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MOLECULAR THEORETICAL EQUATION OF STATE FOR APPLICATIONS TO
SELECTED PURE LIQUIDS AND DENSE FLUIDS OF NATURAL GAS,
PETROLEUM HYDROCARBONS AND COAL CHEMICALS

The University of Oklahoma

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MOLECULAR THEORETICAL EQUATION OF STATE FOR APPLICATIONS TO
SELECTED PURE LIQUIDS AND DENSE FLUIDS OF NATURAL GAS,
PETROLEUM HYDROCARBONS AND COAL CHEMICALS

A DISSERTATION
SUBMITTED TO THE GRADUATE FACULTY
in partial fulfillment of the requirements for the
degree of
DOCTOR OF PHILOSOPHY

BY
SAWITREE BINTASAN KANCHANAKPAN

Norman, Oklahoma

1984

MOLECULAR THEORETICAL EQUATION OF STATE FOR APPLICATIONS TO
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PETROLEUM HYDROCARBONS AND COAL CHEMICALS
A DISSERTATION APPROVED FOR
THE SCHOOL OF CHEMICAL ENGINEERING AND MATERIALS SCIENCE

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ABSTRACT

A new equation of state applicable to both nonpolar and polar compounds has been developed. It is modeled after the nonspherical square-well potential. The repulsive pressure is approximated by contributions from the underlying hard convex molecular core and is represented by the hard convex body equation of Nezbeda. Based on the distribution function theories of liquids, the attractive part of pressure exhibited by anisotropic molecules is derived. This procedure leads to a compact, theoretically-based equation of state - a compromise between statistical mechanical rigor and engineering practicality. The equation is first developed to calculate the thermodynamic properties of nonpolar compounds and slightly polar compounds such as normal paraffins, i-butane, and benzene. The results are in close agreement with the experimental measurements on density, vapor pressure and enthalpy values. The equation is extended to polar and associative compounds through the mean-potential model by making the energy parameter of the square-well potential a temperature dependence.

The equation is applied to over sixty selected substances including hydrocarbons (from methane to eicosane), natural gas components (CO_2 , H_2S , N_2), alcohols,

amines, ethers, ketones, and nitrogen-, oxygen-, and sulfur-containing coal compounds. The accuracy in liquid density and vapor pressure prediction, in most cases, is within 1%. Comparison with similar equations of state, such as Peng-Robinson and B&A equations shows that the present equation is uniformly superior.

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Chapter I

INTRODUCTION

In 1873, van der Waals proposed an equation of state which has since become the basis for numerous empirical and theoretical modifications to describe the thermodynamic behavior of fluids. The pressure equation of van der Waals can be written as:

$$P = P_r + P_a = \frac{RT}{V-Nb} - \frac{a}{V^2} \quad (1)$$

where P is the pressure, V the molar volume, R the universal gas constant, N the number of moles, and T the absolute temperature. The first term on the right-hand side of Equation (1), $P_r = RT/(V-Nb)$, represents the pressure due to repulsive forces between the impenetrable rigid spheres of volume b . The second term, $P_a = -a/V^2$, is due to a uniform intermolecular attraction where 'a' is a parameter characterizing the strength of the attraction. Since the van der Waals equation fails to give accurate representation of experimental thermodynamic data of real fluids, many modifications have been proposed. Empirical or semi-empirical modifications of the van der Waals equation

usually involved the introduction of temperature and/or density dependence of the parameters a and b resulting in an improvement over the original equation. Examples are the Redlich-Kwong equation, the Soave-Redlich-Kwong equation, and the familiar Peng-Robinson (PR) equation where

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)+b(v-b)} \quad (2)$$

$a(T)$ is a function of critical temperature, reduced temperature and an acentric factor. These equations of state are attractive to industrial uses because they are simple and accurate when applied to small hydrocarbons and light gases. However, the disadvantages of these equations are their failure to predict accurately the liquid densities and the properties of polar compounds. These properties become more and more important to engineering design calculations. This research, therefore, focuses on the improvement of the liquid and dense fluid property calculations of both small and large, polar and nonpolar compounds.

Another approach to the development of an equation of state is through statistical mechanics - the study of the fundamental connection between the macroscopic properties of a substance and the forces between the constituent molecules - the intermolecular forces. However, there is still a lack

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of knowledge of the exact form of the intermolecular forces. Therefore, it is generally approached by assuming an algebraic form for the dependence of the intermolecular force upon intermolecular separation; calculating bulk physical properties through the appropriate molecular theory; and finally comparing these calculations with the experimental data for the same physical property. Agreement between the two sets of data is supposed to indicate the correctness of the assumed intermolecular force law (Maitland, 1981).

In order to calculate thermodynamic properties of fluid by means of the intermolecular potential functions, the following assumptions are usually made (Reed & Gubbins, 1973, Umesl, 1983):

1. Intermolecular pair-potential energies are those for an isolated pair of molecules. This assumption is valid only at low densities.
2. Total energy is a sum of all possible isolated-pair energies (pairwise additivity).
3. Pair-potential energy depends only on the distance between centers of mass (valid only for monatomic molecules).
4. Some approximate analytic equations, containing one or more molecular constants characteristic of the type of molecule may be used for the potential energy as a function of the distance between a pair of molecular centers.

The work of van der Waals suggests that the general form of the intermolecular potential energy function be

$$\phi(r) = \phi_r(r) + \phi_a(r) \quad (3)$$

where the intermolecular pair-potential, $\phi(r)$ is a sum of a positive contribution - the repulsive force, $\phi_r(r)$, and a long-range negative contribution - the attractive force, $\phi_a(r)$. The general shape of the pair-potential is shown in Figure 1. σ is the separation at which the potential energy is zero. r_0 is the separation at which the energy attains its minimum value ϵ which is the usual measure of the strength of the interaction.

As mentioned earlier, in order to calculate the macroscopic properties from the microscopic properties, the assumptions of an analytic form for the relationship between pair-potential energy and the intermolecular separation are made. Normally, these functions are written with a number of parameters whose values are to be determined by imposing the condition that the calculated and the experimental data for a particular physical property should be in agreement. Numerous models of the intermolecular potential have been proposed: the simple models - the hard spheres and the square-well model, and the more complicated ones - the Stockmayer potential (see Maitland et al., 1981). However, there is no model available that can satisfactorily

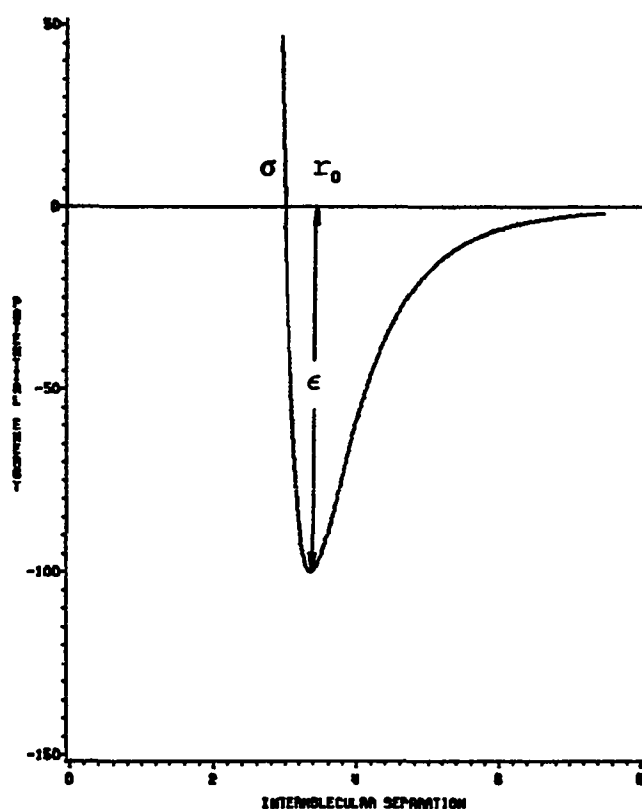


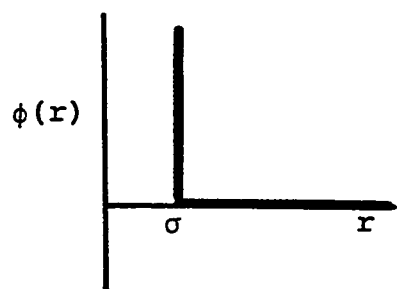
Figure 1: GENERAL SHAPE OF A PAIR-POTENTIAL ENERGY FUNCTION

characterize all the properties of interest for a wide variety of fluids. Figure 2 shows some pair-potential models for spherical molecules (Hirschfelder et al., 1954).

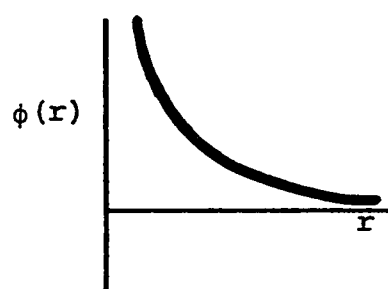
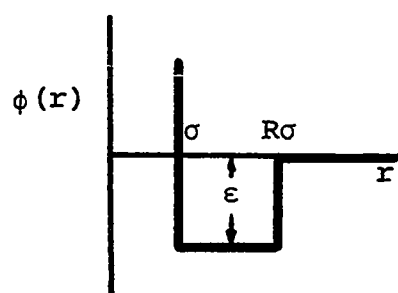
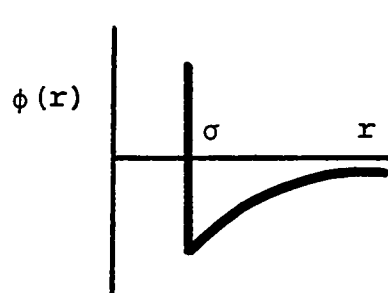
The objective of this work is to utilize the modern theories of statistical mechanics to develop an equation of state which is valid for pure nonpolar and polar molecules with a fair degree of accuracy. Such an equation of state is used in engineering design calculations to estimate thermodynamic properties of a wide variety of fluids. The

new equation, modeled after the nonspherical square-well potential, is derived in Chapter II from the statistical mechanical virial equation of state. The repulsive part is approximated by the expression of hard convex bodies. The attractive part is obtained by introducing the density and temperature dependence approximations to the pair correlation function.

The newly developed equation is first tested for pure normal paraffins from methane to n-eicosane in Chapter III. The values of the adjustable parameters for each compound are obtained from a multiproperty analysis of available thermodynamic property data. The equation is then tested for other nonpolar compounds, such as ethylene, propylene, benzene, etc. The prediction results, as well as the values of the parameters, are reported in Chapter III. The extension of the new equation to the pure polar and associative compounds by assigning a semi-theoretical temperature dependence to the energy parameter, ϵ , is discussed in Chapter II. The results are reported in Chapter III. Comparisons of the predictions with some other equations of state are also given in Chapter III, followed by the conclusions and recommendations in Chapter IV.



Rigid spheres

Point centers of
repulsionSquare-well
potential

Sutherland model

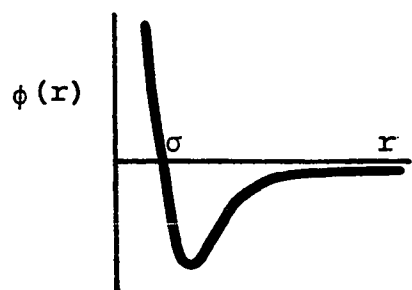
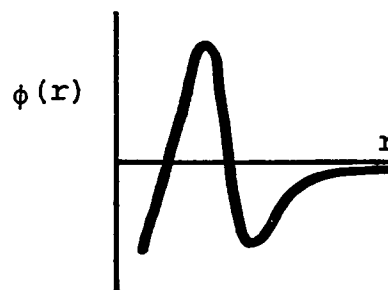
Lennard-Jones
potentialBuckingham
potential

Figure 2: MODEL PAIR-POTENTIALS

Chapter II

DEVELOPMENT OF THE EQUATION OF STATE

From statistical mechanics, the relationship between the macroscopic property of a system - pressure and the properties of the particles contained in a system of N identical particles interacting according to a potential $U(r^N)$, in a volume V , at temperature T , is given by an expression

$$P = \frac{k T}{Q} \left[\frac{\delta Q}{\delta V} \right]_T \quad (4)$$

where Q is the configurational partition function

$$Q = \int \dots \int \exp \{ -U(r^N)/kT \} dr^N. \quad (5)$$

The symbol r^N represents the N vector coordinates $r_1, r_2, \dots, r_N$ of the N particles. If the potential $U(r^N)$ is written as a sum of pair-potentials, $\phi(r)$; Equation (4) becomes

$$\frac{p}{NkT} = 1 - \frac{\rho}{6kT} \int_0^\infty r^3 \frac{d\phi(r)}{dr} g(r) 4\pi dr \quad (6)$$

where k is the Boltzmann constant, r is the intermolecular distance, ρ is the particle density, N/V , and $g(r)$ is the radial distribution function (which measures the probability of finding a particle at a given distance from a fixed particle in the fluid). In addition to the distance r , $g(r)$ is also a function of density and temperature (and composition for mixtures),

$$g(r; \rho, T) = \frac{N(N-1)}{\rho^2 Z} \int \dots \int \exp\{-\beta U^N\} dr_3 \dots dr_N \quad (7)$$

The configuration integral Z is defined as

$$Z = \int \dots \int \exp\{-\beta U^N\} dr_1 \dots dr_N \quad (8)$$

The function $g(r)$ has two important uses: one is used to discuss the structure of fluid and the other is to obtain the thermodynamic properties of the system. Equation (6) is known as the virial equation of state.

We can see that Equation (6) includes the ideal gas term, 1, and a contribution from the two-body interactions

of the system. When the three-body and higher order interactions are present, additional terms written as integrals, including many-body distribution functions, are added to the right-hand side of Equation (6).

The actual calculation of either the configurational integral Q , or the radial distribution function g (which depends on ϕ) usually involves considerable difficulties even for the simple pair-potential model molecules such as hard spheres or square-wells. Therefore, various approximation theories on the intermolecular potential model, the radial distribution function, and the relation between them have been introduced. The approximations are such as the hypernetted chain equation, the Percus-Yevick equation, and the Mean Spherical Approximation (Reijhart, 1976).

The square-well potential model is one of the intermolecular potential models frequently used in the study and development of an equation of state, for example, Alder et al. (1972), Reijnhart (1976), Chen and Kreglewski (1977), and Simmick et al. (1979). It represents the pair-potential energy function by a set of line segments which offers considerable mathematical convenience in evaluating properties from statistical mechanical formulas (Reed & Gubbins, 1973). Besides their simplicity, the equations of state based on the square-well potential model have proven to be a qualitatively reasonable approximation to real

simple fluids compared with the Monte Carlo and molecular dynamic computer simulation results (Smith et al., 1977).

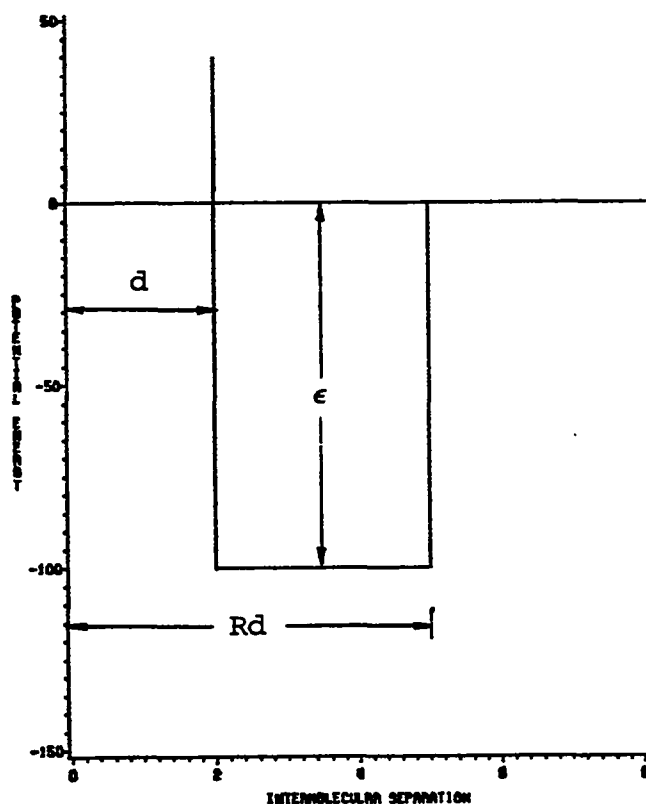


Figure 3: SQUARE-WELL PAIR-POTENTIAL

From Figure 3, d is the collision diameter between two molecules. $d(R-1)$ is the well-width where R is the ratio of the ranges of the attractive and the repulsive parts of the potential. ϵ is the well-depth of the potential measuring the attractive strength of the pair-potential. For a one-component isotropic system, d is equal to the molecular diameter of hard spheres.

Equation (6) can be integrated analytically for the spherical square-well potential.

$$\begin{aligned} \frac{P V}{N k T} = & 1 + \frac{2 \pi}{3} \rho d^3 g_{sw}(d^+) \\ & - \frac{2 \pi}{3} \rho d^3 R^3 \{ g_{sw}(Rd^+) + g_{sw}(Rd^-) \} \end{aligned} \quad (9)$$

$$\text{let } y(r) = g(r) \exp\{\beta \phi(r)\} \quad (10)$$

where $\beta = 1/kT$. Equation (9) becomes

$$\begin{aligned} \frac{P V}{N k T} = & 1 + \frac{2 \pi}{3} \rho d^3 \exp\{\beta \epsilon\} y(d) \\ & - \frac{2 \pi}{3} \rho d^3 R^3 \{\exp(\beta \epsilon) - 1\} y(Rd) \end{aligned} \quad (11)$$

In the equation of state proposed by Reinhardt (1976), an equation of hard spheres was used to represent the

repulsive part of the square-well potential. The expression of the attractive part was obtained by making an approximation of the square-well distribution function with the distribution function of hard spheres, which can be obtained analytically, for example, from the Percus-Yevick's theory (Peter et al., 1979). The equation was tested for its ability to describe the P-V-T data of methane. Satisfactory results were obtained, except in the low density region and in the neighborhood of the critical point.

The first two terms on the right-hand side of Equation (11) are the repulsive contribution. These two terms can be approximated by the equation of hard spheres for an isotropic system (Smith et al., 1977, Reijnhart, 1976, and Henderson, 1979).

$$\frac{P}{NkT} = Z_{hs} - \frac{4\pi}{6} \rho d^3 R^3 y(Rd) \{ \exp(\beta\epsilon) - 1 \} \quad (12)$$

where Z_{hs} is the compressibility factor of hard spheres. The values of Z_{hs} can be evaluated analytically by using, for example, the Carnahan-Starling equation of state (Carnahan and Starling, 1969).

In order to apply Equation (12) to a real fluid system, the behavior of $y(r)$ (or $g(r)$) must be known. This

knowledge is provided in the distribution function theories (Hansen and McDonald, 1976, Lee and Chung, 1983):

1. The radial distribution function can be written as a Maclaurin's expansion about $\rho = 0$:

$$\begin{aligned} g(r; \rho, T) &= \sum_{n=0}^{\infty} g_n \rho^n \\ &= g_0 + g_1 \rho + g_2 \rho^2 + \dots \end{aligned} \quad (13)$$

where g_0 represents the interaction of molecular pairs, g_1 the interaction of molecular trio, etc. Each g is a function of r and T only (Reed & Gubbins, 1973). For low densities, the radial distribution function may be approximated by (Reijnhart, 1976)

$$g(r) \approx g_0 = \exp \{ - \beta \phi(r) \} \quad (14)$$

which leads to

$$\lim_{\rho \rightarrow 0} y(r) = 1 \quad (15)$$

2. $y(r)$ is related to other correlation functions through the following equation:

$$y(r) = \exp \{ h(r) - C(r) + B(r) \} \quad (16)$$

where $h(r)$ is the total correlation function, $C(r)$ the direct correlation function, and $B(r)$ the bridge function. Their cluster series, up to the second order in density, are:

$$h(r) - C(r) + B(r) = \underbrace{\text{diag 1}}_{1\ 2} + \underbrace{\text{diag 2}}_{1\ 2} + \underbrace{\text{diag 3}}_{1\ 2} + \underbrace{\text{diag 4}}_{1\ 2} + \frac{1}{2} \underbrace{\text{diag 5}}_{1\ 2} + \frac{1}{2} \underbrace{\text{diag 6}}_{1\ 2} + O(\rho^3) \quad (17)$$

where the bond $\text{---}\overset{\circ}{\underset{1}{\text{O}}}\text{---}\overset{\circ}{\underset{2}{\text{O}}}\text{---}$ represents the Mayer factor $f(r) = \exp \{-\beta\phi(r) - 1\}$. The cluster integrals are functions of temperature and the expansion is in terms of density.

If all orders of the expansion are kept, an exact theory for the attractive term can be obtained. However, in practice, in order to make calculations for real fluids, some simplifications are needed. Approximate closures of the above series (where one or more diagrams on the right-hand side of Equation (17) are missing) are, for example, the Percus-Yevick closure and the hypernetted chain closure. In this work, an approximation of $y(r)$ is introduced based on Equation (16) and (17). It will be discussed in the next section.

In the case of anisotropic systems, the interaction between two nonspherical molecules is still separated into a short-range repulsive and a long-range attractive force. But in addition to the center to center distance $\{R_{12}\}$, the square-well parameters $\{d, R, \epsilon\}$ also depend on the relative orientations of the molecules, i.e. the Euler angles ω_1 and ω_2 . The pair-potential between two nonspherical molecules has the general form of

$$\phi(1, 2) = \phi(R_{12}, \omega_1, \omega_2) \quad (18)$$

where $\omega_i = \phi_i \theta_i \chi_i$ (or $\phi_i \theta_i$ for linear molecules) is the orientation of molecule i as shown in Figure 4.

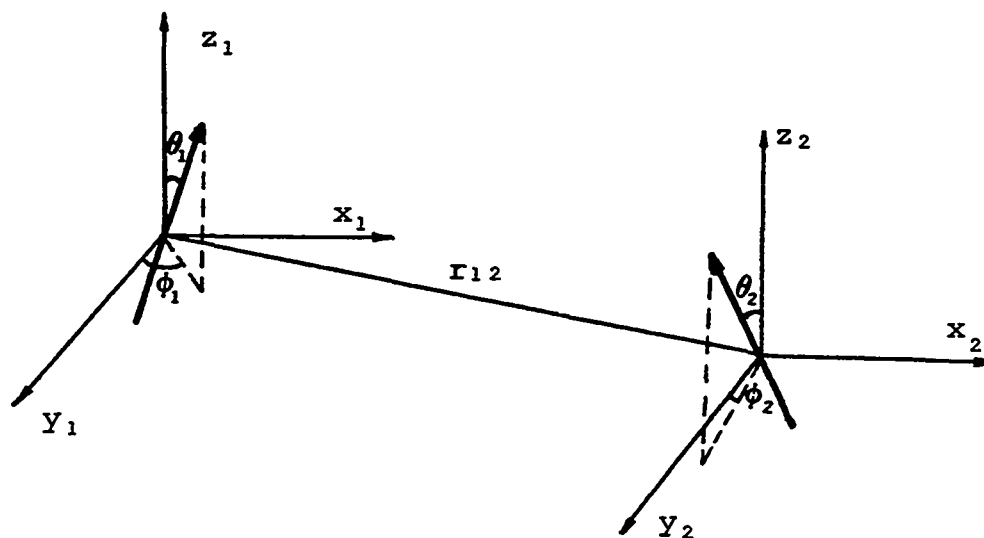


Figure 4: GEOMETRY OF A PAIR OF CONVEX BODIES

The effect of orientation dependent interactions of asymmetric molecules may not be very significant in the gas phase where molecules are widely separated. The spherically symmetric potential, such as the Lennard-Jones potential, can adequately describe the behavior of such system. However, at higher densities and in the liquid phase, the interactions between the nonspherical molecules become significant. Therefore, the nonspherical effects must be included in the intermolecular potential. Figure 5 and 6 show the typical orientations of the nonspherical molecules and the potential energies between nitrogen molecules corresponding to various orientations in Figure 5 as a function of the distance between the centers of molecules (Kihara and Ichimaru, 1976).

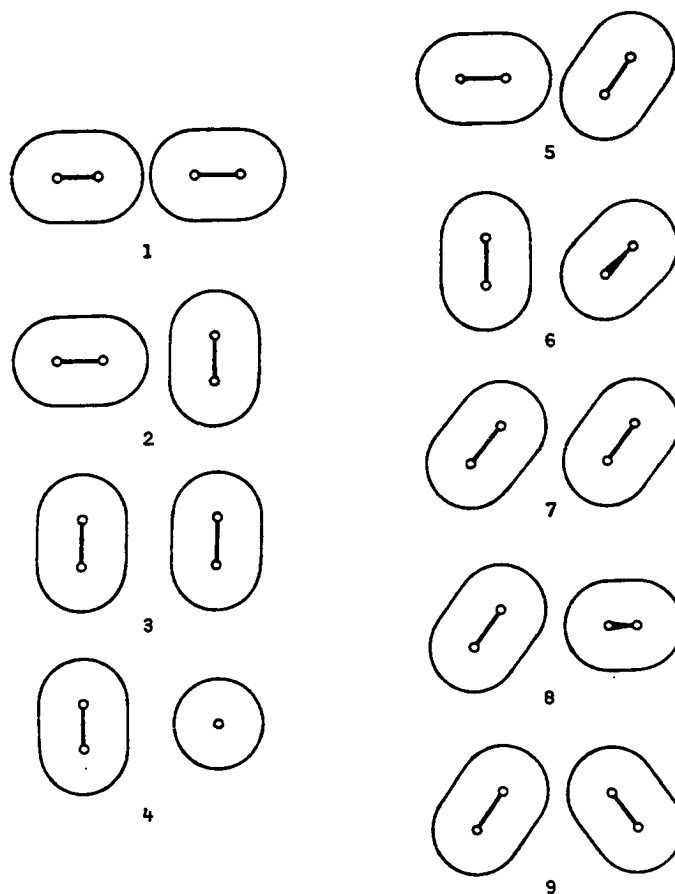


Figure 5: NINE TYPICAL ORIENTATIONS OF MOLECULES

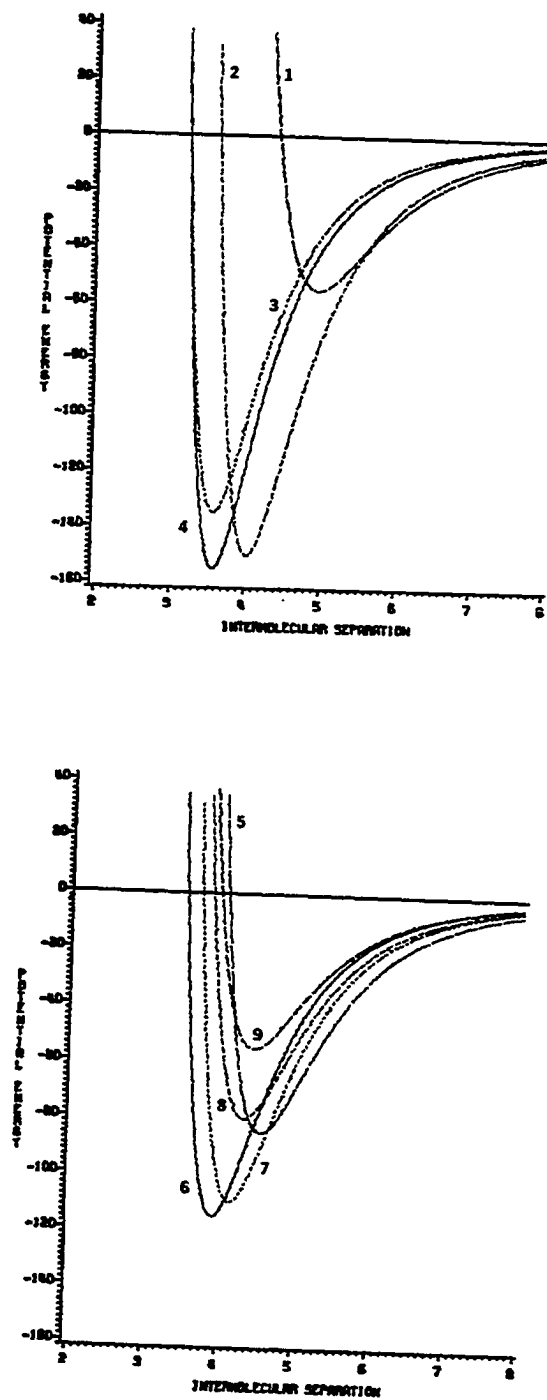


FIGURE 6: POTENTIAL BETWEEN NITROGEN MOLECULES
AT VARIOUS ORIENTATIONS

2.1 EQUATION OF STATE FOR NONPOLAR COMPOUNDS

Equation (12), previously introduced for spherically symmetric molecules, can be readily extended to the nonspherical system. First, by replacing the repulsive part of Equation (12) - Z_{hs} by the compressibility factor or hard convex bodies - Z_{hc} . Second, the angle-dependent parameters in the attractive part of Equation (12) are replaced by the angular-average values:

$$\langle V(R_{12}, \omega_1, \omega_2) \rangle = \frac{1}{(4\pi)^2} \int \int V(R_{12}, \omega_1, \omega_2) d\omega_1 d\omega_2 \quad (19)$$

$$= \frac{1}{(4\pi)^2} \int_0^\pi d\theta_1 \sin\theta_1 \int_0^{2\pi} d\phi_1 \int_0^\pi d\theta_2 \sin\theta_2 \int_0^{2\pi} d\phi_2 V(R_{12}, \omega_1, \omega_2) \quad (20)$$

where $\langle \quad \rangle$ indicates the average value over the orientations of any parameter V . Equation (18) becomes:

$$\frac{P}{NkT} = Z_{hc}$$

$$- \frac{4\pi}{6} \langle Rd \rangle^3 \rho \{ \exp (\beta \langle \epsilon \rangle) - 1 \} y(\langle Rd \rangle) \quad (21)$$

Upon employing the mean value theorem in calculus, the angular average can be evaluated at the mean values of the Euler angles, ω_1 and ω_2 . Equation (21) becomes

$$\frac{P}{NkT} = Z_{hc}$$

$$- \frac{4\pi}{6} \bar{Rd}^3 \rho \{ \exp (\beta \bar{\epsilon}) - 1 \} y(\bar{Rd}) \quad (22)$$

where the overbar indicates function at the mean values.

