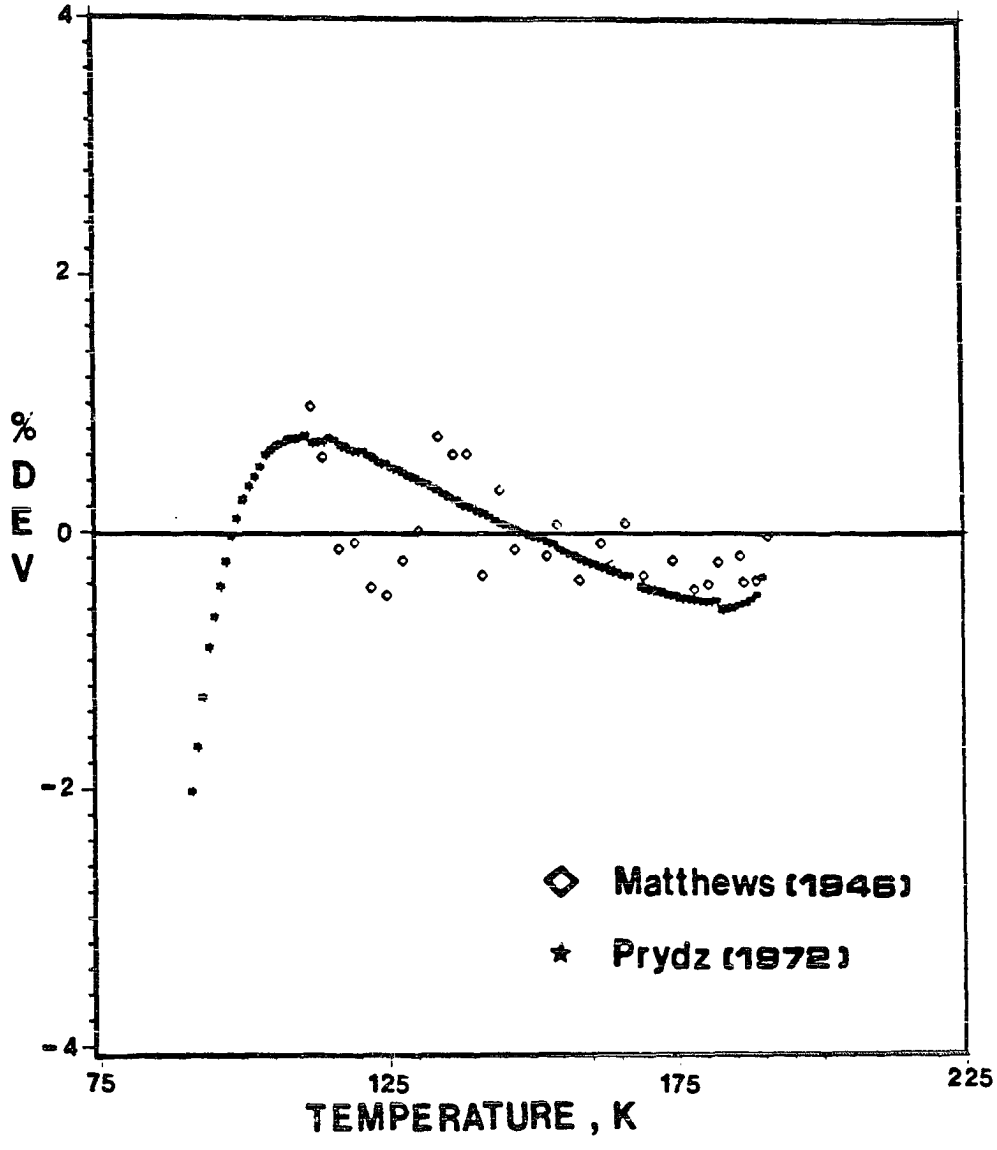


FIGURE 14
PLOT OF THE % DEVIATION OF VAPOR PRESSURE VS TEMPERATURE FOR METHANE

A typical graphical comparison of the PVT behavior with the experimental is shown for propane in the pressure-density diagram (Figure 15) for different isotherms including the critical. Equation (9) is not purely empirical in nature; it has some theoretical basis. Thus, the equation has the advantages of the both approaches. It can be generalized to wide ranges of fluids, like the theoretical equations of state, and also can predict the thermodynamic properties of fluids of interest fairly accurately, like empirical type equations of state.

