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DEVELOPMENT OF THE MOST GENERAL DENSITY-CUBIC EQUATION OF STATE

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DEVELOPMENT OF THE MOST GENERAL DENSITY-CUBIC EQUATION OF STATE

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ABSTRACT

The most general density-cubic equation of state is derived through a mathematical analysis. The adequacy of the density dependence to describe the thermodynamic behavior of real fluids over all fluid states is demonstrated through a case study of propane thermodynamic behavior along isotherms. Provisional temperature dependence is introduced into the equation of state and the resultant equation of state predicts the thermodynamic behavior of methane, propane, n-heptane and n-octane over wide ranges of temperature and pressure to a high level of accuracy hitherto attainable using only non-cubic equations like the modified Benedict-Webb-Rubin equation of state. The equation of state is later generalized using the thermodynamic property values for the normal straight chain paraffin hydrocarbons methane through n-decane. The generalized equation of state predicts density and vapor pressure values within nine tenths of a percent for methane through n-decane and the enthalpy departure is predicted within 1.7 Btu/lb average absolute deviation. The generalized equation of state is applied to normal saturated hydrocarbons n-undecane through n-eicosane resulting in an overall deviation of 1.87 percent from reported values of density and vapor pressure. When applied to other major natural gas constituents the equation of state predicts the thermodynamic properties density, vapor pressure and enthalpy departure with the same level of accuracy as the modified Benedict-Webb-Rubin equation of state. The equation of state gives a reasonably good description of the thermodynamic behavior of selected key coal chemicals, namely benzene, naphthalene, tetralin, quinoline and phenanthrene. The basic density dependence of the equation of state describes the thermodynamic properties of water when provisional temperature dependence is introduced, to a high level of accuracy over all fluid states.

DEVELOPMENT OF THE MOST GENERAL DENSITY-CUBIC EQUATION OF STATE

CHAPTER I

INTRODUCTION

Many attempts have been made over the years to describe the thermodynamic behavior of real fluids via equations of state. These equations of state have achieved varying degrees of success, enabling us to divide them into three separate classes. In the first class, we have the equations of state which are cubic in density. A few of the more popular density-cubic equations are the van der Waals equation (1873), the Redlich-Kwong equation (1949), the Soave equation (1972) and the Peng-Robinson equation (1976). The density-cubic equations of state give reasonable descriptions of the thermodynamic behavior of real fluids, with each equation being more accurate in the chronological order of appearance in the literature. The Beattie-Bridgeman equation (1928), the Benedict-Webb-Rubin equation (1940) and the Modified Benedict-Webb-Rubin equation (1973) are popular examples of the second class of equations of state. They are non-cubic in density and provide a good description of the thermodynamic behavior of real fluids for all fluid states. In the third class of equations, are the non-analytic equations of state which are highly constrained for each specific fluid (Goodwin, 1975) and give a highly accurate description of real fluid behavior.

In most industrial design situations as well as research measurements of derived properties, the unknown variable is density, whereas the easily measurable properties pressure and temperature, are known. Consequently, the first class of equations, namely the density-cubic equations are of particular interest since they provide an analytical solution for the density, as compared to the more complicated non-cubic and non-analytic equations of state, which require time consuming iterative procedures to solve for the density.

The presently available popular density-cubic equations of state like the Soave and the Peng-Robinson equations provide good descriptions of real fluid behavior in the two phase region and in the gas phase, but in the compressed liquid region they lack by far the accuracy levels attainable using the second class of equations of state.

When we look at the form of the density-cubic equations in the chronological order of appearance in the literature, we find that in general the more recent equations have more density dependence (when expressed in a pressure explicit form) than their precedents. For example, the Redlich-Kwong equation has more density dependence than the van der Waals equation, as seen below

$$P = \frac{\rho RT}{1 - \rho b} - a\rho^2 \qquad \text{(van der Waals)}$$

$$P = \frac{\rho RT}{(1-\rho b)} - \frac{aT^{-\frac{1}{2}}\rho^2}{(1+\rho b)} \qquad \text{(Redlich Kwong)}$$

Similarly, the Peng-Robinson equation of state has more density dependence than the Redlich-Kwong equation

$$P = \frac{\rho RT}{1-\rho b} - \frac{a(T)\,\rho^2}{(1+2b\rho-b^2\rho^2)} \qquad \text{(Peng-Robinson)}$$

In general, the overall performance in fluid properties prediction is greatly enhanced when using the Peng-Robinson equation (45) as compared to the Redlich-Kwong equation and the Redlich-Kwong equation (49) in turn is better than the van der Waals equation. Thus, though the temperature dependence of each equation is different it can be projected that at a particular temperature, a higher density dependence leads to a more accurate equation of state. Continuing in the same vein, it can be stated that the most density dependence (in terms of pressure) that can be introduced into a density-cubic equation will in turn lead to the most accurate cubic equation of state. This fact is very important because if the most general density-cubic equation of state can provide an accuracy level comparable to the second class of equations of state for all fluid states it becomes highly desirable in situations where repetitive calculations for the density are required due to its inherent advantages.

This research presents the derivation of the most general density cubic equation of state. A study of the adequacy of the density dependence in describing real fluid behavior is also presented. Provisional analytical relations for the temperature dependence are developed through a careful study of individual isotherms of propane. The temperature dependent equation is later generalized using the thermodynamic data for normal saturated hydrocarbons from methane through normal decane. The equation of state is then applied to fluids not used in the generalization.

CHAPTER II

THE MOST GENERAL DENSITY-CUBIC EQUATION OF STATE

The most general density-cubic equation of state can be derived as discussed below.

A direct density (or volume) expansion for pressure which is cubic in density is given by the following expression

$$P = a_1 + a_2 \rho + a_3 \rho^2 + a_4 \rho^3 \qquad (1)$$

where P is the absolute pressure, ρ is the molar density and a_1, a_2, a_3, a_4 are parameters which can be temperature dependent. It is known that an expansion of the above form, which is similar to the virial equation of state up to the third virial coefficient, can only describe the low density gas phase behavior of a fluid. An equation for pressure of the above form which can describe both the gas and liquid phase behavior of a fluid can be written as follows

$$P = \sum_{j=1}^{\infty} a_j \rho^{j-1} \qquad (2)$$

However, equation 2 is of infinite order in density. An equation of state which can approximate <u>an infinite series in density using</u>

pressure as the dependent variable and yet requires solution of only a cubic expression for density (given pressure) is a ratio of polynomials

$$P = \frac{a_1 + a_2\rho + a_3\rho^2 + a_4\rho^3}{a_5 + a_6\rho + a_7\rho^2 + a_8\rho^3} \qquad (3)$$

Equation 3 represents the most general form of a density-cubic or, alternatively, volume-cubic mathematical equation, where a_1 through a_8 are parameters which can be temperature and composition dependent. When multiplied out, equation 3 can be shown to yield a cubic in density, as follows

$$(Pa_5 - a_1) + (Pa_6 - a_2)\rho + (Pa_7 - a_3)\rho^2 + (Pa_8 - a_4)\rho^3 = 0 \qquad (4)$$

In terms of the compressibility factor Z (=P/ρRT), equation 3 becomes

$$Z = \frac{(c_1/\rho) + c_2 + c_3\rho + c_4\rho^2}{a_5 + a_6\rho + a_7\rho^2 + a_8\rho^3} \qquad (5)$$

where $c_i = a_i/RT$, i = 1,2,3,4, R is the universal gas constant, and T is the absolute temperature.

Before equation 5 can be subjected to the thermodynamic ideal gas limit that as $\rho \to 0$, $Z \to 1$, c_1 is required to be zero to prevent the divergence of Z as $\rho \to 0$. Letting $c_1 = 0$, we have

$$Z = \frac{c_2 + c_3\rho + c_4\rho^2}{a_5 + a_6\rho + a_7\rho^2 + a_8\rho^3} \qquad (6)$$

Now in the limit as $\rho \to 0$

$$\lim_{\rho \to 0} Z = \frac{c_2}{a_5} \tag{7}$$

To satisfy the thermodynamic requirement as $\rho \to 0$, $Z \to 1$, $c_2$must be equal to a_5. Letting $c_2 = a_5$ and dividing the numerator and denominator on the right-hand side of equation 6 by c_2 we have

$$Z = \frac{1 + \frac{c_3}{c_2}\rho + \frac{c_4}{c_2}\rho^2}{1 + \frac{a_6}{c_2}\rho + \frac{a_7}{c_2}\rho^2 + \frac{a_8}{c_2}\rho^3} \tag{8}$$

Now letting $c_3/c_2 = d_1$, $c_4/c_2 = d_2$, $a_6/c_2 = d_3$, $a_7/c_2 = d_4$, and $a_8/c_2 = d_5$, we have

$$Z = \frac{1 + d_1\rho + d_2\rho^2}{1 + d_3\rho + d_4\rho^2 + d_5\rho^3} \tag{9}$$

Equation 9 represents the most general form for a cubic equation of state in density which satisfies the requirement that in the limit as $\rho \to 0$, $Z \to 1$. The five coefficients d_1, d_2, d_3, d_4, and d_5 must be density independent but can be temperature dependent (for a given pure fluid) and composition dependent (for a mixture).

We can now show that the density-cubic equations presented in the literature are special cases of equation 9. To do so, we choose a few of the most popular cubic equations, namely the van der Waals equation (65), the Redlich Kwong equation (49), the Soave equation (55), the Peng-Robinson equation (45) and Martin's equation (36).

In equation 9, if we let $d_1 = -a/RT$; $d_2 = ab/RT$; $d_3 = -b$ and $d_4 = d_5 = 0$ we have

$$Z = \frac{1 - \frac{a}{RT}\rho + \frac{ab}{RT}\rho^2}{1 - b\rho} \tag{10}$$

or

$$Z = \frac{1 - (1 - b\rho)\ \rho a/RT}{1 - b\rho} \tag{11}$$

$$Z = \frac{1}{1-b\rho} - \frac{a\ \rho}{RT} \tag{12}$$

In terms of P and the specific volume V, equation 12 becomes

$$P = \frac{RT}{V - b} - \frac{a}{V^2} \tag{13}$$

which is the well known van der Waals equation of state (65).

The Redlich-Kwong equation can be shown to be a special case of equation 9 if we let $d_1 = (b - a/RT^{3/2})$, $d_2 = (ab/RT^{3/2})$; $d_3 = 0$; $d_4 = -b^2$, and $d_5 = 0$ we have

$$Z = \frac{1 + (b-a/RT^{3/2})\rho + (ab/RT^{3/2})\rho^2}{(1 - b^2\rho^2)} \tag{14}$$

$$Z = \frac{(1 + \rho b) - (a/RT^{3/2})(1 - \rho b)\rho}{(1 - \rho b)(1 + \rho b)} \tag{15}$$

$$Z = \frac{1}{1 - \rho b} - \frac{(a/RT^{3/2})\ \rho}{1 + \rho b} \qquad (16)$$

In terms of P and the specific volume V, equation 16 becomes

$$P = \frac{RT}{V - b} - \frac{a}{T^{\frac{1}{2}} V(V+b)} \qquad (17)$$

which is the Redlich-Kwong equation of state (49).

The Soave equation (55) expressed below is a modification of the Redlich-Kwong equation only in the temperature dependence and thus is also a special case of equation 9

$$P = \frac{RT}{V - b} - \frac{a(T)}{V(V+b)} \qquad (18)$$

The Peng-Robinson equation (45) is a special case of equation 9 if we let

$d_1 = (2b - a/RT)$; $d_2 = (ab/RT - b^2)$; $d_3 = b$; $d_4 = -3b^2$ and $d_5 = b^3$, so that

$$Z = \frac{1 + (2b - a/RT)\rho + (ab/RT - b^2)\rho^2}{1 + b\rho - 3b^2\rho^2 + b^3\rho^3} \qquad (19)$$

or

$$Z = \frac{1 + 2\rho b - \rho^2 b^2 - a/RT\ (1 - \rho b)\rho}{(1 - \rho b)\ (1 + 2\ \rho b - \rho^2 b^2\ )} \qquad (20)$$

or

$$Z = \frac{1}{(1 - \rho b)} - \frac{(a/RT)\rho}{(1+2\ \rho b - \rho^2\ b^2)} \qquad (21)$$

In terms of P and specific volume, V, equation 21 becomes

$$P = \frac{RT}{V - b} - \frac{a(T)}{V(V + b) + b(V - b)} \tag{22}$$

which is the Peng-Robinson equation of state.

Martin's general cubic equation (36) is also a special case of equation 9 if we let

$$d_1 = (\gamma + \beta - \alpha(T)/RT);\ d_2 = (\gamma\beta + \delta(T)/RT);\ d_3 = (\gamma + \beta);$$

$d_4 = \gamma\beta$; $d_5 = 0$ we have

$$Z = \frac{1 + (\gamma + \beta - \alpha(T)/RT)\rho + (\gamma\beta + \delta(T)/RT)\rho^2}{1 + (\gamma + \beta)\rho + \gamma\beta\rho^2} \tag{23}$$

or

$$Z = 1 - \frac{(\alpha(T)/RT)\rho}{(1 + \beta\rho)(1 + \gamma\rho)} - \frac{(\delta(T)/RT)\rho^2}{(1 + \beta\rho)(1 + \gamma\rho)} \tag{24}$$

In terms of P and the specific volume, V, equation 24 becomes

$$P = \frac{RT}{V} - \frac{\alpha(T)}{(V+\beta)(V+\gamma)} + \frac{\alpha(T)}{V(V+\beta)(V+\gamma)} \tag{25}$$

which is Martin's equation (36).

Thus equation 9 represents the most general form of a density-cubic equation of state.

CHAPTER III

ADEQUACY OF THE DENSITY DEPENDENCE OF THE EQUATION OF STATE

It has been shown that equation 9 is the most general density-cubic equation through a mathematical analysis. But the effort would be futile unless it can be shown that the equation of state can describe the thermodynamic behavior of real fluids quite well.

Due to the cubic nature of the equation of state, the density dependence is restricted, whereas there is no limit on the amount of temperature dependence that can be introduced into the equation. Thus, it is of primary importance to make sure that the density dependence of the equation of state is adequate enough to describe real fluid behavior to a high level of accuracy. For this purpose thermodynamic property values are required along isotherms for wide ranges of temperature and pressure conditions.

Equation 9 can be written in a computationally more convenient form by writing the denominator as a product of a first order term and a quadratic function by setting $d_1 = A_5$, $d_2 = A_2$, $d_3 = A_3 - A_1$, $d_4 = A_4 - A_1A_3$ and $d_5 = -A_1A_4$,

$$Z = \frac{1 + A_5 \rho_r + A_2 \rho_r^2}{(1 - A_1 \rho_r)(1 + A_3 \rho_r + A_4 \rho_r^2)} \qquad (26)$$

where $\rho_r = \rho/\rho_c$

To determine the adequacy of the density dependence of equation 26, values of density, vapor pressure and the partial derivative of pressure with respect to density $(\partial P/\partial \rho)_T$ along isotherms were taken from Goodwin's (26) compilation of the thermodynamic functions for propane. For each isotherm the above property values were used in multi-property regression analysis to obtain an optimum set of values for A_1 through A_5 which gave minimum deviation from Goodwin's values for all the properties considered. Table 1 gives the values of the parameters A_1 through A_5 for a total of twenty four isotherms, while Table 2 gives the average absolute deviations from Goodwin's values for each property for each isotherm.

From Table 2 it can be seen that the most general density-cubic equation predicts density and vapor pressure values with an average absolute deviation of one tenth of one percent in most regions except in the neighborhood of the critical point. It is interesting to note that both the liquid and gas phase behavior of propane are predicted accurately. In principle, it is possible to develop analytical relations for the temperature dependence of equation 26 with sufficient accuracy to approach the accuracy levels in Table 2; this will be discussed in the next chapter. Thus, the density dependence of equation 26 is adequate enough to provide a good description of the thermodynamic behavior of propane for all fluid states, an achievement which hitherto was possible only using equations of state which had higher order density dependence than cubic.

