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# CORRELATION OF THERMODYNAMIC PROPERTIES OF FLUIDS THROUGH GENERALIZED HARD SPHERE-AUGMENTED EQUATION OF STATE

A DISSERTATION

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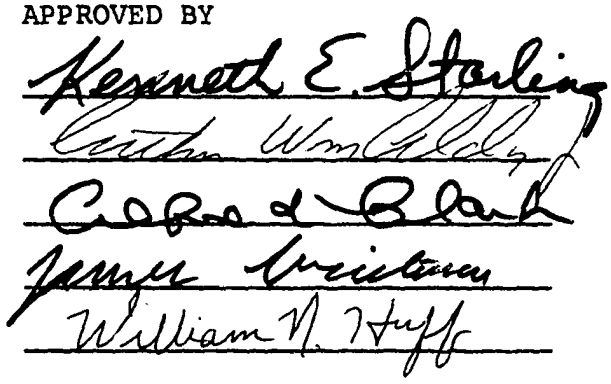
CORRELATION OF THERMODYNAMIC PROPERTIES OF FLUIDS THROUGH

GENERALIZED HARD SPHERE-AUGMENTED EQUATION OF STATE

APPROVED BY



DISSERTATION COMMITTEE

## ABSTRACT

A generalized hard sphere-augmented equation of state has been developed for prediction of thermodynamic properties and phase equilibrium of mixtures as well as pure compounds. The hard sphere volume was expressed in reduced form as a function of acentric factor and reciprocal reduced temperature. The generalized equation of state parameters were determined by multiproperty regression of PVT, enthalpy, vapor pressure, velocity of sound and heat capacity data for pure normal paraffin hydrocarbons methane through octane. A total of more than 2500 data points for pure fluids were tested for polar and non polar compounds, paraffin, olefin, naphthene and aromatic hydrocarbons and nonhydrocarbons. The results are summarized in Table IV-2.

The use of velocity of sound and heat capacity data in addition to PVT, enthalpy and vapor pressure data is demonstrated to be particularly valuable in the low temperature liquid region. Enhancement in the accuracy of temperature and density derivatives of the pressure explicit equation of state is also obtained from the use of the additional types of thermodynamic data.

Two corresponding states principles have been used to apply the generalized equation of state for the prediction of thermodynamic properties of mixtures. The first principle, CSP I, in which mixing rules are formulated for estimates of $T_c$, $v_c$ and $\omega$ for the mixture of interest, is simpler and sufficiently accurate for engineering calculations of density and enthalpy. The second principle CSP II, in which mixing rules for unreduced parameters are developed, is more accurate than CSP I for partial molar property and vapor-liquid equilibrium calculations. The unreduced equation of state parameters are expressed as function of mole fraction by the mixing rules developed in this dissertation.

The interaction parameter values for binary systems, required for the use of CSP II for mixtures, were determined from vapor-liquid equilibrium data and are tabulated in this report. The interaction parameter values for systems not tabulated in the dissertation can be approximated by using the known values for similar systems.

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## CHAPTER I

## INTRODUCTION

The equation of state for calculating pressure P can be considered as the sum of a hard-sphere term $P^o$ and a term P' which accounts for weak, long-range attraction effects[19]

$$P = P^o + P' \qquad (I-1)$$

Such a model corresponds to the form of the van der Waals equation. The intermolecular potential energy of a real fluid system has a steep repulsive part and the range of the attractive force can be considered large relative to the intermolecule spacing at densities greater than the critical density. As a result, for densities greater than the critical, the real fluid system is found to obey Equation I-1.

Carnahan and Starling[15] have formulated an accurate equation of state for an assembly of hard spheres. The computation results are in good agreement with molecular dynamic calculations[3,4]. Still, the Carnahan-Starling

equation requires perturbation for a complete description of real fluid behavior. There are a variety of perturbation calculation schemes. Typical are the introduction of a strength parameter $\lambda$[132] into the attractive part of the intermolecular potential with the free energy expanded as a power series in $\lambda$, around $\lambda = 0$; and the introduction of the variational approach by Mansoori.[71] In spite of many ingenious theoretical attempts, the solution of the classical many-body problem even in fairly good approximation for P' is a herculean task. Approximations are necessary in order to obtain expressions which can be numerically evaluated. In many cases, these approximations were for mathematical convenience rather than for physical reality and hence the soundness of the theoretical basis was contaminated. In addition, to date, theoretical or semi-theoretical equations of state lack the accuracy of the empirical equations of state.

The totally empirical equations of state are developed by correlating experimental thermodynamic property data to minimize the differences between calculated and experimental values. They are, therefore, quite accurate in interpolative calculations. These equations of state are particularly accurate for certain materials from which these equations of state have been developed. The extension of these equations of state to other materials not included in the original correlation is naturally less accurate.

Developments of equations of state for real fluids using Equation I-1 as the starting point have appeared in the literature. Most of the developments are, however, limited either to compressibility factor for noble substances[67] or to gaseous thermodynamic properties of a few substances of industrial interest.[8,59]

The work in this dissertation was undertaken using Equation I-1 to correlate fluid thermodynamic properties (density, enthalpy, fugacity, velocity of sound and heat capacity) in both liquid and gaseous regions. In order to be applicable to a wide range of materials beyond those in the original correlation, Equation I-1 was developed in reduced form, using the three parameter corresponding states principle.

For the past years, the empirical development of equations of state at the University of Oklahoma has centered around simultaneous regression using PVT, enthalpy and vapor pressure data. In this dissertation, velocity of sound and heat capacity data are included in the regression analysis to provide important information regarding property derivatives.

## CHAPTER II

## USE OF VELOCITY OF SOUND AND HEAT CAPACITY DATA IN EQUATION OF STATE CORRELATION

The use of velocity of sound and heat capacity data in addition to density, enthalpy and vapor pressure data in equation of state correlation is particularly valuable in the low temperature liquid region.[121] Cryogenic compressed liquid density data of high accuracy are required to define accurately temperature and density derivatives of thermodynamic properties, even when enthalpy and vapor pressure data are used in correlation development. On the other hand, velocity of sound and heat capacity data provide important information regarding property derivatives, even when such data are available only along an isobar or along the vapor pressure curve.

In the subsequent sections of this chapter, we will demonstrate how the density, enthalpy and vapor pressure data alone cannot serve to define the temperature and density derivatives of thermodynamic properties, and how this drawback can be overcome by including velocity of sound data, or heat capacity data or both. The advantage of using these additional

types of data is illustrated by comparing the calculated value of $(\partial P/\partial T)_\rho$ with the experimental for ethane in Tables II-4 and II-8.

## Density

The traditional development of an equation of state is by the correlation of PVT data. The common situation frequently encountered is that low temperature liquid density data are available only at atmospheric pressure (or perhaps along the vapor pressure curve). Although the correlation is to be used to calculate the density at any T,P condition, isobaric density data provide information for $(\partial\rho/\partial T)_P$ and no information for $(\partial\rho/\partial P)_T$ in the following relation

$$d\rho = \left(\frac{\partial\rho}{\partial T}\right)_P dT + \left(\frac{\partial\rho}{\partial P}\right)_T dP \qquad \text{(II-1)}$$

Thus, in applications of multi-property analysis, information regarding $(\partial\rho/\partial P)_T$ must come from data for properties other than density in the temperature regions where only liquid density data along isobar are available. It should be noted that $(\partial\rho/\partial P)_T$ is very small for low temperature liquids. For example, for ethane at a reduced temperature of 0.5, approximately 100 atmospheres pressure or 1500 psia is required to change the density one percent. Thus, if the liquid density is predicted accurately along the low pressure data isobar, or at saturation, 100 percent error in $(\partial\rho/\partial P)_T$ can be tolerated for density predictions of 1 percent uncertainty

up to about 1500 psia. Noting that

$$\left(\frac{\partial \rho}{\partial T}\right)_P = - \frac{(\partial P/\partial T)_\rho}{(\partial P/\partial \rho)_T} \qquad \text{(II-2)}$$

it can be realized that if $(\partial \rho/\partial P)_T$ and therefore $(\partial P/\partial \rho)_T$ from the correlation is in error, then $(\partial P/\partial T)_\rho$ will be in error by roughly the same factor provided $(\partial \rho/\partial T)_P$ is correlated accurately.

## Enthalpy

When enthalpy data are available at specified T, P conditions, these data provide information regarding both $(\partial H/\partial T)_P$ and $(\partial H/\partial P)_T$ in the relation

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \qquad \text{(II-3)}$$

However, when a pressure explicit equation of state, which uses $(T,\rho)$ as independent variables, is used, the following relations must be applied

$$\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_\rho + \left(\frac{\partial H}{\partial \rho}\right)_T \left(\frac{\partial \rho}{\partial T}\right)_P \qquad \text{(II-4)}$$

$$\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial H}{\partial \rho}\right)_T \div \left(\frac{\partial P}{\partial \rho}\right)_T \qquad \text{(II-5)}$$

For ethane at a reduced temperature of 0.5, 100 percent error in $(\partial H/\partial \rho)_T$ can yield an error of only about 1 percent in the difference between the enthalpy at 1500 psia and the saturated liquid enthalpy, when the density at 1500 psia is

in error by 1 percent. Because enthalpy data generally do not extend above 2000 psia, enthalpy data cannot serve to define $(\partial H/\partial \rho)_T$ for the liquid phase with high accuracy.

## Vapor Pressure

Vapor pressure data provide information about the derivative of pressure with respect to temperature along the vapor pressure curve $(\partial P/\partial T)_\sigma$, therefore, by virtue of the Clapeyron equation

$$\left(\frac{dP}{dT}\right)_\sigma = \frac{H^V - H^L}{T(v^V - v^L)} \qquad \text{(II-6)}$$

the enthalpy of vaporization, $H^V - H^L$, is well established, provided saturated densities are described accurately. However, according to the relation

$$\left(\frac{dP}{dT}\right)_\sigma = \left(\frac{\partial P}{\partial T}\right)_\rho \left[1 - \left(\frac{\partial \rho}{\partial T}\right)_\sigma / \left(\frac{\partial \rho}{\partial T}\right)_P\right] \qquad \text{(II-7)}$$

it is possible to describe $(dP/dT)_\sigma$ within 1 percent while $(\partial P/\partial T)_\rho$ is in error by 100 percent when $(\partial \rho/\partial T)_P$ is exact and $(\partial \rho/\partial T)_\sigma$ is in error by only 1 percent. This situation occurs when the ratio of the derivatives in Equation II-7 is very close to unity. Thus, vapor pressure data cannot be relied upon for the accurate determination of $(\partial P/\partial T)_\rho$.

## Velocity of Sound

Velocity of sound data can be used to particular advantage in thermodynamic correlation development when

liquid density data are available along an isobar or the saturation curve. The velocity of sound, W, is related to the adiabatic compressibility $\beta_S = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_S$,

$$W^2 = \frac{1}{\rho\beta_S} = \left(\frac{\partial P}{\partial \rho}\right)_S \tag{II-8}$$

Using the thermodynamic relation

$$\left(\frac{\partial P}{\partial \rho}\right)_S = \left(\frac{\partial P}{\partial T}\right)_\rho \left(\frac{\partial T}{\partial \rho}\right)_S + \left(\frac{\partial P}{\partial \rho}\right)_T \tag{II-9}$$

$$\left(\frac{\partial T}{\partial \rho}\right)_S = -\left(\frac{\partial S}{\partial \rho}\right)_T \Big/ \left(\frac{\partial S}{\partial T}\right)_\rho = \left(\frac{\partial P}{\partial T}\right)_\rho \Big/ \rho^2 \left(\frac{\partial S}{\partial T}\right)_\rho \tag{II-10}$$

The velocity of sound can be expressed in terms of $(T,\rho)$ as independent variables

$$W^2 = \left(\frac{\partial P}{\partial \rho}\right)_T + \left(\frac{\partial P}{\partial T}\right)_\rho^2 \Big/ \rho^2 \left(\frac{\partial S}{\partial T}\right)_\rho \tag{II-11}$$

It was noted in Equation II-1 that liquid density data along an isobar serve to fix $(\partial\rho/\partial T)_P$, requiring that the correlation predict $(\partial P/\partial\rho)_T$ and $(\partial P/\partial T)_\rho$ to be high or low by approximately the same factor. Thus, if $(\partial S/\partial T)_\rho = C_v/T$ in Equation II-13 is predicted accurately, values of $W^2$ predicted by the correlation will be too large if $(\partial P/\partial T)_\rho$ and $(\partial P/\partial\rho)_T$ are overestimated by the correlation, while $W^2$ will be too small if these derivatives are underestimated by the correlation. Therefore, when liquid velocity of sound and $C_v$ data are used in multiproperty analysis, it is virtually impossible that accurate calculations of $W^2$ and $C_v$ can result when

$(\partial P/\partial T)_\rho$ and $(\partial P/\partial \rho)_T$ are significantly in error, which, as noted, can occur for analysis using liquid enthalpy and vapor pressure.

## Heat Capacity

The use of heat capacity data in correlation is quite valuable for aiding in the determination of the derivatives $(\partial P/\partial T)_\rho$, $(\partial P/\partial \rho)_T$ and $(\partial^2 P/\partial T^2)_\rho$. The use of constant volume heat capacity data in correlation directly aids correlation of $(\partial^2 P/\partial T^2)_\rho$ by virtue of the relation

$$\left(\frac{\partial C_v}{\partial \rho}\right)_T = -\frac{T}{\rho^2}\left(\frac{\partial^2 P}{\partial T^2}\right)_\rho \qquad \text{(II-12)}$$

Also, as noted earlier, $C_v$ data aid correlation of $(\partial S/\partial T)_\rho$ in the relation for the velocity of sound in Equation II-11, since

$$C_v = T\left(\frac{\partial S}{\partial T}\right)_\rho \qquad \text{(II-13)}$$

In the commonly encountered situation where $C_p$ rather than $C_v$ data are available, arguments regarding the value of using velocity of sound and heat capacity data in correlation remain valid. The thermodynamic relation

$$C_p - C_v = \frac{T}{\rho^2}\left(\frac{\partial \rho}{\partial T}\right)_P^2\left(\frac{\partial P}{\partial \rho}\right)_T \qquad \text{(II-14)}$$

can be used with Equation II-13 to derive the following expression for the velocity of sound.

$$W^{-2} = \left(\frac{\partial \rho}{\partial P}\right)_T - \frac{T}{\rho^2 C_p}\left(\frac{\partial \rho}{\partial T}\right)_P^2 \qquad \text{(II-15)}$$

When velocity of sound and constant pressure heat capacity data are used with isobaric density data in correlation, all quantities in Equation II-15 except $(\partial\rho/\partial P)_T$ are fixed by the data, so that $(\partial\rho/\partial P)_T$ is fixed by Equation II-15. Therefore, $(\partial P/\partial\rho)_T$ is correlated since $(\partial P/\partial\rho)_T = (\partial\rho/\partial P)_T^{-1}$. Further, since $(\partial P/\partial\rho)_T$ is correlated, $(\partial P/\partial T)_\rho$ also is correlated since, as noted in Equation II-2, $(\partial P/\partial T)_\rho = -(\partial P/\partial\rho)_T(\partial\rho/\partial T)_P$. In addition, therefore, $C_v$ is correlated by virtue of Equation II-14 and this aids in the correlation of $(\partial^2 P/\partial T^2)_\rho$ by virtue of Equation II-12. Obviously, of course, greater accuracy and thermodynamic consistency would be obtained in correlation if both $C_p$ and $C_v$ rather than only $C_p$ or $C_v$ were used in correlation.

It follows from the preceding discussions that the important functions and derivatives required in correlation of the thermodynamic behavior of pure fluids are obtained only in multiproperty analysis of density, vapor pressure, velocity of sound and heat capacity data. To demonstrate the value of using velocity of sound and heat capacity data in correlation, as discussed herein, correlation of the fluid thermodynamic properties of ethane is considered. Ethane was chosen for this study because it is a fluid of interest in low temperature processing for which, prior to 1970, only fragmentary thermodynamic data existed at cryogenic temperatures. Most

of the thermodynamic data for ethane available prior to 1970 are referred to in the compilation by Canjar and Manning.[18]

The obvious need in the 1960's for more complete data for ethane spurred several experimental density investigations[42,86,104,115], an extensive calorimetric investigation[36] and a vapor pressure investigation to very low temperatures[22]. It therefore is of interest to inquire as to how well one could correlate the thermodynamic behavior of ethane using the fragmentary data available prior to 1970 in comparison to use of the much more complete data available in 1973. The method of demonstration used is to (1) correlate the 1970 data, (2) use the correlation of the 1970 data to compare predicted and experimental properties of the 1973 data, (3) correlate 1973 data, and (4) use the correlation of the 1973 data to compare predicted and experimental properties for the 1973 data.

It will be shown that with the proper use of fragmentary data, correlations accurate enough for engineering applications are possible. However, special care must be taken in choosing the data utilized, to be assured that sufficient information regarding the dependence of properties on temperature and density is included in the data used. For this reason, multiproperty analysis calculations are presented using various combinations of types of data from the set (1) density, (2) vapor pressure, (3) enthalpy, (4) velocity of sound, and (5) heat capacity.

For internal consistency, the multiproperty analysis calculations were performed by utilizing one equation of state. The equation of state used in the correlation of various combinations of types of data is of the following form

$$Z = Z^{o} - \frac{C_1\rho_r + C_2\rho_r^2 + C_3\rho_r^3}{T_r} - \frac{C_4\rho_r + C_5\rho_r^2 + C_6\rho_r^3 + C_7\rho_r^4}{T_r^2} - \frac{C_8\rho_r + C_{11}\rho_r^3}{T_r^3} - \frac{C_9\rho_r + C_{10}\rho_r^2}{T_r^5} \qquad \text{(II-16)}$$

The development of Equation II-16 will be described in detail in Chapter III. In Equation II-16, Z is compressibility factor, $T_r$ is reduced temperature (temperature divided by critical temperature) and $\rho_r$ is reduced density (density divided by critical density). The values of the parameters $C_1$ through $C_{11}$ were determined by the least square method. The hard sphere compressibility factor, $Z^o$, was calculated using the relation

$$Z^{o} = \frac{1 + y + y^2 - y^3}{(1 - y)^3} \qquad \text{(II-17)}$$

$$y = \frac{\pi}{6} N\rho a^3 \qquad \text{(II-18)}$$

where N is Avogadro's number, $\rho$ is molar density in gram mole/$cm^3$, and $a^3$ is hard sphere volume in $\mathring{A}^3$. The hard sphere volume was calculated from the following equation

$$a^3 = A_1 + \frac{A_2}{T_r} + \frac{A_3}{T_r^2} + \frac{A_4}{T_r^3} \qquad \text{(II-19)}$$

The parameters $A_1$ through $A_4$ were held constants for all calculations at the values of $A_1 = 56.8812$, $A_2 = 24.1053$, $A_3 = -6.20769$, and $A_4 = 0.531179$ for ethane. It will be shown in Chapter III that the equation of state parameters $C_1$ through $C_{11}$ and hard sphere volume parameters $A_1$ through $A_4$ can be generalized for other fluids by expressing them as functions of the acentric factor $\omega$.

The expression for $(\partial P/\partial T)_\rho$ was derived from the equation of state and is given by the following equation

$$\frac{1}{R\rho}\left(\frac{\partial P}{\partial T}\right)_\rho = Z^o + T\,\frac{4y + 4y^2 - 2y^3}{a^3(1-y)^4}\left(\frac{\partial a^3}{\partial T}\right) + \frac{C_4\rho_r + C_5\rho_r^2 + C_6\rho_r^3 + C_7\rho_r^4}{T_r^2} + 2\,\frac{C_8\rho_r + C_{11}\rho_r^3}{T_r^3} + 4\,\frac{C_9\rho_r + C_{10}\rho_r^2}{T_r^5} \qquad \text{(II-20)}$$

where R is the universal gas constant, and T is temperature.

## Experimental $(\partial P/\partial T)_\rho$ of Ethane

To evaluate the accuracy of Equation II-16 for the prediction of $(\partial P/\partial T)_\rho$ at a given T, P condition, the experimental values of $(\partial P/\partial T)_\rho$ are needed. Experimental values of this derivative are rare. Values of $(\partial P/\partial T)_\rho$ for ethane were calculated from Pope's isochore data.[86] The isochoric P, T data were first fitted to a third degree polynomial of T in the following form

$$P = B_1 + B_2T + B_3T^2 + B_4T^3 \qquad \text{(II-21)}$$

Herein values of $(\partial P/\partial T)_\rho$ calculated from

$$(\partial P/\partial T)_\rho = B_2 + 2B_3T + 3B_4T^2 \qquad \text{(II-22)}$$

will be referred to as experimental values. In Equation II-22 P is pressure in atmospheres and T is temperature in °K. The values of the parameters $B_1$ through $B_4$, determined by the linear least squares method, are tabulated in Table II-1. The accuracy of the correlation for each isochore was evaluated by comparing the calculated P from Equation II-21 with the experimental P. The deviation percent in P for each isochore is listed in the last column of the table. As noted from the table, the deviation percent in most isochores are less than 1 percent. It is possible that equation of state for ethane could be developed from Equation II-21 by expressing the parameters $B_1$ through $B_4$ as functions of density.

TABLE II-1

SUMMARY OF RESULTS OF FITTING ISOCHORIC P, T DATA TO EQUATION II-21

| Density (g/cc) | Parameter Value | | | | Avg. Abs. Deviation in P (percent) |
|---|---|---|---|---|---|
| | $B_1$ | $B_2$ | $B_3$ | $B_4 \times 10^5$ | |
| 0.033 | -21.91956 | 0.1817 | -0.000122 | 0.00168 | 0.122 |
| 0.242 | -449.61940 | 2.3715 | -0.003828 | 0.45700 | 0.227 |
| 0.290 | -156.7691 | -0.3864 | 0.003461 | 0.00956 | 0.164 |
| 0.389 | -362.0625 | -2.2878 | 0.018071 | -1.71907 | 0.542 |
| 0.436 | -104.8394 | -8.0087 | 0.046975 | -5.40967 | 0.720 |
| 0.462 | -2608.399 | 18.1699 | -0.043493 | 5.48802 | 2.382 |
| 0.491 | -725.4968 | -5.46826 | 0.056385 | -7.6625 | 1.336 |
| 0.512 | -1586.562 | 3.5342 | 0.029352 | -4.60213 | 2.464 |
| 0.537 | -1767.384 | 4.15086 | 0.042165 | -7.62631 | 0.961 |
| 0.563 | -1674.063 | 1.26692 | 0.077554 | -15.24954 | 1.359 |
| 0.575 | -2450.477 | 13.33929 | 0.026376 | -7.517658 | 0.421 |

## Correlation of 1970 Ethane Data

Data used in the correlation include the vapor densities tabulated by Sage and Lacey [101] and Canjar and Manning[18] and atmospheric pressure and saturated liquid densities tabulated by Rossini, et al.[100] Ethane vapor pressure values were taken from Rossini et al.[100] Constant pressure liquid heat capacity values were calculated by standard methods using the saturated liquid heat capacity values reported by Din.[27] The saturated liquid velocity of sound data are the data obtained by Vangeel, et al.[79]

The equation of state parameter values $C_1$ through $C_{11}$ from multiproperty analysis of various combinations of property types are tabulated in Table II-2.

