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THE UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

USE OF MULTICOMPONENT MULTIPROPERTY REGRESSION ANALYSIS IN CORRELATING THERMODYNAMIC PROPERTIES OF FLUIDS AT CRYOGENIC CONDITIONS THROUGH EQUATIONS OF STATE

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

degree of

DOCTOR OF PHILOSOPHY

BY

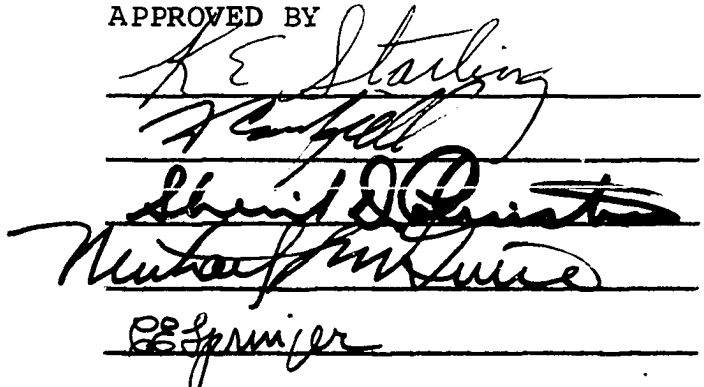
YAN-CHI (DAVID) KWOK

Norman, Oklahoma

1970

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APPROVED BY



DISSERTATION COMMITTEE

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ABSTRACT

Increasing interest and economic investment in processing natural gas at cryogenic conditions demand a critical study in development of an equation of state to correlate the pure component and mixture behavior of the normal hydrocarbons and certain nonhydrocarbons. To this end, a new equation of state containing seventeen parameters was developed from accurate isochoric PVT data of methane. This seventeen-parameter equation also has been successfully applied to propane. The adequacy of the temperature dependence of the new equation was attested by its ability to accurately predict enthalpy departures for methane and propane to reduced temperatures as low as 0.3.

To ensure thermodynamic consistency among properties predicted by the equation of state, a general multicomponent, multiproperty nonlinear regression program was developed. This program allows simultaneous use of density, enthalpy departure and phase equilibrium data for pure components and/or mixtures to determine equation of state parameters.

A modification of the BWR equation, selected from careful study of methane and propane enthalpy data, has been proven capable of predicting the thermodynamic properties of methane

and propane with accuracy comparable to the new equation of state. Because of its simplicity and the existence of mixing rules for the parameters in the original BWR equation, the eleven-parameter modified BWR equation was chosen for further study. In this study, application of the modified BWR equation was extended to ethane, n-butane, n-pentane, n-hexane, n-heptane, ethylene, nitrogen, carbon dioxide and hydrogen sulfide.

A set of generalized parameters which are functions of acentric factor has been developed for the modified BWR equation. The resultant generalized parameters of the modified BWR equation may be used to predict the thermodynamic properties of natural gas at cryogenic conditions with an accuracy suitable for engineering design purposes. An "effective" acentric factor was also developed for isopentane.

To investigate the feasibility of using the general regression analysis to correlate mixture behavior, simultaneous regression on mixture and pure-component thermodynamic properties of the methane-propane system also has been carried out. This general regression analysis method yielded sets of methane and propane parameters which can predict the behavior of this system from -250°F to 250°F with high accuracy. Of more significance, this high accuracy was achieved using simple mixing rules in the modified BWR equation of state without introducing additional unlike interaction parameters.

Finally, a generalized corresponding states chart has been developed to predict liquid enthalpy departures of normal fluids and their mixtures ($0.3 \leq T_r \leq 0.85$). In developing this chart, methane, propane, n-pentane and n-heptane were used as reference fluids. This chart can be used to supplement Yarborough's extension of Curl and Pitzer's correlations.

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USE OF MULTICOMPONENT MULTIPROPERTY REGRESSION ANALYSIS IN CORRELATING THERMODYNAMIC PROPERTIES OF FLUIDS AT CRYOGENIC CONDITIONS THROUGH EQUATIONS OF STATE

CHAPTER I

INTRODUCTION

To correlate the thermodynamic properties of fluids at cryogenic conditions using empirical equations of state, two vitally important developments must be effected.

1. The form of an equation of state must be developed such that it is capable of describing fluid behavior in both the vapor and liquid regions. This may be accomplished by proposing a new equation of state or by modifying an existing equation of state.

2. A unified approach must be developed to enable the determination of a set of self consistent parameters capable of accurately predicting all thermodynamic properties. Traditional use of PVT data in determining equation-of-state parameters may lead to erroneous prediction of enthalpy and phase equilibrium properties.

In the research reported in this dissertation, work has been carried out to develop a new equation of state form

from an empirical study of accurate isochoric PVT data for methane. Efforts also have been devoted to improving the temperature dependence of the original BWR equation. The modification utilized was selected from a careful study of enthalpy data for methane and propane. A general regression program to determine equation-of-state parameters using simultaneously PVT, enthalpy and phase data of mixtures and/or their constituents has been developed.

As a prelude to the presentation of this research, a general discussion of previous equations of state is presented in this chapter.

General Form of an Equation of State

An equation of state may be considered to be an analytic expression describing the compressibility behavior of fluids and has the functional form

$$f\ (P,V,T) \ = \ 0 \qquad (1)$$

Such an equation of state can be explicit in either volume or pressure. Because of mathematical limitations,[43] any equation of state capable of describing coexisting vapor and liquid phases must be explicit in pressure, i.e.

$$P \ = \ f\ (V,T) \qquad (2)$$

Utility of a Corresponding States Equation of State

The well known perfect gas law, though exceedingly simple in form, fails to predict the volumetric behavior

of real gases even at atmospheric pressure and room temperatures.[43] Van der Waals'[130] modification of the perfect gas law in 1873 succeeded, at least qualitatively, in describing the volumetric behavior of fluids in both vapor and liquid phases. Of more importance, van der Waals proposed the corresponding states principle, which postulated that all fluids behave identically at the same reduced conditions.

The corresponding states principle opened a new frontier of research in correlation of equilibrium thermodynamic properties. According to this principle, if an equation of state, free of empiricism, can indeed be formulated for one fluid, then all thermodynamic properties of corresponding states fluids can be derived with confidence. Using reduced variables, such an equation of state can be generalized to encompass all fluids (which obey the corresponding states principle) with a minimum amount of experimental data.

The formidable challenge of storing all thermodynamic and compressibility information of all fluids using a single generalized equation of state has stimulated countless efforts by numerous investigators for the past hundred years. Unfortunately, the goal has proven to be too broad and ambitious. At the present time, no equation of state based on theory alone has been found capable of practical predictions of both vapor and liquid phases. In fact, only a few empirical equations of state are capable of predicting behavior in both the vapor and liquid regions with accuracy approaching experimental uncertainty.

Brief History of Equation of State Development

Abundant literature on equation of state development has appeared in various journals.[88,98,113] Space permits only a brief outline of the general trend in equation of state development.

van der Waals Equation of State

The first significant step in modifying the perfect gas law was taken by van der Waals in 1873.[130] By considering "internal pressure" and "actual volume" of real gases, van der Waals proposed his well known equation of state

$$P = \frac{RT}{V-b} - \frac{a}{V^2} \qquad (3)$$

where a and b are empirical constants. The beauty of this equation lies in its simplicity and ability to predict qualitatively the volumetric behavior of fluids in both the vapor and liquid regions.

Between 1873 and 1917, several attempts were made to modify the van der Waals equation, notably by Clausius[24], Berthelot[15], Dieterici[38], Wohl[139] and Keyes[72]. However, these efforts met with little success because invariably these equations of state assumed a linear dependence of pressure on temperature for isochores.

Redlich-Kwong Equation of State

In 1948 , Redlich and Kwong[107] proposed a two-constant equation of state

$$P = \frac{RT}{(V-b)} - \frac{a}{V(V+b)T^{\frac{1}{2}}} \qquad (4)$$

based on vapor-liquid equilibrium data. Although this equation differs from the van der Waals equation only in the "attractive term" (the term containing the empirical constant a), it has been shown to be superior to other two or three constant equations.[50] Because of its simplicity, the Redlich-Kwong equation has recently been modified and extended to the cryogenic region.[3,133,136]

Beattie-Bridgeman Equation of State

In 1928, Beattie and Bridgeman removed the restriction of isochoric linearity and proposed a five-constant equation of state.[6] The isometric variation between pressure and temperature was represented by

$$P = A + BT + \frac{C}{T^2} \qquad (5)$$

The coefficients A, B, C were then expressed as functions of density. The resulting equation is

$$P = RT\rho + \left(B_oRT - A_o - \frac{CR}{T^2}\right)\rho^2 - \left(bB_oRT - aA_o + \frac{CB_oR}{T^2}\right)\rho^3 + \frac{CbB_oR}{T^2}\rho^4 \qquad (6)$$

where a, A_o, b, B_o and C are parameters. This equation of state is accurate for predicting volumetric behavior of

gases for densities up to one-half the critical density but becomes unreliable near the two-phase region.[18]

Benedict-Webb-Rubin Equation of State

In 1940, Benedict, Webb and Rubin[9] modified the Beattie-Bridgeman equation of state, and extended the number of parameters to eight.

$$P = RT\rho + \left(B_oRT - A_o - \frac{C_o}{T^2}\right)\rho^2 + (bRT - a)\rho^3 + a\alpha\rho^6 + \frac{c\rho^3}{T^2}\left\{(1 + \gamma\rho^2)\exp(-\gamma\rho^2)\right\} \quad (7)$$

This equation was developed specifically for light hydrocarbons and their mixtures for densities up to twice the critical.[10,11,12] This complex equation of state marked the first analytical formulation capable of predicting consistent thermodynamic properties of coexisting vapor and liquid phases. Recently the BWR equation has been successfully extended to nonhydrocarbons[31,49,115] and has been modified to include the cryogenic region.[2,28,54]

Martin-Hou Equation of State

In 1954, Martin and Hou[85] proposed a ten-constant equation of state. Curvatures observed at the low temperature end of the isochores were accounted for by an exponential term

$$P = A + BT + Ce^{-kT/T_c} \quad (8)$$

where k is treated as a constant. Instead of expanding the coefficients A, B and C as functions of density, Martin and Hou used Equation (8) as the temperature dependence of the virial coefficients in a modified truncated virial equation of state

$$P = \sum_{i=1}^{5} \frac{f_i}{(V-b)^i} \tag{9}$$

where $f_i = A_i + B_i T + C_i e^{-kT/T_c}$. It is of interest to note that Kamerlingh Onnes[61] in 1910 proposed the following general empirical equation of state form

$$PV = T\left(1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^4} + \frac{E}{V^6} + \frac{F}{V^8}\right) \tag{10}$$

where the virial coefficients B through F assumed the same temperature dependence form

$$B = b_1 + \frac{b_2}{T} + \frac{b_3}{T^2} + \frac{b_4}{T^4} + \frac{b_5}{T^6} \tag{11}$$

The accuracy and range of the Martin-Hou equation of state are comparable to the BWR equation.[109] However, no mixing rules have yet been proposed for the Martin-Hou equation, and it has not received wide application.

Pings and Sage Equation of State

Use of closed form equations of state with multiparameters suffers the disadvantage of high correlation among their

parameters. Solution for the parameters by least squares analysis may lead to an ill-conditioned regression matrix. To avoid these pitfalls, Pings and Sage[97,98] employed orthogonal polynomials to fit the compressibility data of propane as functions of molal density and temperature. The equation was an infinite series subject to truncation to any degree of accuracy. Pings and Sage used a series with 34 terms to represent propane data virtually within experimental accuracy in the vapor region. Such a procedure has mathematical elegance. However, the necessity of using an excessive number of terms to achieve acceptable accuracy prohibits its general use in engineering calculations.

Strobridge Equation of State

To achieve high accuracy in predicting volumetric behavior of cryogenic nitrogen, Strobridge[125] proposed a sixteen-constant modification of the BWR equation. A root-mean-square error in compressibility factor of 0.87% was reported for densities up to three times the critical density.

Vennix-Kobayashi Equation of State

Recently Vennix and Kobayashi[133] modified Martin-Hou's isometric expression to include an additional exponential term to correct for the observed curvatures of isochores at high temperatures. Accordingly the Vennix-Kobayashi isometric expression takes the form

$$P = A + BT + Ce^{ET} + De^{F/T} \qquad (11)$$

Coefficients A through F were expanded as functions of molal density. The resulting twenty-five-constant equation of state was applied to methane with an average absolute error of 0.047% in density (to temperatures as low as -220°F).

The equation has the following form

$$
\begin{aligned}
P = {} & \rho^2\left[A_1 + A_2\rho + A_3\rho^2 + A_4\rho^3 + A_5\rho^4\right] \\
& + \rho T\left[R + B_1\rho + B_2\rho^2 + B_3\rho^3 + B_4\rho^4 + B_5\rho^5\right] \\
& + \rho^2\left(\rho+\rho_o\right)^2\left[\left(\rho+\rho_o\right)^3 - \left(\alpha+\rho_o\right)^3\right]\left[\left(\beta+\rho_o\right)^3 - \left(\rho+\rho_o\right)^3\right]\cdot \\
& \qquad \exp\left\{G - \left[E_1+E_2\left(\rho+\rho_o\right)^3\right]\left(T-T_o\right)\right\} \qquad (13) \\
& + \rho^2\left[D_1+D_2\rho+D_3\rho^2+D_4\rho^3+D_5\rho^4\right] \exp\left[K-\left(F_1+F_2\rho\right)/T\right]
\end{aligned}
$$

Summary

The foregoing discussion clearly shows the trend towards complexity in equation of state development. Among the equations of state discussed in this chapter, only the Vennix equation extends reliably in cryogenic region to a reduced temperature of 0.7. This equation has been successfully applied to methane only. Application to other fluids is greatly hampered by its highly nonlinear functionality besides its large number of adjustable constants.

It is well known that empirical equations of state cannot be extrapolated reliably (as can be easily realized by predicting the thermodynamic behavior of propane at a reduced

temperature as low as 0.3). In view of these facts, it has become evident that existing equations of state are inadequate for design purposes in the cryogenic region, since they must be extrapolated to this region. To overcome this difficulty, attention has been turned to the development of new equations of state or modification of existing equations.

Also of significance is the fact that all the equations of state discussed so far, with the notable exceptions of the BWR and Redlich-Kwong equations, were developed specifically for PVT prediction without due regard to other thermodynamic properties. This practice is highly undesirable, for the high correlation among the parameters robs thermodynamic consistency from an empirical equation of state developed for only one property.

CHAPTER II

DEVELOPMENT OF THE NEW EQUATION OF STATE

For the development of the new equation of state form, extensive thermodynamic data for methane were utilized. Comprehensive methane PVT data can be found in Din's compilation[41] and the Wilson-Clark-Hyman report[138]. Major data contributions include measurements by Kvalnes and Gaddy[74], Michels and Nederbragt[94], Douslin, et al.[27], Vennix[132] and van Itterbeek[131]. Methane enthalpy data have been reported by Jones, et al.[63], while the vapor pressure of methane has been tabulated by Matthews and Hurd[91].

The extensive and accurate isochoric data from Douslin and Vennix can be used directly and conveniently to discern the temperature dependence of methane isochores. Data from these two sources cover a PVT spectrum from -190°F to 347°F, 1.401 lb mole/ft^3 to 0.047 lb mole/ft^3 and pressures up to 10,000 psia.

Graphical Study of Isochores

To study the temperature dependence of the equation of state, a large scale plot of pressure versus temperature was prepared using the isochoric data of Vennix[132]. Isochoric

data from Douslin, et al.[44] were added to extend seven of Vennix's isochores (from 0.16 lb mole/ft^3 to 0.736 lb mole/ft^3) well into the high temperature and pressure region. It is observed that the isochores may be classified into three families of curves as depicted schematically in Figure 1.

1. The critical isochore and the 1.1558 lb mole/ft^3 isochore show no noticeable deviation from linearity.

2. Isochores with densities less than the critical and greater than 1.1558 lb mole/ft^3 show downward curvature at both ends.

3. Isochores with densities greater than the critical but less than 1.1558 lb mole/ft^3 show linearity from the upper ends (high temperature, high pressure region) to about -80°F, whereupon they show upward curvature as they approach the saturation curve.

Fourteen isotherms of liquid methane density data reported by van Itterbeek, et al.[131] ranging from -257°F to -121°F for pressures up to 4500 psia were crossplotted to obtain isochoric data. For densities less than 1.4 lb mole/ft^3 these isochores show rather erratic curvature, indicating inconsistency in the isothermal data. These data therefore were not used in the present study except for conditions outside the region of the Vennix data.

Analytical Relations for Isochores

Deviations from linearity of isochores have long been observed and various isochoric pressure-temperature (P-T)

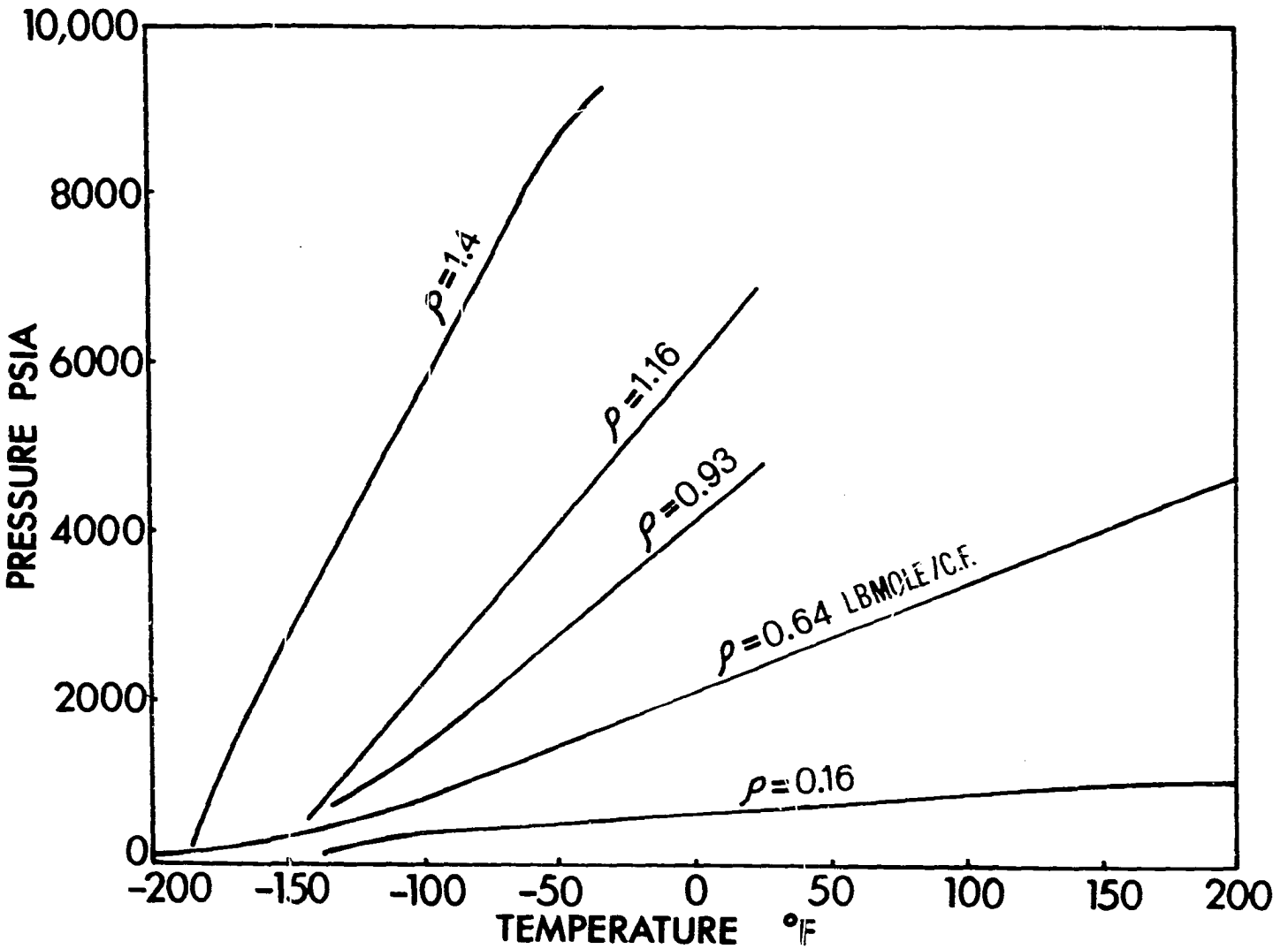


Figure 1. Variation of Pressure with Temperature of Methane Isochores

relationships have been proposed. It is obvious from Figure 1, that curvature does occur at both ends of most isochores. Of more significance, these curvatures are by no means unidirectional. These facts suggest that to adequately describe the temperature dependence of each isochore, it is necessary to introduce at least two different terms to correct for deviations from linearity. As to the analytic form of these correction terms, the isochoric plot fails to provide meaningful information. Vennix[132] used two exponential terms to develop his highly accurate but complex equation of state for methane. Application of the Vennix equation of state to other hydrocarbons is hampered by the lack of extensive PVT data to allow a graphical estimation of some of the nonlinear parameters, in particular ρ_o in Equation (13). In principle, a least squares regression scheme can be used to determine all twenty-five parameters by fitting a PVT surface. However, the presence of eight nonlinear parameters renders such an approach highly difficult in practice.

A primary objective of the present study, then, was to examine the feasibility of using a relatively simple isochoric P-T relationship as the building block in the development of an equation of state. The usefulness of this new equation of state lies in its ability to accurately predict all thermodynamic properties in both vapor and liquid phases as well as in the coexisting vapor and liquid phases.

From statistical mechanical considerations, Zwanzig[146] has shown by perturbation theory, that the Helmholtz free energy can be expressed as an infinite power series in reciprocal temperature. Since pressure can be derived from the residual Helmholtz free energy by

$$P = RT\rho + \rho^2 \left(\frac{\partial \tilde{A}}{\partial \rho}\right)_T \qquad (14)$$

it is obvious that at constant density, pressure can also be taken to assume the same temperature dependent form. (The distinction between the Helmholtz free energy and the residual Helmholtz free energy is elucidated in Appendix C.) Based on these considerations, the pressure-temperature variation of isochores was approximated by the following polynomial

$$P = A + BRT + \sum_{n=1}^{5} \frac{C_n}{T_n} \qquad (15)$$

where $\sum_{n=1}^{5} \frac{C_n}{T_n}$ are the correction terms needed to compensate for deviations from linearity. A general linear least squares program, ORNOR, developed by Hall and Canfield[53], was used to curve fit the individual isochores of Douslin, Vennix and van Itterbeek. The use of ORNOR to discern the temperature dependence of isochores using a polynomial as in Equation (15) offers the following advantages:

1. The coefficients are not functions of the degree of the polynomial. Addition of a new term to the approximating polynomial does not alter any previous calculations.

Thus, the optimum degree of a polynomial can be determined in one computer run.

2. Coefficients in the polynomial are determined without having to solve a set of simultaneous equations, thus avoiding the pitfall of an ill-conditioned regression matrix.

Minimization of the objective function in the ORNOR program is performed with respect to the residuals

$$Q = \Sigma W_i (Y_i - y_i)^2 \tag{16}$$

where W_i is the weighting function taken to be

$$W_i = \frac{1}{Y_i^2} \tag{17}$$

and Y_i and y_i are the observed and calculated responses. It was observed that the use of pressure or a residual quantity such as $(P-RT\rho)/\rho^2$ as the objective function was immaterial. However, use of the latter renders the weighting function meaningless while the former offers more freedom in smoothing the parameters as functions of density.