In this work, Z_{hc} in Equation (22) is replaced by the equation of state for hard convex bodies developed by Nezbeda (1976) and will be referred to as Z_{nez} . The expression of Z_{nez} is obtained from an analysis of the second to the fifth virial coefficients of the hard core molecules.

$$Z_{\text{nez}} = \frac{1 + (3C-2)y + (C^2+C-1)y^2 - C(5C-4)y^3}{(1-y)^3} \quad (23)$$

where C is the hard convex body shape factor, $y = \rho b$ is the packing fraction, ρ is the density, and b is the hard convex molecular volume. For hard spheres, C is equal to 1 and Equation (23) is reduced to the Carnahan-Starling equation of hard spheres. C is greater than 1 for nonspherical molecules.

Substituting Z_{hc} in Equation (22) by Z_{nez} from Equation (23):

$$Z = \frac{1 + (3C-2)y + (C^2+C-1)y^2 - C(5C-4)y^3}{(1-y)^3} - 4 V a^* \rho^* \{ \exp (1/T^*) - 1 \} y (\bar{R}d) \quad (24)$$

where

$$\rho^* = \rho \sigma^3$$

$$T^* = k T / \epsilon$$

$$V a^* = V a / \sigma^3 = \bar{R} d^3 \pi / 6$$

σ^3 is the density-reducing parameter having the unit of volume.

For further evaluation of Equation (24), the following approximation of $y(\bar{R}d)$ is introduced:

$$y(\bar{R}d) = \exp \{ - a' \rho^* / T^* \}. \quad (25)$$

The approximation (Equation (25)) is based on Equation (16), Equation (17), and the knowledge that the radial distribution function depends weakly on temperature but depends strongly on density (Beret and Prausnitz, 1975, Watts and McGee, 1976). a' is a constant specifying the temperature and density dependence. Substituting Equation (25) into Equation (24) leads to the following equation:

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

$$- 4 Va^* \rho^* \{ \exp \{1/T^*\} - 1 \}$$

$$\exp \{ - a' \rho^* / T^* \}. \quad (26)$$

Equation (26) is first applied to n-butane. Comparison between the experimental thermodynamic property data and the calculated values shows good agreement in density prediction. However, poor results are obtained from the predictions of enthalpy and vapor pressure calculations. Further modification of $y(\bar{R}d)$ is accomplished by introducing a density dependence term of higher order to Equation (25):

$$y(\bar{R}d) = \exp \{ -a' \rho^* / T^* \}$$

$$+ \rho^* \exp \{ -a'' \rho^{*2} / T^* \} \quad (27)$$

where a'' is the second constant. The combination of Equation (27) and (26) yields

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

$$- 4 Va^* \rho^* \{ \exp \{1/T^*\} - 1 \}$$

$$\{ \exp \{-a^* \rho^*/T^*\} + \rho^* \exp \{-a^* \rho^{*2}/T^*\} \}. \quad (28)$$

The prediction result of Equation (28) shows a significant improvement over Equation (26), especially in the enthalpy calculation.

In order to test the ability of Equation (28) for the low density prediction, the new equation is used to calculate the second virial coefficients (B_2) of n-butane, where

$$B = (1+3C) b - 4 Va \{ \exp(\bar{\epsilon}/kT) - 1 \}. \quad (29)$$

The parameters used in Equation (29) are determined from the regression analysis of the experimental PVT data mentioned earlier. Comparison of B_2 obtained from Equation (29) and the experimental values of Dymond and Smith (1980) is shown in Figure 6. It is obvious that Equation (29) does not represent the second virial coefficients very well, since the calculated values are much higher than the experimental

values. This may be due to the fact that the second virial of hard convex bodies is too strong for real molecules which are considered softer. Improvement is made by replacing the second virial of the hard convex bodies by an adjustable parameter Br - the effective repulsive contribution of B_2 . This leads to

$$\begin{aligned}
 Z &= Z_{\text{neq}} - (1+3C) y + Br^* \rho^* \\
 &- 4 Va^* \rho^* \{ \exp(1/T^*) - 1 \} \\
 &\{ \exp(-a' \rho^*/T^*) + \rho^* \exp(-a'' \rho^{*2}/T^*) \} \quad (30)
 \end{aligned}$$

where

$$Br^* = Br / \sigma^3$$

and

$$B_2 = Br - 4 Va \{ \exp(\bar{\epsilon}/kT) - 1 \}. \quad (31)$$

Results from Equation (30) show significant improvement over Equation (28) especially in vapor pressure calculations. The deviation of density reduces from 1.73% to 0.70%; vapor pressure deviation reduces from 3.21% to 1.09%; and the enthalpy departure deviation reduces from 0.39 to 0.34 btu/lb. A better prediction of B_2 is also obtained as shown in Figure 6. Figure 7 shows the contributions of the repulsive compressibility factor - Z_r (the first three terms on the right-hand side of Equation (30)) and the attractive compressibility factor - Z_a (the last term on the right hand-side of Equation (30)) to the total compressibility factor Z at two temperatures (T). Z_r is positive and independent of temperature, while Z_a is negative. The absolute value of Z_a decreases as temperature increases. Therefore, the behavior of gas at very high temperature and in liquid phase is dominantly controlled by the repulsive forces between molecules.

The density calculation at each temperature and pressure is obtained by solving the pressure expression of Equation (30): $P = \rho ZRT$ which requires iterations until the convergence criteria is satisfied. The density search technique used in this work was developed by Goin (1978). The enthalpy departure is calculated by the expression derived from the classical thermodynamics (Balzhiser et al., 1972):

$$\frac{H - H^0}{R T} = (Z-1) - \int_0^{\rho^*} T^* \left[\frac{\partial Z}{\partial T^*} \right]_{\rho^*} \frac{d\rho^*}{\rho^*} \quad (32)$$

where

$$\begin{aligned} T^* \int_0^{\rho^*} \left[\frac{\partial Z}{\partial T^*} \right]_{\rho^*} \frac{d\rho^*}{\rho^*} &= -4 Va^* T^* \\ &\left\{ \frac{e^{1/T^*}}{T^*} \left[\frac{e^{-a' \rho^*/T^*}}{a'} - 1 \right] + \frac{e^{-a'' \rho^{*2}/T^*}}{a''} - 1 \right\} \\ &- (e^{1/T^*} - 1) \\ &\left\{ \rho^* \left(e^{-a' \rho^*/T^*} + \frac{\rho^*}{2} e^{-a'' \rho^{*2}/T^*} \right) \right. \\ &\left. + T^* \left(\frac{e^{-a' \rho^*/T^*}}{a'} + \frac{e^{-a'' \rho^{*2}/T^*}}{2a''} - 1 \right) \right\} \quad (33) \end{aligned}$$

The vapor pressure P of a substance at a given temperature is obtained by satisfying the following criteria:

$$P_l = P_v = P$$

and

$$f_l = f_v$$

where l and v are referred to liquid and vapor respectively. The fugacity, f , of a pure component is calculated from the relation:

$$f = RT \exp \left\{ \int_0^{\rho^*} (Z-1) \frac{d\rho^*}{\rho^*} + (Z-1) \right\} \quad (36)$$

where

$$\begin{aligned} \int_0^{\rho^*} (Z-1) \frac{d\rho^*}{\rho^*} = & (5C^2 - 4C - 1) \ln(1-y) \\ & + \frac{(9C^2 - 9C + 2)}{(1-y)} + \frac{(-2C^2 + 4C - 1)}{(1-y)^2} \\ & - (7C^2 - 5C + 1) - (1 + 3C)y \\ & + Br^* \rho^* \\ & - 4Va^* T^* (e^{1/T^*} - 1) \\ & \left\{ \frac{e^{-a'\rho^*/T^*}}{a'} - 1 + \frac{e^{-a''\rho^{*2}/T^*}}{a''} - 1 \right\} \end{aligned} \quad (37)$$

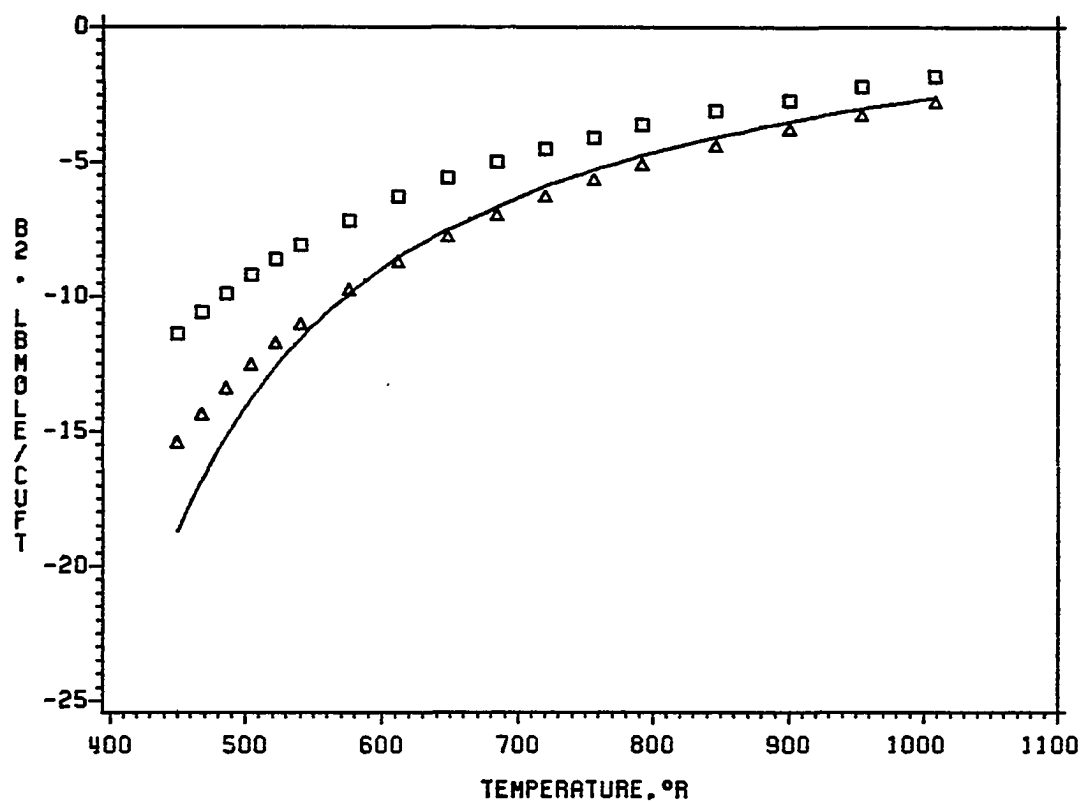


FIGURE 7: COMPARISON OF THE SECOND VIRIAL COEFFICIENTS OF N-BUTANE

— =EXPERIMENTAL, $\square$ =EQUATION (29), Δ =EQUATION (31)

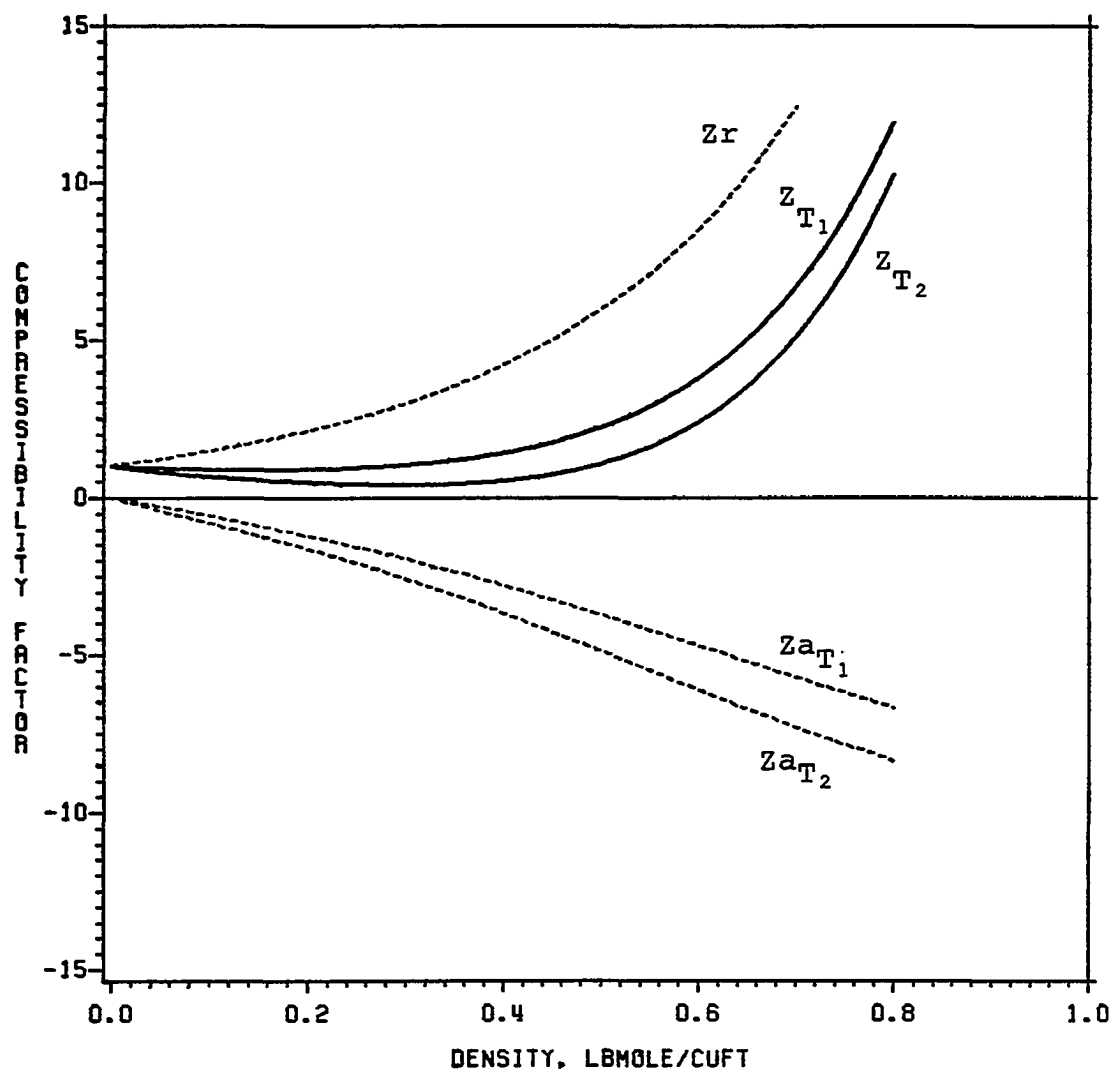


FIGURE 8: PLOT OF THE COMPRESSIBILITY FACTORS VERSUS DENSITY
($T_1 > T_2$)

2.2 EQUATION OF STATE FOR POLAR AND ASSOCIATIVE COMPOUNDS

In previous researches, the development of equations of state for polar fluids can be divided into two categories. One is through empirical algebraic expressions. The other consists of the rigorous statistical mechanical studies of polar fluids. Extension of an equation of state for nonpolar to polar fluids often involves assigning an empirical temperature dependence to the equation-of-state parameters (e.g. Nakamura et al., 1976, Soave, 1979, as cited by Whiting and Prausnitz, 1982) or through the perturbation theory. The latter approach is usually resulting in separating the equation-of-state parameters into the nonpolarity contribution and the polarity contribution (e.g. Watanasiri, 1982, Whiting and Prausnitz, 1982, Umesi, 1983, and Chung, Khan, Lee and Starling, 1984).

In a nonpolar molecule, the centers of negative charges and the positive charges are coincident. Intermolecular pair-potential energies of nonpolar molecules are the summation of a short-range repulsive contribution and a long-range attractive contribution mainly from dispersion energies.

In a polar molecule, the centers of negative and positive charges are not coincident. Therefore, there are additional contributions to the pair-potential energies from the polarization or induction energies and the direct electrostatic energies (associated with dipole, quadrupole

and higher electric moments characterizing the charge distributions of each molecule in an interacting pair).

For a pair of associated molecules, the attraction interaction between them is sufficiently strong to give empirical evidence of the formation of a new molecular species involving both molecules. In addition to all types of energies in polar molecules, there is a contribution from residual valence interactions. Molecules exhibiting residual valence interactions (i.e., hydrogen-bonding) are called associated molecules. Examples are molecules having -OH, >NH or -SH structure such as H₂O, NH₃, alcohols, amines and carboxylic acids (Reed & Gubbins, 1973).

From statistical mechanics, the pair-intermolecular potential energy function of polar molecules may be represented by the Lennard-Jones potential function (nonpolar contribution) together with the contributions of dipole, quadrupole and dipole-quadrupole interactions (Stell et al., 1974, Alem and Mansoori, 1984):

$$\begin{aligned} \phi(r_{12}, \omega_1, \omega_2) = & 4 \epsilon \left\{ \left[\frac{\sigma}{r_{12}} \right]^{12} - \left[\frac{\sigma}{r_{12}} \right]^6 \right\} \\ & + \phi^{\mu\mu}(r_{12}, \omega_1, \omega_2) \\ & + \phi^{\mu Q}(r_{12}, \omega_1, \omega_2) \\ & + \phi^{QQ}(r_{12}, \omega_1, \omega_2) \end{aligned} \quad (38)$$

where, for interacting molecules of the same kind

$$\begin{aligned} \phi^{\mu\mu}(r_{12}, \omega_1, \omega_2) &= -\mu^2 \{ 2 \cos \theta_1 \cos \theta_2 \\ &\quad - \sin \theta_1 \sin \theta_2 \\ &\quad \cos(\phi_1 - \phi_2) \} / r_{12}^3 \end{aligned} \quad (39)$$

$$\begin{aligned} \phi^{\mu Q}(r_{12}, \omega_1, \omega_2) &= -3 \mu Q \{ \cos \theta_1 \cos \theta_2 \\ &\quad - \sin \theta_1 \sin \theta_2 \\ &\quad \cos(\phi_1 - \phi_2) \} / 4 r_{12}^4 \end{aligned} \quad (40)$$

$$\begin{aligned} \phi^{QQ}(r_{12}, \omega_1, \omega_2) &= -3 Q^2 \{ 1 - 5 \cos^2 \theta_1 - 5 \cos^2 \theta_2 \\ &\quad - 15 \cos^2 \theta_1 \cos^2 \theta_2 \\ &\quad + 2 \{ \sin \theta_1 \sin \theta_2 \cos(\phi_1 - \phi_2) \\ &\quad - 4 \cos \theta_1 \cos \theta_2 \} \} / 16 r_{12}^5 \end{aligned} \quad (41)$$

μ is the dipole moment, Q is the quadrupole moment, ω_i is the polar angle of molecule i (see Figure 4).

After introducing the configurational angle-average potential function for polar interactions to the above equations, Equations (39) through (41) become:

$$\langle \phi^{\mu\mu}(r_{12}) \rangle_\omega = -\mu^4 / 3 k T r_{12}^6 \quad (42)$$

$$\langle \phi^{\mu Q}(r_{12}) \rangle_\omega = -\mu^2 Q^2 / k T r_{12}^8 \quad (43)$$

$$\langle \phi^{QQ}(r_{12}) \rangle_{\omega} = -7Q^4 / 3 k T r_{12}^{10} \quad (44)$$

Therefore, the angle-average pair-potential energy function of two identical polar molecules will be

$$\begin{aligned} \langle \phi(r_{12}) \rangle_{\omega} = & 4 \epsilon \left\{ \left[\frac{\sigma}{r_{12}} \right]^{12} - \left[\frac{\sigma}{r_{12}} \right]^6 \right\} \\ & - \frac{\mu^4}{3 k T r_{12}^6} \\ & - \frac{\mu^2 Q^2}{k T r_{12}^8} \\ & - \frac{7 Q^4}{3 k T r_{12}^{10}} \end{aligned} \quad (45)$$

As described by Whiting and Prausnitz (1982), the most important term in the multipolar expansion is the dipole-dipole term. Dropping off the last two terms in Equation (45), the orientation-average pair-potential becomes

$$\begin{aligned} \langle \phi(r_{12}) \rangle_{\omega} = & 4 \epsilon \left\{ \left[\frac{\sigma}{r_{12}} \right]^{12} - \left[\frac{\sigma}{r_{12}} \right]^6 \right\} \\ & - \frac{\mu^4}{3 k T r_{12}^6} \end{aligned} \quad (46)$$

Combining the r^{-6} terms in Equation (46) resulted in

$$\langle \phi(r_{12}) \rangle_{\omega} = 4 \epsilon' \left\{ \left[\frac{\sigma^4}{r_{12}} \right]^{12} - \left[\frac{\sigma^4}{r_{12}} \right]^6 \right\} \quad (47)$$

where

$$\epsilon' = \epsilon \left\{ 1 + \frac{\mu^4}{6kT\epsilon\sigma^6} + \dots \right\} \quad (48)$$

$$\sigma'^6 = \sigma^6 / \left\{ 1 + \frac{\mu^4}{12kT\epsilon\sigma^6} + \dots \right\} \quad (49)$$

The truncated terms are all of higher order in reciprocal temperature. Equation (48) can be approximated as

$$\epsilon' = \epsilon + \frac{\mu^4}{6kT\sigma^6} \quad (50)$$

where the potential well-depth parameter, ϵ' , is a sum of the nonpolar value (ϵ) and the polar contribution ($\mu^4 / 6kT\sigma^6$) which is similar to the relationship of the pair-potential in Equation (46). Therefore, for polar fluids, an effective potential well-depth parameter is assigned as

$$\frac{\epsilon'}{k} = \frac{\epsilon}{k} + \frac{K}{T b^2} \quad \{51\}$$

to take into account the polarity contribution based on the angle-average interaction between point dipoles. b is the closed-packed molar volume and K is a measure of polarity. For nonpolar fluids, $K=0$. A similar approach was successfully employed by Whiting and Prausnitz (1982) and Khan (1983) for extending an equation of state to polar fluids.

Chapter III

RESULTS AND DISCUSSION

The new equation of state is applied to a wide variety of pure fluids found in natural gases, petroleum and coal chemicals. The compounds tested are ranged from straight-chain nonpolar hydrocarbons - normal paraffins; other nonpolar or slightly polar fluids, such as ethylene, isobutane and benzene; to various classes of polar and associative compounds, including carbon dioxide, ammonia, alcohols, ethers, ketones, amines, many nitrogen-, oxygen-, and sulfur- containing compounds with an emphasis on liquid phase properties. In liquid phase, the interactions between polar molecules play a much more important role than in the gas phase where interactions mostly vanish after averaging with respect to molecular orientations (Kihara & Ichimaru, 1976).

Critical properties of each compound are taken either from Reid et al. (1977) or from the sources where the thermodynamic data are obtained. The data sources of all compounds tested are summarized in Table 1, and the physical properties are in Table 2. The values of the adjustable parameters are determined from the multiproperty regression of the experimental thermodynamic property data (density,

vapor pressure, and enthalpy, where available) using the regression program developed by Goin (1978).