TABLE 1

Parameter Values to be used in Equation 26 at each Isotherm

Isotherm K	A_1	A_2	A_3	A_4	A_5
95.0	0.238893	1.98446	-0.109443	-0.014541	-6.85230
100.0	0.238893	1.99047	-0.072851	-0.016547	-6.84378
110.0	0.238893	3.07607	0.196683	-0.058884	-10.2735
120.0	0.238893	2.45458	-0.024084	-0.002970	-8.14833
140.0	0.238893	1.54402	0.086821	-0.059602	-5.10893
160.0	0.238893	2.03587	0.473150	-0.144922	-6.45341
180.0	0.238893	1.62803	0.356993	-0.119238	-5.08307
200.0	0.238893	1.33797	0.277608	-0.102911	-4.11997
220.0	0.238893	1.12157	0.218121	-0.091477	-3.41094
240.0	0.238893	0.956634	0.179106	-0.085520	-2.87692
260.0	0.238893	0.827365	0.163771	-0.086826	-2.46335
280.0	0.238893	0.726484	0.252970	-0.124678	-2.14209
300.0	0.238893	0.625929	0.159633	-0.100661	-1.83994
320.0	0.238893	0.530456	0.268477	-0.159891	-1.57053
340.0	0.238893	0.452896	0.371161	-0.203345	-1.35399
360.0	0.238893	0.402792	0.425081	-0.227933	-1.19976
369.8*	0.286248	0.382062	0.550612	-0.102961	-1.09690
373.15	0.357457	0.354061	0.604742	-0.084248	-1.06924
380.0	0.238893	0.386103	0.347454	-0.190000	-1.10065
400.0	0.238893	0.367507	0.211830	-0.136204	-1.03826
420.0	0.238893	0.309305	0.273097	-0.182537	-0.91335
450.0	0.238893	0.282088	0.197213	-0.159802	-0.828237
500.0	0.238893	0.249403	0.112407	-0.126038	-0.715034
550.0	0.238893	0.168536	0.170428	-0.180027	-0.546128
600.0	0.238893	0.174003	0.078716	-0.126537	-0.509963

* Critical temperature of propane

TABLE 2

Average Absolute Deviations (A.A.D.) of Properties of Propane from Reported Values of Goodwin at Each Isotherm and Pressure Range of Data Used for Determination of Parameters in Equation 26.

Isotherm K	Density			Vapor Pressure	$(\partial P/\partial \rho)_T$		
	No. of Points	Pressure Range kPA	A.A.D.%	A.A.D.%	No. of Points	Pressure Range kPA	A.A.D.%
95.0	8	6600~67320	0.350	4.330	8	6600~67320	10.01
100.0	9	1300~66280	0.012	0.074	9	1300~66280	1.24
110.0	10	4550~73040	0.007	0.010	10	4550~73040	1.71
120.0	11	1710~70130	0.010	0.032	11	1710~70130	2.33
140.0	13	2250~72250	0.014	0.007	13	2250~72250	0.02
160.0	15	2970~73810	0.0001	0.0008	15	2970~73180	0.02
180.0	18	724~73250	0.0005	0.0003	18	724~73250	0.04
200.0	20	2350~72750	0.0007	0.0007	20	2350~72750	0.06
220.0	23	1970~71900	0.0014	0.0008	23	1970~71900	0.10
240.0	29	100~74920	0.019	0.0021	29	100~74920	0.20
260.0	35	103~73330	0.061	0.061	35	103~73330	0.40
280.0	42	110~71760	0.136	0.095	42	110~71760	1.59
300.0	27	240~73300	0.285	0.030	27	240~73300	1.29
320.0	34	255~68900	0.691	0.060	34	255~68900	4.53
340.0	46	270~70030	0.673	0.044	46	270~70030	6.50
360.0	33	565~66410	0.965	0.512	33	565~66410	7.22
369.8	30	1110~64690	4.3895	--	--	--	--
373.15	80	101~101860	1.8987	--	--	--	--
380.0	30	1151~71340	2.780		30	1155~71340	14.35
400.0	29	1220~67780	1.330		29	1220~67780	6.48
420.0	28	1296~64700	0.347		28	1296~64700	2.72
450.0	27	1400~66500	0.177		27	1400~66500	1.68
500.0	25	1580~64350	0.159		25	1580~64350	0.94
550.0	24	1760~70930	0.085		24	1760~70930	0.95
600.0	22	1930~65900	0.120		22	1930~65900	0.42

Comparisons with other cubic equations of state. Traditionally, two of the parameters occuring in a cubic equation of state have been determined using the classical critical constraints, while any remaining parameters have been determined by empirically curve fitting thermodynamic property values (e.g., vapor pressure). In the present work the parameters occurring in equation 26 have been determined through regression analysis of propane thermodynamic property values. Therefore, it is only appropriate that the comparison be made on the same basis, that is, the parameters occurring in each cubic equation which is compared also should be determined from regression analysis in the same manner, using the same thermodynamic data. From Table 2, it can be seen that the deviations increase in the neighborhood of the critical region of propane for equation 26. A comparison in this region of least accuracy for equation 26 would be of interest, to confirm the superiority of equation 26 over all previously reported cubic equations of state. The comparisons are made in two steps, starting with a comparison along the critical isotherm of propane using Goodwin's reported values in the pressure range of 160 psia to 9380 psia. Experimental PVT data have been reported along an isotherm a few degrees above the critical temperature by Beattie et.al., (9), Cherney et.al. (15), Deschner et.al. (18) and Dittmar et.al. (19) in the pressure range of 14.7 psia to 14770 psia. These data were used in the second step for comparison to substantiate the results obtained using Goodwin's values along the critical isotherm. The cubic equations compared are the van der Waals equation (65), the Redlich-Kwong equation (49), Martin's general equation, the Soave equation (55), Abbott's generic equation (1) and the Peng-Robinson equation (45). The results of the study are presented in Table 3. It can be seen that equation 26 emerges as the best density-cubic equation of state according to this comparison.

To show how a constrained cubic equation performs along the critical isotherm as well as isotherms above and below the critical temperature, a set of calculations was made using the Peng-Robinson equation of state (with parameters determined using the relations given by Peng-Robinson), since it is considered to be one of the best equations of state among the previously reported density-cubic equations in the literature. The results are presented in Table 4. A comparison with the results presented in Table 2, shows that equation 26 is by far superior to the constrained Peng-Robinson equation. Although the introduction of analytical temperature dependence into equation 26 will yield a temperature-density explicit equation of state of lower accuracy than the discrete isotherm results in Table 2, with an accurate description of the temperature dependence, the resultant equation of state will still be superior to all previously reported cubic equations due to the fact that it is the most general density-cubic equation of state.

TABLE 3

Results of Performance of Unconstrained Cubic Equations in the Critical Region of Propane

Isotherm K	No. of Points	Pressure Range kPA	Average Absolute Deviation in Density % Van der Waals	 Redlich-Kwong or Soave	 Abbott	 Peng-Robinson	 Martin	 Equation 26
369.8	30	1100~64690	13.07	6.899	5.494	5.599	5.366	4.389
373.15	80	101~101860	8.74	3.59	3.760	4.620	2.720	1.898

TABLE 4

Average Absolute Deviations (A.A.D.) of Predicted Properties of Propane from Reported Values of Goodwin at Each Isotherm for the Peng-Robinson Equation of State

Isotherm K	Density			Vapor Pressure	$(\partial P/\partial \rho)_T$		
	No. of Points	Pressure Range kPA	A.A.D.%	A.A.D.%	No. of Points	Pressure Range kPA	A.A.D.%
160.0	15	2970~73180	5.110	--	15	2970~73180	27.61
200.0	20	2350~72750	6.630	3.466	20	2350~72750	9.41
240.0	29	100~74920	7.334	1.746	29	100~74920	10.42
300.0	27	240~73300	6.070	1.227	27	240~73300	20.17
320.0	34	255~68900	5.370	0.725	34	255~68900	20.44
360.0	33	565~66410	4.500	0.006	33	565~66410	21.24
369.8	30	1110~64690	7.468	--	--	--	--
373.15	80	101~101860	5.050	--	--	--	--
380.0	30	1150~71340	4.480		30	1150~71340	17.91
420.0	28	1296~64700	3.300		28	1296~64700	12.93
450.0	27	1400~66500	2.870		27	1400~66500	11.38
550.0	24	1760~70930	2.110		24	1760~70930	8.55

CHAPTER IV

DEVELOPMENT OF A PROVISIONAL TEMPERATURE DEPENDENCE FOR THE EQUATION OF STATE

The requirement that the equation of state be cubic in density restricts the density dependence, but the temperature dependence is open for analysis, with practical application of the equation of state being the only criteria in restricting the order of the temperature dependence. The evaluation of polynomials consumes very little computing time as compared to repeated calculations using a do-loop and thus, adding more terms to a polynomial in temperature does not for all practical purposes increase the time required for an analytical solution of the cubic equation. In the development of the temperature dependence of the equation of state the goal was to attain a level of accuracy comparable to the second class of equations of state like the Modified Benedict-Webb-Rubin equation of state (56).

In order to determine the form of the temperature dependence, the expressions for the second virial coefficient and third virial coefficient were obtained from equation 26 by expanding it into a polynomial in density. The second and third virial coefficients are given by the following equations

$$B = A_5 - A_3 + A_1 \tag{27}$$

$$C = A_2 - A_4 + A_1A_3 - (A_3 - A_1)A_5 + (A_3 - A_1)^2 \qquad (28)$$

where B and C are the second and third virial coefficients, respectively. It is known (63) that the second and third virial coefficients can be well represented by reciprocal temperature expansions. Since all the five parameters A_1 through A_5 appear in the expressions for the second and third virial coefficients, reciprocal temperature expansions were chosen for the temperature dependence of the equation of state.

In Table 1 the value of parameter A_1 is a constant for all temperatures except very near the critical point and hence it was fixed at that value. The values of A_2 through A_5 were plotted against reduced reciprocal temperature as shown in Figures 1 to 4. Though the plots for A_5 and A_2 give reasonably smooth curves, the plots for A_3 and A_4 show a big scatter of the values. This is probably due to a high correlation between the parameters. In order to avoid the scatter in the plots for A_3 and A_4 against reduced temperature, A_2 and A_5 were fitted to a polynomial in reciprocal temperature and A_3 and A_4 were redetermined for each isotherm using density, vapor pressure and $(\partial P/\partial \rho)_T$ values for propane and plotted against reciprocal reduced temperature. This led to a smoother curve for A_3 and A_4 remained almost a constant. This procedure led to the following temperature dependence for the equation of state

$$Z = \frac{1 + A_5(T_r)\,\rho_r + A_2(T_r)\,\rho_r^2}{(1 - A_1\rho_r)(1 + A_3(T_r)\,\rho_r + A_4\,\rho_r^2)} \qquad (29)$$

where the temperature dependent parameters A_5, A_3 and A_2 are expressed

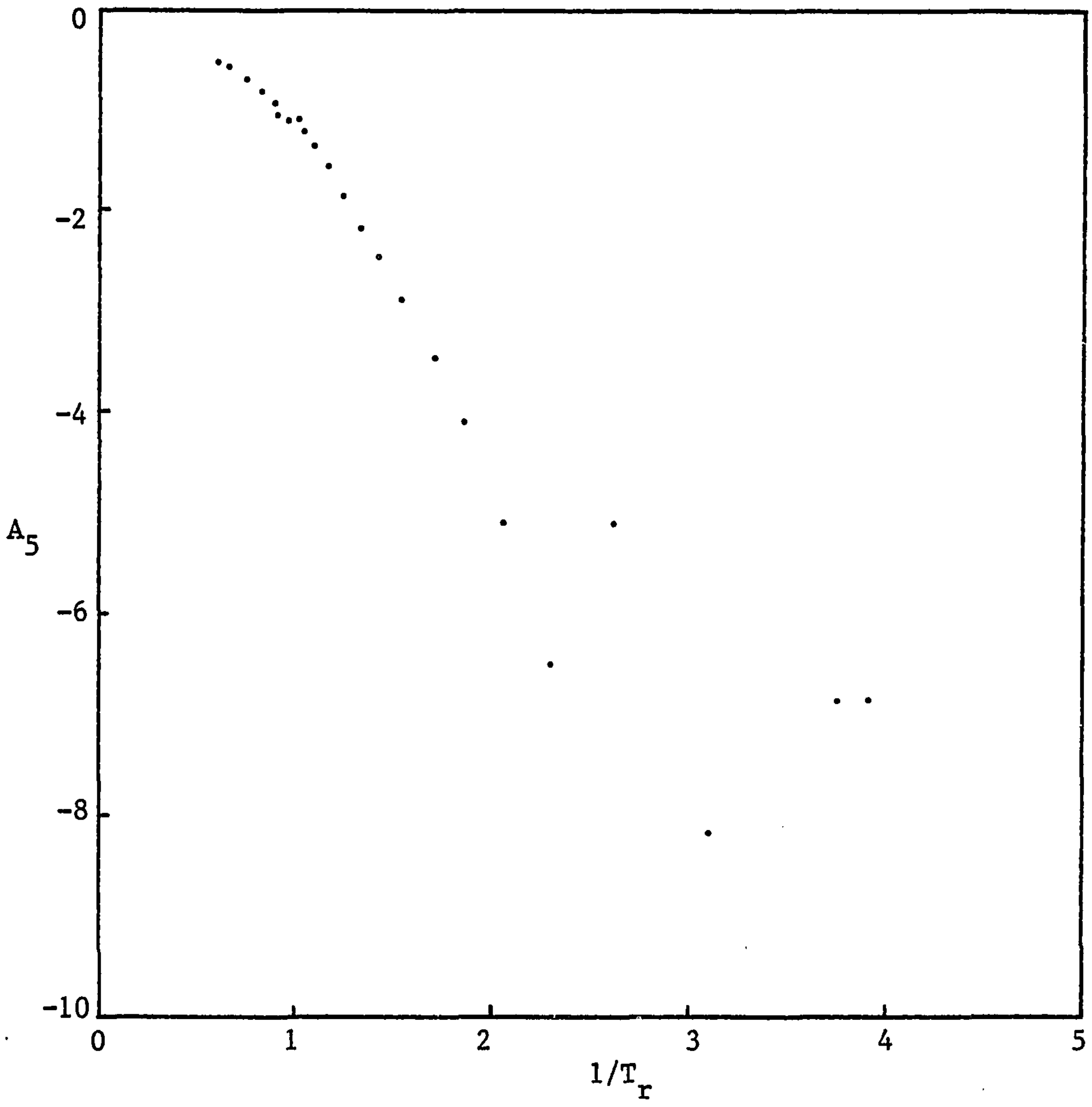

FIGURE 1. Plot of parameter A_5 versus reciprocal reduced temperature.

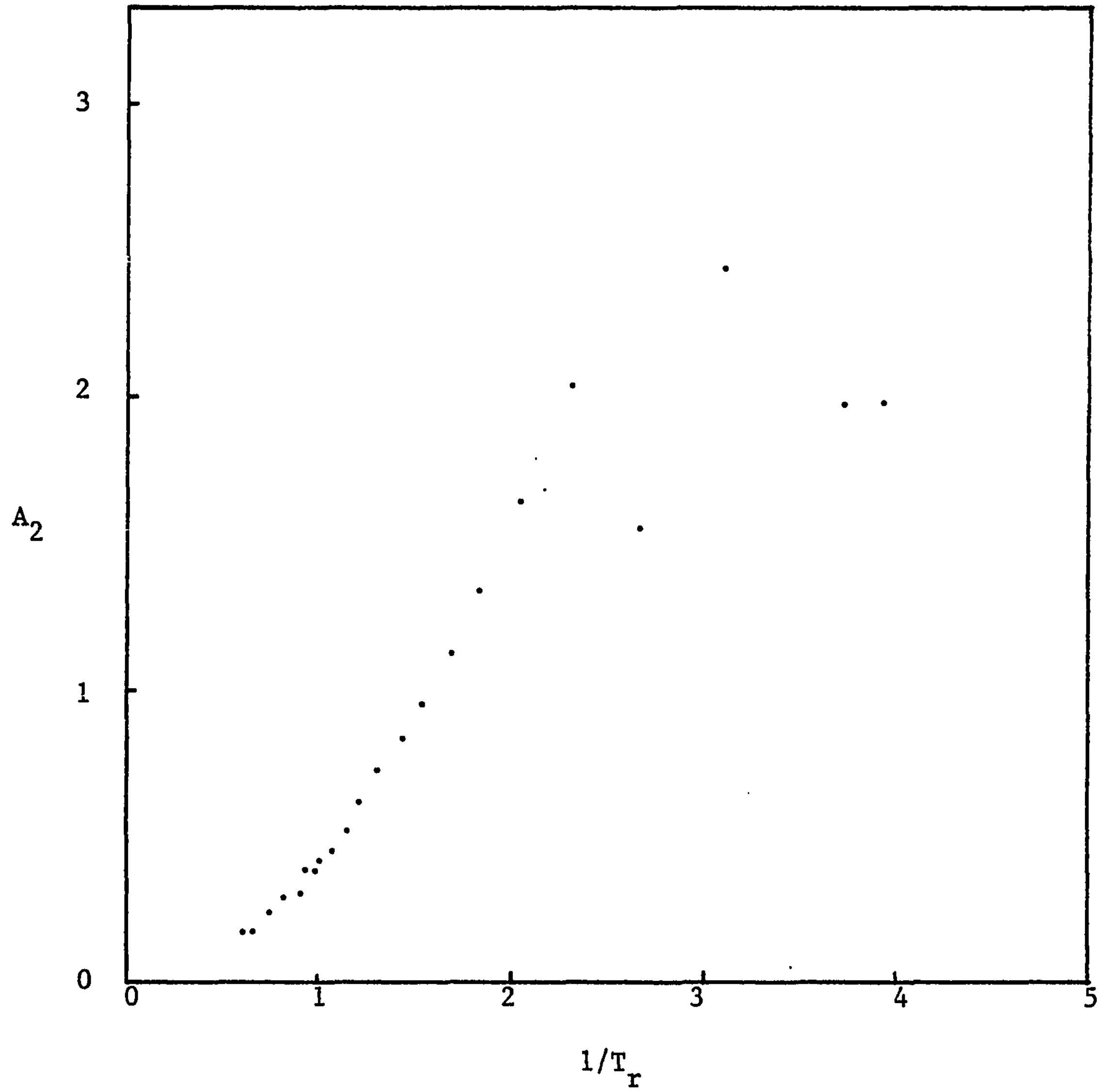

FIGURE 2. Plot of parameter A_2 versus reciprocal reduced temperature.