In Table II-3 are shown the average absolute deviations for the predicted properties using the different sets of parameter values in Table II-2. The various combinations of property types are indicated by parentheses in the table. The first column of results in Table II-3 shows deviations obtained when density regression alone is performed. Other columns in Table II-3 show the results of other various combinations of multiproperty analysis calculations. It is obvious from Table II-3 that when only ethane density data available in 1970 are correlated, the vapor pressure and saturated liquid heat capacity are predicted poorly. These results could be expected on the basis of arguments presented earlier in this chapter. It is evident from the second column of Table II-3 that the

TABLE II-2

EQUATION OF STATE PARAMETER VALUES $C_1$ THROUGH $C_{11}$ FROM MULTIPROPERTY ANALYSIS OF VARIOUS COMBINATIONS OF 1970 ETHANE DATA

| | $\rho$ | $\rho, P_\sigma$ | $\rho, P_\sigma, \Delta H$ | $\rho, P_\sigma, W$ | $\rho, P_\sigma, C_P$ | $\rho, P_\sigma, W, C_P$ |
|---|---|---|---|---|---|---|
| $C_1$ | 0.798010 | 0.836041 | 0.833942 | 0.824257 | 0.893420 | 0.915472 |
| $C_2$ | 0.905919 | 0.913950 | 0.911349 | 0.921250 | 0.927170 | 0.910739 |
| $C_3$ | -0.405921 | -0.405030 | -0.411916 | -0.403359 | -0.363356 | -0.356379 |
| $C_4$ | 1.328032 | 1.305885 | 1.318628 | 1.305310 | 1.174750 | 1.136255 |
| $C_5$ | -1.586213 | -1.595360 | -1.590644 | -1.595644 | -1.658167 | -1.647770 |
| $C_6$ | 1.079429 | 1.076944 | 1.081189 | 1.075809 | 1.029275 | 1.032451 |
| $C_7$ | -0.136878 | -0.142890 | -0.142748 | -0.144528 | -0.135039 | -0.134268 |
| $C_8$ | -0.231066 | -0.246862 | -0.259420 | -0.239402 | -0.123398 | -0.105702 |
| $C_9$ | 0.026807 | 0.012625 | 0.012500 | 0.013592 | 0.000106 | 0.001937 |
| $C_{10}$ | -0.001577 | -0.001420 | -0.001367 | -0.002076 | 0.002305 | 0.001816 |
| $C_{11}$ | -0.050989 | -0.034370 | -0.033373 | -0.034914 | -0.030386 | -0.038231 |

TABLE II-3

DEVIATIONS OF THERMODYNAMIC PROPERTIES FROM MULTIPROPERTY ANALYSIS OF VARIOUS COMBINATIONS OF 1970 ETHANE DATA

| Property | Average Absolute Deviation, Percent | | | | | |
|---|---|---|---|---|---|---|
| $\rho$ | (0.49) | (0.67) | (0.63) | (0.95) | (1.15) | (1.48) |
| $P_\sigma$ | 24.39 | (0.27) | (0.44) | (0.26) | (0.42) | (0.33) |
| $\Delta H$ | 2.68 | 1.11 | (1.03) | 1.12 | 1.34 | 1.33 |
| W | 4.85 | 9.46 | 12.50 | (7.40) | 16.01 | (2.37) |
| $C_p$ | 98.43 | 9.82 | 9.09 | 9.93 | (5.41) | (4.07) |

use of vapor pressure data with density data in multiproperty analysis greatly enhances the resultant correlation. Vapor pressure data have the important effect of putting the gas and liquid phases in the correct regions in the pressure-temperature plane, whereas incomplete density data cannot define these regions clearly. As noted earlier, vapor pressure data also establish the enthalpy of vaporization, so that if the vapor enthalpy is accurately correlated (as is possible if sufficient gas phase PVT data are utilized) then the liquid enthalpy will be correlated accurately. Finally, it can be noted in Table II-3 that the use of velocity of sound and heat capacity data in multiproperty analysis yields overall improvement in the correlation.

Tabulated in Table II-4 are the average absolute percent deviations between the calculated values of $(\partial P/\partial T)_\rho$

TABLE II-4

DEVIATIONS OF $(\partial P/\partial T)_\rho$ FROM MULTIPROPERTY ANALYSIS OF VARIOUS COMBINATIONS OF 1970 ETHANE DATA

| Density g/cc | $\rho, P_\sigma, \Delta H$ | $\rho, P_\sigma, W$ | $\rho, P_\sigma, C_p$ | $\rho, P_\sigma, W, C_p$ |
|---|---|---|---|---|
| 0.033 | 5.16 | 4.79 | 4.31 | 4.20 |
| 0.242 | 5.65 | 5.92 | 3.20 | 3.02 |
| 0.290 | 10.54 | 10.38 | 7.26 | 6.97 |
| 0.389 | 9.07 | 7.78 | 4.49 | 3.95 |
| 0.436 | 8.41 | 6.14 | 3.58 | 3.36 |
| 0.462 | 8.63 | 6.35 | 3.78 | 3.18 |
| 0.491 | 9.89 | 6.28 | 4.28 | 3.70 |
| 0.512 | 10.11 | 5.78 | 3.96 | 3.38 |
| 0.537 | 11.62 | 5.76 | 4.35 | 2.56 |
| 0.563 | 12.76 | 4.98 | 6.45 | 2.85 |
| 0.575 | 13.38 | 4.22 | 8.64 | 2.23 |

from Equation II-20 and the experimental values from Equation II-22. The deviations are compiled for each isochore from multiproperty analysis results of various combinations of property data. It is noted in the table that the equation of state predicted more accurate values of the temperature derivative when the equation of state parameter values were determined by including both velocity of sound and heat capacity data in multiproperty regression.

## Prediction of 1973 Data Using 1970 Correlation

When the fragmentary low temperature data for ethane available prior to 1970 are augmented by the additional data available in 1973, it is possible to critically evaluate the correlation obtained using only the 1970 data. Average

absolute deviations of predictions of properties at the 1973 data points using the 1970 correlation are shown in Table II-5. The data points utilized include the 1970 data plus density data reported by Harrison, et al.[42] and Pope, et al.[86], the vapor pressure data of Carruth and Kobayashi[22] and the enthalpy and heat capacity data of Furtado, et al.[36] It can be noted in Table II-5 that although the 1970 correlation obtained from density alone yields poor predictions of all derived properties, the 1970 correlations from multiproperty analysis yield correlations which can be used for many engineering calculations.

TABLE II-5

PREDICTION OF 1973 ETHANE DATA WITH 1970 CORRELATION

| Property | Average Absolute Deviation, percent | | | | | |
|---|---|---|---|---|---|---|
| $\rho$ | (2.23) | (2.23) | (2.11) | (1.58) | (1.20) | (1.41) |
| $P_\sigma$ | 29.57 | (0.48) | (0.59) | (0.46) | (0.69) | (0.45) |
| $\Delta H$ | 19.63 | 1.50 | (1.44) | 1.46 | 1.97 | 1.80 |
| W | 4.85 | 9.46 | 12.50 | (7.40) | 16.01 | (2.37) |
| $C_p$ | 244.70 | 31.61 | 29.45 | 31.77 | (6.36) | (7.54) |

## Correlation of 1973 Ethane Data

The same procedures used to correlate the data available prior to 1970 were used to correlate the data available in 1973. As in the case of the correlation of 1970 data, the

equation of state parameter values $C_1$ through $C_{11}$ were determined. These are tabulated in Table II-6. The average absolute deviations for each thermodynamic property are shown in Table II-7, and the average absolute deviations of $(\partial P/\partial T)_\rho$ for each isochore from multiproperty analysis of various combinations of property data are listed in Table II-8. It is interesting to note that correlation of density data alone yields poor derived property predictions, even with addition to the fragmentary 1970 ethane liquid density data of the rather extensive compressed liquid density data available in 1973. As with the correlation of 1970 data in Table II-3, multiproperty analysis of vapor pressure data with density data makes a dramatic improvement in the correlation and the addition of velocity of sound and heat capacity data in the multiproperty analysis increases the thermodynamic consistency of the correlation.

In this chapter, we have emphasized the advantage of using velocity of sound and heat capacity data in the prediction of temperature and density derivatives of thermodynamic properties. The conclusion can be drawn from Tables II-4 and II-8. As is noted from the second column of both tables, the correlation of density, enthalpy and vapor pressure data predicts poorly the value of the temperature derivative, $(\partial P/\partial T)_\rho$. Yet, improvement is made by including both heat capacity and velocity of sound data, as shown in the last columns. The improvement is most significant at high density.

TABLE II-6

EQUATION OF STATE PARAMETER VALUES $C_1$ THROUGH $C_{11}$ FROM MULTIPROPERTY ANALYSIS OF VARIOUS COMBINATIONS OF 1973 ETHANE DATA

| | $\rho$ | $\rho, P_\sigma$ | $\rho, P_\sigma, \Delta H$ | $\rho, P_\sigma, W$ | $\rho, P_\sigma, C_p$ | $\rho, P_\sigma, W, C_p$ |
|---|---|---|---|---|---|---|
| $C_1$ | 0.797486 | 0.862342 | 0.849328 | 0.830798 | 0.914776 | 0.954622 |
| $C_2$ | 0.899963 | 0.879435 | 0.891621 | 0.909862 | 0.893793 | 0.849011 |
| $C_3$ | -0.390004 | -0.395564 | -0.401237 | -0.405817 | -0.355322 | -0.336383 |
| $C_4$ | 1.391640 | 1.316305 | 1.313236 | 1.313190 | 1.192448 | 1.168688 |
| $C_5$ | -1.623480 | -1.614098 | -1.605567 | -1.602786 | -1.668506 | -1.665174 |
| $C_6$ | 1.049326 | 1.072613 | 1.070738 | 1.069220 | 1.028473 | 1.027450 |
| $C_7$ | -0.236069 | -0.139964 | -0.138730 | -0.141427 | -0.133623 | -0.131675 |
| $C_8$ | -0.058188 | -0.239783 | -0.236876 | -0.231530 | -0.126719 | -0.120053 |
| $C_9$ | 0.003776 | 0.011283 | 0.011022 | 0.012832 | 0.000726 | 0.002220 |
| $C_{10}$ | 0.004870 | -0.001227 | -0.002414 | -0.002414 | 0.002332 | 0.001921 |
| $C_{11}$ | -0.058188 | -0.033555 | -0.034088 | -0.033870 | -0.031407 | -0.035874 |

TABLE II-7

DEVIATIONS OF THERMODYNAMIC PROPERTIES FROM MULTIPROPERTY ANALYSIS OF VARIOUS COMBINATIONS OF 1973 ETHANE DATA

| Property | Average Absolute Deviation, Percent | | | | | |
|---|---|---|---|---|---|---|
| $\rho$ | (0.77) | (0.98) | (1.02) | (1.37) | (1.18) | (1.19) |
| $P_\sigma$ | 20.13 | (0.26) | (0.42) | (0.54) | (0.55) | (0.24) |
| $\Delta H$ | 5.78 | 1.98 | (1.71) | 1.60 | 2.69 | 3.05 |
| W | 39.74 | 9.69 | 9.90 | (6.43) | 8.95 | (3.45) |
| $C_p$ | 28.14 | 23.80 | 21.40 | 22.08 | (7.89) | (11.25) |

TABLE II-8

DEVIATIONS OF $(\partial P/\partial T)_\rho$ FROM MULTIPROPERTY ANALYSIS OF VARIOUS COMBINATIONS OF 1973 ETHANE DATA

| Density g/cc | $\rho, P_\sigma, \Delta H$ | $\rho, P_\sigma, W$ | $\rho, P_\sigma, C_p$ | $\rho, P_\sigma, W, C_p$ |
|---|---|---|---|---|
| 0.033 | 4.81 | 4.59 | 4.21 | 4.21 |
| 0.242 | 5.83 | 6.41 | 3.18 | 2.50 |
| 0.290 | 10.40 | 10.79 | 7.13 | 6.52 |
| 0.389 | 8.30 | 8.24 | 4.28 | 3.70 |
| 0.436 | 7.29 | 6.86 | 3.49 | 3.38 |
| 0.462 | 7.65 | 7.08 | 3.57 | 3.22 |
| 0.491 | 8.47 | 7.38 | 4.14 | 3.76 |
| 0.512 | 8.56 | 7.09 | 3.77 | 3.41 |
| 0.537 | 9.77 | 7.44 | 3.91 | 2.62 |
| 0.563 | 10.53 | 6.95 | 5.66 | 3.11 |
| 0.575 | 10.85 | 6.29 | 7.68 | 2.82 |

This serves to illustrate how the 1970 correlation, using fragmentary data, predicts as accurately as the 1973 correlation the value of $(\partial P/\partial T)_{\rho}$.

# CHAPTER III

## DEVELOPMENT OF A GENERALIZED HARD-SPHERE AUGMENTED VIRIAL EQUATION OF STATE

In Chapter II the equation of state of the form of Equation II-16 has been used to correlate the thermodynamic properties of ethane. The equation was merely given without exhibiting its detailed derivation. This chapter is devoted to the description of the procedures in the evolution of Equation II-16, which is generally referred to as a hard sphere augmented virial equation of state.

### General Theory

For a system of N molecules in a volume V and the total potential energy U, the configurational Helmholtz free energy A is given by

$$\exp(-\beta A) = (1/N!) \int_V \cdots \int_V \exp(-\beta U)\, d\underline{r}_1 \cdots d\underline{r}_N \qquad \text{(III-1)}$$

where $\beta$ is the Boltzmann constant, and $\int_V d\underline{r}_i$ signifies the integration over the entire configuration space of the $i^{th}$ molecule. The potential energy of this system is considered pairwise additive

$$U = \frac{1}{2} \sum_{i \neq j}^{N} u(i,j) \qquad \text{(III-2)}$$

where i and j indicate the coordinates of species i and j. Also, one could assume that the potential energy may be made up of two parts,

$$U = U^{o}(i,j) + U'(i,j) \qquad \text{(III-3)}$$

where $U^{o}(i,j)$ is the potential energy of an unperturbed system, and $U'(i,j)$ is the potential energy due to perturbation. Then Equation III-1 can be written as

$$\exp(-\beta A) = (1/N!) \int_{V} \cdots \int_{V} \exp\left[-(\beta/2) \sum_{i \neq j}^{N} U^{o}(i,j) - (\beta/2) \sum_{i \neq j}^{N} U'(i,j)\right] d\underline{r}_1 \cdots d\underline{r}_N \qquad \text{(III-4)}$$

The first term in the exponent is a powerful, short-ranged repulsion effect between molecules, whereas the second term is a small, long-ranged and weak attractive effect so that the expression can be expanded in the following form.

$$\exp(-\beta A) = (1/N!) \int_{V} \cdots \int_{V} \exp\left[-(\beta/2) \sum_{i \neq j}^{N} U^{o}(i,j)\right] \times \left[1 - (\beta/2) \sum_{i \neq j}^{N} U'(i,j) + (\beta^2/8)\left(\sum_{i \neq j}^{N} U'(i,j)\right)^2 + \ldots\right] \times d\underline{r}_1 \, d\underline{r}_2 \cdots d\underline{r}_N \qquad \text{(III-5)}$$

The first term in the expansion is merely $\exp(-\beta A^{o})$, where $A^{o}$ is the unperturbed configurational Helmholtz free energy. Since the radial distribution function is defined as

$$g_{o}^{(2)}(i,j) = \frac{v^{2}\int_{v}\cdots\int_{v}\exp\left[-\left(\frac{\beta}{2}\right)\sum_{i\neq j}^{N}U^{o}(i,j)\right]\,d\underline{r}_{1}\cdots d\underline{r}_{N}}{\int_{v}\cdots\int_{v}\exp\left[-\left(\frac{\beta}{2}\right)\sum_{i\neq j}^{N}U^{o}(i,j)\right]\,d\underline{r}_{1}\cdots d\underline{r}_{N}} \tag{III-6}$$

The second term can be rewritten as

$$-\exp(-\beta A^{o})\left[\frac{\beta N(N-1)}{2v^{2}}\right]\int g_{o}^{(2)}(i,j)\;U'(i,j)\;d\underline{r}_{i}\;d\underline{r}_{j} \tag{III-7}$$

where the definition of $A^{o}$ has been inserted and where the $N(N-1)/2$ equivalent terms in the summation have been collected. The evaluation of the other terms requires high-order distribution functions. These many body higher-order distribution functions are very difficult to evaluate to yield satisfactory accuracy. Confining ourselves to the series truncated at the second term (first-order perturbation), we obtain

$$\exp(-\beta A) = \exp(-\beta A^{o})\left[1 - \left(\frac{\beta N^{2}}{2v^{2}}\right)\int g_{o}^{(2)}U'(i,j)\;d\underline{r}_{i}\;d\underline{r}_{j}\right]\cdots \tag{III-8}$$

or

$$A = A^{o} + \frac{2\pi N^{2}}{v}\int_{0}^{\infty} g_{o}^{(2)}(r)\;U'(r)\;r^{2}\,dr + 0(\beta) \tag{III-9}$$

Based on Equation III-9, the other equilibrium thermodynamic properties can be derived by classical thermodynamic relations. By using the definition of pressure P with respect to Helmholtz free energy

$$P = -(\partial A/\partial v)_T \qquad \text{(III-10)}$$

one obtains from Equation III-9 the following expression for the equation of state

$$\left(\frac{Pv}{RT}\right) = \left(\frac{Pv}{RT}\right)^{o} - v\,\frac{(\partial/\partial v)}{RT}\left[(2\pi N^2/v)\int_0^{\infty} r^2\, g_o^{(2)}(r)\, U'(r)\, dr\right] \qquad \text{(III-11)}$$

Equation III-11 is the basic form of equation of state from which Equation II-16 is developed. $(Pv/RT)^{o}$ is the hard sphere equation of state and will be described in the following sections.

## Hard Sphere Equation of State

The hard sphere equation of state is assuming an important role in the study of the behavior of real fluids. In the limits of high temperature and pressure, real fluid behavior can be described by the hard sphere equation of state. The system of hard spheres is characterized by the intermolecular potential function of the form

$$\begin{aligned} U(r) &= 0 \quad \text{for } r \geq a \\ U(r) &= \infty \quad \text{for } r < a \end{aligned} \qquad \text{(III-12)}$$

where a is the hard sphere diameter.

Since the pioneering introduction of the hard sphere system to take into account the volume of fluids by van der Waals a century ago, many hard sphere equations of state have been proposed.[3,39,46,98,113,123,124] These equations are theoretical, numerical or purely empirical. The most prominent theoretical equation was obtained by Reiss, et al.[98] and Thiele[113] by the solution of the Percus-Yevick integral equation, to yield

$$\left(\frac{Pv}{RT}\right)^{o} = \frac{1 + y + y^2}{(1 - y)^3} \qquad \text{(III-13)}$$

where

$$y = \frac{\pi}{6} N\rho a^3 \qquad \text{(III-14)}$$

Equation III-13 is in good agreement with the exact virial series of molecular dynamics experiments by Alder and Wainwright[3,98] up to the fourth virial coefficient.

Carnahan and Starling[20] noted that the numerical coefficients of the virial series can be approximated by integers.

$$\left(\frac{Pv}{RT}\right)^{o} = 1 + 4y + 10y^2 + 18y^3 + 28y^4 + 40y^5 + \ldots \qquad \text{(III-15)}$$

By noting recursive relations the series can be written in the compact formula

$$\left(\frac{Pv}{RT}\right)^{o} = \frac{1 + y + y^2 - y^3}{(1 - y)^3} \qquad \text{(III-16)}$$

The resultant seventh virial coefficient from this treatment agrees closely with the value calculated by Ree and Hoover[97]. Equation III-16 is valid up to the densities of liquid state. The superiority of the Carnahan-Starling hard sphere equation of state is reported in the literature.[21] Equation III-16 is used in this research as the reference system of the hard sphere equation of state.

## Hard Sphere Diameter and Volume

In applying the hard sphere equation of state for calculating thermodynamic properties of fluids, one is naturally encountered with the problem of choosing the hard sphere diameter a, for assessing the value of y. A common choice is to set the hard sphere diameter at the value of the Lennard-Jones parameter $\sigma$. Though values of $\sigma$ are available in the literature, they are different from source to source. Even in the same literature source, two different numbers are available, depending on the methods of determination. The values of $\sigma$ of methane are, for example, 3.758 Å as determined from viscosity data and 4.01 Å as obtained from second virial coefficient data.[45]

The essence of the hard sphere system is, as seen from Equation III-12, to find the value of a at which the hard sphere potential starts. If this value is smaller than that of $\sigma$ and thus the hard sphere potential starts in the very repulsive region of the Lennard Jones potential, it is clear that the expansion will converge more slowly since the

perturbation is very large. A useful procedure is to locate the hard sphere diameter at such a value that the potential energy is twice the mean kinetic energy.[106]

It is necessary that the hard sphere diameter be set at different values at different temperatures. Thus at higher temperatures, when the particles can penetrate further, a smaller hard sphere diameter deep in the repulsive region will keep the potential realistic. Barker and Henderson[6], using a perturbation theory where the inverse steepness of the repulsive potential is the expansion parameter, defined the effective diameter in the following equation

$$a = \int_0^{\sigma} \{1 - \exp\ [- \frac{U(r)}{kT}]\}\ dr \qquad \text{(III-17)}$$

The second virial coefficient is defined as

$$\theta_2 = 2\pi N \int_0^{\infty} \{1 - \exp\ [- \frac{U(r)}{kT}]\}\ r^2\ dr \qquad \text{(III-18)}$$

Comparison of Equations III-17 and III-18 shows that the effective diameter is related to second virial at a given temperature through the potential energy. Vernick[119] derived such a relationship as follows

$$\theta_2 = \frac{2\pi N\sigma^3}{3} [b_2(1) + \frac{b_2(2)}{T^*} + \frac{b_2(3)}{T^{*2}} + \ldots + \frac{b_2(n)}{T^{*n-1}}] \qquad \text{(III-19)}$$

where $T^* = T/(\varepsilon/k)$ ($\varepsilon/k$ is Lennard-Jones parameter)

$b_2(1) = (a/\sigma)^3$

$b_2(n)$ is related to $b_2(1)$ in the recursive form

$$b_2(n) = (-1)^n \, 4^{n-1} \sum_{m=1}^{n} \frac{(-1)^{n-m} b_2(1)^{-(2n+2m-5)}}{(m-1)!\,(n-m)!\,(2n+2m-5)} \qquad \text{(III-20)}$$

Calculations of $B^*$ ($= \theta_2/[2\pi N\sigma^3/3]$) at different values of $(a/\sigma)^3$ were performed and the results are plotted in Figure III-1.[122] It will be noted from this figure that $(a/\sigma)^3$ becomes smaller at higher temperatures, in agreement with the earlier discussion on the temperature dependence of hard sphere diameter. For each isotherm, the curve is extrapolated to the point where the reduced second virial coefficient is the value reported by Hirschfelder, et al.[45] The value of $(a/\sigma)^3$ at this point is calculated. The extrapolated values of $(a/\sigma)$ were correlated by the following polynomial in $1/T^*$.

$$\left(\frac{a}{\sigma}\right) = 0.740997 + \frac{0.372009}{T^*} - \frac{0.246542}{T^{*2}} + \frac{0.082459}{T^{*3}} - \frac{0.010452}{T^{*4}} \qquad \text{(III-21)}$$

Equation III-21 is valid for reduced temperature ($T^*$) from 0.3 to 70.

In order to use Equation III-21 to calculate the hard sphere diameter at a given temperature, we need the values of $\sigma$ and $\varepsilon/k$, the two characteristic Lennard-Jones parameters. As discussed earlier in this section, parameter

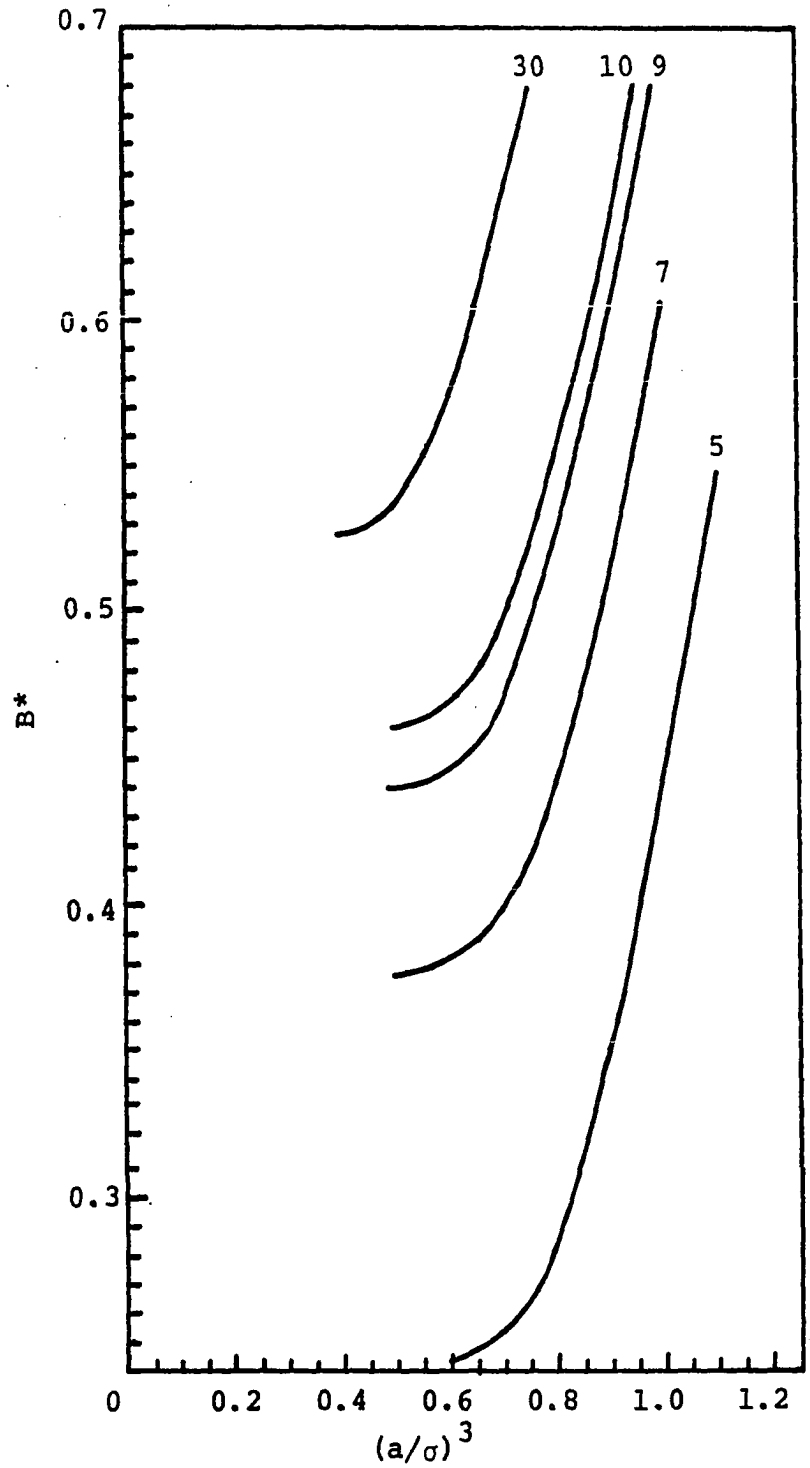


Figure III-1. Plot of B* Against $(a/\sigma)^3$ at Different T*.

values from the literature disagree. Furthermore, a small change in the value of hard sphere diameter will shift the molecule pair potential from repulsive to the attraction region or vice versa. Therefore, in some cases the selected Lennard-Jones parameter values together with the use of Equation III-21 will not place the molecule in the proper region.