TABLE 1

DATA REFERENCES OF NORMAL PARAFFINS, OTHER NONPOLAR, POLAR,
AND ASSOCIATIVE COMPOUNDS

component	property	number of points	data reference(s)
Methane	RHOL	21	Van Itterbeek et al. (1963), Vennix (1966), Yesavage (1968), Matthews (1946), Douslin et al. (1964)
	RHOV	18	
	VP	32	
	ENTH	33	
Ethane	RHOL	39	Sage and Lacey (1950), API-44 (1978), Canjar and Manning (1967)
	RHOV	7	
	VP	46	
	ENTH	85	
Propane	RHOL	130	Sage and Lacey (1950), Canjar and Manning (1967), Huang (1967), API-44 (1978), Yesavage (1968)
	RHOV	4	
	VP	55	
	ENTH	26	
n-Butane	RHOL	31	API-44 (1978), Sage and Lacey (1950), Canjar and Manning (1967)
	RHOV	9	
	VP	52	
	ENTH	39	
n-Pentane	RHOL	24	API-44 (1978), Sage and Lacey (1950), Canjar and Manning (1967)
	RHOV	15	
	VP	45	
	ENTH	38	
n-Hexane	RHOL	41	API-44 (1978), Canjar and Manning (1967), Stewart et al. (1954)
	VP	53	
n-Heptane	RHOL	41	API-44 (1978), Stuart et al. (1950), Kay (1938), Gilliland and Parekh (1942)
	VP	40	
	ENTH	17	

TABLE 1 (CONTINUED)

component	property	number of points	data reference(s)
n-Octane	RHOL	47	Reid et al. (1977), API-44 (1978)
	RHOV	1	
	VP	56	
	ENTH	54	
n-Nonane	RHOL	43	Vargaftik (1975), Reid et al. (1977), API-44 (1978)
	VP	18	
n-Decane	RHOL	32	Sage and Lacey (1950), Vargaftik (1975), API-44 (1978)
	VP	18	
n-Undecane	VP	19	Vargaftik (1975)
n-Dodecane	RHOL	17	Vargaftik (1975), API-44 (1978)
	VP	21	
n-Tridecane	RHOL	17	Vargaftik (1975), Zwolinski and Wilhoit (1971)
	VP	18	
n-Tetra decane	RHOL	14	Vargaftik (1975), Zwolinski and Wilhoit (1971)
	VP	15	
n-Penta decane	RHOL	14	Vargaftik (1975), Zwolinski and Wilhoit (1971)
	VP	14	
n-Hexa decane	RHOL	9	Vargaftik (1975), Zwolinski and Wilhoit (1971)
	VP	10	
n-Hepta decane	RHOL	13	Vargaftik (1975)
	VP	15	
n-Octa decane	RHOL	13	Vargaftik (1975), Zwolinski and Wilhoit (1971)
	VP	15	

TABLE 1 (CONTINUED)

component	property	number of points	data reference(s)
n-Nona decane	RHOL	12	Vargaftik (1975),
	VP	15	Zwolinski and Wilhoit (1971)
n-Eicosane	RHOL	25	Vargaftik (1975),
	VP	15	Zwolinski and Wilhoit (1971)
Ethylene	RHOL	11	API-44 (1978)
	RHOV	29	
	VP	35	Tickner and Lossing (1951),
	ENTH	34	Canjar and Manning (1967)
Propylene	RHOL	22	Farrington and Sage (1949),
	RHOV	35	Michels et al. (1953),
	VP	28	Canjar and Manning (1967)
i-Butane	RHOL	87	Canjar and Manning (1967),
	RHOV	29	Morris et al. (1940),
			Bettie et al. (1950),
			Aston et al. (1940),
	VP	82	Sage and Lacey (1950),
			Connolly (1962),
	ENTH	73	Zwolinsky and Wilhoit (1971), Macknick et al (1978)
i-Pentane	RHOL	13	API-44 (1978),
	RHOV	25	Douslin et al. (1964),
	VP	22	Aston et al. (1940), Silberberg et al. (1959)
Toluene	RHOL	13	Vargaftik (1975),
	VP	33	API-44 (1978)
o-Xylene	RHOL	59	Vargaftik (1975)
	VP	43	
Bicyclo hexyl	VP	23	Weiczorek and Kobayashi (1980)

TABLE 1 (CONTINUED)

component	property	number of points	data reference(s)
Benzene	RHOL	61	Kudchadker et al. (1968), Reid et al. (1977), API-44 (1978), Nicolas et al. (1979), Yaws (1978)
	RHOV	41	
	VP	67	
Fluorene	VP	29	Boublik et al. (1973)
Diphenyl methane	VP	33	Weiczorek and Kobayashi (1980), Wilson et al. (1981)
Dichloro difluoro methane	RHOL	39	ASHRAE (1969)
	RHOV	143	
	VP	40	
	ENTH	40	
Carbon dioxide	RHOL	24	Din (1961), Canjar and Manning (1967)
	RHOV	15	
	VP	33	
	ENTH	39	
Nitrogen	RHOL	11	Canjar and Manning (1967), Streett and Stavely (1968), Mage et al. (1963), Friedman and White (1950)
	RHOV	27	
	VP	19	
	ENTH	77	
Hydrogen sulfide	RHOL	18	Lewis and Frederick (1968), Reamer et al. (1950), Kay and Rambosek (1953), West (1948)
	RHOV	22	
	VP	24	

TABLE 1 (CONTINUED)

component	property	number of points	data reference(s)
Ammonia	RHOL	120	Garnjost (1974),
	RHOV	180	Haar and Gallagher (1977)
	VP	172	
Methyl fluoride	RHOV	131	ASHRAE (1969)
	VP	28	
Butanol	RHOL	32	Kemme and Kreps (1969),
			Ambrose and Townsend (1963),
	VP	92	Ambrose and Sparke (1970),
			Hales and Ellender (1976)
Phenol	RHOL	14	Kudchadker et al. (1977)
	VP	15	
p-Cresol	RHOL	23	Kudchadker et al. (1978a)
	VP	20	
o-Cresol	RHOL	24	Kudchadker et al. (1978a)
	VP	21	
m-Cresol	RHOL	26	Kudchadker et al. (1978a)
	VP	22	
2,3 Xylenol	VP	18	Kudchadker et al. (1978b)
Acetone	RHOL	28	Int. Crit. Tables (1926)
	VP	20	
2-Butanone	VP	16	Collerson et al. (1965)
2- Pentanone	RHOL	18	Collerson et al. (1965),
	VP	18	Meyer and Wagner (1966)

TABLE 1 (CONTINUED)

component	property	number of points	data reference(s)
Dimethyl ether	RHOL RHOV VP	17 17 19	Int. Crit. Tables (1926)
Methyl ethyl ether	RHOL RHOV VP	17 11 18	Int. Crit. Tables (1926)
Diethyl ether	RHOL RHOV VP	22 21 23	Int. Crit. Tables (1926)
Ethyl propyl ether	RHOL VP	17 18	Int. Crit. Tables (1926)
Diphenyl ether	RHOL VP	12 13	Vargaftik (1975)
Acetic acid	RHOL VP	21 23	Int. Crit. Tables (1926)
Methylamine	VP	17	Int. Crit. Tables (1926)
Dimethyl amine	VP	18	Int. Crit. Tables (1926)
Ethylamine	VP	19	Int. Crit. Tables (1926)
Diethyl amine	RHOL VP	17 18	Int. Crit. Tables (1926)
Aniline	RHOL VP	29 34	Kudchadker (1982)
Pyridine	RHOL VP	26 25	Kudchadker (1979)

TABLE 1 (CONTINUED)

component	property	number of points	data reference(s)
4-Methyl pyridine	VP	16	Boublik et al. (1973), Reid et al. (1977)
i- quinoline	RHOL VP	18 63	Viswanath and Wilhoit (1979)
Carbazol	VP	26	Boublik (1973), Kudchadker et al. (1981a)
Acridine	RHOL VP	12 23	Kudchadker et al. (1981a), McNeil (1965)
Formamide	RHOL	67	Int. Crit. Tables (1926)
Ethyl mercaptan	RHOL VP	19 20	Int. Crit. Tables (1926)
Dimethyl sulfide	RHOL VP	20 21	Int. Crit. Tables (1926)
Tetrahydro thiophene	RHOL VP	9 26	Kudchadker et al. (1981b)
Thia naphthene	VP	27	Wieczorek and Kobayashi (1980)
Dibenzo thiophene	VP	19	Sivaraman and Kobayashi (1982)
Dibenzo furan	RHOL VP	42 19	Nasir et al. (1981) Sivaraman and Kobayashi (1982)
Tetrahydro furan	RHOL VP	10 25	Kudchadker et al. (1978c)

RHOL = liquid density
 RHOV = vapor density
 VP = vapor pressure
 ENTH = enthalpy departure

TABLE 2
PHYSICAL PROPERTIES OF NORMAL PARAFFINS.

Component	Molecular weight	Critical Temperature, °R	Critical Pressure, psia	Critical Density, lbmole/cu.ft.
Methane	16.042	343.570	673.100	0.6274
Ethane	30.068	550.000	709.820	0.4218
Propane	44.094	665.640	616.300	0.3121
n-Butane	58.120	765.340	550.700	0.2448
n-Pentane	72.146	845.090	489.500	0.2007
n-Hexane	86.172	913.120	439.700	0.1696
n-Heptane	100.200	972.520	397.000	0.1465
n-Octane	114.220	1023.460	360.600	0.1284
n-Nonane	128.250	1070.170	332.000	0.1150
n-Decane	142.270	1111.570	306.600	0.1037
n-Undecane	156.310	1149.840	285.102	0.0946
n-Dodecane	170.340	1184.940	264.528	0.08956
n-Tridecane	183.370	1216.440	249.832	0.08004
n-Tetradecane	198.390	1249.200	235.136	0.07522
n-Pentadecane	212.450	1272.600	220.440	0.07094
n-Hexadecane	226.450	1290.600	205.744	0.06616
n-Heptadecane	240.470	1319.400	191.048	0.06243
n-Octadecane	254.500	1341.000	174.882	0.05887
n-Nonadecane	268.530	1360.800	161.656	0.05579
n-Eicosane	282.550	1380.600	161.656	0.05302

TABLE 2 (CONTINUED) PHYSICAL PROPERTIES OF NONPOLAR COMPOUNDS.

Component	Molecular weight	Critical Temperature, °R	Critical Pressure, psia	Critical Density, lbmole/cu.ft.
Ethylene	28.050	509.490	728.800	0.50350
Propylene	42.080	657.070	669.000	0.34490
i-Butane	58.120	734.130	526.570	0.24384
i-Pentane	72.146	828.700	490.410	0.20400
Benzene	78.113	1011.888	710.598	0.21250
Toluene	92.142	1065.100	596.820	0.19800
o-Xylene	106.170	1134.360	540.960	0.16920
Bicyclohexyl	166.310	1316.520	371.910	0.10820
Fluorene	166.220	1479.996	523.320	0.10500
Diphenyl methane	168.240	1386.360	414.540	0.11799
Dichloro difluoromethane	120.910	693.000	598.290	0.28769

TABLE 2 (CONTINUED)
 PHYSICAL PROPERTIES OF POLAR AND ASSOCIATIVE COMPOUNDS

Component	Molecular weight	Critical Temperature, °R	Critical Pressure, psia	Critical Density, lbmole/cu.ft.
Carbon dioxide	44.010	547.470	1069.900	0.66410
Nitrogen	28.016	227.070	1296.200	0.69290
Hydrogen sulfide	34.076	672.370	1296.200	0.65710
Ammonia	17.030	729.900	1635.700	0.86148
Methyl fluoride	34.042	572.040	852.600	0.50347
Butanol	74.123	1013.220	640.920	0.22780
Phenol	94.113	1249.700	889.170	0.27300
p-Cresol	108.140	1268.370	746.760	0.22538
o-Cresol	108.140	1255.770	726.180	0.22137
m-Cresol	108.140	1270.530	661.500	0.20010
2,3 Xylenol	122.170	1301.300	710.877	0.17400
Acetone	58.080	914.670	682.080	0.29877
2-Butanone	72.107	964.080	602.700	0.23382
2-Pentanone	86.134	1015.200	564.480	0.20741

TABLE 2 (CONTINUED)

Component	Molecular weight	Critical Temperature, °R	Critical Pressure, psia	Critical Density, lbmole/cu.ft.
Dimethyl ether	46.069	720.000	779.100	0.35073
Methyl ethyl ether	60.096	788.040	637.980	0.28249
Diethyl ether	74.123	840.060	527.730	0.22290
Ethyl propyl ether	88.150	901.080	471.870	0.18272
Diphenyl ether	170.210	1378.800	455.700	0.12139
Acetic acid	60.052	1069.920	839.370	0.36509
Methylamine	31.058	774.000	1081.920	0.44592
Dimethylamine	45.085	787.680	770.280	0.33384
Ethylamine	45.082	820.800	815.850	0.35072
Diethylamine	73.139	893.880	538.020	0.20740
Aniline	93.129	1258.470	770.280	0.22780
Pyridine	79.102	1115.910	827.610	0.24579
4-Methyl pyridine	93.129	1162.800	646.800	0.20007

TABLE 6 (CONTINUED)

Component	Molecular weight	Critical Temperature, °R	Critical Pressure, psia	Critical Density, lbmole/cu.ft.
i-Quinolene	129.160	1445.670	722.486	0.15490
Carbazol	167.200	1620.090	476.280	0.10000
Acridine	179.220	1629.360	441.000	0.11500
Formamide	45.031	985.140	3198.720	0.41512
Ethyl mercaptan	62.134	898.200	796.740	0.30159
Dimethyl sulfide	62.130	905.400	802.620	0.31060
Tetrahydro thiophene	88.168	1137.570	764.400	0.23827
Thianapthene	134.200	1353.600	555.545	0.16210
Tetrahydro furan	72.106	972.270	752.950	0.27870
Dibenzo thiophene	184.270	1618.740	579.180	0.11820
Dibenzofuran	168.190	1508.040	588.000	0.12397

3.1 APPLICATION OF THE EQUATION OF STATE TO NORMAL PARAFFINS

Equation (30) is applied to twenty pure normal paraffins ranging from a simple fluid with one carbon atom - methane, to a long chain molecule with twenty carbon atoms - n-eicosane. Initially, Equation (30) has a total of eight adjustable parameters for each compound: the shape factor (C), the hard convex body volume (b), the effective repulsive contribution of the second virial coefficient (Br), the attractive volume (Va), the energy parameter (ϵ/k), the density-reducing parameter (σ^3), and two constants specifying the temperature and density dependence (a' and a''). These parameters are determined from fitting the available density, vapor pressure and enthalpy data.

From the plot of ϵ/k versus critical temperature T_c , and σ^3 versus critical density ρ_c , for twenty compounds (as shown in Figure 9 and 10), both relations are almost linear. Therefore, following the law of corresponding states, ϵ/k and σ^3 can be correlated to T_c and ρ_c respectively, which results in

$$\epsilon / k = T_c / 2.18601 \quad (52)$$

$$\sigma^3 = 0.572735 / \rho_c \quad (53)$$

The values of critical temperatures and critical densities are listed in Table 2.

The final results are reported in terms of the average absolute deviation (aad) in Table 6 with the values of the corresponding parameters tabulated in Table 3. Generally, Equation (30) gives fairly good agreement with the experimental data. The overall aad of density for nineteen compounds (637 data points) is 0.68% with a maximum of 1.18% for n-pentane. The overall aad of vapor pressure for all twenty compounds (572 data points) is 0.54% with a maximum of 0.99% for methane. For the enthalpy departure calculation, the overall aad is 1.21 Btu/lb for seven fluids with 292 data points.

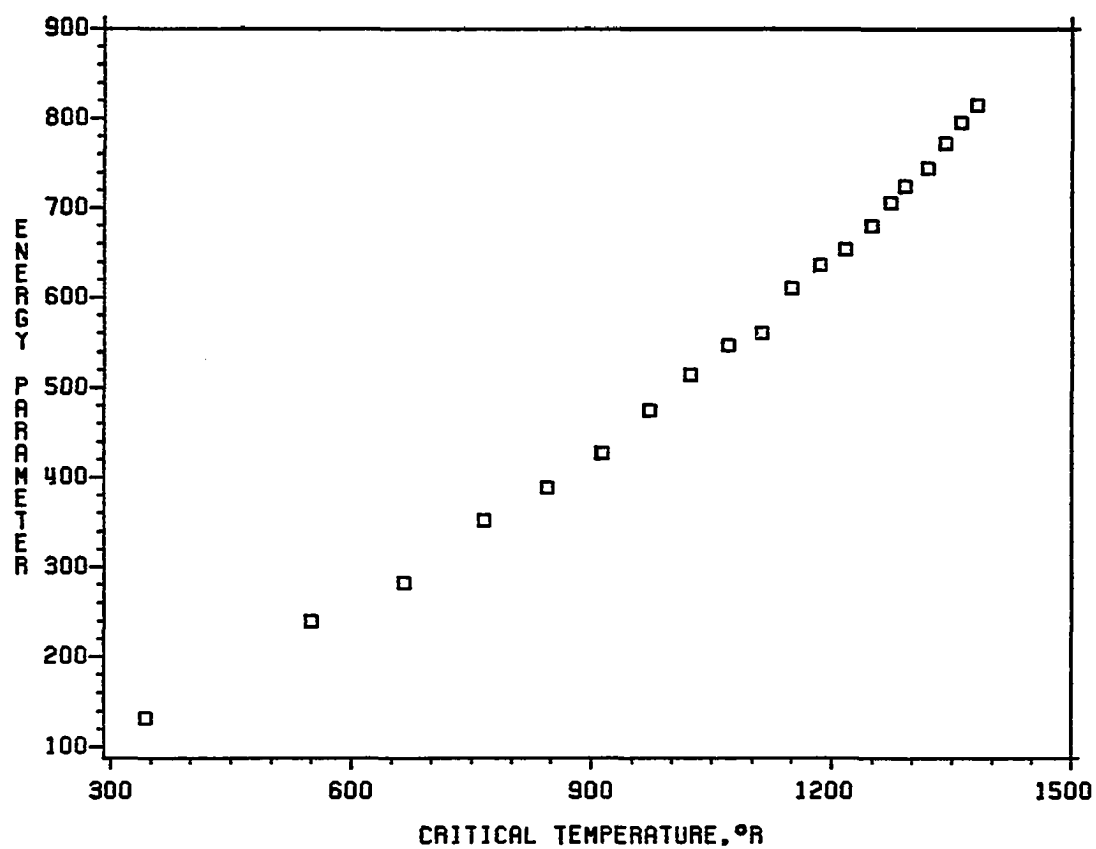


FIGURE 9: PLOT OF THE ENERGY PARAMETERS
VERSUS CRITICAL TEMPERATURE OF N-PARAFFINS

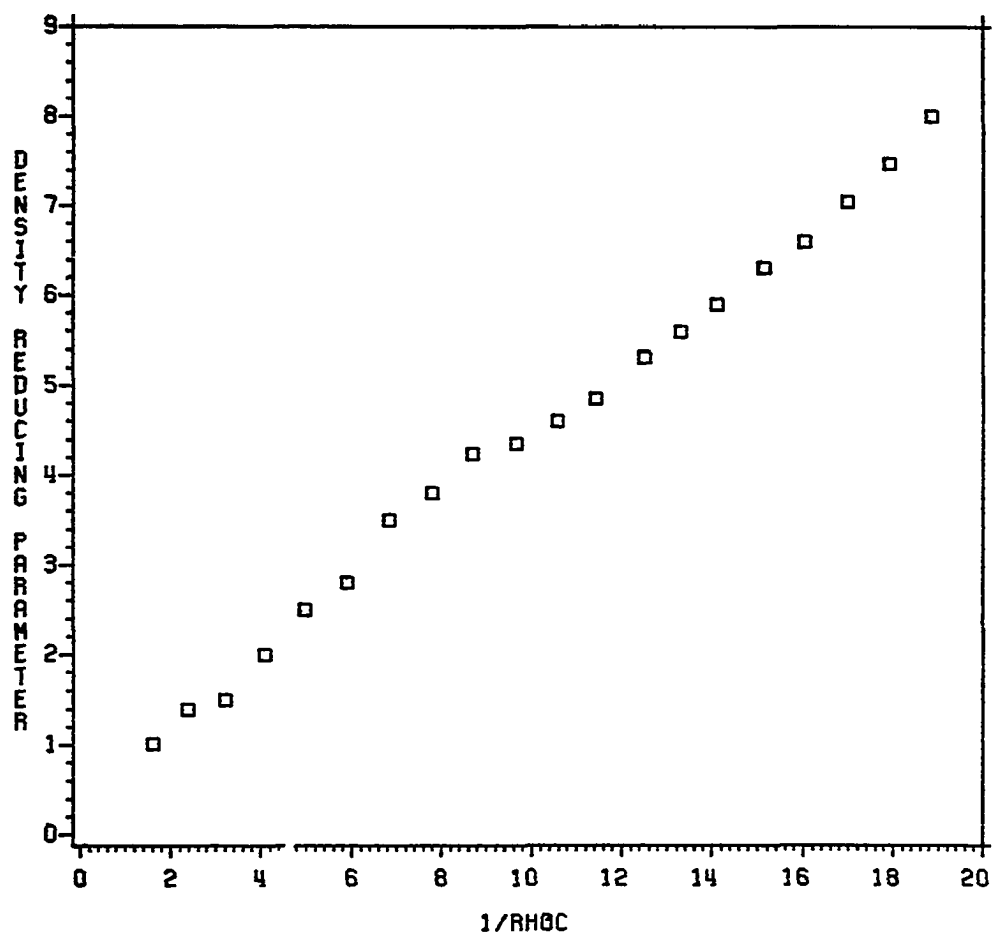


FIGURE 10: PLOT OF THE DENSITY-REDUCING PARAMETERS
VERSUS CRITICAL DENSITY ($RHOC$) OF N-PARAFFINS

3.2 APPLICATION OF THE EQUATION OF STATE TO OTHER NONPOLAR COMPOUNDS

Equation (30) along with Equation (52) and (53) is applied to eleven other nonpolar or slightly polar compounds besides normal paraffins. These compounds represent different classes of fluid including branch-chain hydrocarbons, unsaturated hydrocarbons, ring compounds and halogenated hydrocarbons. The values of the parameters for each compound are summarized in Table 4. The calculation results are given in Table 7. The overall aad of 607 data points of density, 435 points of vapor pressure, and 147 points of enthalpy are 0.7%, 0.59% and 1.20 Btu/lb, respectively.

3.3 APPLICATION OF THE EQUATION OF STATE TO POLAR AND ASSOCIATIVE COMPOUNDS

As described earlier in Chapter II, Equation (30) is extended to polar and associative compounds by making the effective energy parameter " ϵ' /k" temperature dependent:

$$\frac{\epsilon'}{k} = \frac{\epsilon}{k} + \frac{K}{T b^2} \quad (54)$$

where ϵ/k is the nonpolar part of the energy parameter. "K" is the parameter assigned to take into account the contributions of the multipolar and association effects.

Thirty-eight compounds from various classes are tested. The values of the parameters are given in Table 5 along with the prediction results in Table 8. There are a total of 1157 data points of density with the overall aad of 1.23%; 1115 data points of vapor pressure with the overall aad of 0.40%; and 116 points of enthalpy with the overall aad of 1.47 Btu/lb.

TABLE 3
EQUATION OF STATE PARAMETERS FOR NORMAL PARAFFINS.

component	C	b	va	Br	a'	a''
		cu.ft./lbmole				
Methane	1.02008	0.26151	1.30990	1.15550	3.33802	0.333370
Ethane	1.10299	0.37850	2.29115	2.06550	4.13665	0.366547
Propane	1.19523	0.50932	3.09117	3.23730	3.25146	0.335164
n-Butane	1.33117	0.63804	4.14642	4.13475	3.53153	0.325278
n-Pentane	1.37924	0.79020	5.42042	5.40515	3.70428	0.320604
n-Hexane	1.46968	0.91823	6.46905	6.83146	3.42525	0.303150
n-Heptane	1.56411	1.06334	7.85505	7.83293	3.74474	0.294657
n-Octane	1.62814	1.20069	9.66047	10.0424	3.91568	0.312844
n-Nonane	1.73413	1.35103	11.2827	11.2509	4.15130	0.303723
n-Decane	1.79693	1.50789	13.0402	13.0037	4.22387	0.300379

TABLE 3 (CONTINUED)

component	C	b			a'	a''
		Va	Br	cu.ft./lbmole		
n-Undecane	1.88289	1.62949	14.3527	14.3122	4.18223	0.288177
n-Dodecane	1.96885	1.81702	16.8519	16.8044	4.28170	0.296994
n-Tridecane	2.05458	1.97637	18.5097	18.4576	4.37706	0.284677
n-Tetra decane	2.14076	2.11482	21.3019	21.2419	4.49650	0.308393
n-Penta decane	2.21226	2.26042	24.1428	24.0748	4.68490	0.323593
n-Hexa decane	2.29972	2.41321	27.2732	27.1964	4.87208	0.334224
n-Hepta decane	2.38626	2.57808	28.9587	28.8772	4.66210	0.320120
n-Octa decane	2.46985	2.72049	32.3137	32.2227	4.90141	0.337559
n-Nona decane	2.57054	2.88370	34.6525	34.5549	4.76438	0.330740
n-Eicosane	2.65651	3.10348	38.7677	38.6586	4.82883	0.341593

TABLE 4

EQUATION OF STATE PARAMETERS FOR NONPOLAR COMPOUNDS.

component	C	b	Va	Br	a'	a''
		cu.ft./lbmole				
Ethylene	1.05120	0.33912	1.92641	1.82250	3.55652	0.360771
Propylene	1.40083	0.44644	2.91975	2.67811	3.78230	0.352492
i-Butane	1.33986	0.64455	4.38060	3.96152	4.21284	0.351981
i-Pentane	1.33484	0.77994	5.30007	5.42539	3.65174	0.332183
Benzene	2.05852	0.578552	3.86595	3.68515	3.00329	0.263126
Toluene	1.95468	0.71273	5.75532	5.71330	3.75269	0.350970
o-Xylene	1.38407	0.92289	6.56432	7.22017	3.43890	0.312577
Bicyclo hexyl	1.89254	1.56007	13.1454	13.5738	3.65351	0.337325
Fluorene	1.66415	1.33095	13.0545	16.5632	4.14114	0.368505
Diphenyl methane	1.82590	1.34159	11.2469	11.5720	3.74952	0.307503
Dichloro difluoro methane	1.69801	0.49593	3.52230	3.51238	3.44508	0.348992

TABLE 5

EQUATION OF STATE PARAMETERS FOR POLAR AND ASSOCIATIVE
COMPOUNDS.

component	C	b	Va	Br	a'	a''	k *
		cu.ft./lbmole					
Carbon dioxide	2.20215	0.17624	0.91745	0.85635	2.89222	0.398210	1085.26
Nitrogen	1.10870	0.23647	1.25173	1.24820	3.72372	0.308397	0.0
Hydrogen sulfide	1.36413	0.23583	1.47688	1.39930	3.49562	0.359550	0.0
Ammonia	1.49024	0.17169	1.23586	1.03953	4.44942	0.325048	-8.207
Methyl fluoride	1.93017	0.28805	2.25471	2.27156	3.82702	0.389155	-13.015
Butanol	1.13685	0.76824	3.00670	4.64645	0.33349	0.228705	2733.4
Phenol	1.51368	0.66661	3.79188	5.35046	1.44370	0.314044	7193.3

* in units of (°R ft³ / lbmole)

TABLE 5 (CONTINUED)

component	C	b	Va	Br	a'	a''	k
		cu.ft./lbmole					
p-Cresol	1.19434	0.91698	7.36840	5.74190	6.49431	0.365857	15991.0
o-Cresol	1.01932	0.91749	6.98605	6.96638	5.05299	0.348315	5950.1
m-Cresol	1.45342	0.84702	6.43990	6.42176	4.31896	0.326113	19082.0
2,3 Xylenol	1.51523	0.80961	6.09917	6.08200	4.91379	0.358758	42428.0
Acetone	2.41148	0.43883	3.91770	3.79737	3.68117	0.378937	629.52
2- Butanone	1.30404	0.51587	2.98855	2.98013	3.42677	0.237140	4526.0
2- Pentanone	1.34478	0.79359	5.47642	6.69298	2.82656	0.307147	219.09
Dimethyl ether	1.87662	0.38531	2.72600	2.71832	3.23965	0.318131	129.03
Methyl ethyl ether	1.20617	0.58959	3.39435	3.20200	3.69547	0.275984	3429.8

TABLE 5 (CONTINUED)

component	C	b	Va	Br	a'	a''	k
		cu.ft./lbmole					
Diethyl ether	1.86761	0.65631	5.04592	4.33025	4.26846	0.339499	1589.1
Ethyl propyl ether	1.93416	0.76006	6.14702	5.89930	4.04833	0.382782	5017.1
Diphenyl ether	1.54833	1.38196	10.4663	6.78157	5.99501	0.268902	1583.7
Acetic acid	2.77183	0.35892	4.02370	3.87654	4.22370	0.424646	-333.25
Methyl amine	1.08011	0.37660	2.21522	2.20898	3.82267	0.248451	421.52
Dimethyl amine	1.64228	0.47275	3.28492	3.28850	3.43135	0.266224	109.06
Ethyl amine	1.44901	0.45092	3.14337	3.13859	3.70964	0.296325	116.91
Diethyl amine	1.76156	0.72730	5.30042	3.72351	5.05142	0.287329	840.42

TABLE 5 (CONTINUED)

component	C	b	Va	Br	a'	a''	k
		cu. ft./lbmole					
Aniline	1.00785	0.78846	5.21390	6.80805	2.88784	0.275619	-4582.0
Pyridine	2.21624	0.56606	4.50372	4.03843	3.60474	0.281937	-5261.0
4-Methyl pyridine	1.35605	0.92046	6.98800	8.29359	3.48620	0.391816	1739.25
i- quinoline	1.65480	0.91002	6.35645	7.52507	2.81394	0.271196	-8439.56
Carbazol	2.03042	1.58991	14.2401	14.2049	4.07233	0.321177	1178.30
Acridine	1.85980	1.24094	10.9656	15.1920	2.52083	0.288038	-76807.0
Forma- mide	1.08191	0.32804	1.82760	0.28495	3.80991	0.184145	-4618.0
Ethyl mercaptan	2.16017	0.41995	3.22937	3.44313	2.96909	0.372348	234.82
Dimethyl sulfide	1.85038	0.44062	3.23307	2.89645	3.84505	0.393269	1553.4

TABLE 5 (CONTINUED)

component	C	b	Va	Br	a'	a''	k
		cu.ft./lbmole					
Tetra hydro thiophene	1.28571	0.69624	4.76387	4.13763	4.35552	0.291614	-6993.64
Thia napthene	1.38088	0.87804	6.21530	6.84928	3.47042	0.306475	3572.69
Dibenzo thiophene	1.04294	1.10511	13.7391	22.1489	4.42767	0.449223	-28512.0
Tetra hydrofuran	1.56977	0.55088	3.71377	4.04419	2.89819	0.325935	-34.519
Dibenzo furan	2.40006	1.05989	8.57705	9.87446	2.14375	0.280996	-64982.