PROPANE PRESSURE-DENSITY DIAGRAM

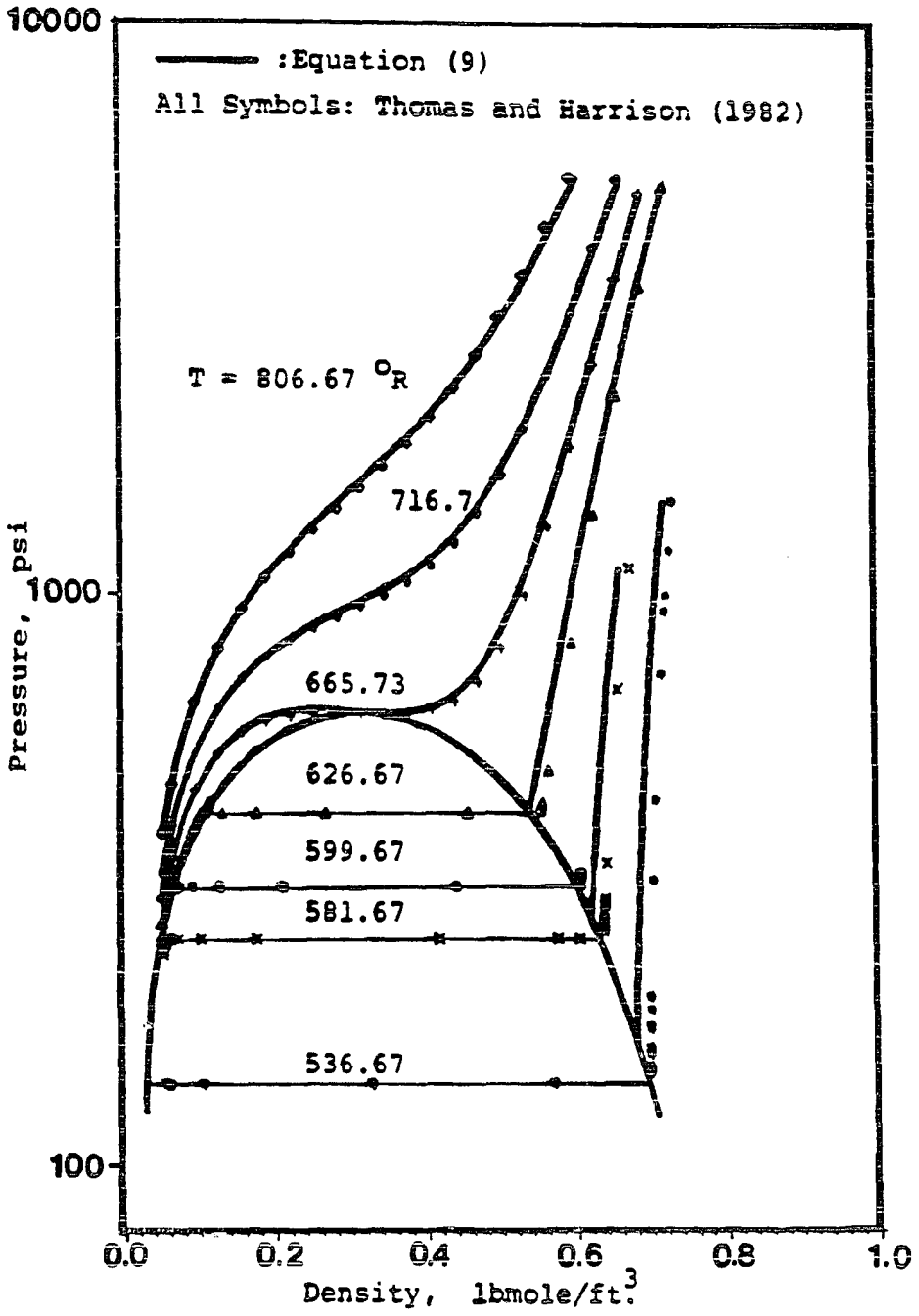


FIGURE 15

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

The newly developed correlation can be applied to fluids commonly encountered in petroleum, natural gas, and related industries. Several significant points are demonstrated by this new equation of state:

1- The equation is applicable to wide ranges of fluids from simple molecules (argon-like) to large, structural molecules (heavy paraffins).

2- The accuracy of the equation for predicting thermodynamic properties is, in general, better than other equations of state of the same class, especially in the high density regions. Furthermore, the equation covers the essential fluid range.