For monatomic fluids, $\sigma$ (also hard sphere diameter) and $\varepsilon/k$ are proportional to the cube root of the critical volume $v_c$ and to the critical temperature $T_c$, respectively. Though $v_c$ is difficult to measure accurately, the published data for $v_c$ are in good agreement in the literature. Therefore, it is more useful to relate the hard sphere diameter or volume directly to the macroscopic $T_c$ and $v_c$.

In this work, the hard sphere volume was obtained from an existing equation of state and was expressed in terms of the reduced temperature, $T_r$, as already elucidated in Equation II-19 for predicting the thermodynamic properties of ethane. Also, the acentric factor, $\omega$, will be utilized to generalize the expression for other materials. An existing equation of state which is capable of predicting thermodynamic properties of fluids in both liquid and vapor phases with high accuracy is an eleven-parameter modified BWR equation proposed by Starling[107] (BWRS). The BWRS equation is written in the form

$$Z = 1 + (B_o - \frac{A_o}{RT} - \frac{C_o}{RT^3} + \frac{D_o}{RT^4} - \frac{E_o}{RT^5})\rho + (b - \frac{a}{RT} - \frac{d}{RT^2})\rho^2$$

$$+ \alpha(\frac{a}{RT} + \frac{d}{RT^2})\rho^5 + \frac{c\rho}{RT^3}(1 + \gamma\rho^2)\exp(-\gamma\rho^2) \qquad \text{(III-22)}$$

The hard sphere diameter was calculated from the BWRS equation. In the limit of high pressure, the attractive force between molecules is small as compared with the repulsive force. Therefore, the hard sphere equation of state can be used to describe real fluid behavior for a system at high pressure. The hard sphere diameter was calculated by setting Equation III-16 equal to Equation III-22 at $\rho_r = 4$ for each temperature from $T_r = 0.2$ to 4.0 with a temperature increment of $\Delta T_r = 0.1$. The calculation procedure was repeated for normal paraffins from methane through octane using the published BWRS parameter values.[61,108] The calculated hard sphere volumes are plotted in Figure III-2 against $T_r$ for each paraffin and were correlated to the following generalized equation to the accuracy of 0.44 percent for normal paraffins methane through heptane.

$$a^3 = A_{11} + \frac{A_{21}}{T_r} + \frac{A_{31}}{T_r^2} + \frac{A_{41}}{T_r^3} + \omega(A_{12} + \frac{A_{22}}{T_r} + \frac{A_{32}}{T_r^2} + \frac{A_{42}}{T_r^3})$$

$$+ \omega^2(A_{13} + \frac{A_{23}}{T_r} + \frac{A_{33}}{T_r^2} + \frac{A_{43}}{T_r^3}) \qquad \text{(III-23)}$$

where the generalized parameter values $A_{ij}$ are

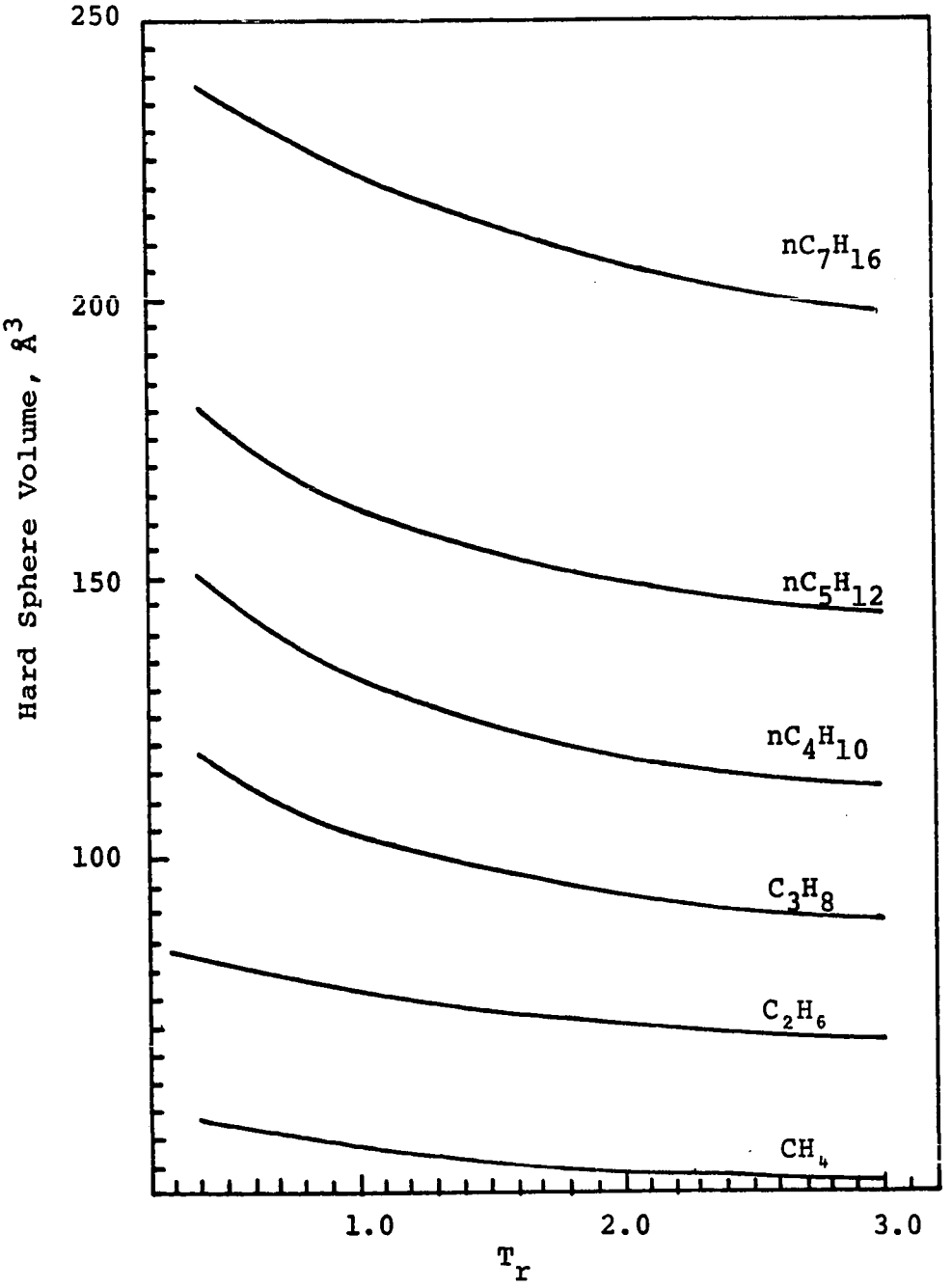


Figure III-2. Temperature Dependence of Hard Sphere Volume for the Normal Paraffins $CH_4$ Through $C_7H_{16}$.

$A_{11}$= 32.83911, $A_{21}$= 18.74099, $A_{31}$= -7.930945, $A_{41}$= 0.980561

$A_{12}$=255.86370, $A_{22}$= 41.68803, $A_{32}$= 43.710640, $A_{42}$=-9.241017

$A_{13}$=440.62930, $A_{23}$=285.44180, $A_{33}$=-276.694500, $A_{43}$=45.938230

It is to be noted that Equation III-23 was extended from Equation II-19 by expressing $A_1$, $A_2$, $A_3$ and $A_4$ as functions of $\omega$.

Equation II-16, when used together with Equation III-23, is capable of predicting the thermodynamic properties of the normal paraffins $CH_4$ through $C_7H_{16}$ with an average absolute deviation of 1 percent for density, enthalpy departure and fugacity. However, the extension of the generalized equation of state thus developed to the materials other than normal paraffins required acentric factors which are quite different from the literature values. Nitrogen, for example, required the value of 0.01 for $\omega$ (compared with the literature value of 0.04) for thermodynamic property predictions.

Referring to Equation III-14, we express y in terms of reduced density by

$$y = \frac{\pi}{6} N\rho_r \ (\rho_c a^3) \qquad \text{(III-24)}$$

The calculated values of $\rho_c a^3$ for individual normal paraffins are plotted against $1/T_r$ in Figure III-3, and against acentric factor for each temperature in Figure III-4. Though, as demonstrated in the figures, the values of $\rho_c a^3$ do not increase with increasing molecular size for certain materials in some temperature ranges, the narrow range of $\rho_c a^3$ (0.4 to

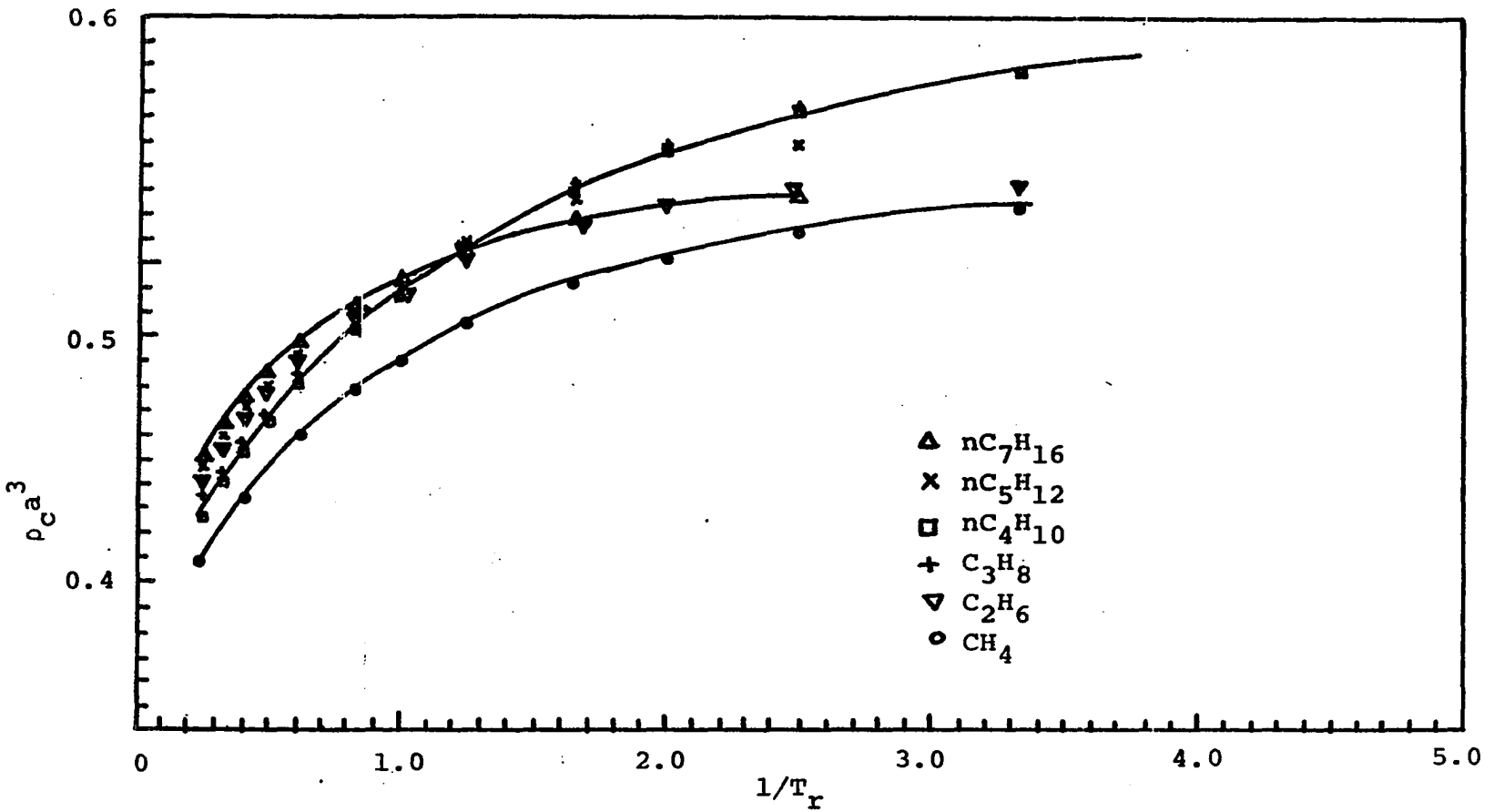


Figure III-3. Plot of $\rho_c a^3$ Against $1/T_r$ for the Normal Paraffins $CH_4$ Through $C_7H_{16}$.

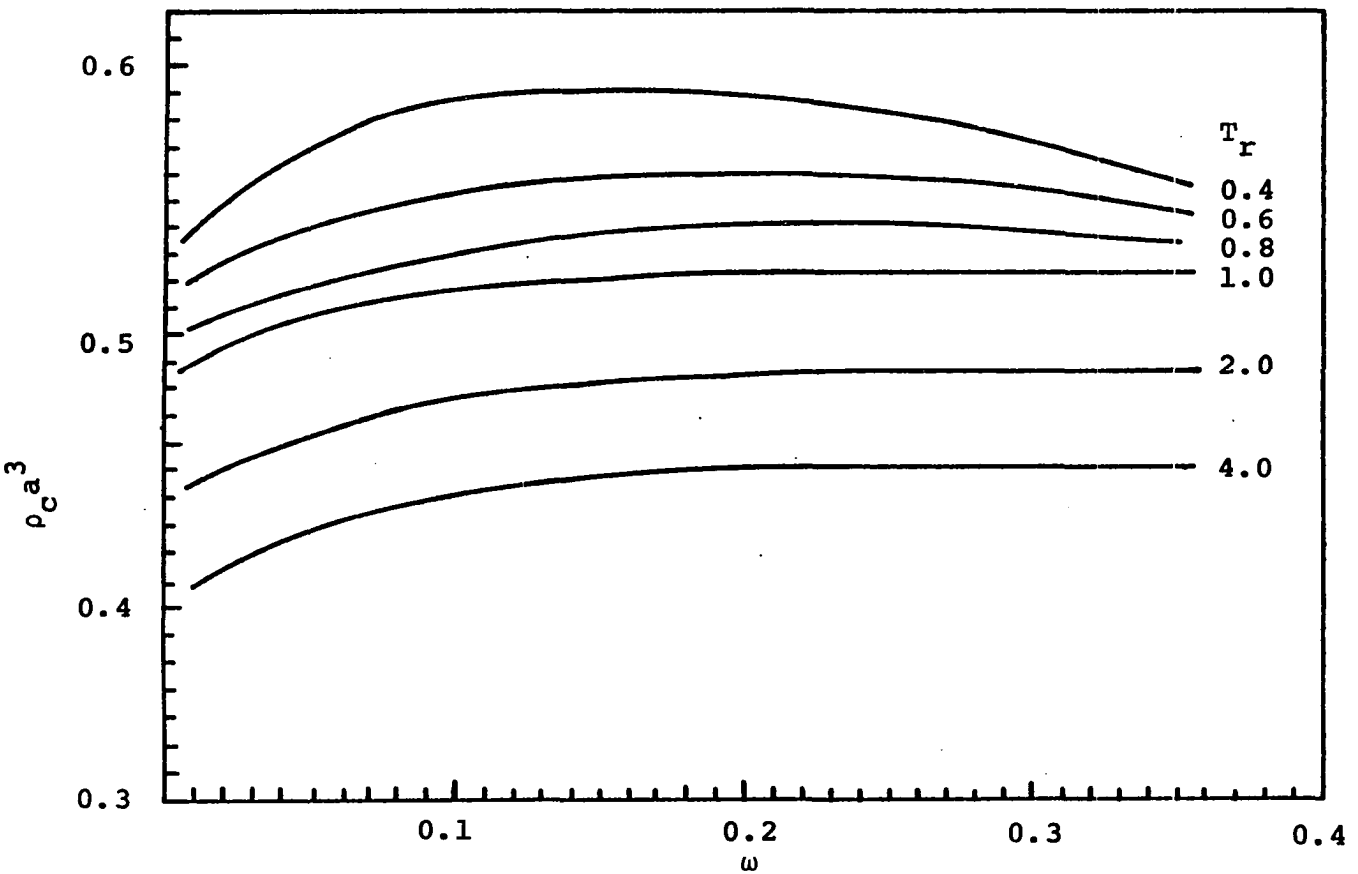


Figure III-4. Plot of $\rho_c a^3$ Against ω at Different $T_r$.

0.6, compared with the values of $a^3$, ranging from 40 for methane to 250 for heptane in Figure III-2), made it possible to fit the curves in Figures III-3 and III-4 to the following equation to the accuracy of 0.8 percent for the normal paraffins methane through octane.

$$\rho_c a^3 = B_1 + \frac{B_2}{T_r} + \frac{B_3}{T_r^2} + \frac{B_4}{T_r^3} + \omega\left(B_5 + \frac{B_6}{T_r} + \frac{B_7}{T_r^2} + \frac{B_8}{T_r^3}\right) + \omega^2\left(B_9 + \frac{B_{10}}{T_r} + \frac{B_{11}}{T_r^2} + \frac{B_{12}}{T_r^3}\right) \qquad \text{(III-25)}$$

The parameter values $B_1$, $B_2$, ..., $B_{11}$ and $B_{12}$ were determined by linear least squares with the following results:

$B_1$=0.380142, $B_2$ = 0.138427, $B_3$ =-0.038418, $B_4$ = 0.003560,

$B_5$=0.015497, $B_6$ = 0.547473, $B_7$ =-0.236621, $B_8$ = 0.030206,

$B_9$=0.401392, $B_{10}$=-1.833072, $B_{11}$= 0.765902, $B_{12}$=-0.092857.

Using the coefficients $B_1$ through $B_{12}$ obtained from normal paraffin data alone, the correlation of the form of Equation III-25, rather than Equation III-23, was extended to other materials using acentric factors slightly different from the literature values. In this case, the value of the acentric factor for nitrogen was 0.039, very near the literature value.

In this report, the final set of parameter values for $B_1$ through $B_{12}$ were obtained by a simultaneous regression with the perturbation parameters $C_1$ through $C_{11}$ in multi-property analysis and are tabulated in Table III-1.

TABLE III-1

GENERALIZED HARD SPHERE AND PERTURBATION EQUATION OF STATE PARAMETER VALUES

Hard Sphere

$B_1 = 0.390265$, $B_2 = 0.141116$, $B_3 = 0.037751$, $B_4 = 0.003337$

$B_5 = -0.000631$, $B_6 = 0.529080$, $B_7 = -0.238688$, $B_8 = 0.029747$

$B_9 = 0.525185$, $B_{10} = -1.799813$, $B_{11} = 0.786241$, $B_{12} = -0.087475$

Perturbation

$C_{11} = 1.281743$, $C_{12} = -2.329622$,

$C_{21} = 0.401326$, $C_{22} = 1.177776$, $C_{23} = 0.507771$

$C_{31} = -0.047881$, $C_{32} = -0.320416$, $C_{33} = -0.137159$

$C_{41} = 0.563276$, $C_{42} = 3.981459$, $C_{43} = -1.370683$

$C_{51} = -0.914930$, $C_{52} = -1.135186$, $C_{53} = -2.316756$

$C_{61} = 0.470129$, $C_{62} = 0.797112$,

$C_{71} = -0.076966$, $C_{72} = -0.044887$

$C_{81} = -1.159513$, $C_{82} = 0.877859$

$C_{91} = 0.001509$, $C_{92} = 0.125768$, $C_{93} = -0.064990$

$C_{101} = -0.000258$, $C_{102} = -0.001768$, $C_{103} = 0.020470$

## Perturbation Equation of State

In the preceding sections, we have developed the hard sphere part of the equation of state. Before proceeding to develop the perturbation part, it is instructive to visualize how significant will be the addition of the perturbation part to the hard sphere part. To this end, Equations III-16, III-24 and III-25, which constitute the whole description of hard sphere fluid at specified T, P conditions, were used to predict density, enthalpy departure and fugacity for methane. The average deviations were 50.64 percent for density (ranging from -3.09 percent at 662°F and 607 psia to -96.61 percent at -253.5°F and 129.7 psia); 141.34 Btu/lb for enthalpy departure (20 Btu/lb at 50°F and 450 psia, 231.7 Btu/lb at -250°F and 2000 psia). The average absolute deviation in saturated fugacity prediction was 0 percent, in that the fugacities in the vapor and liquid phases are identical, an indication that the hard sphere equation of state alone fails to distinguish the two phases. In addition, the fugacities in two phases at a given temperature are greater than the vapor pressure. We chose methane because the methane molecules are nearly spherical. Even though spherical in nature, the behavior of methane is not well described by the hard sphere equation of state and the thermodynamic equations derived therefrom. As will be illustrated in Table IV-2, the addition of perturbation term to the hard sphere part significantly improves the accuracy of predictions of

thermodynamic properties of real fuilds. The average absolute deviations are 0.41 percent, 0.97 Btu/lb and 0.58 percent for density, enthalpy departure and fugacity, respectively, using the same data points.

In this dissertation, the perturbation equation of state was developed with the aid of virial coefficients. The virial equation of state is a series expansion of the compressibility factor,

$$Z = \sum_{i=1} \theta_i \rho^{i-1} \qquad \text{(III-26)}$$

In this relation, the sum starts from i = 1 with $\theta_1 = 1$. The higher virial coefficients $\theta_i$ for i > 1 are functions of temperature for each substance, and are related to the potential functions of intermolecular action by the cluster integrals of Ursell and Mayer. The virial equation of state has theoretical basis. However, the virial coefficients higher than the third (i > 3) have not been developed with accuracy for real fluids. As a result, the practical use of the virial equation of state has been limited to low densities, normally for gases.

The utility of the virial equation of state can be augmented to cover wider density range by reexpressing Equation III-26 as a series of deviation terms from the hard sphere equation,

$$Z = \sum_{i=1} \theta_i^{o} \rho^{i-1} + \sum_{i=1} (\theta_i - \theta_i^{o}) \rho^{i-1} \qquad \text{(III-27)}$$

where the superscript 'o' stands for hard sphere state. The first summation on the right hand side of Equation III-27 is simply the hard sphere compressibility factor $Z^o$. Hence we obtain

$$Z = Z^o + \sum_{i=1} (\theta_i - \theta_i{}^o)\ \rho^{i-1} \qquad \text{(III-28)}$$

The summation in Equation III-28 appears in the form of perturbation to the compressibility factor of the hard sphere fluid. We note from Equations III-11 and III-28 by comparison that

$$-v \frac{(\frac{\partial}{\partial v})}{RT} [(2\pi N^2/v) \int_0^\infty r^2\ g_o^{(2)}(r)\ U'(r)\ dr] = \sum_{i=1} (\theta_i - \theta_i{}^o)\rho^{i-1} \qquad \text{(III-29)}$$

As a first approximation the series on the right hand side of Equation III-29 is truncated after the third virial coefficient. Therefore, Equation III-28 can be written in the approximate form

$$Z = Z^o + (\theta_2 - \theta_2{}^o)\rho + (\theta_3 - \theta_3{}^o)\rho^2 \qquad \text{(III-30)}$$

It is understood that $\theta_1 = \theta_1{}^o = 1$. Later calculations will show that the quantities of both $Z - Z^o$ and $\theta_2 - \theta_2{}^o$ are negative in sign. To plot these two quantities against density on log-log paper, we rewrite Equation III-30 as follows:

$$Z^o = Z + (\theta_2{}^o - \theta_2)\rho - (\theta_3 - \theta_3{}^o)\rho^2 \qquad \text{(III-31)}$$

To calculate the virial coefficients of real fluids, we use the correlation of Pitzer and coworkers[85] for $\theta_2$ and the formulation of Chueh and Prausnitz[24] for $\theta_3$

$$\frac{\theta_2 P_c}{RT_c} = 0.1445 - 0.33/T_r - 0.1385/T_r^2 - 0.0121/T_r^3 + \omega(0.073 + 0.46/T_r - 0.5/T_r^2 - 0.097/T_r^3 - 0.0073/T_r^8) \quad \text{(III-32)}$$

$$\theta_3 \rho_c^2 = \left(\frac{0.232}{T_r^{0.25}} + \frac{0.468}{T_r^5}\right)[1 - \exp(1.0 - 1.89\, T_r^2)] + d \exp[-(2.49 - 2.3\, T_r + 2.7\, T_r^2)] \quad \text{(III-33)}$$

For hard spheres

$$\theta_2^o = \frac{2}{3}\pi N a^3 \quad \text{(III-34)}$$

$$\theta_3^o = \frac{5}{8}(\theta_2^o)^2 \quad \text{(III-35)}$$

The values of $(\theta_2^o - \theta_2)\rho$, and $(\theta_3 - \theta_3^o)\rho^2$ and $Z^o - Z$ were calculated for each normal paraffin methane through octane. The calculated values were plotted against $\rho_r$ with $T_r$ as the parameter. The shapes of the curves were similar for all the substances studied. Thus, only the plots for ethane are presented in Figures III-5, III-6 and III-7.