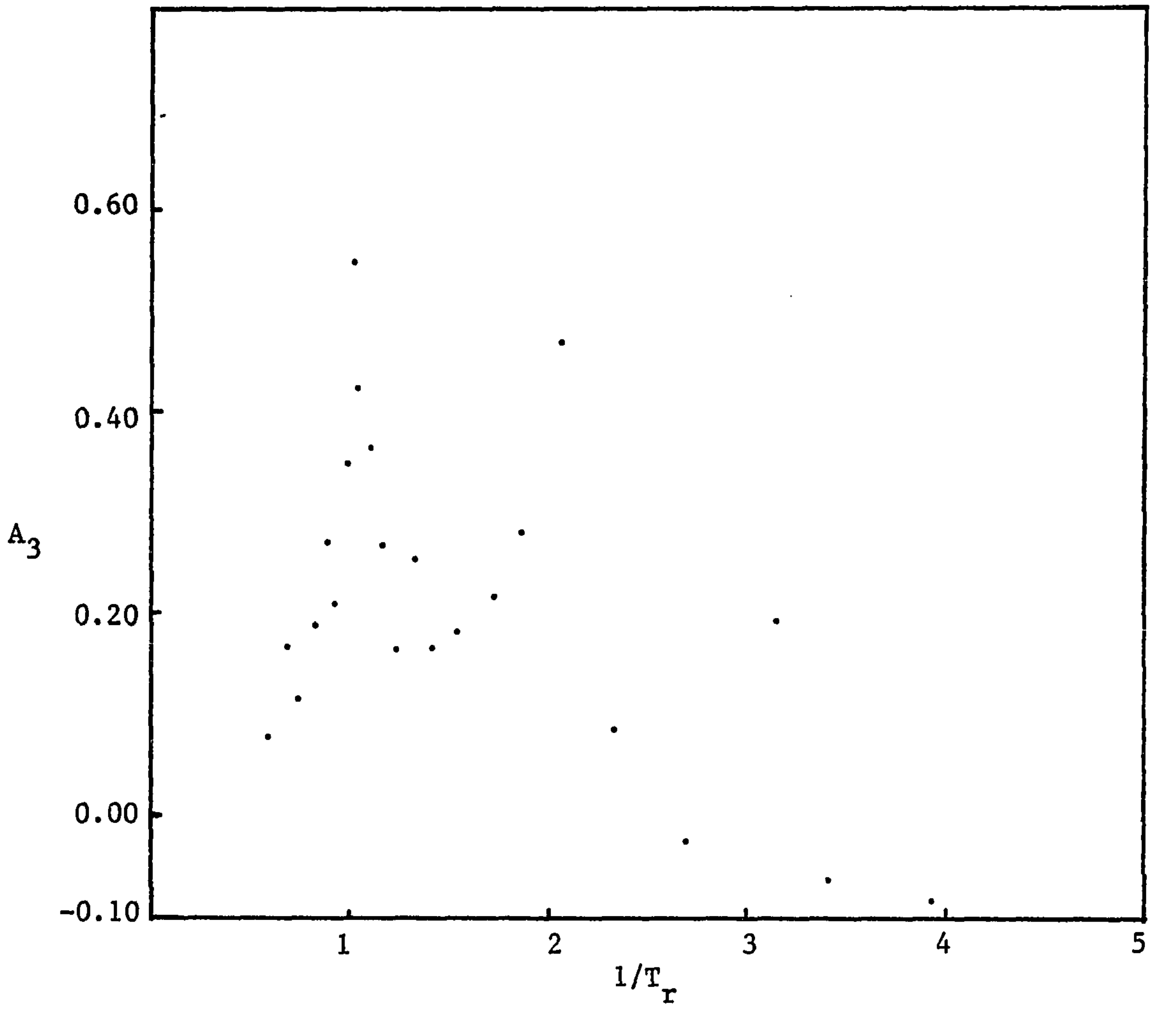

FIGURE 3. Plot of parameter A_3 versus reciprocal reduced temperature.

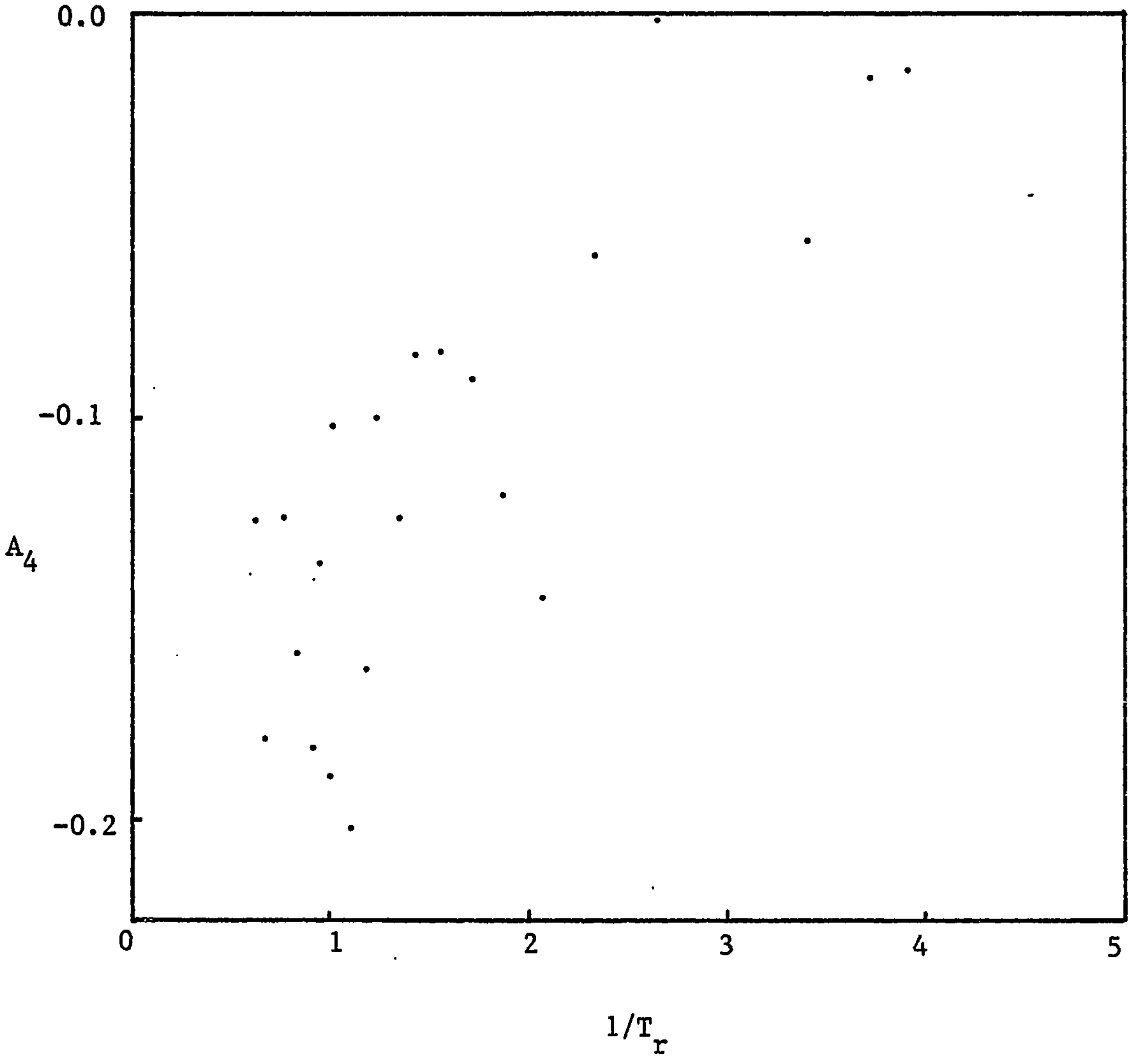

FIGURE 4. Plot of parameter A_4 versus reciprocal reduced temperature.

as follows

$$A_5(T_r) = A_{51} + \frac{A_{52}}{T_r} + \frac{A_{53}}{T_r^2} + \frac{A_{54}}{T_r^3} + \frac{A_{55}}{T_r^4}$$

$$A_2(T_r) = A_{21} + \frac{A_{22}}{T_r} + \frac{A_{23}}{T_r^2} + \frac{A_{24}}{T_r^3}$$

$$A_3(T_r) = A_{31} + \frac{A_{32}}{T_r} + \frac{A_{33}}{T_r^2} + \frac{A_{34}}{T_r^3}$$

The parameters occuring in equation 29 were redetermined using thermodynamic property values over a wide range of temperature and pressure conditions. Equation 29 predicts propane density covering a wide range of fluid states from a reduced temperature of 0.24 to a reduced temperature of 1.62 and up to a reduced pressure of 17 with an average absolute deviation of about half a percent. Vapor pressure values from $T_r = 0.27$ to the critical temperature are predicted within half a percent. The derivatives ($\partial P/ \partial T)\rho$ and ($\partial P/\partial \rho)_T$ calculated using Goodwin's non-analytic equation (26) are predicted within 5 percent by equation 29. The equation of state parameters for propane are presented in Table 5.

The results for propane are compared with those obtained using the Modified Benedict-Webb-Rubin equation of state (56) and the Peng-Robinson equation of state and are presented in Table 6. Before the discussion of the results it has to be stated that the Peng-Robinson equation of state is a generalized equation whereas equation 29 and the Modified Benedict-Webb-Rubin equation are for a specific fluid.

TABLE 5

Reduced Parameters for use in Equation 29

Parameter	Value for Propane
A_1	0.239000
A_{21}	-0.182160
A_{22}	0.368512
A_{23}	0.243401
A_{24}	-0.031339
A_{31}	-0.082134
A_{32}	0.528881
A_{33}	-0.139924
A_{34}	0.012492
A_4	-0.188000
A_{51}	0.091565
A_{52}	-0.034023
A_{53}	-1.451970
A_{54}	0.238376
A_{55}	-0.011072

TABLE 6

Deviations of Predicted Properties of Propane from Reported Values of Goodwin and Comparison of Results between Equation 29, Peng-Robinson and Modified BWR Equations of State

Property	No. of Points	Temperature Range, R	Pressure Range psia	Av. Abs. Percent Deviation		
				Equation 29	Peng-Robinson	MBWR
Density	332	162.0~1080.0	$0.22\text{x}10^{-6}$~10636	0.584	4.662	0.890
Vapor Pressure	23	180.0~665.64	$0.46\text{x}10^{-5}$~616.3	0.440	2.19*	0.458
$(\partial P/\partial T)_{\rho}$	166	162.0~1080.0	29.7 ~10624	5.766	9.23	28.43
$(\partial P/\partial \rho)_{T}$	164	162.0~1080.0	16.5 ~10624	4.212	22.97	10.002

* Vapor Pressure Calculation does not converge below 324 R.

The large deviation in density for the Peng-Robinson equation is due to its inability to predict the compressed liquid region accurately. Also the latter equation of state could not be used to calculate vapor pressures below 324 R. From the comparison presented in Table 6 it can be concluded that equation 29 is quite superior to the Peng-Robinson equation due to its ability to predict the liquid phase densities and the low temperature vapor pressures accurately. Equation 29 is on par with the Modified Benedict-Webb-Rubin equation of state in its ability to predict the properties of propane in the overall region of fluid states but at the same time it has the added advantage of computational speed due to the simple analytical solution for the density.

CHAPTER V

APPLICATION OF THE EQUATION OF STATE TO SELECTED INDIVIDUAL PURE FLUIDS

One of the basic requirements for an equation of state to achieve widespread use in research and industry is the ability to predict the thermodynamic behavior of a wide range of fluids. After having developed the temperature dependence of the equation of state using thermodynamic property values for propane the equation of state is applied to selected lower and higher members of the normal saturated hydrocarbon series. This procedure not only helps to ascertain the applicability of equation 29 to fluids other than propane but it also provides the basis for later generalization of the equation of state.

Methane was chosen as one of the fluids since it is the first member of the normal saturated hydrocarbon series and n-heptane and n-octane were selected as the higher members of the series.

Experimental density, vapor pressure and enthalpy departure data were used in multiproperty regression analysis to determine the optimum set of parameters in equation 29 which gave minimum deviations from the experimental values for all the properties considered.

$$Z = \frac{1 + A_5(T_r)\ \rho_r + A_2(T_r)\ \rho_r^2}{(1 - A_1\rho_r)(1 + A_3(T_r)\ \rho_r + A_4\ \rho_r^2)} \qquad (29)$$

where the temperature dependent parameters A_5, A_3 and A_2 are expressed as follows

$$A_5(T_r) = A_{51} + \frac{A_{52}}{T_r} + \frac{A_{53}}{T_r^2} + \frac{A_{54}}{T_r^3} + \frac{A_{55}}{T_r^4}$$

$$A_2(T_r) = A_{21} + \frac{A_{22}}{T_r} + \frac{A_{23}}{T_r^2} + \frac{A_{24}}{T_r^3}$$

$$A_3(T_r) = A_{31} + \frac{A_{32}}{T_r} + \frac{A_{33}}{T_r^2} + \frac{A_{34}}{T_r^3}$$

Table 7 lists the values of the parameters for each fluid. The results obtained for the fluids considered using the most general density-cubic equation of state are presented in Tables 8 to 10 along with a comparison with the results obtained using the Peng-Robinson and the Modified Benedict-Webb-Rubin equations of state.

From the results it can be seen that the most general density-cubic equation of state performs quite well for fluids other than propane and thus it is amenable to generalization. In comparison to the Peng-Robinson equation, equation 29 describes the low temperature vapor pressures and the liquid densities quite well and it is comparable to the Modified Benedict-Webb-Rubin equation in the overall fluid states.

TABLE 7

Reduced Parameters for Methane, n-Heptane and n-Octane

Parameter	Parameter Value		
	Methane	n-Heptane	n-Octane
A_1	0.239000	0.241042	0.244282
A_{21}	-0.224680	-0.220132	-0.119012
A_{22}	0.428590	0.426032	-0.299461
A_{23}	0.205501	0.241123	0.683564
A_{24}	-0.034396	-0.020819	0.075546
A_{31}	-0.082134	-0.076883	0.407431
A_{32}	0.528881	0.515652	0.351472
A_{33}	-0.139924	-0.140302	0.106380
A_{34}	0.012492	0.012955	0.052481
A_4	-0.188000	-0.187943	-0.193307
A_{51}	0.026275	0.249747	0.289404
A_{52}	-0.013015	-0.136615	0.540259
A_{53}	-1.431860	-1.537200	-1.280060
A_{54}	0.322188	0.205520	-0.556054
A_{55}	-0.029629	-0.006019	-0.001416

TABLE 8

Deviations of Predicted Properties of Methane using Equation 29 and Comparison of Results between Equation 29, Peng-Robinson and Modified BWR Equations of State

Property	No. of Points	Temperature Range, R	Pressure Range, psia	Av. Abs. Percent Deviation		
				Equation 29	Peng-Robinson	MBWR
Density	41	206.2~1121.7	129.7~2324.7	0.256	5.320	0.322
Vapor Pressure	29	200.9~ 343.2	14.7~ 668.7	0.308	0.660	0.441
Enthalpy Departure	38	209.7~ 509.7	450.0~2000.0	0.559*	2.404*	0.68*

* Deviations in Btu/lb

TABLE 9

Deviations of Predicted Properties of n-Heptane using Equation 29 and Comparison of Results between Equation 29, Peng-Robinson and Modified BWR Equations of State

Property	No. of Points	Temperature Range, R	Pressure Range, psia	Av. Abs. Percent Deviation		
				Equation 29	Peng-Robinson	MBWR
Density	41	370 ∿ 920	14.7 ∿ 3082	0.461	1.47	0.645
Vapor Pressure	44	347 ∿ 957	0.0001 ∿ 350	1.374	0.920[*]	1.850
Enthalpy Departure	17	972 ∿ 1167	79 ∿ 2363	1.657[**]	1.06[**]	0.756[**]

[*] Vapor Pressure Calculation does not converge below 598 R.

[**] Deviations in Btu/lb.