The isochoric P-T relation which yields the best fit was found to be

$$P = A + BRT + \frac{C}{T^2} + \frac{D}{T^3} + \frac{E}{T^4} \tag{18}$$

The results of using this relation are shown in Table 1 together with results reported by Vennix.[132] It can be seen that a fifth degree polynomial can fit the Vennix data with an accuracy which is generally better than Equation (12) except for the 1.40 lb mole/ft^3 isochore. This is not too disturbing because an absolute deviation of 0.69 per cent was detected at -179.97°F and 845.7 psia. This is about five times the absolute average deviation for the whole isochore. Removal of the above data point improved the absolute average root-mean deviation from 0.142% to 0.011%.

Final Choice for the Temperature Dependence of Isochores

To ensure the continuity of density dependence of the parameters in Equation (18) up to 2.5 times the critical, five of van Itterbeek's interpolated isochores (from 1.511 lb mole/ft^3 to 1.639 lb mole/ft^3) were included to obtain plots of parameters versus density. It was observed that parameters obtained from van Itterbeek's data showed large scattering. Also because of the large standard deviation of parameter E in Equation (18), its density dependence was not well defined. Also at this stage, the density dependent relation for each parameter in Equation (18) would generate three to five coefficients in the final equation of state. With these considerations as guide lines, it was decided to approximate the P-T relation of isochores by

TABLE 1

COMPARISON OF ISOCHORIC EQUATIONS FOR PREDICTING METHANE PVT DATA OF VENNIX

		$P = A + BRT + \frac{C}{T^2} + \frac{D}{T^3} + \frac{E}{T^4}$		$P = A + BT + ce^{ET} + De^{F/T}$	
DENSITY ($lb.\ mole/ft^3$)	NO. OF DATA PT.	MAX. ABS. DEV. %	AVG. ABS. DEVIATION %	MAX. ABS. DEV. %	AVG. ABS. DEVIATION %
0.16	14	0.0072	0.00343	0.03	0.02
0.405	10	0.0065	0.0027	0.03	0.01
0.4514	19	0.0333	0.0107	0.04	0.02
0.6150	13	0.0363	0.0075	0.04	0.01
0.6382	18	0.0378	0.0126	0.04	0.02
0.6966	19	0.0326	0.0109	0.03	0.01
0.7355	20	0.0179	0.00685	0.02	0.01
0.8017	14	0.0374	0.0216	0.03	0.02
0.8601	27	0.052	0.0221	0.03	0.02
0.934	16	0.0289	0.0160	0.01	0.01
1.0313	15	0.084	0.0299	0.05	0.02
1.0974	15	0.076	0.0190	0.08	0.03
1.1558	20	0.032	0.00816	0.03	0.01
1.2492	16	0.0589	0.0199	0.08	0.03
1.3271	12	0.0425	0.0159	0.05	0.02
1.4010	13	0.689	0.142	0.07	0.03
1.4010	12	0.0338	0.0112		

$$P = A + BRT + \frac{C}{T^2} + \frac{D}{T^3} \qquad (19)$$

Table 2 shows the result of fitting Equation (19) to the previously described methane data set. Results using the Beattie-Bridgeman isochoric expression are also presented for comparison. It can be seen that Equation (18) offers significant improvement in describing the temperature dependence of the Douslin-Vennix isochores. The accuracy of interpolation of van Itterbeek's isochores does not justify a meaningful comparison between Equations (19) and (5). While Equation (19) may not express exactly the temperature-dependence of isochores, it does represent their general shape adequately.

It is worthwhile to note that the isochoric expression in Equation (19) bears remarkable resemblance to the temperature dependence of the second virial coefficient

$$B_2 = A + BT + \frac{C}{T^2} + \frac{D}{T^4} \qquad (20)$$

proposed by Claitor and Crawford[23], and later used by Bloomer and Rao[16]. However, these investigators treated the coefficients in Equation (19) as constants rather than as functions of density. Martin[89] has remarked that the two algebraic correction terms such as the ones appearing in Equation (19) could be combined to form a single exponential term such as ce^{-kT_r}, with k as a constant.

TABLE 2

COMPARISON OF ISOCHORIC EQUATIONS FOR PREDICTING PVT DATA
OF DOUSLIN, VENNIX and VAN ITTERBEEK

		$P = A + BRT + \frac{C}{T^2} + \frac{D}{T^3}$		$P = A + BRT + \frac{C}{T^2}$	
DENSITY (lb. mole/ft^3)	NO. OF DATA PT.	MAX. ABS. DEV. %	ABS. AVG. DEVIATION %	MAX. ABS. DEV. %	ABS. AVG. DEVIATION %
0.1596	29	0.043	0.029	0.075	0.030
0.4047	25	0.088	0.051	0.150	0.067
0.4514	31	0.174	0.074	0.147	0.077
0.6149	20	0.044	0.0114	0.324	0.148
0.6382	24	0.063	0.019	0.445	0.188
0.6966	24	0.104	0.043	0.560	0.234
0.7355	25	0.110	0.033	0.598	0.203
0.8017	14	0.110	0.042	0.272	0.166
0.8601	27	0.13	0.056	0.413	0.217
0.934	16	0.85	0.042	0.390	0.216
1.0313	15	0.112	0.043	0.390	0.214
1.0974	15	0.025	0.026	0.395	0.239
1.1558	20	0.053	0.018	0.521	0.221
1.2492	16	0.06	0.019	0.456	0.260
1.3271	12	0.058	0.022	0.340	0.180
1.401	12	0.058	0.036	0.395	0.198
1.511	14	8.23	1.59	3.59	1.70
1.540	14	1.00	0.313	1.30	0.455
1.563	14	1.93	0.402	1.94	0.412
1.589	13	1.22	0.525	1.28	0.530
1.639	11	1.87	0.887	1.89	0.911

This is a valid proposition provided a lesser degree of accuracy can be accepted in describing the pressure-temperature variations of isochores. To obtain comparable accuracy among isochores, it is necessary to treat k as a function of density. In this case, mathematical simplicity suggests the preference of using Equation (19) as the temperature dependence of the equation of state.

Use of Enthalpy Data to Verify the Temperature Dependence of Isochores

Recent accurate enthalpy data from the University of Michigan[63,141] form a valuable source of information concerning the temperature dependence of an equation of state. The enthalpy departure expression can be derived from the residual Helmholtz free energy $\tilde{A}$ by the following thermodynamic relationship:

$$H-H^\circ = -T^2 \left(\frac{\partial \tilde{A}/T}{\partial T}\right)_\rho + \frac{P}{\rho} - RT \qquad (21)$$

It is obvious that the enthalpy departure assumes the same temperature dependence as pressure, i.e.

$$H-H^\circ = A' + B'T + \frac{C'}{T^2} + \frac{D'}{T^3} \qquad (22)$$

where A', B', C', and D' are empirical constants. To show this is indeed the case, two isochoric enthalpy-temperature plots were constructed. Jones'[63] liquid methane enthalpy values as corrected by Yesavage[141] were interpolated at

temperature-pressure values corresponding to Vennix's 0.934 lb mole/ft^3 and van Itterbeek's 1.64 lb mole/ft^3 isochores. The results are shown in Figures 2 and 3 respectively.

Comparing Figures 1, 2, and 3, it can be seen that enthalpy and pressure do show the same temperature-dependence. Unfortunately, corresponding density values at the temperature-pressure conditions of the enthalpy data are not reported in the literature and the enthalpy data cannot be used directly to derive an equation of state implicit in density and temperature. However, once an equation of state form is developed from PVT data, enthalpy data can be used to check the adequacy of the assumed temperature dependence. Inadequacy of the temperature dependence emerges when the proposed equation of state fails to predict enthalpy behavior with accuracy comparable to the accuracy of predicted volumetric behavior. Detailed discussions of the use of enthalpy data to modify the temperature dependence of an existing equation of state are available in references 28 and 75.

Density Dependence of the Equation of State

The density dependence of parameters A, B, C and D of Equation (19) are shown in Figures 4, 5, 6 and 7. Among the five van Itterbeek interpolated isochores, only the 1.64 lb mole/ft^3 ($2.6\rho_c$) isochore was amenable to correlation.

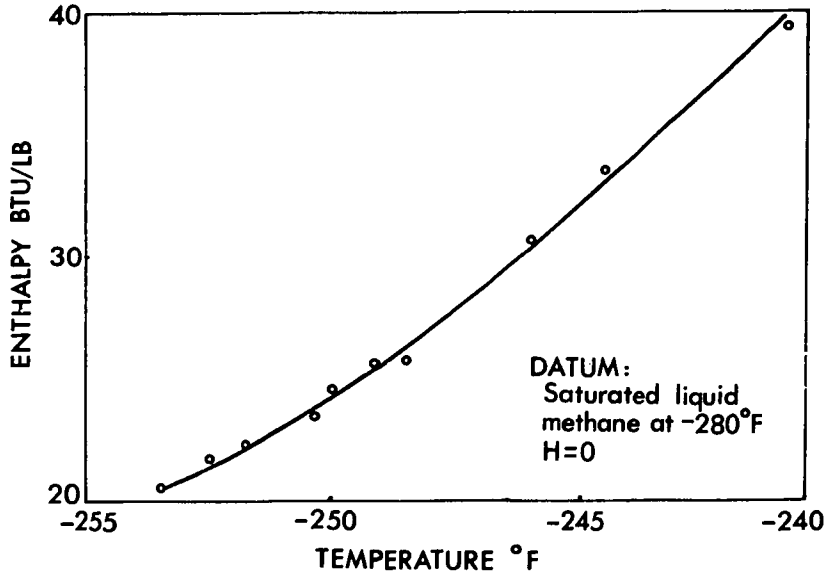


Figure 2. Enthalpies of Methane at Constant Density (0.934 lb mole/ft^3)

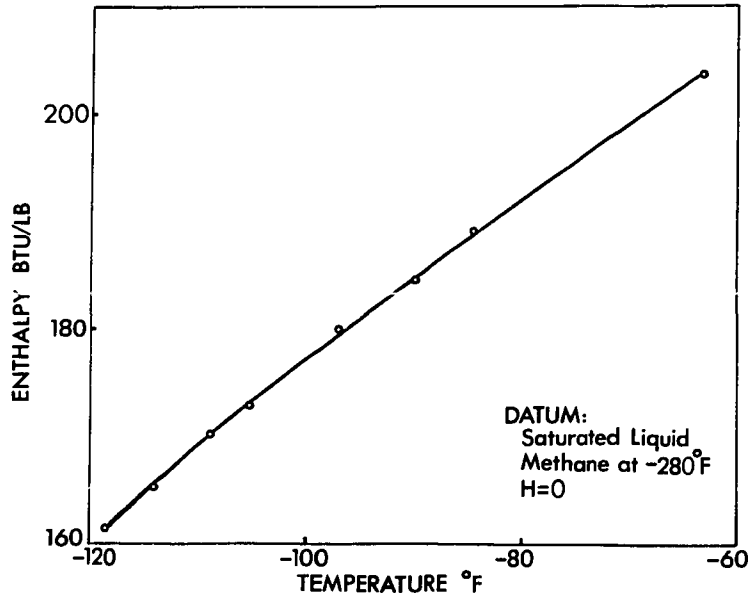


Figure 3. Enthalpies of Methane at Constant Density (1.64 lb mole/ft^3)

It is of interest to note the opposing effect of the density dependence of parameters C and D in Figures 6 and 7. Since the curvatures at both ends of the isochores are not unidirectional, it is logical to consider accounting for the curvatures by a combination of two terms.

The density dependence of parameters A, B, C and D can be adequately described by the following analytic functions,

$$A = A_1\rho^2 + A_2\rho^3 + A_3\rho^6 \tag{23}$$

$$\left(\frac{B}{\rho} - 1\right) = B_1\rho + B_2\rho^2 + B_3\rho^3 + B_4\rho^4 \tag{24}$$

$$\frac{C}{\rho^2} = C_5 + \left(C_1\rho + C_2\rho^3 + C_3\rho^5\right) \exp\left(- C_4\rho^2\right) \tag{25}$$

$$\frac{D}{\rho^2} = D_5 + \left(D_1\rho + D_2\rho^2 + D_3\rho^3\right) \exp\left(- D_4\rho\right) \tag{26}$$

The choice of the above functions reduces the equation of state to the perfect gas law as density approaches zero. The resulting equation of state can be readily differentiated and integrated with respect to density and temperature.

Thermodynamic Relations for the New Equation of State

The new equation of state, explicit in pressure has the following form

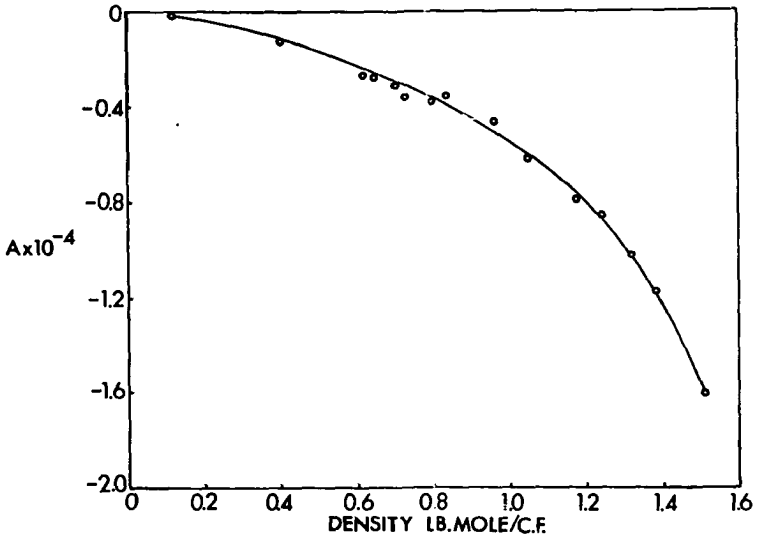


Figure 4. Density Dependence of A in Equation (19)

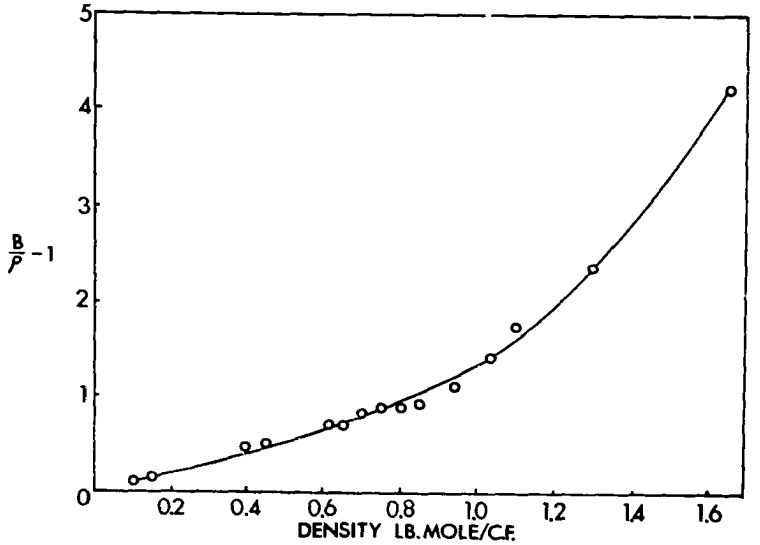


Figure 5. Density Dependence of B in Equation (19)

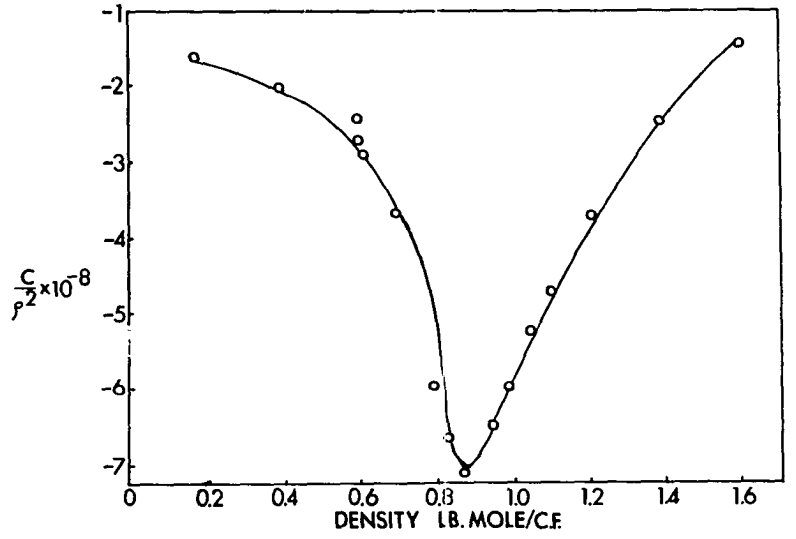


Figure 6. Density Dependence of C in Equation (19)

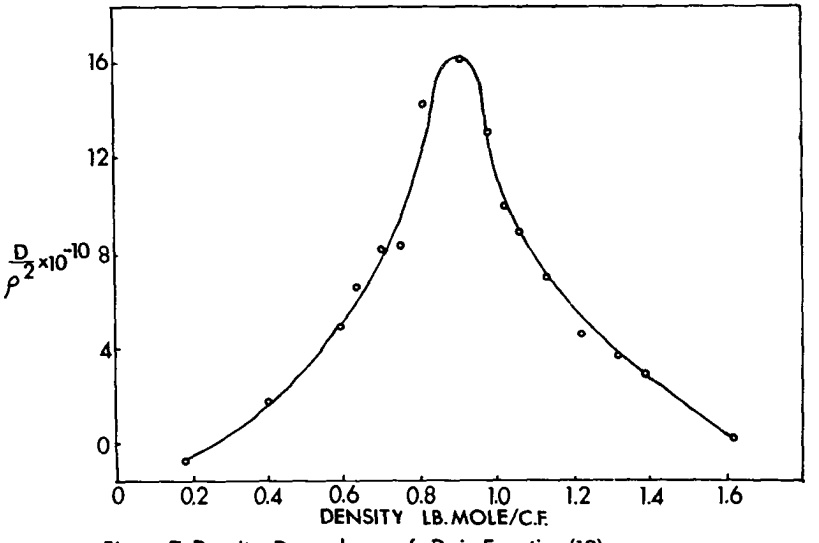


Figure 7. Density Dependence of D in Equation (19)

$$P = RT\rho + \left(A_1\rho^2 + A_2\rho^3 + A_3\rho^6\right) +$$

$$\left(B_1\rho^2 + B_2\rho^3 + B_3\rho^4 + B_4\rho^5\right) RT +$$

$$\frac{C_5\rho^2}{T^2} + \frac{\rho^2}{T^2} \exp\left(- C_4\rho^2\right)\left(C_1\rho + C_2\rho^3 + C_3\rho^5\right) +$$

$$\frac{D_5\rho^2}{T^3} + \frac{\rho^2}{T^3} \exp\left(- D_4\rho\right)\left(D_1\rho + D_2\rho^2 + D_3\rho^3\right) \qquad (27)$$

Derivations of thermodynamic property functions from the pressure equation are presented in Appendix C. Hence only the final equations for enthalpy departure, fugacity and entropy departure will be presented here.

Enthalpy Departure Equation

$$
\begin{aligned}
H-H^\circ = {} & \left(2A_1\rho + \frac{3}{2}A_2\rho^2 + \frac{6}{5}A_3\rho^5\right) + \left(B_1\rho + B_2\rho^2 + B_3\rho^3 + B_4\rho^4\right)RT + \\
& \frac{3C_1}{2C_4T^2} + \frac{3C_2}{2C_4^2T^2} + \frac{3C_3}{C_4^3T^2} + \frac{4C_5\rho}{T^2} + \\
& \frac{C_1\rho^2}{T^2}\exp\left(-C_4\rho^2\right)\left(1 - \frac{3}{2C_4\rho^2}\right) + \\
& \frac{C_2\rho^4}{T^2}\exp\left(-C_4\rho^2\right)\left(1 - \frac{3}{2C_4\rho^2} - \frac{3}{2C_4^2\rho^4}\right) + \\
& \frac{C_3\rho^6}{T^2}\exp\left(-C_4\rho^2\right)\left(1 - \frac{3}{2C_4\rho^2} - \frac{3}{C_4^2\rho^4} - \frac{3}{C_4^3\rho^6}\right) + \\
& \frac{4D_1}{D_4^2T^3} + \frac{8D_2}{D_4^3T^3} + \frac{24D_3}{D_4^4T^3} + \frac{5D_5\rho}{T^3} + \qquad (28) \\
& \frac{D_1\rho^2}{T^3}\exp\left(-D_4\rho\right)\left(1 - \frac{4}{D_4\rho} - \frac{4}{D_4^2\rho^2}\right) + \\
& \frac{D_2\rho^3}{T^3}\exp\left(-D_4\rho\right)\left(1 - \frac{4}{D_4\rho} - \frac{8}{D_4^2\rho^2} - \frac{8}{D_4^3\rho^3}\right) + \\
& \frac{D_3\rho^4}{T^3}\exp\left(-D_4\rho\right)\left(1 - \frac{4}{D_4\rho} - \frac{12}{D_4^2\rho^2} - \frac{24}{D_4^3\rho^3} - \frac{24}{D_4^4\rho^4}\right)
\end{aligned}
$$

Fugacity Equation

$$RT\ell nf = RT\ell n(RT\rho) + \left(2A_1\rho + \frac{3}{2}A_2\rho^2 + \frac{6}{5}A_3\rho^6\right) +$$

$$\left(2B_1\rho + \frac{3}{2}B_2\rho^2 + \frac{4B_3\rho^3}{3} + \frac{5B_4\rho^4}{4}\right)RT +$$

$$\frac{C_1}{2C_4T^2} + \frac{C_2}{2C_4^2T^2} + \frac{C_3}{C_4^3T^2} + \frac{2C_5\rho}{T^2} +$$

$$\frac{C_1}{2C_4T^2}\exp\left(-C_4\rho^2\right)\left(2C_4\rho^2-1\right) + \frac{C_2}{2C_4^2T^2}\exp\left(-C_4\rho^2\right)\left(2C_4^2\rho^4-C_4\rho^2-1\right) +$$

$$\frac{C_3}{C_4^3T^2}\exp\left(-C_4\rho^2\right)\left(C_4^3\rho^6-\frac{1}{2}C_4^2\rho^4 - C_4\rho^2 - 1\right) +$$

$$\frac{D_1}{D_4^2T^3} + \frac{2D_2}{D_4^3T^3} + \frac{6D_3}{D_4^4T^3} + \frac{2D_5\rho}{T^3} + \qquad (29)$$

$$\frac{D_1}{D_4^2T^3}\exp\left(-D_4\rho\right)\left(D_4^2\rho^2 - D_4\rho - 1\right) +$$

$$\frac{2D_2}{D_4^3T^3}\exp\left(-D_4\rho\right)\left(\frac{D_4^3\rho^3}{2} - \frac{D_4^2\rho^2}{2} - D_4\rho - 1\right) +$$

$$\frac{6D_3}{D_4^4T^3}\exp\left(-D_4\rho\right)\left(\frac{D_4^4\rho^4}{6} - \frac{D_4^3\rho^3}{6} - \frac{D_4^2\rho^2}{2} - D_4\rho - 1\right)$$

Entropy Departure Equation

$$S-S^\circ = -R\ell nRT\rho - \left(B_1\rho + B_2\rho^2 + \frac{B_3\rho^3}{3} + \frac{B_4\rho^4}{4}\right) R$$

$$+ \frac{C_1}{C_4T^3} + \frac{C_2}{C_4^2T^3} + \frac{2C_3}{C_4^3T^3} + \frac{2C_5\rho}{T^3}$$

$$- \frac{C_1}{C_4T^3} \exp\left(-C_4\rho^2\right)$$

$$- \frac{C_2}{C_4^2T^3} \exp\left(-C_4\rho^2\right)\left(C_4\rho^2 + 1\right) -$$

$$\frac{2C_3}{C_4^3T^3} \exp\left(-C_4\rho^2\right)\left(\frac{C_4^2\rho^4}{2} + C_4\rho^2 + 1\right) \qquad (30)$$

$$+ \frac{3D_1}{D_4^2T^4} + \frac{6D_2}{D_4^3T^4} + \frac{18D_3}{D_4^3T^4} + \frac{3D_5\rho}{T^4}$$

$$- \frac{3D_1}{D_4^2T^4} \exp\left(-D_4\rho\right)\left(D_4\rho + 1\right) -$$

$$\frac{6D_2}{D_4^3T^4} \exp\left(-D_4\rho\right)\left(\frac{D_4^2\rho^2}{2} + D_4\rho + 1\right) -$$

$$\frac{18D_3}{D_4^3T^4} \exp\left(-D_4\rho\right)\left(\frac{D_4^3\rho^3}{6} + \frac{D_4^2\rho^2}{2} + D_4\rho + 1\right)$$

CHAPTER III

PRINCIPLES OF MULTICOMPONENT MULTIPROPERTY NONLINEAR REGRESSION ANALYSIS IN EQUATION OF STATE DEVELOPMENT

Once the equation-of-state form is formulated, the remaining task is to determine its parameters. If an equation of state is purely theoretical, the parameters are non-adjustable and the set is unique, satisfying the condition of thermodynamic consistency. However, for an empirical equation of state such is not the case. The work of Opfell, Pings and Sage[98] on determination of BWR equation-of-state parameters clearly shows that there may, in fact, be several sets of parameters capable of correlating thermodynamic behavior of a given fluid to varying degrees of accuracy.