3- The equation has been extended to polar and associating fluids with reasonable success.

4- Only a few molecular parameters are required for each substance. Also, these parameters have some physical significance so that it is possible to estimate their values where few or no experimental data are available.

Since the parameters were determined from data reduction, a first and most important step is to determine what experimental data are to be fitted. For pure components, there are a number of possible alternatives. For this work, vapor pressure, liquid and vapor density were considered to be the most available and reliable data. Second virial coefficient data was not considered because reliable data are not readily available for many fluids of interest.

The reduction of the number of characterization parameters is very desirable. If for each class of compounds α, ϵ/k, and κ can be correlated as functions of measurable quantities or even as functions of quantities already determined for the tested compounds, the equation of state will be totally generalized. Further work on the generalization of parameters is recommended.

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APPENDIX A

TABLE A.1 : Detailed Calculations of Enthalpy Departure for Dichloro-difluoro Methane.

No.	Experimental H-H Btu/lb.	Calculated H-H Btu/lb.	Percent Deviation	Temperature Deg. R	Pressure Psia
1	-83.446	-82.820	-.74986	307.67	.14000
2	-82.763	-82.351	-.49752	314.67	.20000
3	-81.806	-81.644	-.19863	324.67	.33000
4	-80.869	-80.900	.03887	334.67	.52000
5	-79.949	-80.127	.22237	344.67	.79000
6	-79.046	-79.329	.35806	354.67	1.1800
7	-78.156	-78.511	.45378	364.67	1.7200
8	-77.280	-77.678	.51542	374.67	2.4400
9	-76.413	-76.833	.54978	384.67	3.3900
10	-75.557	-75.980	.55991	394.67	4.6100
11	-74.708	-75.119	.55034	404.67	6.1900
12	-73.867	-74.254	.52351	414.67	8.1500
13	-73.033	-73.385	.48251	424.67	10.590
14	-72.286	-72.601	.43545	433.67	13.230
15	-71.791	-72.077	.39873	439.67	15.270
16	-70.969	-71.203	.33045	449.67	19.190
17	-70.149	-70.328	.25424	459.67	23.850
18	-69.331	-69.450	.17098	469.67	29.340
19	-68.514	-68.570	.08209	479.67	35.740
20	-67.695	-67.686	-.01258	489.67	43.150
21	-66.872	-66.799	-.10861	499.67	51.670
22	-66.044	-65.906	-.20914	509.67	61.390
23	-65.206	-65.006	-.30716	519.67	72.430
24	-64.357	-64.096	-.40522	529.67	84.890
25	-63.491	-63.175	-.49729	539.67	98.870
26	-62.606	-62.241	-.58394	549.67	114.49
27	-61.696	-61.289	-.66015	559.67	131.86
28	-60.755	-60.315	-.72320	569.67	151.11
29	-59.776	-59.317	-.76792	579.67	172.35
30	-58.752	-58.287	-.79112	589.67	195.71
31	-57.671	-57.219	-.78377	599.67	221.32
32	-56.525	-56.105	-.74190	609.67	249.31
33	-55.295	-54.933	-.65439	619.67	279.82
34	-53.964	-53.688	-.51157	629.67	313.00
35	-52.508	-52.349	-.30376	639.67	349.00
36	-50.890	-50.884	-.012773	649.67	387.98
37	-49.057	-49.241	.37527	659.67	430.09
38	-46.912	-47.324	.87707	669.67	475.52
39	-44.248	-44.908	1.4907	679.67	524.43
40	-40.235	-40.972	1.8327	689.67	577.03

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Table A.2 : Detailed Calculations of Vapor Pressure for Ammonia

