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

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## THE UNIVERSITY OF OKLAHOMA

 GRADUATE COLLEGEA NEW GENERALIZED EQUATION OF STATE FOR POLAR AND NONPOLAR PURE FLUIDS

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

BY

MAHMOUD A. MAGSOUD KHAN
Norman, Oklahoma
1983

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



In The Name Of God,
Most Gracious Ans Most Merciful

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## ABSTRACT


#### Abstract

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


# A NEW GENERALIZED EQUATION OF STATE FOR <br> POLAR AND RONPOLAR PURE FLUIDS 

## CHAPTER I

INIROMIICIION


#### Abstract

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


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

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

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

Over the years, several attempts have been made to describe the thermodynamic behavior of real fluids via equations of state. These equations of state have achieved varying degrees of success, enabling one to divide them into three separate classes. In the first class, one has the equations of state which are cubic in density. A few of the popular density-cubic equations of state are the van der Waals equation(1873), the Redilich-Kwong equation(1949), the Soave-Redilch-Kwong equation(1972), the Peng-Robinson equation(1976), and the Kumar-Starling equation(1982). This type of equations give reasonable description of the thermodyamic behavior of real fluids, with each equation
being more accurate in the chronological order of appearance in the literature. The second class of equations of state is those which are non-cubic in density and provide a good description of the thermodynamic behavior of real fluids for all fluid states. The Beattie-Bridgeman equation(1928), the Beneaict-intbon-Rijin (BWR) equation(1940) and the Modified prar equation(i973) are exampies of this class of equations. The third class is tine equaitions of state which are highly constrained for each specific fluid. Examples of this class of equations are the Keenan and Keyes equation of state for water (1963), the Goodwin equation of state for propane (1977), and the Ewers and Wagner equation of state for oxygen (1981). This class of equations give a highly accurate description of the specific real fluid behaviors.

This research presents the development of a new three parameter generalized equation of state for the accurate calculation of the thermodynamic properties (density, enthalpy departure and vapor pressure) of pure nonpolar fluids for the gaseous and liquid regions of reduced temperatures from 0.24 to 3.3 and reduced pressures to 480. This equation is of the perturbation type and is based on the enipirical equation of state for argon developed by
et al.(1980), but minied by employing the concepts of hard convex body (HCB) model and the hard-chain molecular theory for large, structural molecules. The constants for the temperature and density dependence of the equation of state are generalized using the experimental data for saturated hydrocarbons from ethane to normai decane. The development of the equation of state with a little review about the perturbation theory and hard convas body equations of state are discussed in chapter II. Prediction of the thermodynamic properiies of different classes of fluids not used in the generalization is tested using the heavier normal paraffins, normal undecane to normal eicosane, and other types of hydrocarbons, unsaturated hydrocarbons and ring compounds. Nonhydrocarbons, hydrogen and nitrogen, were also tested. The use of the resultant equation of state has been extended to polar and associating pure fluids by applying the mean-potential model. This introduced a fourth parameter which was determined from the experimental PVT data for the fluid of interest. Results of these tests are given in chapter III. The values of the characteristic parameters for all compounds tested are also reported in chapter III.

## CHAPTER II

## DEVETORNLAT OE THE EOURTYON OF STATE


#### Abstract

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


$$
\begin{equation*}
Z=Z^{(0)}+\omega Z^{(1)} \tag{1}
\end{equation*}
$$

Where ${ }^{(0)}$ is the compressibility factor of a monoatomic (spherdcal molecule) fluid and $z^{(1)}$ represents the deviation of the compressibility factor of the real fluid from $2^{(0)}$. Whe acentric factor, $\omega$, $1 s$ the characterization parameter
for the nonsphericity of the molecule. $Z^{(0)}$ and $Z^{(1)}$ are functions of reduced temperature and reduced pressure. Pitzer type correlations usually give a good prediction of the thermodynamic properties for normal fluids. This approach, however, has been proven inadequate when calculations are made in the critical region and for liquids at low temperatures (Lee and Kesler,1975). Since the acentric factor, $\omega$, cannot completely reflect the molecular shape and the steric effect which become more important at high densities, the use of the the acentric factor as a characterization parameter and monoatomic fluids as reference make this approach hard to extend to large, structurally complex molecules in high density regions. One type of modification given by Lee and Kesler (1975) uses two reference systers instead of using only one reference. The Lee-Kesler correlation expresses the compressibility factor of any fluid in terms of the compressibility factor of a simple fluid, $z^{(0)}$, and the compressibility factor of a reference fluid, $Z^{(r)}$, as follow;

$$
\begin{equation*}
z=z^{(0)}+\frac{\omega}{\omega^{(r)}}\left(z^{(r)}-z^{(0)}\right) \tag{2}
\end{equation*}
$$

Both $Z(0)$ and $Z(r)$, given by the same function form, have
been expressed by a modified Bur equation of state. Equacion (2) can be applied to a wider range of compounds than equation (i). The secoñ type of modificaition uses parameters other than the acentric factor to chaxacierize the steric effect and the multipolar effect. other characterization parameters, such as the orientation parameter, $\gamma,(S t a y i l n g$ et $1 ., 1978$ ) and the shape factor, Ф, (Leland et al., 1952 ) for the steric effect and the Stiel polar factor (Re1d, Prausnitz, and Sherwood, 1977) for polar effect, have been applied in the correlation of thermodynamic properties.

It is the intent of this work to use a structure parameter and a polar parameter to characterize the steric effect and polar effect, respectiveiy. The structure parameter, $\alpha$, used in this work was adopted from the recently deveioped hard-convex-body (HCB) equation of state given by Eoublik (1981),

$$
\begin{equation*}
z=1+\frac{y}{(1-y)}+\frac{3 \alpha^{*} y}{(1-y) 2}+\frac{3 \alpha^{*^{2}} y^{2}-\alpha^{*}\left(6 \alpha^{*}-5\right) y^{3}}{(1-y)^{3}} \tag{3}
\end{equation*}
$$

frere $y$ is the packing sraction defined as the volume occupied by the convex bodies per unit volume of the fluid.

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

$$
\begin{equation*}
\alpha^{*}=\frac{\overline{\bar{p}} s}{3 \bar{v}} \tag{4}
\end{equation*}
$$

where $\bar{R}$ is the radius of curvature, $S$ is the surface area, ane $\bar{F}$ is the hard-convex-boay volune. For an $\alpha^{*}$ value equal to unity, equation (3) reduces to the Carnahan-Siarling equation of state for hard sphere (1972). Equation (3) can be approximately represented by the hard-chain equation of state,

$$
\begin{equation*}
z=1+a^{*} \frac{4 u-2 y^{2}}{(1-y)^{3}} \tag{5}
\end{equation*}
$$

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


PLOT OF 2 BOUBLJK AND Z(EQN. 5)
VERSUS REDUCED DENSITY FOR DIFFERENTA*VALUES.

EQUATION OF STATE FOR NORMAL PARAFFINS:

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

$$
\begin{equation*}
Z=1+\alpha\left(Z_{\text {conf. }}^{(0) \text { rep. }}+Z_{\text {conf. }}^{(0) \text { att }}\right) \tag{6}
\end{equation*}
$$

where $\mathbf{z}_{\text {conf. }}^{(0) \text { rep. }}$ and $\mathbf{z}_{\text {conf. }}^{(0) \text { att. }}$ are the configurational compressibility factor of the repulsive part and attractive part, respectively. Combining the repulsive and attractive parts into the total $z_{\text {conf. }}^{(0)}$. equation (6) becones

$$
\begin{equation*}
Z=1+\alpha Z_{\text {conf. }}^{(0)} \tag{7}
\end{equation*}
$$

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

$$
\begin{equation*}
z=i+2(0) \tag{8}
\end{equation*}
$$

Twu, Lee and Starling (1980) have fitted the constants in a temperatureodensity function chosen for equation (8) by using argon data (ubersity and vapor pressure). This equation of state is capable of predicting the properties of simple fluids at low reduced temperatures ( $T_{\mathrm{T}}=0.3$ ) and high reciuced pressures ( $P_{\mathrm{r}}=132$ ). In this work the constants of Twu-Iee-Starling correlation were modified using the molecular hard-core volume ( $V^{*}$ ) as the reducing parameter For density, which is more realistic than using the Lennard-Jones(12-6) parameter, $\sigma$, for nonspherical molecules.

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

$$
\begin{equation*}
Z=1+\alpha Z_{\text {conf. }}^{(0)}+(\alpha-1) Z_{\text {CONF. }}^{(p)} \tag{9}
\end{equation*}
$$

The coneigurational compressibility gactors of both the isotropic fluid, $z_{\text {conf. }}^{(0)}$, and the perturbation contribution, $z_{\text {conf }}^{(p)}$, have been represenced herein by the Strobridge form,

$$
\begin{aligned}
& Z_{\text {CONF, }}=\left(A_{1}+-\frac{A_{2}}{T^{2}}+-\frac{A_{3}}{T_{2}^{2}}+-\frac{A_{0}}{T_{3}}+-\frac{A_{C}}{T_{5}}\right) \rho^{\circ} \\
& +\left(A_{\epsilon}+-A_{T}-\right) \rho^{02}+A_{8} \rho^{\circ}
\end{aligned}
$$

$$
\begin{align*}
& +\left(\frac{A_{12}}{T^{33}}+\frac{A_{13}}{T^{4}}+\frac{A_{21}}{T}\right): \boldsymbol{p}^{\circ 4} \exp \left(-\hat{A}_{16} \boldsymbol{p}^{2}\right) \\
& +\quad-A_{15} \boldsymbol{P}^{5} \tag{10}
\end{align*}
$$

Where

$$
P^{*}=P U^{*} \quad \text { and } \quad T^{*}=k T / \epsilon
$$

$\epsilon / \mathrm{k}$ and $V^{*}$ are the characteristic energy parameter and Characteristic volume, respectively.

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

$$
\begin{equation*}
\frac{H-H^{D}}{R T}=z-1-\int_{0}^{p} T\left|\frac{\partial z}{\partial T}\right|_{p} \frac{\partial p}{\rho} \tag{11}
\end{equation*}
$$

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

$$
\begin{equation*}
\frac{S-S^{\circ}}{R}=-\ln (\rho R T)-\int_{0}^{p}\left[(z-1)+T\left\{\frac{\partial z}{\partial T}\right\}_{\rho}\right] \frac{\partial \rho}{\rho} \tag{12}
\end{equation*}
$$

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

$$
\begin{align*}
\frac{H-H^{\circ}}{R T} & =(Z-1)+\left(\frac{A_{2}}{T^{\star}}+\frac{2 A_{3}}{T^{* 2}}+\frac{3 A_{4}}{T^{\star 3}}+\frac{5 A_{5}}{T^{* 5}}\right) \hat{\rho}^{\star} \\
& +0.5 \frac{A_{7}}{T^{*}} \rho^{\star 2}+\frac{1}{2 A_{16}}\left(\frac{3 A_{9}}{T^{* 3}}+\frac{4 A_{10}}{T^{\star 4}}+\frac{5 A_{11}}{T^{* 5}}\right)\left[1-\exp \left(-A_{16} 0^{* 2}\right)\right] \\
& +\frac{1}{2 A_{16}} 2\left(\frac{3 A_{12}}{T^{* 3}}+\frac{4 A_{13}}{T^{\star 4}}+\frac{5 A_{14}}{T^{\star 5}}\right)\left[1-\left(1+A_{16} 0^{* 2}\right) \exp \left(-A_{16} 0^{\star 2}\right)\right]  \tag{13}\\
& +\frac{1}{5} \frac{A_{15}}{T^{\star}} \rho^{* 5}
\end{align*}
$$

and for entropy departure,

$$
\begin{align*}
\frac{S-S^{0}}{R} & =-\ln (\rho R T)-\left(A_{1}-\frac{A_{3}}{T^{* 2}}-\frac{2 A_{4}}{T^{* 3}}-\frac{4 A_{5}}{T^{* 5}}\right) \rho^{*}-\frac{1}{2 A_{6}} C^{* 2}+1 / 3 A_{8} \rho^{* 3} \\
& +\frac{1}{2 A_{16}}\left[\frac{2 A_{9}}{T^{* 3}}+\frac{3 A_{10}}{T^{\star 4}}+\frac{4 A_{11}}{T^{\star 5}}\right]\left[1-\exp \left(-A_{16} \rho^{* 2}\right)\right] \\
& +\frac{1}{2 A_{16}^{2}}\left[\frac{2 A_{12}}{T^{* 3}}+\frac{3 A_{13}}{T^{\star 4}}+\frac{4 A_{14}}{T^{* 5}}\right]\left[1-\left(1+A_{16} \rho^{* 2}\right) \exp \left(-A_{16} 0^{* 2}\right)\right] \tag{14}
\end{align*}
$$

where $H^{\circ}$, $S^{\circ}$ are the ideal gas enthalpy and entropy at the same temperature of the fluid and unit pressure.