The objective here is to determine a set of parameters which describe accurately PVT, enthalpy departure and phase equilibrium behavior of pure components and/or their mixtures. If the above three thermodynamic properties are described within experimental accuracy, other related properties such as entropy, fugacity, heat capacity, enthalpy and entropy of vaporization and enthalpy and entropy of mixing can be predicted with confidence.

Mathematical Framework

The general mathematical framework using the least squares formalism as the basis for multiproperty multicomponent regression analysis has been presented in reference 119. For completeness, the main ideas are recapitulated.

Let the functional relationship of an equation of state for a mixture of n-components be

$$f(R,T,\rho,[x],[A]) = 0 \tag{31}$$

where R is a thermodynamic property (e.g., density, enthalpy, fugacity), T is the absolute temperature, ρ is the molal density, [x] is the set of mole fractions and [A]is a set of true-valued mixture parameters. A set of true-valued parameters is defined as the set which, when substituted into Equation (31) yields the experimental value of R provided the functionality of Equation (31) represents the true model of R. This set, of course, is not known.

Denote the least squares estimate of [A] by $[\bar{A}]$ Equation (31) becomes

$$f(R,T,\rho,[x],[\bar{A}]) + \epsilon = 0 \tag{32}$$

The use of $[\bar{A}]$ in Equation (31) represents the regression

surface of R and ϵ is the least squares error of R from the regression surface.

The model chosen for the regression analysis assumes that the independent variables can be measured exactly, and the errors in a thermodynamic property occur randomly. These random errors are assumed to be uncorrelated ($\epsilon_i \neq \epsilon_j$), and follow a normal distribution with zero mean and variance σ^2 (unknown, but assumed to be the same for each data point).[45] Let $\mu(R)$, $\sigma^2(R)$ be the expected value and variance of R respectively. The probability distribution function (PDF) of R is[70]

$$P(R) = \frac{1}{\sqrt{2\pi\sigma^2(R)}} \exp\left[-\frac{[R-\mu(R)]^2}{2\sigma^2(R)}\right] \qquad (33)$$

In a multiproperty regression analysis, it is necessary to distinguish different properties at different states. Let R_{kj} be the k^{th} property at the j^{th} state or data point. Assuming the PDF of each individual property is independent, the PDF of a set of thermodynamic properties becomes

$$P\{R_{kj}\} = \prod_k \prod_j^{NP} P(R_{kj})$$

$$= \prod_k \prod_j^{NP} \frac{1}{\left(2\pi\sigma^2(R_{kj})\right)^{\frac{1}{2}}} \exp\left(-\sum_{kj}\sum \frac{[R_{kj}-\mu(R_{kj})]^2}{2\sigma^2(R_{kj})}\right) \qquad (34)$$

where NP is the number of data points for each individual property.

To apply the concept of least squares regression analysis, it is necessary to assume that the equation of state, with a set of true-valued parameters, yields the true value of the property in question. Let the calculated true value of the property in question be η_{kj}, i.e.

$$\eta_{kj} = f_{kj}(T,\rho,[x],[A]) \tag{35}$$

Using the true-valued parameters in Equation (30), the expected values of thermodynamic properties are

$$\mu(R_{kj}) = \eta_{kj} \tag{36}$$

Furthermore, if the experimental data are accurate and their random errors are small, it is not unreasonable to assume the standard deviation of the data to be proportional to their means, i.e.

$$\sigma(R_{kj}) = \beta_k \eta_{kj} \tag{37}$$

where β_k is the proportionality constant for the k^{th} property. The quantity β_k is a measure of the relative accuracy among different thermodynamic properties. Substitution of Equations (36) and (37) into Equation (34) involves η_{kj} which must be calculated by an equation of state using a set of true-valued parameters. Since the

set of true-valued parameters are not known, it is necessary to make a further simplifying assumption, and treat the standard deviation of the data as proportional to the experimental values, i.e.,

$$\sigma(R_{kj}) = \beta_k R_{kj} \tag{38}$$

Use of estimated parameters $[\bar{A}]$ in Equation (35) yields estimated values of the property in question. Equations (35), (36), (38) become

$$\bar{\eta}_{kj} = f_{kj}(T,\rho,[x],[\bar{A}]) \tag{39}$$

$$\bar{\mu}(R_{kj}) = \bar{\eta}_{kj} \tag{40}$$

$$\bar{\sigma}(R_{kj}) = \beta_k R_{kj} \tag{41}$$

Substituting Equations (39), (40), (41) into Equation (34) gives

$$P\{R_{kj}\} = \prod_k \prod_j^{NP} \frac{1}{\sqrt{2\pi\beta_k^2 R_{kj}^2}} \exp\left[-\frac{1}{2}\sum_k \frac{1}{\beta_k^2}\sum_j^{NP}\left[1 - \frac{\bar{\eta}_{kj}}{R_{kj}}\right]^2\right] \tag{42}$$

Maximimizing the probability distribution function to obtain the maximum likelihood estimation of parameters corresponds to minimizing the negative of the argument of the exponential expression in Equation (42). The function to be minimized is

$$Q^* = \sum_k \frac{1}{\beta_k^2} \sum_j \left[1 - \frac{\bar{\eta}_{kj}}{R_{kj}}\right]^2 \tag{43}$$

Since the β_k are measures of the relative accuracy among different thermodynamic properties, they have the meaning of a weighting function. Defining the weighting function W_k,

$$W_k = \left(\frac{\beta_1}{\beta_k}\right)^2 \tag{44}$$

and

$$Q^* = \frac{Q}{\beta_1^2} \tag{45}$$

Equation (43) becomes

$$Q = \sum_k W_k \sum_j^{NP} \left[1 - \frac{\bar{\eta}_{kj}}{R_{kj}}\right]^2 \tag{46}$$

which is the familiar sum of the weighted squares of the residuals of R_{kj}.

In the absence of constraints such as critical conditions of pure components, a necessary condition for a minimum function Q is given by

$$\sum_k W_k \sum_j \left[1 - \frac{\bar{\eta}_{kj}}{R_{kj}}\right] \frac{1}{R_{kj}} \frac{\partial \bar{\eta}_{kj}}{\partial \bar{A}_{mn}} = 0 \tag{47}$$

where $\bar{A}_{mn}$ is the least squares estimate of the n^{th} parameter for the m^{th} component. Equation (47) forms the set of normal equations to be solved in the least squares regression analysis. If the normal equations are linear with respect to the parameters, the solution is straightforward. However, most existing equations of state are nonlinear. In such cases, iterative schemes must be used to effect a solution. The present work employs the Gauss-Newton linearization procedure because of its simplicity.

Gauss-Newton Linearization[55]

Let $\bar{A}_{mn_o}$ be the guessed values for $\bar{A}_{mn}$. Expanding $\bar{\eta}_{kj}$ in a Taylor series to the first approximation results in

$$\bar{\eta}_{kj} = \bar{\eta}_{kj}\{\bar{A}_o\} + \sum_{r}^{NC}\sum_{s}^{M}\left[\frac{\partial\bar{\eta}_{kj}}{\partial\bar{A}_{rs}}\right]_o \left(\bar{A}_{rs} - \bar{A}_{rs_o}\right) \qquad (48)$$

where r = 1,2...NC and s = 1,2,...M. NC is the number of components and M is the number of regression parameters. The subscript zero denotes that the quantity is to be evaluated at the guessed value $\bar{A}_o$.

Substituting Equation (48) in Equation (47) results in a set of normal equations linear in the correction terms $\left(\bar{A}_{rs} - \bar{A}_{rs_o}\right)$.

$$\sum_k W_k \sum_j \frac{1}{R^2_{kj}} \left[\frac{\partial \bar{\eta}_{kj}}{\partial A_{mn}}\right]_o \sum_r \sum_s \left[\frac{\partial \bar{\eta}_{kj}}{\partial \bar{A}_{rs}}\right]_o \left(\bar{A}_{rs} - \bar{A}_{rs_o}\right) =$$

$$\sum_k W_k \sum_j \frac{1}{R_{kj}} \left[1 - \frac{\bar{\eta}_{kj}}{R_{kj}}\right]_o \left[\frac{\partial \bar{\eta}_{kj}}{\partial \bar{A}_{mn}}\right]_o \tag{49}$$

The correction terms $\left(\bar{A}_{rs} - \bar{A}_{rs_o}\right)$ can be solved for by matrix inversion. The resultant new values of $\bar{A}_{rs}$ can be used as improved estimates in a subsequent iteration. This procedure is repeated until $\left(\bar{A}_{rs} - \bar{A}_{rs_o}\right)$ becomes arbitrarily small.

In matrix notation Equation (49) reads

$$\underline{A}\ \underline{B} = \underline{C} \tag{50}$$

The elements of the square coefficient matrix $\underline{A}$ are

$$A_{gh} = \sum_k W_k \sum_j \frac{1}{R^2_{kj}} \left[\frac{\partial \bar{\eta}_{kj}}{\partial \bar{A}_{mn}}\right]_o \left[\frac{\partial \bar{\eta}_{kj}}{\partial A_{rs}}\right]_o \tag{51}$$

and the elements of the column matrices $\underline{B}$ and $\underline{C}$ are

$$B_h = \left(\bar{A}_{rs} - \bar{A}_{rs_o}\right) \tag{52}$$

$$C_g = \sum_k W_k \sum_j \frac{1}{R_{kj}} \left[1 - \frac{\bar{\eta}_{kj}}{R_{kj}}\right]_o \left[\frac{\partial \bar{\eta}_{kj}}{\partial \bar{A}_{mn}}\right]_o \tag{53}$$

where $g = M(m-1) + n$ (54)

$h = M(r-1) + s$ (55)

and M is the number of regression parameters in the pure component equation of state.

The solution of Equation (50) by matrix inversion is

$$\underline{B} = \underline{A}^{-1}\,\underline{C} \tag{56}$$

where $\underline{A}^{-1}$ is the inverse of $\underline{A}$.

Estimates of the generalized covariances and variances[5] can be obtained from the elements of the inverse square matrix by

$$\overline{\text{cov}}\left(\overline{A}_{mn},\overline{A}_{rs}\right) = \left(\overline{\beta}_1\right)^2 A^{-1}_{gh} \tag{57}$$

$$\overline{\text{var}}\left(\overline{A}_{mn},\overline{A}_{mn}\right) = \left(\overline{\beta}_1\right)^2 A^{-1}_{gg} \tag{58}$$

respectively. $\overline{\beta}_1$, the estimated standard deviation or uncertainty of the first property in the multiproperty regression analysis may be obtained by

$$\overline{\beta}_1^2 = \frac{1}{(N-U)} \sum_k W_k \sum_j \left[1 - \frac{\overline{\eta}_{kj}}{R_{kj}}\right]^2 \tag{59}$$

where N is the total number of data points and U is the total number of parameters to be determined.

This general mathematical framework provides a uniform approach for determining a set of thermodynamically consistent parameters for any proposed equation of state using simultaneously pure components and/or mixtures data of any systems of interest.

CHAPTER IV

DEVELOPMENT OF PVT-ENTHALPY DEPARTURE-PHASE EQUILIBRIUM REGRESSION PROGRAM

A general nonlinear regression program for treating PVT and enthalpy departure data[17,27] has been extended in this work to include phase equilibrium data. The program can handle pure component and/or mixture data. In the case of a binary mixture, the program permits regression on parameters of component 1 and/or component 2. Also, any additional thermodynamic property data such as Joule-Thomson coefficients can be incorporated into the general program in a straightforward manner. The program is written in Fortran IV for the IBM 360 computer. Because of limitations of the University of Oklahoma IBM 360/40 computer on computer core storage and running time, the program is written for a binary mixture. Generalization to more components can be effected very simply.

The general nonlinear regression program has three components.

(1) Main program or "driver"

(2) Thermodynamic property subprograms

(3) Subroutines

Main Program

The main program serves as the driver for all thermodynamic property subprograms which in turn have common access to the subroutines. Figure 8 shows the block diagram for this general multicomponent multiproperty nonlinear regression program. Its main functions are:

1. Read input information pertinent to nonlinear regression analysis such as convergence criterion, number of regression parameters, parameter values and the maximum number of iterations.
2. Initialize the size of a matrix W(K,L) where K denotes the number of regression parameters in question, and L denotes the size of the augmented matrix.
3. Check for the presence of data for each thermodynamic property and provide all linkages among the thermodynamic property subprograms and subroutines to form the set of composite linearized normal equations involving the thermodynamic properties of interest.
4. Solve for the correction terms $\left(\bar{A}_{rs} - \bar{A}_{rs_o}\right)$ and check for convergence.
5. Request output summary in case of convergence.

The logic of the main program are displayed in a flow sheet (Figure 9) and the computational steps are given in

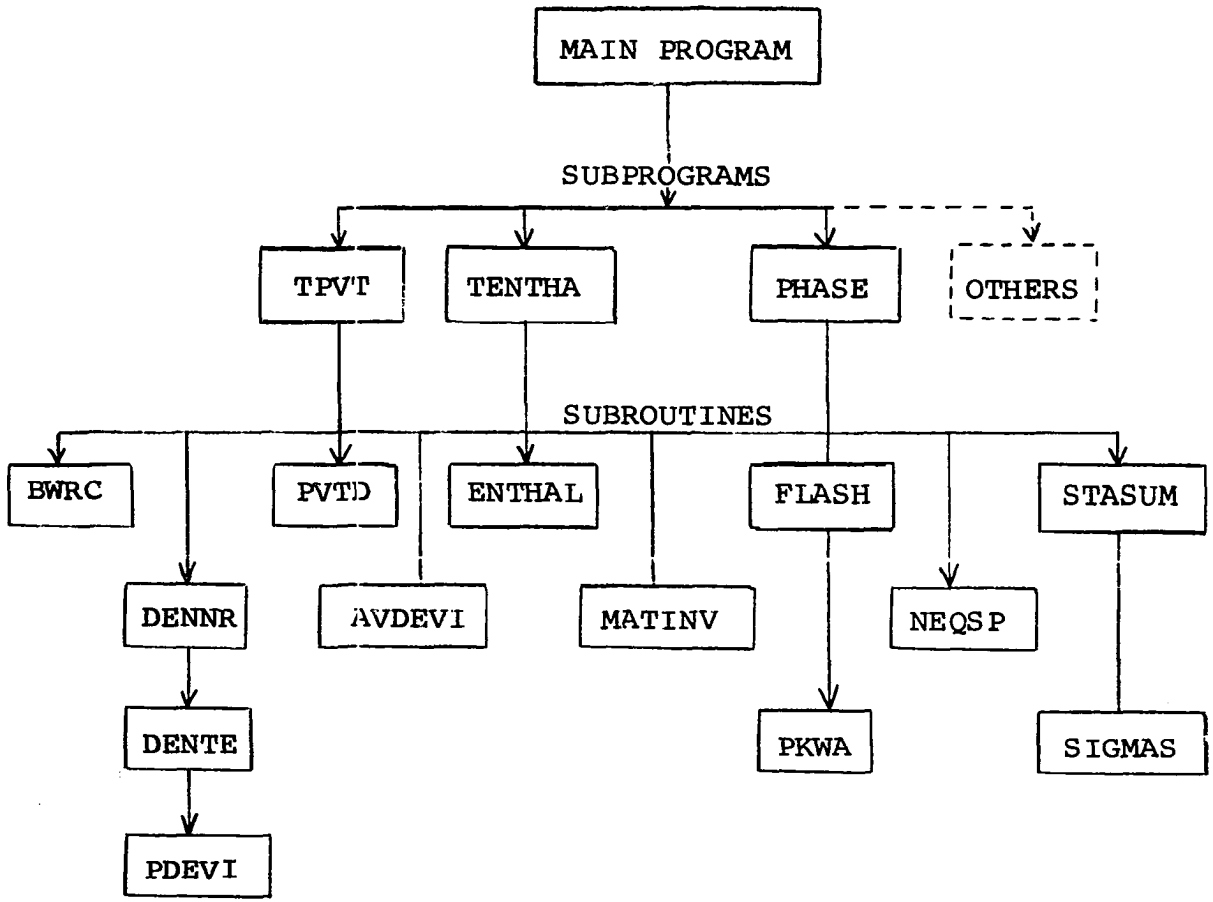


Figure 8. Block Diagram for the General Multicomponent Multiproperty Regression Program.

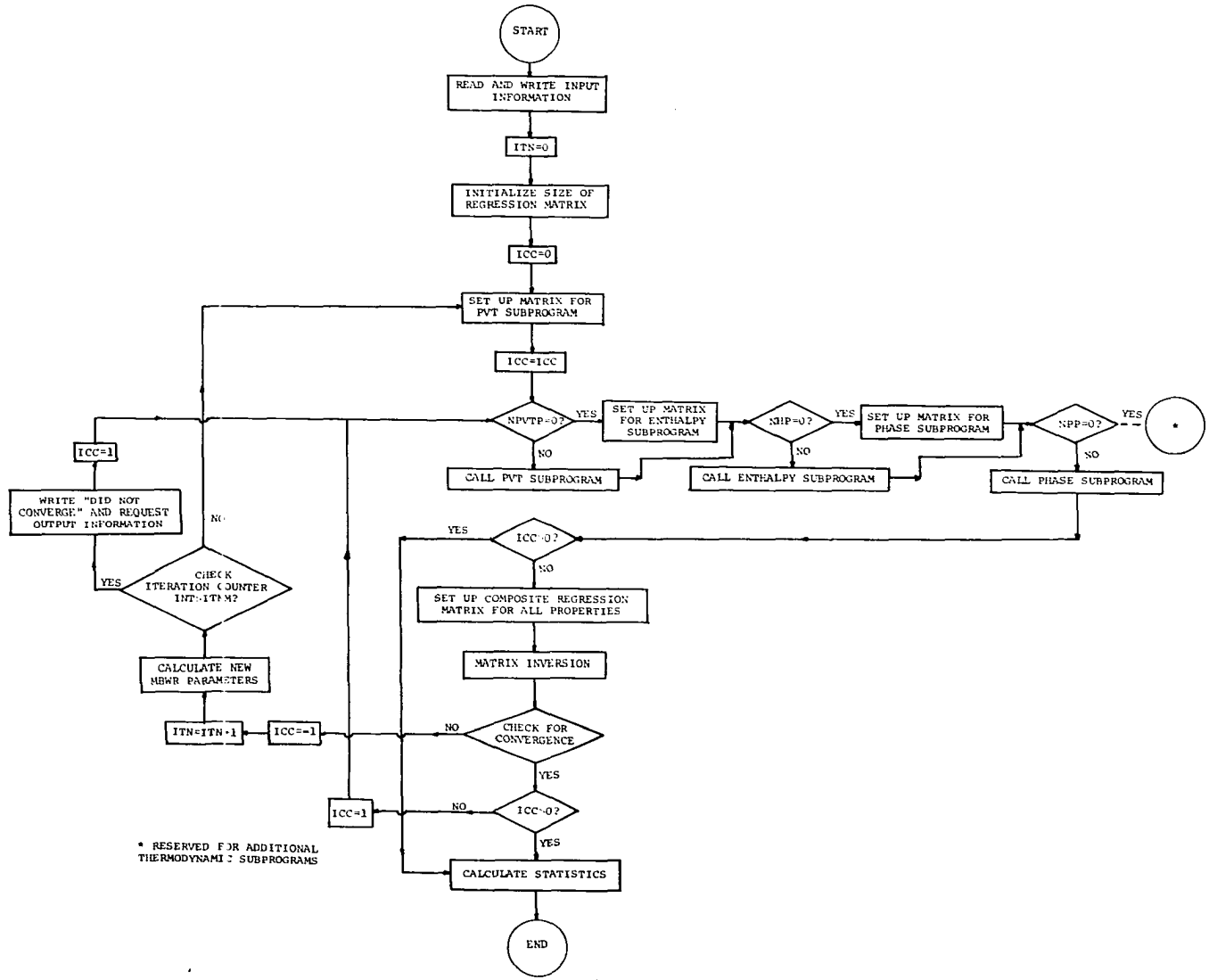


Figure 9. Flow Sheet for Main Program.

Appendix A. Nomenclature appearing in the flow sheets are presented in Appendix B.

Subprograms

Each subprogram handles regression analysis on one thermodynamic property. Its main functions are:

1. Read input data which include temperatures, pressures, experimental values of the thermodynamic property, mole fractions and density keys indicating a gas or liquid phase.
2. Convert data into proper units, e.g. temperatures from degrees Fahrenheit to degrees Rankine.
3. Calculate thermodynamic property by an equation of state.
4. Form the set of "linearized normal equations".
5. Calculate average absolute deviation for the data set.
6. Write output summary when convergence in the correction terms $\left(\bar{A}_{rs} - \bar{A}_{rs_o}\right)$ occurs or the last iteration specified has been reached.

Since all subprograms have identical functions, the following sections will be devoted to discussion of the choice of dependent variable and the formation of the normal equations individually.