TABLE 10

Deviations of Predicted Properties of n-Octane using Equation 29 and Comparison of Results between Equation 29, Peng-Robinson and Modified BWR Equations of State

Property	No. of Points	Temperature Range, R	Pressure Range, psia	Av. Abs. Percent Deviation		
				Equation 29	Peng-Robinson	MBWR
Density	54	389.7 ∿ 970	14.7 ∿ 239	1.10	3.92	1.821
Vapor Pressure	63	390 ∿ 1019.7	0.0003 ∿ 350	1.55	1.51*	2.51
Enthalpy Departure	68	535 ∿ 1060	200 ∿ 1400	1.17**	2.83**	2.18**

*Vapor Pressure calculation does not converge below 608 R.

**Deviations in Btu/lb.

CHAPTER VI

DEVELOPMENT OF A GENERALIZED EQUATION OF STATE USING DATA FOR METHANE THROUGH n-DECANE

The most general density-cubic equation of state has been shown to describe the thermodynamic behavior of methane, propane, n-heptane and n-octane quite well. To extend the usefulness of this equation of state for which parameters have been determined only for a limited number of fluids, it is desirable to have available a practical means of generating parameters for other fluids of interest.

In the three parameter corresponding states theory proposed by Pitzer (47) the compressibility factor, Z can be expressed in a power series in the acentric factor ω, with the expansion truncated after the first order term,

$$Z = Z_o + Z_1\omega + . . . \tag{30}$$

$$Z_o = Z_o\ (T_r,\ P_r) \tag{31}$$

$$Z_1 = Z_1(T_r,\ P_r) \tag{32}$$

where $T_r = T/T_c$ and $P_r = P/P_c$.

For simple fluids like argon the acentric factor is zero and the compressibility factor is given by Z_o. For other fluids the acentric factor is calculated from the following defining relation given by Pitzer,

$$\omega = -\log P_r - 1.000$$

where P_r is the reduced vapor pressure at $T_r = 0.70$. $Z_o + Z_1\omega$ represents the compressibility factor for fluids which deviate from the simple fluid behavior. This theory has been successfully applied to a wide class of fluids.

A similar approach has been taken for the generalization of equation 29, repeated here

$$Z = \frac{1 + A_5(T_r)\ \rho_r + A_2(T_r)\ \rho_r^2}{(1 - A_1\rho_r)(1 + A_3(T_r)\rho_r + A_4\rho_r^2)} \qquad (29)$$

where the temperature dependent parameters A_5, A_2 and A_3 are expressed as follows

$$A_5(T_r) = A_{51} + \frac{A_{52}}{T_r} + \frac{A_{53}}{T_r^2} + \frac{A_{54}}{T_r^3} + \frac{A_{55}}{T_r^4}$$

$$A_2(T_r) = A_{21} + \frac{A_{22}}{T_r} + \frac{A_{23}}{T_r^2} + \frac{A_{24}}{T_r^3}$$

$$A_3(T_r) = A_{31} + \frac{A_{32}}{T_r} + \frac{A_{33}}{T_r^2} + \frac{A_{34}}{T_r^3}$$

The values of A_1 and A_4 obtained for methane, propane, n-heptane and n-octane were plotted against the acentric factor, ω as shown in figures 5 and 6. The values of $A_5(T_r)$, $A_2(T_r)$ and $A_3(T_r)$ were plotted against the acentric factor at various reduced temperatures as shown in

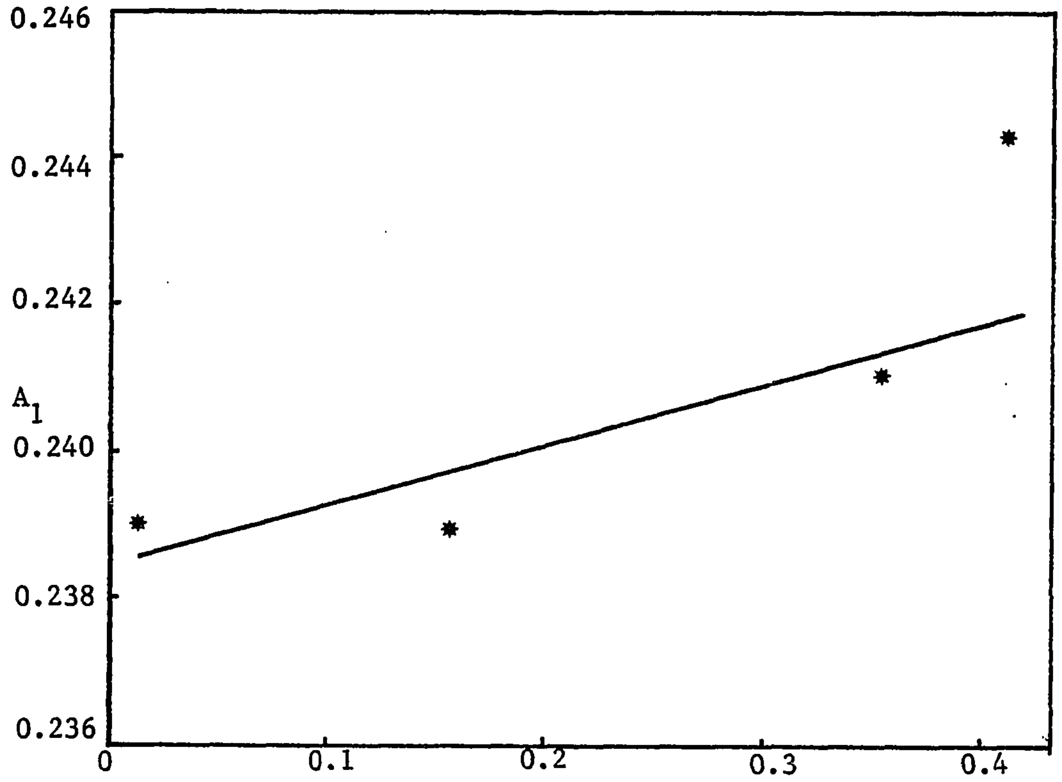

FIGURE 5. Plot of parameter A_1 versus acentric factor, ω

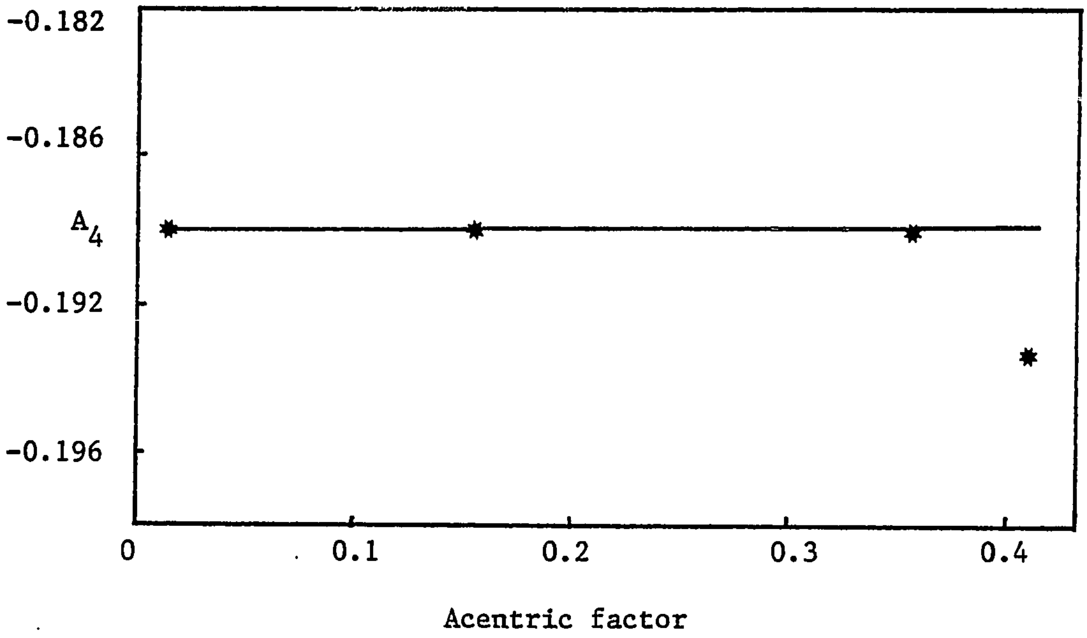

FIGURE 6. Plot of parameter A_4 versus acentric factor, ω

figures 7,8 and 9. From figures 5 and 6 it can be infered that A_1 is a function of the acentric factor and A_4 is practically a constant. The parameters $A_5(T_r)$, $A_3(T_r)$ and $A_2(T_r)$ show almost a linear dependence on the acentric factor except at the low reduced temperatures where a higher order dependence on the acentric factor may be required. In the initial process of the generalization the following relationships were chosen for the parameters

$$A_1 = b_{11} + b_{12}\omega \qquad (33)$$

$$A_2(T_r) = b_{21}(T_r)(1 + b_{22}\omega + b_{23}\omega^2) \qquad (34)$$

$$A_3(T_r) = b_{31}(T_r)(1 + b_{32}\omega + b_{33}\omega^2) \qquad (35)$$

$$A_4 = b_{41} \qquad (36)$$

$$A_5(T_r) = b_{51}(T_r)(1 + b_{52}\omega + b_{53}\omega^2) \qquad (37)$$

Experimental density and vapor pressure data for methane through n-decane over a wide range of fluid states were used in multiproperty regression analysis to obtain an optimum set of parameters in the generalized equation of state, which gave minimum deviation in the density and vapor pressure values. To obtain a good set of initial values for the parameters occuring in the generalized equation, previously determined parameter values for propane were used in equations 33 to 37 as follows

$$b_{21}(T_r) = A_2(T_r)_{C_3}$$

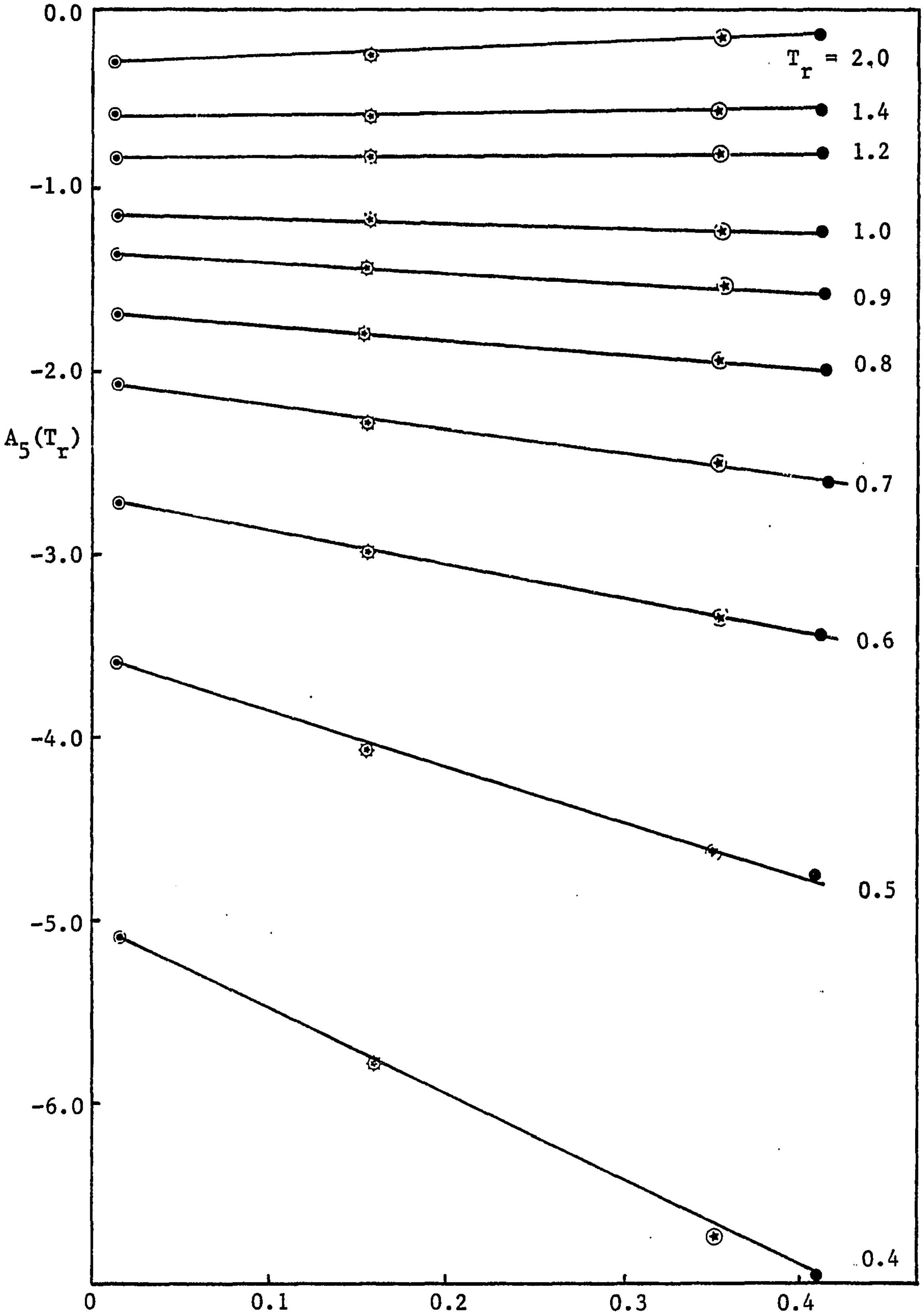

FIGURE 7. Plot of the parameter $A_5(T_r)$ versus acentric factor at various reduced temperatures

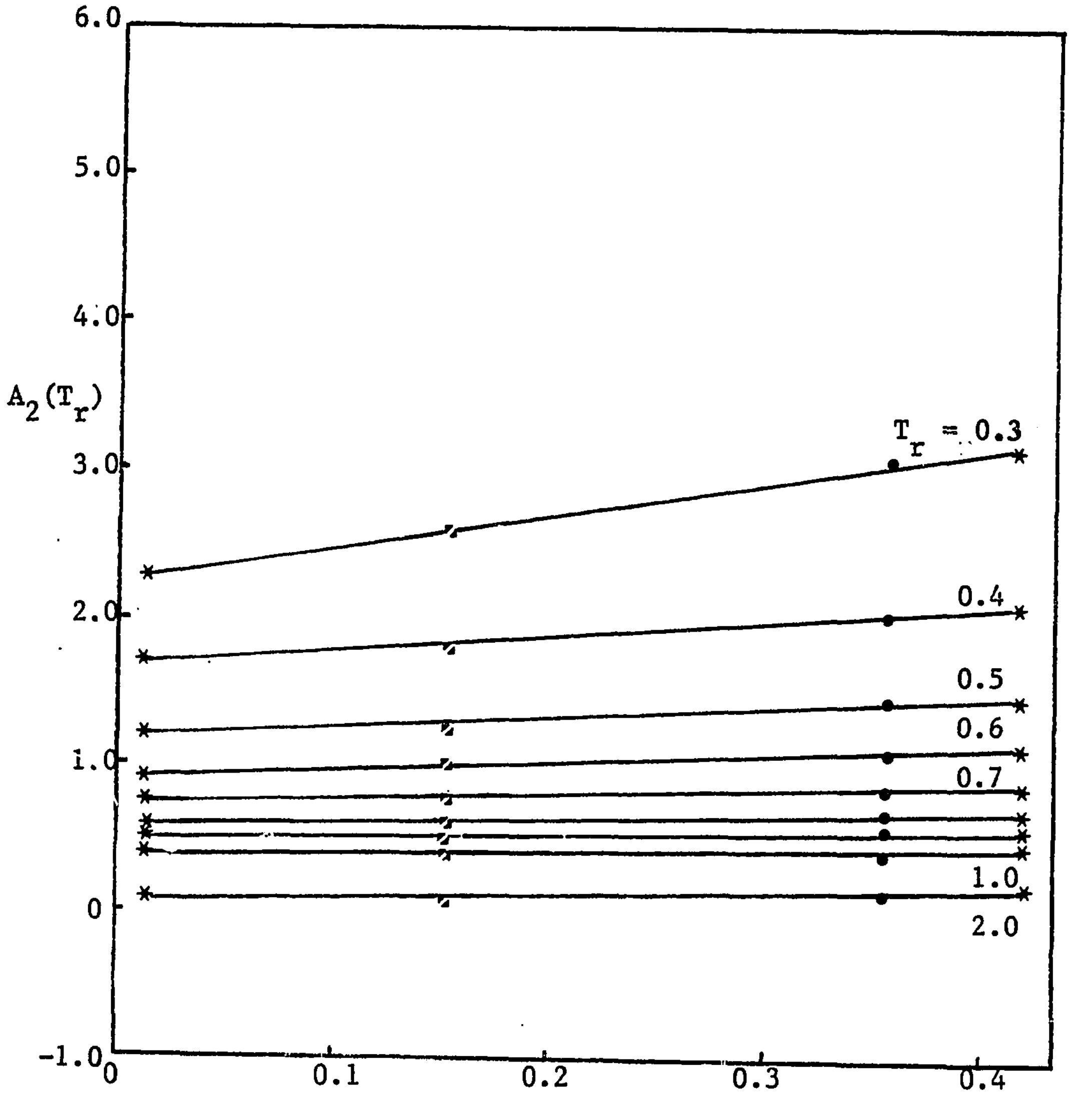

Figure 8. Plot of the parameter $A_2(T_r)$ versus acentric factor, ω at various reduced temperatures