TABLE 6

PREDICTIONS OF THE THERMODYNAMIC PROPERTIES OF NORMAL PARAFFINS.

component	property	number of points	temperature range, °R	pressure range, psia	aad
Methane	RHO	39	206.2-1121.7	129.7-2071.6	0.93
	VP	32	200.9-343.2	14.7-668.72	0.99
	ENTH	33	209.7-509.7	450.0-2000.0	1.50
Ethane	RHO	46	239.7-769.7	14.7-10000.0	0.95
	VP	46	249.7-549.7	0.49-709.80	0.62
	ENTH	85	299.7-769.7	200.0-3000.0	1.42
Propane	RHO	134	162.0-716.7	14.7-10593.0	0.82
	VP	55	259.8-665.9	0.019-617.7	0.19
	ENTH	26	309.7-709.7	500.0-2000.0	1.96
n-Butane	RHO	40	259.7-889.7	14.7-7000.0	0.56
	VP	52	349.7-739.7	0.17-437.30	0.80
	ENTH	39	559.7-889.7	200.0-5000.0	0.12
n-Pentane	RHO	39	299.7-919.7	14.7-10000.0	1.18
	VP	45	401.5-845.6	0.193-489.5	0.67
	ENTH	38	559.7-919.7	200.0-10000.0	1.06
n-Hexane	RHO	41	319.7-779.7	14.7-3977.0	0.57
	VP	53	395.7-914.2	0.02-439.70	0.39
n-Heptane	RHO	41	369.7-919.7	14.7-3081.5	0.77
	VP	40	415.8-956.9	0.008-350.0	0.77
	ENTH	17	971.9-1166.4	78.7-2363.1	0.90
n-Octane	RHO	48	389.7-969.7	14.7-239.0	0.72
	VP	56	414.7-1019.7	0.001-350.0	0.80
	ENTH	54	534.7-1059.7	200.0-1400.0	0.70
n-Nonane	RHO	43	455.7-1031.7	0.002-7251.8	0.67
	VP	18	442.2-814.7	0.001-29.65	0.05
n-Decane	RHO	32	559.7-919.7	200.0-6000.0	0.47
	VP	18	629.7-646.6	0.505-30.00	0.04

TABLE 6 (CONTINUED)

component	property	number of points	temperature range, °R	pressure range, psia	aad
n-Undecane	VP	19	624.7-899.7	0.182-29.60	0.06
n-Dodecane	RHO	17	581.7-869.7	0.016-12.63	0.30
	VP	21	559.7-1186.5	0.032-262.5	0.22
n-Tridecane	RHO	17	617.7-905.8	0.024-12.93	0.28
	VP	18	617.7-1218.9	0.024-15.29	0.27
n-Tetra decane	RHO	14	707.7-941.7	0.18-13.54	0.21
	VP	15	707.7-959.7	0.18-16.93	0.14
n-Penta decane	RHO	14	743.7-977.7	0.24-14.44	0.29
	VP	14	743.7-995.7	0.24-17.90	0.21
n-Hexa decane	RHO	9	833.7-977.7	1.00-10.09	0.17
	VP	10	833.7-995.7	1.00-12.66	0.17
n-Hepta decane	RHO	13	779.7-995.7	0.18-8.89	0.34
	VP	15	779.7-1049.7	0.18-17.1	0.21
n-Octa decane	RHO	13	815.7-1031.7	0.25-10.1	0.27
	VP	15	815.7-1067.7	0.25-15.4	0.45
n-Nona decane	RHO	12	833.7-1031.7	0.23-7.36	0.36
	VP	15	833.7-1085.7	0.23-14.2	0.23
n-Eicosane	RHO	25	671.7-1031.7	725.0-7251.8	0.98
	VP	15	851.7-1121.7	0.22-16.100	0.42

RHO = density

VP = vapor pressure

ENTH = enthalpy departure

aad = average absolute deviation; in % for density and vapor
pressure calculation, in btu/lb for enthalpy departure
calculation

TABLE 7

PREDICTIONS OF THE THERMODYNAMIC PROPERTIES OF NONPOLAR COMPOUNDS.

component	property	number of points	temperature range, °R	pressure range, psia	aad
Ethylene	RHO	40	209.7-719.7	14.7-2000.0	0.91
	VP	35	239.7-509.7	0.885-742.1	0.94
	ENTH	34	339.7-719.7	100.0-200.0	2.00
Propylene	RHO	57	409.7-909.7	16.2-2939.2	1.28
	VP	28	264.5-656.9	0.039-670.3	0.80
i-Butane	RHO	116	349.7-986.6	14.7-5000.0	0.16
	VP	82	334.7-733.9	0.183-526.8	0.15
	ENTH	73	559.7-939.7	14.7-4408.8	1.26
i-Pentane	RHO	38	399.7-851.6	14.7-882.50	0.84
	VP	22	439.7-829.8	1.205-494.7	0.29
Benzene	RHO	102	504.0-981.0	0.768-574.5	0.14
	VP	67	504.0-1012.7	0.768-713.9	0.35
Toluene	RHO	13	491.7-689.7	0.130-14.44	0.31
	VP	33	491.7-1049.7	0.130-547.2	0.89
o-Xylene	RHO	59	536.7-986.7	14.5-5800.0	0.31
	VP	43	455.7-1136.8	0.004-552.1	0.25
Bicyclo hexyl	VP	23	763.6-1039.0	1.391-50.30	0.36
Fluorene	VP	29	926.2-1103.7	4.031-33.35	0.51
Diphenyl methane	VP	33	764.3-1109.7	0.566-61.00	0.85
Dichloro difluoro methane	RHO	182	307.7-919.7	0.14-440.00	0.47
	VP	40	307.7-689.7	0.14-577.03	0.53
	ENTH	40	307.7-689.7	0.14-577.03	0.26

TABLE 8

PREDICTIONS OF THE THERMODYNAMIC PROPERTIES OF POLAR AND
ASSOCIATIVE COMPOUNDS

component	property	number of points	temperature range, °R	pressure range, psia	aad
Carbon dioxide	RHO	39	437.7-743.7	220.5-5580.0	0.39
	VP	33	389.7-544.7	75.15-1032.0	0.81
	ENTH	39	437.7-743.7	441.0-7350.0	1.76
Nitrogen	RHO	38	139.2-699.7	14.7-8936.36	0.79
	VP	19	150.6-226.7	29.06-492.20	0.69
	ENTH	77	159.7-509.7	200.0-2500.0	1.33
Hydrogen sulfide	RHO	40	499.7-799.7	100.0-2000.0	0.53
	VP	24	383.3-672.4	14.7-1306.00	0.39
Ammonia	RHO	300	428.0-1077.0	12.71-11816.	2.37
	VP	172	398.6-726.50	5.35-1592.00	0.08
Methyl fluoride	RHO	131	269.7-899.70	0.62-623.40	0.82
	VP	28	269.7-538.33	0.62-701.40	0.49
Butanol	RHO	32	455.7-864.27	0.145-156.79	0.56
	VP	92	532.3-1002.4	0.106-588.09	0.85
Phenol	RHO	14	581.7-1211.7	0.047-739.50	0.78
	VP	15	581.7-1249.7	0.047-888.85	1.33
p-Cresol	RHO	23	563.7-1211.4	0.0073-478.5	0.25
	VP	20	599.7-1175.7	0.0335-371.2	0.55
o-Cresol	RHO	24	563.7-1247.7	0.0179-697.6	0.25
	VP	21	563.7-1139.7	0.0179-332.2	0.54
m-Cresol	RHO	26	527.7-1247.7	0.0013-555.3	0.43
	VP	22	581.7-1247.7	0.0174-555.3	0.54
2,3 Xylenol	VP	18	635.7-1283.7	0.077-638.00	1.26

TABLE 8 (CONTINUED)

component	property	number of points	temperature range, °R	pressure range, psia	aad
Acetone	RHO	28	491.7-905.70	14.70-648.27	0.62
	VP	20	592.6-914.70	14.70-690.90	0.24
2-Butanone	VP	16	578.33-650.9	4.790-19.340	0.006
2-Pentanone	RHO	18	593.6-692.65	2.965-19.338	0.017
	VP	18	593.6-692.65	2.965-19.338	0.008
Dimethyl ether	RHO	34	449.01-707.6	14.70-680.61	2.70
	VP	19	449.01-720.1	14.70-764.40	0.46
Methyl ethyl ether	RHO	28	505.17-779.7	14.70-595.35	3.25
	VP	18	505.17-788.7	14.70-637.98	0.23
Diethyl ether	RHO	43	491.7-839.07	3.576-517.9	1.85
	VP	23	491.7-840.51	3.576-522.9	0.35
Ethyl propyl ether	RHO	17	602.2-887.67	14.7-423.36	0.55
	VP	18	602.2-900.99	14.7-471.87	0.28
Diphenyl ether	RHO	12	941.7-1139.7	12.06-86.13	0.17
	VP	13	941.7-1157.7	12.06-99.18	0.27
Acetic acid	RHO	21	704.9-1049.7	14.7-719.27	0.52
	VP	23	704.9-1070.5	14.7-840.99	0.36
Methylamine	VP	17	487.8-774.09	14.7-1081.9	0.27
Dimethyl amine	VP	18	504.6-787.95	14.7-759.99	0.21
Ethylamine	VP	19	521.5-821.43	14.7-816.34	0.19

TABLE 8 (CONTINUED)

component	property	number of points	temperature range, °R	pressure range, psia	add
Diethyl amine	RHO	17	591.4-869.67	14.7-441.00	0.50
	VP	18	591.4-887.67	14.7-505.68	0.80
Aniline	RHO	29	491.7-1211.7	0.0014-585.8	0.44
	VP	34	491.7-1167.5	0.0014-440.6	0.76
Pyridine	RHO	26	455.7-1103.7	0.020-775.45	0.76
	VP	25	455.7-1103.7	0.020-755.45	0.88
4-Methyl pyridine	VP	16	668.6-753.5	3.41-14.74	0.20
i- quinoline	RHO	18	599.7-959.7	0.015-21.15	0.30
	VP	63	599.7-1427.7	0.015-667.0	0.44
Carbazol	VP	26	932.3-1211.7	1.07-31.90	0.71
Acridine	RHO	12	707.7-1103.7	0.012-13.08	0.25
	VP	23	724.6-1139.7	0.019-19.14	0.43
Formamide	RHO	67	518.7-581.7	324.8-34800.0	0.13
Ethyl mercaptan	RHO	19	553.7-869.7	14.7-648.3	0.28
	VP	20	553.7-887.7	14.7-742.3	0.27
Dimethyl sulfide	RHO	20	556.1-887.7	14.7-690.9	0.32
	VP	21	556.1-905.5	14.7-802.6	0.47
Tetrahydro thiophene	RHO	9	491.7-617.7	0.079-2.76	0.43
	VP	26	491.7-1137.5	0.079-754.0	0.26
Thia naphthene	VP	27	763.9-1135.1	2.23-153.7	0.28

TABLE 8 (CONTINUED)

component	property	number of points	temperature range, °R	pressure range, psia	add
Dibenzo thiophene	VP	19	764.6-1093.5	0.068-15.36	0.28
Dibenzo furan	RHO	42	704.8-1013.7	74.1-3394.9	0.64
	VP	19	783.6-1112.5	0.75-42.316	0.64
Tetrahydro furan	RHO	10	455.6-599.67	0.28-12.064	0.27
	VP	25	455.6-972.27	0.28-752.55	0.32

3.4 DISCUSSION OF RESULTS

In the previous section, the final results of the new equation of state, applied to 69 compounds, are reported in Table 6, 7 and 8 in terms of the average absolute deviation. Generally, Equation (30) gives fairly good agreement with the experimental values, especially the vapor pressure calculations. All together, there are 2229 data points of density, 2122 data points of vapor pressure, and 555 points of enthalpy data. The average absolute deviation predicted by Equation (30) is 0.95%, 0.47% and 1.26 btu/lb, respectively. The second virial coefficient calculations of Equation (30) are also in fairly good agreement with the smoothed experimental values of Dymond and Smith (1980) for both polar and nonpolar compounds. Comparison of the second virial coefficients (B_2) of six normal paraffins: methane, ethane, propane, n-butane, n-pentane, and n-hexane is shown in Figure 11. The calculated values are very close to the experimental values, especially for small molecules. However, the deviation becomes slightly larger in the low temperature region as the size of molecule increases. Figure 12 is the comparison of B_2 among four other nonpolar compounds: ethylene, propylene, i-butane, and i-pentane. Figure 13 shows the comparison of B_2 for three polar compounds: nitrogen, carbon dioxide, and methyl fluoride. The calculated values are generally in good agreement with

the experimental values, especially for ethylene and methyl fluoride.

Figure 14 is the plot of the experimental second virial coefficients of propane and the values calculated from five different equations of state, including Equation (30). Equation (A1) is the van der Waals equation of state; Equation (A2) is the Peng-Robinson equation; Equation (A3) is the BACK (Boublik-Alder-Chen-Kreglewski) equation developed by Chen and Kreglewski (1977); and Equation (A4) is the equation of state for polar and nonpolar compounds developed by Khan (1983), based on the concept of perturbed hard chain theory and the hard convex body equation of state. The BACK equation is the augmented van der Waals-type equation of state having similar form as Equation (30). That is, the repulsive compressibility factor is represented by the hard convex body equation of Boublik (1975), combined with an attractive expression, which is a power series in (U/kT) and (V^*/V) of Alder et al. (1972). The forms of Equation (A1) to (A4) are summarized in Appendix A. In the high temperature region (above 850 °R), the predictions of all five equations agree well with the experimental data, especially Equation (A3) and (A4). In moderate temperature region (from 500 to 850 °R), Equation (30) gives the closest values to the experimental data. Meanwhile, at temperature below 500 °R, Equation (30), along with Equation (A2) and (A3), has about the same accuracy.

Equation (A4) is slightly better in this region, while the prediction from the van der Waals equation becomes inaccurate at low temperatures.

Further comparisons of the thermodynamic property calculations of Equation (30) with Equation (A2) and (A4) are reported in Table 9 for 38 compounds. Table 10 is the comparison of Equation (30) with the BAC equation for 14 compounds. The values of the parameters used in Equation (A3) and (A4) are those reported by the authors. The thermodynamic property predictions of Equation (30) are generally more accurate than Peng-Robinson's and BAC's, for both polar and nonpolar compounds. Improvement of Equation (30) over the Peng-Robinson equation becomes significant as the size of molecules increases. A similar trend is also observed from the BAC equation, in which the prediction is quite accurate for small globular molecules but not so accurate for heavy, long-chain type molecules such as n-decane. Equation (A4), in general, can describe the P-V-T behavior of paraffin hydrocarbons and some polar compounds quite accurately. Equation (A4), as reported by Khan (1983), is superior to the Perturbed-Hard-Chain equation of state developed by Donohue and Prausnitz (1978). However, the accuracy achieved by Equation (30) is, for the most part, as good as, or better than Equation (A4). The overall error of density, vapor pressure, and enthalpy predicted by Equation (30) are compared with Equation (2) and Equation

{4) at the end of Table 9. The comparison with BACK equation is shown at the end of Table 10.

Figure 15 shows the density calculation of n-butane at various isotherms. The result shows good agreement in both vapor and liquid density regions. Similar results are obtained from the liquid density calculation of o-xylene and the saturation density calculation of phenol, as shown in Figure 16 and 17, respectively. The experimental saturation density of dimethyl ether is compared with the values calculated from Equation (30), Equation (A2), and Equation (A4) in Figure 18. Figure 19 is the comparison of the saturation density of benzene between the experimental values and the calculated values from Equation (30), Equation (A2), and Equation (A3). Both figures show the effectiveness of Equation (30) in predicting both vapor and liquid densities. The improvement over the Peng-Robinson equation is very obvious in the liquid region due to the hard convex body expression used in describing the repulsive pressure in Equation (30).

The newly developed equation of state is particularly effective in predicting the vapor pressures of both polar and nonpolar compounds. For sixty-nine fluids tested, the deviations in vapor pressure calculations are within 1% or less, except two compounds where the deviations are slightly over 1% (phenol, 1.33% and 2,3 xylenol, 1.26%). This accuracy can be seen in Figure 20, a plot of the calculated

vapor pressures versus the observed values for six normal paraffins, and in Figure 21, for some polar compounds. Figure 22, 23, and 24 show the comparisons of vapor pressure calculations of n-decane, n-eicosane, and aniline, respectively. The results confirm that the vapor pressure prediction of Equation (30) is as good as or better than the other equations studied.

Values of the parameters of the new equation of state are now available for 69 compounds as summarized in Table 3, 4, and 5. There are six parameters for each nonpolar compound, and seven parameters for each polar and associative compound. Although these parameters are obtained empirically from the regression analysis of the experimental data, they are not totally arbitrary. Some of them have physical meanings and are closely related to other physical properties such as molecular weight or critical volume.

For normal paraffins, the shape factor (C) and the hard convex body volume (b) increase almost linearly with the carbon number. The increase in molecular weight, critical volume, and van der Waals volume (Bondi, 1968) of normal paraffins has the same nature as the increase in carbon number due to each additional CH group. Therefore, C and b of normal paraffins are also closely related to the molecular weight and the critical volume as shown in Figure 25, 26, and 27. The parameters Br and Va of normal

paraffins are also closely related to the above properties, as shown in Figure 28 and 29. Figure 30 shows the relation between B_r and V_a . The linear relation between the hard convex body volume and the critical volume of normal fluids also agrees with the study of Bienkowski and Chao (1975). Figure 31, 32, and 33 show the increase of b , B_r , and V_a of normal paraffins and some other polar and nonpolar compounds with the critical volume. The relation between B_r and V_a of compounds other than normal paraffins is approximately linear as shown in Figure 34. The regular behavior of these parameters will play a significant role in finding suitable correlations of the parameters. These correlations can add remarkably to the usefulness of the equation of state, especially in an application to mixture systems.

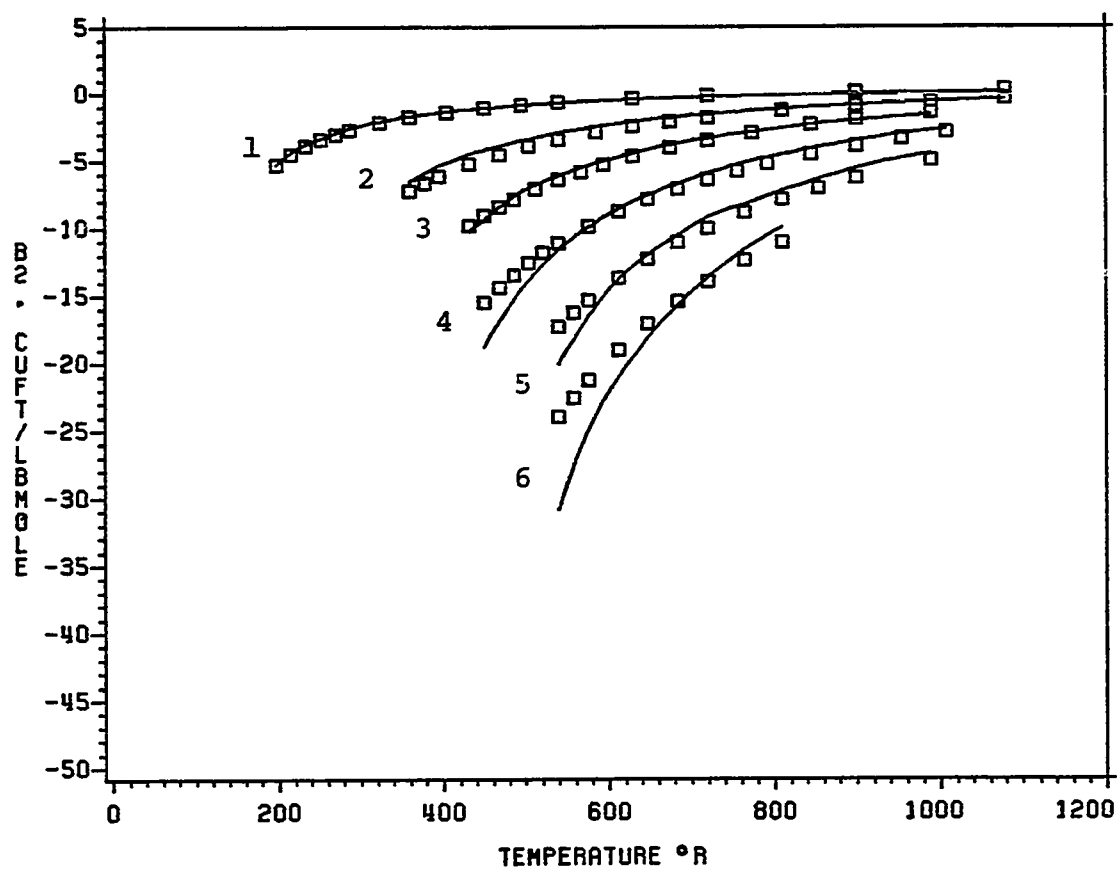


FIGURE 11: COMPARISON OF THE SECOND VIRIAL COEFFICIENTS
OF NORMAL PARAFFINS

— = EXPERIMENTAL, $\square$ = EQUATION (30)
1=METHANE, 2=ETHANE, 3=PROPANE
4=N-BUTANE, 5=N-PENTANE, 6=N-HEXANE

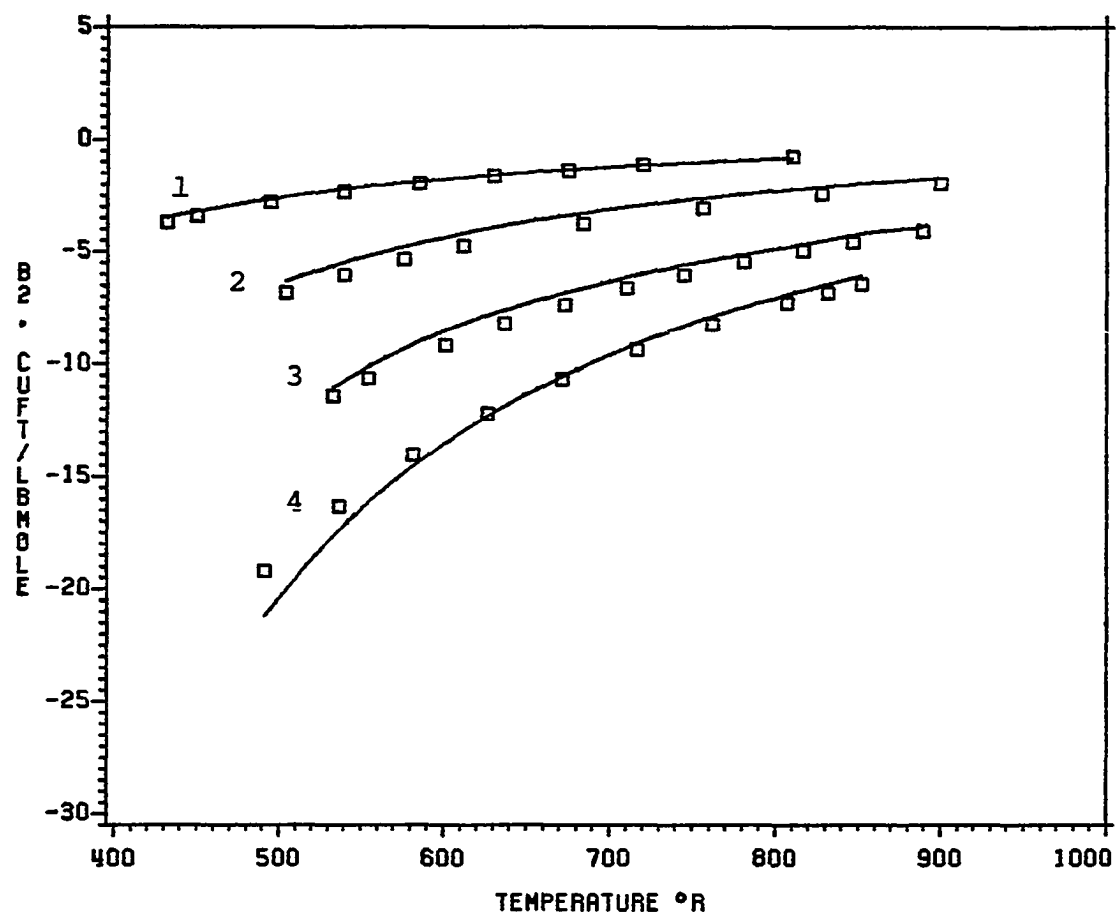


FIGURE 12: COMPARISON OF THE SECOND VIRIAL COEFFICIENTS
OF NONPOLAR COMPOUNDS

— = EXPERIMENTAL, $\square$ = EQUATION (30)
1=ETHYLENE, 2=PROPYLENE, 3=1-BUTANE, 4=1-PENTANE

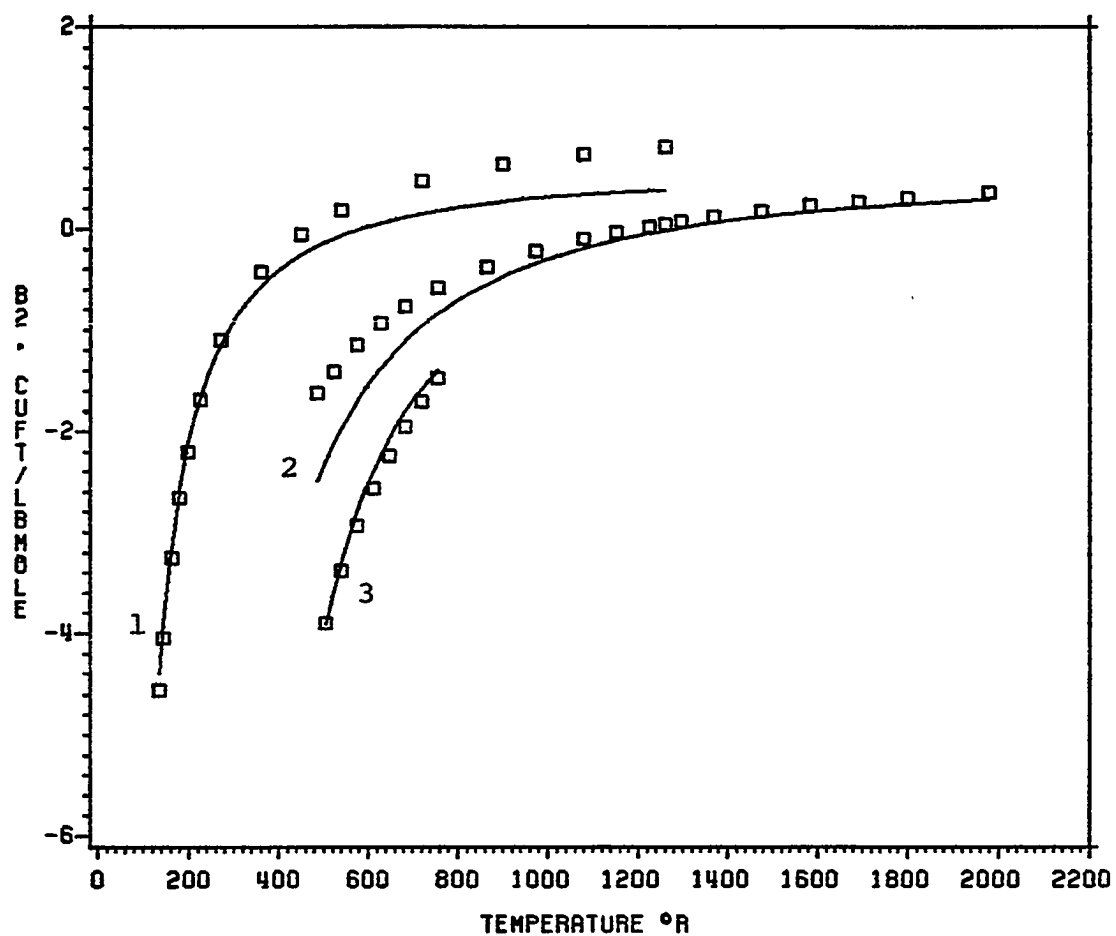


FIGURE 13: COMPARISON OF THE SECOND VIRIAL COEFFICIENTS
OF POLAR COMPOUNDS

— = EXPERIMENTAL, $\square$ = EQUATION (30)