Plotted in Figure III-5 is the dependence of $(\theta_2^o - \theta_2)\rho$ on temperature and density. This quantity becomes larger as

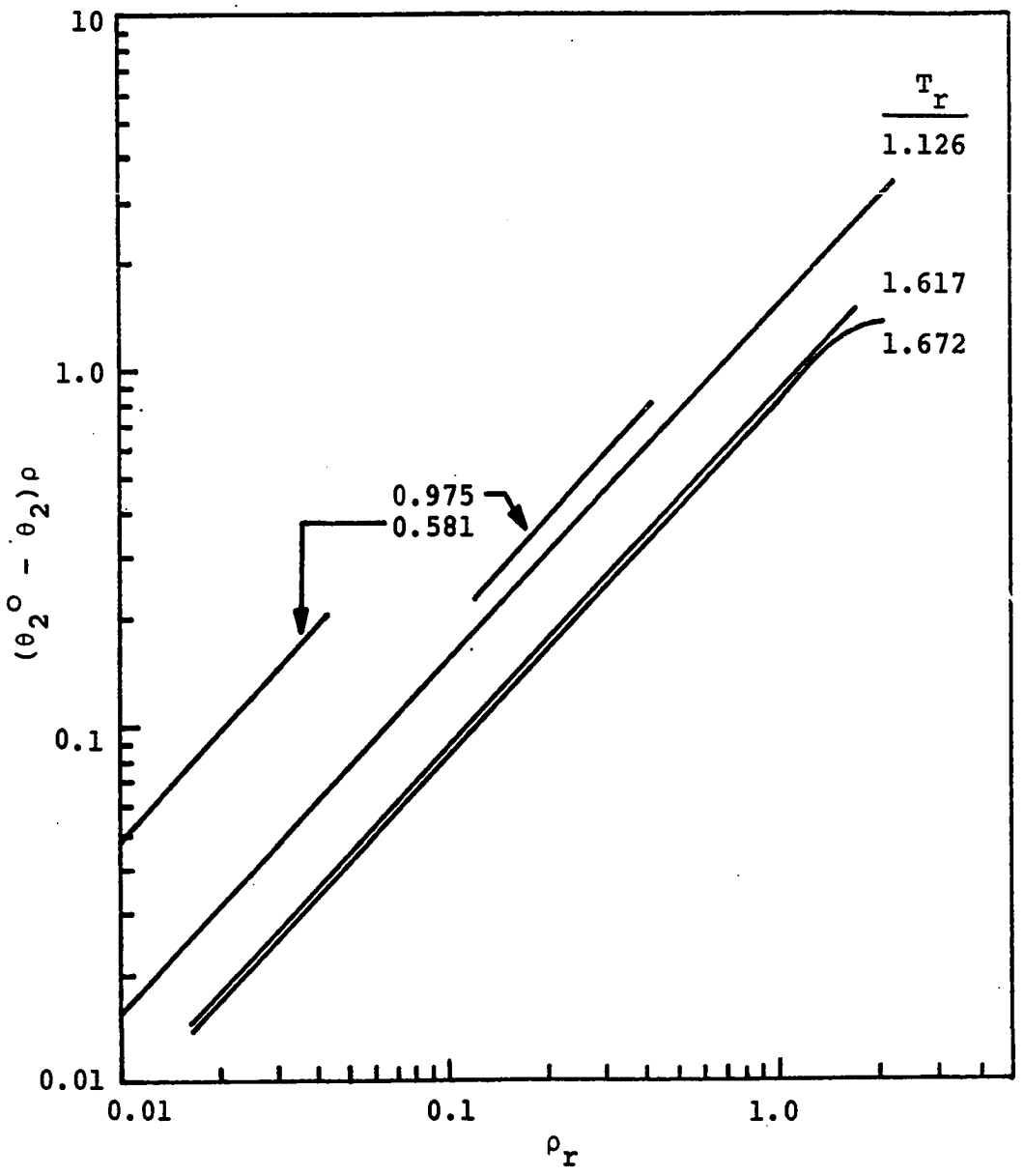


Figure III-5. Density and Temperature Dependence of $(\theta_2^o - \theta_2)\rho$ for $C_2H_6$.

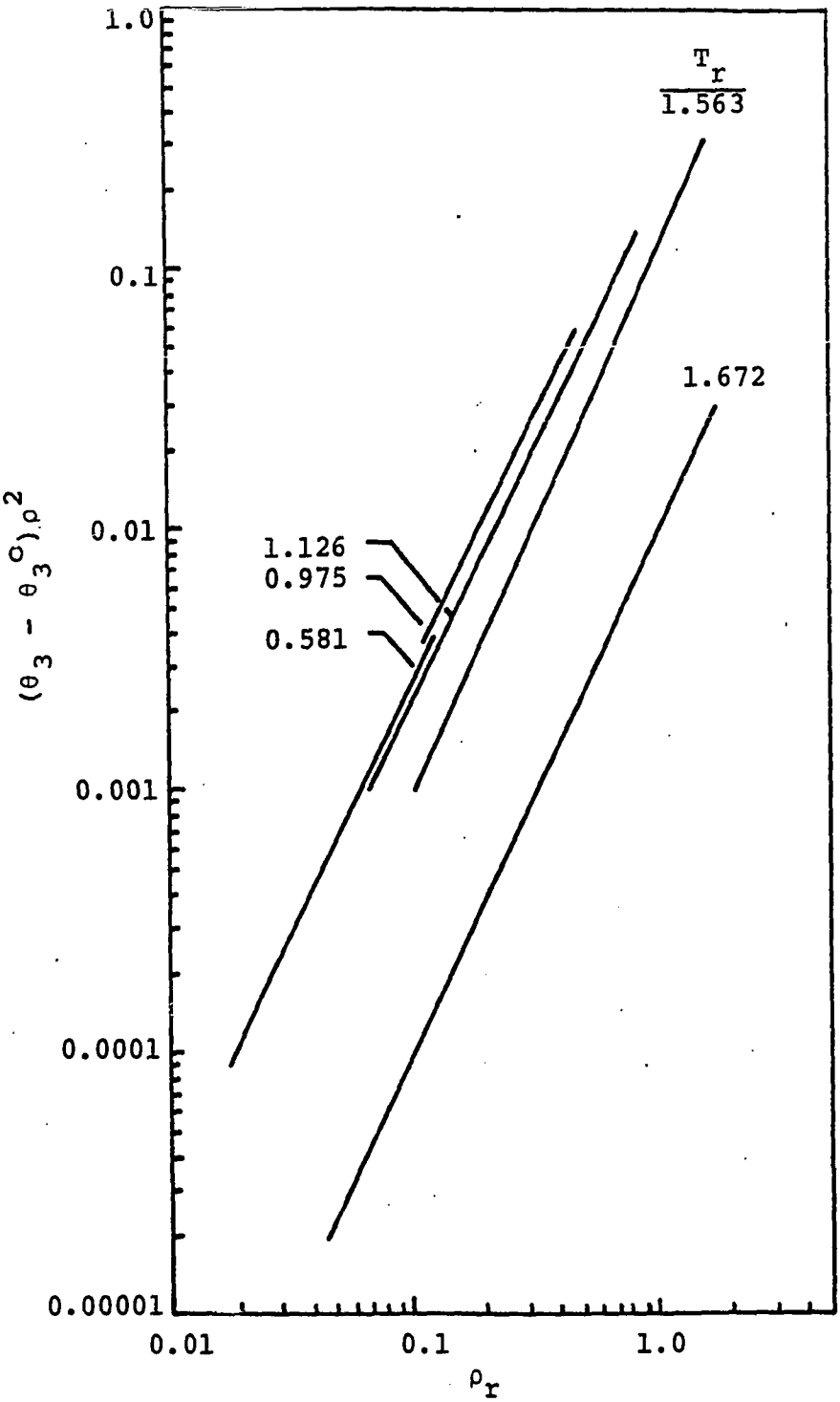


Figure III-6. Density and Temperature Dependence of $(\theta_3 - \theta_3^o)\rho^2$ for $C_2H_6$.

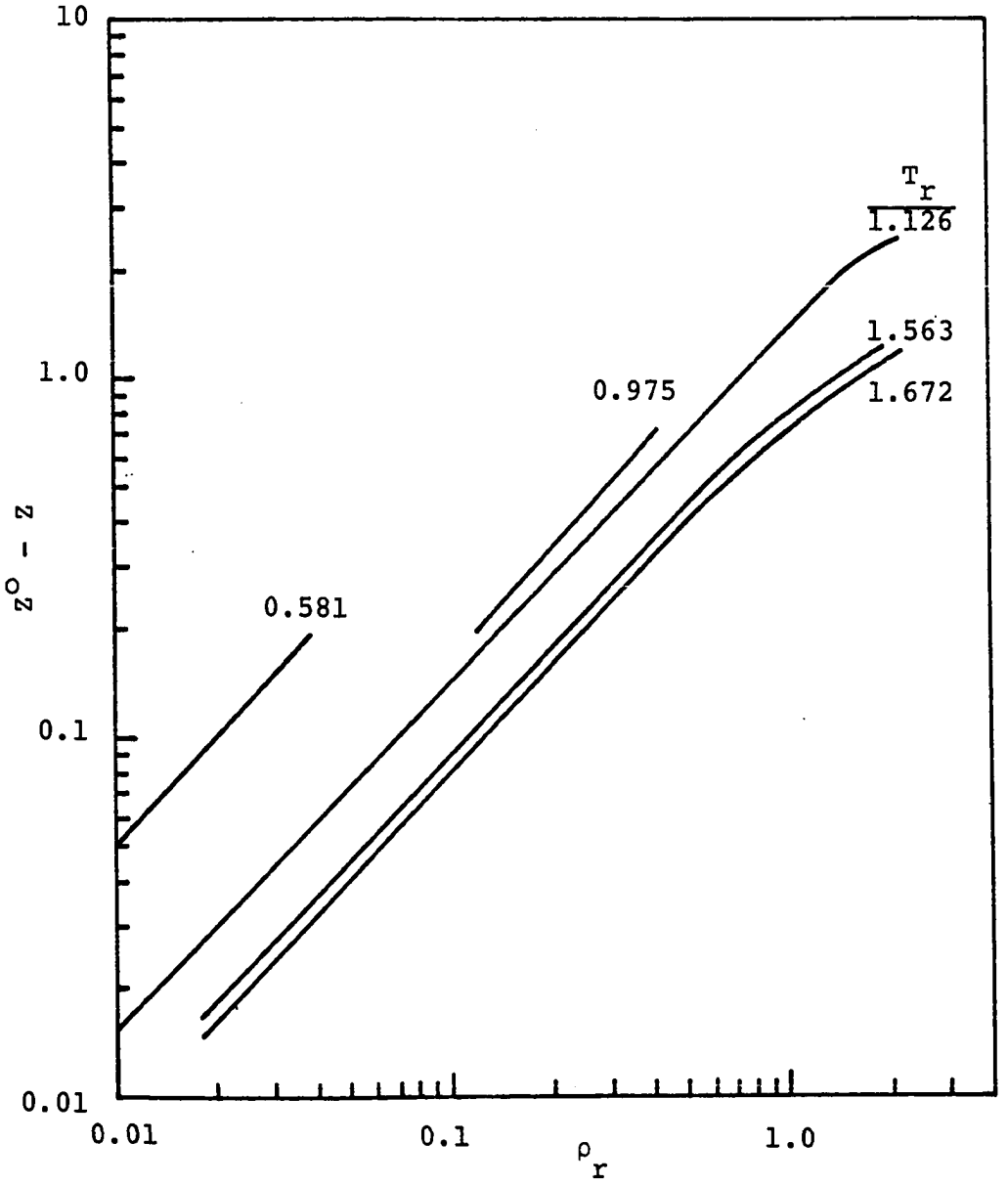


Figure III-7. Density and Temperature Dependence of $Z^O - Z$ for $C_2H_6$.

temperature decreases. The curves are linear in all regions, except downward curvature is noted for $T_r = 1.672$ at $\rho_r$ larger than 1. In Figure III-6, we plot $(\theta_3 - \theta_3^o)\rho^2$. This plot yields straight lines for all densities and temperatures. It can be noted that the value of $(\theta_3 - \theta_3^o)\rho^2$ increases with decreasing temperature, as in the case of Figure III-5. However, the trend is reversed as the critical temperature is reached. The combination of Figure III-5 and III-6 is plotted in Figure III-7. The combination gives $Z^o - Z$. Virtually, Figure III-7 is the same as Figure III-5, except that additional downward curves are observed for lower temperatures (down to $T_r = 1.126$ in the figure) at high density. Also, the decreasing of $(\theta_3 - \theta_3^o)\rho^2$ with decreasing temperature is not exhibited for $Z^o - Z$. The appearance of strong downward curvature is an indication that the third virial coefficient becomes significant at high density. The magnitude of $(\theta_3 - \theta_3^o)\rho^2$ is so small that the truncated virial equation of state after the second virial term is adequate for fluids at low density.

From the study of Figures III-5, III-6 and III-7 we conclude that it is more advantageous to correlate the combination of $(\theta_2^o - \theta_2)\rho$ and $(\theta_3 - \theta_3^o)\rho^2$ than to correlate them individually on the grounds that the unique decreasing effect of $(\theta_3 - \theta_3^o)\rho^2$ with decreasing temperature can be neglected. If now the Lennard-Jones potential is considered as a perturbation on the hard sphere potential, each of the

virial coefficients and sum of them, as seen from Figure III-7, can be expressed as a power series in the reciprocal temperature. In this work we adopt the following power series in $\rho_r$ and $T_r$ for $Z^o - Z$

$$Z^o - Z = \sum_i \sum_j \frac{(C_j \rho_r^j)_i}{T_r^i} \qquad \text{(III-36)}$$

This power series was used to correlate individually the compressibility factors of the normal paraffins $CH_4$ through $C_8H_{18}$ with i ranging from 1 to 3 and j from 1 to 4. The average absolute deviation varied from 0.4 percent for ethane to 2.0 percent for heptane. The correlation was performed by the least squares method to determine the parameters. Though the parameter values are different for each of the fluids studied, some of the parameters were commonly small or large for all paraffins. After neglecting the parameters of small effect, we arrive at

$$Z = Z^o - \frac{C_1\rho_r + C_2\rho_r^2 + C_3\rho_r^3}{T_r} - \frac{C_4\rho_r + C_5\rho_r^2 + C_6\rho_r^3 + C_7\rho_r^4}{T_r^2} - \frac{C_8\rho_r + C_{11}\rho_r^3}{T_r^3} \qquad \text{(III-37)}$$

In the subsequent process of fitting vapor pressure data to Equation III-37 to evaluate the fugacities in vapor and liquid phases, we found it necessary to add more terms of higher power in temperature. We also found that though the value of $C_{11}$ is not small in the correlation of ethane

thermodynamic property data (Table II-2 and II-6), it turned out to be small in the generalized correlation and can be neglected. After these adjustments, Equation III-37 is modified to the form

$$Z = Z^{o} - \frac{C_1\rho_r + C_2\rho_r^2 + C_3\rho_r^3}{T_r} - \frac{C_4\rho_r + C_5\rho_r^2 + C_6\rho_r^3 + C_7\rho_r^4}{T_r^2} - \frac{C_8 T_r}{T_r^3} - \frac{C_9\rho_r + C_{10}\rho_r^2}{T_r^5} \qquad \text{(III-38)}$$

The formulation in Equation III-38 is the equation of state used in this dissertation for the correlation of thermodynamic properties of pure fluids and mixtures.

Initially, the dimensionless parameters $C_1$, $C_2$, ..., $C_9$ and $C_{10}$ were all assumed to be linear functions of acentric factor in the generalized thermodynamic correlation of compounds with different molecular size.

$$C_i = C_{i1} + C_{i2}\omega \quad (i = 1, 2, \ldots, 9, 10)$$

It was found subsequently that some of the parameters require higher powers of $\omega$ for good fits of vapor pressure data, as follows

$$
\begin{aligned}
C_1 &= C_{11} + C_{12}\omega \\
C_2 &= C_{21} + C_{22}\omega + C_{23}\omega^2 \\
C_3 &= C_{31} + C_{32}\omega + C_{33}\omega^2 \\
C_4 &= C_{41} + C_{42}\omega + C_{43}\omega^3 \\
C_5 &= C_{51} + C_{52}\omega + C_{53}\omega^2 \\
C_6 &= C_{61} + C_{62}\omega \\
C_7 &= C_{71} + C_{72}\omega \\
C_8 &= C_{81}\omega + C_{82}\omega^2 \\
C_9 &= C_{91}\omega + C_{92}\omega^2 + C_{93}\omega^3 \\
C_{10} &= C_{101} + C_{102}\omega + C_{103}\omega^3
\end{aligned}
\qquad \text{(III-39)}
$$

Optimal Parameter Values from Multiproperty Analysis

In the foregoing presentation, we have formulated, based on corresponding states principle, a generalized three parameter equation of state. The remaining task is to determine its parameters from multiproperty analysis. Multiproperty regression analysis is a procedure by which a least squares fit is made simultaneously to experimental data for different types of thermodynamic properties. The mathematical framework for multiproperty analysis has been presented by Starling and Wolfe.[109] Only a few remarks will be made regarding the iteration procedure utilized in this work.

To optimize the parameters of the equation of state, the following objective function was minimized

$$\chi = \sum_i W_i \left[ \sum_j \left( 1 - \frac{(\phi_{ij})_c}{(\phi_{ij})_e} \right)^2 \right] \qquad \text{(III-40)}$$

In this relationship, $(\phi_{ij})_c$ and $(\phi_{ij})_e$ are the calculated and experimental values, respectively, at the $j^{th}$ data point for the $i^{th}$ type of thermodynamic property; $W_i$ is a weighting factor for the $i^{th}$ property. The equation of state parameters, which are to be determined by regression, enter the objective function through $(\phi_{ij})_c$. The thermodynamic properties selected for regression analysis are density, enthalpy departure, saturated vapor pressure, heat capacity and velocity of sound. The latter two type properties are data along the saturated vapor pressure curve, with weighting factors less than one.

After the thermodynamic functions, which are derived from the equation of state, are linealized with respect to each of the parameters, the curvature matrix is constructed to find the optimal parameter increments for next iteration. The Marquardt Algorithm[72] is used in this work. The diagonal elements of the matrix are multiplied by $1 + \lambda$; the value of the constant factor $\lambda$ should be chosen small enough to take advantage of the analytical solution, but large enough that $\chi$ decreases. The iteration schemes are

1. Guess initial parameter values C and compute $\chi(C)$.
2. Start initially with $\chi = 0.001$.
3. Compute $\Delta C$ from matrix inversion and evaluate $\chi(C + \Delta C)$ at the value of $\lambda$.

4. If $\chi(C + \Delta C) > \chi(C)$, increase $\lambda$ by a factor of 10 and repeat Step 3.
5. If $\chi(C + \Delta C) < \chi(C)$, decrease $\lambda$ by a factor of 10 and repeat Step 3, using the new parameter values which are obtained by adding $\Delta C$ to the current values.
6. The iteration continues until a specified convergence criterion is satisfied.

The twelve hard sphere parameters of Equation III-25 and twenty-six perturbation parameters of Equation III-39 were determined simultaneously by multiproperty analysis, using the iteration scheme outlined above. The resultant parameter values are tabulated in Table III-1.

# CHAPTER IV

## PREDICTION OF THERMODYNAMIC PROPERTIES OF PURE FLUIDS FROM GENERALIZED EQUATION OF STATE

In the development of the generalized equation of state discussed in Chapter III, we derived the thermodynamic functions from the equation of state using the fundamental thermodynamic relationships. The derived thermodynamic functions were used to correlate various types of thermodynamic data under consideration to find the optimal equation of state parameter values. In this chapter, the calculation procedures for prediction of density, using the Newton-Raphson method, are presented. The equations for prediction of fugacity, enthalpy departure, entropy departure, velocity of sound and heat capacity are derived from the equation of state for pure fluids and the basic thermodynamic relationships used are presented with the derivations. The usefulness of the derived thermodynamic functions are tested for 26 pure compounds, including paraffins, olefins, hydrogen sulfide, oxides, nitrogen, aromatics and water. The average absolute deviations of these calculated thermodynamic functions from the experimental values for each substance are tabulated in

Table IV-2 together with the temperature and pressure ranges of the data.

## Density

The equation of state presented in Equation III-38 is implicit in density. Thus, the calculation of density at given T, P conditions from the equation of state requires iterations. The Newton-Raphson scheme is used in this work. The equation of state was first expanded in a polynomial to degree eight of density $\rho$ in descending order. The first derivative of the polynomial with respect to density, required in the Newton-Raphson method, was generated by Horner's scheme[43] from the nine well established polynomial coefficients. The procedures for iteration to find real roots of a polynomial were outlined by Lapidus[62] and are used in this dissertation. A fixed value of $\Delta\rho$ (-0.001 gram mole/cc for liquid and 0.001 for the case of gas) is supplied in calculation routine. The value of pressure P is then calculated from Equation III-38, starting at $\rho = 3.4\rho_c$ gram mole/cc for liquid and $\rho = 0$ for gas, changing $\rho$ by adding $\Delta\rho$ until a change in the sign of the value of P is found. This is an indication of the rough location of a real root. By backing up one $\Delta\rho$ interval, the resultant $\rho$ is used as the starting value in the iteration. The iteration continues until the convergence criterion is satisfied.

## Fugacity

The fugacity function is defined by the equations

$$\ln f = \ln f^{o} + \frac{1}{RT}\int_{P^{o}}^{P} v\, dP \qquad \text{(IV-1)}$$

and

$$f^{o} = P^{o} \quad \text{as} \quad P^{o} \to 0$$

the integration being along an isotherm. From these equations and the equation of state, the expression of fugacity is readily obtained.

$$\ln f = \ln RT\rho + \frac{11 + 15y - 21y^{2} + 7y^{3}}{6(1-y)^{3}} - \frac{11}{6}$$

$$- \frac{1}{T_r}\left(2C_1\rho_r + \frac{3}{2}C_2\rho_r^{2} + \frac{4}{3}C_3\rho_r^{3}\right)$$

$$- \frac{1}{T_r^{2}}\left(2C_4\rho_r + \frac{3}{2}C_5\rho_r^{2} + \frac{4}{3}C_6\rho_r^{3} + \frac{5}{4}C_7\rho_r^{4}\right)$$

$$- \frac{1}{T_r^{3}}\left(2C_8\rho_r\right) - \frac{1}{T_r^{5}}\left(2C_9\rho_r + \frac{3}{2}C_{10}\rho_r^{2}\right) \qquad \text{(IV-2)}$$

For consistency in units, f is in atmospheres, $\rho$ is in gram mole/cc, T is in °K, and R = 82.0544 (cc)(atm)/(gram-mole)(°K).

## Enthalpy Departure

The fundamental equation for calculation of the enthalpy departure of any homogeneous substance when the independent variables are T and V is

$$H - H^{O} = PV - RT - \int_{V^{\infty}}^{V} P\, dV + \int_{V^{\infty}}^{V} \left[T\left(\frac{\partial P}{\partial T}\right)_V\right] dV \qquad \text{(IV-3)}$$

Starting from the equation of state by substituting the expressions of PdV and $(\partial P/\partial T)_V$ into Equation IV-3, and performing integrations between the limits of $V^{\infty}$ and V, one has the following thermodynamic function for enthalpy departure

$$\begin{aligned} H - H^{O} = RTZ - RT - RT(T\alpha') \frac{4y - 2y^2}{(1 - y)^3 \alpha} \\ - \frac{RT}{T_r}\left(C_1\rho_r + \frac{C_2\rho_r^2}{2} + \frac{C_3\rho_r^3}{3}\right) \\ - \frac{2RT}{T_r^2}\left(C_4\rho_r + \frac{C_5\rho_r^2}{2} + \frac{C_6\rho_r^3}{3} + \frac{C_7\rho_r^4}{4}\right) \\ - \frac{3RT}{T_r^3} C_8\rho_r - \frac{5RT}{T_r^5}\left(C_9\rho_r + \frac{C_{10}\rho_r^2}{2}\right) \end{aligned} \qquad \text{(IV-4)}$$

where $T\alpha' \equiv T\left(\frac{\partial \alpha}{\partial T}\right)$

$$\begin{aligned} = - \frac{1}{\rho_c}\left(\frac{B_2}{T_r} + \frac{2B_3}{T_r^2} + \frac{3B_4}{T_r^3}\right) - \frac{\omega}{\rho_c}\left(\frac{B_6}{T_r} + \frac{2B_7}{T_r^2} + \frac{3B_8}{T_r^3}\right) \\ - \frac{\omega^2}{\rho_c}\left(\frac{B_{10}}{T_r} + \frac{2B_{11}}{T_r^2} + \frac{3B_{12}}{T_r^3}\right) \end{aligned} \qquad \text{(IV-5)}$$

$$\alpha = (\rho_c a^3)/\rho_c \qquad \text{(IV-6)}$$

$(\rho_c a^3)$ has been correlated as functions of reduced temperature and acentric factor in Equation III-25.