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

$$
\begin{equation*}
A_{i}=B_{i}^{(0)}+(\alpha-1) B_{i}^{(p)}, \quad i=1,16 \tag{15}
\end{equation*}
$$

where $B_{i}(0)$ is the constant for $Z_{\text {conf }}^{(0)}$. and $B_{i}^{(p)}$ is the constant for ${\underset{y}{c o n f}}_{(\mathrm{p})}^{(0)} \quad$ The constants for $\mathcal{Z}_{\text {conf }}^{(0)}$ are converted from the Twu-Lee-Starling correlation(1980) and the constants for $Z_{\text {conf }}^{(p)}$. are determined from the thermodynamic property data including vapor pressure, density, and enthalpy departure of normal paraffins (ethane to normal decane) with the parameters ( $\epsilon / k, \alpha$, and $v^{*}$ ) fixed as linear functions of carbon number. The numerical values of the constants, $B_{i}^{(0)}$ and $B_{i}^{(p)}$, used in equation (9) are given in Table 2.1. The benavior of the universal functions ${\underset{c}{c o n f}}_{(0)}^{(0)}$ and $\underset{\text { conf. }}{(p)} \quad$ is shown in Figures 2 and 3. for different isotherms. It can be seen that $Z_{\text {conf }}^{(p)}$. contributes only in the high density region ( $\theta^{*}$ (0.3) where the fluid properties iecome more sensitive to differences of moiecular shape. For larger molecules, the reduced density range increases and also the $\alpha$-value. Therefore, the

| Universal constants $B_{i}^{(0)}$ and $B_{i}^{(p)}$ to be used ins equation (9) |  |  |
| :---: | :---: | :---: |
| 1 | $\mathrm{B}_{\mathrm{i}}(0)$ | $\mathrm{B}_{\mathrm{i}} \mathrm{p}^{\text {) }}$ |
| 1 | 2.5023740 | 0.53182 |
| 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 |

## COMPRESSIBIITY FACTOR <br> CONTRIBUTION ZO



FIGURE 2.
PLOT OF 20 AS A FUNCTION OF REDUCED DERSTTY AND REDUCED TEMPERATURE

COMPRESSIBILITY FACTOR CONTRIBUTION ZP


FIGURE 3
PLOT OF ZP ASA
FUNCTION OF REDUCED DENSITY
AND TEMPERATURE
(p)

Zconf. term becomes more important for larger and more complicated molecules.

ENUATION OF STAIE FOR MUTIPOLAR AND ASSOCIATING FLUIDS:

According to the treatment of pople(1954), the pair potential for polar fluids is divided into two parts; a reference potential Uo which is spherical and therefore a function only of interparticle distance, $\Psi_{i j}$, and a perturbation potential ${ }_{I_{1}}$, which is a function of the angular variables, $\omega_{i}$ and $\omega_{j}$,

$$
\begin{equation*}
U\left(r_{i j}, \omega_{i}, \omega_{j}\right)=U\left(r_{i j}\right)+\lambda U_{1}\left(r_{i j} ; \omega_{i}, \omega_{j}\right) \tag{16}
\end{equation*}
$$

Where $\lambda$ is a perturbation parameter. The Stockmayer pair potential is

$$
\begin{align*}
& U\left(r_{i j}\right)=4 \epsilon\left(\left\{\frac{\sigma}{r_{i j}}\right)^{12}-\left(\frac{\sigma}{r_{i j}}\right)^{6}\right)  \tag{17}\\
& U_{1}\left(r_{i j} ; \omega_{i}, \omega_{j}\right)=\frac{\mu_{i} \mu_{i}}{r_{i j}^{3}}\left(\sin \theta_{i} \sin \theta_{j} \cos \phi_{i j}-2 \cos \theta_{i} \cos \theta_{j}\right) \tag{18}
\end{align*}
$$

and

$$
\lambda=1
$$

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

$$
\begin{equation*}
A=A_{0}+R_{2}+A 3+\cdots \tag{19}
\end{equation*}
$$

The first-order term, A1, disappears because the reference potential $U 0$ is defined as the angular average of the total potential $U$ (i.e, the angular average of $U$ is zero). Ao is the free energy of isotropic fluids. The expressions for A2 and $A 3$ involve the stese variables, intermolecular pocentisi parameters, and certain integrals, $J$ and $K$, for the reference fluid. Details of the derivation of the equations for these terms, as well as expressions for other thermodynamic properties are given by Twa (1976). As an example the J-integral is given as

$$
\begin{equation*}
J^{(n)}=\int_{0}^{\infty} d r^{*} \mathbf{r}^{*^{-(n-2)}} g^{(0)}\left(I^{*}\right) \tag{20}
\end{equation*}
$$

where $J$ is the two-body proxe pluid integral, $F^{*}$ is the recuced intermolecuiar separation, $g(0)$ is the pair
correlation function for the reference system, and - $n-2)$ is the power of the distance in the multipolar potential. The $J$ and $K$ integrals for the Lennard-Jones (12-6) reference have been evaluated by Gubbins and coworkers (Twu et al., 1976: Gray et al.,1978: Gubinas añ Twifisis); Niccias et al.,1979). With these integrals correlated as functions of reduced temperature and reduced density, the perturbation theory has been successfully applied to real fluids of moderate polarity and molecules of simple structure. Another problem for the perturbation theory is that the series of the perturbation expansion converges slowly as the dipole moment increases. The application of Pade resummation suggested by Stell, Rasaiah and Narang (1972) can help the series (19) converge faster. However, for highly polar fluids, if a simple reference model is used, the perturbation terms become greater than the reference term which makes the series divergent. Therefore, unless a more sophisticated reference term is used, perturbation theory still cannot be easily applied to highly polar compounds ( $\left.\mu^{*} \gg 1\right)$.

For practical purposes, this work employs the mean-potential model, instead of the statistical mechanicai
perturbation theory, to approach this problem. The orientation-averaged pair potential gor polar molecules is given (Reed and Gubbins,1973) as:

$$
\begin{equation*}
U^{\text {ave. }}=4 \epsilon\left(\left(\frac{\sigma}{r}\right)^{i 2}-\left(\frac{\sigma}{r}\right)^{6}\right)-\frac{1}{r^{6}}\left(\frac{\mu_{a}^{\hat{2}} \mu_{b}^{2}}{3 k T}+\mu_{a}^{2} a_{b}+\mu_{b}^{2} a_{a}\right) \tag{21}
\end{equation*}
$$

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

$$
\begin{equation*}
U^{a v e}=\Delta \epsilon^{\prime}\left(\left(\frac{0^{\prime}}{r}\right)^{12}-\left(\frac{0^{\prime}}{r}\right)^{6}\right) \tag{22}
\end{equation*}
$$

where

$$
\begin{gather*}
\epsilon^{\prime}=\left(1+\frac{i_{a}^{2} \mu_{b}^{2}}{6 \mathrm{kT} \mathrm{\varepsilon}(\sigma)^{6}}+\cdots\right)  \tag{23a}\\
\left(\sigma^{\prime}\right)^{6}=\sigma^{6} /\left(1+\frac{\mu_{a}^{2} \mu_{b}^{2}}{12 \mathrm{kTE}(\sigma)^{6}}+\cdots\right) \tag{23b}
\end{gather*}
$$

Where $\mu_{i}$ is the dipole moment, and $\otimes_{a, b}$ is the dipole polarizability. Since the hard-core vodume, $y^{*}$ was used

Instead of $\sigma^{3}$, the relationship of equation (23b) is not applicable in this work. The relationship of (23a) for the energy parametar was employed in equation fis). For many polar species, one of the mosi imporeant terms in the酎tipole expansion is the dipole-dipole term. Thus it was chosen to lump all orientational contributions to pure-fauid properties into a single term based on the angle-averaged interaction between point dipoles. To this term: \& simple temperarure dependence was assigned. Thus the energy parameter, $\epsilon / k$, was changed to $\varepsilon^{\prime} / k$, which is a function of temperature plus another parameter, $K$, as

$$
\begin{equation*}
\frac{\epsilon^{\prime}}{k}=\frac{\epsilon}{k}+\frac{k}{T\left(U^{*}\right)^{2}} \tag{24}
\end{equation*}
$$

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

When equations (13) and (1A) were derived for nonpolar fluizs, they involved the derivative of the compressibility factor witin respect to temperature (see equations il sne 12). From the definition of $\mathrm{T}^{*}$, one can easidy prove that

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

This relation holds true as long as $T$ is nondimensionlajzed to $T^{*}$ by diviaing it by a constant. In the case of nompolar fluids, this constant is equal to $\epsilon \prime k$, the energy parameter which is constant for a given fluid. Equation (24), however, indicates that $\epsilon^{\prime} / k$ for polar fluids is a function of temperature. This has been taken care of by using the relation

$$
\begin{equation*}
T\left(\frac{\partial Z}{\partial T}\right)_{P}=T\left(\frac{\partial Z}{\partial T^{*}}\right)_{F}\left(\frac{\partial T^{*}}{\partial T}\right)_{F} \tag{26}
\end{equation*}
$$

Which when the expression for polar compounds is used Changes to

$$
\begin{equation*}
T\left(\frac{\partial Z}{\partial T}\right)=\left(1+\frac{K}{T^{*}(E / K)^{2}\left(V^{*}\right)^{2}}\right) T^{*}\left(\frac{\partial Z}{\partial T^{*}}\right) \tag{27}
\end{equation*}
$$

Equation (27) above reduces to (35) for nonpolar sluids since $x=0$.

## APPLICATION OF THE GENERALIZED EQUATION OF STATE TO PURE COAPOUNDS

The neu genexalized comrelation is applied io a wide variety of compounds including hydrocarbon. nonhydrocarbor. halogenated hydrocarbon, ring compounds, hydrogen, nitrogen. carbon dioxide, ethers, acetone, alcohols, ammonia and water. Tables 3.1 and 3.2 list the compounds used in the application and their data source(s).

In order to calculate the thermodynamic properties of a compound (e.g. density, enthalpy departure, etc. ...) at a given temperature and pressure, the density has to be determined. The density is calculated implicitly by solving equation (9). The density search technique used in this work is described by Goin (i978). Other thermodynamic properties can be caiculated using the obtained density ir: the expressions derived by classical thermodynamic relatior:s (e.g. equations (11) and (12) of chapter II). To calculate the vapor pressure for a compound at a given temperature, one calculates the fugacity of the compound in the vapor phase and the fugacity in the liguid ohase at an assumed initial pressure. Since the fugacities in both phases are equal at the vapor pressure, the initial pressure can be

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

| Compound | Property | No. Of points | Data reference(s) |
| :---: | :---: | :---: | :---: |
| H゙athane | $E$ | 128 | Matinews (1946), |
|  |  |  | Prydz and Goodwin(1972) |
|  | den. | 41 | Van Itterieck et ai. (1963). |
|  |  |  | Douslin et ai.(1964). |
|  |  |  | Vennix(1967) |
|  | $\mathrm{H}-\mathrm{H}^{\mathrm{O}}$ | 38 | Jones(1963), Yesavage(1968) |
| Ethane | P | 46 | API-44(1953), |
|  |  |  | Canjar and Manning(1967) |
|  | den. |  | Sace 쿨 구릌(1950), |
|  |  |  | API-44(1953), |
|  |  |  | Canjar and Manning (1967) |
|  | $\mathrm{H}-\mathrm{H}^{\circ}$ | S8 | Sage and Lacey(1950), |
|  |  |  | Starling et al. (1978). |
| Propane | $p$ | 59 | API-44(!953), |
|  |  |  | Canjar and maming (1957) |
|  | den. | 41 | Sage and Lacey(1950), |
|  |  |  | API-44(1953), <br> Huang et al. (1967) |
|  | den. | 70 | Goodwin(1977) |
|  |  | 145 | Thomas ane Harrison (1982) |
|  | $\mathrm{H}-\mathrm{H}^{\circ}$ | 39 | Yesavage (1968), <br> Kwok et al.(1971) |
| n-Butane | P | 38 | API-44(1953), |
|  |  |  | Canjar and Manning(1967) |
|  | den. | 40 | Sage and Lacey(1950), |
|  |  |  | API-44(1953) <br> Sage and Lacey(1950) |
|  | $\mathrm{H}-\mathrm{H}^{\circ}$ | 39 | Sage and Lacey(1950) |
| n-Pentane | P | 50 | API-44(1953), |
|  |  |  | Canjar and manning (1967) |
|  | den. | 41 | Sage and Iacey(1950). |
|  |  |  | API-44(1953) |
|  | $\mathrm{H}-\mathrm{H}^{\mathrm{O}}$ | 39 | Sage and Lacey(1950) |