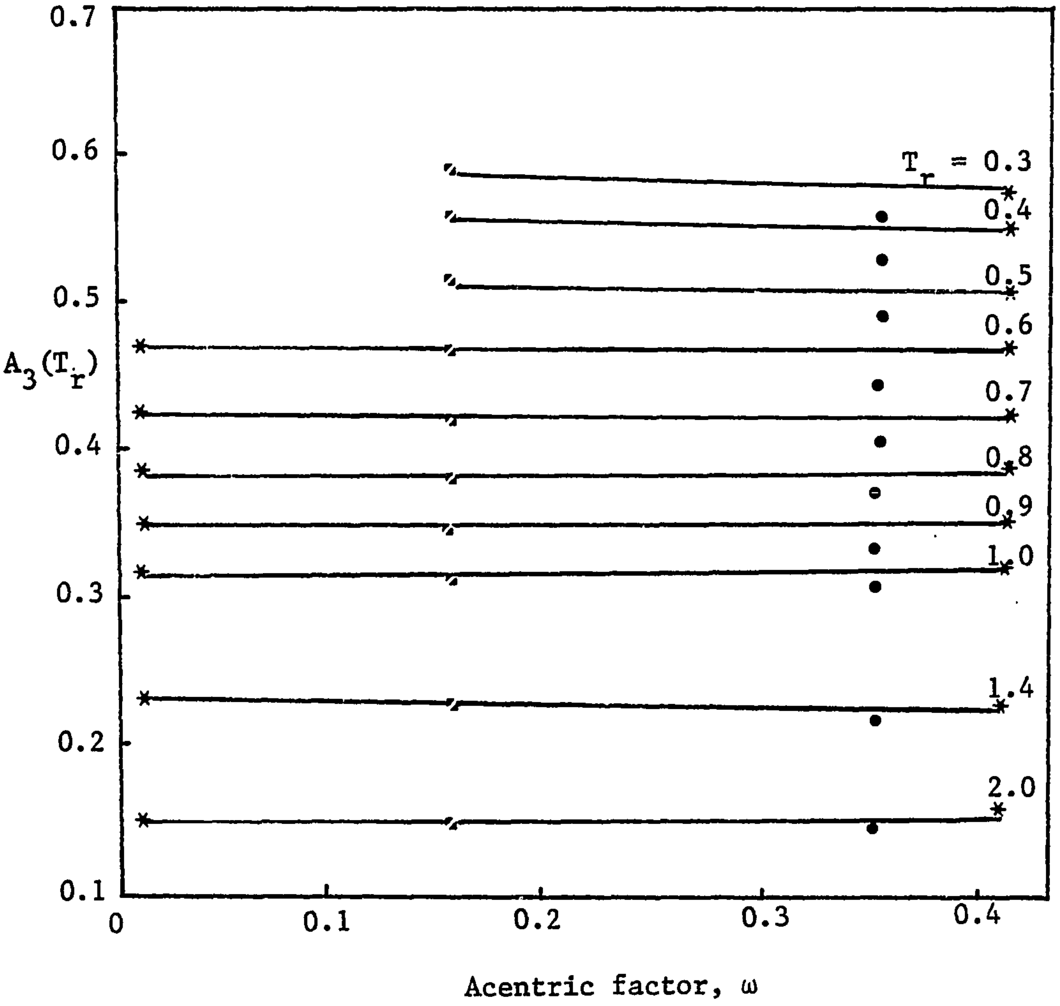

FIGURE 9. Plot of the parameter $A_3(T_r)$ versus acentric factor, ω at various reduced temperatures.

$$b_{31}(T_r) = A_3(T_r)_{C_3}$$

$$b_{51}(T_r) = A_5(T_r)_{C_3}$$

$$b_{41} = A_{4C_3}$$

$$b_{11} = A_{1C_3}$$

and ω was replaced by $(\omega - \omega_{C_3})$.

The reason for the choice of propane instead of methane parameter values is due to the fact that the data for propane exist at lower reduced temperatures than those of methane. A regression analysis for the rest of the parameters occuring in equations 32 to 37 using the density and vapor pressure data of methane through n-decane gave an overall average absolute deviation of about 1.8 percent. With this result as a starting point, the generalized equation of state was further developed following the methodology presented by Goin (25) to achieve an accuracy level comparable to the generalized Modified Benedict-Webb-Rubin equation of state cast in a three parameter corresponding states framework (57). This led to the following equation of state which gave an overall average absolute deviation of 1.05 percent from the experimental values of vapor pressure and density for all the fluids considered, namely methane through n-decane.

$$Z = \frac{1 + A_5(T_r)\,\rho_r + A_2(T_r)\,\rho_r^2}{(1 - A_1\,\rho_r)(1 + A_3(T_r)\,\rho_r + A_4\,\rho_r^2)} \tag{38}$$

where

$$A_5(T_r) = \left(a_{51} + \frac{a_{52}}{T_r} + \frac{a_{53}}{T_r^2} + \frac{a_{54}}{T_r^3} \right) \left[1 + \left(a_{55} + \frac{a_{56}}{T_r} + \frac{a_{57}}{T_r^2} \right) \omega \right]$$

$$A_2(T_r) = \left(a_{21} + \frac{a_{22}}{T_r} + \frac{a_{23}}{T_r^2} + \frac{a_{24}}{T_r^3} \right) \left[1 + a_{25}\omega \right]$$

$$A_3(T_r) = \left(\frac{a_{31}}{T_r} + \frac{a_{32}}{T_r^2} + \frac{a_{33}}{T_r^3} \right) \left[1 + \left(a_{34} + \frac{a_{35}}{T_r} \right) \omega + a_{36}\, \omega^2 \right]$$

$$A_1 = a_{11}$$

$$A_4 = a_{41}$$

However, when equation 38 was used to generate enthalpy departure values for the fluids methane through n-octane the deviations from the experimental values were of the order of 3 Btu/lb. An acceptable value would be around 2 Btu/lb, which is the result obtained when using the Modified Benedict-Webb-Rubin equation of state. The probable reason for the larger deviations is the fact that the functions of acentric factor within the brackets in the above equations for $A_2(T_r)$, $A_5(T_r)$ and $A_3(T_r)$ are highly dependent on the values of the temperature functions within the parentheses, a situation which magnifies itself in the calculation of the enthalpy departure where temperature derivatives of the functions are required.

To correct this problem the functions for $A_3(T_r)$, $A_5(T_r)$ and $A_2(T_r)$ were written in a linear form in the acentric factor and selected enthalpy data were included along with the vapor pressure and density data previously used to develop the following equation of state

$$Z = \frac{1 + A_5(T_r)\,\rho_r + A_2(T_r)\,\rho_r^2}{(1 - A_1\rho_r)(1 + A_3(T_r)\,\rho_r + A_4\,\rho_r^2} \qquad (39)$$

$$A_5(T_r) = \left(\frac{a_{51}}{T_r^{\,2}} + \frac{a_{52}}{T_r^{\,3}}\right) + \left(\frac{a_{53}}{T_r} + \frac{a_{54}}{T_r^{\,3}} + \frac{a_{55}}{T_r^{\,4}} + \frac{a_{56}}{T_r^{\,8}}\right)\omega$$

$$A_2(T_r) = \left(a_{21} + \frac{a_{22}}{T_r} + \frac{a_{23}}{T_r^{\,2}}\right) + \left(\frac{a_{24}}{T_r} + \frac{a_{25}}{T_r^{\,2}} + \frac{a_{26}}{T_r^{\,8}}\right)\omega$$

$$A_3(T_r) = \left(\frac{a_{31}}{T_r} + \frac{a_{32}}{T_r^{\,2}}\right) + \left(\frac{a_{33}}{T_r} + \frac{a_{34}}{T_r^{\,2}} + \frac{a_{35}}{T_r^{\,3}} + \frac{a_{36}}{T_r^{\,4}}\right)\omega$$

$$A_1 = a_{11}$$

$$A_4 = a_{41}$$

The intuition to add a high order temperature dependence term for $A_5(T_r)$ and $A_2(T_r)$ came from the work by Tsonopoulos (63) on the second virial coefficients of non-polar and polar fluids and their mixtures. Equation 39 predicts the density and vapor pressure data of methane through n-decane with an average absolute deviation of 1.0 percent from the experimental values. The enthalpy departure values are predicted within 1.7 Btu/lb average absolute deviation.

The value of the acentric factor, ω depends on the source from which it is obtained. For example the value of the acentric factor for methane has been quoted as 0.0072, 0.008 and 0.0115 in three sources

(43, 50, 44) of which the first and the last value are by the same principal author along with different co-authors. This is because the value of the acentric factor depends upon the accuracy of the vapor pressure value at a reduced temperature of 0.7 and the accuracy of the critical temperature and critical pressure for that fluid. Usually the vapor pressure at the reduced temperature of 0.7 is not reported and hence the vapor pressure is either interpolated from other reported values or it is obtained from a vapor pressure equation. In any case the accuracy of an empirical equation of state like the most general density-cubic equation depends on the values of the acentric factor used in the determination of the rest of the parameters. Thus, in order to make the value of the acentric factor compatible with the equation of state an effective value of the acentric factor which we call 'γ' was determined for each fluid from regression analysis of thermodynamic properties retaining the other parameters in the equation at the same value. When the values of γ were substituted for ω in equation 39 the overall deviation in density and vapor pressure values for methane through n-decane reduced to 0.9 percent. The uncertainty in the enthalpy departure values is 1.68 Btu/lb. The physical properties of the fluids along with the values of ω and γ are presented in Table 11. The values of the parameters in equation 39 are reported in Table 12. A summary of the results obtained using ω and γ, the range of data used and the sources from which the data has been obtained are presented in Table 13.

The generalized equation (equation 39) is compared with the results obtained by using the generalized Modified Benedict-Webb-Rubin equation (57) and the Peng-Robinson equation using identical data sets

TABLE 11

Characterization Parameters for Methane through n-Decane to be used with the Generalized Equation of State

Fluid	Critical Temp., °R	Critical Density, lbmole/ cu.ft.	Molecular Weight	Acentric Factor, ω	Effective Acentric Factor, γ
Methane	343.24	0.6274	16.042	0.0115	0.0115
Ethane	549.70	0.4218	30.068	0.0980	0.0980
Propane	665.64	0.3096	44.094	0.1520	0.1520
n-Butane	765.34	0.2448	58.120	0.1930	0.1956
n-Pentane	845.09	0.2007	72.146	0.2510	0.2480
n-Hexane	913.02	0.1696	86.172	0.2960	0.2974
n-Heptane	972.52	0.1465	100.198	0.3510	0.3476
n-Octane	1023.46	0.1284	114.224	0.3940	0.3940
n-Nonane	1070.17	0.1150	128.240	0.4440	0.4469
n-Decane	1111.57	0.1037	142.276	0.4970	0.4874

TABLE 12

Generalized Parameters used in Equation 39

i	a_{1i}	a_{2i}	a_{3i}	a_{4i}	a_{5i}
1	0.261470	-0.177989	0.578522	-0.263225	-1.097760
2		0.267322	-0.041516		0.041857
3		0.247866	-1.561630		0.521565
4		-0.236432	2.455580		-1.063570
5		0.411015	-1.280740		0.193772
6		0.000276	0.233100		-0.001081

TABLE 13

Prediction of Thermodynamic Properties of Methane through n-Decane using Equation 39

(ρ= density, $H-H^0$ = enthalpy departure, P_σ = vapor pressure)

Fluid	Property	No. of Points	Temperature Range, °R	Pressure Range, psia	Av. Abs. Dev.*		Data Reference
					ω	γ	
Methane	ρ	41	206.17 ∿ 1121.7	129.70 ∿ 2324.7	1.159	1.159	21,66,68
	P_σ	29	200.99 ∿ 343.16	14.696 ∿ 668.72	1.048	1.048	37
	$H-H^0$	38	209.67 ∿ 509.67	450 ∿ 2000	1.787	1.787	29,74
Ethane	ρ	46	239.67 ∿ 769.67	14.7 ∿ 8000.0	1.567	1.591	2,14,53
	P_σ	46	249.67 ∿ 549.68	0.49 ∿ 709.80	1.022	1.022	2,14
	$H-H^0$	98	299.67 ∿ 769.67	200 ∿ 3500	1.561	1.561	53
Propane	ρ	70	162.0 ∿ 1080.0	16.48 ∿ 10636.0	0.620	0.620	26
	P_σ	21	216.0 ∿ 665.64	0.0004 ∿ 616.30	0.873	0.873	26
	$H-H^0$	39	209.67 ∿ 709.67	500 ∿ 2000	1.464	1.464	74
n-Butane	ρ	40	259.67 ∿ 889.67	14.7 ∿ 7000.0	0.549	0.511	2,53
	P_σ	38	364.67 ∿ 765.29	0.342 ∿ 550.7	0.850	0.479	2,14
	$H-H^0$	39	559.67 ∿ 889.67	200 ∿ 5000.0	0.687	0.653	53

TABLE 13

(continued)

Fluid	Property	No. of points	Temperature Range, °R	Pressure Range, psia	Av. Abs Dev.*		Data Reference
					ω	γ	
n-Pentane	ρ	41	259.67 ∿ 919.67	14.7 ∿ 10000.0	0.841	0.868	2,53
	P_σ	50	323.28 ∿ 845.59	0.003 ∿ 489.50	1.272	1.156	2,14
	$H-H^0$	39	559.67 ∿ 919.67	200 ∿ 10000.0	1.215	1.083	53
n-Hexane	ρ	41	319.67 ∿ 739.67	14.70 ∿ 2980.0	0.257	0.267	2,58
	P_σ	53	395.75 ∿ 919.17	0,020 ∿ 439.70	0.982	0.844	2,14
n-Heptane	ρ	41	369.67 ∿ 919.67	14.7 ∿ 3081.5	0.384	0.420	2,61
	P_σ	44	346.93 ∿ 956.87	0.00013 ∿ 350.0	1.618	0.730	2,30
	$H-H^0$	17	971.97 ∿ 1069.2	78.770 ∿ 2363.1	1.224	1.200	24
n-Octane	ρ	50	389.67 ∿ 969.7	14.7 ∿ 239.0	1.120	1.120	2,22
	P_σ	47	393.67 ∿ 989.67	0.0004 ∿ 283.0	1.331	1.331	2,41,75
	$H-H^0$	68	534.67 ∿ 1059.7	200.0 ∿ 1400	2.95	2.95	33
n-Nonane	P_σ	24	402.75 ∿ 814.67	0.00012 ∿ 29.65	1,84	1.585	2
n-Decane	ρ	32	559.67 ∿ 919.67	200.0 ∿ 6000.0	0.334	0.343	53
	P_σ	24	438.30 ∿ 859.67	0.0002 ∿ 30.0	1.507	1.448	2

* % for ρ, P_σ, Btu/lb for $H-H^0$

in Table 14. It can be seen that equation 39 is as good as the MBWR equation of state and that it is superior to the Peng-Robinson equation of state. In almost all cases where low temperature vapor pressure data have been compared the Peng-Robinson equation invariably fails to converge to the correct solution. The large deviations in the density are due to the Peng-Robinson equation's inability to predict the compressed liquid densities accurately. The Peng-Robinson equation of state was developed using vapor pressure data from the normal boiling point up to the critical point (45) and thus it fails to converge at the lower temperatures and hence comparisons of the vapor pressures are not reported except for methane. In the range of the normal boiling point to the critical point the vapor pressures are predicted quite accurately by the Peng-Robinson equation as reported in their paper (45). It is not the intention of this research to play down the Peng-Robinson equation or other cubic equations but to show that the most general density-cubic equation is much better in predicting the thermodynamic behavior of the fluids investigated thus far than any previously reported cubic equation of state.