## Entropy Departure

The entropy departure of a compound is defined by the following thermodynamic relation

$$S - S^{o} = \int_{V^{\infty}}^{V} \left(\frac{\partial P}{\partial T}\right)_{V} dV - \int_{V^{\infty}}^{V} R \, d \ln V \qquad \text{(IV-7)}$$

The thermodynamic function $(\partial P/\partial T)_V$ was derived from the equation of state and is expressed in Equation IV-11. After mathematical substitution and integrations between limits, the following equation is obtained for entropy departure

$$\begin{aligned} S - S^{o} = {} & -R \ln (\rho RT) - R \frac{4y - 3y^{2}}{(1 - y)^{2}} \\ & - \frac{2RyT\alpha'}{\alpha(1-y)^{3}} (2 - y) \\ & - \frac{R}{T_r^{2}} \left(C_4\rho_r + \frac{C_5\rho_r^{2}}{2} + \frac{C_6\rho_r^{3}}{3} + \frac{C_7\rho_r^{4}}{4}\right) \\ & - \frac{2RC_8\rho_r}{T_r^{3}} - \frac{R}{T_r^{5}} \left(4C_9\rho_r + 2C_{10}\rho_r^{2}\right) \end{aligned} \qquad \text{(IV-8)}$$

The entropy departure, derived herein, will be used for velocity of sound in the following section.

## Velocity of Sound

As already expressed in Equation II-11, the velocity of sound is thermodynamically related to the derivatives of P with respect to $\rho$, of P with respect to T and of S with

respect to T. The equation is repeated here.

$$W^2 = \left(\frac{\partial P}{\partial \rho}\right)_T + \frac{\left(\frac{\partial P}{\partial T}\right)_\rho^2 / \rho^2}{\left(\frac{\partial S}{\partial T}\right)_\rho} \qquad \text{(IV-9)}$$

The expression for each term in above equation will be derived from the equation of state.

$\underline{(\partial P/\partial \rho)_T}$

$$\left(\frac{\partial P}{\partial \rho}\right)_T = RT \frac{1 + 4y + 4y^2 - 4y^3 + y^4}{(1 - y)^4} - RT \left( \frac{2C_1\rho_r + 3C_2\rho_r^2 + 4C_3\rho_r^3}{T_r} + \frac{2C_4\rho_r + 3C_5\rho_r^2 + 4C_6\rho_r^3 + 5C_7\rho_r^4}{T_r^2} + \frac{2C_8\rho_r}{T_r^3} + \frac{2C_9\rho_r + 3C_{10}\rho_r^2}{T_r^5} \right) \qquad \text{(IV-10)}$$

$\underline{(\partial P/\partial T)_\rho/\rho}$

$$\frac{(\partial P/\partial T)_\rho}{\rho} = RZ^o + RT\alpha' \frac{Y}{\alpha} \frac{4 + 4y - 2y^2}{(1 - y)^4} + R\frac{C_4\rho_r + C_5\rho_r^2 + C_6\rho_r^3 + C_7\rho_r^4}{T_r^2} + R\frac{2C_8\rho_r}{T_r^3} + R\frac{4C_9\rho_r + 4C_{10}\rho_r^2}{T_r^5} \qquad \text{(IV-11)}$$

$(\partial S/\partial T)_\rho$

The entropy of a substance can be calculated by adding $S^o$ to the entropy departure

$$S = S^o + (S - S^o) \tag{IV-12}$$

where $S^o$ is the entropy of the substance in the ideal gas state at the given temperature and at unit pressure. Thus, the derivative of Equation IV-12 with respect to T at constant density gives two parts

$$\left(\frac{\partial S}{\partial T}\right)_\rho = \left(\frac{\partial S^o}{\partial T}\right)_\rho + \left[\frac{\partial (S - S^o)}{\partial T}\right]_\rho \tag{IV-13}$$

From thermodynamic relations for ideal gas, we have

$$\left(\frac{\partial S^o}{\partial T}\right)_\rho = \left(\frac{\partial S^o}{\partial T}\right)_P + \left(\frac{\partial S^o}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_\rho \tag{IV-14}$$

$$\left(\frac{\partial S^o}{\partial P}\right)_T = -\frac{R}{P} \tag{IV-15}$$

$$\left(\frac{\partial P}{\partial T}\right)_\rho = \frac{R}{V} \tag{IV-16}$$

By substituting Equations IV-15 and IV-16 into Equation IV-14, one obtains the following equation for the ideal gas

$$\left(\frac{\partial S^o}{\partial T}\right)_\rho = \left(\frac{\partial S^o}{\partial T}\right)_P - \frac{R}{T} \tag{IV-17}$$

From Equation IV-17 we note that the derivation of $(\partial S^o/\partial T)_\rho$ requires the derivation of $(\partial S^o/\partial T)_P$. In this report, the

correlation of $S^o$ published by Passut, et al.[83] was used to derive the expression for $(\partial S^o/\partial T)_p$. The correlation is of the following form

$$S_o = \beta_1 \ln \frac{T_R}{T_B} + 2\beta_2 (T_R - T_B) + \frac{3}{2} \beta_3 (T_R^2 - T_B^2)$$

$$+ \frac{4}{3} \beta_4 (T_R^3 - T_B^3) + \frac{5}{4} \beta_5 (T_R^4 - T_B^4) + \beta_6 \qquad \text{(IV-18)}$$

where $T_R$ is temperature in °R. $T_B$ is the base temperature for the entropy, taken at 1°R. $\beta_1$ through $\beta_6$ are a set of parameter values, characteristic of individual substances. Taking the temperature derivative of Equation IV-18 we have

$$\left(\frac{\partial S^o}{\partial T}\right)_p = \frac{\beta_1}{T_R} + 2\beta_2 + 3\beta_3 T_R + 4\beta_4 T_R^2 + 5\beta_5 T_R^3 \qquad \text{(IV-19)}$$

The derivation of $(\partial S^o/\partial T)_\rho$ is complete by subtracting R/T from Equation IV-19, thus,

$$\left(\frac{\partial S^o}{\partial T}\right)_\rho = 1.8\ M \left(\frac{\beta_1}{T_R} + 2\beta_2 + 3\beta_3 T_R + 4\beta_4 T_R^2 + 5\beta_5 T_R^3\right)$$

$$- R/T \qquad \text{(IV-20)}$$

Where M is molecular weight. 1.8 M is incorporated into Equation IV-20 to give the units of cal/gram-mole-$K^2$.

$\left[\frac{\partial (S - S^o)}{\partial T}\right]_\rho$

Since the entropy departure has been well established in Equation IV- 8, the temperature derivative of entropy

departure at constant density is readily obtained.

$$\left[\frac{\partial(S - S^{o})}{\partial T}\right]_{\rho} = -\frac{R}{T} - \frac{R\alpha'}{\alpha(1-y)^{3}}(4y - 2y^{2})$$

$$- \frac{2Ry}{\alpha(1-y)^{4}}(T\alpha'' + \alpha')(2 - 3y + y^{2})$$

$$- \frac{2Ry}{\alpha^{2}(1-y)^{4}}\alpha'(T\alpha')(5y - 2y^{2})$$

$$+ \frac{R}{TT_{r}^{2}}\left(2C_{4}\rho_{r} + C_{5}\rho_{r}^{2} + \frac{2C_{6}\rho_{r}^{3}}{3} + \frac{C_{7}\rho_{r}^{4}}{2}\right)$$

$$+ \frac{6RC_{8}\rho_{r}}{TT_{r}^{3}} + \frac{R}{TT_{r}^{5}}(20C_{9}\rho_{r} + 10C_{10}\rho_{r}^{2}) \qquad \text{(IV-21)}$$

Now that $(\partial S^{o}/\partial T)_{\rho}$ and $[\partial(S - S_{o})/\partial T]_{\rho}$ have been derived, the sum of these two functions gives the expression for $(\partial S/\partial T)_{\rho}$

$$\left(\frac{\partial S}{\partial T}\right)_{\rho} = 1.8\ M\left(\frac{\beta_{1}}{T_{R}} + 2\beta_{2} + 3\beta_{3}T_{R} + 4\beta_{4}T_{R}^{2} + 5\beta_{5}T_{R}^{3}\right)$$

$$- 2\,\frac{1.987}{T} - \frac{R\alpha'}{\alpha(1-y)^{3}}(4y - 2y^{2})$$

$$- \frac{2Ry}{\alpha(1-y)^{4}}(T\alpha'' + \alpha')(2 - 3y + y^{2})$$

$$- \frac{2Ry}{\alpha^{2}(1-y)^{4}}\alpha'(T\alpha')(5y - 2y^{2}) + \frac{R}{TT_{r}^{2}}\left(2C_{4}\rho_{r} + C_{5}\rho_{r}^{2}\right.$$

$$\left. + \frac{2C_{6}\rho_{r}^{3}}{3} + \frac{C_{7}\rho_{r}^{4}}{2}\right) + \frac{6RC_{8}\rho_{r}}{TT_{r}^{3}} + \frac{R}{TT_{r}^{5}}(20C_{9}\rho_{r}$$

$$+ 10C_{10}\rho_{r}^{2}) \qquad \text{(IV-22)}$$

## Heat Capacity

In this section, the heat capacity departure at constant pressure is derived from the equation of state. The heat capacity departure at constant pressure is defined as the change of the enthalpy departure with temperature at constant pressure

$$C_p - C_p^o = \left[\frac{\partial (H - H^o)}{\partial T}\right]_P \qquad \text{(IV-23)}$$

Since the enthalpy departure is function of temperature and density, the temperature derivative of the enthalpy departure is of the following form

$$\left[\frac{\partial (H - H^o)}{\partial T}\right]_P = \left[\frac{\partial (H - H^o)}{\partial T}\right]_\rho + \left[\frac{\partial (H - H^o)}{\partial \rho}\right]_T \left(\frac{\partial \rho}{\partial T}\right)_P \qquad \text{(IV-24)}$$

Using the identity,

$$\left(\frac{\partial \rho}{\partial T}\right)_P = - \frac{(\partial P/\partial T)_\rho}{(\partial P/\partial \rho)_T} \qquad \text{(IV-25)}$$

and substituting Equation IV-24 into Equation IV-23, we have

$$C_p - C_p^o = \left[\frac{\partial (H - H^o)}{\partial T}\right]_\rho - \left[\frac{\partial (H - H^o)}{\partial \rho}\right]_T \frac{(\partial P/\partial T)_\rho}{(\partial P/\partial \rho)_T} \qquad \text{(IV-26)}$$

The expressions for $(\partial P/\partial T)_\rho$ and $(\partial P/\partial \rho)_T$ have been derived in the previous section for velocity of sound, and are given in Equations IV-11 and IV-10, respectively. Thus, only the derivations for $[\partial (H - H^o)/\partial T]_\rho$ and $[\partial (H - H^o)/\partial \rho]_T$

are needed here to give the complete formulation of $(C_p - C_p^o)$. Taking the temperature and density derivatives of the enthalpy departure, we find

$$\left[\frac{\partial(H-H^o)}{\partial T}\right]_\rho = -R + RZ + \frac{R(T\alpha')}{\alpha}\frac{4y + 4y^2 - 2y^3}{(1-y)^4}\left(1 - \frac{T\alpha'}{\alpha}\right)$$

$$- \frac{R}{\alpha}\frac{4y - 2y^2}{(1-y)^3}\left[\frac{2B_3}{\rho_c T_r^2} + \frac{6B_4}{\rho_c T_r^3} + \frac{\omega}{\rho_c}\left(\frac{2B_7}{T_r^2} + \frac{6B_8}{T_r^3}\right)\right.$$

$$\left. + \frac{\omega^2}{\rho_c}\left(\frac{2B_{11}}{T_r^2} + \frac{6B_{12}}{T_r^3}\right) - \frac{(T\alpha')^2}{\alpha}\right]$$

$$+ \frac{R}{T_r}\left(C_1\rho_r + C_2\rho_r^2 + C_3\rho_r^3\right)$$

$$+ \frac{2R}{T_r^2}\left(2C_4\rho_r + \frac{3}{2}C_5\rho_r^2 + \frac{4}{3}C_6\rho_r^3 + \frac{5}{4}C_7\rho_r^4\right)$$

$$+ \frac{3R}{T_r^3}\left(3C_8\rho_r\right) + \frac{5R}{T_r^5}\left(5C_9\rho_r + \frac{6}{2}C_{10}\rho_r^2\right) \qquad \text{(IV-27)}$$

$$\left[\frac{\partial(H-H^o)}{\partial\rho}\right]_T = RT\frac{\partial Z}{\partial\rho} - RT(T\alpha')\frac{\pi N}{6}\frac{4 + 4y - 2y^2}{(1-y)^4}$$

$$- \frac{RT}{T_r\rho_c}\left(C_1 + C_2\rho_r + C_3\rho_r^2\right)$$

$$- \frac{2RT}{T_r^2\rho_c}\left(C_4 + C_5\rho_r + C_6\rho_r^2 + C_7\rho_r^3\right)$$

$$- \frac{3RT}{T_r^3\rho_c}C_8 - \frac{5RT}{T_r^5\rho_c}\left(C_9 + C_{10}\rho_r\right) \qquad \text{(IV-28)}$$

where

$$\frac{\partial Z}{\partial \rho} = \frac{2y(2 + 2y - y^2)}{\rho(1 - y)^4} - \frac{C_1 + 2C_2\rho_r + 3C_3\rho_r^2}{\rho_c T_r} - \frac{C_4 + 2C_5\rho_r + 3C_6\rho_r^2 + 4C_7\rho_r^3}{\rho_c T_r^2} - \frac{C_8}{\rho_c T_r^3} - \frac{C_9 + 2C_{10}\rho_r}{\rho_c T_r^5}$$

So, knowing the thermodynamic functions for each term in Equation IV-26, the heat capacity departure $(C_p - C_p^o)$ can be calculated at T, P conditions.

As seen from Equation IV-23, the heat capacity at constant pressure $C_p$ can be evaluated by adding the ideal gas heat capacity $C_p^o$ to $(C_p - C_p^o)$. In this work, $C_p^o$ is calculated according to the following equation proposed by Passult, et al.[83]

$$C_p^o = M(\beta_1 + 2\beta_2 T_R + 3\beta_3 T_R^2 + 4\beta_4 T_R^3 + 5\beta_5 T_R^4) \quad \text{(IV-29)}$$

The units of $C_p^o$ in Equation IV-29 are Btu/lb mole °R.

The heat capacity at constant pressure is related to other heat capacities by the following thermodynamic relationships. For the saturated liquid heat capacity $C_\sigma$,

$$C_\sigma = C_p - \frac{(\partial P/\partial T)_\rho}{(\partial P/\partial \rho)_T} \frac{\rho^V(H^V - H^L)}{\rho^L(\rho^L - \rho^V)} \quad \text{(IV-30)}$$

For the heat capacity at constant volume $C_v$,

$$C_V = C_p - \frac{T(\partial P/\partial T)_\rho^2}{\rho^2(\partial P/\partial \rho)_T} \qquad \text{(IV-31)}$$

The superscripts V and L refer to vapor and liquid, respectively.

## Physical Properties of Pure Fluids

The equation of state developed in this dissertation for correlating thermodynamic properties is generalized, using the three parameter corresponding states principle, in the desire that it be useful for a wide range of substances. Thus, the use of the equation of state requires the three characteristic parameters, $T_c$, $\rho_c$ and $\omega$ in addition to the given T, P conditions. The characteristic parameters are tabulated along with molecular weight for each pure fluid in Table IV-1. The values of $\omega$ in Table IV-1 are considerably different from the reported values in standard references. They are also in disagreement with the optimal values for the BWRS equation.[41] The values of $\omega$ herein were adjusted such that the present equation of state would predict thermodynamic properties with minimum deviation.

## Summary of Pure Component Property Predictions

The capability of the equation of state developed herein for predicting the thermodynamic properties of pure fluids using the equations derived in this chapter is summarized in Table IV-2. A total of 26 pure fluids are tested. The fluids include polar and non-polar compounds, paraffin,

TABLE IV-1

PHYSICAL PROPERTIES OF PURE FLUIDS

| Fluid | Critical Temp. °F | Critical Density, lb-mole/ cu.ft. | Molecular Weight | Acentric Factor |
|---|---|---|---|---|
| Methane | -116.43 | 0.6274 | 16.042 | 0.0132 |
| Ethane | 90.03 | 0.4218 | 30.068 | 0.102 |
| Propane | 206.13 | 0.3121 | 44.094 | 0.154 |
| n-Butane | 305.67 | 0.2448 | 58.12 | 0.201 |
| i-Butane | 274.96 | 0.2373 | 58.12 | 0.183 |
| n-Pentane | 385.42 | 0.2007 | 72.146 | 0.253 |
| i-Pentane | 369.00 | 0.2027 | 72.146 | 0.190 |
| n-Hexane | 453.45 | 0.1696 | 86.172 | 0.2997 |
| n-Heptane | 512.85 | 0.1465 | 100.198 | 0.353 |
| n-Octane | 563.79 | 0.1284 | 114.224 | 0.4135 |
| n-Nonane | 610.5 | 0.1150 | 128.25 | 0.515 |
| n-Decane | 651.9 | 0.1037 | 142.276 | 0.476 |
| Ethylene | 49.82 | 0.5035 | 28.05 | 0.101 |
| Propylene | 197.4 | 0.3449 | 42.08 | 0.150 |
| Benzene | 552. | 0.2401 | 78.108 | 0.218 |
| Cyclohexane | 535.6 | 0.2027 | 84.156 | 0.2155 |
| Toluene | 605.0 | 0.1924 | 92.134 | 0.260 |
| Nitric Oxide | -135.69 | 1.0764 | 30.01 | 0.485 |
| Carbon Dioxide | 87.8 | 0.6641 | 44.01 | 0.215 |
| Nitrous Oxide | 97.77 | 0.6483 | 44.02 | 0.160 |
| Ethylene Oxide | 382.71 | 0.4524 | 44.05 | 0.168 |
| Sulfur Dioxide | 315.5 | 0.5118 | 64.06 | 0.31 |
| Nitrogen | -232.6 | 0.6929 | 28.016 | 0.039 |
| Hydrogen Sulfide | 212.7 | 0.6571 | 34.076 | 0.11 |
| Methyl Chloride | 289.65 | 0.4366 | 50.49 | 0.17 |
| Water | 704.93 | 1.1148 | 18.02 | 0.375 |

TABLE IV-2

PREDICTION OF PURE FLUID THERMODYNAMIC PROPERTIES
USING GENERALIZED EQUATION OF STATE

| Fluid | Property | References | Data Point | Temp. Range °F | Press. Range psia | Avg. Abs. Dev. |
|---|---|---|---|---|---|---|
| Methane | ρ | 31,117,118 | 41 | -253/662 | 129/2325 | 0.41 |
| | f | 22,89 | 30 | -320/-116 | 0.19/669 | 0.58 |
| | ΔH | 49,129 | 39 | -250/50 | 450/2000 | 0.97 |
| | W | 79 | 13 | -244/-136 | 28/481 | 8.77 |
| | C | 116 | 9 | -235/-192 | 39/145 | 4.50 |
| Ethane | ρ | 18,86,100 | 41 | -230/310 | 14.7/10278 | 1.12 |
| | f | 18,22,100 | 41 | -270/90 | 0.0047/709 | 0.83 |
| | ΔH | 36,88,101 | 69 | -240/340 | 200/3000 | 0.78 |
| | W | 79 | 21 | -187/44 | 1.5745/410 | 4.75 |
| | C | 116 | 17 | -215/-47 | 0.37/98 | 5.02 |
| Propane | ρ | 47,100,101 | 41 | -250/526 | 14.7/2405 | 0.65 |
| | f | 18,22,100,114 | 49 | -280/206 | .000004/617 | 1.59 |
| | ΔH | 129 | 39 | -250/250 | 500/2000 | 1.51 |
| | C | 116 | 18 | -224/-46 | 0.0029/14 | 6.44 |
| n-Butane | ρ | 100,101 | 41 | -220/430 | 14.7/7000 | 0.65 |
| | f | 18,100 | 39 | -110/306 | 0.176/551 | 0.51 |
| | ΔH | 101 | 39 | 100/430 | 200/5000 | 0.81 |
| | C | 116 | 28 | -89/57 | 3.9/73.3 | 3.27 |
| i-Butane | ρ | 100,101 | 68 | -110/480 | 14.7/3000 | 2.00 |
| | f | 100,114 | 28 | -136/275 | 0.097/529 | 1.26 |
| n-Pentane | ρ | 100,101 | 41 | -200/460 | 14.7/10000 | 1.06 |
| | f | 18,22,100 | 39 | -89/385 | 0.0427/490 | 0.60 |
| | ΔH | 101 | 39 | 100/460 | 200/10000 | 1.11 |
| | W | 79 | 6 | 67/321 | 8/279 | 4.91 |
| | C | 76 | 13 | -28/80.3 | 0.606/11 | 5.08 |
| i-Pentane | ρ | 31,100,105 | 37 | -60/392 | 14.7/883 | 1.43 |
| | f | 5,100 | 31 | -123/370 | 0.014/495 | 3.27 |
| n-Hexane | ρ | 100,110 | 41 | -140/340 | 14.7/2980 | 0.74 |
| | f | 18,22,100 | 42 | -64/455 | 0.02/440 | 0.86 |
| | W | 79 | 5 | -4.3/140 | 0.26/11 | 8.70 |
| | C | 76 | 9 | 8.3/129 | 0.41/9 | 4.71 |

TABLE IV-2--Continued

| Fluid | Property | References | Data Point | Temp. Range °F | Press. Range psia | Avg. Abs. Dev. |
|---|---|---|---|---|---|---|
| n-Heptane | ρ | 100,112 | 41 | -90/460 | 14.7/3082 | 0.45 |
| | f | 22,53,100 | 32 | 6.8/497 | 0.08/350 | 0.40 |
| | W | 79 | 6 | -4.3/176 | 0.056/8.2 | 10.42 |
| | c | 76 | 16 | 71/206 | 0.75/14 | 3.07 |
| | ΔH | 38 | 17 | 512/707 | 79/2363 | 1.01 |
| n-Octane | ρ | 34,100 | 54 | -70/510 | 14.7/239 | 1.32 |
| | f | 22,80,100 | 51 | 41.5/560 | 0.07/350 | 0.64 |
| | ΔH | 64,80 | 69 | 75/600 | 200/1400 | 2.47 |
| n-Nonane | f | 100 | 15 | 100/353 | 0.18/29 | 3.56 |
| n-Decane | ρ | 101 | 32 | 100/460 | 200/6000 | 3.10 |
| Ethylene | ρ | 18,78,100 | 41 | -250/260 | 14.7/2000 | 2.71 |
| | f | 18,100,114 | 35 | -220/50 | 0.88/742 | 2.01 |
| | ΔH | 10 | 38 | -120/260 | 100/2000 | 2.35 |
| Propylene | ρ | 18,33,77,100 | 61 | -50/450 | 16/2939 | 1.80 |
| | f | 18,100,114 | 28 | -195/197 | 0.04/670 | 0.78 |
| Cyclohexane | ρ | 84 | 25 | 68/500 | 1.2/462 | 0.65 |
| | f | 84,100 | 48 | 50/520 | 0.9/531 | 0.84 |
| | ΔH | 66 | 33 | 300/680 | 200/1400 | 1.71 |
| Benzene | ρ | 82 | 63 | 464/545 | 375/923 | 2.25 |
| | f | 82,100 | 37 | 45/553 | 0.76/715 | 0.63 |
| Toluene | f | 100 | 26 | 45/280 | 0.2/30 | 0.41 |
| | ΔH | 128 | 83 | 50/650 | 50/2500 | 2.57 |
| Nitrogen | ρ | 18,111 | 41 | -321/240 | 14.7/8936 | 0.68 |
| | f | 35 | 19 | -309/-233 | 29/492 | 0.39 |
| | ΔH | 69 | 39 | -300/0 | 500/2500 | 0.76 |
| Hydrogen Sulfide | ρ | 68,95 | 41 | 40/340 | 100/2000 | 1.76 |
| | f | 55,125 | 24 | -76/213 | 14.7/1306 | 1.11 |
| Carbon Dioxide | ρ | 28 | 41 | -22/284 | 220/5580 | 1.01 |
| | f | 18 | 33 | -70/88 | 75/1070 | 0.65 |
| | ΔH | 28 | 39 | -22/284 | 441/7350 | 2.59 |
| Nitrous Oxide | ρ | 25,73 | 124 | -22/302 | 88/3233 | 1.07 |

TABLE IV-2--Continued

| Fluid | Property | References | Data Point | Temp. Range °F | Press. Range psia | Avg. Abs. Dev. |
|---|---|---|---|---|---|---|
| Sulfur Dioxide | ρ | 118,120 | 62 | -60/482 | 1.5/4408 | 1.77 |
| Methyl Chloride | ρ | 65,125 | 60 | -80/437 | 2/4408 | 3.31 |
| Ethylene Oxide | ρ | 127 | 54 | 70/370 | 22/936 | 3.56 |
| Water | ρ | 56 | 26 | 32/700 | 0.089/3094 | 4.17 |
| | f | 56 | 26 | 200/700 | 11.5/3094 | 5.83 |

olefin, naphthene and aromatic hydrocarbons and nonhydrocarbons. Total 1150 data points for density ($\rho$), 673 points for vapor pressure data (f), 543 points for enthalpy departure ($\Delta H$), 51 data points for velocity of sound (W) and 110 data points for saturated heat capacity (C) were included in the test. The data points cover wide ranges of temperature and pressure, with the lowest temperature of -320°F for methane and nitrogen and the highest pressure of 10,278 psia for ethane. The deviations are reported in average absolute deviation percent for each pure fluid for each property, except the enthalpy departure, which is in Btu/lb. The deviations are listed in the last column of the table. The overall average absolute deviations are 1.66 percent for $\rho$, 1.21 percent for f, 1.67 Btu/lb for $\Delta H$, 6.84 percent for W and 4.46 percent for C. The deviations in $\rho$, f and $\Delta H$ could have been smaller without W and C being included in the regression. The seemingly large deviations in velocity of sound and heat capacity are due partly to the ideal entropy value calculated from Equation IV-18. Artificial manipulation was made to change the value of $(\partial S^{o}/\partial T)$ in Equation IV-20 and, consequently, changes in the deviations of W and C were noted. The multiplication factor of 1.8 in Equation IV-20 was taken off purposely and the deviations then decreased to 2.8 percent and 6.3 percent for n-$C_6H_{14}$ and n-$C_7H_{16}$, respectively. This is an indication that the correlation of ideal entropy in Equation IV-18 is accurate, yet $(\partial S^{o}/\partial T)$ in Equation IV-20 might be in error.