Table 3.1, (continued)

| Compound | Property | No. OE points | Data reference(s) |
| :---: | :---: | :---: | :---: |
| n-HEMane | F | 53 | API-44(1953), |
|  |  |  | Canjar and Manning(1967) |
|  | den. | 41 | ADI-44(1953), |
|  |  |  | Stewart et al. (1954) |
| n-Heptane | $\begin{aligned} & \mathrm{P} \\ & \text { den. } \end{aligned}$ | $\begin{aligned} & 44 \\ & 41 \end{aligned}$ | Kay(1938), ARI-44(i953), Stuart et al.(1950), <br>  |
|  |  |  |  |
|  |  |  |  |
|  | $\mathrm{H}-\mathrm{H}^{\mathrm{O}}$ | 17 | Gillana and Pareikh(1942) |
| n-Octane | P | 64 | Young (1900), |
|  |  |  | Mundel (1913), |
|  |  |  | API-44(1953) |
|  | den. | 54 | Felsing and Watson(1942), |
|  |  | 62 | API-44(1953) Lenoir et al.(1968) |
| n-Nonane | $\begin{aligned} & p \\ & \text { den. } \end{aligned}$ | $\begin{aligned} & 21 \\ & 75 \end{aligned}$ | API-44(1953) |
|  |  |  | Vargaftik(1975) |
| n-Decane | $\begin{aligned} & p \\ & \text { den. } \end{aligned}$ | $\begin{aligned} & 24 \\ & 32 \end{aligned}$ | API-44(1953) |
|  |  |  | Sage and Lacey(1950) |
| n-Undecane to <br> n-Eicosane | P <br> den. | $\begin{aligned} & 164 \\ & 157 \end{aligned}$ | Vargaftik(1975) |
|  |  |  | Vargaftik(1975) |
| Isobutane | P | 64 | Dana et al.(1926), |
|  |  |  | Sage and Lacey(1938), |
|  |  |  | Aston et al. (1940), |
|  |  |  | Hackñer ec ai. (i945), |
|  |  |  | Beattie et al.(1949), |
|  |  |  | Connolly(1962), |
|  |  |  | Zwolinski and Wilhoit(1971) |
|  | den. | 321 | Sage and Lacey(1938), |
|  |  |  | Morris et al.(1940), Sage and Lacey(1950), |
|  |  |  | Rossini et al.(1953), |
|  |  |  | Canjaz and Manning(1967), |
|  |  |  | Naxman et al. (istib) |
|  |  | 24 | geattie et al. (1950), |
|  |  |  | Canjar and Manning(1967) |


| Compound | Property | No. Of points | Data reference(s) |
| :---: | :---: | :---: | :---: |
| Isopentane | P den. | 72 128 | Aston and Shumann(1942), <br> Rossini et al.(1953) <br> Rossini et al.(1953), <br> Silberberg et al.(1959), <br> Douslin et al.(1964) |
| Ethylene | $p$ <br> den. $\mathrm{H}-\mathrm{H}^{\mathrm{O}}$ | 35 41 38 | Tickner and Lossing(1951), <br> Rossini et al.(1953), <br>  <br> Michels et al.(1953), <br> Rossini et al.(1953), <br> Canjar and Manning(1967) <br> Canjar and Manning(1967) |
| Propylene | P den. | 28 61 | Tickner and Lossing(1951), Rossini et al.(1953), <br> Canjar and Manning(1967) <br> Farrington and Sage(1949), <br> Michels et al.(1953), <br> Rossini et al.(1953), <br> Canjar and Manning(1967) |
| Cyclohexane | $p$ <br> den. | 43 26 | Vargaftik(1975), <br> Reid et al(1977), <br> API-44(1978) <br> Vargaftik(1975), <br> Peid et al. (1977), <br> API-44(1978) |
| Benzene | $\begin{aligned} & \mathrm{P} \\ & \text { den. } \end{aligned}$ | $\begin{aligned} & 36 \\ & 60 \end{aligned}$ | Vargaftik(1975) Chan (1978) |
| o-x̆yiene | $\begin{aligned} & \mathbf{F} \\ & \text { den. } \end{aligned}$ | $\begin{aligned} & 44 \\ & 59 \end{aligned}$ | Varga£tik(1975) <br> Vargaftik(1975) |


| Compound | Property | No. of points | Data reference(s) |
| :---: | :---: | :---: | :---: |
| Toluene | P deni. | $\begin{aligned} & 33 \\ & 13 \end{aligned}$ | Vargaftic (1975) Vargaftic (1975) |
| Dichlorodifluoro methane | p den. $\mathrm{H}-\mathrm{H}^{\mathrm{O}}$ | $\begin{array}{r} 40 \\ 189 \\ 40 \end{array}$ | ASHRAE (1969) ASHRAE (1969) ASHRAE (1969) |
| Argon | P den. | 64 1423 | Clark et al.(1951) <br> Michels ot 21 (1959) <br> Michels and Wijker (1949), <br> Michels et al.(1958), <br> Van Itterbeek et al.(1960), <br> Van Itterbeek et al.(1963), <br> Van Itterbeek et al.(1964), <br> Street and Staveley (1968), <br> Van Witzenburgh et al.(1968). <br> Crawford and Daniels (1969), <br> Goldman and Scrase (1969), <br> Terry et al.(1969) |

Table 3.2
Multipolar and associating compounds data sources.

| Compound | Property | No. OE points | Data reference(s) |
| :---: | :---: | :---: | :---: |
| Nitrogen | P <br> den. $\mathrm{H}-\mathrm{H}^{\mathrm{O}}$ | $\begin{aligned} & 17 \\ & 41 \\ & 87 \end{aligned}$ | Friedman, A.S.(1950) <br> Canjar and Manning(1967) <br> Streett and Staveley(1968) <br> Mage et al. (1963) |
| Hydrogen | p den. | $\begin{array}{r} 24 \\ 180 \end{array}$ | Vargaftik(1975) <br> Vargaftik(1975) |
| Carbon Dioxide |  | $\begin{aligned} & 18 \\ & 41 \\ & 39 \end{aligned}$ | ```Canjar and Manning(1967) Din (1961) Din (1961)``` |
| Sulfur Dioxide | $\begin{aligned} & \mathbf{P} \\ & \text { den. } \end{aligned}$ | $\begin{aligned} & 20 \\ & 309 \end{aligned}$ | Kang et al.(1961) <br> Kang et al.(1961) |
| Hydrogen Sulfide | P | 24 | West (1948), |
|  | den. | 41 | Kay and Rambosek (1953) <br> Reamer and Sage(1950), <br> Lewis and Fredericks(1968) |
| Hydrogen Chloride | P | 14 | Frank et al.(1962), Thomas(1962) |
|  | den. | 150 | Frank et al.(1962), <br> Thomas(1962) |
| Methyl Fluoride | $P$ <br> den. | $\begin{array}{r} 28 \\ 107 \end{array}$ | ASHRAE (1969) <br> ASHRAE (1969) |
| Difluoro- | $p$ | 16 | ASHRAE (1969) |
| monochloro methane | den. | 17 | ASHRAE (1969) |
| Dichloromonofluoro methane | $\begin{aligned} & \mathrm{p} \\ & \text { den. } \end{aligned}$ | $\begin{array}{r} 51 \\ 300 \end{array}$ | ASHRAE (1969) <br> ASHRAE (1969) |



Table 3.2 (continued)

| Compound | Property | No. of points | Data reference(s) |
| :---: | :---: | :---: | :---: |
| Phenol | P den. | $\begin{array}{r} 15 \\ 15 \end{array}$ | Kudchadker et al.(1977) <br> Kudchadker et al.(1977) |
| 2;A-Xylenol | p <br> denl. | $\begin{array}{r} 32 \\ 5 \end{array}$ | Kudchadker et al.(1978) Kudchadker $\cong$ t al.(1978) |
| Water | P | 66 | Obsorne et al.(1939) |
|  | density | 385 | Keyes and Smith(1934), Keyes et al.(1936), Obsorne et al.(1939), Kennedy(1957), Holser and Kennedy(1958), Kell and Whalley(1965), Keenan et al.(1969) |
|  | $\mathrm{H}-\mathrm{H}^{\circ}$ | 256 | Callendar and Egerton(1960), Keenan et al.(1969) |
| * $\mathrm{P}=$ vapor pressure, den. = density, |  |  |  |
| denl. = liquid density, denv. = vapor density, |  |  |  |

adjusied until the equality of the vapor phase fugacity and liguid phase fugacity is obtained. This final obtained pressure is the desired vapor pressure.

The characterization parameters for the compounds tested are not measurable properties and are therefore determined from reduction of experimental vapor pressure. enthalpy departure, and density data whenever available. The inclusion of more than one property in the test of the applicability of the equation of state is important because in order for the generalized equation to be used effectively in process design, it must be capable of predicting accurate vapor pressures, densities, and other derived properties for process-strean fiuias the temperature dependence of the equation can be critically tested with the use of enthalpy data because the entahlpy expression, equation (11), sentasns the temperature derivative of the compressibility factor, Z. Furthermore, if only one property, e.g. density, is used in determining the parameters, an excellent fit could be obtained but the resulting paramaters might have one or two disadvantages. The first one is when these parameters are applied to another property, e.g. vapor pressure, the equation prediction accuracy might be
drastically deteriorated. This is because the effect of the value of each parameter on a given property is not the same as on another. The second drawback is that the values obtained might not be systematic with values obtained for another compound of the same class and hence, the generalization of the equation of state becomes ever: tougher. These phenomena were notably observed during the development of the equation. A discussion on the values of the characterization parameters and their effect on the accuracy of the thermodynamic property predicions is presented in chapter IV.

APPLICATION OF THE EQUATION OF STATE TO NORMAL PARAFFINS:

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

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

| Compound | $\begin{gathered} E / k \\ \text { Heg. } \mathrm{R} \end{gathered}$ | cu.ft./lbuole | 0 | $k$ |
| :---: | :---: | :---: | :---: | :---: |
| Methane | 270.804 | 0.25905 | 1.03331 | 0.0 |
| Etrane | 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 | 534.300 | 0.60388 | 2.05819 | 0.0 |
| n-hexane | 556.517 | 0.69323 | 2.30282 | 0.0 |
| n-Hepiane | 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-\%\%ptadecane | 860.173 | 1.67600 | 4.87238 | 0̀.00 |
| n-Octadecane | 664.333 | 1.76534 | 5.09688 | 0.0 |
| n-Nonadecane | 665.679 | 1.85469 | 5.37682 | 0.0 |
| n-Elcosane | 666.379 | 1.94403 | 5.68279 | 0.0 |

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

| Compound | $\begin{gathered} \varepsilon / k \\ \operatorname{Deg} \cdot R \end{gathered}$ | $\begin{gathered} V^{*} \\ \text { cu. รั./1bmole } \end{gathered}$ | 昭 | ${ }^{+}$ |
| :---: | :---: | :---: | :---: | :---: |
| Isobutane | 486.253 | 0.526474 | 1.75444 | 0.0 |
| Isopentane | 533.891 | 0.813340 | 1.93374 | 0.0 |
| Ethylene | 368.844 | 0.290322 | 1.35634 | 0.0 |
| Propylene | 448.552 | 0.385617 | 1.60734 | 0.0 |
| Cyciohexane | 642.239 | 0.611280 | 1.91294 | 0.0 |
| Benzene | 669.312 | 0.506596 | 1.82792 | 0.0 |
| o-Xylene | 690.512 | 0.698227 | 2.31868 | 0.0 |
| Toluene | 658.809 | 0.610572 | 2.16520 | 0.0 |
| Dichlorodifluoromethane | 459.703 | 0.441159 | 1.75124 | 0.0 |
| Hydrogen | 56.0699 | 0.129691 | 1.01372 | $-7.3172$ |
| Argon | 215.634 | 0.199450 | 1.00000 | 0.0 |
| Nitrogen | 168.969 | 0.210863 | 1.22598 | 0.0 |
| Carbon Diokide | 358.899 | 0.209042 | 1.36653 | 930.242 |
| Sulfur Dioxide | 499.896 | 0.248729 | 1.77884 | 737.352 |
| Hyarogen Sulfide | 496.486 | 0.254407 | 1.02500 | 1590.420 |
| Hydrogen Chloride | 426.049 | 0.226240 | 1.01000 | 1421.630 |
| Methyl Fluoride | 351.61 | 0.292249 | 1.66552 | 720.803 |
| Difiuoro-moño chloromethane | 451.387 | 0. 376581 | 1.27521 | 4534.430 |
| ${ }^{\text {i }}$ in units of ( OR ft./lbmole) ${ }^{2}$ |  |  |  |  |


| Table 3.3, 〈continued) |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
| Compound | $\varepsilon / k$ Deg. $R$ | $\text { cu. ft. } / 1 \text { bmole }$ | 0 | $\underset{\sim}{0}+$ |
| Dichloro-mono Eluoromethane | 529.761 | 0.392497 | 1.85043 | 168.985 |
|  | 505.499 |  | 9.754i0 | 2877.160 |
| Dimethylether | 480.569 | 0.402000 | 1.33792 | 5113.510 |
| Diethylether | 523.728 | 0.546213 | 2.09362 | 1369:090 |
| Acetone | 599.138 | 0.448461 | 1.62079 | 8145.340 |
| Ammonia | 492.043 | 0.153614 | 1.65667 | 257.410 |
| Aniline | 767.357 | 0.549676 | 2.05710 | 14413.400 |
| Methanol | 525.791 | 0.267275 | 2.11110 | 4235.920 |
| Ethanol | 476.325 | 0.333049 | 2.15532 | 10992.000 |
| Propanol | 506.038 | 0.404247 | 2.47944 | 12032.800 |
| Phenol | 703.892 | 0.520417 | 2.32465 | 16426.500 |
| 2,4-xylenol | 739.692 | 0.805834 | 1.77258 | 96141.70 |
| Water | 789.390 | 0.108835 | 1.83760 | 185.84 |
| ${ }^{+}$in units of $\left({ }^{\circ} \mathrm{R} \mathrm{ft}{ }^{3} / \mathrm{I}\right.$ Ibmole) ${ }^{2}$ |  |  |  |  |

Table 3.4
Prediction of thermodynamic properties for noromal paraffins.