No.	Temperature Deg. R	Experimental Pressure, Psia	Calculated Pressure, Psia	Percent Deviation
1	518.87	106.07	107.24	1.0977
2	527.66	124.28	125.57	1.0371
3	536.62	145.32	146.64	0.9104
4	536.80	145.77	147.08	0.9014
5	545.54	168.92	170.13	0.7108
6	545.66	169.19	170.46	0.7468
7	554.76	196.02	197.25	0.6301
8	554.69	195.94	197.05	0.5661
9	563.52	225.04	225.93	0.3973
10	563.52	225.01	225.93	0.4073
11	563.64	225.49	226.35	0.3778
12	572.51	257.81	258.43	0.2390
13	572.59	258.12	258.74	0.2406
14	572.78	258.90	259.47	0.2216
15	581.72	295.12	295.22	0.0312
16	581.80	295.35	295.54	0.0656
17	581.86	295.72	295.82	0.0353
18	590.66	335.05	334.54	-0.1515
19	599.75	379.62	378.38	-0.3271
20	599.76	379.69	378.42	-0.3338
21	599.76	379.76	378.42	-0.3505
22	599.76	379.63	378.40	-0.3221
23	599.77	379.74	378.46	-0.3353
24	608.76	428.11	425.84	-0.5290
25	608.77	428.12	425.88	-0.5228
26	617.68	480.39	476.90	-0.7273
27	617.68	480.38	476.90	-0.7240
28	398.55	5.35	5.22	-2.3448
29	398.84	5.39	5.27	-2.1857
30	400.43	5.69	5.57	-2.1782
31	400.43	5.69	5.57	-2.1524
32	404.43	6.48	6.37	-1.7056
33	405.01	6.61	6.50	-1.7463
34	405.72	6.76	6.65	-1.6404
35	406.00	6.81	6.71	-1.4814
36	409.02	7.51	7.40	-1.3925
37	411.44	8.10	8.00	-1.2158

Table A.2 (continued)

No.	Temperature Deg. R	Experimental Pressure, Psia	Calculated Pressure, Psia	Percent Deviation
38	412.03	8.24	8.15	-1.0497
39	412.21	8.29	8.20	-1.0348
40	412.41	8.35	8.25	-1.1725
41	412.46	8.36	8.27	-1.1493
42	412.63	8.40	8.31	-1.0346
43	413.55	8.64	8.56	-0.9779
44	415.26	9.11	9.03	-0.9414
45	419.22	10.26	10.20	-0.6174
46	419.28	10.28	10.22	-0.6572
47	419.28	10.28	10.22	-0.6572
48	421.74	11.06	11.00	-0.5142
49	421.74	11.05	11.00	-0.4481
50	421.74	11.05	11.00	-0.3977
51	421.74	11.06	11.00	-0.5007
52	421.74	11.05	11.00	-0.4586
53	421.74	11.06	11.00	-0.4695
54	421.74	11.05	11.00	-0.4586
55	421.74	11.05	11.00	-0.4451
56	421.74	11.05	11.00	-0.4586
57	421.75	11.06	11.00	-0.4868
58	421.75	11.06	11.01	-0.4822
59	421.75	11.05	11.01	-0.4287
60	421.75	11.06	11.01	-0.4861
61	421.76	11.06	11.01	-0.4135
62	423.95	11.80	11.75	-0.3831
63	425.50	12.33	12.30	-0.2538
64	425.71	12.40	12.38	-0.1668
65	425.75	12.42	12.39	-0.2498
66	425.80	12.45	12.41	-0.2712
67	425.82	12.44	12.42	-0.1892
68	427.85	13.20	13.18	-0.1580
69	428.87	13.59	13.57	-0.1360
70	430.29	14.14	14.14	-0.0121
71	430.96	14.41	14.41	-0.0001
72	431.61	14.67	14.67	0.0222
73	431.64	14.70	14.69	-0.0700
74	431.64	14.68	14.69	0.0509
75	431.65	14.70	14.69	-0.0308
76	431.65	14.70	14.69	-0.0080
77	431.66	14.70	14.70	-0.0230
78	431.67	14.70	14.70	0.0130

Table A.2 (continued)