The equation of state was developed using only data for the normal paraffins methane through heptane, with 89 points for density, 81 for vapor pressure data, 70 for enthalpy data, 51 for velocity of sound and 57 for saturated heat capacity being included in the regression for determining the optimal equation of state parameter values. The consistent accuracy of predictions for wide classes of fluids indicates that the properties of other fluids can be predicted with confidence.

# CHAPTER V

## PREDICTION OF MIXTURE THERMODYNAMIC PROPERTIES USING CORRESPONDING STATES PRINCIPLE I

In Chapter IV we have used the generalized equation of state to predict the thermodynamic properties of 26 pure fluids with accuracy more than adequate for engineering calculations. This was expected since the equation of state was developed, using solely thermodynamic data of pure fluids. Industrial fluids in the chemical process industry are mostly mixtures. It is natural to ask how accurate the equation of state is for mixtures. This chapter and Chapter VI are devoted to the extension of the equation of state to mixtures.

For applications of an equation of state to mixtures, there are two possible routes. The first method is to use rules for calculating pseudo characterization parameters for $T_c$, $v_c$ and $\omega$ for the mixtures. The second method is to assume the unreduced mixture parameters $Q_k$ are functions of mole fractions and pure component parameters $C_k$. To distinguish these two methods, the first one is called corresponding states principle I (CSP I) and the second, corresponding states principle II (CSP II). In this chapter, only CSP I is described. The application of CSP II to mixtures,

particularly for vapor-liquid calculations, will be illustrated in Chapter VI.

The theorem of corresponding states, when used with the pseudocritical concept, forms one of the most widely used techniques in industry for the prediction of the thermodynamic properties of mixtures over wide ranges of conditions. A review of the corresponding states principle was presented by Leland, et al.[63] with 150 references cited.

As in the case of pure fluids, the use of Equation III-38 for a mixture requires values of $T_c$, $v_c$ and $\omega$ for the mixture in interest. Experimental values of $T_c$, $v_c$ and $\omega$ of mixtures at different compositions are rare. Furthermore, unlike the case of pure fluids, the values of $T_r$ and $\rho_r$, when reduced by the experimental $T_c$ and $\rho_c$ of the mixture, generally will not give good predictions of the thermodynamic properties for the mixture. Instead, the values of $T_r$ and $\rho_r$, when reduced by appropriate pseudocritical properties, give satisfactory results. The pseudocritical concept is based on the supposition that a single pure fluid may exist which possesses the same properties as the mixture. The critical properties of this pure fluid are then the proper pseudocritical properties of the mixture.

The pseudocritical concept was first introduced by Kay.[52] In Kay's rules the pseudocritical temperature and pressure are taken as mole-fraction averages of pure component criticals. For the past 35 years, other rules, more complex

but generally more accurate, have appeared in the literature.

The following set of equations were used in this section for calculating pseudocritical properties and acentric factors for mixtures.

$$T_c = \sum_{i=1}^{NC} \sum_{j=1}^{NC} x_i \, x_j \, T_{c_{ij}} \tag{V-1}$$

$$v_c = \sum_{i=1}^{NC} \sum_{j=1}^{NC} x_i \, x_j \, v_{c_{ij}} \tag{V-2}$$

$$\omega = \sum_{i=1}^{NC} \sum_{j=1}^{NC} x_i \, x_j \, \omega_{ij} \tag{V-3}$$

where $x_i$ is the mole fraction of $i^{th}$ component in the mixture.

$$T_{c_{ij}} \quad (i = j) = T_{c_i} \tag{V-4}$$

$$T_{c_{ij}} \quad (i \neq j) = \frac{1}{2} \left(T_{c_i} + T_{c_j}\right) K_{ij} \tag{V-5}$$

$$v_{c_{ij}} \quad (i = j) = v_{c_i} \tag{V-6}$$

$$v_{c_{ij}} \quad (i \neq j) = \frac{1}{2} \left(v_{c_i} + v_{c_j}\right) \tag{V-7}$$

$$\omega_{ij} \quad (i = j) = \omega_i \tag{V-8}$$

$$\omega_{ij} \quad (i \neq j) = \left(\omega_i \, \omega_j\right)^{1/2} \tag{V-9}$$

The parameter $K_{ij}$ is an empirical interaction coefficient which is characteristic of the i-j interaction. The values of $K_{ij}$ for binary systems were published by Barner.[7] Though the mixing rules for $v_{c_{ij}}$ and $\omega_{ij}$ by Barner are different from those proposed herein, the values of $K_{ij}$ presented by Barner can be used either directly or slightly modified for Equation V-5. In the past, attention has been directed toward the formulation of $T_{c_{ij}}$ in efforts to correlate the thermodynamic properties of mixtures. The use of the geometric mean rule correction was proposed by Chueh and Prausnitz[23]

$$T_{c_{ij}} = (T_{c_i} T_{c_j})^{1/2} (1 - k_{ij}) \qquad \text{(V-10)}$$

Again, $k_{ij}$ is an empirical interaction coefficient, determined from second virial coefficients. The values of $k_{ij}$ for some binary systems are tabulated in the literature. The values of $k_{ij}$ are different from those of $K_{ij}$. We have chosen Equation V-5 for CSP I in that, as mentioned earlier, the values of $K_{ij}$ available in the literature can be used either directly for some binaries or slightly modified for some systems to yield better prediction of mixture density and enthalpy. It was found that the use of Equation V-10 along with the original values of $k_{ij}$ results in calculated mixture enthalpies which are much smaller than the experimental values. Of course, $k_{ij}$ can be modified to adjust the calculated mixture properties if Equation V-10 is used. However, the modification was much larger than that of $K_{ij}$. The optimal values

for $k_{ij}$ for Equation V-10 were negative, in contrast to the positive values reported by Cheuh, et al.

Using the mixing rules for CSP I, as formulated in Equations V-1 to V-9, the equation of state was utilized to calculate mixture densities and enthalpies. The results are presented in Table V-1 and Table V-2, respectively. Also, the $K_{ij}$ values are listed at the bottom of each table.

Table V-1 summarizes the results of mixture density predictions for three binaries of nine different compositions at temperatures from -238°F to 477°F and pressures from 50 to 5000 psia. The total number of data points was 209, with an average absolute deviation from the experimental data of 1.37 percent. The data points selected for the binaries of $C_2H_6$-$nC_4H_{10}$ and $C_2H_6$-$nC_7H_{16}$ are at phase boundaries. The results indicate that the generalized equation of state, which was originally developed from pure component data, can adequately predict densities of mixtures even with quite different molecular size.

Tabulated in Table V-2 are the results of enthalpy departure predictions for 22 mixtures, either binary or ternary systems. The temperature ranges from -250°F to 680°F and pressure ranges from 50 psia to 2500 psia. The total number of data points was 1239 with an average absolute deviation of 2.09 Btu/lb. The results show that the generalized equation of state can be extended to mixtures of different chemical nature, such as paraffin-aromatic systems. The

TABLE V-1

PREDICTION OF MIXTURE DENSITIES USING CORRESPONDING STATES PRINCIPLE I

| System Composition (mole %) | Ref. | Data Points | Temp. Range °F | Press. Range psia | Avg. Abs. Dev. % |
|---|---|---|---|---|---|
| $CH_4$ - $C_3H_8$ | 48 | | | | |
| 75.3-24.7 | | 24 | -238/32 | 1000/5000 | 1.14 |
| 50.0-50.0 | | 27 | -184/32 | 500/5000 | 0.76 |
| 22.1-77.9 | | 25 | -184/32 | 500/5000 | 0.72 |
| $C_2H_6$ - $nC_4H_{10}$ | 54 | | | | |
| 82.2-17.8 | | 22 | 24.7/157 | 75/750 | 0.79 |
| 45.1-54.9 | | 24 | 33.0/242 | 75/725 | 1.24 |
| 17.5-82.5 | | 24 | 43.5/280 | 75/575 | 2.35 |
| $C_2H_6$ - $nC_7H_{16}$ | 53 | | | | |
| 77.1-22.9 | | 21 | 45/350 | 100/1250 | 1.97 |
| 58.7-41.3 | | 20 | 36/413 | 50/1150 | 2.00 |
| 26.5-73.5 | | 24 | 52/477 | 50/700 | 1.74 |

Interaction parameter values $K_{ij}$. Barner's values are included in parentheses if different.

| | | |
|---|---|---|
| $CH_4$ - $C_3H_8$ | 1.02 | (1.07) |
| $C_2H_6$ - $nC_4H_{10}$ | 1.05 | (1.03) |
| $C_2H_6$ - $nC_7H_{16}$ | 1.13 | |

TABLE V-2

PREDICTION OF MIXTURE ENTHALPIES USING CORRESPONDING STATES PRINCIPLE I

| System Composition (mole %) | Ref. | Data Points | Temp Range °F | Press. Range psia | Avg. Abs. Dev. Btu/lb |
|---|---|---|---|---|---|
| $CH_4$ - $N_2$ | 73 | | | | |
| 56.6-43.4 | | 54 | -250/250 | 250/2000 | 0.84 |
| $CH_4$ - $C_3H_8$ | | | | | |
| 94.8- 5.2 | 13,70 | 25 | -250/300 | 250/2000 | 1.31 |
| 88.3-11.7 | 73 | 47 | -250/250 | 250/2000 | 1.44 |
| 72.0-28.0 | 73 | 45 | -250/250 | 250/2000 | 1.60 |
| 49.4-50.6 | 129 | 45 | -250/250 | 250/2000 | 2.73 |
| 23.4-76.6 | 129 | 50 | -250/250 | 250/2000 | 3.29 |
| $C_2H_6$ - $C_3H_8$ | 88 | | | | |
| 76.3-23.7 | | 29 | -240/240 | 250/2000 | 0.90 |
| 49.8-50.2 | | 28 | -240/240 | 250/2000 | 1.25 |
| 27.6-72.4 | | 17 | -240/240 | 250/2000 | 1.40 |
| $CH_4$ - Toluene | 49 | | | | |
| 50.0-50.0 | | 33 | 300/600 | 50/2500 | 0.97 |
| $CH_4$-$C_2H_6$-$C_3H_8$ | 37 | | | | |
| 36.6-31.1-32.8 | | 28 | -240/240 | 250/2000 | 1.92 |
| $nC_5H_{12}$ - $C_6H_{12}$ | 66 | | | | |
| 79.3-20.7 | | 115 | 280/680 | 200/1400 | 1.50 |
| 61.2-38.8 | | 118 | 280/680 | 200/1400 | 1.75 |
| 38.5-61.5 | | 115 | 300/680 | 200/1400 | 1.81 |
| 19.7-80.3 | | 108 | 400/680 | 200/1400 | 3.45 |

TABLE V-2--Continued

| System Composition (mole %) | Ref. | Data Points | Temp. Range °F | Press. Range psia | Avg. Abs. Dev. Btu/lb |
|---|---|---|---|---|---|
| $nC_5H_{12}$-$C_6H_{12}$-$C_6H_6$ | | | | | |
| | 64 | | | | |
| 20.0-20.2-59.8 | | 43 | 380/600 | 200/1400 | 3.65 |
| 33.3-33.4-33.3 | | 40 | 340/600 | 200/1400 | 2.87 |
| 60.1-20.0-19.9 | | 59 | 320/600 | 200/1400 | 2.56 |
| $nC_5H_{12}$-$nC_8H_{18}$ | 65 | | | | |
| 80.9-19.1 | | 66 | 75/600 | 200/1400 | 3.08 |
| 59.7-40.3 | | 66 | 75/600 | 200/1400 | 2.30 |
| 39.2-60.8 | | 47 | 75/600 | 200/1400 | 2.78 |
| 21.8-78.2 | | 61 | 75/600 | 200/1400 | 2.94 |

Interaction parameter values $K_{ij}$. Barner's values are included in parentheses if different.

| | | | | | |
|---|---|---|---|---|---|
| $CH_4$-$N_2$ | 0.97 | | $nC_5H_{12}$-$C_6H_6$ | 0.95 | |
| $CH_4$-$C_2H_6$ | 1.04 | (1.03) | $nC_5H_{12}$-$C_6H_{12}$ | 1.01 | (1.0) |
| $CH_4$-$C_3H_8$ | 1.10 | (1.07) | $nC_5H_{12}$-$nC_8H_{18}$ | 1.03 | (1.02) |
| $CH_4$-toluene | 1.26 | | $C_6H_6$-$C_6H_{12}$ | 0.93 | |
| $C_2H_6$-$C_3H_8$ | 1.01 | (1.02) | | | |

summary in Table V-2 also indicates that extension to ternary systems are applicable, using only binary interaction parameter constants.

# CHAPTER VI

## PREDICTION OF MIXTURE THERMODYNAMIC PROPERTIES USING CORRESPONDING STATES PRINCIPLE II

In Chapter V we have extended the equation of state to mixtures for predicting density and enthalpy departure, using corresponding states principle I. CSP I is convenient to use, since it utilizes the equation of state for pure fluids directly, without any revision, and requires only mixing rules for $v_c$, $T_c$ and $\omega$ of the mixture of interest. However, the application of CSP I to vapor-liquid equilibrium prediction was less successful than in the prediction of bulk properties. Accurate prediction of partial molar properties and phase equilibrium requires accurate dependence of the properties on composition. The composition dependence of these properties occurs through the composition dependence of the equation of state parameters which characterize the fluids. This approach is different from CSP I in that the composition dependence of thermodynamic properties occurs through the characteristic constants of $v_c$, $T_c$ and $\omega$ in CSP I.

### Mixture Equation of State

The equation of state in Equation III-38 can be rewritten in the unreduced form, so that it can be treated

by the corresponding state principle II for mixtures.

$$P = \frac{RT}{v}\frac{1 + y + y^2 - y^3}{(1 - y)^3} - R\left(\frac{Q_1}{v^2} + \frac{Q_2}{v^3} + \frac{Q_3}{v^4}\right)$$

$$- \frac{R}{T}\left(\frac{Q_4}{v^2} + \frac{Q_5}{v^3} + \frac{Q_6}{v^4} + \frac{Q_7}{v^5}\right) - \frac{R}{T^2}\left(\frac{Q_8}{v^2}\right)$$

$$- \frac{R}{T^4}\left(\frac{Q_9}{v^2} + \frac{Q_{10}}{v^3}\right) \qquad \text{(VI-1)}$$

where the unreduced parameters $Q_1$, $Q_2$, ..., $Q_9$ and $Q_{10}$ of the perturbation are

$$Q_1 = \frac{C_1 T_c}{\rho_c} = (C_{11} + C_{12}\omega)\frac{T_c}{\rho_c}$$

$$Q_2 = \frac{C_2 T_c}{\rho_c^2} = (C_{21} + C_{22}\omega + C_{23}\omega^2)\frac{T_c}{\rho_c^2}$$

$$Q_3 = \frac{C_3 T_c}{\rho_c^3} = (C_{31} + C_{32}\omega + C_{33}\omega^2)\frac{T_c}{\rho_c^3}$$

$$Q_4 = \frac{C_4 T_c^2}{\rho_c} = (C_{41} + C_{42}\omega + C_{43}\omega^3)\frac{T_c^2}{\rho_c}$$

$$Q_5 = \frac{C_5 T_c^2}{\rho_c^2} = (C_{51} + C_{52}\omega + C_{53}\omega^2)\frac{T_c^2}{\rho_c^2}$$

$$Q_6 = \frac{C_6 T_c^2}{\rho_c^3} = (C_{61} + C_{62}\omega)\frac{T_c^2}{\rho_c^3}$$

$$Q_7 = \frac{C_7 T_c^2}{\rho_c^4} = (C_{71} + C_{72}\omega)\frac{T_c^2}{\rho_c^4}$$

$$Q_8 = \frac{C_8 T_c^3}{\rho_c} = (C_{81}\omega + C_{82}\omega^2)\frac{T_c^3}{\rho_c}$$

$$Q_9 = \frac{C_9 T_c^5}{\rho_c} = (C_{91}\omega + C_{92}\omega^2 + C_{93}\omega^3)\ \frac{T_c^5}{\rho_c}$$

$$Q_{10} = \frac{C_{10} T_c^5}{\rho_c^2} = (C_{101} + C_{102}\omega + C_{103}\omega^3)\ \frac{T_c^5}{\rho_c^2} \qquad \text{(VI-2)}$$

Equations VI-1 and VI-2 apply to pure fluids as well as mixtures. In the case of mixture, we need mixing rules for $\alpha$ and $Q_1$, etc. For a mixture containing NC components,

$$\alpha = \sum_{i=1}^{NC} \sum_{j=1}^{NC} x_i\, x_j\, \alpha_{ij}$$

$$Q_1 = \sum_i^{NC} \sum_j^{NC} x_i x_j\, T_{c_{ij}}\, v_{c_{ij}}\, (C_{11} + C_{12}\omega_{ij})$$

$$Q_4 = \sum_i^{NC} \sum_j^{NC} x_i\, x_j\, T_{c_{ij}}^2\, v_{c_{ij}}\, (C_{41} + C_{42}\omega_{ij} + C_{43}\omega_{ij}^3)$$

$$Q_8 = \sum_i^{NC} \sum_j^{NC} x_i\, x_j\, T_{c_{ij}}^3\, v_{c_{ij}}\, (C_{81}\omega_{ij} + C_{82}\omega_{ij}^2)$$

$$Q_9 = \sum_i^{NC} \sum_j^{NC} x_i\, x_j\, T_{c_{ij}}^5\, v_{c_{ij}}\, (C_{91}\omega_{ij} + C_{92}\omega_{ij}^2 + C_{93}\omega_{ij}^3)$$

$$Q_2 = C_{21}\left[\sum_i^{NC} x_i\, (T_{c_i}\, v_{c_i}^2)^{1/3}\right]^3 + C_{22}\left[\sum_i^{NC} x_i (T_{c_i}\, v_{c_i}^2\, \omega_i)^{1/3}\right]^3$$

$$+ C_{23}\left[\sum_i^{NC} x_i\, (T_{c_i}\, v_{c_i}^2\, \omega_i^2)^{1/3}\right]^3$$

$$Q_5 = C_{51}\left[\sum_i^{NC} x_i\, (T_{c_i}^2\, v_{c_i}^2)^{1/3}\right]^3 + C_{52}\left[\sum_i^{NC} x_i (T_{c_i}^2\, v_{c_i}^2\, \omega_i)^{1/3}\right]^3$$

$$+ C_{53}\left[\sum_i^{NC} x_i\, (T_{c_i}^2\, v_{c_i}^2\, \omega_i^2)^{1/3}\right]^3$$

$$Q_{10} = C_{101} \left[\sum_{i}^{NC} x_i \left(T_{c_i}^5 \, v_{c_i}^2\right)^{1/3}\right]^3$$

$$+ C_{102} \left[\sum_{i=1}^{NC} x_i \left(T_{c_i}^5 \, v_{c_i}^2 \, \omega_i\right)^{1/3}\right]^3$$

$$+ C_{103} \left[\sum_{i=1}^{NC} x_i \left(T_{c_i}^5 \, v_{c_i}^2 \, \omega_i^3\right)^{1/3}\right]^3$$

$$Q_3 = C_{31} \left[\sum_{i}^{NC} x_i \left(T_{c_i} \, v_{c_i}^3\right)^{1/4}\right]^4 + C_{32} \left[\sum_{i}^{NC} x_i \left(T_{c_i} v_{c_i}^3 \omega_i\right)^{1/4}\right]^4$$

$$+ C_{33} \left[\sum_{i=1}^{NC} x_i \left(T_{c_i} \, v_{c_i}^3 \, \omega_i^2\right)^{1/4}\right]^4$$

$$Q_6 = C_{61} \left[\sum_{i=1}^{NC} x_i \left(T_{c_i}^2 \, v_{c_i}^3\right)^{1/4}\right]^4 + C_{62} \left[\sum_{i=1}^{NC} x_i \left(T_{c_i}^2 v_{c_i}^3 \omega_i\right)^{1/4}\right]^4$$

$$Q_7 = C_{71} \left[\sum_{i=1}^{NC} x_i \left(T_{c_i}^2 \, v_{c_i}^4\right)^{1/5}\right]^5 + C_{72} \left[\sum_{i=1}^{NC} x_i \left(T_{c_i}^2 v_{c_i}^4 \omega_i\right)^{1/5}\right]^5$$

The mixing rules for $\alpha$, $Q_1$, $Q_2$, ..., $Q_9$ and $Q_{10}$ in the above eleven equations are denoted Equation VI-3, where

$$\alpha_{ij} \quad (i = j) = \alpha_i$$

$$\alpha_{ij} \quad (i \neq j) = \frac{1}{2} (\alpha_i + \alpha_j)(1 - n_{ij})$$

$$T_{c_{ij}} \quad (i = j) = T_{c_i}$$

$$T_{c_{ij}} \quad (i \neq j) = (T_{c_i} \, T_{c_j})^{1/2} \, (1 - k_{ij})$$

$$v_{c_{ij}} \quad (i = j) = v_{c_i}$$

$$v_{c_{ij}} \quad (i \neq j) = (v_{c_i} \; v_{c_j})^{1/2} \; (1 - \ell_{ij})$$

$$\omega_{ij} \quad (i = j) = \omega_i$$

$$\omega_{ij} \quad (i \neq j) = (\omega_i \; \omega_j)^{1/2} \; (1 - m_{ij}) \qquad \text{(VI-4)}$$

The interaction parameters between species "i" and "j", $k_{ij}$, $\ell_{ij}$, $m_{ij}$ and $n_{ij}$, are measures of deviations from ideal solution behavior due to the interaction between $i^{th}$ and $j^{th}$ components. Though small in magnitude, the interaction parameters play an important role in improvement of the accuracy of mixture thermodynamic property predictions. The improvement is even more significant for vapor-liquid equilibrium calculations. Unlike the case of CSP I, the use of CSP II requires four interaction parameters, as demonstrated in Equation VI-4. Furthermore, a preliminary determination of all four parameters for the methane-propane system indicated that the parameter value for $k_{ij}$ was uniquely different from values available in the literature.[15,23,41] This is contrary to $K_{ij}$, which can be estimated with confidence from Barner's table. Therefore, a comprehensive determination of the parameter values for binary systems is necessary to make the equation of state through CSP II applicable to mixtures. The interaction parameter values are valid exclusively for the equation of state proposed in this dissertation.

The early stages of investigation revealed that vapor-liquid equilibrium predictions are most sensitive to

$n_{ij}$. Gunn[40] and Robinson[99] have pointed out that the values of $\ell_{ij}$ and $m_{ij}$ are very small compared to the value of $k_{ij}$. Hence, the values of both $\ell_{ij}$ and $m_{ij}$ were set at zero in this early work. The determination of two interaction parameters instead of four also saves computing time substantially.

## Determination of Optimal Interaction Parameter Values

The interaction parameter values were determined from experimental data. The mixture thermodynamic properties of interest are density, enthalpy departure and vapor-liquid equilibrium. Therefore, in order to have equally good correlation of all types of properties, experimental mixture data for all properties should be included to determine the optimal interaction parameter values. Fortunately, the BWRS results have concluded that the sensitivity of density and enthalpy to $k_{ij}$ is small. In addition, CSP II is devised particularly for vapor-liquid calculations. Therefore, only vapor-liquid equilibrium data for binary systems were used in the determination of optimal parameter values. Accordingly, the following objective function was minimized.

$$\chi = \sum_{i}^{NC} \sum_{j}^{NP} \left[1 - \frac{(K_{ij})_c}{(K_{ij})_e}\right]^2 \qquad \text{(VI-5)}$$

where $(K_{ij})_c$ and $(K_{ij})_e$ are the calculated and experimental K values, respectively, at the $j^{th}$ point for $i^{th}$ component in the mixture. The objective function depends upon not only the mathematical model through $(K_{ij})_c$ but also the

selection of experimental data and the number of data points used.