1= NITROGEN, 2= CARBON DIOXIDE, 3= METHYL FLUORIDE

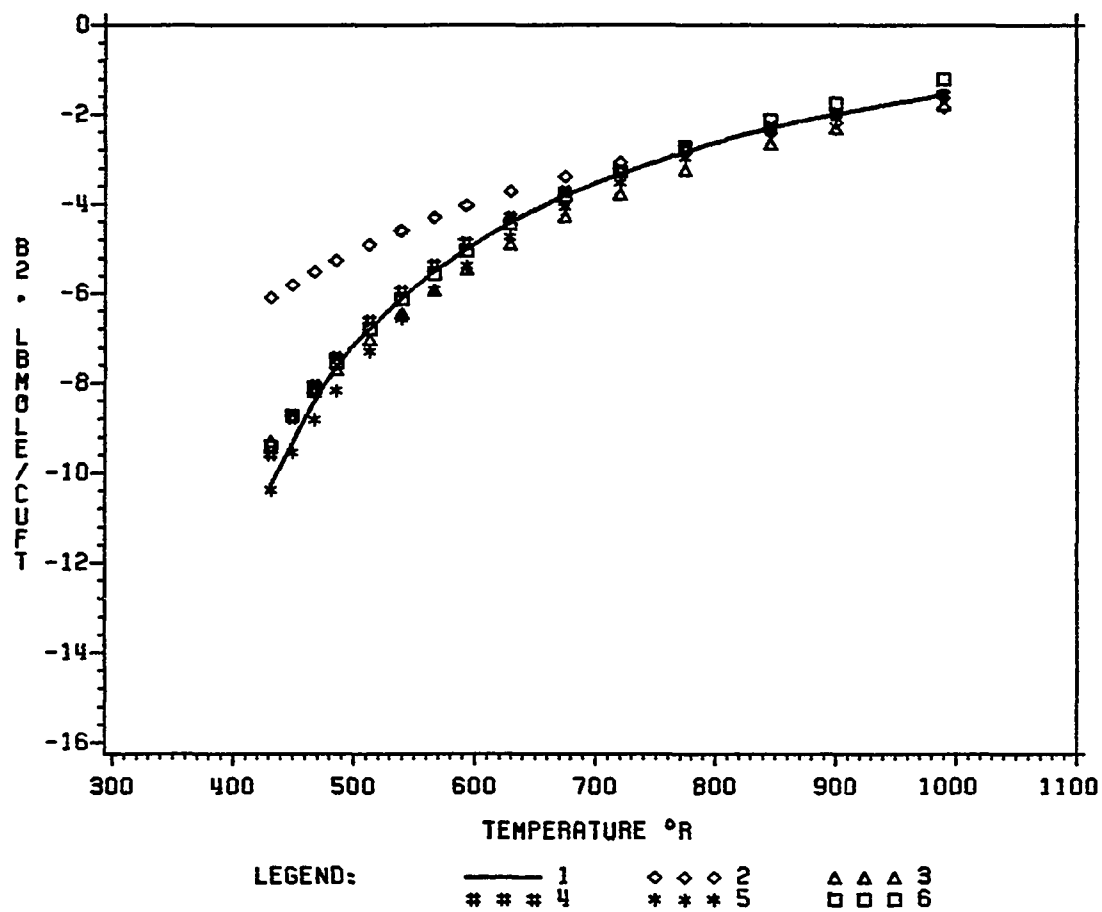


FIGURE 14: COMPARISON OF THE SECOND VIRIAL COEFFICIENTS OF PROPANE

1=EXPERIMENTAL, 2=EQUATION (A1), 3=EQUATION (A2),
4=EQUATION (A3), 5=EQUATION (A4), 6=EQUATION (A5)

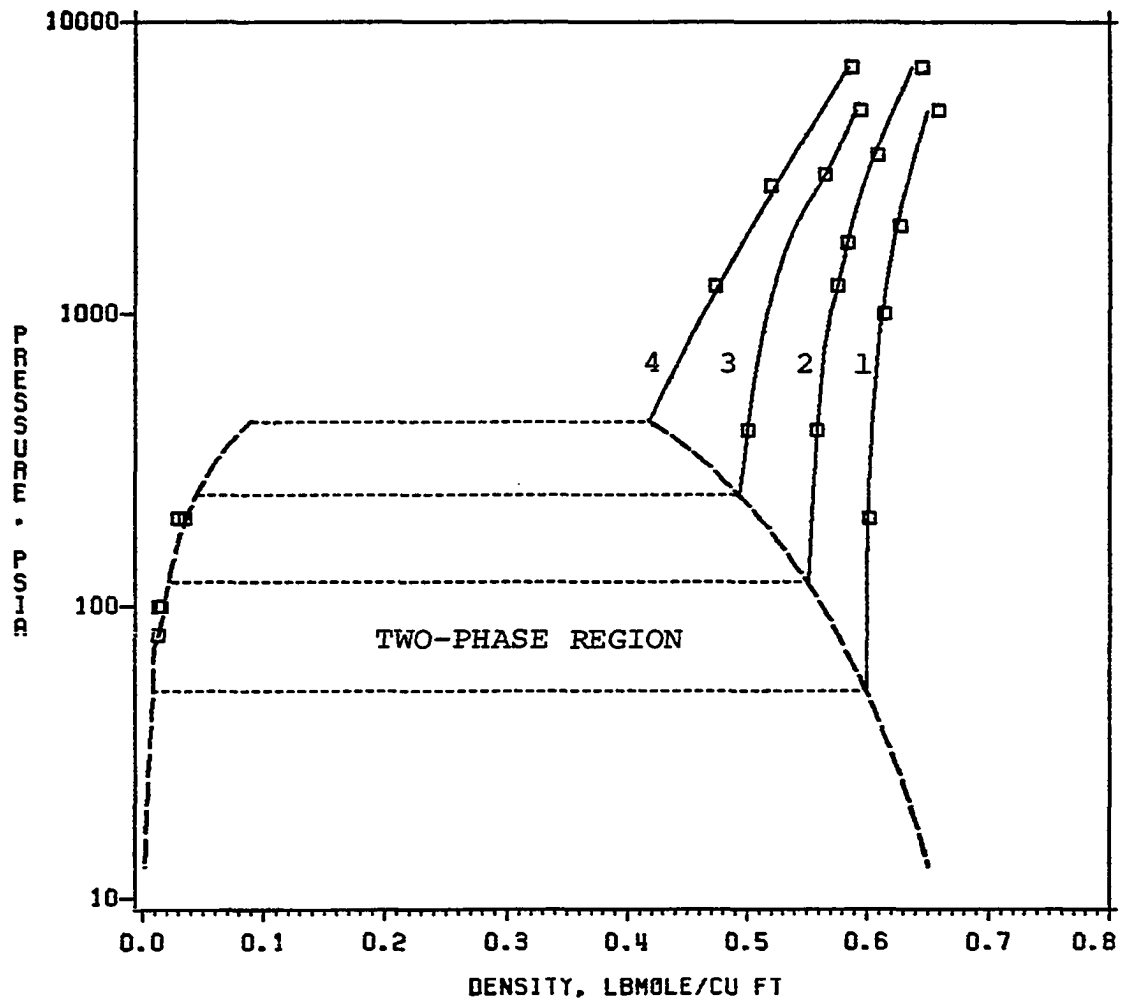


FIGURE 15: DENSITY CALCULATIONS OF N-BUTANE

— = EXPERIMENTAL, □ = EQUATION (30)
 1=559.7 °R, 2=619.7 °R, 3=679.7 °R, 4=739.7 °R

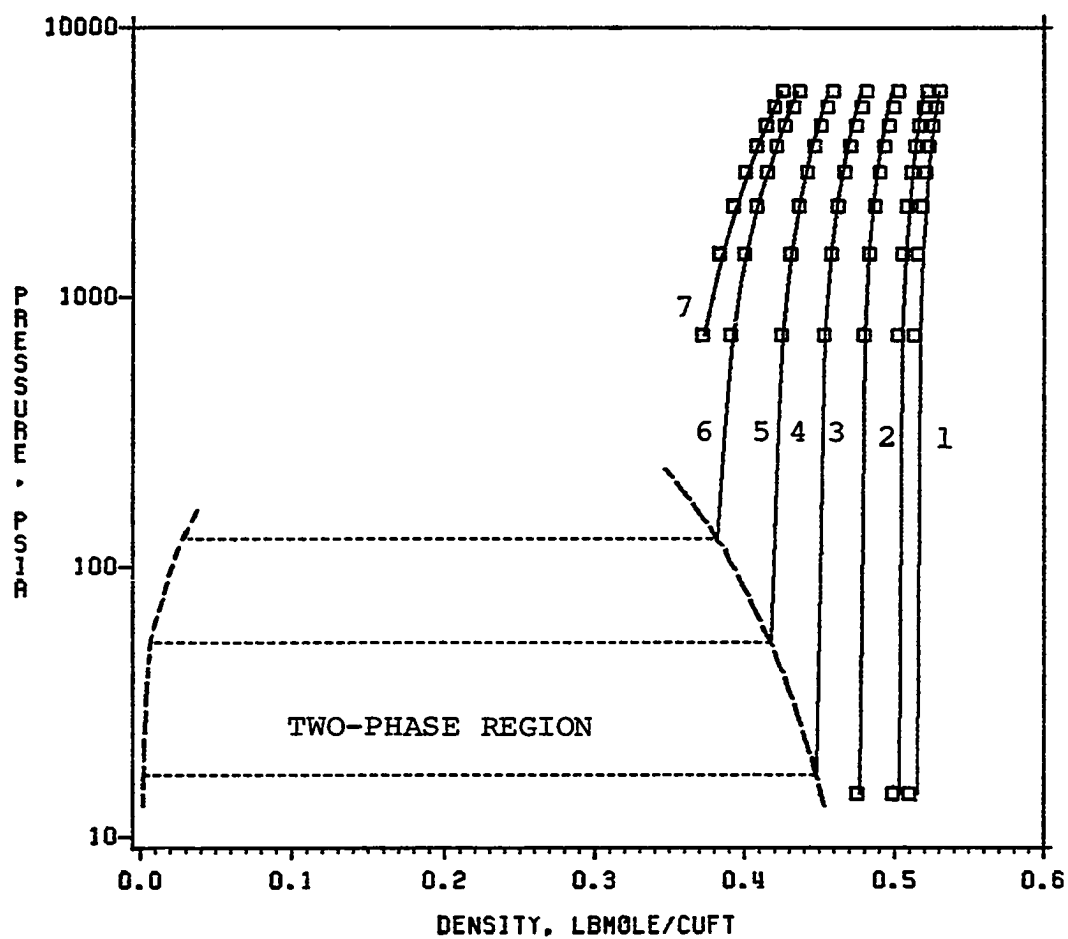


FIGURE 16: LIQUID DENSITY CALCULATIONS OF O-XYLENE

— = EXPERIMENTAL, □ = EQUATION (30)
 1=536.7 °R, 2=581.7 °R, 3=671.7 °R, 4=761.7 °R
 5=851.7 °R, 6=941.7 °R, 7=986.7 °R

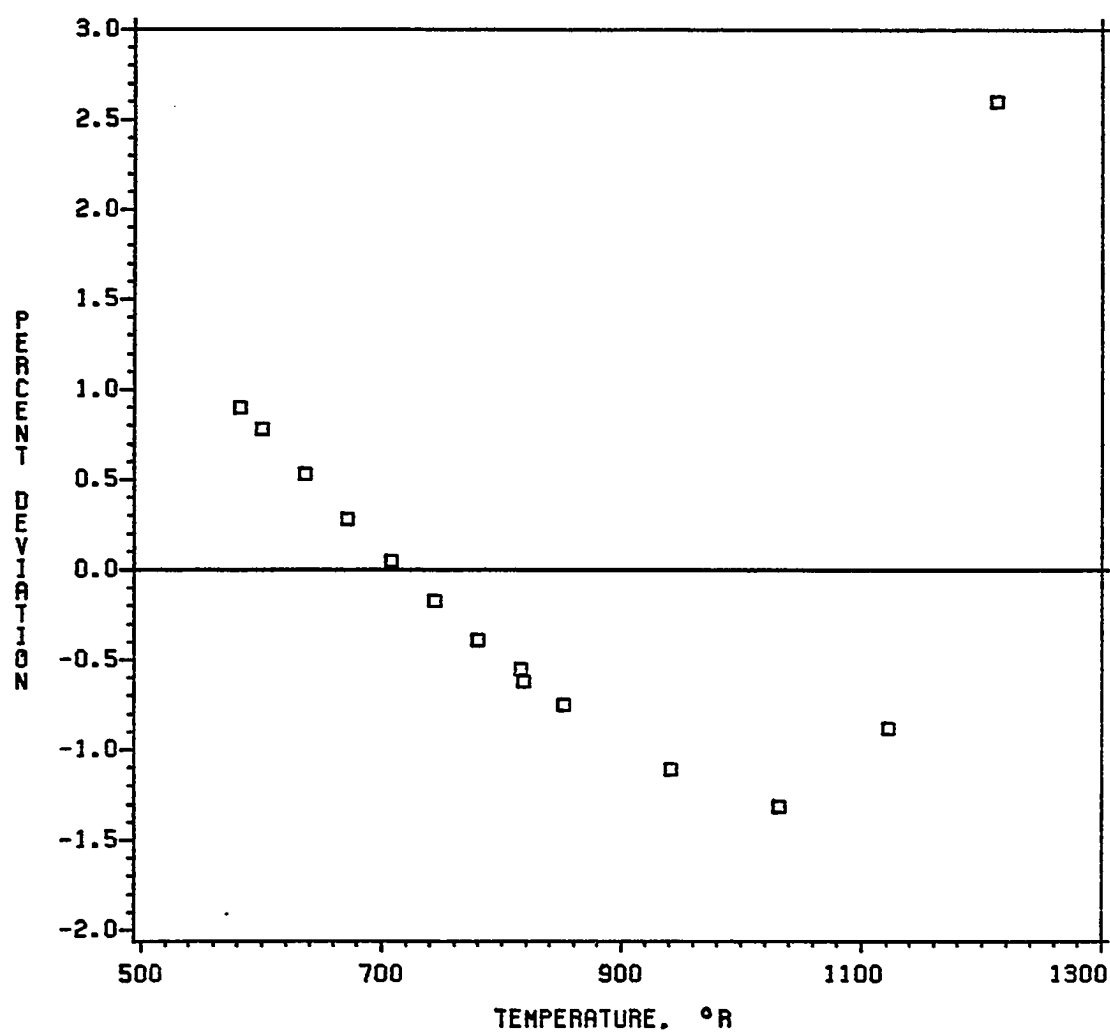


FIGURE 17: PERCENT DEVIATION OF SATURATION DENSITY CALCULATIONS
OF PHENOL

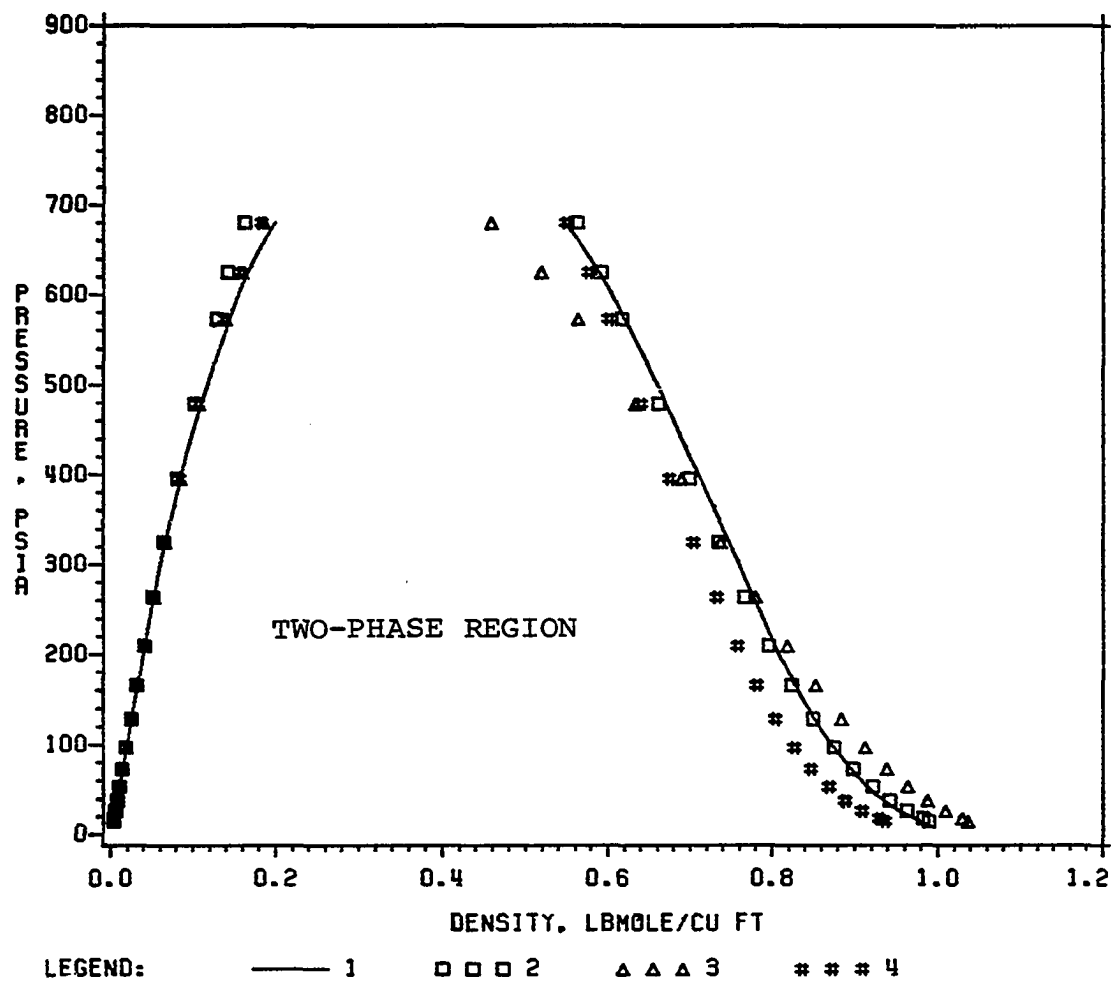


FIGURE 18: COMPARISON OF THE SATURATION DENSITIES
OF DIMETHYL ETHER

1 = EXPERIMENTAL, 2 = EQUATION (30),
3 = EQUATION (A2), 4 = EQUATION (A4)

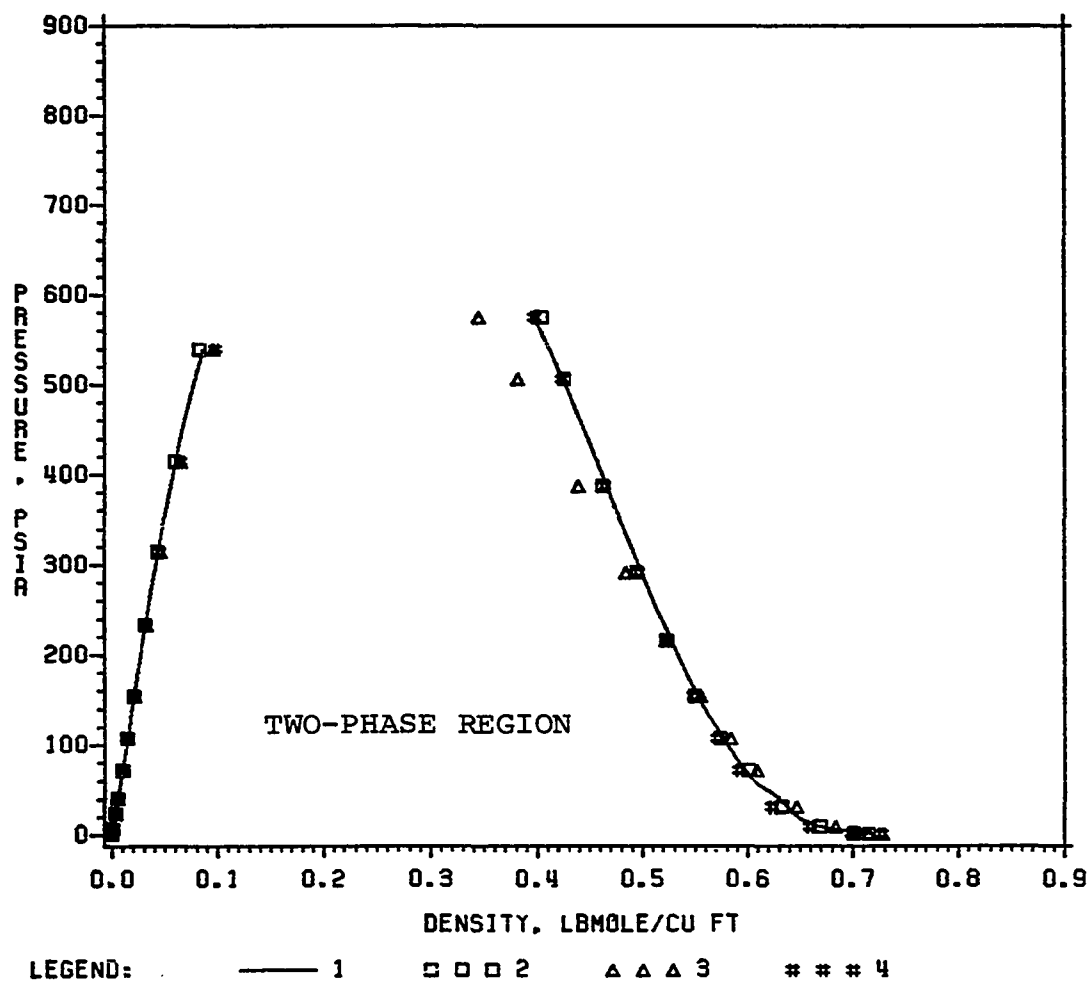


FIGURE 19: COMPARISON OF THE SATURATION DENSITIES OF BENZENE

1 = EXPERIMENTAL, 2 = EQUATION (30)
3 = EQUATION (A2), 4 = EQUATION (A3)