No.	Temperature Deg. R	Experimental Pressure, Psia	Calculated Pressure, Psia	Percent Deviation
79	431.74	14.73	14.73	0.0204
80	431.76	14.72	14.74	0.1244
81	431.77	14.72	14.74	0.1438
82	431.80	14.74	14.75	0.0985
83	431.82	14.76	14.76	0.0085
84	431.85	14.76	14.77	0.0890
85	431.87	14.76	14.78	0.1225
86	431.87	14.78	14.78	0.0247
87	431.87	14.78	14.78	0.0190
88	432.08	14.87	14.87	0.0407
89	436.89	16.97	17.01	0.2586
90	437.56	17.27	17.32	0.2950
91	437.63	17.32	17.36	0.2273
92	437.68	17.35	17.39	0.2203
93	437.70	17.34	17.39	0.2693
94	437.86	17.42	17.47	0.3012
~~95~~	~~446.59~~	~~21.93~~	~~22.07~~	~~0.6176~~
96	446.61	21.94	22.08	0.6124
97	446.63	21.97	22.09	0.5710
98	446.66	21.98	22.11	0.5945
99	446.67	21.97	22.11	0.6260
100	446.69	21.99	22.12	0.6197
101	450.63	24.31	24.50	0.7552
102	450.69	24.35	24.53	0.7434
103	455.67	27.58	27.82	0.8550
104	455.68	27.59	27.82	0.8301
105	455.68	27.59	27.82	0.8657
106	455.68	27.58	27.83	0.9008
107	455.69	27.60	27.83	0.8309
108	464.60	34.22	34.57	1.0132
109	464.64	34.24	34.60	1.0347
110	464.65	34.24	34.61	1.0562
111	464.68	34.27	34.63	1.0408
112	464.68	34.28	34.63	1.0384
113	473.64	42.15	42.64	1.1498
114	473.65	42.15	42.64	1.1694
115	473.66	42.18	42.66	1.1378
116	473.67	42.17	42.66	1.1731
117	473.68	42.16	42.68	1.2246
118	482.57	51.32	51.98	1.2888
119	482.64	51.43	52.06	1.2290
120	482.65	51.43	52.07	1.2492

Table A.2 (continued)

No.	Temperature Deg. R	Experimental Pressure, Psia	Calculated Pressure, Psia	Percent Deviation
121	482.65	51.44	52.08	1.2402
122	482.66	51.44	52.09	1.2497
123	482.67	51.47	52.10	1.2198
124	491.67	62.28	63.07	1.2654
125	491.67	62.27	63.07	1.2823
126	491.67	62.28	63.07	1.2722
127	491.67	62.28	63.07	1.2746
128	491.67	62.27	63.07	1.2844
129	491.67	62.29	63.07	1.2580
130	491.67	62.28	63.07	1.2722
131	491.67	62.29	63.07	1.2580
132	500.71	74.86	75.80	1.2456
133	500.71	74.84	75.80	1.2768
134	500.62	74.72	75.66	1.2604
135	509.65	89.16	90.24	1.2135
136	509.70	89.25	90.32	1.2079
137	509.73	89.30	90.37	1.1932
138	518.67	105.64	106.84	1.1353
139	518.95	106.18	107.37	1.1213
140	527.69	124.38	125.65	1.0157
141	527.69	124.38	125.66	1.0294
142	536.68	145.51	146.79	0.8820
143	536.97	146.22	147.51	0.8796
144	545.65	169.22	170.45	0.7234
145	563.65	225.48	226.38	0.3979
146	581.65	295.01	294.97	-0.0137
147	599.65	379.38	377.87	-0.3962
148	617.66	480.81	476.79	-0.8361
149	635.66	600.98	593.77	-1.1998
150	653.67	742.53	730.66	-1.5978
151	671.67	907.90	890.20	-1.9504
152	689.68	1099.70	1074.70	-2.2763
153	707.68	1322.30	1287.80	-2.6109
154	716.69	1446.80	1407.00	-2.7513
155	725.69	1581.30	1534.80	-2.9426
156	729.29	1638.60	1589.20	-3.0173
157	591.17	337.28	336.87	-0.1216
158	600.06	381.11	379.93	-0.3113
159	608.98	429.23	427.06	-0.5047
160	617.93	481.92	478.44	-0.7232

Table A.2 (continued)

No.	Temperature Deg. R	Experimental Pressure, Psia	Calculated Pressure, Psia	Percent Deviation
121	482.65	51.44	52.08	1.2402
161	626.83	538.95	534.04	-0.9106
162	635.67	600.41	593.84	-1.0943
163	644.67	668.27	659.70	-1.2827
164	653.56	740.83	729.81	-1.4882
165	663.03	824.47	810.66	-1.6745
166	672.85	918.57	901.50	-1.8583
167	681.80	1011.20	990.92	-2.0079
168	690.74	1110.90	1086.40	-2.2004
169	699.61	1217.20	1188.70	-2.3418
170	708.49	1331.80	1298.10	-2.5298
171	717.43	1456.00	1417.10	-2.6665
172	726.46	1591.60	1546.10	-2.8586

Average Absolute Deviation = 0.86 % ,

Number of Points = 172

APPENDIX B

Table B.1
Values of parameters for use with equation (9).