The objective function is minimized using the gradient-search method of least squares.[12] All the parameters $k_{ij}$ and $n_{ij}$ are incremented simultaneously, with the relative magnitude adjusted so that the resultant direction of travel in parameter space is along the direction of maximum variation of $\chi$.

Mathematically, the gradient search method for determining parameter values can be summarized in the following equations

$$(\nabla\chi)_n = \frac{\partial\chi}{\partial c_n} \simeq \frac{\chi(c_n + f\Delta c_n) - \chi(c_n)}{f\Delta c_n} \qquad \text{(VI-6)}$$

$$\gamma_n = \frac{(\partial\chi/\partial c_n)\ \Delta c_n}{\sum_{k=1}^{2} \left(\frac{\partial\chi}{\partial c_k}\ \Delta c_k\right)^2} \qquad \text{(VI-7)}$$

$$\delta c_n = -\gamma_n\ \Delta c_n \qquad \text{(VI-8)}$$

In these expressions, we use the notation $c_1$ and $c_2$ to represent $k_{ij}$ and $n_{ij}$, respectively. The calculation procedures for arriving at $\delta c_n$ are summarized in the following paragraphs.

Initiate the procedure by guessing $c_n$ and $\Delta c_n$. The value of the objective function $\chi$ is computed from Equation VI-5 at this choice of $c_n$ and is denoted $\chi(1)$. The variation of $\chi$ in the immediate neighborhood is sampled according to

Equation VI-6 with f = 0.1. Then, the gradient components can be calculated from Equation VI-7. The value of $\chi$ at the first search points, $c_n + 0.1\Delta c_n$, is denoted $\chi(2)$. Since the gradient components are already known, the searching vector $\delta c_n$ can be evaluated from Equation VI-8 accordingly.

The size of the step $\Delta c_n$ should be tested. If the value of $\chi$ at $c_n + \delta c_n$ is larger than that at $c_n$, the magnitude of all step size $\Delta c_n$ are cut in half and the gradient recomputed. The parameters $c_n$ are then incremented by $0.1\ \delta c_n$ until the value of $\chi$ starts to increase. After each increment, if $\chi$ has not increased, the previous values of $\chi$ are relabelled so that $\chi(1)$, $\chi(2)$, and $\chi(3)$ are always the last three evaluations of $\chi$.

When the minimum in $\chi$ along the gradient is straddled, as detected by an increase in $\chi$, parabolic interpolation to find parameter values is computed from the following formula

$$c_n(\text{optimal}) = c_n(3) - \Delta c_n \left[\frac{\chi(3) - \chi(2)}{\chi(3) - 2\chi(2) + \chi(1)} + \frac{1}{2}\right] \qquad \text{(VI-9)}$$

Then, the value of $\chi$ at the final point is evaluated. The examination of the change in $\chi$ from the previous iteration decides whether another iteration along the new gradient is advisable.

Following the iteration scheme just outlined in the above, we have determined $k_{ij}$ and $n_{ij}$ for 33 binary systems, using the experimental vapor-liquid equilibrium data which

are tabulated in Table VI-2. The optimal values of $k_{ij}$ and $n_{ij}$ are presented in Table VI-1.

Thermodynamic Functions of Mixtures for CSP II

The thermodynamic functions derived from the equation of state for pure fluids in Chapter III can be used directly for mixtures, if the corresponding states principle I is utilized. The only exception is that the expression for vapor-liquid equilibrium should be rederived. In order to apply corresponding states principle II to mixtures, all thermodynamic functions should be rederived from the unreduced equation of state, using the notation involving $Q_k$ as in Equation VI-1.

The density calculation subroutine for pure fluids and CSP I can be used for CSP II by substituting $Q_i$ for the corresponding $C_i$ (i = 1, 2, ..., 9, 10). Similarly, the equation for the enthalpy departure for mixtures following CSP II is of the same form as pure fluids

$$H - H^{O} = RTZ - RT - RT\,(T\alpha')\,\frac{4y - 2y^2}{\alpha(1-y)^3}$$
$$- \frac{RT}{T}\left(Q_1\rho + \frac{Q_2}{2}\rho^2 + \frac{Q_3}{3}\rho^3\right)$$
$$- \frac{2RT}{T^2}\left(Q_4\rho + \frac{Q_5}{2}\rho^2 + \frac{Q_6}{3}\rho^3 + \frac{Q_7}{4}\rho^4\right)$$
$$- \frac{3RT}{T}Q_8\rho - \frac{5RT}{T^5}\left(Q_9\rho + \frac{Q_{10}}{2}\rho^2\right) \qquad \text{(VI-10)}$$

TABLE VI-1

INTERACTION PARAMETER VALUES OF $k_{ij}$ AND $n_{ij}$ FOR CORRESPONDING STATES PRINCIPLE II[1]

| System i | System j | $k_{ij}$ | $n_{ij}$ |
|---|---|---|---|
| Methane | Ethane | 0.000284 | 0.020057 |
| | Propane | 0.007682 | 0.058532 |
| | n-Butane | 0.000264 | 0.079954 |
| | n-Pentane | 0.000259 | 0.009983 |
| | i-Pentane | 0.000241 | 0.039904 |
| | n-Heptane | 0.000240 | 0.087790 |
| | n-Octane | 0.000240 | 0.087791 |
| Ethane | Propane | 0.057257 | 0.090290 |
| | n-Butane | 0.000058 | 0.012758 |
| | n-Pentane | -0.007886 | 0.020508 |
| | n-Hexane | -0.010449 | 0.039903 |
| | n-Heptane | -0.010117 | 0.000020 |
| | i-Butane | -0.005490 | 0.002144 |
| Propane | i-Butane | 0.000320 | 0.009980 |
| | n-Pentane | 0.000097 | 0.003129 |
| n-Butane | n-Heptane | -0.000299 | 0.002879 |
| n-Pentane | n-Heptane | -0.000247 | 0.000043 |
| Nitrogen | Methane | 0.002120 | 0.000029 |
| | Ethane | 0.001976 | 0.000115 |
| | n-Butane | 0.001642 | 0.009945 |
| | n-Hexane | 0.001493 | 0.039886 |
| | n-Heptane | 0.001453 | 0.079721 |
| | Carbon Dioxide | 0.000280 | -0.000005 |
| Hydrogen Sulfide | Methane | 0.000301 | -0.009989 |
| | Propane | 0.007554 | 0.004313 |
| | n-Pentane | -0.018836 | 0.005006 |
| Carbon Dioxide | Methane | 0.000289 | -0.009987 |
| | Ethane | 0.000293 | -0.009994 |
| | Propane | 0.000306 | -0.021976 |
| | n-Butane | 0.000311 | -0.000001 |
| | n-Pentane | 0.000314 | 0.009999 |
| | Hydrogen Sulfide | 0.000306 | -0.019978 |
| | i-Butane | 0.000330 | -0.009980 |

TABLE VI-2

SUMMARY OF RESULTS OF BINARY K-VALUES

| Component 1 | Component 2 | Ref. | Data Pts. | Temp. Range (°F) | Press. Range (psia) | Avg. Abs. Dev. % K-Value 1 | Avg. Abs. Dev. % K-Value 2 |
|---|---|---|---|---|---|---|---|
| $CH_4$ | - $C_2H_6$ | 126 | 18 | -200/-100 | 27/740 | 6.10 | 5.57 |
| | $C_3H_8$ | 89,126 | 19 | -150/-75 | 150/939 | 4.00 | 13.07 |
| | $nC_4H_{10}$ | 50 | 17 | -140/50 | 229/1597 | 4.53 | 16.80 |
| | $nC_5H_{12}$ | 90 | 9 | 220/220 | 1001/1999 | 16.38 | 3.45 |
| | $iC_5H_{12}$ | 90 | 21 | 160/280 | 499/2191 | 15.54 | 5.60 |
| | $nC_7H_{16}$ | 91 | 19 | 40/460 | 200/3500 | 11.95 | 17.34 |
| | $nC_8H_{18}$ | 57 | 21 | 77/302 | 147/1029 | 10.22 | 13.19 |
| $C_2H_6$ | - $C_3H_8$ | 29 | 28 | -230/0 | .0026/205 | 9.50 | 13.06 |
| | $nC_4H_{10}$ | 74 | 19 | 150/250 | 470/805 | 1.89 | 3.31 |
| | $nC_5H_{12}$ | 92 | 9 | 40/160 | 50/900 | 1.20 | 7.98 |
| | $nC_6H_{14}$ | 130 | 14 | 150/350 | 224/1110 | 5.56 | 8.57 |
| | $nC_7H_{16}$ | 75 | 19 | 150/350 | 524/1235 | 4.80 | 4.02 |
| | $iC_4H_{10}$ | 10 | 15 | 100/250 | 155/779 | 4.33 | 3.56 |
| $C_3H_8$ | -$iC_4H_{10}$ | 44 | 13 | 20/200 | 19/554 | 2.29 | 3.40 |
| | $nC_5H_{12}$ | 102 | 20 | 160/370 | 60/650 | 2.56 | 6.52 |
| $nC_4H_{10}$ | -$nC_7H_{16}$ | 93 | 4 | 200/350 | 100/200 | 1.03 | 2.23 |
| $nC_5H_{12}$ | -$nC_7H_{16}$ | 51 | 14 | 267/498 | 147/444 | 2.25 | 6.56 |
| $N_2$ | - $CH_4$ | 16 | 13 | -255/-130 | 50/710 | 6.74 | 4.95 |
| | $C_2H_6$ | 32 | 12 | -210/-100 | 100/1000 | 6.54 | 17.69 |
| | $nC_4H_{10}$ | 2 | 12 | 100/300 | 518/4020 | 7.01 | 13.04 |
| | $nC_6H_{14}$ | 87 | 13 | 160/340 | 500/5000 | 17.77 | 8.98 |
| | $nC_7H_{16}$ | 1 | 9 | 175/360 | 2022/10025 | 7.24 | 14.50 |
| | $CO_2$ | 131 | 10 | -41/32 | 514/2015 | 7.03 | 2.60 |

TABLE VI-2--Continued

| Component 1 | Component 2 | Ref. | Data Pts. | Temp. Range (°F) | Press. Range (psia) | Avg. Abs. Dev. % K-Value 1 | Avg. Abs. Dev. % K-Value 2 |
|---|---|---|---|---|---|---|---|
| $H_2S$ - | $CH_4$ | 58,96 | 15 | 40/160 | 200/1900 | 3.32 | 10.78 |
| | $C_3H_8$ | 17 | 24 | -68/160 | 20/400 | 7.27 | 5.80 |
| | $nC_5H_{12}$ | 103 | 9 | 40/160 | 20/700 | 4.75 | 11.88 |
| $CO_2$ - | $CH_4$ | 30 | 13 | -65/29 | 400/1000 | 5.18 | 10.94 |
| | $C_2H_6$ | 60 | 12 | -60/60 | 114/814 | 21.55 | 13.83 |
| | $C_3H_8$ | 94 | 9 | 40/160 | 100/100 | 2.70 | 7.72 |
| | $C_3H_8$ | 94 | 9 | -40/32 | 50/400 | 7.82 | 5.23 |
| | $nC_4H_{10}$ | 94 | 9 | 100/220 | 100/900 | 9.33 | 3.04 |
| | $nC_5H_{12}$ | 11 | 22 | 40/220 | 33/1300 | 6.20 | 15.60 |
| | $H_2S$ | 14 | 31 | 23/176 | 294/1176 | 12.10 | 2.87 |
| | $iC_4H_{10}$ | 9 | 15 | 100/250 | 105/1042 | 4.61 | 7.16 |

The use of Equation VI-10 needs an additional mixing rule for $T\alpha'$. As in the case of $\alpha$, the following rules are written for $T\alpha'$

$$T\alpha' = \sum_{i}^{NC} \sum_{j}^{NC} x_i x_j (T\alpha')_{ij} \qquad \text{(VI-11)}$$

where

$$(T\alpha')_{ij} = \frac{1}{2} [(T\alpha')_i + (T\alpha')_j](1 - n_{ij}) \qquad \text{(VI-12)}$$

For vapor-liquid equilibrium calculations, the fugacity of the $k^{th}$ component in a mixture is related to the equation of state by the following equation

$$RT \ln \frac{f_k}{x_k P} = \int_V^\infty [(\frac{\partial P}{\partial n_k})_{T,v,n_{j\neq k}} - \frac{RT}{V}] dV - RT \ln Z \qquad \text{(VI-13)}$$

where Z is the compressibility factor for the mixture, V is the volume of the phase, $x_k$ is the mole fraction of $k^{th}$ component in the phase, which may be either vapor or liquid, and $n_k$ is the number of moles of the $k^{th}$ component in the phase. The most ponderous mathematical operation in Equation VI-13 is the evaluation of $(\partial P/\partial n_k)_{T,V,n_{j\neq k}}$, which is to be derived from the mixture equation of state in Equation VI-1. After straightforward but tedious mathematical operations, we arrive at the following expressions for the fugacity of $k^{th}$ component in the mixture.

$$\ln\left(\frac{f_k}{x_k P}\right) = \frac{(8y - 4y^2)(1/\alpha)(\partial\alpha/\partial n_k) + 3 + 7y - 9y^2 + 3y^3}{2(1-y)^3} - 1.5$$

$$- \frac{1}{T}\left(2Q_1\rho + \frac{3}{2}Q_2\rho^2 + \frac{4}{3}Q_3\rho^3\right)$$

$$- \frac{1}{T^2}\left(2Q_4\rho + \frac{3}{2}Q_5\rho^2 + \frac{4}{3}Q_6\rho^3 + \frac{5}{4}Q_7\rho^4\right)$$

$$- \frac{1}{T^3}(2Q_8\rho) - \frac{1}{T^5}\left(2Q_9\rho + \frac{3}{2}Q_{10}\rho^2\right)$$

$$- \frac{1}{T}\left[\rho\left(\frac{\partial Q_1}{\partial n_k}\right) + \frac{\rho^2}{2}\left(\frac{\partial Q_2}{\partial n_k}\right) + \frac{\rho^3}{3}\left(\frac{\partial Q_3}{\partial n_k}\right)\right]$$

$$- \frac{1}{T^2}\left[\rho\left(\frac{\partial Q_4}{\partial n_k}\right) + \frac{\rho^2}{2}\left(\frac{\partial Q_5}{\partial n_k}\right) + \frac{\rho^3}{3}\left(\frac{\partial Q_6}{\partial n_k}\right) + \frac{\rho^4}{4}\left(\frac{\partial Q_7}{\partial n_k}\right)\right]$$

$$- \frac{1}{T^3}\rho\left(\frac{\partial Q_8}{\partial n_k}\right) - \frac{1}{T^5}\left[\rho\left(\frac{\partial Q_9}{\partial n_k}\right) + \frac{\rho^2}{2}\left(\frac{\partial Q_{10}}{\partial n_k}\right)\right]$$

$$- R \ln Z \qquad \text{(VI-14)}$$

where

$$\left(\frac{\partial\alpha}{\partial n_k}\right) = 2\sum_{j=1}^{NC} x_j\,\alpha_{kj} - 2\alpha$$

$$\left(\frac{\partial Q_1}{\partial n_k}\right) = 2\sum_{j=1}^{NC} x_j\,T_{c_{kj}}\,v_{c_{kj}}\,(C_{11} + C_{12}\omega_{kj}) - 2Q_1$$

$$\left(\frac{\partial Q_4}{\partial n_k}\right) = 2\sum_{j=1}^{NC} x_j\,T_{c_{kj}}^2\,v_{c_{kj}}\,(C_{41} + C_{42}\omega_{kj} + C_{43}\omega_{kj}^3) - 2Q_4$$

$$\left(\frac{\partial Q_8}{\partial n_k}\right) = 2\sum_{j=1}^{NC} x_j\,T_{c_{kj}}^3\,v_{c_{kj}}\,(C_{81}\omega_{kj} + C_{82}\omega_{kj}^2) - 2Q_8$$

$$\left(\frac{\partial Q_9}{\partial n_k}\right) = 2\sum_{j=1}^{NC} x_j\,T_{c_{kj}}^5\,v_{c_{kj}}\,(C_{91}\omega_{kj} + C_{92}\omega_{kj}^2 + C_{93}\omega_{kj}^3)$$

$$- 2Q_9$$

$$\left(\frac{\partial Q_2}{\partial n_k}\right) = 3C_{21}\left[\sum_{i=1}^{NC} x_i \left(T_{c_i} v_{c_i}^2\right)^{1/3}\right]^2 \left(T_{c_k} v_{c_k}^2\right)^{1/3}$$

$$+ 3C_{22}\left[\sum_{i=1}^{NC} x_i \left(T_{c_i} v_{c_i}^2 \omega_i\right)^{1/3}\right]^2 \left(T_{c_k} v_{c_k}^2 \omega_k\right)^{1/3}$$

$$+ 3C_{23}\left[\sum_{i=1}^{NC} x_i \left(T_{c_i} v_{c_i}^2 \omega_i^2\right)^{1/3}\right]^2 \left(T_{c_k} v_{c_k}^2 \omega_k^2\right)^{1/3} - 3Q_2$$

$$\left(\frac{\partial Q_5}{\partial n_k}\right) = 3C_{51}\left[\sum_{i=1}^{NC} x_i \left(T_{c_i}^2 v_{c_i}^2\right)^{1/3}\right]^2 \left(T_{c_k}^2 v_{c_k}^2\right)^{1/3}$$

$$+ 3C_{52}\left[\sum_{i=1}^{NC} x_i \left(T_{c_i}^2 v_{c_i}^2 \omega_i\right)^{1/3}\right]^2 \left(T_{c_k}^2 v_{c_k}^2 \omega_k\right)^{1/3}$$

$$+ 3C_{53}\left[\sum_{i=1}^{NC} x_i \left(T_{c_i}^2 v_{c_i}^2 \omega_i^2\right)^{1/3}\right]^2 \left(T_{c_k}^2 v_{c_k}^2 \omega_k^2\right)^{1/3} - 3Q_5$$

$$\left(\frac{\partial Q_{10}}{\partial n_k}\right) = 3C_{101}\left[\sum_{i=1}^{NC} x_i \left(T_{c_i}^5 v_{c_i}^2\right)^{1/3}\right]^2 \left(T_{c_k}^5 v_{c_k}^2\right)^{1/3}$$

$$+ 3C_{102}\left[\sum_{i=1}^{NC} x_i \left(T_{c_i}^5 v_{c_i}^2 \omega_i\right)^{1/3}\right]^2 \left(T_{c_k}^5 v_{c_k}^2 \omega_k\right)^{1/3}$$

$$+ 3C_{103}\left[\sum_{i=1}^{NC} x_i \left(T_{c_i}^5 v_{c_i}^2 \omega_i^3\right)^{1/3}\right]^2 \left(T_{c_k}^5 v_{c_k}^2 \omega_k^3\right)^{1/3} - 3Q_{10}$$

$$\left(\frac{\partial Q_3}{\partial n_k}\right) = 4C_{31}\left[\sum_{i=1}^{NC} x_i \left(T_{c_i} v_{c_i}^3\right)^{1/4}\right]^3 \left(T_{c_k} v_{c_k}^3\right)^{1/4}$$

$$+ 4C_{32}\left[\sum_{i=1}^{NC} x_i \left(T_{c_i} v_{c_i}^3 \omega_i\right)^{1/4}\right]^3 \left(T_{c_k} v_{c_k}^3 \omega_k\right)^{1/4}$$

$$+ 4C_{33}\left[\sum_{i=1}^{NC} x_i \left(T_{c_i} v_{c_i}^3 \omega_i^2\right)^{1/4}\right]^3 \left(T_{c_k} v_{c_k}^3 \omega_k^2\right)^{1/4} - 4Q_3$$

$$\left(\frac{\partial Q_6}{\partial n_k}\right) = 4C_{61}\left[\sum_{i=1}^{NC} x_i\left(T_{c_i}^2 v_{c_i}^3\right)^{1/4}\right]^3 \left(T_{c_k}^2 v_{c_k}^3\right)^{1/4}$$

$$+ 4C_{62}\left[\sum_{i=1}^{NC} x_i\left(T_{c_i}^2 v_{c_i}^3 \omega_i\right)^{1/4}\right]^3 \left(T_{c_k}^2 v_{c_k}^3 \omega_k\right)^{1/4} - 4Q_6$$

$$\left(\frac{\partial Q_7}{\partial n_k}\right) = 5C_{71}\left[\sum_{i=1}^{NC} x_i\left(T_{c_i}^2 v_{c_i}^4\right)^{1/5}\right]^4 \left(T_{c_k}^2 v_{c_k}^4\right)^{1/5}$$

$$+ 5C_{72}\left[\sum_{i=1}^{NC} x_i\left(T_{c_i}^2 v_{c_i}^4 \omega_i\right)^{1/5}\right]^4 \left(T_{c_k}^2 v_{c_k}^4 \omega_k\right)^{1/5} - 5Q_7$$

## Prediction of K-Values for Binary Systems

A total of 33 binary systems were employed to test the capability of the generalized equation of state for predicting vapor-liquid equilibrium. The data points for the binary systems are summarized in Table VI-2. The binary systems have been used mainly for determining $k_{ij}$ and $n_{ij}$, the values of which are tabulated in Table VI-1. The K-value of the $i^{th}$ component in the mixture is calculated from the following equation

$$K_i = \frac{f_i^L (y_e)_i}{f_i^V (x_e)_i} \qquad \text{(VI-15)}$$

where $f_i^L$ and $f_i^V$ are the fugacities of $i^{th}$ component in the liquid and vapor phases, respectively, and are calculated from Equation VI-14; $(y_e)_i$ and $(x_e)_i$ are the experimental compositions of the $i^{th}$ component in vapor and liquid phases, respectively. The calculated K-value is then compared with

the experimental, and the average absolute deviation percent of the K-value for each component for each binary system is evaluated and tabulated in the last two columns of Table VI-2. Because of the problem of evaluating the accuracy of experimental K-value data, the deviation percent of K-values reported herein are uncertain. Thus, most K-values are reported graphically in the literature. As a typical example, the calculated K-values of the $CH_4$ - $C_3H_8$ system are plotted in Figure VI-1. Inspection of the figure shows that the trends of the calculated K-values are in good agreement with the experimental. Plots for other systems reveal the same trends.

## Calculation of Phase Compositions for Binary Systems

Flash calculations are performed for three binary systems of $CH_4$ - $C_3H_8$, $CH_4$ - $N_2$ and $N_2$ - $C_2H_6$ for calculating phase compositions of the components in the mixtures. The calculated phase compositions for each component are compared numerically with the experimental values in Tables VI-3, VI-4 and VI-5. The deviations of K-values, as reported in Table VI-2, are 13.07 percent for $C_3H_8$ in the $CH_4$ - $C_3H_8$ system and 17.69 percent for $C_2H_6$ in the $N_2$ - $C_2H_6$ system, yet a direct comparison of calculated compositions with the experimental values indicates that they are in good agreement, in relation to expected uncertainties in measuring phase compositions.