| Fluid Pr | Prop. | No. of Data Points | Temperature <br> Range; ${ }^{\circ} \mathrm{R}$ | Pressure <br> Range: <br> Psia | $\frac{\text { A.A.D. }}{\text { Eq. (9) }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Methane | P | 128 | 163.5-342.0 | 1.774-655.7 | 0.41 |
|  | den. | 40 | 206.2-1122. | 129.7-506.5 | 0.54 |
|  | $\mathrm{H}-\mathrm{H}^{\circ}$ | 38 | 209.7-509.7 | 450.0-2000. | 0.51 |
| Ethane | P | 46 | 249.7-549.7 | 0.489-709.80 | 0.65 |
|  | den. | 43 | 219.7-769.7 | 14.70-9000.0 | 1.98 |
|  | ${\mathrm{H}-\mathrm{H}^{\circ} \mathrm{O}}^{\text {d }}$ | 98 | 299.7-769.7 | 200.0-3000.0 | 1.65 |
| Propane | P | 59 | 211.4-665.9 | 0.0002-617.5 | 1.09 |
|  | den* | 145 | 536.7-806.7 | 147.6-5372.8 | 1.78 |
|  | den** | 70 | 162.0-1080. | 15.24-10624. | 1.44 |
|  | den. | 41 | 209.7-986.7 | 14.70-3910.0 | 1.55 |
|  | $\mathrm{H}-\mathrm{H}^{\text {O }}$ | 39 | 209.7-709.7 | 500.0-2000.0 | 0.97 |
| n-Butane | P | 38 | 364.7-765.3 | . 3420-550.70 | 0.89 |
|  | den: | 40 | 259.7-889.7 | 14.70-7000.0 | 1.32 |
|  | $\mathrm{H}-\mathrm{H}^{\mathrm{O}}$ | 39 | 559.7-889.7 | 200.0-5000.0 | 0.74 |
| n-Pentane | P | 50 | 323.3-845.6 | .00299-489.5 | 1.38 |
|  | den: | 41 | 259.7-919.7 | 14.700-10000. | 1.98 |
|  | $\mathrm{H}-\mathrm{H}^{\circ}$ | 39 | 559.7-919.7 | 200.00-10000. | 1.60 |
| n-Hexane | P | 53 | 395.8-914.2 | 0.0200-439.7 | 1.01 |
|  | den. | 41 | 319.7-799.7 | 14.700-3977. | 2.14 |
| n-Heptane | P | 44 | 346.9-956.9 | .00014-350.0 | 1.97 |
|  | den. | 41 | 369.7-919.7 | 14.700-3082. | 1.61 |
|  | $\mathrm{H}-\mathrm{H}^{\circ}$ | 17 | 971.9-1156. | 78.800-2363. | 0.89 |
| n-Octane | $p$ | 64 | 389.9-1020. | . 00033-350.0 | 1.72 |
|  | den. | 54 | 389.7-969.7 | 14.700-239.0 | 2.58 |
|  | $\mathrm{H}-\mathrm{H}^{\circ}$ | 62 | 534.7-1060. | 200.00-1400. | 1.38 |

\# Thomas and Harrison Experimencal Data (1982).
** Generated Goodwin Data (1977).

Table 3.4 (continued)

| Fluid Er | Erop. | \$0. Of Data Points | Temperature Range, ${ }^{\circ}$ ? | Pressure Range, Psia | A.A.D. \% <br> Eg. (9) |
| :---: | :---: | :---: | :---: | :---: | :---: |
| n-Monane | P den. | $\begin{aligned} & 21 \\ & 75 \end{aligned}$ | $\begin{aligned} & 426.3-814.7 \\ & 455.7-1032 . \end{aligned}$ | $\begin{aligned} & .00048-29.65 \\ & .00226-72518 . \end{aligned}$ | $\begin{aligned} & 1.66 \\ & 2.89 \end{aligned}$ |
| n-Decane | $\mathbf{P}$ <br> den. | $\begin{array}{r} 24 \\ . \quad 32 \end{array}$ | $\begin{aligned} & 432.3-859.7 \\ & 559.7-919.7 \end{aligned}$ | $\begin{aligned} & .00022-30.00 \\ & 200.00-6000 . \end{aligned}$ | $\begin{aligned} & 2.05 \\ & 1.60 \end{aligned}$ |
| n-Undecane | $p$ | 19 | 624.7-899.7 | 0.182-29.600 | 0.55 |
| n-Dodecane | $p$ <br> den. | $\begin{aligned} & 22 \\ & 17 \end{aligned}$ | $\begin{aligned} & 581.7-1187 . \\ & 581.7-869.7 \end{aligned}$ | $\begin{aligned} & 0.016-363.52 \\ & 0.016-12.626 \end{aligned}$ | $\begin{aligned} & 3.24 \\ & 1.04 \end{aligned}$ |
| n-Tridecane | P <br> den. | $\begin{aligned} & 19 \\ & 17 \end{aligned}$ | $\begin{aligned} & 617.7-1219 . \\ & 617.7-905.7 \end{aligned}$ | $\begin{aligned} & 0.0242-249.5 \\ & 0.0242-12.93 \end{aligned}$ | $\begin{aligned} & 2.36 \\ & 0.93 \end{aligned}$ |
| n-Tetradecane | e $p$ den. | $\begin{array}{r} 16 \\ . \quad 14 \end{array}$ | $\begin{aligned} & 707.7-1251 . \\ & 707.7-941.7 \end{aligned}$ | $\begin{aligned} & 0.180-235.00 \\ & 0.180-13.540 \end{aligned}$ | $\begin{aligned} & 2.42 \\ & 0.78 \end{aligned}$ |
| n-Pentadecane | $\begin{aligned} & \mathrm{P} \\ & \mathrm{den} . \end{aligned}$ | $\begin{array}{r} 14 \\ . \quad 14 \end{array}$ | $\begin{aligned} & 743.7-995.7 \\ & 743.7-977.7 \end{aligned}$ | $\begin{aligned} & 0.2384-17.91 \\ & 0.2384-14.44 \end{aligned}$ | $\begin{aligned} & 0.59 \\ & 1.03 \end{aligned}$ |
| n-Hexadecane | $P$ <br> den. | $\begin{array}{r} 10 \\ \cdot \quad 9 \end{array}$ | $\begin{aligned} & 833.7-995.7 \\ & 833.7-977.7 \end{aligned}$ | $\begin{aligned} & 1.003-12.659 \\ & 1.003-10.094 \end{aligned}$ | $\begin{aligned} & 0.81 \\ & 1.31 \end{aligned}$ |
| n-Heptadecane | $\text { e } \begin{aligned} & P \\ & \text { den. } \end{aligned}$ | $\begin{array}{r} 16 \\ \cdot \quad 13 \end{array}$ | $\begin{aligned} & 779.7-1050 . \\ & 779.7-995.7 \end{aligned}$ | $\begin{aligned} & 0.181-17.106 \\ & 0.181-8.8910 \end{aligned}$ | $\begin{aligned} & 0.73 \\ & 1.03 \end{aligned}$ |
| n-Ôç̇ãecane | $\bar{F}$ <br> Cen. | $\begin{array}{r} 15 \\ . \quad 13 \end{array}$ | $\begin{aligned} & 815.7-1068 . \\ & 815.7-1032 . \end{aligned}$ | $\begin{aligned} & 0.254-15.458 \\ & 0.254-10.090 \end{aligned}$ | $\begin{aligned} & 0.77 \\ & 1.13 \end{aligned}$ |
| n-Nonadecane | P <br> den. | $\begin{array}{r} 16 \\ . \quad 12 \end{array}$ | $\begin{aligned} & 833.7-1104 . \\ & 833.7-1032 . \end{aligned}$ | $\begin{aligned} & 0.236-17.332 \\ & 0.2357-7.367 \end{aligned}$ | $\begin{aligned} & 0.79 \\ & 1.55 \end{aligned}$ |
| n-Eicosane | $\begin{aligned} & \mathrm{g} \\ & \text { den. } \end{aligned}$ | $\begin{array}{r} 17 \\ .48 \end{array}$ | $\begin{aligned} & 851.7-1395 . \\ & 671.7-1032 . \end{aligned}$ | $\begin{aligned} & 0.222-161.57 \\ & 725.2-72518 . \end{aligned}$ | $\begin{aligned} & 2.96 \\ & 4.08 \end{aligned}$ |

** $\mathrm{P}=\mathrm{vapor}$ pressure, den. =density, $\mathrm{H}-\mathrm{H}^{\circ}=$ enthalpy departure, Btu/lb.
points were calculated using the parameters obtained from the other experimental data. The generated data from Goodwin equation of state for propane was also tested to see how good the equation is when the data inciudes higher ranges of temperatures and pressures than thóse used for determining the characterization parameters. For the twenty compounds applied (methane to normal eicosane), the average absolute relative deviation (AARD\%) for vapor pressure and density predictions are 1.23 ; and 1.58 \% respectively. For enthalpy departure the average absolute difference is 1.24 Btu/lb.

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

For an equation of state to achieve widespread use in research and industry its ability so predict the thermodynamic properties of a wide range of gluids is essential. A number of compounds representing different classes of fluids not used in the determination of the equation of state constants were applied. Branch-chain hydrocarbons, unsaturated hydrocarbons, ring compounds. halogenated hydrocarbons, and nonhydrocarbon fluias were
tested. Table 3.3 gives the values of the parameters for each fluid used and Table 3.5 gives the results of the tests along with the number of data points and temperature and pressure ranges. The $\bar{A} \hat{R} N \mathrm{~N} \%$ for vapor pressure and density for aỉ tweive fiuids are i.û For enthalpy departure, the auerage absolute difference is 0.49 Btu/lb. From these results, it can be seen that the new equation performs quite well for fluids not used in the generalization. A typical point by point calculation for enthalpy departure for dichloro-difluoro methane is presented in Table A. 1

Table 3.5
Prediction of thermodynamic properties for nonpolar compounds．

| Fluid F | Prop． | No．of Uata Points | Temperature Range，${ }^{\circ} \mathrm{R}$ | Pressure Range． Psia | $\frac{\text { A.A.D. } \%}{\text { Eq. (O) }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Isobutane | p | 64 | 334．7－734． | 0．183－526．6 | 0.72 |
|  | $\mathrm{H}-\mathrm{H}^{\mathrm{O}}$ | 24 | 559．7－939．7 | 250．0－3000． | 0.95 |
|  | den． | 321 | 349．7－1032． | 14．70－5000． | 1.53 |
| Isopentane | $F$ | 72 | 314．05－829． | ．0036－490．4 | 0.99 |
|  | den． | 128 | 400．16－852． | ．3034－2674． | 1.81 |
| Ethylene | P | 35 | 239．67－510． | 0．885－742．1 | 0.63 |
|  | $\mathrm{H}-\mathrm{H}^{\circ}$ | 38 | 339．67－720． | 100．0－2000． | 0.75 |
|  | den． | 41 | 209．67－720． | 14．69－2000． | 0.99 |
| Propylene | P | 28 | 264．47－657． | 0．039－670．3 | 1.37 |
|  | den． | 61 | 409．68－910． | 16．19－2939． | 1.36 |
| Cyclo－ Hexane | P | 43 | 509．7－930． | 0．918－371．0 | 0.56 |
|  | den． | 26 | 519．7－960． | 1．212－461．9 | 1.60 |
| Benzene | P | 36 | 504．7－996． | 0．760－636．9 | 1.23 |
|  | den． | 60 | 923．7－1104． | 375．3－867．4 | 1.59 |
| O－Xylene | P | 41 | 473．7－1137． | 0．011－552．3 | 0.56 |
|  | den． | 59 | 536．7－986．7 | 14．50－5800． | 1.13 |
| Toluene | P | 33 | 491．7－1060． | 0．130－547．4 | 1.73 |
|  | den． | 13 | 491．7－689．7 | 0．130－547．4 | 0.91 |
| Dichloro－ diflugro meどゥane | P | 40 | 307．7－689．7 | 0．140－577．0 | 0.58 |
|  | H－4\％ | 40 | 307．7－689．7 | 0．140－577．0 | 0.31 |
|  | den． | 189 | 307．7－919．7 | 0．140－440．0 | 1.03 |
| Argon | P | 64 | 150．8－271．4 | 9．863－709．3 | 0.20 |
|  | den． | 1423 | 154．1－761．9 | 12．04－93723． | 0.26 |

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

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

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

| Fluid | Prop. | No. of Data Points | Temperature Range, ${ }^{\circ} R$ | pressure Range, Psia | A. A.D. \% --------- <br> Eq : (9) |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Nitrogen | $F$ <br> $\mathrm{H}-\mathrm{H}^{\mathrm{O}}$ <br> den. | $\begin{aligned} & 17 \\ & 87 \\ & 41 \end{aligned}$ |  | $\begin{aligned} & 29.06-454.41 \\ & 200.0-2500.0 \\ & 14.69-8936.4 \end{aligned}$ | $\begin{aligned} & 0.60 \\ & 0.34 \\ & 0.30 \end{aligned}$ |
| Hydrogen | $\begin{aligned} & \mathrm{p} \\ & \text { den. } \end{aligned}$ | $\begin{array}{r} 24 \\ 180 \end{array}$ | $\begin{array}{r} 25.2-59.84 \\ 720.0-1440 \end{array}$ | $\begin{aligned} & 1.081-190.9 \\ & 14.50-3626 . \end{aligned}$ | $\begin{aligned} & 5.20 \\ & 0.44 \end{aligned}$ |
| Carbon Dioxide | $\mathrm{P}$ $\mathrm{H}-\mathrm{H}^{0}$ <br> den. | $\begin{aligned} & 18 \\ & 39 \\ & 41 \end{aligned}$ |  | 75.15-1070. 441.0-4410. 220.5-4410. | $\begin{aligned} & 0.43 \\ & 1.72 \\ & 0.67 \end{aligned}$ |