Compound	ε/k Deg. R	$V^* = V^*(Vc)$ cu.ft./lbmole	α	κ^+
Isobutane	487.827	0.508450	1.76899	0.0
Isopentane	533.225	0.587121	1.96124	0.0
Ethylene	365.770	0.300716	1.36677	0.0
Propylene	449.3993	0.390422	1.59874	0.0
Cyclohexane	635.224	0.590205	1.97000	0.0
Benzene	660.813	0.567860	1.80554	0.0
o-Xylene	690.724	0.686214	2.32408	0.0
Toluene	650.052	0.664992	2.18779	0.0
Dichloro-difluoromethane	460.874	0.447065	1.73731	0.0
Nitrogen	174.547	0.222960	1.12833	0.0
Carbon Dioxide	342.390	0.253539	1.10786	2731.16
Sulfur Dioxide	502.490	0.297582	1.59629	1554.53
Hydrogen Sulfide	498.403	0.255115	1.02176	1621.04
Hydrogen Chloride	429.080	0.233079	1.01000	1359.75
Methyl Fluoride	359.085	0.300735	1.47789	1253.83
Difluoro-mono chloromethane	447.737	0.366256	1.34859	3700.73
Dichloro-mono fluoromethane	528.564	0.414657	1.77033	1075.95

Table B.1, (continued)
Values of parameters for use with equation (9).

Compound	ε/k Deg. R	$V^*=V^*(Vc)$ cu.ft./lbmole	α	κ [+]
Methylethylether	510.922	0.453350	1.72823	2873.48
Dimethylether	471.145	0.385695	1.48366	3560.59
Diethylether	523.436	0.546173	2.10754	1128.67
Acetone	601.190	0.434469	1.62078	7693.37
Ammonia	504.662	0.219652	1.01867	3056.58
Aniline	759.403	0.530380	2.20407	9585.33
Methanol	553.043	0.291294	1.70665	6508.30
Ethanol	469.410	0.368389	1.79799	18692.80
Propanol	517.075	0.449419	2.04580	20721.20
Phenol	716.179	0.513138	2.26150	15594.20
Water	782.270	0.194110	1.62692	1277.48

[+] in units of $({}^{o}R\ ft.^3/lbmole)^2$

Table B.2
Prediction of thermodynamic properties for nonpolar compounds.

Fluid	Prop.	No. of Data Points	Temperature Range, °R	Pressure Range, Psia	$V^{*}=V^{*}(Vc)$ A.A.D. %
Isobutane	P	64	334.7-734.13	0.183-526.57	1.64
	H-H°	24	559.7-939.67	250.0-3000.0	1.25
	den.	321	349.7-1031.7	14.70-5000.0	2.81
Isopentane	P	72	314.65-828.7	0.0036-490.4	2.10
	den.	128	400.16-851.7	0.3034-2674.	4.06
Ethylene	P	35	239.67-509.5	0.885-742.10	0.76
	H-H°	38	339.67-719.7	100.0-2000.0	1.59
	den.	41	209.67-719.7	14.69-2000.0	0.78
Propylene	P	28	264.47-656.9	0.039-670.27	1.64
	den.	61	409.68-909.7	16.19-2939.2	1.49
Cyclo-Hexane	P	43	509.7-929.7	0.918-371.0	1.73
	den.	26	519.7-959.7	1.212-461.9	3.31
Benzene	P	36	504.67-995.7	0.760-636.93	6.48
	den.	60	923.67-1104.	375.31-867.4	7.55
o-Xylene	P	41	473.67-1137.	0.011-552.30	0.82
	den.	59	536.67-986.7	14.50-5800.0	1.79
Toluene	P	33	491.7-1049.7	0.130-547.40	2.26
	den.	13	491.7-689.67	0.130-547.40	8.73
Dichloro-difluoro methane	P	40	307.67-689.7	0.140-577.03	0.97
	H-H°	40	307.67-689.7	0.140-577.03	0.36
	den.	189	307.67-919.7	0.140-440.00	1.18
Nitrogen	P	17	150.6-224.2	29.06-454.41	1.59
	H-H°	87	159.7-509.7	200.0-2500.0	0.67
	den.	41	139.3-699.7	14.69-8936.4	0.39

** P = vapor pressure, den = density,

$H-H^{\circ}$ = enthalpy departure, Btu/lb

Table B.3
Prediction of thermodynamic properties of multipolar and associating compounds.