TABLE 14

Comparison of Results between Equation 39, Generalized MBWR and the Peng-Robinson Equation of State

Fluid	Property	Av. Abs. Dev. (% for ρ, P_σ, Btu/lb for $H-H^0$)		
		Equation 39	Peng-Robinson	MBWR
Methane	ρ	1.156	5.330	0.650
	P_σ	1.048	0.660	0.680
	$H-H^0$	1.787	2.404	1.390
Ethane	ρ	1.591	5.350	1.230
	P_σ	1.022	--	1.100
	$H-H^0$	1.561	1.612	0.980
Propane	ρ	0.620	3.836	1.010
	P_σ	0.873	--	0.460
	$H-H^0$	1.464	3.607	1.450
n-Butane	ρ	0.511	3.650	0.550
	P_σ	0.479	--	0.530
	$H-H^0$	0.653	1.359	0.500

TABLE 14

(continued)

Fluid	Property	Av. Abs. Dev. (% for ρ, P_σ, Btu/lb for $H-H^0$		
		Equation 39	Peng-Robinson	MBWR
n-Pentane	ρ	0.868	3.142	1.150
	P_σ	1.156	--	1.030
	$H-H^0$	1.083	1.791	0.630
n-Hexane	ρ	0.267	1.594	0.530
	P_σ	0.844	--	0.980
n-Heptane	ρ	0.420	1.470	0.650
	P_σ	0.730	--	0.750
	$H-H^0$	1.200	1.060	0.740
n-Octane	ρ	1.121	3.920	1.180
	P_σ	1.331	--	1.160
	$H-H^0$	2.950	2.830	1.850
n-Nonane	P_σ	1.585	--	1.460
n-Decane	ρ	0.342	4.711	1.090
	P_σ	1.448	--	0.770

CHAPTER VII

APPLICATION OF THE GENERALIZED EQUATION OF STATE TO THE NORMAL SATURATED HYDROCARBONS n-UNDECANE THROUGH n-EICOSANE

The generalized equation of state was developed using data for methane through n-decane, but the purpose of the generalization is to make the equation of state applicable to other fluids of interest with a minimum input of information.

To use the generalized equation of state to calculate the thermodynamic properties of a fluid the critical temperature, the critical density and the value of the effective acentric factor, γ are required. In most cases the value of γ is very close to the value of the acentric factor, ω. For the fluids studied in this research the effective acentric factor, γ has been determined through the use of thermodynamic property data. For other fluids the value of ω can be used, which is defined by the following well known relation of Pitzer

$$\omega \equiv - \log P_r - 1.000$$

where P_r is the reduced vapor pressure at a reduced temperature of 0.70. The values of the acentric factor have also been tabulated and are available from several sources in the literature (43, 50).

The critical temperature, the critical density and the acentric factor for the saturated hydrocarbons n-undecane, n-dodecane, n-tridecane, n-tetradecane, n-pentadecane, n-hexadecane, n-heptadecane, n-octadecane, n-nonadecane and n-eicosane were obtained from the literature (50). These values were used in equation 39 repeated here to generate thermodynamic property values namely, vapor pressure and density

$$Z = \frac{1 + A_5(T_r)\,\rho_r + A_2(T_r)\,\rho_r^2}{(1 - A_1\,\rho_r)(1 + A_3(T_r)\,\rho_r + A_4\rho_r^2)} \qquad (39)$$

$$A_5(T_r) = \left(\frac{a_{51}}{T_r^{\,2}} + \frac{a_{52}}{T_r^{\,3}}\right) + \left(\frac{a_{53}}{T_r} + \frac{a_{54}}{T_r^{\,3}} + \frac{a_{55}}{T_r^{\,4}} + \frac{a_{56}}{T_r^{\,8}}\right)\omega$$

$$A_2(T_r) = \left(a_{21} + \frac{a_{22}}{T_r} + \frac{a_{23}}{T_r^{\,2}}\right) + \left(\frac{a_{24}}{T_r} + \frac{a_{25}}{T_r^{\,2}} + \frac{a_{26}}{T_r^{\,8}}\right)\omega$$

$$A_3(T_r) = \left(\frac{a_{31}}{T_r} + \frac{a_{32}}{T_r^{\,2}}\right) + \left(\frac{a_{33}}{T_r} + \frac{a_{34}}{T_r^{\,2}} + \frac{a_{35}}{T_r^{\,3}} + \frac{a_{36}}{T_r^{\,4}}\right)\omega$$

$$A_1 = a_{11}$$

$$A_4 = a_{41}$$

where Z is the compressibility factor, ρ_r is the reduced density ($\rho_r = \rho/\rho_c$), T_r is the reduced temperature ($T_r = T/T_c$) and a_{ij} are the generalized equation of state parameters.

When compared with the experimental vapor pressure and density values the overall deviation for the ten fluids was around 5 percent, with large deviations occuring at the higher end of the hydrocarbon series. However, when the effective acentric factor, γ was obtained for each of the above fluids from the thermodynamic properties information, the overall average absolute deviation dropped to 1.87 percent.

The physical properties of the fluids and the values of ω and γ are presented in Table 15. A summary of the results including the ranges of temperature and pressure of the data used are presented in Table 16.

From the results presented in Table 16 it can be concluded that the generalized equation of state, when applied to fluids outside the range of those used in the development of the equation, does quite well in predicting the thermodynamic properties. The use of an effective acentric factor, γ improves the results considerably and at the same time the use of ω gives a reasonable result, taking into account the fact that the data for n-undecane through n-eicosane are not as accurate as the data for methane through n-decane.

TABLE 15

Characterization Parameters for n-Undecane through n-Eicosane to be used with the Generalized Equation of State

Fluid	Critical Temp., °R	Critical Density, lbmole/ cu.ft.	Molecular Weight	Acentric Factor, ω	Effective Acentric Factor, γ
n-Undecane	1149.84	0.09460	156.313	0.535	0.5338
n-Dodecane	1184.94	0.08756	170.340	0.562	0.5781
n-Tridecane	1216.44	0.08004	188.367	0.623	0.6185
n-Tetradecane	1249.20	0.07522	198.394	0.679	0.6531
n-Pentadecane	1272.60	0.07094	212.421	0.706	0.7107
n-Hexadecane	1290.60	0.06616	226.448	0.742	0.7793
n-Heptadecane	1319.40	0.06243	240.475	0.770	0.7997
n-Octadecane	1341.00	0.05887	254.502	0.790	0.8406
n-Nonadecane	1360.80	0.05579	268.529	0.827	0.8862
n-Eicosane	1380.60	0.05303	282.556	0.907	0.9298

TABLE 16

Prediction of Thermodynamic Properties of n-Undecane through n-Eicosane using Equation 39

(ρ= density, P_σ = vapor pressure)

Fluid	Property	No. of Points	Temperature Range, °R	Pressure Range, psia	Av. Abs. Dev., %		Data Reference
					ω	γ	
n-Undecane	P_σ	19	624.67 ∿ 899.67	0.182 ∿ 29.60	0.654	0.620	67
n-Dodecane	ρ	17	581.67 ∿ 869.70	0.016 ∿ 12.63	2.064	0.817	67
	P_σ	22	581.67 ∿1186.5	0.016 ∿ 262.52	6.312	2.253	
n-Tridecane	ρ	17	617.70 ∿ 905.70	0.024 ∿ 12.93	1.501	1.449	67
	P_σ	19	617.70 ∿1218.9	0.024 ∿ 249.5	1.778	0.790	
n-Tetradecane	ρ	14	707.70 ∿ 941.70	0.180 ∿ 13.540	3.179	2.922	67
	P_σ	16	707.70 ∿1251.0	0.180 ∿ 235.00	7.792	0.796	
n-Pentadecane	ρ	14	743.70 ∿ 977.70	0.238 ∿ 14.44	4.118	4.162	67
	P_σ	14	743.70 ∿ 995.70	0.238 ∿ 17.91	1.544	0.317	

TABLE 16

(continued)

Fluid	Property	No. of Points	Temperature Range, $^{\circ}$R	Pressure Range, psia	Av. Abs. Dev., %		Data Reference
					ω	γ	
n-Hexadecane	ρ	9	833.70 ∿ 977.70	1.003 ∿ 10.094	3.412	3.728	67
	P_{σ}	10	833.70 ∿ 995.70	1.003 ∿ 12.659	9.992	0.242	
n-Heptadecane	ρ	13	779.70 ∿ 995.70	0.181 ∿ 8.891	4.236	4.491	67
	P_{σ}	16	779.67 ∿ 1049.70	0.181 ∿ 17.106	4.875	0.378	
n-Octadecane	ρ	13	815.70 ∿ 1031.70	0.254 ∿ 10.090	4.148	4.561	67
	P_{σ}	15	815.70 ∿ 1067.70	0.254 ∿ 15.470	14.54	0.203	
n-Nonadecane	ρ	12	833.67 ∿ 1031.7	0.236 ∿ 7.367	4.484	4.947	67
	P_{σ}	16	833.67 ∿ 1103.7	0.236 ∿ 17.332	16.360	0.771	
n-Eicosane	P_{σ}	17	851.67 ∿ 1395.3	0.222 ∿ 161.6	5.573	3.143	67

CHAPTER VIII

PREDICTION OF PROPERTIES OF MAJOR NATURAL GAS CONSTITUENTS USING THE GENERALIZED EQUATION OF STATE

The thermodynamic properties of the normal saturated hydrocarbons methane, ethane, propane, n-butane, n-pentane, n-hexane, n-heptane and the higher members of the series which occur in natural gas systems, were shown to be predicted accurately by the generalized equation of state. Here, the generalized equation of state is applied to other major fluids found in natural gas systems, namely isobutane, isopentane, carbon dioxide, hydrogen sulfide and nitrogen and to ethylene and propylene. Isobutane and isopentane are also primary candidate working fluids in low temperature Rankine Cycles, particularly Geothermal Cycles (73).

The generalized equation of state, repeated here, is expressed as follows

$$Z = \frac{1 + A_5(T_r)\,\rho_r + A_2(T_r)\,\rho_r^2}{(1 - A_1\,\rho_r)(1 + A_3(T_r)\,\rho_r + A_4\rho_r^2)} \qquad (39)$$

$$A_5(T_r) = \left(\frac{a_{51}}{T_r^{\,2}} + \frac{a_{52}}{T_r^{\,3}}\right) + \left(\frac{a_{53}}{T_r} + \frac{a_{54}}{T_r^{\,3}} + \frac{a_{55}}{T_r^{\,4}} + \frac{a_{56}}{T_r^{\,8}}\right)\omega$$

$$A_2(T_r) = \left(a_{21} + \frac{a_{22}}{T_r} + \frac{a_{23}}{T_r^2} \right) + \left(\frac{a_{24}}{T_r} + \frac{a_{25}}{T_r^2} + \frac{a_{26}}{T_r^8} \right) \omega$$

$$A_3(T_r) = \left(\frac{a_{31}}{T_r} + \frac{a_{32}}{T_r^2} \right) + \left(\frac{a_{33}}{T_r} + \frac{a_{34}}{T_r^2} + \frac{a_{35}}{T_r^3} + \frac{a_{36}}{T_r^4} \right) \omega$$

$$A_1 = a_{11}$$

$$A_4 = a_{41}$$

where Z is the compressibility factor, ρ_r is the reduced density ($\rho_r=\rho/\rho_c$), T_r is the reduced temperature ($T_r = T/T_c$) and a_{ij} are the generalized parameters presented in Table 12. The characterization parameters for isobutane, isopentane, ethylene, propylene, carbon dioxide, hydrogen sulfide and nitrogen are presented in Table 17. The values of the effective acentric factor, γ were determined using experimental density, vapor pressure and enthalpy departure values in multiproperty regression analysis for each fluid. In most cases the value of γ is very close to that of ω, as shown in Table 17.

The average absolute deviations and the ranges of data used for isobutane and isopentane are presented in Table 18. In Table 19 the results for ethylene and propylene are presented. The results for carbon dioxide, hydrogen sulfide and nitrogen are presented in Table 20. These results are comparable with those obtained for the normal straight chain hydrocarbons methane through n-decane, though the fluids in Table 18 to 20 were not used for the development of the generalized equation of state.

TABLE 17

Characterization Parameters for Isobutane, Isopentane, Ethylene, Propylene, Carbon dioxide, Hydrogen sulfide and Nitrogen to be used with the Generalized Equation of State

Fluid	Critical Temp., °R	Critical Density lbmole/cft	Molecular Weight	Acentric Factor, ω	Effective Acentric Factor, γ
Isobutane	734.13	0.2438	58.120	0.1760	0.1833
Isopentane	828.67	0.2027	72.146	0.2270	0.2251
Ethylene	509.49	0.5035	28.05	0.0850	0.0993
Propylene	657.07	0.3449	42.08	0.1480	0.1473
Carbon dioxide	547.47	0.6641	44.01	0.2250	0.2117
Hydrogen sulfide	672.37	0.6571	34.076	0.1000	0.1079
Nitrogen	227.07	0.6929	28.016	0.0400	0.0392

TABLE 18

Prediction of Thermodynamic Properties of Isobutane and Isopentane using Equation 39

(ρ = density, $H-H^0$ = enthalpy departure, P_σ = vapor pressure)

Fluid	Property	No. of Points	Temperature Range, °R	Pressure Range, psia	Av. Abs. Dev., %		Data Reference
					ω	γ	
	ρ	354	333.8 ∿ 1032	0.18 ∿ 5000	0.93	0.93	12,40,51,52,53,70
Isobutane	P_σ	64	335 ∿ 734.13	0.18 ∿ 526.6	2.64	0.49	7,16,17,52,69,76,70
	$H-H^0$††	24	560 ∿ 940	250 ∿ 3000	0.93	1.13	10,14
	ρ	116	224.9 ∿ 851.67	0.3×10^{-6} ∿ 2674	1.24	1.22	21,51,54
	P_σ	64	390.9 ∿ 828.7	0.211 ∿ 490.4	0.60	0.40	8,51
Isopentane	ΔH*	3	503 ∿ 541.8	6.54 ∿ 14.7	0.33	0.13	8
	B†	10	491.7 ∿ 851.7	—	5.67	5.68	54

* Enthalpy of Vaporization

† Second virial coefficient

†† Deviation in Btu/lb.

TABLE 19

Prediction of Thermodynamic Properties of Ethylene and Propylene using Equation 39

(ρ= density, $H-H^o$ = enthalpy departure, P_σ = vapor pressure)

Fluid	Property	No. of Points	Temperature Range, °R	Pressure Range, psia	Av. Abs. Dev., %		Data Reference
					ω	γ	
Ethylene	ρ	41	209.67 ∿ 719.67	14.7 ∿ 2000	1.79	1.91	14,51,38
	P_σ	36	239.67 ∿ 509.49	0.88 ∿ 742.1	6.84	2.08	14,51,62
	$H-H^{0\dagger}$	38	339.67 ∿ 719.67	100 ∿ 2000	1.69	1.49	14
Propylene	ρ	61	409.68 ∿ 909.67	16.2 ∿ 2939	1.43	1.43	14,39,51
	P_σ	28	264.47 ∿ 656.87	0.04 ∿ 670.3	1.21	1.06	14,51,62

† Deviation in Btu/lb.

TABLE 20

Prediction of Thermodynamic Properties of Carbon dioxide Hydrogen sulfide and Nitrogen using Equation 39

(ρ= density, $H-H^0$ = enthalpy departure, P_σ = vapor pressure)

Fluid	Property	No. of Points	Temperature Range, °R	Pressure Range, psia	Av. Abs. Dev., %		Data Reference
					ω	γ	
Carbon dioxide	ρ	41	437.67 ∿ 743.67	220 ∿ 4410	0.76	0.75	20
	P_σ	33	389.67 ∿ 547.67	75 ∿ 1070	2.42	0.91	14
	$H-H^{0\dagger}$	39	437.67 ∿ 743.67	441 ∿ 7350	2.13	2.12	20
Hydrogen sulfide	ρ	41	499.67 ∿ 799.67	100 ∿ 2000	1.99	2.05	34,48
	P_σ	24	383.27 ∿ 672.37	14.7 ∿ 1306	2.09	1.16	31,71
Nitrogen	ρ	41	139.67 ∿ 699.67	14.7 ∿ 8936	1.40	1.40	14,60
	P_σ	19	159.67 ∿ 226.67	29 ∿ 492	0,90	0.90	23
	$H-H^{0\dagger}$	79	159.67 ∿ 509.67	200 ∿ 2500	0.56	0.56	35

†Deviation in Btu/lb.

The results obtained using equation 39 are compared with those obtained using the Modified Benedict-Webb-Rubin equation of state (57) in Table 21. From the results it can be infered that the most general density-cubic equation of state is comparable to the Modified Benedict-Webb-Rubin equation of state when extended to fluids not used in the development of the generalized equation of state.

TABLE 21

Comparison of Results between Equation 39 and the Generalized MBWR Equation of State

Fluid	Property	Av. Abs. Dev. (% for ρ, P_σ, Btu/lb for $H-H^0$) Equation 39	MBWR
	ρ	0.929	1.90
Isobutane*	P_σ	0.495	1.95
	$H-H^0$	1.128	1.10
	ρ	1.223	1.50
Isopentane*	P_σ	0.399	0.37
	ρ	1.911	2.73
Ethylene	P_σ	2.08	2.08
	$H-H^0$	1.494	1.97
	ρ	1.428	1.58
Propylene	P_σ	1.060	0.69
	ρ	0.75	0.65
Carbon Dioxide	P_σ	0.91	0.76
	$H-H^0$	2.12	2.69

TABLE 21
(continued)

		Av. Abs. Dev. (% for ρ, P_σ, Btu/lb for $H-H^0$)	
Fluid	Property	Equation 39	MBWR
Nitrogen	ρ	1.40	0.27
	P_σ	0.90	0.90
	$H-H^0$	0.56	0.48
Hydrogen sulfide	ρ	2.05	1.85
	P_σ	1.16	0.72

*Identical data sets were not used for comparison.