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

| Fluid Pr | Prop. | No. of Data points | Temperature <br> Range, ${ }^{\circ} \mathrm{K}$ | Pressure <br> Range, <br> Psia | $\frac{\text { A.A.D. \% }}{\text { Eq. (S) }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Sulfur- | P | 20 | 581.7-775.2 | 124.7-1143.7 | 0.29 |
| Dioxide | den. | 309 | 509.7-941.7 | 7.35-4630.5 | 0.83 |
| Hydrogen- | p | 24 | 383.27-672.4 | 14.6s-i306. | ¢. 6.6 |
| Sulfide | den. | 41 | 499.67-799.7 | 100.0-2000.0 | 0.46 |
| Hydrogen- | P | 14 | 491.7-581.7 | 378.3-1163.9 | 0.22 |
| Chloride | den. | 157 | 491.67-1212. | 370.0-29554. | 3.67 |
| Methyl- | P | 28 | 269.7-538.3 | 0.620-701.4 | 1.74 |
| Fluoride | den. | 107 | 269.7-899.7 | 0.620-400.0 | 0.58 |
| Difluoro- | P | 16 | 455.7-664.7 | 35.62-723.2 | 0.69 |
| monochloro methane | den. | 17 | 319.7-859.7 | 0.450-497.3 | 3.84 |
| Dichloro- | P | 51 | 383.7-812.5 | $0.367-812.5$ | 0.51 |
| monofluoro methane | den. | 300 | 491.7-851.7 | 14.50-2901. | 0.57 |
| Methyl- | P | 18 | 505.0-788.0 | 14.70-638.0 | 1.28 |
| ethyl-ether | r den. | 35 | 505.0-788.0 | 14.70-638.0 | 7.82 |
| Dimethyl- | P | 19 | 449.0-720.0 | 14.70-764.0 | 0.53 |
| ether | den. | 37 | 449.0-720.0 | 14.70-764.0 | 4.82 |
| Diethyl- | P | 26 | 474.0-841.0 | 2.170-523.0 | 0.43 |
| echer | den. | 46 | 492.0-841.0 | 3.580-523.0 | 3.82 |
| Acetone | P | 30 | 506.0-915.0 | 1.930-691.0 | 1.80 |
|  | den. | 48 | 492.0-915.0 | 14.70-691.0 | 7.56 |

Table 3.7, (continued)

| Fluid P | Prop. | No. of Data points | Temperature Range, ${ }^{\circ}$ R | Pressure Range. Psia | A.A.D. \% $\qquad$ <br> This Work |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Ammonia | $\begin{aligned} & \mathrm{P} \\ & \text { den. } \end{aligned}$ | $\begin{aligned} & 172 \\ & 307 \end{aligned}$ | $\begin{aligned} & 398.6-726.5 \\ & 429.0=1077 . \end{aligned}$ | $\begin{aligned} & 5.350-1592.0 \\ & i 2.7 i-i i \Delta i ́ n . \end{aligned}$ | $\begin{aligned} & 0.86 \\ & 2.93 \end{aligned}$ |
| Aniline | P den. | $\begin{aligned} & 45 \\ & 35 \end{aligned}$ | $\begin{aligned} & 491.7-1259 . \\ & 491.7-1248 . \end{aligned}$ | $\begin{aligned} & 0.0014-770.15 \\ & 0.0014-725.19 \end{aligned}$ | $\begin{aligned} & 3.33 \\ & 3.30 \end{aligned}$ |
| Methanol | P den. | $\begin{array}{r} 33 \\ 232 \end{array}$ | $\begin{aligned} & 473.7-922.8 \\ & 491.7-923.7 \end{aligned}$ | $\begin{aligned} & 0.299-1143.7 \\ & 0.572-1135.9 \end{aligned}$ | $\begin{aligned} & 7.00 \\ & 4.48 \end{aligned}$ |
| Ethanol | p den. | $\begin{array}{r} 42 \\ 289 \end{array}$ | 527.0-925.1 <br> 491.7-1122. | $\begin{aligned} & 0.831-891.7 \\ & 0.237-10000 . \end{aligned}$ | $\begin{aligned} & 5.16 \\ & 3.84 \end{aligned}$ |
| Propanol | $\begin{aligned} & \mathrm{p} \\ & \text { den. } \end{aligned}$ | $\begin{aligned} & 54 \\ & 38 \end{aligned}$ | $\begin{aligned} & 526.4-966.1 \\ & 635.7-959.7 \end{aligned}$ | $\begin{aligned} & 0.284-749.8 \\ & 7.27-698.12 \end{aligned}$ | $\begin{aligned} & 3.86 \\ & 2.49 \end{aligned}$ |
| Phenol | $\begin{aligned} & \mathrm{p} \\ & \text { den. } \end{aligned}$ | $\begin{aligned} & 15 \\ & 15 \end{aligned}$ | $\begin{aligned} & 581.7-1248 . \\ & 581.7-1248 . \end{aligned}$ | $\begin{aligned} & 0.047-884.5 \\ & 0.047-884.5 \end{aligned}$ | $\begin{aligned} & 3.24 \\ & 2.19 \end{aligned}$ |
| 2,4-Xylenol | $1 \mathrm{P}$ <br> den. | $\begin{array}{r} 32 \\ 5 \end{array}$ | $\begin{aligned} & 545.7-1266 . \\ & 545.7-617.7 \end{aligned}$ | $\begin{aligned} & 0.020-594.5 \\ & 0.020-0.051 \end{aligned}$ | $\begin{aligned} & 5.11 \\ & 0.81 \end{aligned}$ |
| Water | $\begin{aligned} & \mathrm{g} \\ & \mathrm{H}-\mathrm{H}^{0} \\ & \text { den. } \end{aligned}$ | $\begin{array}{r} 66 \\ 256 \\ 385 \end{array}$ | 492.0-1160. <br> 510.0-2860 <br> 492.0-2860. | $\begin{aligned} & 0.089-3090 . \\ & 0.666-15721 . \\ & 0.089-205305 . \end{aligned}$ | $\begin{array}{r} 2.70 \\ 10.30 \\ 2.81 \end{array}$ |

** $P=$ vapor pressure, den. $=$ density,
$\mathrm{H}-\mathrm{H}^{0}=$ enthalpy departure, Btu/lb.

SORTE PROPERTIES OF THE PARAMETERS:

Equation (9) requires three parameters, $\mathrm{V}^{*}, \boldsymbol{\alpha}$, and $\epsilon / k$, for each pure nonpolar compound and one more parameter, $k$, for polar compounds. All these parameters are obiained from recuction of experimental data. The values of $\bar{v}$ for normal paraffins are fiyed as a linear function of carbon number, i.e.,

$$
\begin{equation*}
V^{*}=0.157167+0.0893432 \text { (Carbon Number) } \tag{28}
\end{equation*}
$$

This increase with each additional CH2 group, or carbon, is of the same nature as that of the critical volume, Vc, (see Figure 4). Since the equation was to be applied to other classes of compounds, the idea of relating the $V^{*}$ to CH 2 group was changed to relating it with the critical volume. which is a measurable quantity that is a characteristic of each compound. The characteristic volume parameter also increases linearly with the critical volume. The equation for this dinear relation is

$$
\begin{equation*}
v^{*}=0.10537+0.098222(V c) \tag{29}
\end{equation*}
$$

Where Vc is in $f t^{3} / 1$ bmole. Figure 5 is a plot of the characteristic volume versus the critical volume for normal



Fig. 5 : Plot of V* vs. Critical Volume
paraffins and a few other classes of compounds. The molecular volume parameter values are related to the van der Waals close-packing volume, which can be calculated using the group contribution method given by Bondi (1968). Figure 6 shows the relation of $V^{*}$ with the calculated van der Waals volume. Equation 29 can be used as a starting estimate for tine voiume parameter and this reduces the number of parameters for the equation of state by one. To illustrate this further, compounds other than normal paraffins were used and the property prediction is of reasonable accuracy with a very few exceptions. Appendix B lists the values of the parameters used for the compounds tested along with the results of these tests. The structure parameter ( $\alpha$ ) is unity for spherical molecules (e.g. argon) and greater than unity for structural molecules. For normal paraffins, its value increases linearly with carbon number as illustrated by Figure 7. For branch-chain and unsaturated compounds, its value is smaller than that of same carbon number normal paraffins (e.g., ethane lethylene, propane) propylene, nbutane >iso-butane, and n-pentane >iso-pentane). Figure 8 is a plot of $\epsilon / k$ versus critical temperature for normal paraffins and a few nonpolar compounds. A higher critical cemperature gives a nigher energy parameter but the

## VOLUME OF MOLECULE




FIGURE 7

## ENERGY PARAMETER



FIGURE 8
PLOT OF E $/ K$
versus critical temperature
increase is more for ring compounds. All these plots show that these characterization parameters relate somewhat to molecular properties and are not merely random constants.

CHAPTER IV

## DISCUSSION OF RESULTS


#### Abstract

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


Table
4.1

Comparison of thermodynamic property predictions for nonpolar compounds.

| Flusd | Eroperty | No. os Data Points | \% 2.D. \% |  |
| :---: | :---: | :---: | :---: | :---: |
|  |  |  | This Work | Dب¢ |
| Methane | P | 120 | 0.41 | 0.35 |
|  | den. | $4{ }^{\text {¢ }}$ | 0.54 | 1.37 |
|  | $\mathrm{H}-\mathrm{H}^{\circ}$ | 38 | 0.51 | 2.88 |
| Ethane | $p$ | 46 | 0.65 | 0.98 |
|  | den. | 49 | 1.98 | 1.92 |
|  | $\mathrm{H}-\mathrm{H}^{\circ}$ | 98 | 1.65 | 3.77 |
| Propane | 8 | 59 | 1.09 | 3.13 |
|  | aen.* | 145 | 1.78 | 4.76 |
|  | den** | 70 | 1.44 | 2.71 |
|  | den. | 41 | 1.55 | 2.70 |
|  | $\mathrm{H}^{\mathrm{H}}{ }^{\circ}$ | 39 | 0.97 | 3.84 |
| n-Butane | $p$ | 38 | 0.89 | 0.90 |
|  | den. | 40 | 1.32 | 0.97 |
|  | H-H | 39 | 0.74 | 5.39 |
| n-Pentane | P | 50 | 1.38 | 2.65 |
|  | den. | 41 | 1.98 | 3.16 |
|  | H-H ${ }^{\circ}$ | 39 | 1.60 | 6.04 |
| n-Hexane | 8 | 53 | 1.01 | 2.38 |
|  | den. | 41 | 2.14 | 0.76 |
|  | P | $4{ }_{4}$ | 1.97 | 4.99 |
|  | den. | 41 | 1.61 | 1.86 |
|  | $\mathrm{H}-\mathrm{HO}^{\circ}$ | 17 | 0.89 | 3.51 |
| n-octane | $p$ | 64 | 1.72 | 6.18 |
|  | den: | 54 | 2.58 | 2.53 |
|  | $\mathrm{H}-\mathrm{H}^{\circ}$ | 62 | 1.38 | 5.28 |
| n-nonane | P | 29 | 1.65 | 7.64 |
|  | den. | 75 | 3.89 | 1.76 |
| $n-D e c a n e$ | $P$ | 24. | 2.05 | 6.01 |
|  | den. | 32 | 1.60 | 1.30 |
| * Thomes and harrison data (igo2) <br> ${ }^{* *}$ Goodwin generated data (1977) |  |  |  |  |
|  |  |  |  |  |  |  |

Table 4.1, (continued)

| Fluid Pr | Property | No. of Data Points | A.A.D. \% |  |
| :---: | :---: | :---: | :---: | :---: |
|  |  |  | This mork | PHC |
| n-Dodecane | $\underline{F}$ | 22 | 3.24 | 5.10 |
|  | den. | 17 | 1.04 | 1.51 |
| n-Hexadecane | e $P$ | 10 | 0.81 | 4.30 |
|  | den. | 9 | 1.31 | 3.34 |
| n-Eicosane | P | 17 | 2.96 | 2.29 |
|  | den. | 48 | 4.08 | 4.47 |
| Isobutane | P | 64 | 0.72 | 1.54 |
|  | H- $\mathrm{H}^{\mathbf{O}}$ | 24 | 0.95 | 4.26 |
|  | den. | 321 | 1.53 | 4.65 |
| Isopentane | P | 72 | 0.99 | 2.23 |
|  | den. | 128 | 1.81 | 8.53 |
| Ethylene | P | 35 | 0.63 | 1.17 |
|  | $\mathrm{H}-\mathrm{HO}^{\mathrm{O}}$ | 38 | 0.75 | 2.83 |
|  | den. | 41 | 0.99 | 3.19 |
| Propylene | P | 28 | 1.37 | 27.88 |
|  | den. | 61 | 1.36 | 3.52 |
| Cyclohexane | P | 43 | 0.56 | 1.14 |
|  | deñ. | 26 | 1.60 | 1. 5 ¢ |
| Benzerie | P | 36 | 1.23 | 1.73 |
|  | den. | 60 | 1.59 | 12.39 |
| Toluene | P | 33 | 1.73 | 0.46 |
|  | den. | 13 | -0.91. | 1.53 |
| \$1tscosen | \% | 17 | 0.60 | 0.12 |
|  | Fi-nin | 87 | 0. 34 | 1.05 |
|  | den. | 41 | 0.30 | 1.35 |
| 交 $\boldsymbol{B}$ | = vapor | essure, | den. $=$ de | ty, |
|  |  | py dep | ure ; Btu |  |