PVT Subprogram (TPVT)

When PVT data are used in regression analysis, the obvious and most convenient choise of dependent variable

is either compressibility factor, Z, or pressure. In the case of Z, the functional form of an equation of state becomes

$$\bar{Z}_j = f_z \left(T_j, \rho_j, [x_i]_j, [\bar{A}]\right) \tag{60}$$

and the set of normal equations is

$$W_z \sum_j \left(1 - \frac{\bar{Z}_j}{Z_j}\right) \frac{1}{Z_j} \frac{\partial \bar{Z}_j}{\partial \bar{A}_{mn}} = 0 \tag{61}$$

where Z_j and $\bar{Z}_j$ are the experimental and calculated compressibility factors respectively.

However, for most PVT data, volumetric measurements suffer the most uncertainty relative to temperature and pressure. Based on statistical implication, Bono[17] has aptly demonstrated the superiority in using density as the dependent variable. From practical consideration, in most engineering calculations, density is the unknown and has to be solved for by the equation of state. In the low temperature and pressure liquid region, an equation of state, explicit in pressure, may calculate a negative pressure for a known density whereas it will yield a reasonably accurate density when the temperature and pressure are specified. In such cases, the use of pressure as the dependent variable in the regression analysis is not appropriate. With density as the response, Equation (60) becomes

$$\bar{\rho}_j = f_\rho \left(T_j, P_j, [x_i]_j, [\bar{A}]\right) \tag{62}$$

and the set of normal equation is

$$W_\rho \sum_j \left(1 - \frac{\bar{\rho}_j}{\rho_j}\right)\left(\frac{1}{\rho_j}\right)\left(\frac{\partial \bar{\rho}_j}{\partial \bar{A}_{mn}}\right) = 0 \tag{63}$$

where W_ρ is arbitrarily chosen to be unity and ρ_j is the experimental density at the j^{th} state. The differentiation in Equation (63) can be carried out implicitly, in terms of compressibility factor or pressure

$$\frac{\partial \rho_j}{\partial \bar{A}_{mn}} = \frac{-\left[\frac{\partial \bar{Z}_j}{\partial \bar{A}_{mn}}\right]_{T,\rho,[x_i]}}{\left[\frac{\bar{Z}_j}{\bar{\rho}_j}\right] + \left[\frac{\partial \bar{Z}_j}{\partial \rho_j}\right]_{T,[x_i],[\bar{A}]}} \tag{64}$$

$$= \frac{\left[-\frac{\partial P}{\partial \bar{A}_{mn}}\right]_{T,\rho,[x_i]}}{\left[\frac{\partial P}{\partial \bar{\rho}}\right]_{T,[x_i],[\bar{A}]}} \tag{65}$$

A flow sheet for subprogram TPVT is presented in Figure (10), while the computational steps are presented in Appendix A.

Enthalpy Departure Subprogram (TENTHA)

The choice of the observed response in enthalpy departure regression program is unambiguous. In terms of

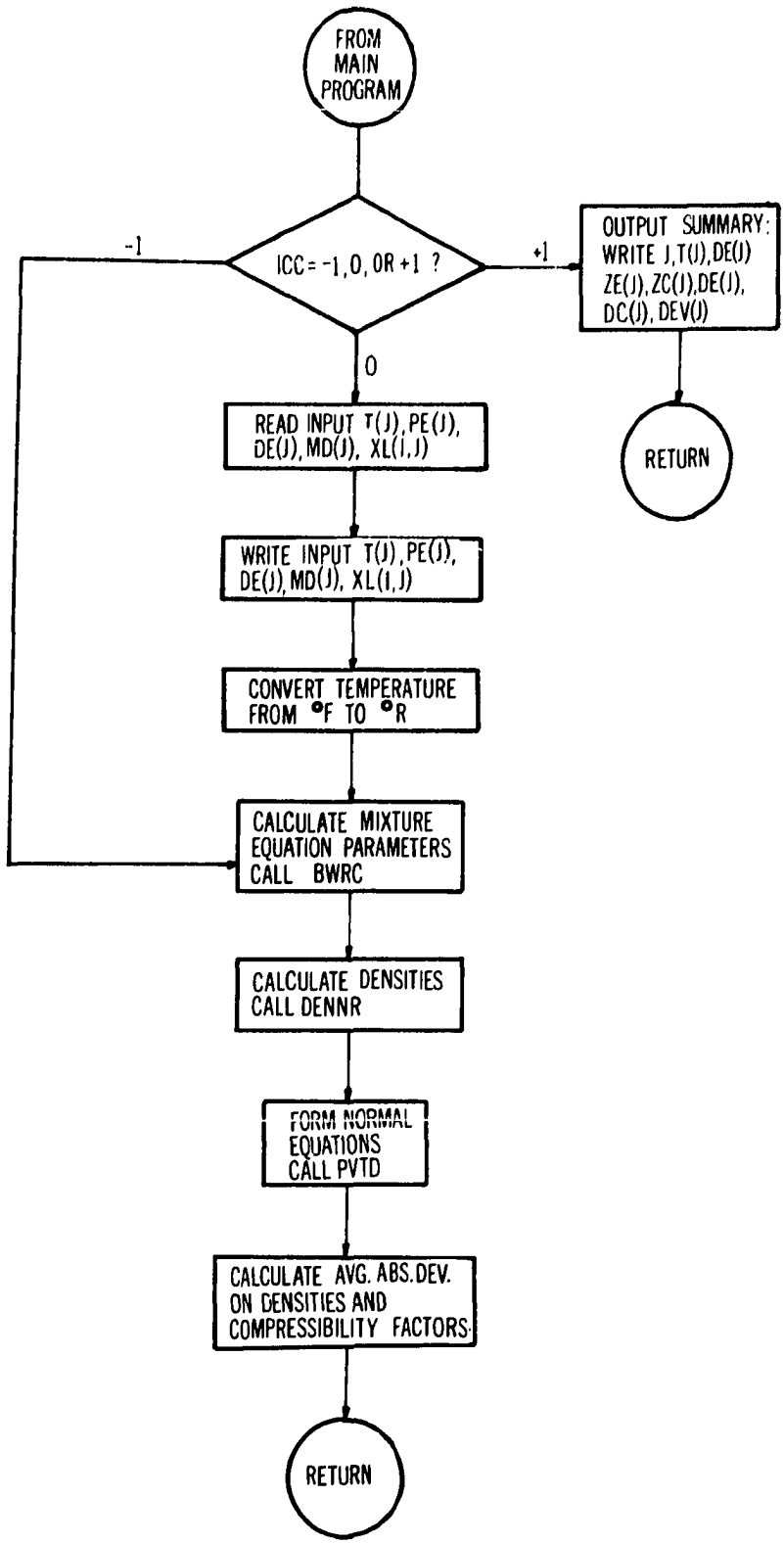


Figure 10. Flow Sheet for PVT Subprogram.

enthalpy departure, Equation (60) becomes

$$\overline{\Delta H}_j = f_{\Delta H}\left(T_j, \rho_j, [x_i]_j, [\overline{A}]\right) \tag{66}$$

In enthalpy departure measurements, seldom are corresponding densities reported. To preserve internal consistency, only calculated densities are used in the enthalpy departure regression program.

The set of normal equations is

$$W_{\Delta H} \sum_j \left(1 - \frac{\overline{\Delta H}_j}{\Delta H_j}\right) \frac{1}{\Delta H_j} \frac{\partial \overline{\Delta H}_j}{\partial \overline{A}_{mn}} = 0 \tag{67}$$

where $W_{\Delta H}$ is arbitrarily chosen to be unity and ΔH_j is the experimental enthalpy departure of the j^{th} state.

A flowsheet for the enthalpy subprogram is presented in Figure 11, while the computational steps are presented in Appendix A.

Phase Equilibrium Subprogram (PHASE)

An equation of state may be used to describe the equilibrium behavior of coexisting vapor and liquid phases. The vapor-liquid equilibrium ratio, or K-value, of the i^{th} component is

$$\overline{K}_i = \frac{\underline{f}_i^{\ell}/x_i}{\underline{f}_i^{g}/y_i} \tag{68}$$

where $\underline{f}_i^{\ell}$, $\underline{f}_i^{g}$ are liquid and gas fugacity of i^{th} component

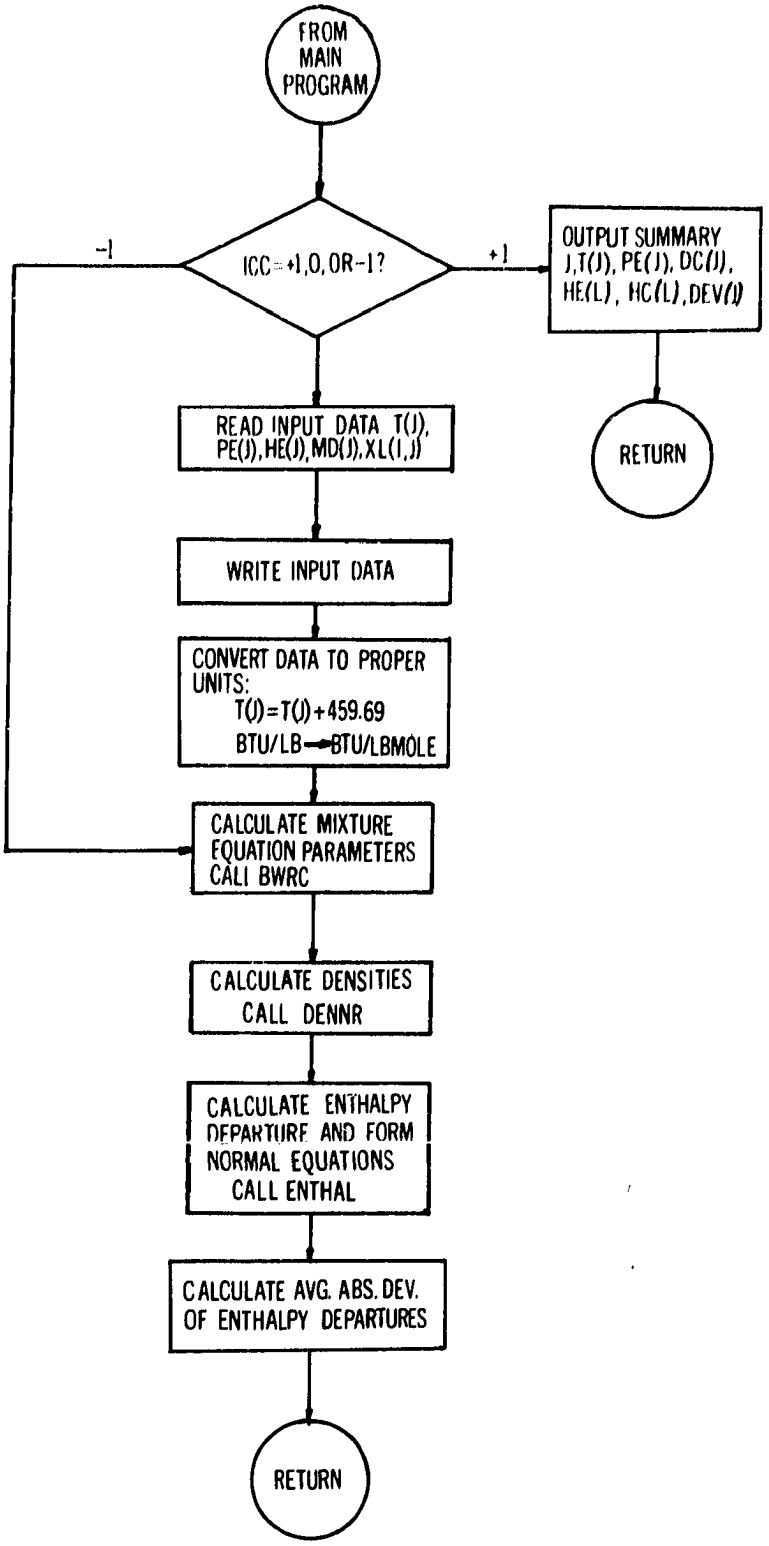


Figure 11. Flow Sheet for Enthalphy Subprogram.

in a mixture. $\bar{K}_i$ is a function of temperature, pressure, pure component as well as mixture parameters.

$$\bar{K}_{ij} = f_K\left(T_j, \rho_j, [x_i], [\bar{A}_i], [\bar{A}]\right) \tag{69}$$

where subscript i is the component index and j is the state index. The set of normal equations is

$$W_K \sum_i^{NC} W_i \sum_j \left[1 - \frac{\bar{K}_{ij}}{K_{ij}}\right] \frac{1}{K_{ij}} \frac{\partial \bar{K}_{ij}}{\partial \bar{A}_{mn}} = 0 \tag{70}$$

here W_K and W_i are arbitrarily taken to be unity. Because of the dual functionalities of K-values with respect to pure-component and mixture parameters, the differentiation in Equation (70) takes the following form

$$\frac{\partial \bar{K}_{ij}}{\partial \bar{A}_{mn}} = \left(\frac{\partial \bar{K}_{ij}}{\partial \bar{A}_{mn}}\right)_{[\bar{A}]} \delta_{im} + \left(\frac{\partial \bar{K}_{ij}}{\partial \bar{A}}\right)_{[\bar{A}_i]} \left(\frac{\partial \bar{A}}{\partial \bar{A}_{mn}}\right) \tag{71}$$

where δ_{im} is the Kronecker delta.

It is obvious from Equation (68) that to preserve internal consistency, the mole fractions and densities in both the liquid and vapor phases should be predicted values. Hence an internal flash calculation is incorporated into the phase equilibrium subprogram to calculate vapor and liquid mole fractions and densities.

For pure components, the experimental K-values assume the value of unity. However, an equation of state would

not be expected to be exact in predicting equal fugacities in both phases along the vapor pressure curve. Hence the ratio of f^{ℓ} and f^{g} may be used as the dependent variable in the nonlinear regression analysis.

A flow sheet of the phase equilibrium subprogram is presented in Figure 12, while the computational steps are listed in Appendix A.

Subroutines

The subroutines perform repetitious calculations required by the subprograms. These are simple computational procedures and hence only their names and a brief description of their functions will be given.

PVTD

This subroutine calculates compressibility factors and forms the set of linearized normal equations using density as the dependent variable.

ENTHAL

This subroutine calculates enthalpy departures and forms the set of linearized normal equations using enthalpy departures as the dependent variable.

PKWA

This subroutine forms the set of linearized normal equations using the liquid-vapor equilibrium ratio, or K-value, as the dependent variable.

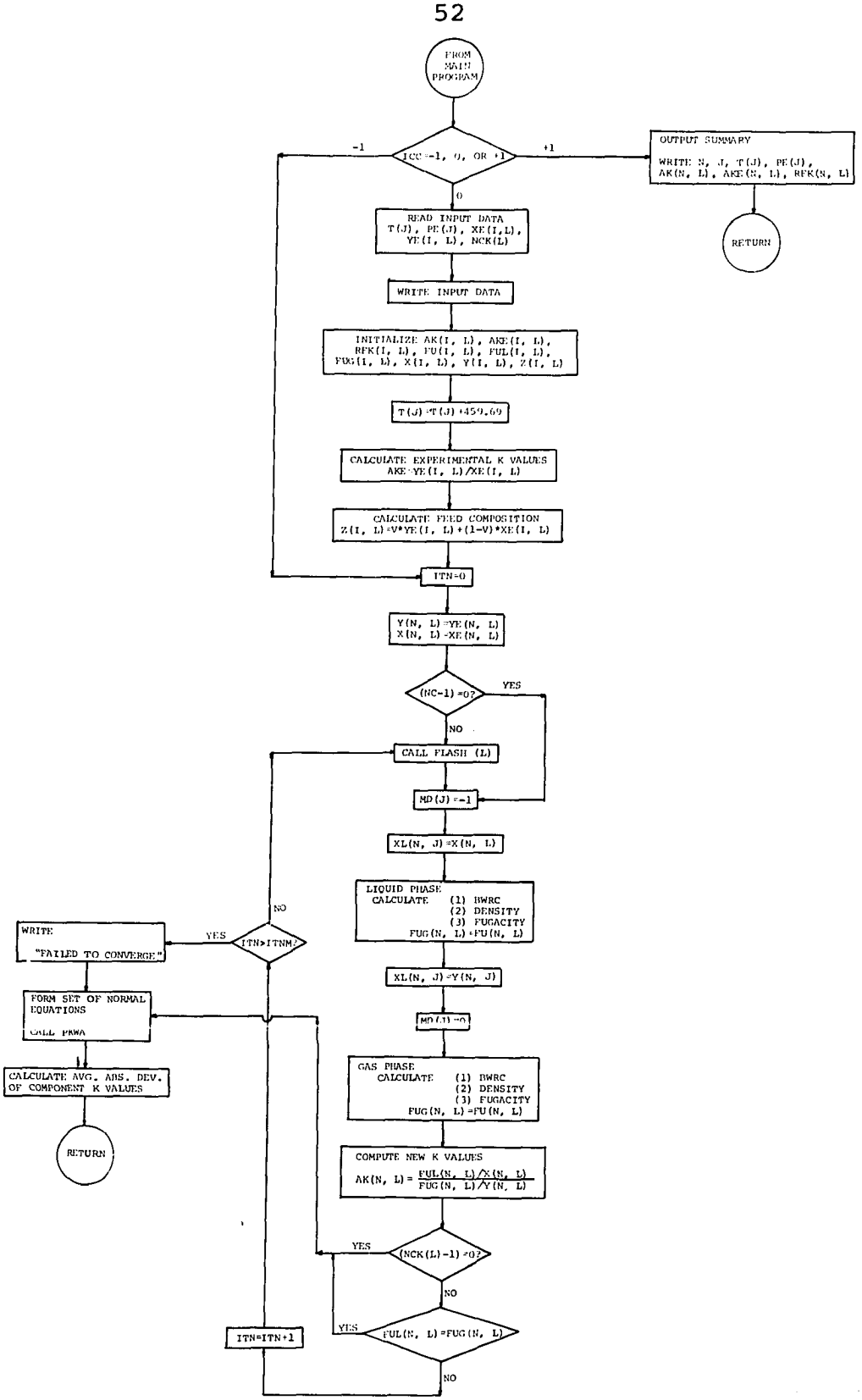


Figure 12. Flow Sheet for Phase Equilibrium Subprogram.

AVDEVI

This subroutine calculates the percent relative deviation for each data point and the average absolute deviation for all data points for each thermodynamic property.

BWRC

This subroutine calculates mixture equation-of-state parameters.

DENNR

This subroutine calculates densities using the Newton-Raphson method. A detailed discussion on this subroutine is given by Bono[17].

DENTE

In cases where the Newton-Raphson method does not converge, the DENNR subroutine calls on DENTE which solves for the density root by trial and error[62].

PDEVI

This subroutine calculates the difference between calculated and experimental pressures.

FLASH

This subroutine performs an internal Newtonian flash calculation in the two-phase region for a mixture. If the equation of state fails to indicate a two-phase region, the flash subroutine assumes predicted K-values to be equal to experimental K-values for that particular state.

NEQSP

This subroutine forms the new regression parameter values by adding the correction terms $\left(\overline{A}_{rs} - \overline{A}_{rs_o}\right)$ to the parameter values of the preceding iteration.

MATINV

This subroutine inverts a matrix in situ using a modification of the Gauss-Jordan reduction method. A detailed discussion of this subroutine is given by Cox[28].

STASUM

This subroutine calculates the variances, covariances and correlation coefficients of the regression parameters.

SIGMAS

This subroutine calculates the standard deviation of the data and the point of maximum deviation.

CHAPTER V

APPLICATION OF MULTIPROPERTY REGRESSION ANALYSIS TO THE NEW EQUATION OF STATE

As discussed in previous chapters, multiproperty regression analysis can be applied to determine parameters in the new equation of state. To enhance the success of any nonlinear regression scheme, it is important that a "reasonable" set of initial guessed values be available.

Use of Linear Least Squares Regression to Obtain Initial Estimates of Equation of State Parameters

Since extensive methane PVT data covering the temperature range of -250°F to 600°F are available, and reasonable estimates of parameters C_4 and D_4 in Equation (27) can be obtained from Figures 6 and 7, it was decided to apply the linear least squares method to determine the remaining parameters. A total of 560 data points were taken from the data of Douslin,[44] Vennix[132] and van Itterbeek.[131] The average absolute deviation for pressure was 0.47%, with a maximum deviation of 6.6%. This set of parameters was then used to calculate densities and enthalpy departures at twenty-two points as a test of the validity of

the new equation of state. Average absolute deviations for densities and enthalpy departures were 19.0% and 130.0% respectively.

These large deviations in predicted densities and enthalpy departures illustrate overwhelmingly the inadequacy of using pressure as the dependent variable in a least squares approach to determine the parameters of an equation of state. The reason for the results obtained is that in the low temperature and pressure region, an equation of state may calculate an erroneous or even negative pressure with an experimental liquid density. Yet for the same condition, an accurate liquid density can be calculated, since pressure changes very rapidly with density in the low temperature liquid region.

Equation of State for Methane

Despite the large deviations in calculated densities and enthalpy departures obtained with the set of parameters determined from linear least squares method, these parameters provide the only logical starting values for the application of multiproperty nonlinear regression analysis. Using this method, a final set of parameters was obtained which yielded an average absolute deviation of 0.304% for density at 40 points, 0.513% for enthalpy departure at 58 points and 0.443% for the fugacities of coexisting vapor and liquid phases at 18 vapor pressure points. The average

absolute deviation of a thermodynamic property R is defined as follows:

$$\frac{1}{NP}\sum_{j}\left|\frac{R_j - \bar{R}_j}{R_j}\right| 100\% \qquad (72)$$

where R_j is the experimental thermodynamic property in the j^{th} state, $\bar{R}_j$ is the least squares estimate of R_j and NP is the number of data points for property R.

Comparison of predicted and experimental values of these properties are presented in Tables 3, 4 and 5.

Use of Simple Corresponding States Principle to Determine Initial Estimates of Equation of State Parameters for Propane

Successful application of Equation (27) to methane does not ensure its usefulness for other fluids. To determine if this equation can be used for other fluids, propane was chosen for study because of industrial interest and because of its extensive PVT[8,42,59,112], enthalpy[141] and vapor pressure[21] data.