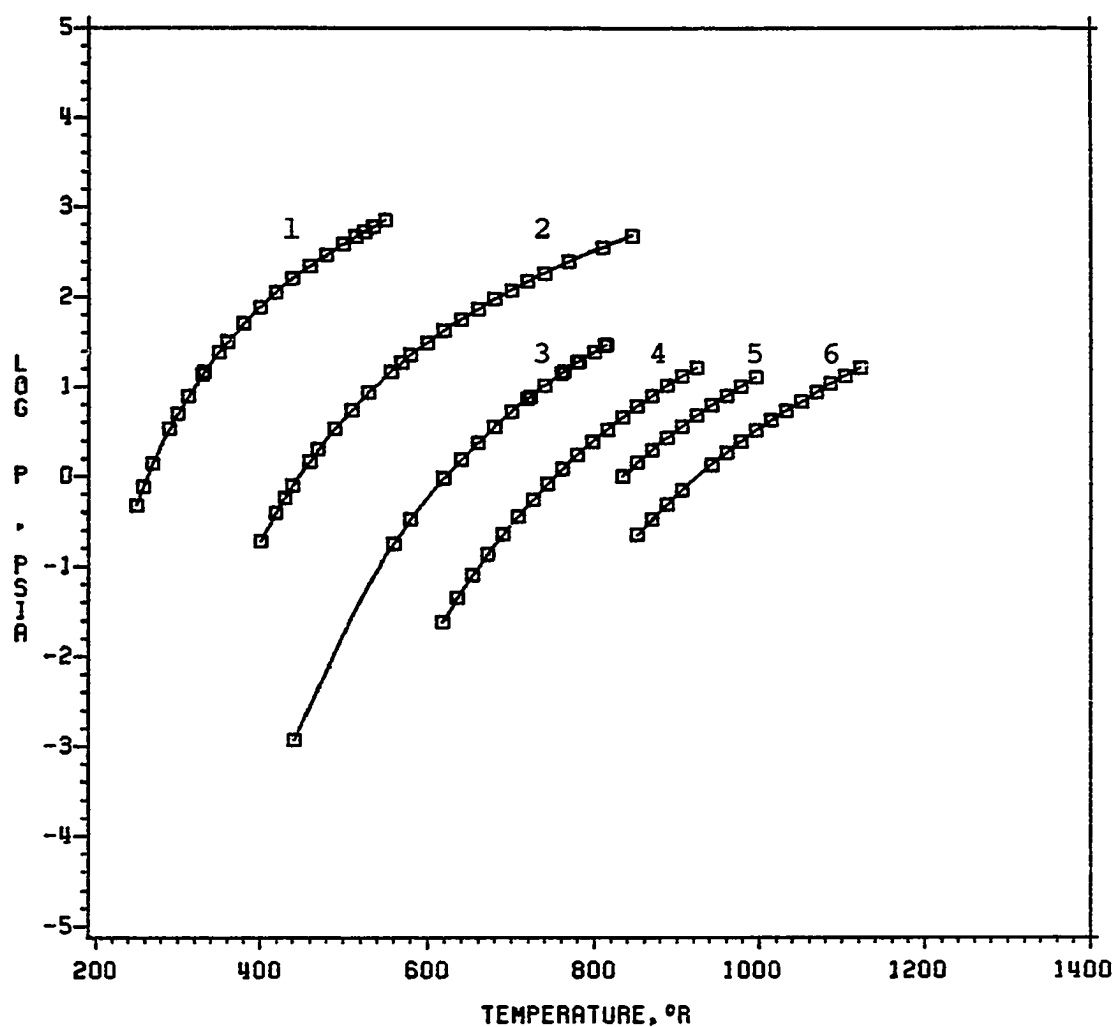


FIGURE 20: VAPOR PRESSURE CALCULATIONS OF NORMAL PARAFFINS

— = EXPERIMENTAL, □ = EQUATION (30)
 1=ETHANE, 2=N-PENTANE, 3=N-NONANE
 4=N-TRIDECANE, 5=N-HEXADECANE, 6=N-EICOSANE

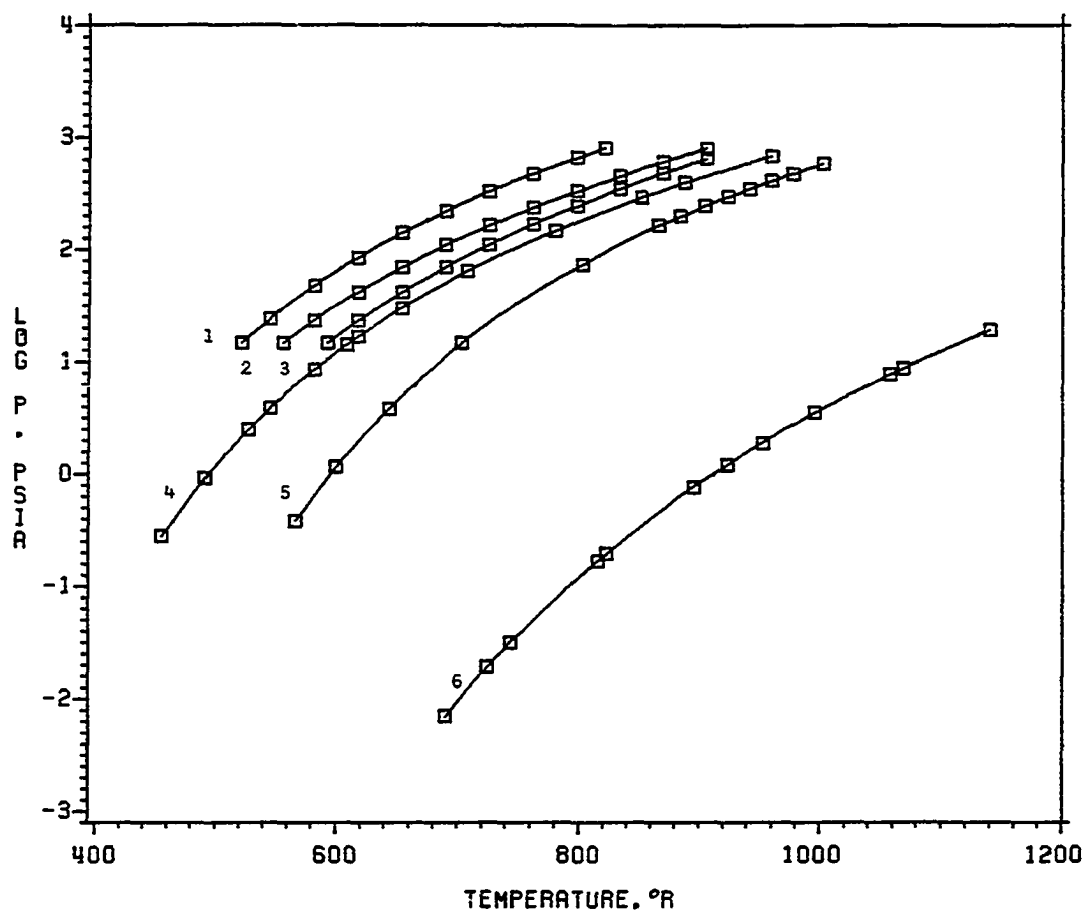


FIGURE 21: VAPOR PRESSURE CALCULATIONS OF POLAR COMPOUNDS

— = EXPERIMENTAL, □ = EQUATION (30)
 1=ETHYLAMINE, 2=DIMETHYL SULFIDE, 3=ACETONE
 4=TETRAHYDROFURAN, 5=BUTANOL, 6=ACRIDINE

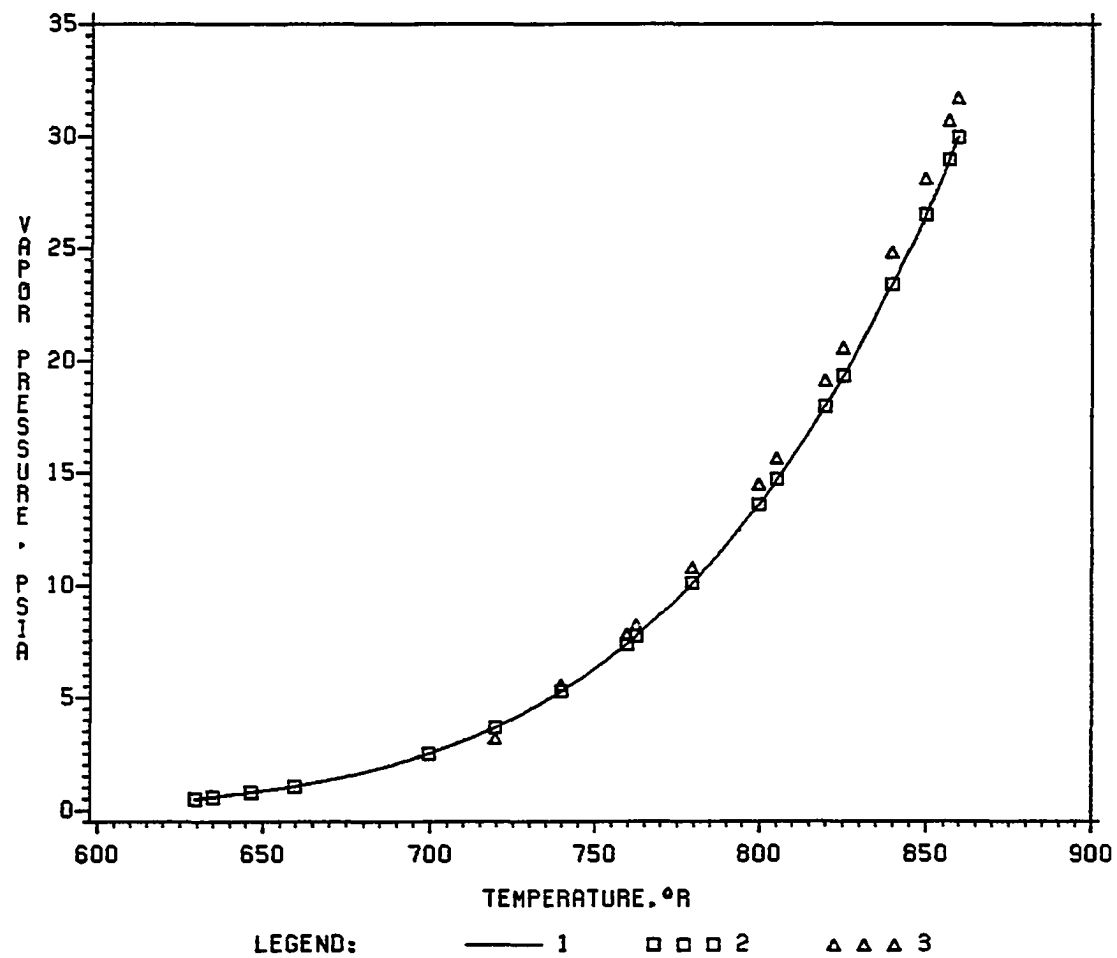


FIGURE 22: COMPARISON OF VAPOR PRESSURE CALCULATIONS
OF N-DECANE

1=EXPERIMENTAL, 2=EQUATION (30), 3=EQUATION (A3)

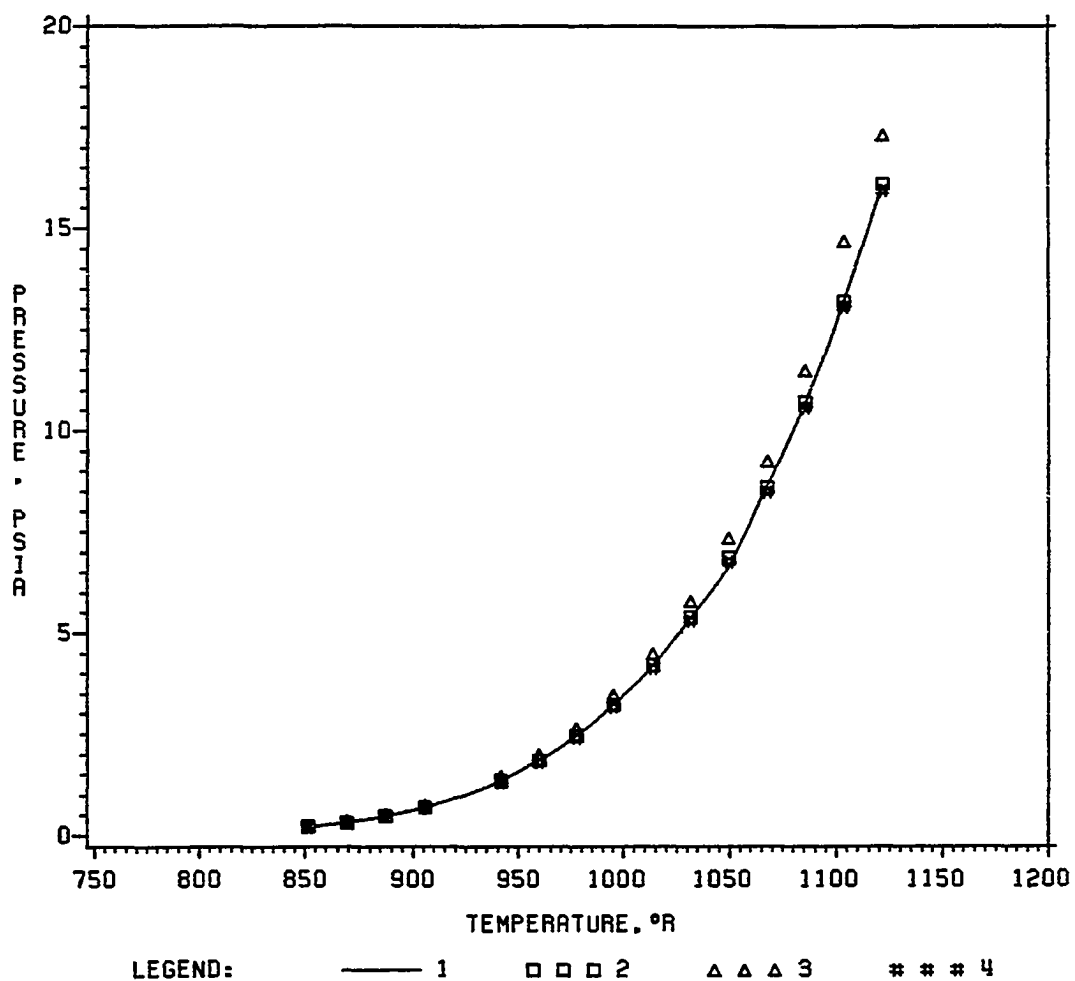


FIGURE 23: COMPARISON OF VAPOR PRESSURE CALCULATIONS
OF N-EICOSANE

1=EXPERIMENTAL. 2=EQUATION (30)
3=EQUATION (A2). 4=EQUATION (A4)

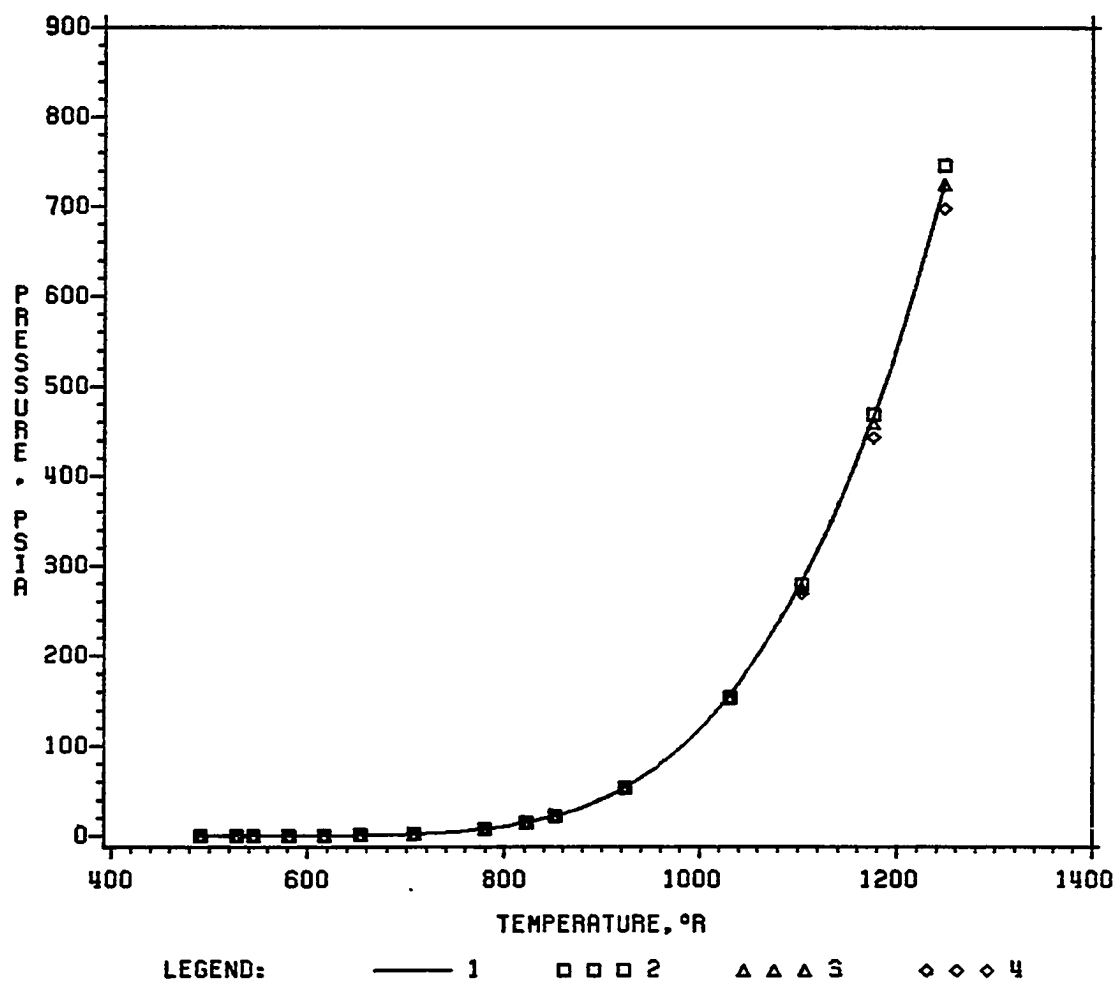


FIGURE 24: COMPARISON OF VAPOR PRESSURE CALCULATIONS OF ANILINE

1 = EXPERIMENTAL, 2 = EQUATION (30)
 3 = EQUATION (A2), 4 = EQUATION (A4)

TABLE 9
COMPARISON OF THE THERMODYNAMIC PROPERTY PREDICTIONS

component	property	number of points	aad		
			eq. (30)	eq. (A4)	eq. (A2)
Methane	RHO	39	0.93	0.55	5.43
	VP	32	0.99	0.38	1.45
	ENTH	33	1.50	0.49	2.13
Ethane	RHO	46	0.95	1.96	5.64
	VP	46	0.62	0.65	2.93
	ENTH	85	1.42	1.43	2.23
Propane	RHO	134	0.82	1.67	4.27
	VP	55	0.79	0.60	3.07
	ENTH	26	1.96	0.91	2.58
n-Butane	RHO	40	0.56	1.31	3.66
	VP	52	0.80	1.02	4.11
	ENTH	39	0.72	0.74	1.11
n-Pentane	RHO	39	1.18	1.82	3.23
	VP	45	0.67	1.16	1.35
	ENTH	38	1.06	1.63	1.56
n-Hexane	RHO	41	0.34	2.14	1.59
	VP	53	0.42	1.01	4.92
n-Heptane	RHO	41	0.77	1.61	1.49
	VP	40	0.77	1.97	1.10
	ENTH	17	0.90	0.89	1.10
n-Octane	RHO	48	0.72	2.33	4.13
	VP	56	0.80	1.16	3.73
	ENTH	54	0.70	0.97	2.41
n-Nonane	RHO	43	0.67	1.53	0.67
	VP	18	0.05	0.34	4.05
n-Decane	RHO	32	0.47	1.60	0.92
	VP	18	0.04	0.92	2.09

TABLE 9 (CONTINUED)

component	property	number of points	aad		
			eq. (30)	eq. (A4)	eq. (A2)
n-Undecane	VP	19	0.06	0.55	5.11
n-Dodecane	RHO	17	0.30	1.04	5.11
	VP	21	0.22	3.24	7.82
n-Tridecane	RHO	17	0.28	0.93	9.14
	VP	18	0.27	2.36	5.19
n-Tetra decane	RHO	14	0.21	0.78	7.78
	VP	15	0.14	2.42	3.79
n-Penta decane	RHO	14	0.29	1.03	8.96
	VP	14	0.21	0.59	4.64
n-Hexa decane	RHO	9	0.17	1.31	10.3
	VP	10	0.17	0.81	13.2
n-Hepta decane	RHO	13	0.34	1.03	13.4
	VP	15	0.21	0.73	9.99
n-Octa decane	RHO	13	0.27	1.13	17.1
	VP	15	0.45	0.77	11.5
n-Nona decane	RHO	12	0.36	1.55	20.1
	VP	15	0.23	0.79	11.1
n-Eicosane	RHO	25	0.98	1.78	17.8
	VP	15	0.42	1.71	8.48

TABLE 9 (CONTINUED)

component	property	number of points	aad		
			eq. (30)	eq. (A4)	eq. (A2)
Ethylene	RHO	40	0.91	0.99	3.19
	VP	35	0.94	0.63	5.22
	ENTH	34	2.00	0.75	2.77
Propylene	RHO	57	1.28	1.36	2.31
	VP	28	0.80	1.37	3.72
i-Butane	RHO	116	0.79	1.00	3.77
	VP	82	0.75	5.93	2.39
	ENTH	73	1.34	1.19	1.67
i-Pentane	RHO	38	0.84	1.33	3.07
	VP	22	0.29	0.81	0.90
Benzene	RHO	102	0.74	2.53	3.35
	VP	67	0.35	1.51	1.21
Toluene	RHO	13	0.31	0.91	0.54
	VP	33	0.89	1.73	2.31
o-Xylene	RHO	59	0.37	1.13	1.17
	VP	43	0.25	0.56	5.27
Dichloro difluoro methane	RHO	182	0.47	1.03	1.69
	VP	40	0.53	0.58	2.50
	ENTH	40	0.26	0.31	1.36
Carbon dioxide	RHO	39	0.39	0.65	1.89
	VP	33	0.81	0.39	0.61
	ENTH	39	1.76	1.73	3.09
Nitrogen	RHO	38	0.79	0.30	4.32
	VP	19	0.69	0.62	3.26
	ENTH	77	1.33	0.29	1.21

TABLE 9 (CONTINUED)

component	property	number of points	aad		
			eq. (30)	eq. (A4)	eq. (A2)
Hydrogen sulfide	RHO	40	0.53	0.46	3.69
	VP	24	0.39	0.66	4.23
Methyl fluoride	RHO	131	0.74	2.69	4.14
	VP	28	0.54	1.73	18.1
Phenol	RHO	14	0.78	2.19	10.5
	VP	15	1.33	3.24	6.11
Acetone	RHO	46	0.62	2.90	13.1
	VP	20	0.24	1.46	0.99
Dimethyl ether	RHO	34	2.90	3.35	3.77
	VP	19	0.26	0.53	3.46
Methyl ethyl ether	RHO	28	3.25	3.61	6.51
	VP	18	0.23	1.32	2.27
Diethyl ether	RHO	43	1.85	3.82	5.11
	VP	23	0.35	0.43	0.95
Aniline	RHO	29	0.44	3.56	2.98
	VP	34	0.76	3.15	8.09
overall prediction	RHO	1668	0.79	1.68	4.16
	VP	1155	0.56	1.47	4.04
	ENTH	555	1.26	0.96	1.91

TABLE 10

COMPARISON OF THERMODYNAMIC PROPERTY PREDICTIONS WITH THE
BACK EQUATION

component	property	number of points	aad	
			eq. (30)	eq. (A3)
Methane	RHO	39	0.93	0.40
	VP	32	0.99	1.07
	ENTH	33	1.50	3.83
Ethane	RHO	46	0.95	1.95
	VP	46	0.62	4.55
	ENTH	85	1.42	3.55
Propane	RHO	116	0.54	1.14
	VP	53	0.65	4.40
	ENTH	26	1.96	5.76
n-Butane	RHO	36	0.42	1.18
	VP	52	0.80	5.08
	ENTH	39	0.72	2.42
n-Pentane	RHO	37	1.11	1.89
	VP	45	0.67	3.85
	ENTH	38	1.06	2.76
i-Pentane	RHO	38	0.84	1.87
	VP	22	0.29	3.16
n-Hexane	RHO	29	0.58	0.97
	VP	49	0.37	3.60
n-Heptane	RHO	36	0.82	2.64
	VP	40	0.77	3.39
	ENTH	17	0.90	1.33
n-Octane	RHO	31	0.49	6.01
	VP	51	0.80	3.59
	ENTH	46	0.90	1.66
n-Decane	RHO	14	0.49	14.3
	VP	13	0.05	6.72

TABLE 10 (CONTINUED)

component	property	number of points	aad	
			eq. (30)	eq. (A3)
Benzene	RHO	102	0.79	1.79
	VP	67	0.29	3.16
Toluene	RHO	13	0.31	1.82
	VP	33	0.89	5.24
Nitrogen	RHO	38	0.79	0.30
	VP	19	0.69	0.33
	ENTH	77	1.33	2.36
Hydrogen sulfide	RHO	40	0.53	0.74
	VP	24	0.39	2.12
overall prediction	RHO	615	0.70	2.15
	VP	546	0.66	3.67
	ENTH	361	1.24	2.93