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

| Fluid | Property | No. of Data poines | A.A.D. \% |  |
| :---: | :---: | :---: | :---: | :---: |
|  |  |  | This Work | PHC |
| Carbon Dioxide | P | 18 | 0.43 | 0.25 |
|  | $\mathrm{H}-\mathrm{H}^{\circ}$ | 39 | 1.72 | 4.45 |
|  | den. | 41 | 0.67 | 2.60 |
| Sulfur- | P | 20 | 0.29 | 1.72 |
| Dioride | den. | 309 | 0.83 | 4.24 |
| HydrogenSulfide | P | 24 | 0.66 | 2.12 |
|  | den. | 41 | 0.46 | 0.43 |
| Ammonia | P | 172 | 0.86 | 1.20 |
|  | den. | 307 | 2.93 | 5.11 |
| Water | P | €6 | 2.83 | 5.97 |
|  | H- ${ }^{\circ}$ | 256 | 10.44 | 17.38 |
|  | den. | 385 | 2.79 | 6.02 |

\#* $P=$ vapor pressure, den. = density,
$H-H^{\circ}=$ entraipy departure, Btu/lb
compounds used in the comparison, although the vapor pressure prediction for methane, ethane, toluene, nitrogen and carbon dioxide are not. However, for these same compounds, the deviation in the density predictions by the new correlation is less than half of that obtained by the PHC equation. Furthermore, equation (9) can be applied to a wider class of compounds such as pherol, acetone, and alcohols. Figure 9 is a plot of calculated vapor pressure compared with observed values for eight polar compounds. The accuracy of equation (9) for vapor pressure prediction will be of benefit for VIE calculations in multicomponent systems. The calculated second virial coefficient from equation (9) for propane is more accurate than popular cubic equations of state, especially in the low temperature region (Figure 10). Figure 11 is a plot of the calculated second virial coefficient compared with the smoothed experimental values (Dymond and Smith,1980) for nine nonpolar compounds. The fit for nitrogen, methane, propene and normal hexane is vexy good for all temperature ranges. For n-butane, npentane, benzene and n-octane, the experimental values of the second virial coefficients are more negative than the caloniated ones in the 100 temperature reyions. The seme observation is noted for polar compounds as illustrated by



FIGURE 10


Figure 11: Calculated and Dbserved Second Virial

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


FIGURE 12
Calculated and observed second virial coefficents


Figure 13 : Plot of the geviation vs density for propane


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

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

## PROPANE PRESSURE-DENSITY DIAGRAM



## CHAPTER V

## CONCLUSIONS AND RECOMMENDATIONS

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

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

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

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

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

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

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

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Appendix A

TABLE A.I : Detailed Calculations of Enthalpy Departure for Dichloro-diflucro methane.

| No. | $\begin{gathered} \text { Experimental } \\ H-H \\ \mathcal{B t u / 1 b .} \end{gathered}$ | $\begin{gathered} \text { Calculated } \\ \text { H-H } \\ \text { Btu/lb. } \end{gathered}$ | Percent Deviation | Temperature Deg. $R$ | $\begin{gathered} \text { Pressure } \\ \text { Psia } \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | -83.446 | -82.820 | -. 74986 | 307.67 | 14000 |
| 2 | -82. 763 | -82. 351 | -. 49752 | 314.67 | . 20000 |
| 3 | -81.806 | -81.644 | -. 19863 | 324.67 | . 33000 |
| $\stackrel{4}{4}$ | -20.869 | -80.900 | . 03887 | 334.67 | .52000 |
| 5 | -79.949 | -80.127 | . 22237 | 344.67 | .79000 |
| 6 | -79.046 | -79.329 | . 35805 | 354.67 | ¢ .1800 |
| 7 | -78.156 | -78.511 | . 45378 | 364.67 | 1.7200 |
| 8 | -77.280 | -77.678 | . 51542 | 374.67 | 2.4400 |
| 9 | -76.413 | -76.833 | . 54978 | 384.67 | 3.3900 |
| 10 | -75.557 | -75.980 | . 55991 | 394.67 | 4.6100 |
| 11 | -74.708 | -75.119 | . 55034 | 404.67 | 6.1900 |
| 12 | -73.867 | -74.254 | . 52351 | 414.67 | 8.1500 |
| 13 | -73,033 | -73.385 | . 48251 | 424.67 | 10.590 |
| 14 | -72.286 | -72.601 | . 43545 | 433.67 | 13.230 |
| 15 | -71.791 | -72.077 | . 39873 | 439.67 | 15.270 |
| 16 | -70.969 | -71.203 | . 33045 | 449.67 | 19.190 |
| 17 | -70.149 | -70.328 | . 25424 | 459.67 | 23.850 |
| 18 | -69.331 | -69.450 | . 17098 | 469.67 | 29.340 |
| 19 | -68.514 | -68.570 | . 08209 | 479.67 | 35.740 |
| 20 | -67.695 | -67.686 | -. 01258 | 489.67 | 43.150 |
| 21 | -66.872 | -66.799 | -. 10861 | 499.67 | 51.670 |
| 22 | -66.044 | -65.906 | -. 20914 | 509.67 | 61.390 |
| 23 | -65.206 | -65.006 | -. 30716 | 519.67 | 72.430 |
| 24 | -64.357 | -64.096 | -. 40522 | 529.67 | 84.890 |
| 25 | -63.491 | -63.175 | -. 49729 | 539.67 | 98.870 |
| 26 | -62.606 | -62.281 | -. 58394 | 543.67 | 114.49 |
| 27 | -61.696 | -61.289 | -. 66015 | 559.67 | 131.86 |
| 28 | -60.755 | -50.315 | -. 72320 | 559.67 | 151.11 |
| 29 | -59.776 | -59.317 | -. 76792 | 579.67 | 172.35 |
| 30 | -58.752 | -58.287 | -. 79112 | 589.67 | 195.71 |
| 31 | -57.671 | -57.219 | -. 78377 | 599.67 | 221.32 |
| 32 | -56.525 | -56.105 | -. 74190 | 609.67 | 249.31 |
| 33 | -55.295 | -54.933 | -. 65439 | 619.67 | 279.82 |
| 34 | -53.964 | -53.688 | -. 51157 | 629.67 | 313.00 |
| 35 | -52.508 | -52.349 | -. 30376 | 639.67 | 349.00 |
| 36 | -50.890 | -50.884 | -. 012773 | 649.67 | 387.98 |
| 37 | -49.057 | -89.241 | . 37527 | 659.67 | 430.69 |
| 38 | -46.512 | -94.324 | . 87707 | 659.67 | 475.52 |
| 39 | -44.2A8 | -8A. 908 | \%.4907 | 679.67 | 524.43 |
| 40 | -40.235 | -40.972 | 1.8327 | 689.67 | 577.03 |
|  | ABS. PERCEND | DIFFEREIGE, | MUMBER 40 |  |  |

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

| No. | Temperature Des. R | Experimental pressiora, Psia | Calculated Fェessure, Psia | Percent Deviacion |
| :---: | :---: | :---: | :---: | :---: |
| 1 | 518.87 | 106.07 | 107.24 | 1.0977 |
| 2 | 527.66 | 124.28 | 125.57 | 1.0371 |
| 3 | 536.62 | 145.32 | 146.64 | 0.9104 |
| 4 | 536.80 | 145.77 | 147.08 | 0.9014 |
| 5 | 545.54 | 168.92 | 170.13 | 0.7108 |
| 6 | 545.66 | 169.19 | 170.46 | 0.7468 |
| 7 | 554.76 | 196.02 | 197.25 | 0.6301 |
| 8 | 554.69 | 195.94 | 197.05 | 0.5661 |
| 9 | 563.52 | 225.04 | 225.93 | 0.3973 |
| 10 | 563.52 | 225.01 | 225.93 | 0.4073 |
| 11 | 553.64 | 225.49 | 225.35 | 0.3778 |
| 12 | 572.51 | 257.81 | 258.43 | 0.2390 |
| 13 | 572.59 | 358.12 | 258.74 | 0.2466 |
| 14 | 572.78 | 258.90 | 259.47 | 0.2216 |
| 15 | 581.72 | 295.12 | 295.22 | 0.0312 |
| 16 | 581.80 | 395.35 | 295.54 | 0.0656 |
| 17 | 581.86 | 295.72 | 295.82 | 0.0353 |
| 18 | 590.66 | 335.05 | 334.54 | -0.1515 |
| 19 | 599.75 | 379.62 | 378.38 | -0.3271 |
| 20 | 599.76 | 379.69 | 378.42 | -0.3338 |
| 21 | 599.76 | 379.76 | 378.42 | -0.3505 |
| 22 | 599.76 | 379.63 | 378.40 | -0.3221 |
| 23 | 599.77 | 379.74 | 378.46 | -0.3353 |
| 24 | 608.76 | 428.11 | 425.84 | -0. 5290 |
| 25 | 608.77 | 428.12 | 425.88 | -0.5228 |
| 26 | 617.68 | 480.39 | 476.90 | -0.7273 |
| 27 | 617.68 | 480.38 | 476.90 | -0.7240 |
| 28 | 398.55 | 5.35 | 5.22 | -2.3448 |
| 29 | 398.84 | 5.39 | 5.27 | -2.1857 |
| -30 | -400.43 | 6.69 | .5.57 | -2.4782 |
| 31 | 400.43 | 5.69 | 5.57 | -2.1524 |
| 32 | 404.43 | 6.48 | 6.37 | -1.7056 |
| 33 | 405.01 | 6.61 | 6.50 | -9.7463 |
| 34 | 405.72 | 6.76 | 6.65 | -1. 6464 |
| 35 | 406.00 | 6.81 | 6.71 | -9.4814 |
| 36 | 405.02 | 7.51 | 7.40 | -9.3925 |
| 37 | 411.44 | 8.10 | 8.00 | -1.2ise |

Table A. 2 (continued)

| N0. | Temperature Deg. R | Experimental pressure, Psia | Calculated Pressure, Psia | Percent Deviation |
| :---: | :---: | :---: | :---: | :---: |
| 38 | 412.03 | 8.24 | 8.15 | -1.0497 |
| 39 | 412.21 | 8.29 | 8.20 | -1.0348 |
| 40 | 412.41 | 8.35 | 8.25 | -1.1725 |
| A1 | 412.45 | 8.36 | 6.27 | -i.1493 |
| 42 | 412.53 | 8.40 | 8.31 | -1.0346 |
| 43 | 413.55 | 8.64 | 8.56 | -0.9779 |
| $4{ }^{4}$ | 415.26 | 9.11 | 9.03 | -0.9414 |
| 45 | 419.22 | 10.26 | 10.20 | -0.6174 |
| 46 | 419.28 | 10.28 | 10.22 | -0.6572 |
| 47 | 419.28 | 10.28 | 10.22 | -0.6572 |
| 48 | 421.74 | 11.06 | 11.00 | -0.5142 |
| 49 | 421.74 | 11.05 | 11.00 | -0.4481 |
| 50 | 421.74 | 11.05 | 11.00 | -0.3977 |
| 51 | 421.74 | 11.06 | 11.00 | -0.5007 |
| 52 | 421.74 | 11.05 | 11.00 | -0.4586 |
| 53 | 421.74 | 11.06 | 11.00 | -0.4695 |
| 54 | 421.74 | 11.05 | 11.00 | -0.4586 |
| 55 | 421.74 | 11.05 | 11.00 | -0.4451 |
| 56 | 421.74 | 11.05 | 11.00 | -0.4586 |
| 57 | 421.75 | 11.06 | 11.00 | -0.4868 |
| 58 | 421.75 | 11.06 | 11.01 | -0.4822 |
| 59 | 421.75 | 11.05 | 11.01 | -0.4287 |
| 60 | 421.75 | 11.06 | 11.01 | -0.4861 |
| 61 | 421.76 | 11.06 | 11.01 | -0.4135 |
| 62 | 423.95 | 11.80 | 11.75 | -0.3831 |
| 63 | 425.50 | 12.33 | 12.30 | -0.2538 |
| 64 | 425.71 | 12.40 | 12.38 | -0.1668 |
| 65 | 425.75 | 12.42 | 12.39 | -0.2498 |
| 66 | 425.80 | 12.45 | 12.41 | -0.2712 |
| 67 | 425.82 | 12.48 | 12.42 | -0.1892 |
| 68 | 427.85 | 13.20 | 13.18 | -0.1580 |
| 69 | 428.87 | 13.59 | 13.57 | -0.1360 |
| 70 | 430.29 | 14.14 | 14.14 | -0.0121 |
| 71 | 430.96 | 14.41 | 14.41 | -0.0009 |
| 72 | 431.61 | 14.67 | 14.67 | 0.0222 |
| 73 | 431.64 | 14.70 | 14.69 | -0.0700 |
| 74 | 431.64 | 14.68 | 14.69 | 0.0509 |
| 75 | 431.65 | 14.70 | 14.69 | -0.0308 |
| 76 | 431.65 | 14.70 | 14.69 | -0.0080 |
| 77 | 431.66 | 14.70 | 14.70 | -0.0230 |
| 78 | 831.67 | 14.70 | 14.70 | 0.0130 |