To obtain an initial set of parameter values to be used in the multiproperty regression analysis, a linear least squares calculation was attempted. Estimated values for the two nonlinear parameters, C_4 and D_4 in Equation (27) were obtained from the corresponding methane parameters using the simple corresponding states principle. A set of 500 PVT points from Beattie[8], Dittmas[42], Sage and Lacey[112] were used. The average absolute deviation for pressure

TABLE 3

COMPARISON OF PREDICTED DENSITIES WITH EXPERIMENTAL VALUES FOR METHANE USING THE NEW EQUATION OF STATE

T (F)	PE (PSIA)	DE (LBMOLE/CF)	DC	DEV	%DEV
-253.5	129.7	1.6316	1.6400	-0.0084	-0.514
-253.5	1093.7	1.6548	1.6582	-0.0034	-0.204
-253.5	1932.2	1.6731	1.6726	0.0005	0.027
-234.8	142.1	1.5731	1.5700	0.0031	0.196
-234.8	652.0	1.5881	1.5830	0.0051	0.318
-234.8	1815.3	1.6192	1.6095	0.0097	0.596
-197.7	188.4	1.4347	1.4285	0.0062	0.434
-197.7	511.5	1.4520	1.4440	0.0080	0.548
-197.7	875.4	1.4691	1.4599	0.0092	0.629
-197.7	1699.2	1.5033	1.4908	0.0125	0.834
-151.9	574.5	1.2333	1.2360	-0.0027	-0.222
-151.9	897.0	1.2718	1.2735	-0.0017	-0.132
-151.9	1541.3	1.3280	1.3275	0.0005	0.036
-151.9	1799.3	1.3461	1.3448	0.0013	0.100
-151.9	2071.6	1.3639	1.3612	0.0027	0.201
-120.9	1565.3	1.1861	1.1935	-0.0074	-0.624
-120.9	2103.4	1.2446	1.2514	-0.0068	-0.545
-144.7	368.0	0.1598	0.1573	0.0025	1.568
-144.7	413.9	1.1551	1.1552	-0.0001	-0.009
-144.7	1881.5	1.3247	1.3242	0.0005	0.036
-99.7	503.5	0.1766	0.1773	-0.0007	-0.405
-99.7	1013.2	0.8584	0.8566	0.0018	0.207
-54.7	562.7	0.1594	0.1600	-0.0006	-0.388
-54.7	1521.4	0.6956	0.6966	-0.0010	-0.139
-54.7	1915.8	0.8573	0.8588	-0.0015	-0.172
26.3	728.1	0.1591	0.1598	-0.0007	-0.464
26.3	1749.3	0.4500	0.4518	-0.0018	-0.403
77.0	344.9	0.0624	0.0626	-0.0002	-0.268
77.0	962.9	0.1872	0.1882	-0.0010	-0.515
122.0	377.1	0.0624	0.0626	-0.0002	-0.285
122.0	1724.1	0.3120	0.3133	-0.0013	-0.433
167.0	409.2	0.0624	0.0626	-0.0002	-0.296
167.0	1925.2	0.3120	0.3131	-0.0011	-0.365
212.0	441.4	0.0624	0.0626	-0.0002	-0.345
212.0	2126.1	0.3120	0.3131	-0.0011	-0.357
257.0	473.2	0.0624	0.0626	-0.0002	-0.312
257.0	2324.7	0.3120	0.3129	-0.0009	-0.291
302.0	405.0	0.0499	0.0501	-0.0002	-0.353
347.0	403.4	0.0468	0.0469	-0.0001	-0.301
347.0	430.2	0.0499	0.0501	-0.0002	-0.362
662.0	606.5	0.0499	0.0501	-0.0002	-0.360

AVERAGE AESOLUTE DEVIATION = 0.3608%

TABLE 4

COMPARISON OF PREDICTED ENTHALPY DEPARTURES WITH EXPERIMENTAL VALUES FOR METHANE USING THE NEW NEW EQUATION OF STATE

T (F)	PE (PSIA)	HE (BTU/LBMOLE)	HC (BTU/LBMOLE)	DEV BTU/LB	%DEV
-250.0	450.0	-3488.07	-3501.75	0.85	-0.39
-200.0	450.0	-3189.67	-3169.94	-1.23	0.62
-150.0	450.0	-2769.34	-2758.10	-0.70	0.41
-100.0	450.0	-513.70	-513.93	0.01	-0.05
-50.0	450.0	-370.91	-372.59	0.10	-0.45
50.0	450.0	-237.76	-235.81	-0.12	0.82
-250.0	600.0	-3484.22	-3492.74	0.53	-0.24
-200.0	600.0	-3193.84	-3163.79	-1.87	0.94
-150.0	600.0	-2797.58	-2774.21	-1.46	0.84
-100.0	600.0	-769.74	-758.80	-0.68	1.42
-50.0	600.0	-513.05	-516.42	0.21	-0.66
0.0	600.0	-392.73	-394.69	0.12	-0.50
-250.0	1000.0	-3457.59	-3468.30	0.67	-0.31
-200.0	1000.0	-3180.04	-3145.51	-2.15	1.09
-150.0	1000.0	-2828.70	-2795.37	-2.08	1.18
-100.0	1000.0	-2127.62	-2096.03	-1.97	1.48
-50.0	1000.0	-996.59	-981.17	-0.96	1.55
0.0	1000.0	-694.98	-692.55	-0.15	0.35
50.0	1000.0	-540.97	-539.85	-0.07	0.21
-250.0	1200.0	-3430.63	-3455.84	1.57	-0.73
-200.0	1200.0	-3156.30	-3135.50	-1.30	0.66
-150.0	1200.0	-2817.39	-2798.84	-1.18	0.67
-100.0	1200.0	-2269.12	-2257.98	-0.69	0.49
0.0	1200.0	-847.71	-850.17	0.15	-0.29
50.0	1200.0	-651.99	-652.49	0.03	-0.08
-250.0	1500.0	-3397.10	-3436.90	2.48	-1.17
-200.0	1500.0	-3127.58	-3119.58	-0.50	0.26
-150.0	1500.0	-2805.12	-2798.59	-0.41	0.23
-100.0	1500.0	-2355.91	-2367.44	0.72	-0.49
-50.0	1500.0	-1597.08	-1614.36	1.08	-1.08
0.0	1500.0	-1075.68	-1084.94	0.58	-0.86
50.0	1500.0	-822.20	-818.89	-0.21	0.40
-250.0	2000.0	-3358.44	-3404.74	2.89	-1.38
-200.0	2000.0	-3096.94	-3091.03	-0.37	0.19
-150.0	2000.0	-2796.94	-2788.39	-0.53	0.31
-100.0	2000.0	-2427.95	-2443.74	0.98	-0.65
-50.0	2000.0	-1933.82	-1933.15	-0.04	0.04
0.0	2000.0	-1417.24	-1414.02	-0.20	0.23
50.0	2000.0	-1077.13	-1072.63	-0.28	0.42

AVERAGE ABSOLUTE DEVIATION = 0.6183%

AVERAGE ABSOLUTE DEVIATION IN BTU/LB = 0.82

TABLE 5

PREDICTION OF SATURATED VAPOR AND LIQUID FUGACITIES FOR METHANE USING THE NEW EQUATION OF STATE

T (F)	PE (PSIA)	FUL (PSIA)	FUG (PSIA)	%DEV
-258.68	14.696	14.3004	14.1312	-1.20
-255.00	17.400	16.8054	16.6527	-0.92
-250.00	21.710	20.7112	20.6327	-0.38
-245.00	26.600	25.2394	25.0992	-0.56
-240.00	32.400	30.4361	30.3298	-0.35
-235.00	39.000	36.3511	36.2062	-0.40
-230.00	46.400	43.0207	42.7101	-0.73
-225.00	54.800	50.4842	49.9898	-0.99
-218.98	66.030	60.5741	59.5793	-1.67
-214.15	76.680	69.5679	68.5044	-1.55
-209.98	86.760	78.0097	76.8304	-0.68
-205.00	101.000	88.9551	88.3503	-1.53
-199.74	115.900	101.4851	100.2686	-1.21
-195.00	132.000	113.7055	112.8343	-0.77
-185.00	169.700	142.3248	141.4677	-0.61
-181.93	182.150	151.8630	150.7209	-0.76
-175.00	214.900	174.8979	174.3690	-0.30
-168.34	248.400	198.7470	197.9740	-0.39
-165.00	267.300	211.4063	210.9246	-0.23
-160.66	290.450	227.6208	226.6788	-0.42
-155.00	329.000	251.8911	251.9132	0.01
-145.89	392.710	292.0752	292.3267	0.09
-139.38	444.970	322.8594	323.8877	0.32
-135.00	482.000	344.3411	345.6277	0.37
-131.77	510.230	360.5940	361.9009	0.36
-125.00	575.000	395.9189	397.7234	0.45
-123.95	587.100	401.7295	403.9395	0.55
-120.22	626.800	422.1050	424.5430	0.57
-116.51	668.720	443.0098	443.0088	0.0

AVERAGE ABSOLUTE DEVIATION = 0.6334%

was 3.2% with several parameters assuming opposite signs from their corresponding parameters for methane. To preserve the opportunity of proposing mixing rules for describing mixture behavior, a new set of propane parameters was estimated from the methane parameters using simple corresponding states principle.

Defining $P = P_c\pi$; $T = T_c\theta$; $\rho = \frac{dP_c}{RT_c}$ 127,128

Equation (27) becomes

$$\pi = \theta d + A_1' d^2 + A_2' d^3 + A_3' d^6 +$$

$$\left(B_1' d + B_2' d^3 + B_3' d^4 + B_4' d^5\right)\theta + \tag{73}$$

$$\frac{C_5' d^2}{\theta^2} + \frac{d^2}{\theta^2} \exp\left(-C_4' d^2\right)\left(C_1' d + C_2' d^3 + C_3' d^5\right) +$$

$$\frac{D_5' d^2}{\theta^3} + \frac{d^2}{\theta^3} \exp\left(-D_4' d\right)\left(D_1' d + D_2' d^2 + D_3' d^3\right)$$

where

$$A_1' = \frac{A_1 P_c}{R^2 T_c^2} \; ; \; A_2' = \frac{A_2 P_c^2}{R^3 T_c^3} \; ; \; A_3' = \frac{A_3 P_c^5}{R^6 T_c^6}$$

$$B_1' = \frac{B_1 P_c}{R T_c} \; ; \; B_2' = \frac{B_2 P_c^2}{R^2 T_c^2} \; ; \; B_3' = \frac{B_3 P_c^3}{R^3 T_c^3}$$

$$B_4' = \frac{B_4 P_c^4}{R^4 T_c^4} \; ; \; C_1' = \frac{C_1 P_c^2}{R^3 T_c^5} \; ; \; C_2' = \frac{C_2 P_c^4}{R^5 T_c^7} \qquad (74)$$

$$C_3' = \frac{C_3 P_c^6}{R^7 T_c^9} \; ; \; C_4' = \frac{C_4 P_c^2}{R^2 T_c^2} \; ; \; C_5' = \frac{C_5 P_c}{R^2 T_c^4}$$

$$D_1' = \frac{D_1 P_c^2}{R^3 T_c^6} \; ; \; D_2' = \frac{D_2 P_c^3}{R^4 T_c^7} \; ; \; D_3' = \frac{D_3 P_c^4}{R^5 T_c^8}$$

$$D_4' = \frac{D_4 P_c}{R T_c} \; ; \; D_5' = \frac{D_5 P_c}{R^2 T_c^5}$$

While the simple corresponding states principle provides an easy means of obtaining initial estimates of parameters for a new material, the results of using these initial estimates are poor. For reduced temperatures less than 0.6, the average absolute deviation in pressures and enthalpy departures was 2.4% for 9 propane PVT points and 646.4% for 10 enthalpy points. For reduced temperature greater than 0.6, the average absolute deviation was 37.9% for 21 PVT points and 71.5% for 20 enthalpy points.

Equation of State for Propane

Application of multiproperty nonlinear regression analysis resulted in a set of parameters which yielded an average absolute deviation of 0.80% in density for 29 PVT points, 0.69% in enthalpy departure for 40 points and 0.34% in fugacity of coexisting phases for 19 vapor pressure points. Comparisons of predicted and experimental values of these properties are presented in Tables 6, 7, 8. As can be seen in Table 6, the calculation of density is not as accurate as the result for methane. To determine what improvement would result, it was decided to fit Equation (27) to propane PVT data only. The average absolute deviation in density was reduced to 0.35% for 46 points. Tables 9 and 10 show comparisons for densities and enthalpy departures using the set of parameters obtained from regression on PVT only. Until a unified set of parameters (which can predict densities, enthalpies and vapor pressures with less than 1% error) is developed in future study, one might consider the use of separate sets of parameters for correlating different thermodynamic properties of propane. A summary of parameters in Equation (27) for methane and propane is shown in Table 11.

Summary

A new equation of state has been developed for methane and propane. This equation is capable of predicting all

TABLE 6

COMPARISON OF PREDICTED DENSITIES WITH EXPERIMENTAL VALUES FOR PROPANE USING THE NEW EQUATION OF STATE

T (F)	PF (PSIA)	DE (LBMOLE/CF)	CC	DEV	%DEV
-250.0	14.7	0.5933	1.0609	-0.0675	-6.791
-220.0	14.7	0.5707	1.0010	-0.0303	-3.119
-190.0	14.7	0.5480	0.5574	-0.0094	-0.993
-160.0	14.7	0.5253	0.5223	0.0030	0.321
-130.0	14.7	0.8981	0.8921	0.0060	0.670
-148.0	1000.0	0.5218	0.5136	0.0082	0.899
-112.0	2000.0	0.5006	0.4848	0.0158	1.758
-76.0	1000.0	0.8610	0.8498	0.0112	1.297
-40.0	2000.0	0.8411	0.8280	0.0131	1.558
-4.0	1000.0	0.7986	0.7927	0.0059	0.737
-4.0	2000.0	0.8114	0.8013	0.0101	1.244
32.0	2000.0	0.7802	0.7744	0.0058	0.739
100.0	500.0	0.6793	0.6922	-0.0129	-1.857
100.0	1000.0	0.6940	0.7030	-0.0090	-1.303
100.0	1500.0	0.7067	0.7124	-0.0057	-0.802
100.0	2000.0	0.7174	0.7207	-0.0033	-0.464
130.0	500.0	0.6365	0.6554	-0.0189	-2.662
130.0	1250.0	0.6662	0.6776	-0.0114	-1.719
130.0	1500.0	0.6743	0.6837	-0.0094	-1.390
130.0	1750.0	0.6812	0.6892	-0.0080	-1.177
160.0	800.0	0.6031	0.6234	-0.0203	-3.361
160.0	1000.0	0.6146	0.6326	-0.0180	-2.927
160.0	1500.0	0.6382	0.6510	-0.0128	-2.005
160.0	2000.0	0.6566	0.6654	-0.0088	-1.336
220.0	500.0	0.1035	0.1043	-0.0008	-0.775
220.0	1500.0	0.5546	0.5621	-0.0075	-1.345
220.0	2000.0	0.5858	0.5942	-0.0084	-1.431
250.0	500.0	0.0901	0.0906	-0.0005	-0.595
250.0	1000.0	0.3893	0.3508	0.0385	9.901
250.0	1500.0	0.5061	0.4947	0.0114	2.244
250.0	2000.0	0.5470	0.5485	-0.0015	-0.274
302.0	425.7	0.0624	0.0625	-0.0001	-0.219
347.0	1180.1	0.2185	0.2235	-0.0050	-2.271
347.0	1406.8	0.2809	0.2792	0.0017	0.594
437.0	535.1	0.0624	0.0626	-0.0002	-0.323
437.0	2104.6	0.3121	0.3041	0.0080	2.558
482.0	3910.0	0.4370	0.4238	0.0132	3.020
527.0	605.9	0.0624	0.0625	-0.0001	-0.220
527.0	1132.8	0.1249	0.1259	-0.0010	-0.823
527.0	1872.0	0.2185	0.2188	-0.0003	-0.130
527.0	2404.9	0.2809	0.2769	0.0040	1.436

AVERAGE ABSOLUTE DEVIATION = 1.6980%

TABLE 7

COMPARISON OF PREDICTED ENTHALPY DEPARTURES WITH EXPERIMENTAL VALUES FOR PROPANE USING THE NEW EQUATION OF STATE

T (F)	PP (PSIA)	HE (BTU/LBMOLE)	HC	DEV BTU/LB	%DEV
-25C.C	5CC.C	-10071.07	-10041.63	-0.21	C.CS
-25C.C	1CCC.C	-9901.70	-10016.00	0.55	-0.24
-25C.C	15CC.C	-9916.74	-9970.44	1.22	-0.54
-25C.0	2CCC.C	-9890.28	-9924.25	0.77	-0.34
-2CC.C	5CC.C	-9599.26	-9561.41	-0.86	0.39
-2CC.C	1CCC.C	-9519.89	-9501.15	-0.42	0.20
-2CC.C	15CC.C	-9449.34	-9440.66	-0.20	0.09
-2CC.C	2CCC.C	-9414.07	-9379.91	-0.77	C.36
-15C.C	5CC.C	-9131.86	-9156.84	0.57	-0.27
-15C.C	1CCC.C	-9052.50	-9090.25	0.86	-0.42
-15C.C	15CC.C	-8981.95	-9023.35	0.94	-0.46
-15C.C	2CCC.C	-8937.85	-8956.09	0.41	-0.20
-1CC.0	5CC.C	-8642.42	-8659.67	0.39	-0.20
-1CC.C	1CCC.C	-8602.73	-8591.02	-0.27	0.14
-1CC.0	15CC.C	-8523.37	-8521.80	-0.04	0.02
-5C.C	5CC.C	-8227.94	-8164.00	-1.45	C.78
-5C.C	1CCC.C	-8152.98	-8096.63	-1.28	0.69
-5C.C	15CC.C	-8082.43	-8029.25	-1.23	C.67
-5C.C	2CCC.C	-8038.33	-7958.94	-1.80	C.99
C.C	1CCC.C	-7712.04	-7635.01	-1.75	1.00
C.C	15CC.C	-7650.30	-7571.05	-1.80	1.04
C.C	2CCC.C	-7610.62	-7505.37	-2.39	1.38
5C.C	5CC.C	-7324.01	-7246.25	-1.76	1.06
5C.C	15CC.C	-7196.14	-7142.78	-1.21	C.74
5C.C	2CCC.C	-7169.68	-7085.33	-1.91	1.19
1CC.0	5CC.C	-6794.88	-6773.05	-0.50	0.32
1CC.C	15CC.C	-6733.15	-6719.18	-0.32	0.21
1CC.0	2CCC.C	-6719.92	-6679.19	-0.95	0.62
15C.0	5CC.C	-6124.65	-6177.95	1.21	-0.87
15C.0	1CCC.C	-6204.02	-6242.16	0.86	-0.61
15C.0	15CC.C	-6181.98	-6260.07	1.77	-1.26
2CC.C	5CC.C	-1843.13	-1792.49	-1.15	2.75
2CC.C	1CCC.C	-5494.11	-5491.88	-0.05	0.04
2CC.C	15CC.C	-5670.48	-5688.89	0.42	-0.32
2CC.C	2CCC.C	-5745.45	-5765.71	0.46	-0.35
25C.C	5CC.C	-1314.00	-1292.65	-0.48	1.62
25C.0	1CCC.C	-4246.25	-3853.42	-8.91	9.25
25C.C	15CC.C	-4964.98	-4836.64	-2.91	2.58
25C.0	2CCC.C	-5172.22	-5147.81	-0.55	0.47

AVERAGE ABSOLUTE DEVIATION = C.8522%

AVERAGE ABSOLUTE DEVIATION IN BTU/LB = 1.17

TABLE 8

PREDICTION OF SATURATED VAPOR AND LIQUID FUGACITIES FOR PROPANE USING THE NEW EQUATION OF STATE

T (F)	PE (PSIA)	FUL (PSIA)	FUG (PSIA)	%DEV
-140.00	0.605	0.5968	0.6127	2.59
-130.00	0.932	0.9210	0.9271	0.66
-120.00	1.394	1.3794	1.3841	0.34
-110.00	2.030	2.0101	2.0112	0.06
-100.00	2.887	2.8571	2.8528	-0.15
-90.00	4.017	3.9670	3.9570	-0.33
-80.00	5.481	5.4027	5.3795	-0.43
-70.00	9.680	9.4620	9.4162	-0.49
-42.73	14.696	14.2268	14.1669	-0.42
-30.00	20.338	19.4935	19.4318	-0.32
-20.00	25.395	24.1514	24.0888	-0.26
-10.00	31.376	29.5725	29.5280	-0.15
0.0	38.371	35.8267	35.8039	-0.06
10.00	46.470	42.9688	42.9655	-0.01
20.00	55.807	51.0599	51.0932	0.07
30.00	66.460	60.1506	60.2132	0.10
40.00	78.577	70.2946	70.4029	0.15
50.00	92.231	81.5370	81.6709	0.16
60.00	107.590	93.9159	94.0931	0.19
70.00	124.730	107.4672	107.6659	0.18
80.00	143.820	122.2242	122.4460	0.18
90.00	164.990	138.2073	138.4500	0.18
100.00	188.320	155.4387	155.6522	0.14
110.00	214.020	173.9308	174.1021	0.10
120.00	242.190	193.6938	193.7642	0.04
130.00	273.080	214.7276	214.6792	-0.02
140.00	306.760	237.0208	236.7647	-0.11
145.00	325.370	248.6730	248.5798	-0.04
150.00	343.520	260.5574	260.0398	-0.20
155.00	363.110	272.7825	272.1028	-0.25
160.00	383.450	285.3003	284.3943	-0.32
165.00	404.730	298.1116	296.9810	-0.38
170.00	426.890	311.2021	309.8057	-0.45
175.00	450.010	324.5569	322.8726	-0.52
180.00	474.060	338.1514	336.1377	-0.60
185.00	499.020	351.9419	349.5591	-0.68
190.00	525.100	365.8516	363.1653	-0.74
195.00	552.230	376.8860	376.8831	0.0
206.36	617.470	408.3892	408.3833	0.0

AVERAGE ABSOLUTE DEVIATION = 0.3095%

TABLE 9

COMPARISON OF DENSITIES PREDICTED USING PARAMETERS OF THE NEW EQUATION DETERMINED FROM PVT DATA WITH EXPERIMENTAL VALUES FOR PROPANE

T (F)	PE (PSIA)	DE (LBMOLE/CF)	DC	DEV	%DEV
-250.0	14.7	0.5933	0.5931	0.0002	0.021
-220.0	14.7	0.5707	0.5759	-0.0052	-0.932
-190.0	14.7	0.5480	0.5510	-0.0030	-0.222
-160.0	14.7	0.5253	0.5250	0.0003	0.032
-130.0	14.7	0.4981	0.4987	-0.0006	-0.067
-148.0	1000.0	0.5218	0.5214	0.0004	0.039
-112.0	2000.0	0.9006	0.8981	0.0024	0.270
-76.0	3000.0	0.8610	0.8600	0.0010	0.114
-40.0	4000.0	0.8411	0.8391	0.0020	0.237
-4.0	5000.0	0.7986	0.7972	0.0014	0.169
-4.0	6000.0	0.8114	0.8094	0.0020	0.248
32.0	6000.0	0.7802	0.7789	0.0013	0.169
100.0	500.0	0.6793	0.6794	-0.0001	-0.019
100.0	1000.0	0.6940	0.6943	-0.0003	-0.045
100.0	1500.0	0.7067	0.7068	-0.0001	-0.016
100.0	2000.0	0.7174	0.7178	-0.0004	-0.057
130.0	500.0	0.6365	0.6373	-0.0008	-0.130
130.0	1250.0	0.6662	0.6670	-0.0008	-0.113
130.0	1500.0	0.6743	0.6747	-0.0004	-0.066
130.0	1750.0	0.6812	0.6819	-0.0007	-0.098
160.0	800.0	0.6031	0.6052	-0.0021	-0.344
160.0	1000.0	0.6146	0.6167	-0.0021	-0.334
160.0	1500.0	0.6382	0.6394	-0.0012	-0.188
160.0	2000.0	0.6566	0.6571	-0.0005	-0.069
220.0	500.0	0.1035	0.1027	0.0008	0.796
220.0	1500.0	0.5546	0.5531	0.0015	0.275
220.0	2000.0	0.5858	0.5857	0.0002	0.029
250.0	500.0	0.0901	0.0897	0.0004	0.400
250.0	1000.0	0.3893	0.3850	0.0043	1.115
250.0	1500.0	0.5061	0.4982	0.0079	1.570
250.0	2000.0	0.5470	0.5446	0.0024	0.448
302.0	425.7	0.0624	0.0623	0.0001	0.139
347.0	1180.1	0.2185	0.2190	-0.0005	-0.209
347.0	1406.8	0.2809	0.2807	0.0002	0.053
437.0	535.1	0.0624	0.0622	0.0002	0.285
437.0	2104.6	0.3121	0.3085	0.0032	1.012
482.0	3510.6	0.4370	0.4361	0.0009	0.214
527.0	665.8	0.0624	0.0622	0.0002	0.400
527.0	1132.8	0.1249	0.1244	0.0005	0.428
527.0	1672.0	0.2185	0.2181	0.0004	0.165
527.0	2404.9	0.2809	0.2804	0.0005	0.187