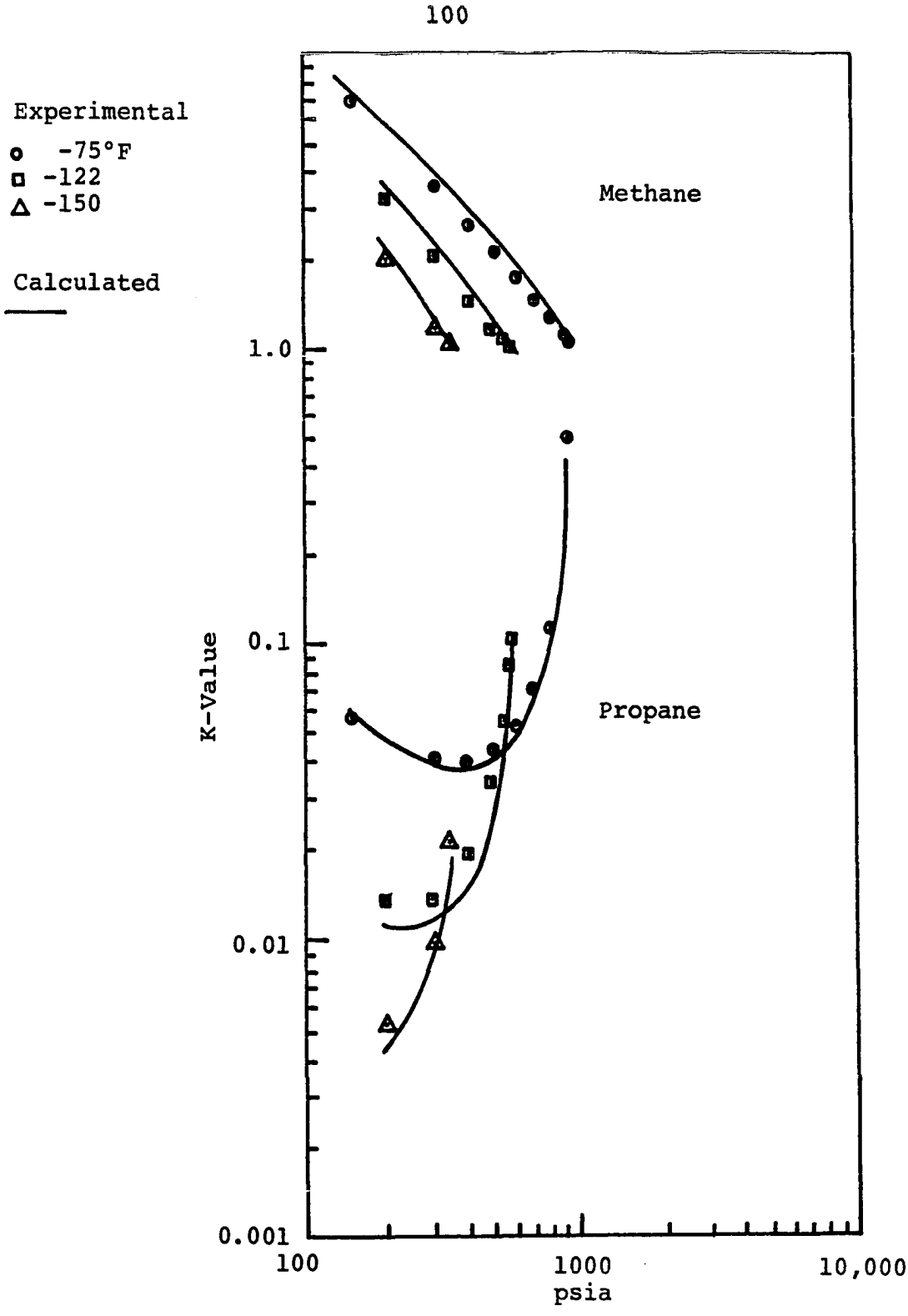


Figure VI-1. Comparison of Calculated and Experimental K-Values for $CH_4$ - $C_3H_8$ System.

TABLE VI-3

COMPARISON OF PREDICTED AND EXPERIMENTAL PHASE COMPOSITIONS FOR $CH_4$ - $C_3H_8$ SYSTEM

(Component Indices: 1 = $CH_4$, 2 = $C_3H_8$)

| Component Index | Liquid Mole % | | Vapor Mole % | |
|---|---|---|---|---|
| | Exptl. | Calc. | Exptl. | Calc. |
| -75°F, 102 psia | | | | |
| 1 | 8.99 | 8.77 | 92.88 | 92.86 |
| 2 | 91.01 | 91.23 | 7.12 | 7.14 |
| -75°F, 300 psia | | | | |
| 1 | 27.09 | 25.80 | 96.98 | 97.04 |
| 2 | 72.91 | 74.20 | 3.02 | 2.96 |
| -75°F, 500 psia | | | | |
| 1 | 45.80 | 42.04 | 97.60 | 97.71 |
| 2 | 54.20 | 57.96 | 2.40 | 2.29 |
| -150°F, 100 psia | | | | |
| 1 | 22.70 | 20.95 | 99.505 | 99.57 |
| 2 | 77.30 | 79.05 | 0.495 | 0.43 |
| -150°F, 200 psia | | | | |
| 1 | 49.09 | 44.63 | 99.73 | 99.76 |
| 2 | 50.91 | 55.37 | 0.27 | 0.24 |
| -150°F, 300 psia | | | | |
| 1 | 84.23 | 82.06 | 99.845 | 99.84 |
| 2 | 15.77 | 17.93 | 0.155 | 0.16 |
| -116.6°F, 615 psia | | | | |
| 1 | 96.14 | 96.14 | 99.52 | 99.63 |
| 2 | 3.86 | 3.86 | 0.48 | 0.37 |
| -113.6°F, 75 psia | | | | |
| 1 | 10.52 | 9.96 | 97.18 | 97.38 |
| 2 | 89.48 | 90.04 | 2.82 | 2.62 |

TABLE VI-4

COMPARISON OF PREDICTED AND EXPERIMENTAL PHASE COMPOSITIONS FOR $CH_4$ - $N_2$ SYSTEM

(Component Indices: 1 - $CH_4$, 2 = $N_2$)

| Component Index | Liquid Mole % | | Vapor Mole % | |
|---|---|---|---|---|
| | Exptl. | Calc. | Exptl. | Calc. |
| -130°F, 576 psia | | | | |
| 1 | 97.456 | 97.31 | 95.069 | 95.21 |
| 2 | 2.544 | 2.69 | 4.931 | 4.79 |
| -130°F, 689 psia | | | | |
| 1 | 89.40 | 87.73 | 85.75 | 87.42 |
| 2 | 10.60 | 12.27 | 14.25 | 12.58 |
| -150°F, 370.5 psia | | | | |
| 1 | 99.405 | 99.27 | 98.062 | 98.20 |
| 2 | 0.595 | 0.73 | 1.938 | 1.80 |
| -170°F, 250 psia | | | | |
| 1 | 99.025 | 98.956 | 95.548 | 96.81 |
| 2 | 0.975 | 1.044 | 4.452 | 3.19 |
| -170°F, 647 psia | | | | |
| 1 | 63.17 | 59.69 | 47.16 | 39.69 |
| 2 | 36.83 | 40.31 | 52.84 | 60.31 |
| -170°F, 710 psia | | | | |
| 1 | 54.73 | 52.50 | 48.22 | 49.80 |
| 2 | 45.27 | 47.50 | 51.78 | 50.20 |
| -210.45°F, 548 psia | | | | |
| 1 | 27.05 | 26.98 | 16.33 | 12.08 |
| 2 | 72.95 | 73.02 | 83.76 | 87.91 |

TABLE VI-5

COMPARISON OF PREDICTED AND EXPERIMENTAL PHASE COMPOSITIONS FOR $N_2$ - $C_2H_6$ SYSTEM

(Component Indices: 1 = $N_2$, 2 = $C_2H_6$)

| Component Index | Liquid Mole % | | Vapor Mole % | |
|---|---|---|---|---|
| | Exptl. | Calc. | Exptl. | Calc. |
| -180°F, 700 psia | | | | |
| 1 | 22.50 | 23.96 | 98.45 | 98.45 |
| 2 | 77.50 | 76.04 | 1.55 | 1.55 |
| -110°F, 808 psia | | | | |
| 1 | 17.56 | 18.45 | 91.54 | 92.15 |
| 2 | 82.44 | 81.55 | 8.46 | 7.85 |
| -150°F, 200 psia | | | | |
| 1 | 4.845 | 5.15 | 94.778 | 95.20 |
| 2 | 95.155 | 94.85 | 5.222 | 4.80 |
| -190°F, 100.5 psia | | | | |
| 1 | 3.178 | 3.42 | 97.867 | 98.32 |
| 2 | 96.822 | 96.58 | 2.133 | 1.68 |
| -190°F, 300 psia | | | | |
| 1 | 9.698 | 10.57 | 98.937 | 99.10 |
| 2 | 90.303 | 89.43 | 1.063 | 0.90 |
| -190°F, 601 psia | | | | |
| 1 | 20.58 | 22.18 | 98.656 | 98.95 |
| 2 | 79.42 | 77.82 | 1.344 | 1.05 |
| -210°F, 100 psia | | | | |
| 1 | 3.87 | 4.20 | 99.164 | 99.38 |
| 2 | 96.13 | 95.80 | 0.836 | 0.62 |
| -210°F, 300 psia | | | | |
| 1 | 11.92 | 13.19 | 99.444 | 99.62 |
| 2 | 88.08 | 86.81 | 0.556 | 0.38 |
| -210°F, 500 psia | | | | |
| 1 | 21.26 | 23.20 | 99.308 | 99.52 |
| 2 | 78.80 | 76.80 | 0.692 | 0.48 |

## Prediction of K-Values for Multicomponent Systems

The calculation of K-values for binary systems is extended herein to two ternary systems, $CH_4$ - $C_2H_6$ - $C_3H_8$ and $N_2$ - $CH_4$ - $C_2H_6$ and to a quinary system of normal paraffins $CH_4$ to $C_5H_{12}$. The calculated K-values are compared numerically with the experimental values for the ternary systems in Tables VI-6 and VI-7. For the quinary system, the results are compared graphically in Figure VI-2. Again, as in the case of binary systems, the magnitudes and trends of the calculated values are in good agreement with the experimental data. Thus, Equation VI-11 is applicable to multicomponent systems, using only binary interaction parameter values.

## Estimate of Interaction Parameter Value $k_{ij}$ and $n_{ij}$

In Table VI-1 we have tabulated the interaction parameter values of $k_{ij}$ and $n_{ij}$ for 33 binary systems. The interaction parameter values for a binary system that is not listed in the table can be approximated using the values for a similar system. The binary system $nC_5H_{12}$ - $nC_7H_{16}$, for example, is similar to the binary system $nC_4H_{10}$ - $nC_7H_{16}$. For a test we have used the interaction parameter values for $nC_4H_{10}$ - $nC_7H_{16}$ to calculate the K-values for the $nC_5H_{12}$ - $nC_7H_{16}$ system. The resultant deviations are 2.6 percent for $nC_5H_{12}$ and 7.18 percent for $nC_7H_{16}$ (compared to 2.25 percent for $nC_5H_{12}$ and 6.56 percent for $nC_7H_{16}$, using the optimal interaction parameter value for the $nC_5H_{12}$ - $nC_7H_{16}$ system).

Similarly, since the values of $k_{ij}$ and $n_{ij}$ are not available for $C_3H_8$ - $nC_4H_{10}$ in the table, the values required in the quinary system have been approximated by using the values for the $C_2H_6$ - $nC_4H_{10}$ system.

TABLE VI-6

COMPARISON OF CALCULATED AND EXPERIMENTAL K-VALUES FOR $CH_4$ - $C_2H_6$ - $C_3H_8$ SYSTEM[126]

(1 = $CH_4$; 2 = $C_2H_6$; 3 = $C_3H_8$)

| Temperature and Pressure | Component | K-Value | |
|---|---|---|---|
| | | Exptl. | Calc. |
| 50°F, 600 psia | 1 | 3.2058 | 3.8834 |
| | 2 | 0.8427 | 0.8086 |
| | 3 | 0.3171 | 0.3021 |
| 50°F, 1000 psia | 1 | 1.8175 | 1.9843 |
| | 2 | 0.7455 | 0.7165 |
| | 3 | 0.3778 | 0.3560 |
| 0°F, 1100 psia | 1 | 1.4966 | 1.5474 |
| | 2 | 0.5869 | 0.5640 |
| | 3 | 0.2841 | 0.2727 |
| -50°F, 400 psia | 1 | 2.9941 | 3.3457 |
| | 2 | 0.3402 | 0.3475 |
| | 3 | 0.0798 | 0.0813 |
| -50°F, 1000 psia | 1 | 1.1780 | 1.1907 |
| | 2 | 0.5650 | 0.5307 |
| | 3 | 0.3250 | 0.3066 |
| -100°F, 600 psia | 1 | 1.3121 | 1.3141 |
| | 2 | 0.2288 | 0.2090 |
| | 3 | 0.0522 | 0.0576 |
| -150°F, 200 psia | 1 | 1.9078 | 2.1401 |
| | 2 | 0.0802 | 0.0639 |
| | 3 | 0.0097 | 0.0063 |

TABLE VI-7

COMPARISON OF CALCULATED AND EXPERIMENTAL K-VALUES FOR $N_2$ - $CH_4$ - $C_2H_6$ SYSTEM[26]

(1 - $N_2$; 2 = $CH_4$; 3 = $C_3H_8$)

| Temperature and Pressure | Component | K-Value | |
|---|---|---|---|
| | | Exptl. | Calc. |
| -100°F, 500 psia | 1 | 8.4321 | 7.2194 |
| | 2 | 1.4977 | 1.7204 |
| | 3 | 0.1359 | 0.1314 |
| -100°F, 1000 psia | 1 | 3.6143 | 3.4335 |
| | 2 | 1.0499 | 1.0831 |
| | 3 | 0.1409 | 0.1437 |
| -100°F, 1000 psia | 1 | 1.9606 | 1.9536 |
| | 2 | 0.9993 | 1.0047 |
| | 3 | 0.3630 | 0.3246 |
| -200°F, 500 psia | 1 | 3.6662 | 3.3160 |
| | 2 | 0.4479 | 0.4705 |
| | 3 | 0.0116 | 0.0110 |
| -200°F, 500 psia | 1 | 2.2747 | 2.2084 |
| | 2 | 0.4399 | 0.4426 |
| | 3 | 0.0232 | 0.0193 |

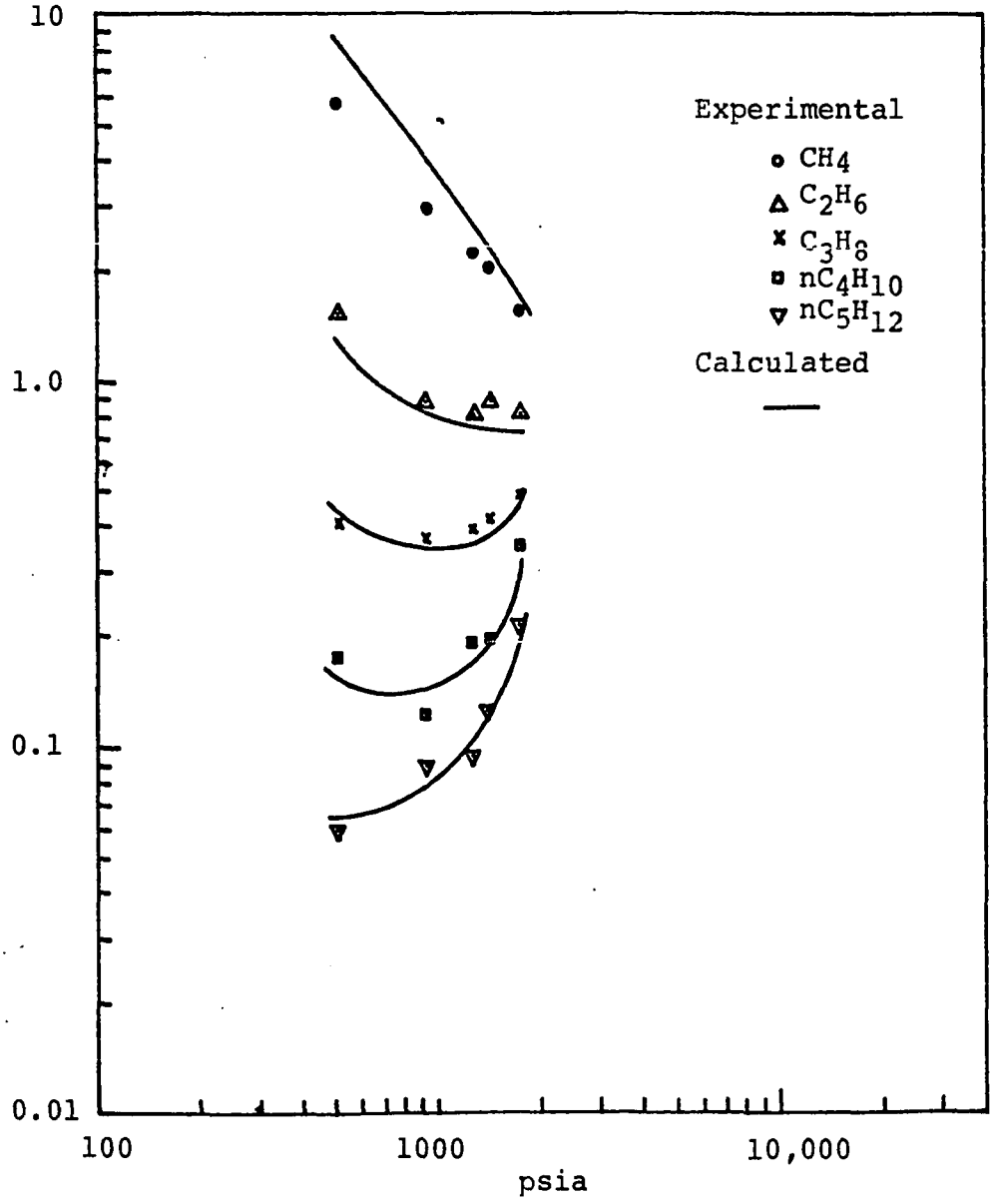


Figure VI-2. Comparison of Calculated and Experimental K-Values for $CH_4$-$C_2H_6$-$C_3H_8$-$nC_4H_{10}$-$nC_5H_{12}$ System at 100°F.

# CHAPTER VII

## CONCLUSIONS

The primary objective of this research has been the development of a generalized hard sphere-augmented equation of state for predicting thermodynamic properties of mixtures as well as pure fluids. A test of the generality has been made for a variety of fluids with satisfactory results, as summarized in Table IV-2. The test shows that the generalized equation of state is applicable in the cryogenic region to reduced temperatures as low as 0.27.

Prediction of the thermodynamic properties of a fluid not included in the original correlation, then, involves simply determination of an "effective" acentric factor for the fluid. The values of the "effective" acentric factor for the fluids studied in this research are tabulated in Table IV-1. It is within this context that the "effective" acentric factor becomes a more general characterization parameter. The gap existing between the "effective" and literature values could be drawn closer by defining reduced values of hard sphere volume such that they are universal constants for all fluids. Introduction of a fourth parameter into the reduced hard sphere volume might be a possibility.

The generalized equation of state parameter values were determined by multiproperty regression of PVT, enthalpy, vapor pressure, velocity of sound and heat capacity data. The major advantage of using velocity of sound and heat capacity data in equation of state correlation is the enhancement obtained in the accuracy of temperature and density derivatives of the pressure explicit equation of state. As shown in Chapter II, the use of velocity of sound and heat capacity data in correlation can be particularly valuable when only isobaric or saturated liquid density data are available at low temperatures. Multiproperty analysis calculations in Chapter II demonstrate that for ethane the accuracy and thermodynamic consistency of derived properties is enhanced when velocity of sound and heat capacity data are used with vapor pressure and density data. It is also shown that even the multiproperty analysis of the fragmentary data for ethane available prior to 1970 yields reasonable predictions of cryogenic compressed liquid behavior even though virtually no compressed liquid data were included in the data correlated.

The generalized equation of state has been extended to mixtures using two corresponding states principles, CSP I and CSP II. In CSP I, mixing rules are utilized to estimate the characteristic parameters $v_c$, $T_c$ and $\omega$ for the mixture. This principle is virtually the method by which the generalized equation of state is developed for pure fluids. CSP I

is convenient to use and has been employed successfully for mixture density and enthalpy calculations.

For the prediction of partial molar properties and phase equilibrium, CSP II is more accurate than CSP I. The composition dependence of CSP II occurs through the composition dependence of the equation of state parameters. Using CSP II, calculations of K-values and equilibrium vapor-liquid compositions by flash were performed for binary, ternary and quinary systems. The results show that the calculated values are in good agreement with the experimental in trend and magnitude.

In both corresponding state principles, the generalized equation of state can be readily extended to mixtures of more than two components using merely binary interaction parameter values.

## NOMENCLATURE

| | |
|---|---|
| $A$ | Helmholtz free energy |
| $\mathring{A}$ | Angstrom |
| $A_1, A_2, A_3, A_4$ | Hard sphere volume correlation parameters for ethane in Equation II-19 |
| $A_{ij}$ | Generalized hard sphere volume correlation parameters (i = 1, 2, 3, 4; j = 1, 2, 3) |
| $a^3$ | Hard sphere volume, $(\mathring{A})^3$ |
| $a$ | Hard sphere diameter, $\mathring{A}$ |
| $B_1, B_2, B_3, B_4$ | Correlation parameters for isochoric ethane P, T data in Equation II-21 |
| $B^*$ | Reduced second virial coefficient |
| $B_i$ | Generalized correlation parameters for $\rho_c a^3$ (i = 1, 2, ..., 11, 12) |
| $C_i$ | Generalized equation of state parameters in Equation III-39 (i = 1, 2, ..., 103) |
| $C_v$ | Heat capacity at constant volume |
| $C_p$ | Heat capacity at constant pressure |
| $C_\sigma$ | Saturated heat capacity along vapor pressure curve |
| $d$ | Differential operator |

| | |
|---|---|
| d | Parameter for the generalized correlation of the third virial coefficient in Equation III-33 |
| f | Fugacity |
| f | Adjustable parameter in Equation VI-6 |
| $f_i$ | Fugacity of $i^{th}$ component in a mixture |
| $g_o^{(2)}$ | Radial distribution function |
| H | Enthalpy |
| $H - H^o$ | Enthalpy departure |
| $\Delta H$ | $H - H^o$ |
| $K_{ij}$ | Vapor-liquid equilibrium constant for $i^{th}$ component in a mixture at $j^{th}$ data point |
| $K_{ij}$ | Characteristic constant of $T_{c_{ij}}$ for i-j interaction in CSP I |
| $k_{ij}$ | Characteristic constant of $T_{c_{ij}}$ for i-j interaction in CSP II |
| k | Boltzmann constant |
| ln | Natural logarithm |
| $\ell_{ij}$ | Characteristic constant of $v_{c_{ij}}$ for i-j interaction in CSP II |
| M | Molecular weight |
| $m_{ij}$ | Characteristic constant of $\omega_{ij}$ for i-j interaction in CSP II |
| N | Avogadro's number |
| N | Number of molecules in the system of volume V |
| NC | Number of components in a mixture |

| | |
|---|---|
| NP | Number of data points |
| $n_k$ | Number of moles of $k^{th}$ component in a mixture |
| $n_{ij}$ | Characteristic constant of hard sphere for i-j interaction in CSP II |
| P | Absolute pressure |
| $Q_k$ | Unreduced equation of state parameters (k = 1, 2, ..., 9, 10) |
| R | Universal gas constant |
| r | Distance between molecules |
| S | Entropy |
| $\Delta S$ | $S - S^o$ |
| T | Absolute temperature, °K |
| $T_B$ | Base temperature for $S^o$ and $C_p{}^o$ correlations, 1°R |
| $T_R$ | Absolute temperature, °R |
| $T_r$ | Reduced temperature, $T/T_c$ |
| T* | Reduced temperature, $T/(\varepsilon/k)$ |
| $T_{c_{ij}}$ | Critical temperature characteristic of i-j interaction |
| U | Potential energy of a system |
| u | Pairwise potential energy between molecules |
| V | Total volume of a system |
| v | Molar volume |
| W | Velocity of sound |
| $W_i$ | Weighting factor of $i^{th}$ type of thermodynamic property |

| | |
|---|---|
| $x_i$ | Mole fraction of $i^{th}$ component in a mixture |
| $x_i$ | Mole fraction of $i^{th}$ component in liquid |
| $y_i$ | Mole fraction of $i^{th}$ component in vapor |
| Z | Compressibility factor |
| $v_{c_{ij}}$ | Critical volume characteristic of i-j interaction |

Greek Letters

| | |
|---|---|
| $\alpha$ | $\rho_c a^3/\rho_c$ |
| $\alpha'$ | $\partial\alpha/\partial T$ |
| $\alpha''$ | $\partial\alpha'/\partial T$ |
| $\alpha_{ij}$ | Hard sphere volume characteristic of i-j interaction |
| $\beta$ | $1/kT$ |
| $\beta_i$ | Parameters for $S^o$ and $C_p^o$ correlations (i = 1, 2, 3, 4, 5) |
| $\beta_s$ | Adiabatic compressibility |
| $\varepsilon/k$ | Lennard-Jones parameter |
| $\theta_i$ | $i^{th}$ virial coefficient |
| $\lambda$ | Adjustable parameter for matrix inversion |
| $\rho$ | Molar density, gram-mole/cc |
| $\rho_r$ | Reduced density |
| $\sigma$ | Lennard-Jones parameter, Å |
| $\phi_{ij}$ | Value of $j^{th}$ rype of thermodynamic property at $i^{th}$ data point |
| $\chi$ | Objective function |

| | |
|---|---|
| $\omega$ | Acentric factor |
| $\omega_{ij}$ | Acentric factor characteristic of i-j interaction |

Subscripts

| | |
|---|---|
| c | Critical state |
| c | Calculated value |
| e | Experimental value |
| $\sigma$ | Property at saturation |

Superscripts

| | |
|---|---|
| L | Liquid phase |
| V | Vapor phase |
| o | Hard sphere system |
| o | Ideal gas state |
| ' | Perturbation system |

Abbreviations

| | |
|---|---|
| Avg. Abs. Dev. | Average absolute deviation |
| Btu | British thermal unit |
| cal | Metric thermal unit |
| calc. | Calculated |
| CSP I | Corresponding states principle I |
| CSP II | Corresponding states principle II |
| cu. ft. | Cubic feet |
| Dev % | Deviation percent |
| exp | Exponential function |

| | |
|---|---|
| Exptl. | Experimental |
| g/cc | Gram per cubic centimeter |
| °F | Degree Fahrenheit |
| °K | Degree Kelvin |
| lb | Pound |
| Press. | Pressure |
| psia | Absolute pound-force per square inch |
| Pts. | Points |
| °R | Degree Rankin |
| Ref. | References |
| Temp. | Temperature |

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