Table A. 2 (continued)

| No. | Temperature Deg. R | Experimental Pressure, Esia | Calculated Pressure, Psia | Percent Deviation |
| :---: | :---: | :---: | :---: | :---: |
| 79 | 431.74 | 14.73 | 14.73 | 0.0204 |
| 80 | 431.76 | 14.72 | 14.74 | 0.1284 |
| 81 | 431.77 | 14.72 | 14.74 | 0.1438 |
| 82 | 431.80 | 14.74 | 14.75 | 0.0985 |
| 83 | $43 i .62$ | 14.76 | 14.76 | 0.0085 |
| 84 | 431.85 | 14.76 | 14.77 | 0.0890 |
| 85 | 431.87 | 14.76 | 14.78 | 0.1225 |
| 86 | 431.87 | 14.78 | 14.78 | 0.0247 |
| 87 | 431.87 | 14.78 | 14.78 | 0.0190 |
| 88 | 432.08 | 14.87 | 14.87 | 0.0407 |
| 89 | 436.89 | 16.97 | 17.01 | 0.2586 |
| 90 | 437.56 | 17.27 | 17.32 | 0.2950 |
| 91 | 437.63 | 17.32 | 17.36 | 0.2273 |
| 92 | 437.68 | 17.35 | 17.39 | 0.2203 |
| 93 | 437.70 | 17.34 | 17.39 | 0.2693 |
| 94 | 437.86 | 17.42 | 17.47 | 0.3012 |
| -95. | -446.59 | -21.93 | 22.07 | -0.6476 |
| 96 | 446.61 | 21.94 | 22.08 | 0.6124 |
| 97 | 446.63 | 21.97 | 22.09 | 0.5710 |
| 98 | 485.66 | 21.98 | 22.11 | 0.5945 |
| 99 | 446.67 | 21.97 | 22.11 | 0.6260 |
| 100 | 446.69 | 21.99 | 22.12 | 0.6197 |
| 101 | 450.63 | 24.31 | 24.50 | 0.7552 |
| 102 | 450.69 | 24.35 | 24.53 | 0.7434 |
| 103 | 455,67 | 27.58 | 27.82 | 0.8550 |
| 104 | 455.58 | 27.59 | 27.82 | 0.8301 |
| 105 | 455.68 | 27.59 | 27.82 | 0.8657 |
| 106 | 455.68 | 27.58 | 27.83 | 0.9008 |
| 107 | 955.69 | 27.60 | 27.83 | 0.8309 |
| 108 | 464.60 | 34.22 | 34.57 | 1.0132 |
| 109 | 464.64 | 34.24 | 34.60 | 1.0347 |
| 110 | 464.65 | 34.24 | 34.61 | 1.0562 |
| 111 | 454.68 | 34.27 | 34.53 | 1.0408 |
| 112 | 464.68 | 34.28 | 34.63 | 1.0384 |
| 113 | 473.64 | 42.15 | 42.64 | 1.1498 |
| 114 | 473.65 | 42.15 | 42.64 | 1.1694 |
| 115 | 473.66 | 42.18 | 42.66 | 1.1378 |
| 116 | 473.67 | 42.17 | 82.66 | 1.1731 |
| 117 | 473.68 | 42.16 | 42.68 | 1.2246 |
| 118 | 482.57 | 51.32 | 51.98 | 1.2888 |
| 119 | 482.64 | 51.43 | 52.06 | 1.2290 |
| \$20 | 482.65 | 51.43 | 52.07 | 1.2492 |

Table A. 2 (continued)

| $N 0$. | Temperature Deg. R | Experimental Pressure, Psia | Calculated Pressure, Psia | Percent Deviation |
| :---: | :---: | :---: | :---: | :---: |
| 121 | 482.65 | 51.44 | 52.08 | 1.2402 |
| 122 | $482.6{ }^{4}$ | 51.4 ¢â | 52.09 | 1. 2 2997 |
| 123 | 482.67 | 51.47 | 52.10 | 1.2198 |
| 124 | 491.67 | 62.28 | 63.07 | 1.2654 |
| 125 | 491.67 | 62.27 | 63.07 | 1.2823 |
| 126 | 491.67 | 62.28 | 63.07 | 1.2722 |
| 127 | 491.67 | 62.28 | 63.07 | 1.2746 |
| 128 | 491.67 | 62.27 | 63.07 | 1.2844 |
| 129 | 491.67 | 62.29 | 63.07 | 1.2580 |
| 130 | 491.67 | 62.28 | 63.07 | 1.2722 |
| 131 | 491.67 | 62.29 | 63.07 | 1.2580 |
| 132 | 500.71 | 74.86 | 75.80 | 1.2456 |
| 133 | 500.71 | 74.84 | 75.80 | 1.2768 |
| 134 | 500.62 | 74.72 | 75.66 | 1.2604 |
| 135 | 509.65 | 89.16 | 90.24 | 1.2135 |
| 136 | 509.70 | 89.25 | 90.32 | 1.2079 |
| 137 | 509.73 | 89.30 | 90.37 | 1.1932 |
| 138 | 518.67 | 105.64 | 106.84 | 1.1353 |
| 139 | 518.95 | 106.18 | 107.37 | 1.1213 |
| 140 | 527.69 | 124.38 | 125.65 | 1.0157 |
| 141 | 527.69 | 124.38 | 125.66 | 1.0294 |
| 142 | 536.68 | 145.51 | 146.79 | 0.8820 |
| 143 | 536.97 | 146.22 | 147.51 | 0.8796 |
| 144 | 545.65 | 169.22 | 170.45 | 0.7234 |
| 145 | 563.65 | 225.48 | 226.38 | 0.3979 |
| 146 | 581.65 | 295.01 | 294.97 | -0.0137 |
| 147 | 599.65 | 379.38 | 377.87 | -0.3962 |
| 148 | 517.56 | 480.81 | 475.79 | -0.836! |
| 149 | 635.66 | 600.98 | 593.77 | -1.1998 |
| 150 | 653.67 | 742.53 | 730.66 | -1.5978 |
| 151 | 671.67 | 907.90 | 890.20 | -1.9504 |
| 152 | 685.68 | 1099.70 | 1074.70 | -2.2763 |
| 153 | 707.68 | 1322.30 | 1287.80 | -2.6109 |
| 154 | 716.69 | 1446.80 | 1407.00 | -2.7513 |
| 155 | 725.69 | 1581.30 | 1534.80 | -2.9426 |
| 156 | 729.39 | 1638.60 | 1589.20 | -3.0173 |
| 157 | 591.17 | 337.28 | 336.87 | -0.1216 |
| 158 | 600.06 | 381.11 | 379.93 | -0.3113 |
| 159 | 608.98 | 429.23 | 427.06 | -0.5047 |
| 160 | 617.93 | 481.92 | 478.44 | -0.7232 |

Table A. 2 (continued)


| Compound | $\begin{gathered} \varepsilon / k \\ \text { Deg. } R \end{gathered}$ | $\begin{gathered} V^{*}=V^{*}(V C) \\ c u . f t . / l b m o l e \end{gathered}$ | $\alpha$ | K |
| :---: | :---: | :---: | :---: | :---: |
| Isobutane | 487.827 | 0.508950 | 1.75899 | 0.0 |
| Isopentane | 533.225 | 0.587121 | 1.96124 | 0.0 |
| Ethylene | 365.770 | 0.300716 | 1.36677 | 0.0 |
| Propylene | 449.3993 | 0.390422 | 1.59874 | 0.0 |
| Cyclohexane | 635.224 | 0.590205 | 1.97000 | 0.0 |
| Benzene | 660.813 | 0.567860 | 1.80554 | 0.0 |
| o-Xylene | 690.724 | 0.686214 | 2.32408 | 0.0 |
| Toluene | 550.052 | 0.664992 | 2.18779 | 0.0 |
| Dichlorodifluoromethane | 460.874 | 0.447065 | 1.73731 | 0.0 |
| Nitrogen | 174.547 | 0.222960 | 1.12833 | 0.0 |
| Carbon Dioxide | 342.390 | 0.253539 | 1.10786 | 2731.16 |
| Sulfur Dioxide | 502.480 | 0.297582 | 1.59629 | 1554.53 |
| Hydrogen Sulfide | 498.403 | 0.255115 | 1.02176 | 1621.04 |
| Hydrogen Chloride | 429.080 | 0.233079 | 1.01000 | 1359.75 |
| Methyl Fluoride | 359.085 | 0.300735 | 1.47789 | 1253.83 |
| Difluoro-mono chloromethane | 447.737 | 0.368256 | 1.34859 | 3700.73 |
| Dichloro-mono fluorometnane | 528.55A | 0.814657 | 1.77033 | 1075.35 |


| Compound | $\begin{gathered} \varepsilon / k \\ \text { neg. R } \end{gathered}$ | $\begin{gathered} \mathrm{V}^{\star}=\mathrm{V}^{*}(\mathrm{Vc}) \\ \mathrm{cu} . \mathrm{ft} .1 \mathrm{lbmol} \end{gathered}$ | $\alpha$ | K |
| :---: | :---: | :---: | :---: | :---: |
| wethylethylether | 510.922 | 0.453350 | 1.72823 | 2873.48 |
| Dimethylether | 471.145 | 0.385695 | 1.48366 | 3560.59 |
| Diethylecher | 523.436 | 0.546173 | 2.10754 | 1128.67 |
| Acetone | 601.190 | 0.434469 | 1.62078 | 7693.37 |
| Ammonia | 504.662 | 0.219652 | 1.01867 | 3056.58 |
| Aniline | 759.403 | 0.530380 | 2.20407 | 9585.33 |
| Methanol | 553.043 | 0.291294 | 1.70665 | 6508.30 |
| Ethanol | 469.410 | 0.368389 | 1.79799 | 18692.80 |
| Propanol | 517.075 | 0.449419 | 2.04580 | 20721.20 |
| Phenol | 716.179 | 0.513138 | 2.26150 | 15594.20 |
| Water | 782.270 | 0.194110 | 1.62692 | 1277.48 |
| ${ }^{\text {in }}$ units of 1 | R ft . ${ }^{\text {/ }} 1$ | nole) ${ }^{2}$ |  |  |

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

| Fluid | Prop. | No. of La亡a Points | Temperature Range, on | Pressure Range, Psia | $\begin{aligned} & V^{7}=V^{7}(V C) \\ & \text { A.A.D. } \end{aligned}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | p | 64 | 334.7-734.13 | 0.183-526.57 | 1.54 |
| Isobutane | $\mathrm{H}-\mathrm{H}^{\circ}$ | 24 | 559.7-939.67 | 250.0-3000.0 | 1.25 |
|  | den. | 321 | 349.7-1031.7 | 14.70-5000.0 | 2.81 |
| Isopentane | P | 72 | 314.65-828.7 | 0.0036-490.4 | 2.10 |
|  | den. | 128 | 400.16-851.7 | 0.3034-2674. | 4.06 |
|  | P | 35 | 239.67-509.5 | 0.885-742.10 | 0.76 |
| Ethylene | $\mathrm{H}-\mathrm{HO}^{\mathrm{O}}$ | 38 | 339.67-719.7 | 100.0-2000.0 | 1.59 |
|  | den. | 41 | 209.67-719.7 | 14.69-2000.0 | 0.78 |
| Propylene | P | 28 | 254.47-656.9 | 0.039-670.27 | 1.64 |
|  | den. | 61 | 409.68-909.7 | 16.19-2939.2 | 1.49 |
| Cyclo- | P | 43 | 509.7-929.7 | 0.918-371.0 | 1.73 |
| Hexane | den. | 26 | 519.7-959.7 | 1.212-461.9 | 3.31 |
| Benzene | P | 36 | 504.67-995.7 | $0.760-636.93$ | 6.48 |
|  | den. | 60 | 923.67-1104. | 375.31-867.4 | 7.55 |
| o-Xyiene | P | 41 | 473.67-1137. | 0.011-552.30 | 0.82 |
|  | den. | 59 | 536.67-986.7 | 14.50-5800.0 | 1.79 |
| Toluene | P | 33 | 491.7-1049.7 | 0.130-547.40 | 2.26 |
|  | den. | 13 | 491.7-689.67 | 0.130-547.40 | 8.73 |
| Dichlorodifluoro methane | $p$ | 40 | 307.67-689.7 | 0.140-577.03 | 0.97 |
|  | $\mathrm{H}-\mathrm{H}^{\circ}$ | 40 | 307.67-689.7 | 0.140-577.03 | 0.36 |
|  | den. | 189 | 307.67-919.7 | 0.140-440.00 | 1.18 |
| Nitrogen | F | 17 | 150.6-224.2 | 29.06-454.41 | 1.59 |
|  | $\mathrm{H}-\mathrm{H}^{\text {+ }}$ | 87 | 159.7-509.7 | 200.0-2500.0 | 0.67 |
|  | den. | 41 | 139.3-699.7 | 14.69-8936.4 | 0.39 |

nぇ $P=$ vapor pressure, den $=$ density,
$H-H^{\circ}=$ enthalpy departure, Btu/lb