AVERAGE ABSOLUTE DEVIATION = 0.2766%

TABLE 10

COMPARISON OF ENTHALPY DEPARTURES PREDICTED USING PARAMETERS OF THE NEW EQUATION DETERMINED FROM PVT DATA WITH EXPERIMENTAL VALUES FOR PROPANE

T (F)	PE (PSIA)	HE (BTU/LBMOLE)	HC	DEV BTU/LB	%DEV
-250.0	500.0	-10071.07	32070.31	-955.72	418.44
-250.0	1000.0	-9951.70	32156.88	-955.88	421.84
-250.0	1500.0	-9916.74	32241.00	-956.09	425.12
-250.0	2000.0	-9890.28	32323.38	-957.36	426.82
-200.0	500.0	-9599.26	6266.16	-359.81	165.28
-200.0	1000.0	-9519.89	6340.22	-359.69	166.60
-200.0	1500.0	-9449.34	6414.01	-359.76	167.88
-200.0	2000.0	-9414.07	6481.61	-360.63	168.91
-150.0	500.0	-9131.66	-2822.39	-143.09	69.09
-150.0	1000.0	-9052.50	-2751.03	-142.91	69.61
-150.0	1500.0	-8981.95	-2679.56	-142.93	70.17
-150.0	2000.0	-8937.65	-2607.54	-143.55	70.82
-100.0	500.0	-8642.42	-6184.05	-55.75	28.45
-100.0	1000.0	-8602.73	-6115.79	-56.40	28.91
-100.0	1500.0	-8523.37	-6047.02	-56.16	29.05
-50.0	500.0	-8227.94	-7329.68	-20.37	10.92
-50.0	1000.0	-8152.98	-7266.54	-20.10	10.87
-50.0	1500.0	-8082.43	-7202.16	-19.96	10.89
-50.0	2000.0	-8038.32	-7136.71	-20.45	11.22
0.0	1000.0	-7712.04	-7488.88	-5.06	2.89
0.0	1500.0	-7650.30	-7432.06	-4.95	2.85
0.0	2000.0	-7610.62	-7373.01	-5.39	3.12
50.0	500.0	-7324.01	-7332.71	0.20	-0.12
50.0	1500.0	-7196.14	-7251.64	1.26	-0.77
50.0	2000.0	-7169.68	-7203.44	0.77	-0.47
100.0	500.0	-6794.88	-6895.98	2.29	-1.49
100.0	1500.0	-6733.15	-6874.38	3.20	-2.10
100.0	2000.0	-6719.92	-6845.04	2.84	-1.86
150.0	500.0	-6124.65	-6256.61	2.99	-2.15
150.0	1000.0	-6204.02	-6346.96	3.24	-2.30
150.0	1500.0	-6181.98	-6381.03	4.51	-3.22
200.0	500.0	-1643.13	-1653.71	0.24	-0.57
200.0	1000.0	-5494.11	-5604.21	2.50	-2.00
200.0	1500.0	-5670.48	-5780.07	2.49	-1.93
200.0	2000.0	-5745.45	-5855.63	2.50	-1.92
250.0	500.0	-1314.00	-1361.35	1.07	-3.60
250.0	1000.0	-4246.25	-4285.72	0.90	-0.93
250.0	1500.0	-4564.98	-5029.17	1.36	-1.21
250.0	2000.0	-5172.22	-5250.39	1.77	-1.51

AVERAGE ABSOLUTE DEVIATION = 71.9978

AVERAGE ABSOLUTE DEVIATION IN BTU/LB =157.34

TABLE 11

PARAMETERS OF THE NEW EQUATION OF STATE FOR METHANE AND PROPANE

PARAMETER*	METHANE	PROPANE (FOR ΔH and VP)	PROPANE (FOR PVT ONLY)
A_1	-0.7608515625E 04	-0.3086141797E 05	-0.3539348047E 05
A_2	-0.1228517890E 00	-0.1674793549E 03	-0.2573193750E 05
A_3	0.1556539795E 04	0.5716621094E 05	0.1154304375E 06
B_1	0.7377123833E 00	0.1982285500E 01	0.2106225937E 01
B_2	0.6177854538E 00	0.1141969681E 01	0.3235265732E 01
B_3	0.1136284471E 00	0.2697813988E 01	0.5705714226E 01
B_4	-0.3268250227E 00	-0.3638399243E 00	-0.6527409554E 01
C_1	-0.1076610080E 09	-0.3591914496E 10	-0.2798654400E 08
C_2	0.5894108160E 09	0.1938610176E 11	0.7068994765E 11
C_3	-0.2869066240E 09	-0.1941427323E 12	-0.3649344635E 12
C_4	0.1157861710E 01	0.4817086220E 01	0.4884107590E 01
C_5	-0.2519371520E 09	-0.4160454144E 10	-0.1163040768E 10
D_1	0.2228189266E 12	0.1517777794E 14	0.3096398791E 13
D_2	0.9920610304E 11	0.2449961753E 14	0.5155554591E 14
D_3	-0.9990576538E 11	-0.6295446733E 11	-0.2820659374E 14
D_4	0.2152213097E 01	0.3173298836E 01	0.3250006676E 01
D_5	-0.2658851200E 08	-0.8517675254E 12	-0.1161565307E 13

*These parameters are consistent with the following units: pressure in psia, volume in ft^3/lb mole, temperature in °R. The gas constant is 10.7319

thermodynamic properties of methane and propane with an uncertainty in the neighborhood of 1.0% for vapor, liquid and coexisting phases. Its development arises from a careful study of isochoric PVT data for methane. A polynomial power series in reciprocal temperature proves to be mathematically simpler than proposed exponential functions for describing the temperature dependence of isochoric PVT data. The temperature dependence of this new equation of state, though developed from PVT data for methane, is shown to be adequate when applied to enthalpy data for methane and propane. This is significant, because the enthalpy data for propane extend to reduced temperatures as low as 0.3, which is far below the region of application of most equations of state.

The use of multiproperty nonlinear regression analysis in equation of state development guarantees thermodynamic consistency. That is, the resultant equation will accurately predict the behavior of all properties, not just one property, such as pressure, to which the equation was fit in the traditional method of equation of state development. Multiproperty analysis, as used here, also ensures consistency of equation of state parameters among different materials with regard to their signs. None of the above vitally necessary features in equation of state development can be achieved using the traditional linear least squares approach with pressure or compressibility factor as the dependent variable.

CHAPTER VI

THE MODIFIED BWR EQUATION OF STATE

The new equation of state developed in the preceeding chapters has been shown to successfully correlate all thermodynamic properties for methane and propane over wide ranges of conditions. Nevertheless, there are a number of disadvantages to a continued pursuit of this new equation of state.

The major disadvantage of pursuing the new equation of state is the fact that an excessive amount of computer time is presently required to determine the equation parameters for a new material. This situation occurs because the initial estimates of parameters used in the nonlinear regression program must be reasonably close to optimal values in order for the Gauss-Newton iteration scheme to converge in a finite number of interations. This problem is exaggerated by the fact that the new equation contains seventeen parameters. Although this problem may be solved in the future, it remains a serious limitation at the present time. It should be noted that this problem is also encountered for the Vennix[133] equation of state, which contains twenty-five parameters.

An additional disadvantage of pursuing the new equation of state is the fact that considerable effort would be required for its extension to predict behavior of mixture, aside from applications in corresponding states calculations. To apply an equation of state directly to describe mixture behavior, appropriate mixture parameters must be used. Mixture parameters are usually expressed as functions of mole fractions and pure component parameters of the mixture constituents, and, in some cases, unlike interaction parameters. These expressions for mixture parameters, which are referred to as mixing rules, must be developed for any equation of state before it can be applied to mixtures. To date, mixing rules have been developed for very few of the many equations of state which have been developed for pure compounds. It is probable that a very formidable effort would be required to define appropriate mixing rules for the new equation of state developed in this dissertation. Obviously, this constitutes a disadvantage to the continued pursuit of this equation, especially in light of the fact that an eleven parameter modified BWR equation, which is of comparable accuracy has been developed concurrent with the development of the seventeen parameter equation. For these reasons, emphasis in this research was shifted from the new seventeen parameter equation of state to the eleven parameter modified BWR equation.

Considerable effort has been expended in investigating the potential of modifying the original BWR equation[17,27]. The modification selected results in an eleven-parameter equation which can predict the thermodynamic properties of methane and propane with accuracy comparable to Equation (27). Because of its simplicity and the existence of mixing rules for the original BWR parameters, the modified BWR equation was chosen to explore the potential of using an analytic expression to correlate the low temperature behavior of fluids.

Modification of the BWR Equation of State

Literature Review

Benedict and coworkers[10], in correlating low temperature vapor pressure, suggested treating the parameter C_o

$$P = RT\rho + \left(B_oRT - A_o - \frac{C_o}{T^2}\right)\rho^2 + (bRT-a)\rho^3 + \alpha a\rho^6 + \frac{c\rho^3}{T^2}(1+\gamma\rho^2)\exp(-\gamma\rho^2) \qquad (75)$$

of the above equation as a function of temperature. Following this advice, Barner and Schreiner reported improvement in correlating the low temperature behavior of hydrocarbons[2]. Zudkevitch and Kaufmann[145] applied a similar method to argon with success. Other modifications of the original BWR equation include treating B_o, γ, A_o and c as temperature dependent[4,49,54]. Among the parameters treated as

temperature dependent, C_o seems to be most promising in improving the prediction of thermodynamic properties in the cryogenic region. Unfortunately, the above investigators did not formulate an analytic expression for the temperature dependent form of C_o but rather chose to use discrete values derived from low temperature vapor pressure data.

The Present Modification of the BWR Equation

Research initiated at the University of Oklahoma has concentrated on deriving the temperature dependence of C_o from enthalpy data[27]. The use of enthalpy data to discern the temperature dependence of an equation of state in general has been elucidated in Chapter II. Detailed discussion on the use of methane and propane enthalpy data to improve the temperature dependence of the original BWR equation of state can be found in references 22 and 64. For completeness, only the final results will be discussed.

To improve predictions of the enthalpy behavior of methane and propane in both the low temperature and critical regions, it was found beneficial to treat C_o and a in Equation (6) as temperature dependent. Based on theoretical considerations of Zwanzig's perturbation theory[146] and supported by empirical results using regression analysis on isothermal enthalpy data of methane and propane, the temperature dependent forms of C_o and a may be described by

$$C_o^* = C_o - \frac{D_o}{T} + \frac{E_o}{T^2} \tag{76}$$

$$a^* = a + \frac{d}{T} \tag{77}$$

where C_o^* and a^* are values of C_o and a obtained from enthalpy regression analysis of isotherms. D_o, E_o and d are the additional parameters.

Thermodynamic Relations Derived from the Modified BWR Equation of State

Replacing C_o and a of the original BWR equation (Equation (75)) by Equations (76) and (77), the pressure expression of the modified BWR equation has the following form

$$P = \rho RT + \left(B_oRT - A_o - \frac{C_o}{T^2} + \frac{D_o}{T^3} - \frac{E_o}{T^4}\right)\rho^2 + \left(bRT - a - \frac{d}{T}\right)\rho^3 + \alpha\left(a + \frac{d}{T}\right)\rho^6 + \frac{c\rho^3}{T^2}(1 + \gamma\rho^2)\exp(-\gamma\rho^2) \ . \tag{78}$$

Residual Helmholtz Free Energy Equation

From Equation (c-14), the residual Helmholtz free energy is

$$\tilde{A} = \left(B_oRT - A_o - \frac{C_o}{T^2} + \frac{B}{T^3} - \frac{D_o}{T^4}\right)\rho + \left(bRT - a - \frac{F}{T}\right)\frac{\rho^2}{2} + \left(a + \frac{F}{T}\right)\frac{\alpha\rho^5}{5} + \frac{c\rho^2}{T^2}\left\{\frac{1-\exp(-\gamma\rho^2)}{\gamma\rho^2} - \frac{\exp(-\gamma\rho^2)}{2}\right\} \tag{79}$$

Thermodynamic relationships expressing enthalpy departure, fugacity and entropy departure in terms of the residual Helmholtz free energy have been presented in Appendix C. Hence only the final forms of the above thermodynamic property expressions using the modified BWR equation will be presented.

Enthalpy Departure Equation

$$H-H^\circ = \left(B_oRT - 2A_o - \frac{4C_o}{T^2} + \frac{5D_o}{T^3} - \frac{6E_o}{T^4}\right)\rho + \frac{1}{2}\left(2bRT - 3a - \frac{4d}{T}\right)\rho^2 + \frac{1}{5}\alpha\left(6a + \frac{7d}{T}\right)\rho^5 + \frac{c}{\gamma T^2}\left[3 - \left(3 + \frac{1}{2}\gamma\rho^2 - \gamma^2\rho^4\right)\exp\left(-\gamma\rho^2\right)\right] \quad (80)$$

Fugacity Equation

$$RT\ \ell n\ f = RT\ \ell n\ (\rho RT) + 2\left(B_oRT - A_o - \frac{C_o}{T^2} + \frac{D_o}{T^3} - \frac{E_o}{T^4}\right)\rho + \frac{3}{2}\left(bRT - a - \frac{d}{T}\right)\rho^2 + \frac{6\alpha}{5}\left(a + \frac{d}{T}\right)\rho^5 + \frac{c}{\gamma T^2}\left[1 - \left(1 - \frac{1}{2}\gamma\rho^2 - \gamma^2\rho^4\right)\exp\left(-\gamma\rho^2\right)\right] \quad (81)$$

Entropy Departure Equation

$$(S-S^\circ) = -R\,\ell n(\rho RT) - \left(B_o R + \frac{2C_o}{T^3} - \frac{3D_o}{T^4} + \frac{4E_o}{T^5}\right)\rho$$

$$- \frac{1}{2}\left(bRT + \frac{d}{T^2}\right)\rho^2 + \frac{\alpha d\rho^5}{5T^2} \qquad (82)$$

$$+ \frac{2c}{\gamma T^3}\left[1 - \left(1 + \frac{1}{2}\gamma\rho^2\right)\exp\left(-\gamma\rho^2\right)\right]$$

CHAPTER VII

APPLICATION OF MULTIPROPERTY REGRESSION ANALYSIS TO HYDROCARBONS USING MODIFIED BWR EQUATION

The modified BWR equation was applied to seven normal paraffins, methane through n-heptane, and ethylene. PVT, enthalpy departure and vapor pressure data were used simultaneously to determine the equation-of-state parameters for these hydrocarbons with the exception of n-hexane, for which no experimental nor meaningful derived enthalpy values are available.

Sets of parameters in British engineering units of the modified and original BWR equations are presented in Tables 12 and 13. In calculating low temperature saturated vapor and liquid fugacities, discrete values of C_o as reported by Benedict and coworkers are not used. This policy is adopted to emphasize the successful development of an analytic expression for the temperature dependent form of C_o to correlate low temperature densities, enthalpy departures and vapor pressures.

Predictions of thermodynamic properties of the above hydrocarbons are discussed individually in the following sections.

TABLE 12

MODIFIED BWR EQUATION-OF-STATE PARAMETERS* FOR INDIVIDUAL HYDROCARBONS

	METHANE	ETHANE	PROPANE	N-BUTANE	N-PENTANE	N-HEXANE	N-HEPTANE	ETHYLENE
B_o	0.7232[illegible] 00	[illegible] 00	[illegible] 00	0.218122E 01	0.237633E 01	0.242347E 01	0.174372E 01	0.852574E 00
A_o	0.792023E 04	0.125374E 05	0.178597E 05	0.424434E 05	0.550792E 05	0.341105E 05	0.581235E 05	0.129024E 05
C_o	0.271[illegible] 09	0.305936E 10	0.772153E 10	0.126513E 11	0.206236E 11	0.498629E 11	0.672038E 11	0.164359E 10
γ	0.144[illegible] 01	0.2[illegible] 01	0.341195E 01	0.753051E 01	0.117147E 02	0.176030E 02	0.252947E 02	0.233657E 01
b	0.929[illegible] 03	0.362133E 04	0.526635E 04	0.733335E 04	0.133293E 05	0.254335E 05	0.462517E 05	0.251551E 04
a	0.257[illegible] 04	0.24[illegible] 05	0.348339E 05	0.461053E 05	0.108031E 06	0.423901E 06	0.609419E 06	0.163518E 05
α	0.46[illegible] 00	[illegible] 00	0.176666E 01	0.452533E 01	0.774133E 01	0.108720E 02	0.162419E 02	0.683715E 00
c	0.437222E 09	0.713791E 10	0.244355E 11	0.619255E 11	0.124300E 12	0.226077E 12	0.452262E 12	0.479561E 10
D_o	0.137737E 11	0.253342E 12	0.421549E 12	0.387404E 12	0.836455E 12	0.567968E 13	0.809593E 13	0.569169E 11
d	0.474[illegible] 05	[illegible] 06	0.143572E 03	0.266794E 03	0.453363E 03	0.334171E 03	0.316115E 07	0.885764E 06
E_o	0.301122E 11	0.130786E 14	0.250712E 14	0.798594E 13	0.333932E 14	0.516311E 15	0.415947E 13	0.161706E 11

*These parameters are consistent with the following units: pressure in psia, volume in ft^3/lb mole, temperature in °R. The gas constant used is 10.7335.

TABLE 13

ORIGINAL BWR EQUATION-OF-STATE PARAMETERS* FOR INDIVIDUAL HYDROCARBONS[11]

	METHANE	ETHANE	PROPANE	N-BUTANE	N-PENTANE	N-HEXANE	N-HEPTANE	ETHYLENE
B_o	0.443243E 00	1.131354E 01	0.155434E 01	0.199211E 01	0.251095E 01	0.284335E 01	0.319782E 01	0.331983E 00
A_o	0.699258E 04	0.136737E 05	0.251154E 05	0.380296E 05	0.459263E 05	0.544341E 05	0.660706E 05	0.125936E 05
C_o	0.275763E 09	0.213427E 10	0.620393E 10	0.121305E 11	0.259172E 11	0.405562E 11	0.579341E 11	0.160228E 10
γ	0.153761E 01	0.332733E 01	0.564524E 01	0.572447E 01	0.121385E 02	0.171115E 02	0.230942E 02	0.236844E 01
b	0.867325E 00	0.265413E 01	0.577355E 01	0.112635E 02	0.171441E 02	0.233032E 02	0.349317E 02	0.220673E 01
a	0.239412E 04	0.213532E 05	0.572440E 05	0.113705E 06	0.245148E 06	0.429901E 06	0.626106E 06	0.156455E 05
α	0.511720E 00	0.190144E 01	0.244577E 01	0.452648E 01	0.743992E 01	0.115534E 02	0.179055E 02	0.731561E 00
c	0.498106E 09	0.641314E 10	0.232473E 11	0.619256E 11	0.161305E 12	0.226077E 12	0.483427E 12	0.413363E 10

*These parameters are consistent with the following units: pressure in psia, volume in ft^3/lb mole, temperature in °R. The gas constant used is 10.7335.

Methane

Source of Data

Review of sources of experimental data for methane has been given in Chapter II.

Results from Regression Analysis

Densities. A total of 40 points were taken from van Itterbeek's[131] data (-253.5°F to -153.7°F), Vennix's[132] data (-144.7°F to 26.3°F) and Douslin's[44] data (77°F to 257°F). The average absolute deviation was 0.315%. Original BWR equation predictions were compared with the same data set, and the average absolute deviation was 1.14%. Comparisons of predicted and experimental densities using the modified and original BWR equations are presented in Tables 14 and 15. Topographical plots of deviations are presented in Figures 14 and 15. Legends for these topographical plots are given in Figure 13.

Enthalpy Departures. Fifty-eight points were taken from Jones'[63] data as corrected by Yesavage.[141] The average absolute deviation was 0.453%. Original BWR equation predictions were compared with the same data set, and the average absolute deviation was 9.28%. Comparisons of predicted and experimental enthalpy departures using the modified and original BWR equations are presented in Tables 16 and 17. Topographical plots of deviations are presented in Figures 16 and 17.