CHAPTER IX

PREDICTION OF PROPERTIES OF SELECTED PURE COAL FLUIDS

In recent years, due to the high price of oil, the use of coal as an important or rather primary source of energy has received great attention. In the very near future the mental image of coal as a solid fuel will gradually change to that of a liquid which will be pumped from a liquefaction plant close to the mining site through pipelines just as oil is pumped through pipelines today. In this context, the economic design of coal liquefaction demonstration plants requires the use of design data. Since very little design information is available at this point in time, it is necessary to develop correlations which can help in the design of these plants.

As the generalized equation of state has been developed in a framework which allows the use of other characterization parameters such as dipole moment etc., the equation of state is applied here to some selected pure coal fluids, namely benzene, naphthalene, tetralin, quinoline and phenanthrene to test the applicability of this equation for later use in the prediction of the thermodynamic properties of defined and undefined coal mixtures. The fluids were so chosen as to cover a broad class of aromatic hydrocarbons, namely single ring, two ring and three ring fluids. Naphthalene, tetralin and quinoline are two ring aromatic hydrocarbons; in addition, tetralin and quinoline are polar fluids. Phenanthrene was chosen from the class of three ring aromatic hydrocarbons.

The characterization parameters for use in the generalized equation of state are presented in Table 22. Table 23 presents the results for the fluids considered using literature values for the acentric factor, ω, and also using the values for the effective acentric factor, γ, determined from regression analysis of the experimental data.

From the results presented in Table 23 it can be seen that the generalized equation of state predicts the vapor pressure and density of these complex fluids to a reasonable level of accuracy.

TABLE 22

Characterization Parameters for Benzene, Naphthalene, Tetralin, Quinoline and Phenanthrene to be used with the Generalized Equation of State

Fluid	Critical Temp., °R	Critical Density lbmole/cft	Molecular Weight	Acentric Factor, ω	Effective Acentric Factor, γ
Benzene	1011.89	0.24136	78.1134	0.2125	0.2138
Naphthalene	1347.03	0.15099	128.1732	0.3020	0.3004
Tetralin	1296.27	0.14166	132.2048	0.2970	0.3168
Quinoline	1407.87	0.15515	129.1610	0.330	0.2587
Phenanthrene	1571.67	0.11278	178.233	0.540	0.4641

TABLE 23

Prediction of Thermodynamic Properties of Selected Pure Coal Fluids using Equation 39

Fluid	Property	No. of Points	Temperature Range, °R	Pressure Range, psia	Av. Abs. Dev.,%		Data Reference
					ω	γ	
Benzene	ρ	60	923.7 ∿ 1103.7	374.3 ∿ 867.4	1.828	1.821	2
	P_σ	36	504.7 ∿ 995.7	0.76 ∿ 639.9	0.582	0.502	2
Naphthalene	ρ	18	648.0 ∿ 1800.0	14.7 ∿ 290.1	2.61	2.62	4
	P_σ	15	810.3 ∿ 1279.7	4.2 ∿ 490.0	3.23	3.12	72
Tetralin	ρ	17	540.0 ∿ 1800.0	14.7 ∿ 1450.7	2.796	2.631	5
	P_σ	16	810.3 ∿ 1279.7	6.74 ∿ 488.0	4.928	2.634	72
Quinoline	ρ	17	576.0 ∿ 1800.0	14.7 ∿ 1450.4	3.621	4.24	3
	P_σ	8	959.7 ∿ 1309.7	23.8 ∿ 407.0	14.01	5.68	72
Phenanthrene	ρ	7	671.7 ∿ 1031.7	0.0004 ∿ 10.022	3.716	4.65	6
	P_σ	12	865.8 ∿ 1309.7	0.650 ∿ 99.0	19.20	4.64	72

CHAPTER X

APPLICABILITY OF THE MOST GENERAL DENSITY-CUBIC EQUATION OF STATE TO POLAR FLUIDS

The generalized equation of state which has been developed in a three parameter corresponding states framework for non-polar fluids can be extended to polar and associative fluids if adequate characterization is provided for the effects of polarity and hydrogen bonding. This leads to a multi-parameter corresponding states framework where the equation of state, and in turn the parameters in the cubic equation can be expressed as

$$A_i(T_r) = A_{i1}(T_r) + A_{i2}(T_r,\omega) + A_{i3}(T_r, \mu^*) + A_{i4}(T_r,\alpha) + \ldots \quad (40)$$

where μ^* is the reduced dipole moment and α is a measure of the associative effects. Thus far, the equation of state extends up to the second term. When the equation of state is used in the present form to predict the properties of fluids like water and ammonia which are highly polar and associative the deviations in the properties are relatively high. For ammonia the overall average absolute deviation is around 4 percent for vapor pressure and density over all fluid states with a 9 Btu/lb deviation on the enthalpy departure. The overall deviation for water is about 8 percent. In restricted regions the equation of state can be shown to perform better, but in order to get an accurate description of polar and associative fluids over all fluid states, additional characterization parameters like the reduced dipole moment μ^* are required. Before attempting this task the applicability of the basic equation formulation has to be tested. For this purpose a provisional temperature dependence for the most general density-cubic equation of state was developed exclusively for water. This equation of state is presented below

$$Z = \frac{1 + A_5(T_r)\,\rho_r + A_2(T_r)\,\rho_r^2}{(1 - A_1\,\rho_r)(1 + A_3(T_r)\,\rho_r + A_4\,\rho_r^2)} \tag{41}$$

where the temperature dependent parameters $A_5(T_r)$, $A_2(T_r)$ and $A_3(T_r)$ are expressed as

$$A_5(T_r) = A_{51} + \frac{A_{52}}{T_r} + \frac{A_{53}}{T_r^2} + \frac{A_{54}}{T_r^3} + \frac{A_{55}}{T_r^4} + \frac{A_{56}}{T_r^5} + \frac{A_{57}}{T_r^6} + A_{58}T_r$$

$$A_2(T_r) = \frac{A_{21}}{T_r} + \frac{A_{22}}{T_r^2} + \frac{A_{23}}{T_r^3} + \frac{A_{24}}{T_r^5} + \frac{A_{25}}{T_r^6} + A_{26}T_r$$

$$A_3(T_r) = A_{31} + A_{32}T_r$$

Table 24 presents the parameters for water for use in equation 41. The above form of the temperature dependence for the equation gives accurate results for water density and vapor pressure whereas the enthalpy departures have a greater uncertainty from the reported values over all fluid states as shown in Table 25. A systematic study of the thermo-

TABLE 24

Parameters for water to be used in Equation 41

Parameter	Parameter Value
A_1	0.248539
A_{21}	-0.280423
A_{22}	0.606953
A_{23}	0.086806
A_{24}	-0.035691
A_{25}	0.006724
A_{26}	-0.012962
A_{31}	1.05855
A_{32}	-0.248420
A_4	-0.063821
A_{51}	0.117006
A_{52}	1.128286
A_{53}	-2.442082
A_{54}	0.0713956
A_{55}	-0.128320
A_{56}	0.143604
A_{57}	-0.027056
A_{58}	0.052152

TABLE 25

Prediction of Thermodynamic Properties of Water using Equation 41

Property	No. of Points	Temperature Range, °R	Pressure Range, psia	Average Absolute Deviation	Data Reference
Density	335	540 ∿ 2860	0.7 ∿ 20305	0.94%	28,32
Vapor pressure	66	491.7 ∿ 1160	0.09 ∿ 3090	0.27%	28,32
Satd. Liquid Density	60	492 ∿ 1023	0.09 ∿ 1161	0.56%	28,32
Vapor Enthalpy Departure	158	560 ∿ 2860	0.7 ∿ 7781	2.71 Btu/lb	28,32
Liquid Enthalpy Departure	49	510 ∿ 1460	452.6 ∿ 15203	2.12%	28,32

dynamic properties of water along isotherms similar to the study of propane can lead to a more accurate equation of state than equation 41. However, this study demonstrates the capability of the most general density-cubic equation in predicting the properties of highly polar and associative fluids like water.

CHAPTER XI

CONCLUSIONS

This research presents the most general density-cubic equation of state. All previously reported cubic equations are only special cases of the most general density-cubic equation of state. A detailed study of the thermodynamic properties of propane along isotherms showed that the density dependence of the equation of state was adequate enough to describe propane thermodynamic behavior over all fluid states.

The introduction of a provisional temperature dependence into the equation of state led to an equation which provided an accurate description of the thermodynamic behavior of methane, propane, n-heptane and n-octane, thus making the equation of state amenable to generalization.

The generalization of the equation of state was carried out to provide a flexible equation of state, where the temperature dependence and in effect the equation of state can be changed to accommodate the thermodynamic behavior of polar fluids, etc.

The generalized equation of state was applied to 32 pure fluids consisting mainly of non-polar hydrocarbons. Where comparisons have been made the generalized equation of state is superior to the Peng-Robinson equation of state and it is as good as the Modified Benedict-

Webb-Rubin equation of state. It has also been shown that the basic density dependence of the equation of state is capable of describing the thermodynamic behavior of water, which is polar and associative, to a reasonable level of accuracy in the overall fluid states. Finally, the most general density-cubic equation of state has been shown to perform as well as a non-cubic equation of state such as the Modified Benedict-Webb-Rubin equation of state in the overall fluid states.

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APPENDIX A

EXPRESSIONS FOR DERIVED THERMODYNAMIC PROPERTIES

The classical relationships for the derived properties were converted into a reduced form in terms of the variables $\rho_r = \rho/\rho_c$ and $T_r = T/T_c$. For example the classical relationship for the enthalpy departure of a pure fluid is given by

$$H-H^0 = P/\rho - RT + \int_0^\rho \{ P - T(\partial P/\partial T)_\rho \} \frac{d\rho}{\rho^2} \qquad \text{A.1}$$

In terms of the reduced temperature T_r, the reduced density ρ_r and the compressibility factor Z equation A.1 becomes

$$\frac{H-H^0}{RT_c} = T_r(Z-1) - T_r^2 \int_0^{\rho_r} (\partial Z/\partial T_r)_{\rho_r} d \ln \rho_r \qquad \text{A.2}$$

The expression for the entropy departure is given by

$$\frac{S-S^0}{R} = - \int_0^{\rho_r} (Z-1) d \ln \rho_r - T_r \int_0^{\rho_r} (\partial Z/\partial T)_{\rho_r} d \ln \rho_r - \ln P/Z \qquad \text{A.3}$$

The internal energy departure expression is

$$\frac{U-U^0}{RT_c} = -T_r^2 \int_0^{\rho_r} (\partial Z/\partial T_r)_{\rho_r} d \ln \rho_r \qquad \text{A.4}$$

The Helmholtz free energy departure expression is

$$\frac{A-A^0}{RT_c} = T_r \int_0^{\rho_r} (Z-1)\, d \ln \rho_r + T_r \ln P/Z \qquad \text{A.5}$$

Gibbs free energy departure expression is

$$\frac{G-G^0}{RT_c} = T_r \int_0^{\rho_r} (Z-1)\, d \ln \rho_r + T_r \ln P/Z + T_r (Z-1) \qquad \text{A.6}$$

The fugacity expression is

$$\ln (f/P) = \int_0^{\rho_r} (Z-1)\, d \ln \rho_r - \ln Z + (Z-1) \qquad \text{A.7}$$

when the integrals $\int_0^{\rho_r} (Z-1)\, d \ln \rho_r$ and $\int_0^{\rho_r} (\partial Z/\partial T_r)_{\rho_r} d \ln \rho_r$ are evaluated from the equation of state, all of the above properties can be determined. The equation of state expressions for the two integrals are given below.

The generalized equation of state, repeated here is expressed as

$$Z = \frac{1 + A_5(T_r)\, \rho_r + A_2(T_r)\, \rho_r^2}{(1 - A_1 \rho_r)(1 + A_3(T_r)\, \rho_r + A_4 \rho_r^2\,)} \qquad (39)$$

$$A_5(T_r) = \left(\frac{a_{51}}{T_r^{\,2}} + \frac{a_{52}}{T_r^{\,3}} \right) + \left(\frac{a_{53}}{T_r} + \frac{a_{54}}{T_r^{\,3}} + \frac{a_{55}}{T_r^{\,4}} + \frac{a_{56}}{T_r^{\,8}} \right) \omega$$

$$A_2(T_r) = \left(a_{21} + \frac{a_{22}}{T_r} + \frac{a_{23}}{T_r^{\,2}} \right) + \left(\frac{a_{24}}{T_r} + \frac{a_{25}}{T_r^{\,2}} + \frac{a_{26}}{T_r^{\,8}} \right) \omega$$

$$A_3(T_r) = \left(\frac{a_{31}}{T_r} + \frac{a_{32}}{T_r^{\,2}} \right) + \left(\frac{a_{33}}{T_r} + \frac{a_{34}}{T_r^{\,2}} + \frac{a_{35}}{T_r^{\,3}} + \frac{a_{36}}{T_r^{\,4}} \right) \omega$$

$$A_4 = a_{11}$$

$$A_1 = a_{11}$$

where Z is the compressibility factor, T_r is the reduced temperature, ρ_r is the reduced density and a_{ij} are the generalized parameters presented in Table 12. ω is the acentric factor which is replaced by the effective acentric factor γ for the fluids considered in this research.

The expression for the integral $\int_0^{\rho_r} (Z-1) d \ln \rho_r$ is given as follows

$$\int_0^{\rho_r} (Z-1) d \ln \rho_r = -F \ln (1-A_1 \rho_r) + \frac{(F-1)}{2} \ln (1 + A_3(T_r) \rho_r + A_4 \rho_r^2)$$

$$\frac{+ A_3(T_r)(F - 1)/2 + (A_4 F - A_2(T_r))/A_1}{\sqrt{A_3^{\,2}(T_r) - 4 A_4}}$$

$$\ln \left\{ \frac{2 + (A_3(T_r) + \overline{A_3^{\,2}(T_r) - 4 A_4}) \rho_r}{2 + (A_3(T_r) - A_3^{\,2}(T_r) - 4 A_4) \rho_r} \right\} \qquad \text{A.8}$$

where $F = \dfrac{A_5(T_r) A_1 + A_1^{\,2} + A_2(T_r)}{A_3(T_r) A_1 + A_1^{\,2} + A_4}$

The temperature derivatives of the functions $A_5(T_r)$, $A_2(T_r)$ and $A_3(T_r)$ are given as follows

$$\frac{dA_5(T_r)}{dT_r} = -\left(\frac{2a_{51}}{T_r^3} + \frac{3a_{52}}{T_r^4}\right) - \left(\frac{a_{53}}{T_r^2} + \frac{3a_{54}}{T_r^4} + \frac{4a_{55}}{T_r^5} + \frac{8a_{56}}{T_r^9}\right)\omega \qquad \text{A.9}$$

$$\frac{dA_2(T_r)}{dT_r} = -\left(\frac{a_{22}}{T_r^2} + \frac{2a_{23}}{T_r^3}\right) - \left(\frac{a_{24}}{T_r^2} + \frac{2a_{25}}{T_r^3} + \frac{8a_{26}}{T_r^9}\right)\omega \qquad \text{A.10}$$

$$\frac{dA_3(T_r)}{dT_r} = -\left(\frac{a_{31}}{T_r^2} + \frac{2a_{32}}{T_r^3}\right) - \left(\frac{a_{33}}{T_r^2} + \frac{2a_{34}}{T_r^3} + \frac{3a_{35}}{T_r^4} + \frac{4a_{36}}{T_r^5}\right)\omega \qquad \text{A.11}$$

Let us define

$$S_1 = \frac{dA_5(T_r)}{dT_r} - \frac{dA_3(T_r)}{dT_r}$$

$$S_2 = A_3(T_r)\frac{dA_5(T_r)}{dT_r} + \frac{dA_2(T_r)}{dT_r} - A_5(T_r)\frac{dA_3(T_r)}{dT_r}$$

$$S_3 = A_4\frac{dA_5(T_r)}{dT_r} + A_3(T_r)\frac{dA_2(T_r)}{dT_r} - A_2(T_r)\frac{dA_3(T_r)}{dT_r}$$

$$S_4 = A_4\frac{dA_2(T_r)}{dT_r}$$

$$K = 1/A_1$$

$$P_1 = S_1 + S_2K + S_3K^2 + S_4K^3$$

$$P_2 = 1 + A_3K + A_4K^2$$

$$P_a = P_1/P_2^{\,2}$$

$$P_x = 1 + A_3(T_r)\rho_r + A_4\,\rho_r^2$$

$$Q_1 = 4A_4 - A_3^{\,2}(T_r)$$

Then the expression for the integral $\int_0^{\rho_r} (\partial Z/\partial T_r)_{\rho_r}\, d\ln\rho_r$ is given as

$$\begin{aligned}
\int_0^{\rho_r} (\partial Z/\partial T_r)_{\rho_r}\, d\ln\rho_r = {} & -K\Big\{P_a \ln(1-A_1\rho_r) + \frac{\rho_r}{Q_1P_x}\Big[\Big(S_3 - (A_3(T_r) \\
& - A_4K)\frac{dA_2(T_r)}{dT_r} - A_4P_1/P_2\Big)(A_3(T_r) + 2A_4\rho_r) + \Big(S_2 + S_3K - \\
& \frac{dA_2(T_r)}{dT_r}(1 - A_4K^2) - P_1/P_2(A_3(T_r) + A_4K)\Big)\Big(2A_4 - A_3(T_r) \\
& (A_3(T_r) + A_4\rho_r)\Big)\Big] - \frac{P_a}{2}\ln(P_x) + \Big[\frac{2S_2A_4}{Q_1} + \frac{S_3}{Q_1}(2A_4K - A_3(T_r)) \\
& + \frac{S_4}{Q_1}\big(A_3(T_r)\,(A_3(T_r)/A_4 - K) - 2\,(1 - A_4K^2)\big) - \frac{P_1A_4}{Q_1P_2}(A_3(T_r) \\
& + 2A_4K) + \frac{dA_2(T_r)}{dT_r} - P_a(A_3(T_r)/2 + A_4K)\Big] \ln\Big(\big(2 + (A_3(T_r) \\
& + \sqrt{-Q_1})\rho_r\big)/\big(2 + (A_3(T_r) - \sqrt{-Q_1})\,\rho_r\big)\Big)\Big\}
\end{aligned} \tag{A.12}$$

Since the two integrals $\int_0^{\rho_r} (Z-1)d\ln\rho_r$ and $\int_0^{\rho_r} (\partial Z/\partial T_r)_{\rho_r} d\ln\rho_r$

along with Z occur in the expressions for the above mentioned derived thermodynamic properties, a good description of the density, vapor pressure and enthalpy departure of a fluid ensures good descriptions of all the other derived properties.