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

| Fluid | Prop. | No. of Data Points | Temperature <br> Range, ${ }^{\circ} \mathrm{R}$ | gressure <br> Range, <br> Psia | $V^{*}=V^{*}(\mathrm{VC})$ A.A.D. |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Carbon | P | 18 | 389.8-547.7 | 75.15-1070.0 | 1.14 |
| Dioxide | $\mathrm{H}-\mathrm{H}^{\circ}$ | 39 | 437.7-743.7 | 441.0-4410.0 | 1.87 |
|  | den. | 41 | 437.7-743.7 | 220.5-4410.0 | 5.28 |
| Sulfur- | $p$ | 20 | 581.7-775.2 | 124.7-1143.7 | 2.03 |
| Dioxide | den. | 309 | 509.7-941.7 | 7.35-4630.5 | 4.92 |
| HydrogenSulfide | P | 24 | 383.27-672.4 | 14.69-1306.0 | 0.65 |
|  | den. | 41 | 499.67-799.7 | 100.0-2000.0 | 0.47 |
| HydrogenChloride | P | 14 | 491.7-581.7 | 378.3-1163.9 | 0.21 |
|  | den. | 157 | 491.67-1212. | 370.0-29554. | 5.04 |
| MethylFluoride | P | 28 | 269.7-538.3 | 0.620-701.4 | 2.24 |
|  | den. | 107 | 269.7-899.7 | $0.620-400.0$ | 0.67 |
| Difluoromonochloro methane | $P$ | 16 | 455.7-664.7 | 35.62-723.2 | 0.41 |
|  | den. | 17 | 319.7-859.7 | 0.450-497.3 | 3.98 |
| Dichloromonofluoro methane | P | 51 | 383.7-812.5 | 0.367-812.5 | 0.56 |
|  | den. | 300 | 491.7-851.7 | 14.50-2901. | 3.02 |
| Methyl-ethyl-ather | P | 18 | 505.0-788.0 | 14.70-638.0 | 1.75 |
|  | den. | 35 | 505.0-788.0 | 14.70-538.0 | 7.40 |
| Dimethylether | $P$ | 19 | 449.0-720.0 | 14.70-764.0 | 0.63 |
|  | den. | 37 | 449.0-720.0 | 14.70-764.0 | 4.80 |
| Diethylether | $p$ | 26 | 474.0-841.0 | $2.170 \cdots 523.0$ | 0.43 |
|  | den. | 46 | 482.0-841.0 | 3.580-523.0 | 3.82 |
| Acetone | P | 30 | 506.0-915.0 | 1.930-691.0 | 1.76 |
|  | den. | 48 | 492.0-915.0 | 14.70-591.0 | 7.84 |

Table B.3, (continued)

| Fluid | Prop. | No. Of Data Points | Temperature Range, ${ }^{\circ}$ R | Pressure $\quad$ V Range, Psia | $\begin{aligned} & V^{*}=V^{*}(V C) \\ & \text { A.A.D. } \% \end{aligned}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Ammonia | P den. | $\begin{aligned} & 172 \\ & 307 \end{aligned}$ | $\begin{aligned} & 398.6-726.5 \\ & 428.0-1077.0 \end{aligned}$ | $\begin{aligned} & 5.350-1592.0 \\ & 12.71-11816 . \end{aligned}$ | $\begin{aligned} & 2.25 \\ & 6.25 \end{aligned}$ |
| Anjline | P <br> den. | $\begin{aligned} & 45 \\ & 35 \end{aligned}$ | $\begin{aligned} & 491.7-1258.5 \\ & 491.7-1247.7 \end{aligned}$ | $\begin{aligned} & 0.0014-770.15 \\ & 0.0014-725.19 \end{aligned}$ | $\begin{array}{ll} 5 & 2.94 \\ 9 & 4.63 \end{array}$ |
| Methanol | P den. | $\begin{array}{r} 33 \\ 232 \end{array}$ | $\begin{aligned} & 473.7-922.8 \\ & 491.7-923.7 \end{aligned}$ | $\begin{aligned} & 0.299-1143.7 \\ & 0.572-1135.9 \end{aligned}$ | $\begin{array}{r} 15.13 \\ 4.55 \end{array}$ |
| Ethanol | $P$ den. | $\begin{array}{r} 42 \\ 289 \end{array}$ | $\begin{aligned} & 527.0-925.10 \\ & 491.7-1122.0 \end{aligned}$ | $\begin{aligned} & 0.831-891.7 \\ & 0.237-10000 . \end{aligned}$ | $\begin{aligned} & 5.71 \\ & 4.57 \end{aligned}$ |
| Propanol | P den. | $\begin{aligned} & 54 \\ & 38 \end{aligned}$ | $\begin{aligned} & 526.41-966.1 \\ & 635.7-959.7 \end{aligned}$ | $\begin{aligned} & 0.284-749.8 \\ & 7.27-698.12 \end{aligned}$ | $\begin{aligned} & 5.16 \\ & 3.88 \end{aligned}$ |
| Phenol | P <br> den. | $\begin{aligned} & 15 \\ & 15 \end{aligned}$ | $\begin{aligned} & 581.7-1247.7 \\ & 581.7-1247.7 \end{aligned}$ | $\begin{aligned} & 0.047-884.5 \\ & 0.047-884.5 \end{aligned}$ | $\begin{aligned} & 5.45 \\ & 2.82 \end{aligned}$ |
| Water | $\mathrm{P}$ <br> $\mathrm{H}-\mathrm{H}^{\circ}$ den. | $\begin{array}{r} 66 \\ 256 \\ 385 \end{array}$ | $\begin{aligned} & 492.0-1160 . \\ & 510.0-2860 . \\ & 492.0-2860 . \end{aligned}$ | $\begin{aligned} & 0.089-3090 . \\ & 453.0-15721 \\ & 0.089-20305 \end{aligned}$ | 15.17 34.21 28.63 |

** $p=$ vapor pressure, den. = density,
H-Ho $=$ enthaipy departure, Dtu/lb

Appendix C

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

| Compound | Deg. R | $\stackrel{\mathrm{V}}{\mathrm{cu} . \mathrm{ft} . / 1 \mathrm{bmole}}$ | c | $q / 0$ |
| :---: | :---: | :---: | :---: | :---: |
| Methane | 273.842 | 0.317877 | 1.0000 | 1.4494 |
| Ethane | 403.974 | 0.441023 | 1.2743 | 2.1375 |
| Propane | 464.6:5 | 0.594652 | i. 4746 | 2.4583 |
| n-Butane | 519.732 | 0.739839 | 1.5248 | 2.7517 |
| n-Pentane | 556.362 | 0.882687 | 1.8152 | 2.9435 |
| n -Hexane | 587.754 | 1.035840 | 1.9720 | 3.1095 |
| $n$-Heptane | 610.902 | 1.176313 | 2.1581 | 3.2325 |
| n-Octane | 631.872 | 1.341875 | 2.2986 | 3.3433 |
| n-Nonane | 638.874 | 1.484419 | 2.5576 | 3.3801 |
| n-Decane | 651.744 | 1.612851 | 2.7544 | 3.4483 |
| n -Dodecane | 688.010 | 1.937590 | 2.9579 | 3.6404 |
| n -Hexadecane | 716.814 | 2.554940 | 3.6693 | 3.7926 |
| n-Eicosane | 741.996 | 3.13113 | 4.2876 | 3.9260 |
| Isobutane | 495.882 | 0.737922 | 1.6225 | 2.6237 |
| Isopentane | 554.562 | 0.878452 | 1.7124 | 2.9345 |
| Ethylene | 377.586 | 0.388527 | 1.2483 | 1.6465 |
| Propylene | 445.590 | 0.530115 | 1.6615 | 1.9436 |
| Cyclohexane | 672.174 | 0.908006 | 1.6575 | 3.1644 |



| Component | Molecular Height | Critical Temperature Deg. $R$ | Critical Pressure Psia | Critical Density lbmoles/cft. |
| :---: | :---: | :---: | :---: | :---: |
| Ethane | 30.068 | 549.70 | 709.82 | 0.4218 |
| Propane | A4.094 | 655.64 | 616.30 | 0.30096 |
| n-Butane | 58:120 | 765.3A | 550.70 | 0.2448 |
| n-Pentane | 72.146 | 845.09 | 489.50 | 0.2007 |
| n-Hexane | 86.172 | 914.20 | 439.70 | 0.1696 |
| n-Heptane | 100.198 | 972.52 | 397.00 | 0.1465 |
| n-Octane | 114.200 | 1023.46 | 360.60 | 0.1284 |
| n-Nonane | 128.250 | 1070.17 | 332.00 | 0.1150 |
| n-Decane | 142.276 | 1111.57 | 306.60 | 0.1037 |
| n-Undecane | 156.313 | 1149.84 | 285.10 | 0.0946 |
| n-Dodecane | 170.340 | 1186.50 | 264.53 | 0.08756 |
| n-Tridecane | 184.367 | 1218.90 | 249.83 | 0.08004 |
| n-Tetradecane | 198.394 | 1250.50 | 235.14 | 0.07522 |
| n-Pentadecane | 212.448 | 1272.60 | 220.44 | 0.07094 |
| n-Hexadecane | 226.448 | 1290.60 | 205.74 | 0.06616 |
| n-Heptadecane | 240.475 | 1319.40 | 191.05 | 0.06243 |
| n-Octadecane | 254.502 | 1341.00 | 174.88 | 0.05887 |
| n-Monadecane | 268.529 | 1360.80 | 161.66 | 0.05589 |
| n-Elcosane | 282.556 | 1380.60 | 148.00 | 0.05303 |

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

| Componert | molecular Height | $\begin{gathered} \text { Critical } \\ \text { Temperature } \\ \text { Deg. } \end{gathered}$ | Critical Pressure Dsia | Critical Density 1bmeles/cft |
| :---: | :---: | :---: | :---: | :---: |
| Methane | 16.043 | 343.24 | 673.1 | 0.62740 |
| Isobutane | 58.120 | 734.13 | 526.57 | 0.24384 |
| Isopentane | 72.146 | 828.70 | 490.41 | 0.20400 |
| Ethylene | 28.050 | 505.49 | 728.80 | 0.50350 |
| Propylene | 42.080 | 657.07 | 669.0 | 0.34490 |
| Cyclohexane | 84.160 | 996.30 | 590.78 | 0.20270 |
| Benzene | 78.113 | 1011.89 | 710.41 | 0.21250 |
| Toluene | 92.141 | 1065.06 | 596.66 | 0.19756 |
| 0-Xylene | 106.168 | 1134.36 | 540.85 | 0.15818 |
| Dichlorodi- | 120.914 | 693.27 | 598.13 | 0.28768 |
| fluoromethane |  |  |  |  |
| Hydrogen | 2.016 | 59.31 | 188.11 | 0.96938 |
| Argon | 39.948 | 271.46 | 706.88 | 0.83720 |
| Nitrogen | 28.016 | 227.07 | 492.3 | 0.69290 |
| Carbon Dioxide | 44.010 | 547.47 | 1069.9 | 0.66410 |
| Sulfur Dioxide | 64.060 | 775.44 | 1143.4 | 0.51172 |
| Hydrogen Sulfide | de 34.076 | 672.37 | 1296.2 | 0.65710 |
| Hydrogen Chioride | de 36.461 | 584.28 | 1205.1 | 0.77072 |
| Wethyl Fluoride | 34.033 | 572.04 | 852.37 | 0.50345 |


| component Mor | Molecular <br>  | Critical Temperature Deg. $R$ | Critical Pressure Psia | Critical Density ibmoles/cft |
| :---: | :---: | :---: | :---: | :---: |
| Difluoromono- | 86.467 | 664.76 | 721.57 | 0.37688 |
| chloromethane |  |  |  |  |
| Dichloromono- | 102.923 | 812.84 | 749.50 | 0.31785 |
| Eluoromethane |  |  |  |  |
| Methyl Ethyl Ether | r 60.069 | 788.04 | 637.81 | 0.28248 |
| Dimethyl Ether | 46.069 | 720.00 | 778.89 | 0.35072 |
| Diethyl Ether | 74.123 | 840.06 | 520.68 | 0.22296 |
| Acetone | 58.080 | 914.58 | 681.90 | 0.29870 |
| Ammonia | 17.030 | 729.90 | 1635.70 | 0.86148 |
| Aniline | 93.129 | 1258.47 | 770.70 | 0.23125 |
| Methanol | 32.042 | 922.68 | 1174.10 | 0.52905 |
| Ethanol | 46.069 | 929.15 | 925.85 | 0.37382 |
| Propanol | 60.096 | 966.06 | 749.50 | 0.28571 |
| Phenol | 94.113 | 1249.55 | 889.17 | 0.27261 |
| 2,4-Xylenol | 122.167 | 1273.68 | 638.14 | 0.16351 |
| Water | 18.015 | 1165.30 | 3208.00 | 1.11020 |

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