TABLE 14

COMPARISON OF PREDICTED DENSITIES USING THE MBWR EQUATION WITH EXPERIMENTAL VALUES FOR METHANE

T (F)	PE (PSIA)	DE (LBMOLE/CF)	DC	DEV	%DEV
-253.5	129.7	1.6316	1.6378	-0.0062	-0.378
-253.5	1093.7	1.6548	1.6584	-0.0036	-0.215
-253.5	1932.2	1.6731	1.6745	-0.0014	-0.086
-234.8	142.1	1.5731	1.5720	0.0011	0.070
-234.8	652.0	1.5881	1.5862	0.0019	0.121
-234.8	1815.3	1.6192	1.6148	0.0044	0.274
-197.7	188.4	1.4347	1.4326	0.0021	0.144
-197.7	511.5	1.4520	1.4485	0.0035	0.242
-197.7	875.4	1.4691	1.4646	0.0045	0.308
-197.7	1699.3	1.5033	1.4960	0.0073	0.485
-151.9	574.5	1.2333	1.2383	-0.0050	-0.406
-151.9	897.0	1.2718	1.2739	-0.0021	-0.169
-151.9	1541.3	1.3280	1.3260	0.0020	0.147
-151.9	1799.3	1.3461	1.3428	0.0033	0.245
-151.9	2071.6	1.3639	1.3588	0.0051	0.375
-120.9	1565.3	1.1861	1.1875	-0.0014	-0.121
-120.9	2103.4	1.2446	1.2425	0.0021	0.169
-144.7	368.0	0.1598	0.1589	0.0009	0.579
-144.7	413.9	1.1551	1.1606	-0.0055	-0.476
-144.7	1881.5	1.3247	1.3207	0.0040	0.304
-99.7	503.5	0.1766	0.1783	-0.0017	-0.946
-99.7	1013.2	0.8584	0.8571	0.0013	0.154
-54.7	562.7	0.1594	0.1604	-0.0010	-0.609
-54.7	1521.4	0.6956	0.6929	0.0027	0.387
-54.7	1915.8	0.8573	0.8523	0.0050	0.581
26.3	728.1	0.1591	0.1600	-0.0009	-0.564
26.3	1749.3	0.4500	0.4515	-0.0015	-0.341
77.0	344.9	0.0624	0.0626	-0.0002	-0.267
77.0	962.9	0.1872	0.1883	-0.0011	-0.592
122.0	377.1	0.0624	0.0626	-0.0002	-0.285
122.0	1724.1	0.3120	0.3132	-0.0012	-0.398
167.0	409.2	0.0624	0.0626	-0.0002	-0.297
167.0	1925.2	0.3120	0.3128	-0.0008	-0.252
212.0	441.4	0.0624	0.0626	-0.0002	-0.346
212.0	2126.1	0.3120	0.3125	-0.0005	-0.170
257.0	473.2	0.0624	0.0626	-0.0002	-0.312
257.0	2324.7	0.3120	0.3121	-0.0001	-0.036
302.0	405.0	0.0499	0.0501	-0.0002	-0.352
347.0	403.4	0.0468	0.0469	-0.0001	-0.300
347.0	430.2	0.0499	0.0501	-0.0002	-0.360
662.0	606.5	0.0499	0.0501	-0.0002	-0.356

AVERAGE ABSOLUTE DEVIATION = 0.3223%

TABLE 15

COMPARISON OF PREDICTED DENSITIES USING THE OBWR EQUATION WITH EXPERIMENTAL VALUES FOR METHANE

T (F)	PE (PSIA)	DE (LBMOLE/CF)	DC	DEV	%DEV
-253.5	129.7	1.6316	1.6296	0.0020	0.124
-253.5	1093.7	1.6548	1.6477	0.0071	0.430
-253.5	1932.2	1.6731	1.6621	0.0110	0.657
-234.8	142.1	1.5731	1.5560	0.0171	1.088
-234.8	652.0	1.5881	1.5689	0.0192	1.212
-234.8	1815.3	1.6192	1.5950	0.0242	1.493
-197.7	188.4	1.4347	1.4081	0.0266	1.853
-197.7	511.5	1.4520	1.4232	0.0288	1.981
-197.7	875.4	1.4691	1.4386	0.0305	2.077
-197.7	1699.3	1.5033	1.4686	0.0347	2.306
-151.9	574.5	1.2333	1.2121	0.0212	1.719
-151.9	897.0	1.2718	1.2476	0.0242	1.901
-151.9	1541.3	1.3280	1.2989	0.0291	2.190
-151.9	1799.3	1.3461	1.3153	0.0308	2.288
-151.9	2071.6	1.3639	1.3309	0.0330	2.419
-120.9	1565.3	1.1861	1.1658	0.0203	1.714
-120.9	2109.4	1.2446	1.2196	0.0250	2.009
-144.7	368.0	0.1598	0.1584	0.0014	0.846
-144.7	413.9	1.1551	1.1336	0.0215	1.858
-144.7	1881.5	1.3247	1.2939	0.0308	2.325
-99.7	503.5	0.1766	0.1767	-0.0001	-0.060
-99.7	1013.2	0.8584	0.8275	0.0309	3.594
-54.7	562.7	0.1594	0.1592	0.0002	0.137
-54.7	1521.4	0.6956	0.6830	0.0126	1.810
-54.7	1915.8	0.8573	0.8477	0.0096	1.125
26.3	728.1	0.1591	0.1591	0.0000	0.003
26.3	1749.3	0.4500	0.4489	0.0011	0.234
77.0	344.9	0.0624	0.0624	-0.0000	-0.058
77.0	962.9	0.1872	0.1874	-0.0002	-0.099
122.0	377.1	0.0624	0.0625	-0.0001	-0.103
122.0	1724.1	0.3120	0.3124	-0.0004	-0.132
167.0	409.2	0.0624	0.0625	-0.0001	-0.140
167.0	1925.2	0.3120	0.3125	-0.0005	-0.154
212.0	441.4	0.0624	0.0625	-0.0001	-0.213
212.0	2126.1	0.3120	0.3126	-0.0006	-0.205
257.0	473.2	0.0624	0.0625	-0.0001	-0.202
257.0	2324.7	0.3120	0.3126	-0.0006	-0.178
302.0	405.0	0.0499	0.0500	-0.0001	-0.275
347.0	403.4	0.0468	0.0469	-0.0001	-0.240
347.0	430.2	0.0499	0.0500	-0.0001	-0.298
662.0	606.5	0.0499	0.0501	-0.0002	-0.368

AVERAGE ABSOLUTE DEVIATION = 1.0272%

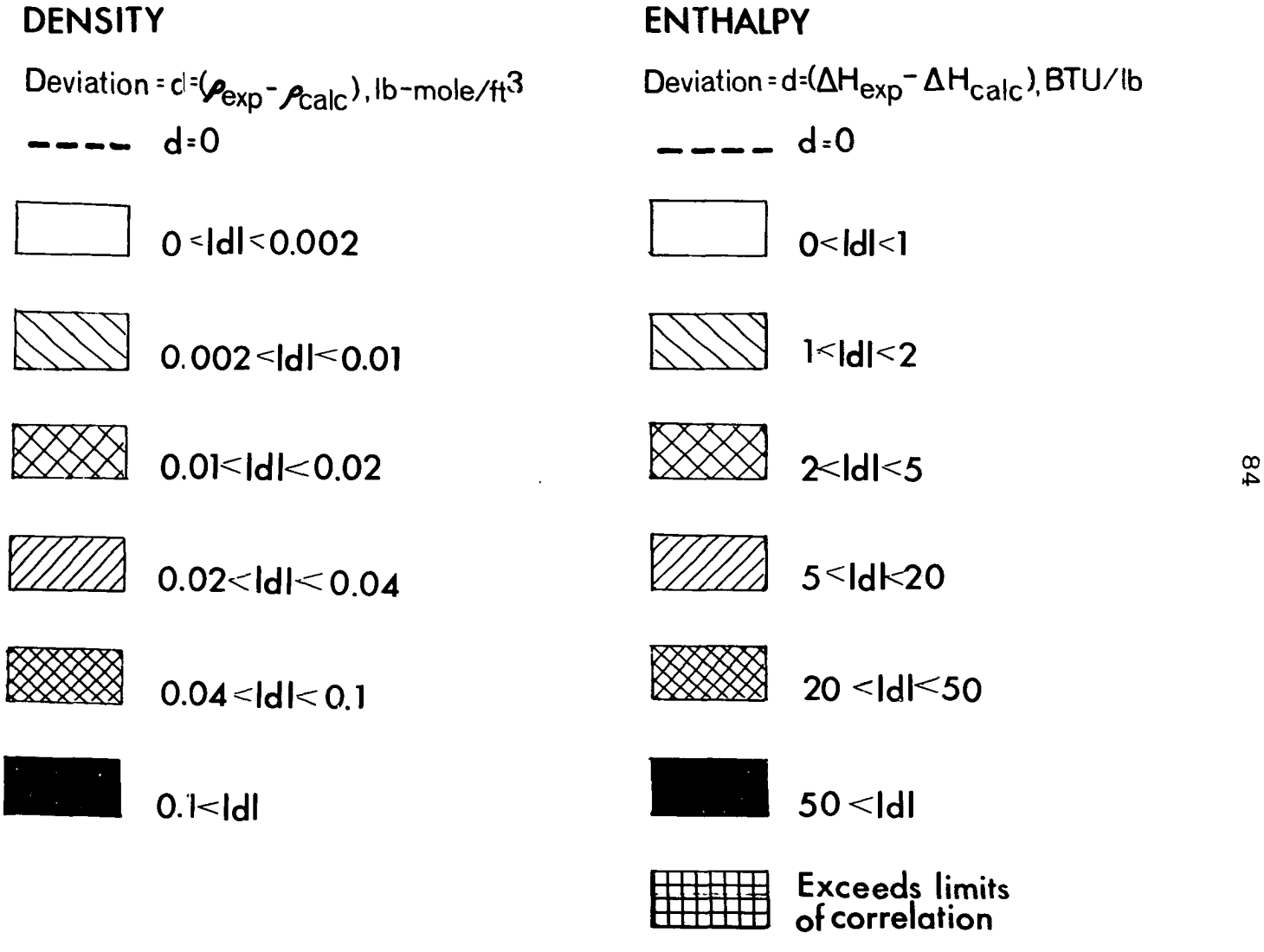


Figure 13. Legends for the Topographical Plots.

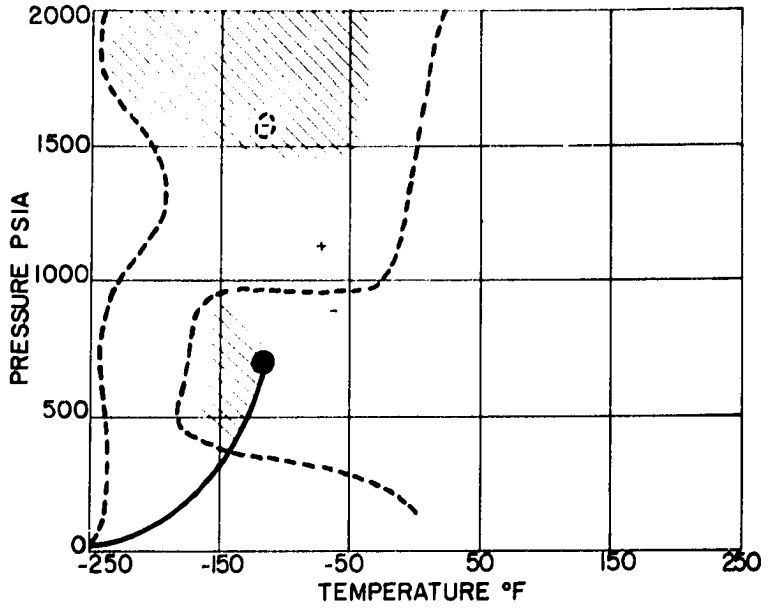


Figure 14. Comparison of Densities Calculated by the Modified BWR Equation with Experimental Values for Methane

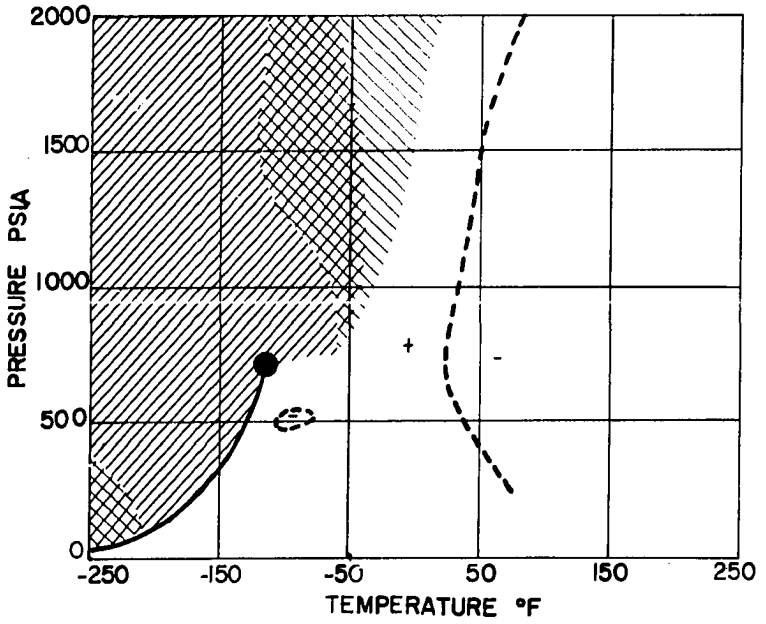


Figure 15. Comparison of Densities Calculated by the Original BWR Equation with Experimental Values for Methane

TABLE 16

COMPARISON OF PREDICTED ENTHALPY DEPARTURES USING THE MBWR EQUATION WITH EXPERIMENTAL VALUES FOR METHANE

T (F)	PE (PSIA)	HF (BTU/LBMOL F)	HC (BTU/LBMOL F)	DEV BTU/LB	%DEV
-250.0	450.0	-3487.85	-3471.84	-1.00	0.46
-200.0	450.0	-3189.47	-3165.81	-1.47	0.74
-150.0	450.0	-2769.17	-2766.30	-0.18	0.10
-100.0	450.0	-513.66	-515.13	0.09	-0.29
-50.0	450.0	-370.89	-371.31	0.03	-0.11
50.0	450.0	-237.74	-234.87	-0.18	1.21
-250.0	600.0	-3484.00	-3462.26	-1.36	0.62
-200.0	600.0	-3193.64	-3159.74	-2.11	1.06
-150.0	600.0	-2797.40	-2781.72	-0.98	0.56
-100.0	600.0	-769.69	-769.95	0.02	-0.03
-50.0	600.0	-513.02	-517.67	0.29	-0.90
0.0	600.0	-392.71	-394.47	0.11	-0.45
-250.0	1000.0	-3457.37	-3436.33	-1.31	0.61
-200.0	1000.0	-3179.84	-3141.79	-2.37	1.20
-150.0	1000.0	-2828.52	-2803.22	-1.58	0.89
-100.0	1000.0	-2127.49	-2094.83	-2.04	1.54
-50.0	1000.0	-996.53	-988.88	-0.48	0.77
0.0	1000.0	-694.94	-696.42	0.09	-0.21
50.0	1000.0	-540.94	-541.92	0.06	-0.18
-250.0	1200.0	-3430.42	-3423.15	-0.45	0.21
-200.0	1200.0	-3156.10	-3132.01	-1.50	0.76
-150.0	1200.0	-2817.62	-2807.47	-0.63	0.36
-100.0	1200.0	-2268.98	-2260.72	-0.51	0.36
0.0	1200.0	-847.66	-855.25	0.47	-0.90
50.0	1200.0	-651.95	-655.80	0.24	-0.59
-250.0	1500.0	-3396.89	-3403.18	0.39	-0.19
-200.0	1500.0	-3127.39	-3116.51	-0.68	0.35
-150.0	1500.0	-2804.94	-2808.76	0.24	-0.14
-100.0	1500.0	-2355.77	-2368.43	0.79	-0.54
-50.0	1500.0	-1596.98	-1608.74	0.73	-0.74
0.0	1500.0	-1075.62	-1089.04	0.84	-1.25
50.0	1500.0	-822.15	-823.34	0.07	-0.14
-250.0	2000.0	-3358.23	-3369.33	0.69	-0.33
-200.0	2000.0	-3096.75	-3088.78	-0.50	0.26
-150.0	2000.0	-2796.76	-2801.73	0.31	-0.18
-100.0	2000.0	-2427.79	-2445.87	1.13	-0.74
-50.0	2000.0	-1933.70	-1927.40	-0.39	0.33
0.0	2000.0	-1417.15	-1413.18	-0.25	0.28
50.0	2000.0	-1077.06	-1076.34	-0.05	0.07

AVERAGE ABSOLUTE DEVIATION = 0.5293%

AVERAGE ABSOLUTE DEVIATION IN BTU/LB = 0.68

TABLE 17

COMPARISON OF PREDICTED ENTHALPY DEPARTURES USING THE OBWR EQUATION WITH EXPERIMENTAL VALUES FOR METHANE

T (F)	PF (PSIA)	HF (BTU/LBMOLE)	HC (BTU/LBMOLE)	DEV BTU/LB	%DEV
-250.0	450.0	-3487.85	-4335.05	52.81	-24.29
-200.0	450.0	-3189.47	-3412.09	13.88	-6.98
-150.0	450.0	-2769.17	-2796.49	1.70	-0.99
-100.0	450.0	-513.66	-520.49	0.43	-1.33
-50.0	450.0	-370.89	-369.15	-0.11	0.47
50.0	450.0	-237.74	-228.69	-0.56	3.81
-250.0	600.0	-3484.00	-4326.48	52.52	-24.18
-200.0	600.0	-3193.64	-3406.60	13.27	-6.67
-150.0	600.0	-2797.40	-2812.91	0.97	-0.55
-100.0	600.0	-769.69	-770.90	0.08	-0.16
-50.0	600.0	-513.02	-512.99	-0.00	0.01
0.0	600.0	-392.71	-386.92	-0.36	1.47
-250.0	1000.0	-3457.37	-4303.19	52.73	-24.46
-200.0	1000.0	-3179.84	-3390.10	13.11	-6.61
-150.0	1000.0	-2828.52	-2835.25	0.42	-0.24
-100.0	1000.0	-2127.49	-2045.33	-5.12	3.86
-50.0	1000.0	-996.53	-968.62	-1.74	2.90
0.0	1000.0	-694.94	-680.30	-0.91	2.11
50.0	1000.0	-540.94	-526.45	-0.90	2.68
-250.0	1200.0	-3430.42	-4291.32	53.67	-25.10
-200.0	1200.0	-3156.10	-3380.98	14.02	-7.13
-150.0	1200.0	-2817.62	-2839.50	1.36	-0.78
-100.0	1200.0	-2268.98	-2231.43	-2.34	1.65
0.0	1200.0	-847.66	-834.38	-0.83	1.57
50.0	1200.0	-651.95	-636.99	-0.93	2.29
-250.0	1500.0	-3396.89	-4273.26	54.63	-25.90
-200.0	1500.0	-3127.39	-3366.41	14.90	-7.64
-150.0	1500.0	-2804.94	-2840.57	2.22	-1.27
-100.0	1500.0	-2355.77	-2339.76	-1.00	0.68
-50.0	1500.0	-1596.98	-1574.76	-1.39	1.39
0.0	1500.0	-1075.62	-1062.57	-0.81	1.21
50.0	1500.0	-822.15	-800.31	-1.36	2.66
-250.0	2000.0	-3358.23	-4242.55	55.13	-26.33
-200.0	2000.0	-3096.75	-3340.12	15.17	-7.96
-150.0	2000.0	-2796.76	-2832.86	2.25	-1.29
-100.0	2000.0	-2427.79	-2412.06	-0.98	0.65
-50.0	2000.0	-1933.70	-1895.94	-2.35	1.95
0.0	2000.0	-1417.15	-1384.66	-2.03	2.29
50.0	2000.0	-1077.06	-1049.85	-1.70	2.53

AVERAGE ABSOLUTE DEVIATION = 6.0443%

AVERAGE ABSOLUTE DEVIATION IN BTU/LB = 11.30

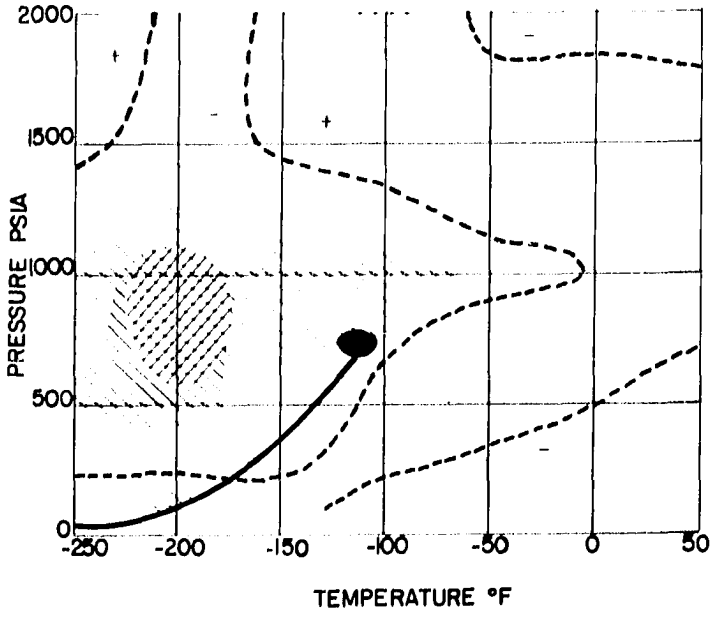


Figure 16. Comparison of Enthalpy Departures Calculated by the Modified BWR Equation with Experimental Values for Methane.

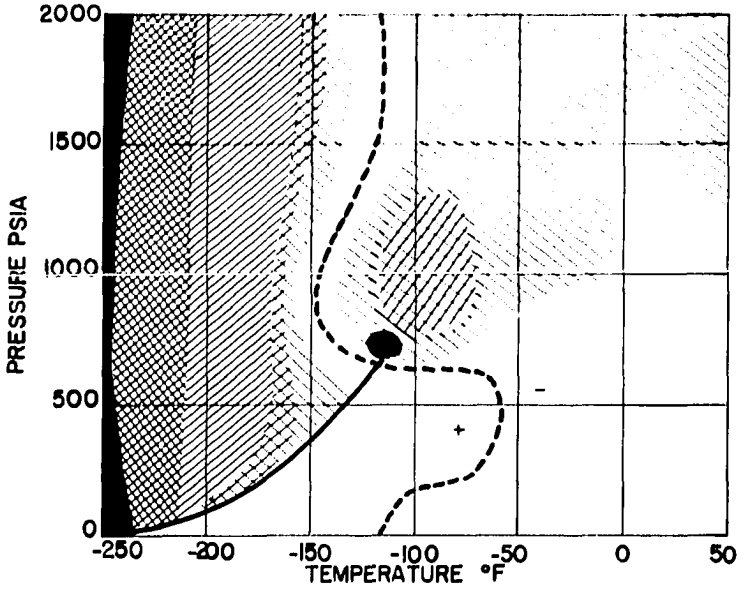


Figure 17. Comparison of Enthalpy Departures Calculated by the Original BWR Equation with Experimental Values for Methane.

Vapor Pressures. A total of 17 points were taken from Matthews and Hurd[91] (-250.0°F to -230.0°F) and Vennix[137] (-218.98°F to -116.51°F). The average absolute deviation was 0.26%. Original BWR equation predictions were compared with the same data set, and the average absolute deviation was 5.61%. Prediction of fugacities along the vapor pressure curve using the modified and original BWR equations are presented in Tables 18 and 19 respectively. It may be noted that at conditions other than the critical point, zero percent deviation in fugacity prediction means the failure of the equation of state to indicate a two-phase region.

Ethane

Source of Data

Comprehensive compilation of the thermodynamic properties of ethane have been presented by Michels, Straaten and Dawson[95], Din, et al.[41], Sage and Lacey[112] and Canjar and Manning[21].