APPENDIX B

DENSITY SOLUTION OF THE CUBIC EQUATION WHEN TEMPERATURE AND PRESSURE ARE SPECIFIED

The most general density-cubic equation of state is expressed as

$$Z = \frac{1 + A_5(T_r)\,\rho_r + A_2(T_r)\,\rho_r^2}{(1 - A_1\rho_r)(1 + A_3(T_r)\rho_r + A_4\rho_r^2)} \qquad \text{B.1}$$

For the purpose of solving for the density the temperature dependent parameters can be treated as constants. In terms of pressure P, equation B.1 becomes

$$P = \frac{\rho_r RT\rho_c(1 + A_5\rho_r + A_2\rho_r^2)}{(1 - A_1\rho_r)(1 + A_3\rho_r + A_4\rho_r^2)} \qquad \text{B.2}$$

Equation B.2 can be expressed as a cubic equation in density

$$\frac{P}{RT\rho_c} + \left(\frac{A_3 - A_1}{RT\rho_c} - A_5\right)\rho_r + \left(\frac{A_4 - A_1A_3}{RT\rho_c} - A_2\right)\rho_r^2 - A_4A_1\rho_r^3 = 0 \qquad \text{B.3}$$

Let

$-P/(RT\rho_cA_4A_1) = r$, $(A_5 - (A_3 - A_1)/RT\rho_c)/A_4A_1 = q$,

$(A_2 - (A_4 - A_1A_3)/RT\rho_c)/A_4A_1 = p$, then we have

$$\rho_r^3 + p\rho_r^2 + q\rho_r + r = 0 \qquad \text{B.4}$$

Equation B.4 can be reduced to

$$x^3 + ax + b = 0 \qquad \text{B.5}$$

by substituting for ρ_r the value $x - p/3$ (64). Here

$$a = (3q - p^2)/3 \text{ and } b = (2p^3 - 9pq + 27r)/27$$

The solution of the cubic equation has been adapted here to the problem of solving for the liquid and vapor roots in an equation of state from the general solution presented by Uspensky (64).

Equation B.5 can be solved by setting $x = u + v$. On substituting this expression into B.5 and rearranging, u and v have to satisfy the equation

$$u^3 + v^3 + (a + 3uv)(u + v) + b = 0 \qquad \text{B.6}$$

with two unknowns. This problem is indeterminate unless another relation between u and v is given. For this relation we take

$$3uv + a = 0$$

or

$$uv = -a/3$$

Then it follows $u^3 + v^3 = -b$

so that the solution of the cubic equation B.5 can be obtained by solving the system of two equations

$$u^3+v^3 = -b, \quad uv = -a/3 \qquad B.7$$

Taking the cube of the latter equation we have

$$u^3 v^3 = -a^3/27 \qquad B.8$$

From equations B.7 and B.8 we know the sum and the product of the two unknown quantities u^3 and v^3. These quantities are the roots of the quadratic equation

$$t^2 + bt - a^3/27 = 0 \qquad B.9$$

Denoting them by A and B, we have then

$$A = -b/2 + \sqrt{b^2/4 + a^3/27}$$

$$B = -b/2 - \sqrt{b^2/4 + a^3/27}$$

Now

$$u^3 = A \text{ and } v^3 = B$$

The three possible values of u will be

$$u = \sqrt[3]{A}, \quad u = \omega \sqrt[3]{A}, \quad u = \omega^2 \sqrt[3]{A}$$

where $\omega = (-1 + i\sqrt{3})/2$ is an imaginary cube root of unity and the three possible values for v are

$$v = \sqrt[3]{B}, \; v = \omega \sqrt[3]{B} \text{ and } v = \omega^2 \sqrt[3]{B}$$

but the correct combination of u and v gives the solution for the cubic equation B.5. Due to the assumption $uv = -a/3$ the product of the cube roots of A and B has to satisfy this relation. Thus if $\sqrt[3]{B}$ satisfies the relation

$$\sqrt[3]{A} \cdot \sqrt[3]{B} = -a/3$$

then the three roots of the cubic equation are given by

$$x_1 = \sqrt[3]{A} + \sqrt[3]{B}$$

$$x_2 = \omega \sqrt[3]{A} + \omega^2 \sqrt[3]{B}$$

$$x_3 = \omega^2 \sqrt[3]{A} + \omega \sqrt[3]{B}$$

The above formulas are known as Cardan's formulas. When $4a^3 + 27b^2 > 0$, there will be one real and two conjugate imaginary roots.

When $4a^3 + 27b^2 = 0$, there will be three real roots of which at least two are equal.

When $4a^3 + 27b^2 < 0$, there will be three real and unequal roots.

In situations where the determinant $4a^3 + 27b^2$ is less than or equal to zero, the solution of the cubic equation can be obtained trigonometrically (46). In this case the roots are given by

$$x_k = \pm 2 \sqrt{-a/3} \, \mathrm{Cos} \{ \phi/3 + 2\pi k/3 \}, \; k = 0,1,2$$

where $\phi = \mathrm{Cos}^{-1} \sqrt{(-27b^2/4a^3)}$ and the upper sign applies if $b < 0$, the lower if $b > 0$.

The largest root gives the liquid density and the smallest root gives the vapor density.

APPENDIX C

SOURCE LISTING OF EQUATION OF STATE

FUNCTION SUBPROGRAMS

```
c     The following function subprograms have to be used in the
c     Ezfit program developed by K.M.Goin to calculate pure
c     fluid properties using the generalized Kumar-Starling
c     equation of state
c     Procedures for using the following are explained in
c     K.M.Goin's dissertation (Univ. of Oklahoma,1978)
c     Function pres(t,rho) calculates the pressure at a given
c     temperature and density
      function pres(t,rho)
      common /prm/rgas,renrgy,tcrit,pcrit,rhoc,w,alpha,beta,xmw
     1 ,a(40),b(7),nterms,nparm,numb,rtop,rmidl,rmidv
      rhos=beta*rho/rhoc
      tstar=alpha*t/tcrit
      x=1/tstar
      a7=(((a(5)*x*x*x*x+a(17))*x+a(14))*x*x+a(13))*x
      a9=(((a(2)*x+a(10))*x+a(18))*x+a(15))*x
      a8=((a(1)*x*x*x*x*x+a(16))*x+a(19))*x
      ap2=((a(9)*x+a(8))*x+a(7))+a8*w
      ap3=((a(12)*x+a(11))*x)+a9*w
      ap5=(a(4)*x+a(3))*x*x+a7*w
      ap1=a(20)
      ap4=a(6)
      cp=1-ap1*rhos
      bp=1+ap3*rhos+ap4*rhos**2
      ap=1+ap5*rhos+ap2*rhos**2
      dp=bp*cp
      z=ap/dp
      pres=z*rho*rgas*t
      return
      end
```

```
c     Function fil(t,rho) calculates the integral (z-1)dln(rho)
c     which is used in the calculation of the fugacity
c     coefficient
      function fil(t,rho)
      common /prm/rgas,renrgy,tcrit,pcrit,rhoc,w,alpha,beta,xmw
     1  ,a(40),b(7),nterms,nparm,numb,rtop,rmidl,rmidv
      tstar=alpha*t/tcrit
      rhos=beta*rho/rhoc
      if(rhos.gt.3.8) rhos=3.8
      x=1/tstar
      a7=(((a(5)*x*x*x*x+a(17))*x+a(14))*x*x+a(13))*x
      a9=(((a(2)*x+a(10))*x+a(18))*x+a(15))*x
      a8=((a(1)*x*x*x*x*x*x+a(16))*x+a(19))*x
      ap2=((a(9)*x+a(8))*x+a(7))+a8*w
      ap3=((a(12)*x+a(11))*x)+a9*w
      ap5=(a(4)*x+a(3))*x*x+a7*w
      ap1=a(20)
      ap4=a(6)
      f=(ap5*ap1+ap1*ap1+ap2)/(ap3*ap1+ap1*ap1+ap4)
      q=sqrt(ap3*ap3-4*ap4)
      sp=1-ap1*rhos
      bp=1+rhos*(ap3+ap4*rhos)
      if(bp.le.0.0) bp=0.1e-05
      if(sp.le.0.0) sp=0.1e-05
      d2=(rhos*(ap3+q)+2)/(rhos*(ap3-q)+2)
      if(d2.lt.0.0) d2=0.1e-05
      d3=0.5*ap3*(f-1)+(ap4*f-ap2)/ap1
      d4=d3/q*alog(d2)
      fil=-f*alog(sp)+0.5*(f-1)*alog(bp)+d4
      return
      end
```

```
c     Function fi2(t,rho) calculates the integral dz/dt dln(rho)
c     which is used in the calculation of the enthalpy
c     departure
      function fi2(t,rho)
      common /prm/rgas,renrgy,tcrit,pcrit,rhoc,w,alpha,beta,xmw
     1  ,a(40),b(7),nterms,nparm,numb,rtop,rmidl,rmidv
      tstar=alpha*t/tcrit
      rhos=beta*rho/rhoc
      x=1/tstar
      if(rhos.gt.3.9) rhos=3.9
      a7=(((a(5)*x*x*x+a(17))*x+a(14))*x*x+a(13))*x
      a9=(((a(2)*x+a(10))*x+a(18))*x+a(15))*x
      a8=((a(1)*x*x*x*x*x+a(16))*x+a(19))*x
      ap2=((a(9)*x+a(8))*x+a(7))+a8*w
      ap3=((a(12)*x+a(11))*x)+a9*w
      ap5=(a(4)*x+a(3))*x*x+a7*w
      ap1=a(20)
      ap4=a(6)
      ap33=-(2*a(12)*x+a(11))*x**2
      bp33=-(((4.0*a(2)*x+3.0*a(10))*x+2.0*a(18))*x+a(15))*x*x
      ap22=-(2.0*a(9)*x+a(8))*x**2
      bp22=-((8.0*a(1)*x*x*x*x*x+2.0*a(16))*x+a(19))*x*x
      a19=8.0*a(5)*x*x*x
      ap21=ap22+bp22*w
      bp55=-(((a19*x+4*a(17))*x+3*a(14))*x*x+a(13))*x*x
      ap55=-(3.0*a(4)*x+2.0*a(3))*x*x*x
      ap51=ap55+bp55*w
      ap31=ap33+bp33*w
      s1=ap51-ap31
      s2=ap51*ap3+ap21-ap31*ap5
      s3=ap51*ap4+ap21*ap3-ap31*ap2
      s4=ap21*ap4
      ak=1./ap1
      p1=((s4*ak+s3)*ak+s2)*ak+s1
      p2=1+(ap4*ak+ap3)*ak
      pa=p1/p2/p2
      px=1+(ap4*rhos+ap3)*rhos
      q1=4.0*ap4-ap3*ap3
      q2=sqrt(-q1)
      y1=alog((2+(ap3+q2)*rhos)/(2+(ap3-q2)*rhos))/q2
      gp=pa*alog(1-ap1*rhos)
      hp=(s3-ap21*(ap3-ap4*ak)-ap4*pa*p2)*(ap3+2*ap4*rhos)
      bp=(hp+(s2+s3*ak-ap21*(1-ap4*ak*ak)-pa*p2*(ap3+ap4*ak))
     **(2*ap4-ap3*(ap3+ap4*rhos)))*rhos/q1/px
      dp=-0.5*pa*alog(px)
      ep=(2*ap4*s2+s3*(2*ap4*ak-ap3)-s4*(2*(1-ap4*ak*ak)-ap3
     **(ap3/ap4-ak))-(ap3+2*ap4*ak)*pa*p2*ap4)
      cp=(ep/q1+ap21-pa*(0.5*ap3+ap4*ak))*y1
      fi2=-ak*(gp+bp+dp+cp)
      return
      end
```

```
c     Function densl(t,p) calculates the liquid density by
c     solving for the liquid root in the cubic equation
c     analytically at a given temperature and pressure
      function densl(t,p)
      complex r1,r2,y1,det,vier,funf,d,v3,dd,ra,rb
      data trd,d,dd/0.333333,(-0.5,0.8660254),(-0.5,-0.8660254)/
      common /prm/rgas,renrgy,tcrit,pcrit,rhoc,w,alpha,beta,xmw
     1 ,a(40),b(7),nterms,nparm,numb,rtop,rmidl,rmidv
      data vap,bap/4.1888,2.0945/
      tstar=t/tcrit
      x=1./tstar
      a7=(((a(5)*x*x*x+a(17))*x+a(14))*x*x+a(13))*x
      a9=(((a(2)*x+a(10))*x+a(18))*x+a(15))*x
      a8=((a(1)*x*x*x*x*x+a(16))*x+a(19))*x
      ap2=((a(9)*x+a(8))*x+a(7))+a8*w
      ap3=((a(12)*x+a(11))*x)+a9*w
      ap5=(a(4)*x+a(3))*x*x+a7*w
      ap1=a(20)
      ap4=a(6)
      fac=p/(rgas*t*rhoc)
      div=fac*ap1*ap4+ap2
      p1=(ap5+fac*(ap1*ap3-ap4))/div
      q1=(1+fac*(ap1-ap3))/div
      r=-fac/div
      sa=(3.*q1-p1**2)/3.
      sb=(2.*p1**3-9.*p1*q1+27.*r)/27.0
      pet=(sb**2/4.+sa**3/27.)
      if(pet.gt.0.0) go to 22
      theta=arcos(2.59807*sb/(sa*sqrt(-sa)))
      tt=2.0*sqrt(-sa/3.0)
      th=theta/3.0
      rhos=(tt*cos(th)-p1/3.0)
      if(rhos.gt.4.0) go to 27
      densl=rhos*rhoc
      return
 27   th=th+vap
      rhos=(tt*cos(th)-p1/3.0)
      if(rhos.gt.4.0.or.rhos.lt.0.0) rhos=3.0
      densl=rhos*rhoc
      return
 22   un=sqrt(pet)
      pa=-sb/2+un
      pb=-sb/2-un
      if(pa.gt.0.0) go to 50
      if(pa.eq.0.0) go to 30
 10   ra=-sb/2+un
```

```
c     Function densl(t,p) continued.....
      vier=clog(ra)
      r1=cexp(trd*vier)
      go to 40
 30   r1=0.0
 40   if(pb.eq.0.0) go to 60
      rb=-sb/2-un
      funf=clog(rb)
      r2=cexp(trd*funf)
      go to 70
  60  r2=0.0
      go to 70
 50   r1=pa**trd
      if(pb.gt.0.0) go to 80
      if(pb.eq.0.0) go to 77
      rb=-sb/2-un
      funf=clog(rb)
      r2=cexp(trd*funf)
      go to 70
 77   r2=0.0
      go to 70\
 80   r2=pb**trd
 70   if(sa/3.gt.0.0) go to 20
      y1=(r1+r2-p1/3)*rhoc
      go to 15
  20  v3=dd*r2
      y1=(r1+v3-p1/3)*rhoc
 15   densl=real(y1)
      return
      end
```