Fluid	Prop.	No. of Data Points	Temperature Range, °R	Pressure Range, Psia	$V^*=V^*(Vc)$ A.A.D. %
Carbon Dioxide	P	18	389.8-547.7	75.15-1070.0	1.14
	$H-H^o$	39	437.7-743.7	441.0-4410.0	1.87
	den.	41	437.7-743.7	220.5-4410.0	5.28
Sulfur-Dioxide	P	20	581.7-775.2	124.7-1143.7	2.03
	den.	309	509.7-941.7	7.35-4630.5	4.92
Hydrogen-Sulfide	P	24	383.27-672.4	14.69-1306.0	0.65
	den.	41	499.67-799.7	100.0-2000.0	0.47
Hydrogen-Chloride	P	14	491.7-581.7	378.3-1163.9	0.21
	den.	157	491.67-1212.	370.0-29554.	5.04
Methyl-Fluoride	P	28	269.7-538.3	0.620-701.4	2.24
	den.	107	269.7-899.7	0.620-400.0	0.67
Difluoro-monochloro methane	P	16	455.7-664.7	35.62-723.2	0.41
	den.	17	319.7-859.7	0.450-497.3	3.98
Dichloro-monofluoro methane	P	51	383.7-812.5	0.367-812.5	0.56
	den.	300	491.7-851.7	14.50-2901.	3.02
Methyl-ethyl-ether	P	18	505.0-788.0	14.70-638.0	1.75
	den.	35	505.0-788.0	14.70-638.0	7.40
Dimethyl-ether	P	19	449.0-720.0	14.70-764.0	0.63
	den.	37	449.0-720.0	14.70-764.0	4.80
Diethyl-ether	P	26	474.0-841.0	2.170-523.0	0.43
	den.	46	492.0-841.0	3.580-523.0	3.82
Acetone	P	30	506.0-915.0	1.930-691.0	1.76
	den.	48	492.0-915.0	14.70-691.0	7.84

Table B.3, (continued)

Fluid	Prop.	No. of Data Points	Temperature Range, ^{o} R	Pressure Range, Psia	$V^{*}=V^{*}(Vc)$ A.A.D. %
Ammonia	P	172	398.6-726.5	5.350-1592.0	2.25
	den.	307	428.0-1077.0	12.71-11816.	6.25
Aniline	P	45	491.7-1258.5	0.0014-770.15	2.94
	den.	35	491.7-1247.7	0.0014-725.19	4.63
Methanol	P	33	473.7-922.8	0.299-1143.7	15.13
	den.	232	491.7-923.7	0.572-1135.9	4.55
Ethanol	P	42	527.0-925.10	0.831-891.7	5.71
	den.	289	491.7-1122.0	0.237-10000.	4.57
Propanol	P	54	526.41-966.1	0.284-749.8	5.16
	den.	38	635.7-959.7	7.27-698.12	3.88
Phenol	P	15	581.7-1247.7	0.047-884.5	5.45
	den.	15	581.7-1247.7	0.047-884.5	2.82
	P	66	492.0-1160.	0.089-3090.	15.17
Water	$H-H^{o}$	256	510.0-2860.	453.0-15721.	34.21
	den.	385	492.0-2860.	0.089-20305.	28.63

** P = vapor pressure, den. = density,

$H-H^{o}$= enthalpy departure, Btu/lb

APPENDIX C

Table C.1
Values of parameters for use with the PHC equation.

Compound	T Deg. R	V cu.ft./lbmole	c	q/c
Methane	273.942	0.317877	1.0000	1.4494
Ethane	403.974	0.441023	1.2743	2.1376
Propane	464.616	0.594652	1.4746	2.4583
n-Butane	519.732	0.739839	1.6248	2.7517
n-Pentane	556.362	0.882687	1.8152	2.9435
n-Hexane	587.754	1.035840	1.9720	3.1095
n-Heptane	610.902	1.176313	2.1581	3.2325
n-Octane	631.872	1.341875	2.2986	3.3433
n-Nonane	638.874	1.484419	2.5576	3.3801
n-Decane	651.744	1.612851	2.7544	3.4483
n-Dodecane	688.010	1.937590	2.9579	3.6404
n-Hexadecane	716.814	2.554940	3.6693	3.7926
n-Eicosane	741.996	3.13113	4.2876	3.9260
Isobutane	495.882	0.737922	1.6225	2.6237
Isopentane	554.562	0.878452	1.7124	2.9345
Ethylene	377.586	0.388527	1.2463	1.6465
Propylene	445.590	0.530115	1.6615	1.9436
Cyclohexane	672.174	0.908006	1.6575	3.1644

Table C.1, (continued)