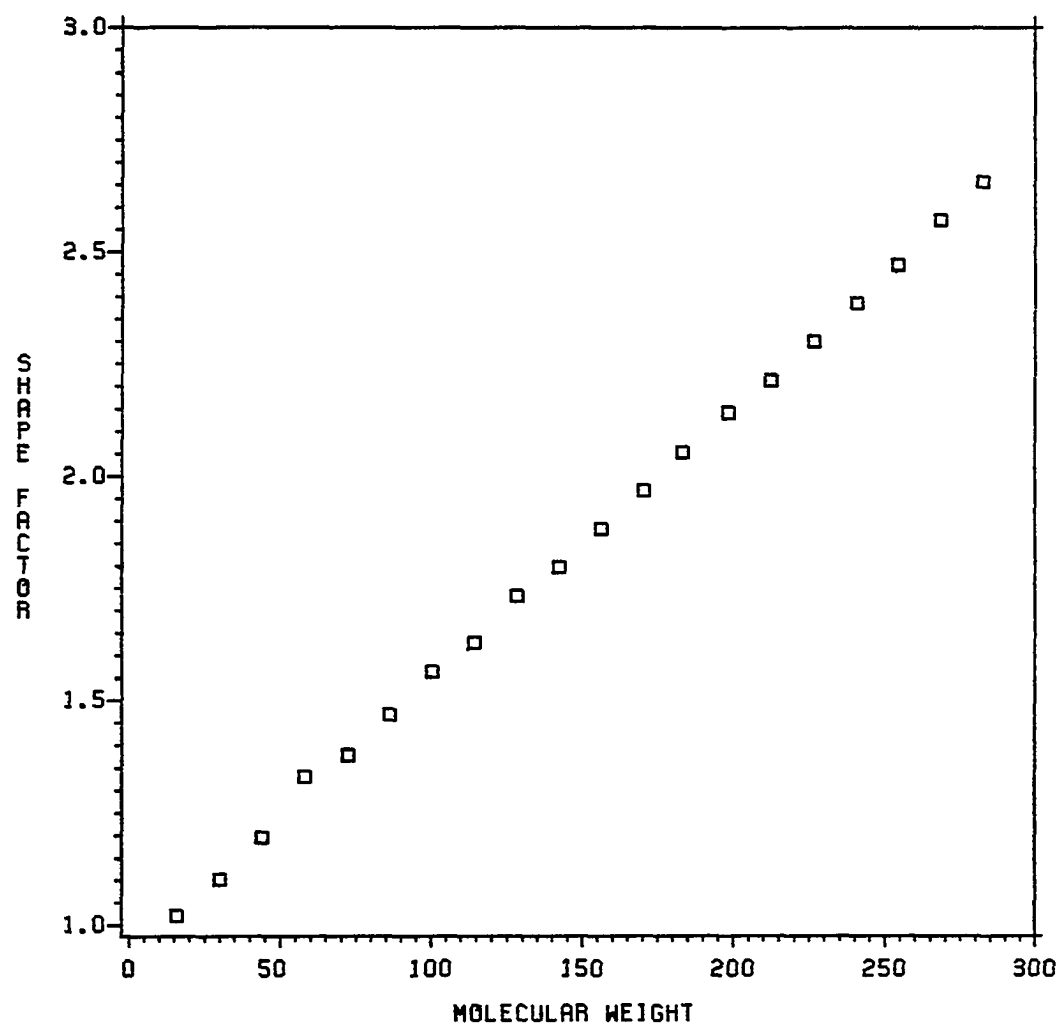


FIGURE 25: PLOT OF THE SHAPE FACTOR VERSUS
MOLECULAR WEIGHT OF N-PARAFFINS

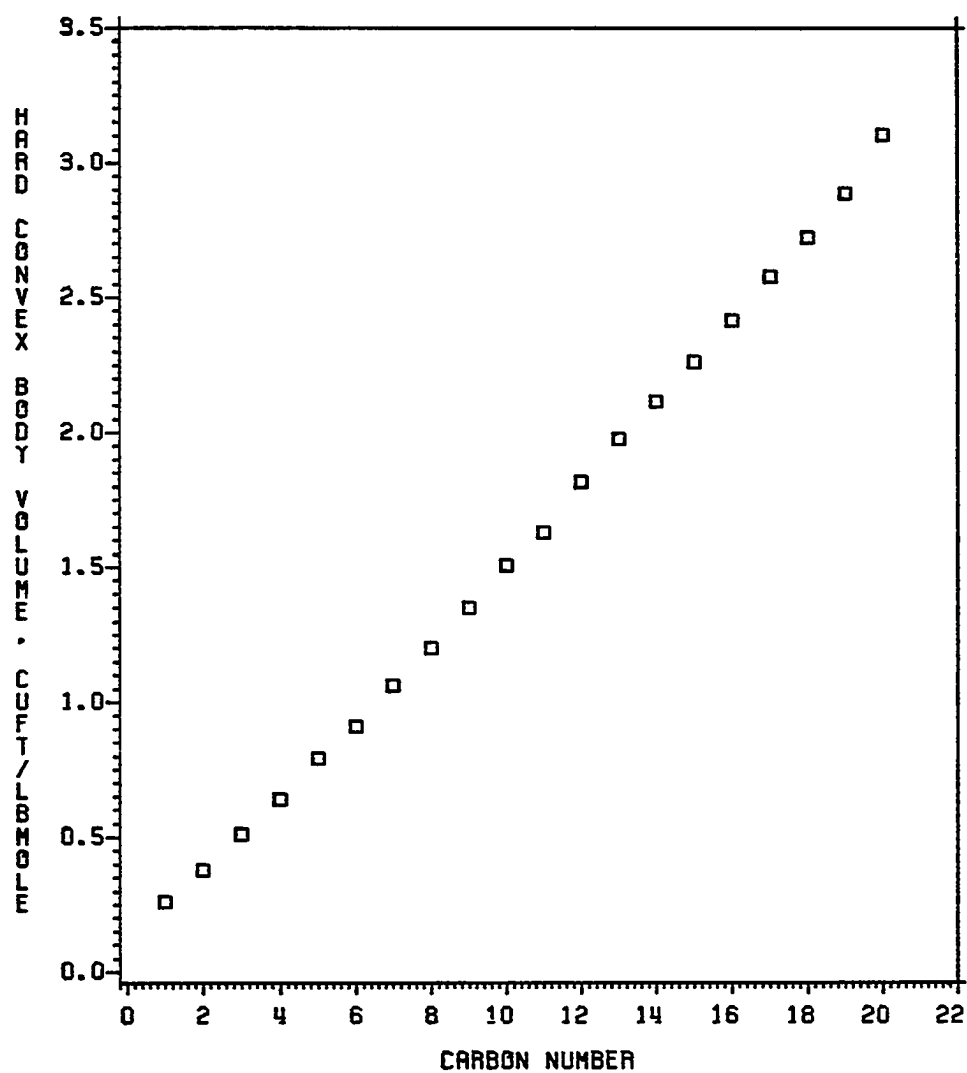


FIGURE 26: PLOT OF THE HARD CONVEX BODY VOLUME VERSUS CARBON NUMBER OF N-PARAFFINS

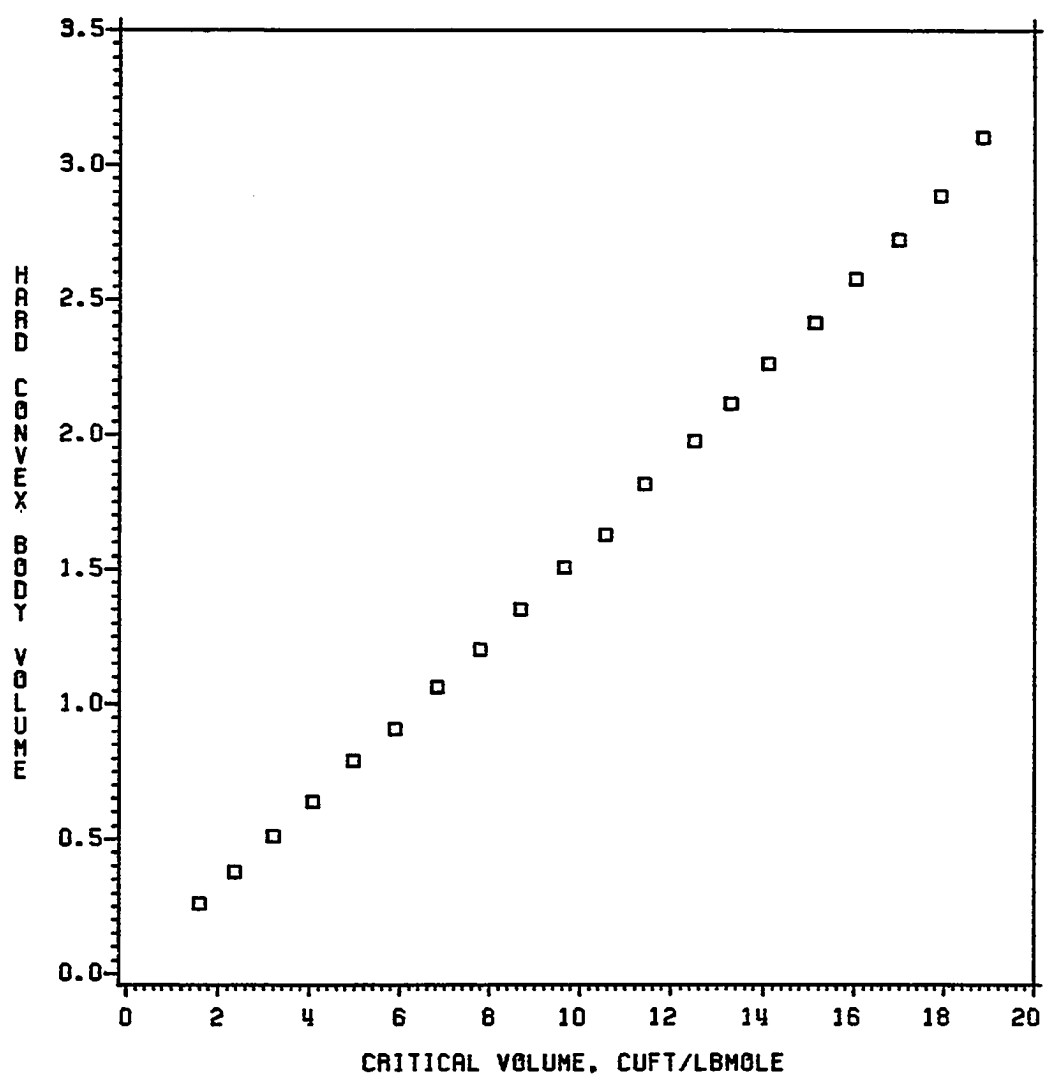


FIGURE 27: PLOT OF THE HARD CONVEX BODY VOLUME
VERSUS CRITICAL VOLUME OF N-PARAFFINS

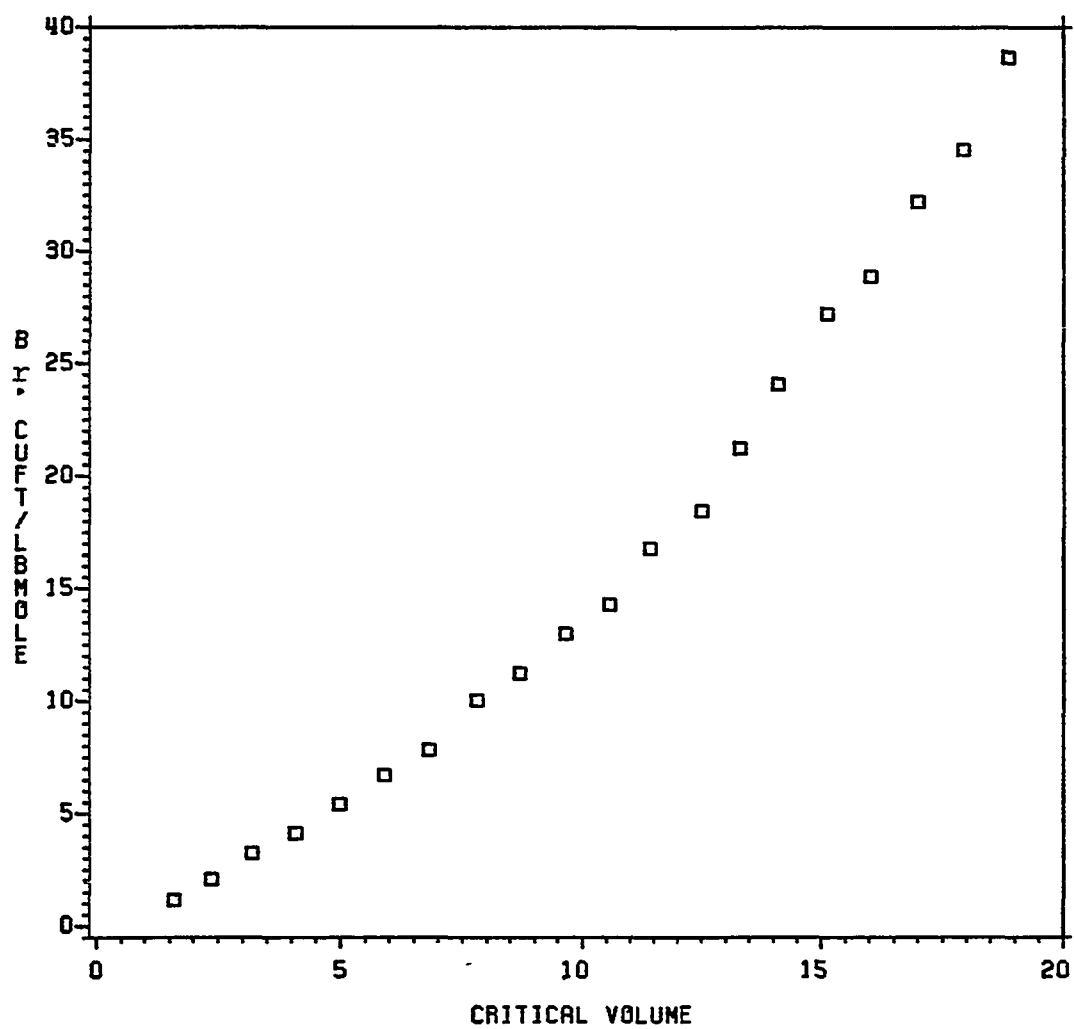


FIGURE 28: PLOT OF B_r VERSUS CRITICAL VOLUME
OF N-PARAFFINS

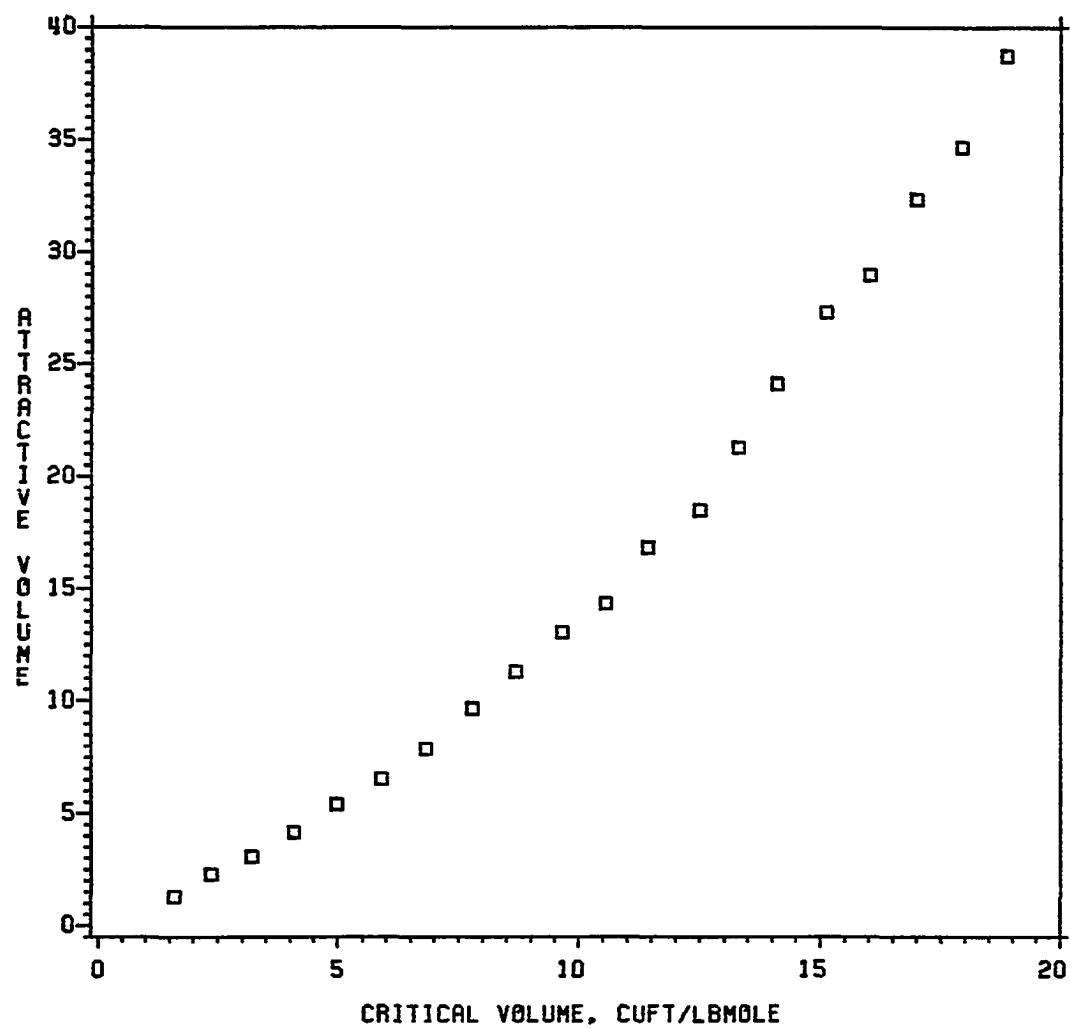


FIGURE 29: PLOT OF THE ATTRACTIVE VOLUME VERSUS
CRITICAL VOLUME OF N-PARAFFINS

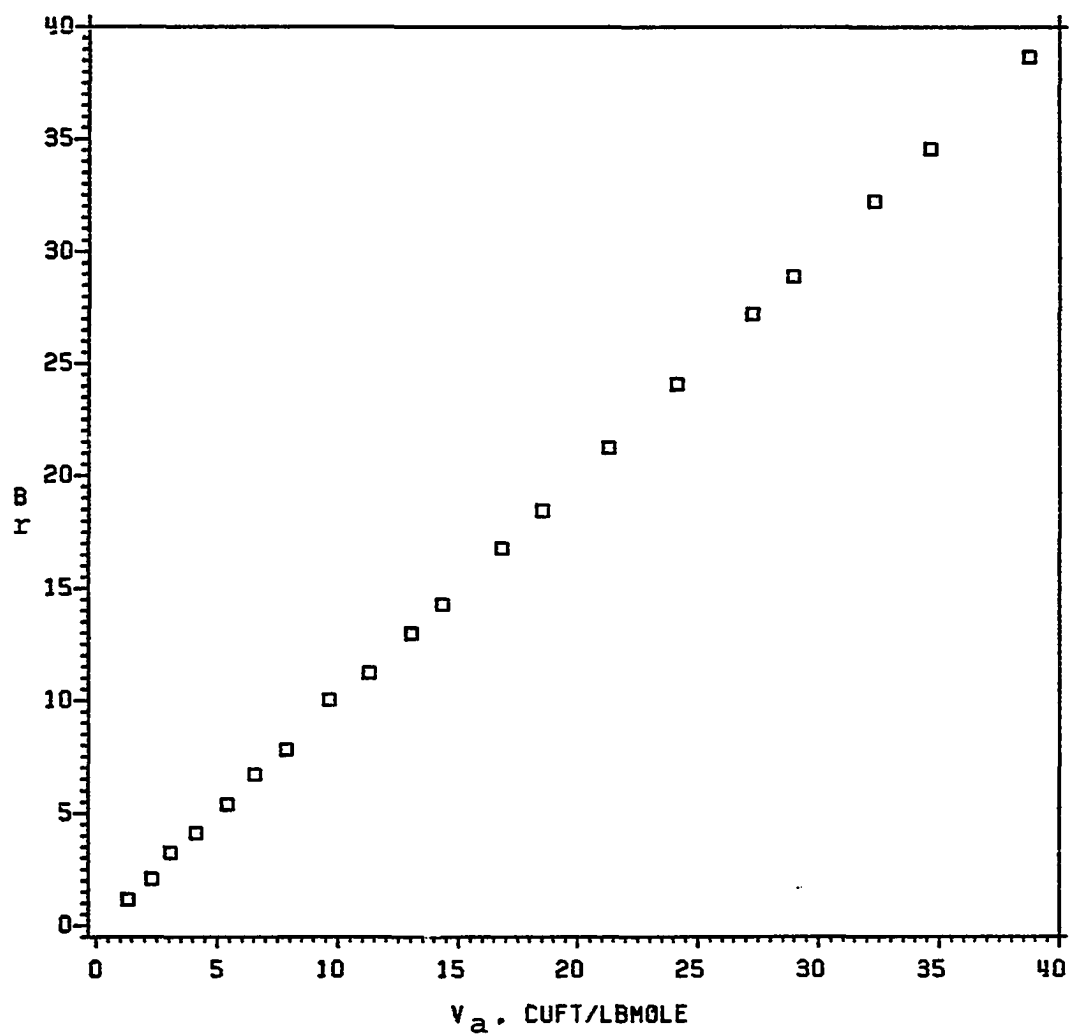


FIGURE 30: PLOT OF Br VERSUS V_a OF NORMAL PARAFFINS

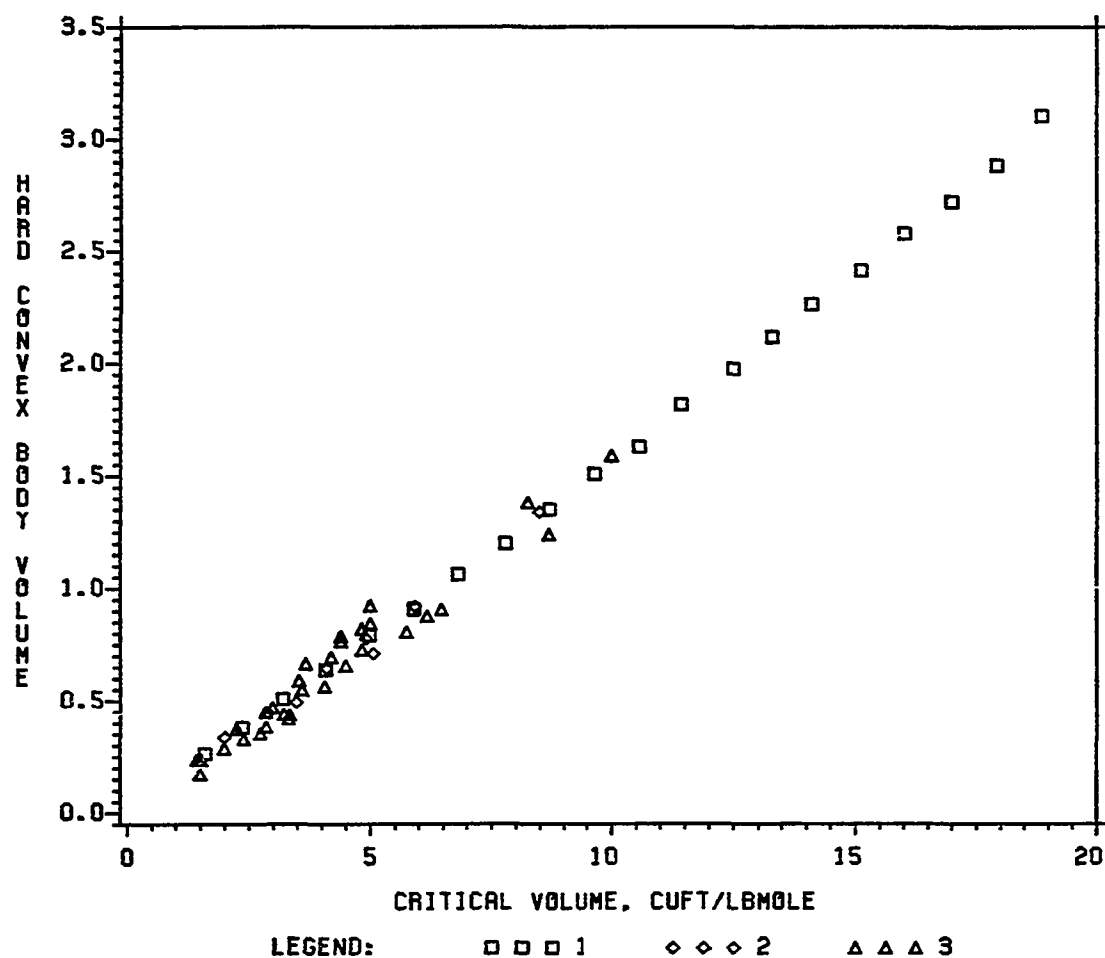


FIGURE 31: PLOT OF THE HARD CONVEX BODY VOLUME VERSUS
CRITICAL VOLUME

1=N-PARAFFINS, 2=OTHER NONPOLARS, 3=POLAR COMPOUNDS

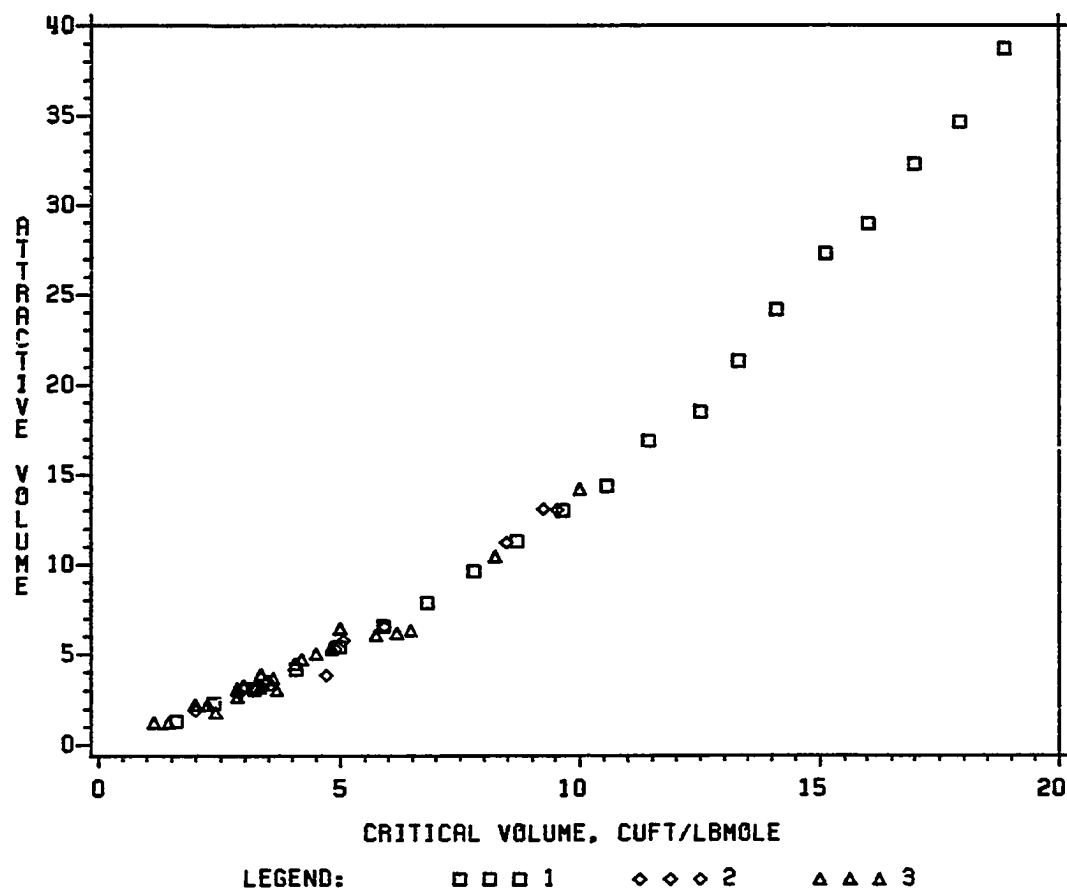


FIGURE 32: PLOT OF THE ATTRACTIVE VOLUME VERSUS
THE CRITICAL VOLUME

1=N-PARAFFINS, 2=OTHER NONPOLARS, 3=POLAR COMPOUNDS

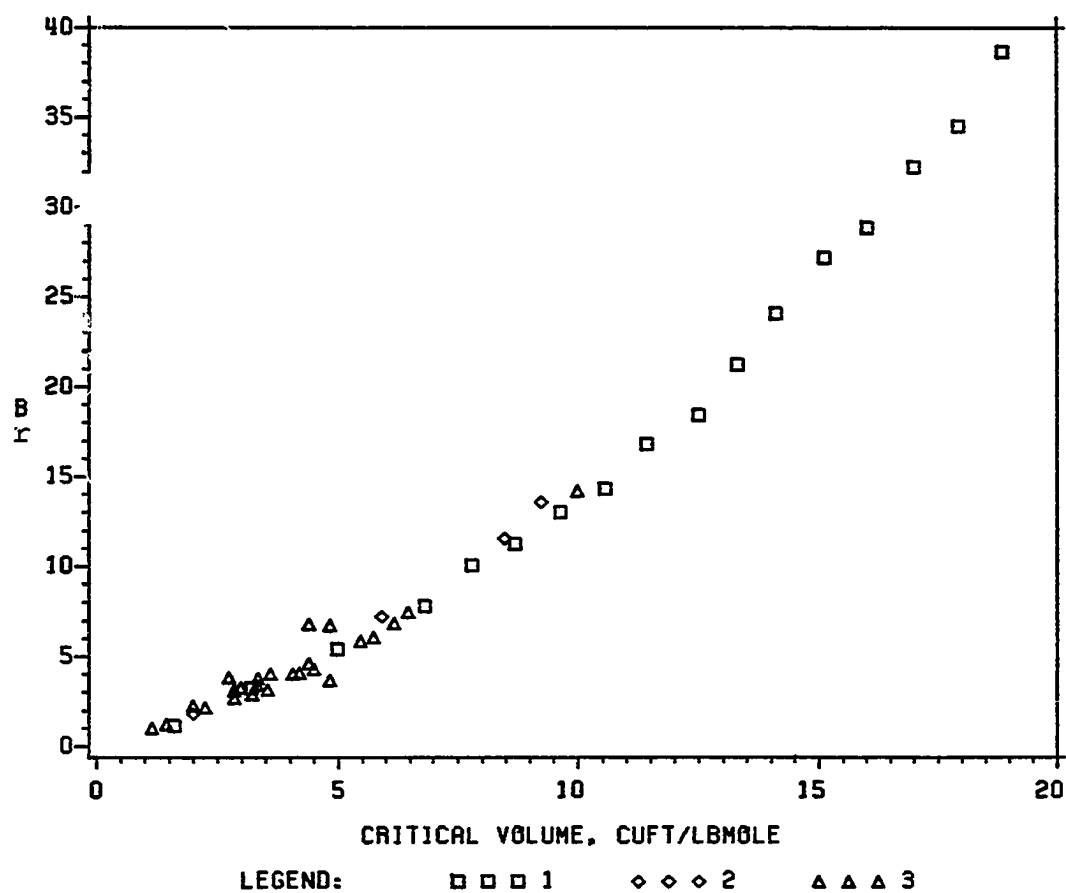


FIGURE 33: PLOT OF B_r VERSUS CRITICAL VOLUME

1=N-PARAFFINS, 2=OTHER NONPOLARS, 3=POLAR COMPOUNDS

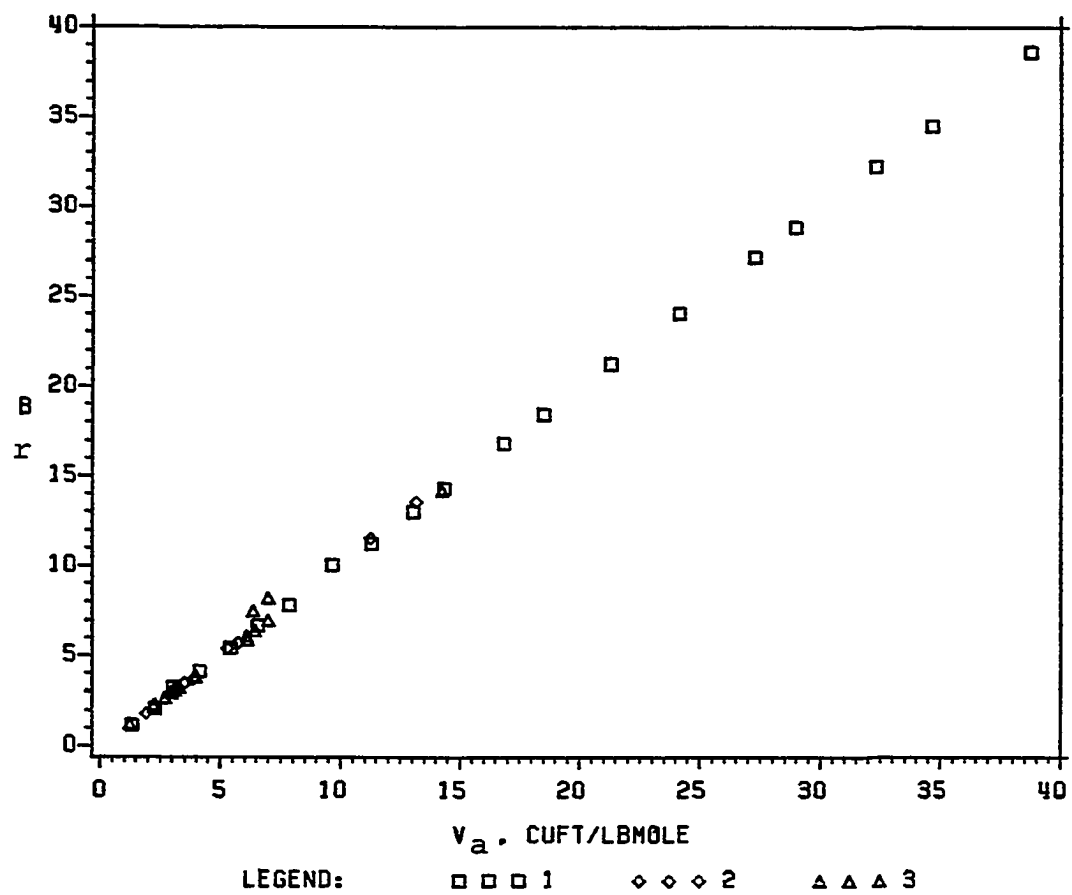


FIGURE 34: PLOT OF Br VERSUS V_a

1=N-PARAFFINS, 2=OTHER NONPOLARS, 3=POLAR COMPOUNDS

Chapter IV

CONCLUSIONS

Thermodynamic properties of fluids of different structures and electrostatic interactions are accurately predicted by the equation of state presented in this thesis. The fluids tested include some petroleum hydrocarbons, compounds found in natural gas, and some coal chemicals. These compounds represent various classes of fluids: polar, nonpolar, associative, aromatic compound, straight-chain, ring compound, hydrocarbon, nonhydrocarbon, etc. The new equation is developed based on statistical mechanical theories which relate thermodynamic properties to the molecular interactions. The intermolecular potential is assumed to be of the square-well model. The molecular nonsphericity and the size of molecule are taken into account explicitly by the parameters C and D in the hard convex body expression. The effect of the molecular orientation on the square-well parameters are taken into account through angle-averaging.

The new equation not only has a simple functional form but also offers a very good accuracy in the prediction of thermodynamic properties as compared to other equations such as the Peng-Robinson or the BAC equation. As mentioned

earlier, the improvement is significant in the predictions of gases at high temperatures, liquid phase properties, and the overall predictions of large molecular fluids. In addition to the ability to describe the P-V-T behavior of both polar and nonpolar compounds over a wide range of temperatures and pressures, the new equation offers a fairly good accuracy in the predictions of the enthalpy and the second virial coefficients.

Development of an equation of state of pure fluids is the groundwork for an application to mixtures of different types of compounds, which is the practical interest in engineering design calculations. An equation of state that works for both polar and nonpolar pure compounds of different sizes should lead to a good prediction of similar and dissimilar mixture systems, such as nonpolar-nonpolar, polar-polar, and nonpolar-polar mixtures, provided the appropriate mixing rules are used. The regular behavior of the parameters provides a possibility of correlating them with some known properties or measurable quantities. A generalization of the adjustable parameters will benefit the property calculations of mixture systems. Improvement of the equation of state studied can be made, in the future, by several options. For example, a term of higher order in density can be added to the approximation of $y(r)$ in Equation (17) and (27). A dependent of the hard convex body volumes on temperatures for a 'soft' molecule can be taken

into consideration, as suggested by Bienkowski and Chao (1975). For highly polar and strong hydrogen-bonding compounds such as methanol and water, a simple temperature-dependence of the effective energy parameter ϵ'/k in Equation (51) and the polarity parameter K may not be sufficient to account for such systems. Therefore, modifications of these terms might be necessary.

Appendix A

SUMMARY OF THE EQUATIONS OF STATE REFERENCED

THE VAN DER WAALS EQUATION (Balzhiser, 1972)

$$P + \frac{a}{V^2} (V - b) = RT \quad (A1)$$

where $a = \frac{27}{64} R^2 \frac{T_c^2}{P_c}$

and $b = \frac{R T_c}{8 P_c}$

THE PENG-ROBINSON EQUATION (Peng and Robinson, 1976)

$$Z = \frac{V}{V-b} - \frac{a(T) V}{RT(V(V-b) + b(V-b))} \quad (A2)$$

where $a(T) = 0.45724 \frac{R^2 T_c^2}{P_c} (T_r, \omega)$

$$\alpha = (1 + K (1 - T_r^{1/2}))^2$$

$$K = 0.37464 + 1.54226 \omega - 0.26992 \omega^2$$

$$b = 0.07780 \frac{RT_c}{P_c}$$

THE BACK EQUATION (Boublik-Alder-Chen-Kreglewski Equation)

(Chen & Kreglewski, 1977; Sirmick, Lin and Chao, 1979)

$$Z = Z_h + Z_a \quad (A3)$$

$$Z_h = \frac{1 + (3\alpha - 2)y + (3\alpha^2 - 3\alpha + 1)y^2 - \alpha^2 y^3}{(1 - y)^3}$$

$$Z_a = \sum_n \sum_m D_{nm} (U/kT)^n (v'/v)^m$$

$$y = 0.74048 v'/v$$

$$v' = v'' (1 - C \exp(-3U'/kT))^3$$

$$U = u' (1 + n'/kT)$$

$$n'/k = 0.60 \omega T_c$$

TABLE A1: UNIVERSAL CONSTANTS D_{nm} FOR EQUATION (A3)

D11	=	-8.8043
D12	=	4.164627
D13	=	-48.203555
D14	=	140.43620
D15	=	-195.23339
D16	=	113.515
D21	=	2.9396
D22	=	-6.0865383
D23	=	40.137956
D24	=	-76.230797
D25	=	-133.70055
D26	=	860.25349
D27	=	-1535.3224
D28	=	1221.4261
D29	=	-409.10539
D31	=	-2.8225
D32	=	4.7600148
D33	=	11.257177
D34	=	-66.382743
D35	=	69.248785
D41	=	0.3400
D42	=	-3.18750
D43	=	12.231796
D44	=	-12.110681

TABLE A2: PARAMETERS OF EQUATION (A3) FOR $C = 0.12$

component	v^m cc/mole	α	u^s/k K	n^s/k K
Methane	21.576	1.00	190.29	1.00
Ethane	31.118	1.037	298.03	19.0
Propane	42.598	1.041	353.11	34.0
n-Butane	53.855	1.051	399.56	51.0
n-Pentane	65.751	1.0566	435.93	70.72
i-Pentane	64.958	1.0565	432.20	62.71
n-Hexane	77.228	1.072	468.33	90.11
n-Heptane	89.351	1.0799	491.00	113.77
n-Octane	96.556	1.0981	517.52	134.50
n-Decane	110.72	1.1349	558.07	181.57
Benzene	54.383	1.0587	532.12	71.50
Toluene	67.013	1.0621	532.12	91.24
Nitrogen	19.457	1.00	123.66	3.0
Hydrogen Sulfide	20.672	1.044	373.66	15.0

THE KHAN'S EQUATION (Khan, 1983)

$$Z = 1 + \alpha Z_c + (\alpha - 1) Z_c \quad (A4)$$

$$\begin{aligned} Z_c = & \left(\frac{A1}{T^*} + \frac{A2}{T^{*2}} + \frac{A3}{T^{*3}} + \frac{A4}{T^{*4}} + \frac{A5}{T^{*5}} \right) \rho^* \\ & + \left(A6 + \frac{A7}{T^*} \right) \rho^{*2} + A8 \rho^{*3} \\ & + \left(\frac{A9}{T^{*3}} + \frac{A10}{T^{*4}} + \frac{A11}{T^{*5}} \right) \rho^{*2} \exp(-A16 \rho^{*2}) \\ & + \left(\frac{A12}{T^{*3}} + \frac{A13}{T^{*4}} + \frac{A14}{T^{*5}} \right) \rho^{*4} \exp(-A16 \rho^{*2}) \\ & + \frac{A15}{T^*} \rho^{*5} \end{aligned}$$

where $\rho^* = \rho V^*$; $T^* = kT/\epsilon$

$$A_i = \alpha Bi^0 + (\alpha - 1) Bi^P$$

TABLE A3: UNIVERSAL CONSTANTS OF EQUATION (A4)

i	Bi^0	Bi^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

TABLE A4: VALUES OF PARAMETERS USED WITH EQUATION (A4)

Compound	$\epsilon/k, R$	V^* cu.ft./lbmole	α	K
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 A4 (CONTINUED)

compound	$\epsilon/k, R$	v^* cu.ft./lbmole	α	K
Ethylene	368.844	0.290322	1.35634	0.0
Propylene	448.552	0.385617	1.60734	0.0
i-Butane	486.253	0.526474	1.76444	0.0
i-Pentane	533.891	0.613940	1.93374	0.0
Benzene	669.312	0.506596	1.82792	0.0
Toluene	658.809	0.610572	2.16520	0.0
o-Xylene	690.612	0.698227	2.31868	0.0
Dichloro- difluoromethane	459.703	0.441159	1.75124	0.0
Carbon Dioxide	358.899	0.209042	1.36653	930.242
Nitrogen	168.969	0.210863	1.22598	0.0
Hydrogen Sulfide	498.486	0.254407	1.02500	1590.420
Methyl Fluoride	351.610	0.292249	1.66562	720.803
Phenol	703.892	0.520417	2.32465	16426.500
Acetone	599.138	0.448461	1.62079	8145.340
Dimethyl Ether	480.569	0.402000	1.33792	5113.510
Methyl- Ethyl Ether	505.499	0.444777	1.76410	2877.160
Diethyl Ether	523.728	0.546213	2.09362	1369.090
Aniline	767.357	0.549676	2.05710	14413.400

Appendix B

THERMODYNAMIC PROPERTY CALCULATIONS OF N-OCTANE

TABLE B1: DENSITY CALCULATIONS OF N-OCTANE

Temperature, R	Pressure, psia	Experimental density, lbmole/cu.ft.	Calculated density, lbmole/cu.ft.	Percent deviation
389.670	14.696	0.4177	0.40725	-2.5018
399.670	14.696	0.4153	0.40579	-2.2894
409.670	14.696	0.4129	0.40428	-2.0872
419.670	14.696	0.4105	0.40272	-1.8950
429.670	14.696	0.4081	0.40111	-1.7129
439.670	14.696	0.4057	0.39945	-1.5408
449.670	14.696	0.4032	0.39774	-1.3540
459.670	14.696	0.4008	0.39598	-1.2014
469.670	14.696	0.3983	0.39418	-1.0338
479.670	14.696	0.3959	0.39233	-0.9006
489.670	14.696	0.3934	0.39044	-0.7523
499.670	14.696	0.3909	0.38850	-0.6131
509.670	14.696	0.3884	0.38652	-0.4837
519.670	14.696	0.3859	0.38450	-0.3639
529.670	14.696	0.3835	0.38243	-0.2798
539.670	14.696	0.3810	0.38032	-0.1792
549.670	14.696	0.3786	0.37816	-0.1161
559.670	14.696	0.3762	0.37596	-0.0631
569.670	14.696	0.3737	0.37372	0.0059
579.670	14.696	0.3713	0.37144	0.0372
589.670	14.696	0.3688	0.36911	0.0844
599.670	14.696	0.3662	0.36674	0.1478
609.670	14.696	0.3636	0.36433	0.1998
619.670	14.696	0.3610	0.36187	0.2405
629.670	14.696	0.3583	0.35937	0.2972

TABLE B1 (continued)

Temperature, R	Pressure, psia	Experimental density, lbmole/cu.ft.	Calculated density, lbmole/cu.ft.	Percent deviation
639.670	14.696	0.3557	0.35682	0.3136
649.670	14.696	0.3531	0.35422	0.3173
659.670	14.696	0.3505	0.35158	0.3073
669.670	14.696	0.3477	0.34889	0.3410
679.670	14.696	0.3449	0.34614	0.3608
689.670	14.696	0.3422	0.34335	0.3367
699.670	14.696	0.3393	0.34051	0.3557
709.670	12.928	0.3350	0.33759	0.7336
709.670	14.696	0.3364	0.33761	0.3587
729.670	17.570	0.3290	0.33166	0.8032
749.670	23.420	0.3235	0.32550	0.6183
769.670	30.700	0.3175	0.31909	0.5022
789.670	39.100	0.3115	0.31242	0.2942
809.670	50.000	0.3061	0.30545	-0.2118
829.670	62.000	0.2995	0.29814	-0.4524
849.670	76.500	0.2924	0.29047	-0.6612
859.670	85.000	0.0109	0.01127	3.3803
869.670	95.000	0.2842	0.28239	-0.6382
889.670	116.00	0.2755	0.27380	-0.6156
909.670	140.00	0.2662	0.26462	-0.5924
929.670	169.00	0.2563	0.25473	-0.6123
949.670	201.00	0.2448	0.24397	-0.3410
969.670	239.00	0.2295	0.23205	1.1113

ave. abs. deviation = 0.722626 %
 number of points = 48

TABLE B2: VAPOR PRESSURE CALCULATIONS OF N-OCTANE

Temperature, R	Pressure, psia	Experimental vapor pressure, psia	Calculated vapor pressure, psia	Percent deviation
414.760	0.001415	0.001415	0.001385	-2.0689
428.525	0.002960	0.00296	0.00305	3.0594
529.670	0.2160	0.2160	0.21760	0.7417
539.670	0.2970	0.2970	0.29835	0.4557
549.670	0.4020	0.4020	0.40330	0.3234
559.670	0.5370	0.5370	0.53800	0.1858
569.670	0.7090	0.7090	0.70881	-0.0266
572.90	0.7735	0.7735	0.77285	-0.8371
589.670	1.1920	1.1920	1.18860	-0.2862
599.670	1.5210	1.5210	1.51500	-0.3942
609.670	1.9220	1.9220	1.91230	-0.5036
619.670	2.4060	2.4060	2.39170	-0.5929
629.670	2.9850	2.9850	2.96550	-0.6544
639.670	3.6740	3.6740	3.64710	-0.7322
642.220	3.8674	3.8674	3.83990	-0.7117
649.670	4.4870	4.4870	4.45080	-0.8062
659.670	5.4400	5.4400	5.39210	-0.8810
669.670	6.5490	6.5490	6.48780	-0.9340
679.670	7.8330	7.8330	7.75500	-0.9962
689.670	9.3110	9.3110	9.21240	-1.0590
699.670	11.0020	11.0020	10.8810	-1.1037
709.670	12.9280	12.9280	12.7790	-1.1501
717.88	14.6960	14.6960	14.5260	-1.1557
719.670	15.1100	15.1100	15.9310	-1.1834
729.670	17.5700	17.5700	17.3580	-1.2088
736.22	19.3370	19.3370	19.1070	-1.1881
739.670	20.3300	20.3300	20.0830	-1.2139
749.670	23.4200	23.4200	23.1330	-1.2258
759.670	26.9000	26.9000	26.5300	-1.3736
765.470	29.0050	29.0050	29.6760	-1.1350
769.670	30.7000	30.7000	30.3060	-1.2820
779.670	34.5000	34.5000	34.4860	-0.0410

TABLE B2 (continued)

Temperature, R	Pressure, psia	Experimental vapor pressure, psia	Calculated vapor pressure, psia	Percent deviation
789.670	39.100	39.100	39.097	-0.0070
799.670	44.200	44.200	44.176	-0.0543
809.670	50.000	50.000	49.747	-0.5068
819.670	55.500	55.500	55.829	0.5927
829.670	62.000	62.000	62.489	0.7894
839.670	68.600	68.600	68.732	1.6500
849.670	76.500	76.500	77.607	1.4473
859.670	85.000	85.000	86.149	1.3522
869.670	95.000	95.000	95.395	0.4160
879.670	105.00	105.00	105.39	0.3739
889.670	116.00	116.00	116.20	0.1689
899.670	127.00	127.00	127.82	0.6426
909.670	140.00	140.00	140.31	0.2242
919.670	153.00	153.00	153.76	0.4980
929.670	168.00	168.00	168.14	0.0853
939.670	184.00	184.00	183.82	-0.0955
949.670	201.00	201.00	200.41	-0.2921
959.670	220.00	220.00	218.11	-0.8611
969.670	239.00	239.00	237.12	-0.7877
979.670	260.00	260.00	257.49	-0.9664
989.670	283.00	283.00	279.18	-1.3496
999.670	310.00	310.00	302.46	-2.4338
1009.67	327.00	327.00	326.92	-0.0236
1019.67	350.00	350.00	352.40	0.6849

ave. abs. deviation = 0.80470 %
 number of points = 56

TABLE B3: ENTHALPY DEPARTURE CALCULATIONS OF N-OCTANE

Temperature, R	Pressure, psia	Experimental enthalpy departure, Btu/lb	Calculated enthalpy departure, Btu/lb	Deviation, Btu/lb
534.670	200.00	-155.80	-156.10	0.3019
534.670	360.00	-155.40	-155.62	0.2211
534.670	400.00	-155.20	-155.50	0.3009
534.670	500.00	-155.00	-155.20	0.1997
534.670	600.00	-154.70	-154.90	0.1982
534.670	800.00	-154.20	-154.29	0.0940
534.670	1000.00	-153.70	-153.69	-0.0118
534.67	1400.00	-152.60	-152.47	-0.1273
959.670	200.00	-21.00	-18.231	-0.7689
959.670	500.00	-100.40	-96.978	-3.4216
979.670	400.00	-93.40	-92.030	-1.3704
979.670	500.00	-93.50	-93.114	-0.3960
979.670	600.00	-93.70	-93.984	0.2838
979.670	800.00	-94.50	-95.298	0.7984
979.670	1000.00	-95.70	-96.238	0.5384
979.670	1400.00	-98.20	-97.438	-0.7615
999.670	400.00	-89.00	-87.076	-1.9331
999.670	500.00	-89.90	-88.768	-1.1317
999.670	600.00	-89.20	-90.047	0.8469
999.670	800.00	-92.10	-91.884	-0.2160
999.670	1000.00	-93.40	-93.154	-0.2463
999.670	1400.00	-96.50	-94.759	-1.7411
1009.670	400.00	-85.40	-84.107	-1.2930
1009.670	500.00	-87.10	-86.333	-0.7670
1009.670	600.00	-88.40	-87.910	-0.4902
1009.670	800.00	-89.90	-90.091	0.1912
1009.670	1000.00	-91.90	-91.561	-0.3394
1009.670	1400.00	-95.40	-93.399	-2.0012
1019.670	500.00	-84.30	-83.644	-0.6557
1019.670	600.00	-86.30	-85.627	-0.6727
1019.670	800.00	-88.00	-88.231	0.2314

TABLE B3 (continued)

Temperature, R	Pressure, psia	Experimental enthalpy departure, Btu/lb	Calculated enthalpy departure, Btu/lb	Deviation, Btu/lb
1019.670	1000.00	-90.40	-89.932	-0.4682
1019.670	1400.00	-93.90	-92.026	-1.8741
1029.670	500.00	-81.10	-80.597	-0.5025
1029.670	600.00	-83.40	-83.163	-0.2368
1029.670	800.00	-86.10	-86.298	0.1982
1029.670	1000.00	-88.70	-88.263	-0.4369
1029.670	1400.00	-92.30	-90.639	-1.6614
1039.670	500.00	-77.00	-76.993	-0.0066
1039.670	600.00	-80.80	-80.464	-0.3362
1039.670	800.00	-84.20	-84.280	0.0795
1039.670	1000.00	-87.00	-86.553	-0.4467
1039.670	1400.00	-90.70	-89.238	-1.4624
1049.670	500.00	-72.10	-72.396	0.2958
1049.670	600.00	-77.90	-77.455	-0.4454
1049.670	800.00	-81.90	-82.167	0.2670
1049.670	1000.00	-85.00	-84.798	-0.2021
1049.670	1400.00	-88.80	-87.822	-0.9776
1059.670	200.00	-14.50	-13.862	-0.6377
1059.670	500.00	-66.50	-65.394	-1.1061
1059.670	600.00	-75.00	-74.017	-0.9828
1059.670	800.00	-79.90	-79.946	0.0464
1059.670	1000.00	-83.00	-82.995	-0.0480
1059.670	1400.00	-87.00	-86.393	-0.6069

ave. abs. deviation = 0.700435 Btu/lb
 ave. abs. deviation = 1.02585 %
 number of points = 54

Appendix C

THERMODYNAMIC PROPERTY CALCULATIONS OF DIETHYLAMINE

TABLE C1: DENSITY CALCULATIONS OF DIETHYLAMINE

Temperature, R	Pressure, psia	Experimental density, lbmole/cu.ft.	Calculated density, lbmole/cu.ft.	Percent deviation
591.390	14.700	0.57019	0.57366	0.6093
599.670	17.052	0.56592	0.56926	0.5894
617.670	23.373	0.55653	0.55941	0.5173
635.670	31.311	0.54629	0.54918	0.5293
653.670	41.454	0.53605	0.53855	0.4665
671.670	52.920	0.52580	0.52747	0.3170
689.670	69.090	0.51556	0.51593	0.0712
707.670	87.024	0.50446	0.50384	-0.1234
725.670	108.633	0.49251	0.49116	-0.2744
743.670	133.770	0.47971	0.47780	-0.3991
761.670	163.170	0.46605	0.46365	-0.5142
779.670	196.980	0.45069	0.44858	-0.4674
797.670	233.730	0.43532	0.43232	-0.6894
815.670	277.830	0.41740	0.41471	-0.6448
833.670	326.340	0.39777	0.39518	-0.6517
851.670	379.260	0.37387	0.37284	-0.2764
869.670	441.000	0.34143	0.34642	1.4602

ave. abs. deviation = 0.50596 %
number of points = 17

TABLE C2: VAPOR PRESSURE CALCULATIONS OF DIETHYLAMINE

Temperature, R	Pressure, psia	Experimental vapor pressure, psia	Calculated vapor pressure, psia	Percent deviation
591.390	14.700	14.700	14.663	-0.2527
599.670	17.052	17.052	17.101	0.2865
617.670	23.373	23.373	23.484	0.4758
635.670	31.311	31.311	31.568	0.8212
653.670	41.454	41.454	41.632	0.4287
671.670	52.920	52.920	53.963	1.9708
689.670	69.090	69.090	68.883	-0.2999
707.670	87.024	87.024	86.709	-0.3621
725.670	108.633	108.633	107.780	-0.7808
743.670	133.770	133.770	132.500	-0.9525
761.670	163.170	163.170	161.250	-1.1770
779.670	196.980	196.980	194.490	-1.2625
797.670	233.730	233.730	232.600	-0.4818
815.670	277.830	277.830	276.320	-0.5436
833.670	326.340	326.340	326.140	-0.0611
851.670	379.260	379.260	382.170	0.7668
869.670	441.000	441.000	446.040	1.1434
887.670	505.680	505.680	517.980	2.4329

ave. abs. deviation = 0.80558 %
 number of points = 18

Appendix D

THERMODYNAMIC PROPERTY CALCULATIONS OF TETRAHYDROFURAN

TABLE D1: DENSITY CALCULATIONS OF TETRAHYDROFURAN

Temperature, R	Pressure, psia	Experimental density, lbmole/cu.ft.	Calculated density, lbmole/cu.ft.	Percent deviation
455.670	0.28333	0.80000	0.80451	0.5632
473.670	0.52707	0.79221	0.79597	0.4742
491.670	0.92829	0.78441	0.78741	0.3478
509.670	1.55875	0.77627	0.77893	0.2263
527.670	2.50850	0.76814	0.76864	0.0653
536.670	3.13635	0.76398	0.76385	-0.0172
545.670	3.89035	0.75965	0.75899	-0.0874
563.670	5.83480	0.75082	0.74906	-0.2343
581.670	8.50135	0.74147	0.73887	-0.3511
599.670	12.0640	0.73143	0.72840	-0.4144

ave. abs. deviation = 0.27814 %
number of points = 10

TABLE D2: VAPOR PRESSURE CALCULATIONS OF TETRAHYDROFURAN

Temperature, R	Pressure, psia	Experimental vapor pressure, psia	Calculated vapor pressure, psia	Percent deviation
455.670	0.28333	0.28333	0.28241	-0.3233
473.670	0.52707	0.52707	0.52716	0.0170
491.670	0.92829	0.92829	0.93033	0.2197
509.670	1.55875	1.55875	1.56340	0.2979
527.670	2.50850	2.50850	2.51690	0.3343
536.670	3.13635	3.13635	3.14750	0.3564
545.670	3.89035	3.89035	3.90160	0.2898
563.670	5.83480	5.83480	5.84900	0.2431
581.670	8.50135	8.50135	8.51160	0.1205
599.670	12.0640	12.0640	12.0630	-0.0123
608.670	14.2419	14.2419	14.2310	-0.0746
609.670	14.5000	14.5000	14.4890	-0.0730
617.670	16.7185	16.7185	16.6950	-0.1424
635.670	22.6780	22.6780	22.6200	-0.2544
653.670	30.1890	30.1890	30.0680	-0.4004
671.670	39.4690	39.4690	39.2830	-0.4705
707.670	63.9450	63.9450	64.0750	0.2033
743.670	99.0350	99.0350	99.2500	0.2168
779.670	146.450	146.450	147.240	0.5384
815.670	210.250	210.250	210.720	0.2213
851.670	291.450	291.450	292.380	0.3191
887.670	395.850	395.850	395.560	-0.0740
923.670	524.900	524.900	522.830	-0.3946
959.670	684.400	684.400	678.160	-0.9116
972.270	725.550	725.550	737.710	1.6837

ave. abs. deviation = 0.32770 %
number of points = 25

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