Compound	T Deg. R	V cu.ft./lbmole	c	q/c
Benzene	686.412	0.750187	1.6484	3.00267
Toluene	693.774	0.894983	1.8667	3.11314
Nitrogen	174.094	0.283559	1.1040	0.92111
Carbon Dioxide	368.172	0.269150	1.6699	1.70450
Sulfur Dioxide	504.648	0.332270	1.8733	2.00260
Hydrogen Sulfide	489.402	0.296420	1.3001	2.58940
Ammonia	508.248	0.198719	1.6560	1.88240
Water	758.920	0.147200	2.0140	2.81078

Table C.2 Physical properties of pure components

Component	Molecular Weight	Critical Temperature Deg. R	Critical Pressure Psia	Critical Density lbmoles/cft.
Ethane	30.068	549.70	709.82	0.4218
Propane	44.094	665.64	616.30	0.3096
n-Butane	58.120	765.34	550.70	0.2448
n-Pentane	72.146	845.09	489.50	0.2007
n-Hexane	86.172	914.20	439.70	0.1696
n-Heptane	100.198	972.52	397.00	0.1465
n-Octane	114.200	1023.46	360.60	0.1284
n-Nonane	128.250	1070.17	332.00	0.1150
n-Decane	142.276	1111.57	306.60	0.1037
n-Undecane	156.313	1149.84	285.10	0.0946
n-Dodecane	170.340	1186.50	264.53	0.08756
n-Tridecane	184.367	1218.90	249.83	0.08004
n-Tetradecane	198.394	1250.50	235.14	0.07522
n-Pentadecane	212.448	1272.60	220.44	0.07094
n-Hexadecane	226.448	1290.60	205.74	0.06616
n-Heptadecane	240.475	1319.40	191.05	0.06243
n-Octadecane	254.502	1341.00	174.88	0.05887
n-Nonadecane	268.529	1360.80	161.66	0.05580
n-Eicosane	282.556	1380.60	148.00	0.05303

Table C.2, (continued)
Physical properties of pure components

Component	Molecular Weight	Critical Temperature Deg. R	Critical Pressure Psia	Critical Density lbmoles/cft.
Methane	16.043	343.24	673.1	0.62740
Isobutane	58.120	734.13	526.57	0.24384
Isopentane	72.146	828.70	490.41	0.20400
Ethylene	28.050	509.49	728.80	0.50350
Propylene	42.080	657.07	669.0	0.34490
Cyclohexane	84.160	996.30	590.78	0.20270
Benzene	78.113	1011.89	710.41	0.21250
Toluene	92.141	1065.06	596.66	0.19756
o-Xylene	106.168	1134.36	540.85	0.16918
Dichlorodi-fluoromethane	120.914	693.27	598.13	0.28768
Hydrogen	2.016	59.31	188.11	0.96938
Argon	39.948	271.46	706.88	0.83720
Nitrogen	28.016	227.07	492.3	0.69290
Carbon Dioxide	44.010	547.47	1069.9	0.66410
Sulfur Dioxide	64.060	775.44	1143.4	0.51172
Hydrogen Sulfide	34.076	672.37	1296.2	0.65710
Hydrogen Chloride	36.461	584.28	1205.1	0.77072
Methyl Fluoride	34.033	572.04	852.37	0.50345

Table C.2, (continued)
Physical properties of pure components

Component	Molecular Weight	Critical Temperature Deg. R	Critical Pressure Psia	Critical Density lbmoles/cft.
Difluoromono-chloromethane	86.467	664.76	721.57	0.37688
Dichloromono-fluoromethane	102.923	812.84	749.50	0.31785
Methyl Ethyl Ether	60.069	788.04	637.81	0.28248
Dimethyl Ether	46.069	720.00	778.89	0.35072
Diethyl Ether	74.123	840.06	520.68	0.22296
Acetone	58.080	914.58	681.90	0.29870
Ammonia	17.030	729.90	1635.70	0.86148
Aniline	93.129	1258.47	770.70	0.23125
Methanol	32.042	922.68	1174.10	0.52905
Ethanol	46.069	929.16	925.85	0.37382
Propanol	60.096	966.06	749.50	0.28571
Phenol	94.113	1249.56	889.17	0.27261
2,4-Xylenol	122.167	1273.68	638.14	0.16351
Water	18.015	1165.30	3208.00	1.11020

Reference: Reid, Prausnitz, and Sherwood (1977).