Results from Regression Analysis

Densities. A total of 28 points were taken from API Project 44[111] (-280°F to -130°F), Canjar and Manning (-100°F to 50°F) and Sage and Lacey (100°F to 310°F). The average absolute deviation was 1.29%. Original BWR equation predictions were compared with the same data set, and the average absolute deviation was 1.73%. Comparisons of predicted and experimental densities using the modified and

TABLE 18

PREDICTION OF SATURATED VAPOR AND LIQUID FUGACITIES FOR METHANE USING THE MBWR EQUATION

T (F)	PE (PSIA)	FUL (PSIA)	FUG (PSIA)	%DEV
-258.68	14.696	14.4255	14.1703	-1.80
-255.00	17.400	16.9298	16.7020	-1.36
-250.00	21.710	20.8285	20.6989	-0.63
-245.00	26.600	25.3422	25.1852	-0.62
-240.00	32.400	30.5196	30.4402	-0.26
-235.00	39.000	36.4041	36.3444	-0.16
-230.00	46.400	43.0375	42.8791	-0.37
-225.00	54.800	50.4603	50.1932	-0.53
-218.98	66.030	60.4960	59.8260	-1.12
-214.15	76.680	69.4374	68.7912	-0.94
-209.98	86.760	77.8371	77.1525	-0.89
-205.00	101.000	88.7297	88.7202	-0.01
-199.74	115.900	101.2009	100.6785	-0.52
-195.00	132.000	113.3727	113.2831	-0.08
-185.00	169.700	141.8987	141.9742	0.05
-181.93	182.150	151.4151	151.2361	-0.12
-175.00	214.900	174.3995	174.8874	0.28
-168.34	248.400	198.2152	198.4612	0.12
-165.00	267.300	210.8619	211.3804	0.25
-160.66	290.450	227.0612	227.0833	0.01
-155.00	325.000	251.3244	252.1998	0.35
-145.89	392.710	291.5203	292.3445	0.28
-139.38	444.970	322.3335	323.6216	0.40
-135.00	482.000	343.8469	345.1377	0.37
-131.77	510.230	360.1260	361.2341	0.31
-125.00	575.000	395.5371	396.6375	0.28
-123.95	587.100	401.3564	402.7656	0.35
-120.22	626.800	421.7642	423.1487	0.33
-116.51	668.720	442.6533	442.6543	0.00

AVERAGE ABSOLUTE DEVIATION = 0.4410%

TABLE 19

PREDICTION OF SATURATED VAPOR AND LIQUID FUGACITIES FOR METHANE USING THE OBWR EQUATION

T (F)	PF (PSIA)	FUL (PSIA)	FUG (PSIA)	%DEV
-258.68	14.696	10.0221	14.1246	29.05
-255.00	17.400	12.3099	16.6447	26.04
-250.00	21.710	15.9783	20.6224	22.52
-245.00	26.600	20.3439	25.0964	18.90
-240.00	32.400	25.4620	30.3142	16.01
-235.00	39.000	31.3802	36.1876	13.28
-230.00	46.400	38.1402	42.6896	10.65
-225.00	54.800	45.7813	49.9654	8.37
-218.98	66.030	56.1966	59.5522	5.63
-214.15	76.680	65.5257	68.4746	4.31
-209.98	86.760	74.3156	76.7986	3.23
-205.00	101.000	85.7333	88.3142	2.92
-199.74	115.900	98.8194	100.2330	1.41
-195.00	132.000	111.5889	112.7962	1.07
-185.00	169.700	141.4728	141.4313	-0.03
-181.93	182.150	151.4223	150.6882	-0.49
-175.00	214.900	175.3594	174.3403	-0.61
-168.34	248.400	200.1652	197.9626	-1.11
-165.00	267.300	213.2823	210.9222	-1.12
-160.86	290.450	230.0555	226.7008	-1.49
-155.00	329.000	255.1082	251.9662	-1.25
-145.89	392.710	296.4517	292.4905	-1.35
-139.38	444.970	328.0217	324.1870	-1.19
-135.00	482.000	349.9980	346.0715	-1.13
-131.77	510.230	366.5923	362.4927	-1.13
-125.00	575.000	402.5476	398.7957	-0.94
-123.95	587.100	408.4426	405.1274	-0.82
-120.22	626.800	426.2732	426.2732	0.0
-116.51	668.720	447.9609	447.9612	0.00

AVERAGE ABSOLUTE DEVIATION = 6.07088

original BWR equations are presented in Tables 20 and 21.

Enthalpy Departures. Forty points were taken from Sage and Lacey's compilation (100°F to 310°F). These enthalpy departures were derived from PVT data through rigorous thermodynamic relationships. In the absence of experimental data, these derived enthalpy departures were used to insure the internal consistency of equation-of-state parameters. The average absolute deviation was 1.53%. Original BWR equation predictions were compared with the same data set, and the average absolute deviation was 1.04%. Comparisons of predicted and derived enthalpy departures using the modified and original BWR equations are presented in Tables 22 and 23.

Vapor Pressures. A total of 28 points were taken from API Project 44[111] (-220°F to -130°F) and Canjar and Manning (-127.85°F to 90.0°F). The average absolute deviation was 0.19%. Original BWR equation predictions were compared with the same data set, and the average absolute deviation was 15.59%. Predictions of fugacities along the vapor pressure curve using the modified and original BWR equations are presented in Tables 24 and 25 respectively.

TABLE 20

COMPARISON OF PREDICTED DENSITIES USING THE MBWR EQUATION WITH EXPERIMENTAL VALUES FOR ETHANE

T (F)	PF (PSIA)	DE (LBMOLE/CF)	DC	DEV	%DEV
-220.0	14.7	1.2644	1.3049	-0.0405	-3.201
-190.0	14.7	1.2249	1.2494	-0.0245	-1.998
-160.0	14.7	1.1836	1.1980	-0.0144	-1.214
-130.0	14.7	1.1390	1.1489	-0.0099	-0.865
-100.0	31.6	1.0988	1.1006	-0.0018	-0.167
-70.0	62.0	1.0560	1.0517	0.0043	0.404
-40.0	113.4	1.0077	1.0003	0.0073	0.729
-10.0	189.0	0.9526	0.9440	0.0086	0.908
50.0	441.3	0.8031	0.7903	0.0128	1.590
100.0	400.0	0.0840	0.0853	-0.0013	-1.589
100.0	2500.0	0.8163	0.8231	-0.0068	-0.828
100.0	3000.0	0.8410	0.8474	-0.0064	-0.755
100.0	4000.0	0.8803	0.8841	-0.0038	-0.429
100.0	6000.0	0.9320	0.9347	-0.0027	-0.289
130.0	1000.0	0.3775	0.3784	-0.0009	-0.241
130.0	2000.0	0.7123	0.7144	-0.0021	-0.292
130.0	3000.0	0.7880	0.7945	-0.0065	-0.829
160.0	2500.0	0.6930	0.6938	-0.0008	-0.109
160.0	4000.0	0.7949	0.7964	-0.0015	-0.183
160.0	6000.0	0.8658	0.8670	-0.0012	-0.143
160.0	8000.0	0.9158	0.9133	0.0025	0.275
190.0	2000.0	0.5476	0.5398	0.0078	1.428
190.0	6000.0	0.8326	0.8327	-0.0001	-0.012
190.0	10000.0	0.9268	0.9228	0.0040	0.430
220.0	2500.0	0.5634	0.5571	0.0063	1.124
220.0	5000.0	0.7593	0.7584	0.0009	0.114
220.0	7000.0	0.8313	0.8298	0.0015	0.185
250.0	1000.0	0.1675	0.1707	-0.0032	-1.925
250.0	2000.0	0.4068	0.4078	-0.0010	-0.238
250.0	4000.0	0.6636	0.6591	0.0045	0.677
250.0	6000.0	0.7657	0.7641	0.0016	0.205
280.0	1000.0	0.1536	0.1565	-0.0029	-1.880
280.0	2000.0	0.3595	0.3628	-0.0033	-0.926
280.0	3000.0	0.5236	0.5187	0.0049	0.934
280.0	4000.0	0.6211	0.6164	0.0047	0.756
280.0	7000.0	0.7710	0.7684	0.0026	0.337
310.0	1000.0	0.1429	0.1452	-0.0023	-1.626
310.0	2500.0	0.4092	0.4096	-0.0004	-0.093
310.0	3500.0	0.5373	0.5318	0.0055	1.014
310.0	5000.0	0.6515	0.6466	0.0049	0.758
310.0	9000.0	0.8026	0.7996	0.0030	0.370

AVERAGE ABSOLUTE DEVIATION = 0.7822%

TABLE 21

COMPARISON OF PREDICTED DENSITIES USING THE OBWR EQUATION WITH EXPERIMENTAL VALUES FOR ETHANE

T (F)	PE (PSIA)	DE (LBMOLE/CF)	DC	DEV	%DEV
-220.0	14.7	1.2644	1.3139	-0.0495	-3.919
-190.0	14.7	1.2249	1.2488	-0.0239	-1.954
-160.0	14.7	1.1836	1.1906	-0.0070	-0.594
-130.0	14.7	1.1390	1.1368	0.0022	0.194
-100.0	31.6	1.0988	1.0854	0.0134	1.218
-70.0	63.0	1.0560	1.0346	0.0214	2.022
-40.0	113.4	1.0077	0.9825	0.0252	2.498
-10.0	189.0	0.9526	0.9266	0.0260	2.733
50.0	441.3	0.8031	0.7816	0.0215	2.680
100.0	400.0	0.0840	0.0848	-0.0008	-0.940
100.0	2500.0	0.8163	0.8193	-0.0030	-0.368
100.0	3000.0	0.8410	0.8428	-0.0018	-0.217
100.0	4000.0	0.8803	0.8788	0.0015	0.175
100.0	6000.0	0.9320	0.9288	0.0032	0.344
130.0	1000.0	0.3775	0.3806	-0.0031	-0.817
130.0	2000.0	0.7123	0.7190	-0.0067	-0.945
130.0	3000.0	0.7880	0.7944	-0.0064	-0.808
160.0	2500.0	0.6930	0.7005	-0.0075	-1.082
160.0	4000.0	0.7949	0.7980	-0.0031	-0.388
160.0	6000.0	0.8658	0.8664	-0.0006	-0.066
160.0	8000.0	0.9158	0.9116	0.0042	0.458
190.0	2000.0	0.5476	0.5498	-0.0022	-0.394
190.0	6000.0	0.8326	0.8346	-0.0020	-0.246
190.0	10000.0	0.9268	0.9226	0.0042	0.455
220.0	2500.0	0.5634	0.5664	-0.0030	-0.525
220.0	5000.0	0.7593	0.7641	-0.0048	-0.636
220.0	7000.0	0.8313	0.8332	-0.0019	-0.226
250.0	1000.0	0.1675	0.1690	-0.0015	-0.878
250.0	2000.0	0.4068	0.4099	-0.0031	-0.759
250.0	4000.0	0.6636	0.6681	-0.0045	-0.675
250.0	6000.0	0.7657	0.7706	-0.0049	-0.636
280.0	1000.0	0.1536	0.1550	-0.0014	-0.894
280.0	2000.0	0.3595	0.3628	-0.0033	-0.909
280.0	3000.0	0.5236	0.5259	-0.0023	-0.433
280.0	4000.0	0.6211	0.6257	-0.0046	-0.734
280.0	7000.0	0.7710	0.7755	-0.0045	-0.589
310.0	1000.0	0.1429	0.1439	-0.0010	-0.681
310.0	2500.0	0.4092	0.4115	-0.0023	-0.557
310.0	3500.0	0.5373	0.5392	-0.0019	-0.349
310.0	5000.0	0.6515	0.6559	-0.0044	-0.677
310.0	9000.0	0.8026	0.8068	-0.0042	-0.524

AVERAGE ABSOLUTE DEVIATION = 0.8828%

TABLE 22

COMPARISON OF PREDICTED ENTHALPY DEPARTURES USING THE MBWR EQUATION WITH DERIVED VALUES FOR ETHANE

T (F)	PE (PSIA)	HE (BTU/LBMOLE)	HC	DEV BTU/LB	%DEV
100.0	1750.0	-4203.26	-4282.73	2.65	-1.89
100.0	2000.0	-4249.20	-4329.80	2.68	-1.90
100.0	2250.0	-4280.78	-4361.89	2.70	-1.89
100.0	3000.0	-4331.54	-4407.05	2.51	-1.74
100.0	3500.0	-4341.83	-4412.13	2.34	-1.62
130.0	1250.0	-3426.86	-3376.72	-1.67	1.46
130.0	2000.0	-3993.19	-3967.73	2.48	-1.91
130.0	3000.0	-4090.30	-4146.27	1.86	-1.37
130.0	6000.0	-4039.17	-4126.84	2.92	-2.17
130.0	10000.0	-3726.72	-3820.57	3.12	-2.52
160.0	2000.0	-3514.69	-3550.77	1.20	-1.03
160.0	3000.0	-3784.48	-3865.50	2.70	-2.14
160.0	4000.0	-3863.81	-3956.35	3.08	-2.39
160.0	5000.0	-3871.61	-3969.25	3.25	-2.52
190.0	1250.0	-2024.78	-2104.88	2.67	-3.96
190.0	2000.0	-3196.84	-3121.91	-2.49	2.34
190.0	3500.0	-3674.27	-3663.89	-0.35	0.28
190.0	5000.0	-3756.60	-3763.84	0.24	-0.19
190.0	6000.0	-3743.61	-3757.63	0.47	-0.37
190.0	8000.0	-3648.38	-3667.35	0.63	-0.52
220.0	1000.0	-1329.44	-1342.92	0.45	-1.01
220.0	1500.0	-2160.27	-2152.29	-0.27	0.37
220.0	3000.0	-3365.91	-3271.62	-3.14	2.80
220.0	4000.0	-3544.37	-3477.88	-2.21	1.88
250.0	2000.0	-2427.96	-2394.15	-1.13	1.39
250.0	3000.0	-3038.67	-2984.51	-1.80	1.78
250.0	4500.0	-3323.54	-3304.24	-0.64	0.58
250.0	5000.0	-3357.22	-3346.67	-0.35	0.31
250.0	6000.0	-3379.70	-3383.00	0.11	-0.10
280.0	2000.0	-2131.70	-2114.13	-0.58	0.82
280.0	3000.0	-2786.67	-2718.04	-2.28	2.46
280.0	4000.0	-3053.76	-3004.47	-1.64	1.61
280.0	5000.0	-3169.77	-3140.48	-0.97	0.92
310.0	2000.0	-1904.48	-1882.72	-0.72	1.14
310.0	3000.0	-2562.45	-2476.35	-2.87	3.36
310.0	5000.0	-3029.98	-2940.08	-2.99	2.97
340.0	1000.0	-862.01	-845.35	-0.55	1.93
340.0	2000.0	-1732.11	-1690.65	-1.38	2.39
340.0	3000.0	-2353.42	-2260.02	-3.11	3.97

AVERAGE ABSOLUTE DEVIATION = 1.6936%

AVERAGE ABSOLUTE DEVIATION IN BTU/LB = 1.77

TABLE 23

COMPARISON OF PREDICTED ENTHALPY DEPARTURES USING THE OBWR EQUATION WITH DERIVED VALUES FOR ETHANE

T (F)	PF (PSIA)	HF (BTU/LBMOLE)	HC (BTU/LBMOLE)	DEV BTU/LB	%DEV
100.0	1750.0	-4203.26	-4279.35	2.53	-1.81
100.0	2000.0	-4249.20	-4316.83	2.25	-1.59
100.0	2250.0	-4280.78	-4341.35	2.02	-1.42
100.0	3000.0	-4331.54	-4369.90	1.28	-0.89
100.0	3500.0	-4341.83	-4366.58	0.82	-0.57
130.0	1250.0	-3426.86	-3466.64	1.32	-1.16
130.0	2000.0	-3893.19	-3988.09	3.16	-2.44
130.0	3000.0	-4090.30	-4129.06	1.29	-0.95
130.0	6000.0	-4039.17	-4060.24	0.70	-0.52
130.0	10000.0	-3726.72	-3717.37	-0.31	0.25
160.0	2000.0	-3514.69	-3604.28	2.98	-2.55
160.0	3000.0	-3784.48	-3875.65	3.03	-2.41
160.0	4000.0	-3863.81	-3940.07	2.54	-1.97
160.0	5000.0	-3871.61	-3934.19	2.08	-1.62
190.0	1250.0	-2024.78	-2101.24	2.54	-3.78
190.0	2000.0	-3196.84	-3182.76	-0.47	0.44
190.0	3500.0	-3674.27	-3686.05	0.39	-0.32
190.0	5000.0	-3756.60	-3752.21	-0.15	0.12
190.0	6000.0	-3743.61	-3729.34	-0.47	0.38
190.0	8000.0	-3648.38	-3613.12	-1.17	0.97
220.0	1000.0	-1329.44	-1334.64	0.17	-0.39
220.0	1500.0	-2160.27	-2160.55	0.01	-0.01
220.0	3000.0	-3365.91	-3327.45	-1.28	1.14
220.0	4000.0	-3544.37	-3511.70	-1.09	0.92
250.0	2000.0	-2427.96	-2428.09	0.00	-0.01
250.0	3000.0	-3038.67	-3048.59	0.33	-0.33
250.0	4500.0	-3323.54	-3349.35	0.86	-0.78
250.0	5000.0	-3357.22	-3382.96	0.86	-0.77
250.0	6000.0	-3379.70	-3402.62	0.76	-0.68
280.0	2000.0	-2131.70	-2138.90	0.24	-0.34
280.0	3000.0	-2786.67	-2782.46	-0.14	0.15
280.0	4000.0	-3053.76	-3071.84	0.60	-0.59
280.0	5000.0	-3169.77	-3196.51	0.89	-0.84
310.0	2000.0	-1904.48	-1902.55	-0.06	0.10
310.0	3000.0	-2562.45	-2537.21	-0.84	0.99
310.0	5000.0	-3029.98	-3011.35	-0.62	0.61
340.0	1000.0	-862.01	-846.93	-0.50	1.75
340.0	2000.0	-1732.11	-1708.10	-0.80	1.39
340.0	3000.0	-2353.42	-2316.23	-1.24	1.58

AVERAGE ABSOLUTE DEVIATION = 1.0129%

AVERAGE ABSOLUTE DEVIATION IN BTU/LB = 1.10

TABLE 24

PREDICTION OF SATURATED VAPOR AND LIQUID FUGACITIES FOR ETHANE USING THE MBWR EQUATION

T (F)	PE (PSIA)	FUL (PSIA)	FUG (PSIA)	%DEV
-220.00	0.269	0.2673	0.2685	0.44
-210.00	0.489	0.4846	0.4874	0.59
-200.00	0.842	0.8345	0.8380	0.42
-190.00	1.385	1.3729	1.3754	0.18
-180.00	2.189	2.1688	2.1677	-0.05
-170.00	3.339	3.3037	3.2949	-0.27
-160.00	4.938	4.8705	4.8519	-0.38
-150.00	7.099	6.9737	6.9395	-0.49
-140.00	9.952	9.7249	9.6700	-0.57
-130.00	13.640	13.2418	13.1617	-0.61
-127.85	14.656	14.1104	14.1526	0.30
-120.00	18.480	17.6460	17.6846	0.22
-110.00	24.350	23.0597	23.0952	0.15
-100.00	31.550	29.6011	29.6303	0.10
-90.00	40.270	37.3885	37.4124	0.06
-80.00	50.660	46.5303	46.5172	-0.03
-70.00	62.970	57.1307	57.0923	-0.07
-60.00	77.370	69.2787	69.2030	-0.11
-50.00	94.130	83.0623	82.9793	-0.10
-40.00	113.400	98.5466	98.4411	-0.11
-30.00	135.500	115.7992	115.7188	-0.07
-20.00	160.600	134.8643	134.8133	-0.04
-10.00	189.000	155.7805	155.7985	0.01
0.0	220.800	178.5668	178.5983	0.02
10.00	256.300	203.2368	203.2516	0.01
20.00	295.900	229.7954	229.8263	0.01
30.00	339.700	258.2197	258.1919	-0.01
40.00	388.100	288.4839	288.3623	-0.04
45.00	414.100	304.2878	304.0925	-0.06
50.00	441.300	320.5273	320.2156	-0.10
55.00	469.800	337.1904	336.7446	-0.13
60.00	499.600	354.2610	353.6497	-0.17
65.00	530.800	371.7180	370.9341	-0.21
70.00	563.300	389.5203	388.5242	-0.26
75.00	597.200	407.6116	406.4238	-0.29
80.00	632.700	425.8721	424.6558	-0.29
85.00	670.300	443.3145	443.3145	0.0
90.01	709.800	462.3704	462.3689	-0.00

AVERAGE ABSOLUTE DEVIATION = 0.1832%

TABLE 25

PREDICTION OF SATURATED VAPOR AND LIQUID FUGACITIES FOR ETHANE USING THE OBWR EQUATION

T (F)	PE (PSIA)	FUL (PSIA)	FUG (PSIA)	%DEV
-220.00	0.269	0.0411	0.2684	84.71
-210.00	0.489	0.1120	0.4874	77.03
-200.00	0.842	0.2650	0.8379	68.37
-190.00	1.385	0.5589	1.3752	59.36
-180.00	2.189	1.0728	2.1674	50.50
-170.00	3.339	1.9045	3.2944	42.19
-160.00	4.938	3.1681	4.8512	34.69
-150.00	7.099	4.9894	6.9387	28.09
-140.00	9.952	7.5012	9.6692	22.42
-130.00	13.640	10.8392	13.1613	17.64
-127.65	14.696	11.6780	14.1524	17.48
-120.00	18.480	15.1378	17.6856	14.41
-110.00	24.350	20.5244	23.0990	11.15
-100.00	31.550	27.1226	29.6390	8.49
-90.00	40.270	35.0439	37.4291	6.37
-80.00	50.660	44.3877	46.5462	4.64
-70.00	62.970	55.2468	57.1396	3.31
-60.00	77.370	67.6957	69.2763	2.28
-50.00	94.130	81.8059	83.0887	1.54
-40.00	113.400	97.6291	98.5990	0.98
-30.00	135.500	115.2129	115.9415	0.63
-20.00	160.600	134.5926	135.1205	0.39
-10.00	189.000	155.7933	156.2148	0.27
0.0	220.800	178.8314	179.1528	0.18
10.00	256.300	203.7132	203.9806	0.13
20.00	295.900	230.4491	230.7734	0.14
30.00	339.700	259.0229	259.4104	0.15
40.00	388.100	289.4287	289.9170	0.17
45.00	414.100	305.3101	305.8438	0.17
50.00	441.300	321.6345	322.1846	0.17
55.00	469.800	338.4016	338.9563	0.16
60.00	499.600	355.5979	356.1289	0.15
65.00	530.800	373.2229	373.7114	0.13
70.00	563.300	391.2495	391.6318	0.10
75.00	597.200	409.6621	409.8943	0.06
80.00	632.700	428.4485	428.5276	0.02
85.00	670.300	447.6206	447.6189	-0.00
90.01	709.800	467.0295	467.0305	0.00

AVERAGE ABSOLUTE DEVIATION = 14.7022%

Propane

Source of Data

Comprehensive compilations of the thermodynamic properties of propane have been presented by Din[40], Sage and Lacey[112], Canjar and Manning[21]. Recent contributions include PVT measurements by Dawson and McKetta[34], Dittmar and coworkers[42] and Huang[57]. Accurate enthalpy data were reported by Yesavage[141].

Results from Regression Analysis

Densities. A total of 30 points were taken from API Project 44[111] (-250°F to -130°F), Huang (-148°F to 32°F) and Sage and Lacey (100°F to 460°F). The average absolute deviation was 1.16%. Original BWR equation predictions were compared with the same data set, and the average absolute deviation was 1.6%. Comparisons of predicted and experimental densities using the modified and original BWR equations are presented in Tables 26 and 27. Topographical plots of deviations are presented in Figures 18 and 19.

Enthalpy Departures. Forty points were taken from Yesavage (-250°F to 250°F). The average absolute deviation was 0.40%. Original BWR equation predictions were compared with the same data set, and the average absolute deviation was 51.34%. Comparisons of predicted and experimental enthalpy departures using the modified and original BWR equations are presented in Tables 28 and 29.

TABLE 26

COMPARISON OF PREDICTED DENSITIES USING THE MBWR EQUATION WITH EXPERIMENTAL VALUES FOR PROPANE

T (F)	PF (PSIA)	DE (LBMOLE/CF)	DC	DEV	%DEV
-250.0	14.7	0.9933	1.0168	-0.0235	-2.368
-220.0	14.7	0.9707	0.9800	-0.0093	-0.961
-190.0	14.7	0.9480	0.9476	0.0004	0.038
-160.0	14.7	0.9253	0.9182	0.0071	0.762
-130.0	14.7	0.8981	0.8908	0.0073	0.810
-148.0	1000.0	0.9218	0.9127	0.0091	0.986
-112.0	2000.0	0.9006	0.8890	0.0116	1.284
-76.0	1000.0	0.8610	0.8531	0.0079	0.915
-40.0	2000.0	0.8411	0.8349	0.0063	0.744
-4.0	1000.0	0.7986	0.7948	0.0038	0.475
-4.0	2000.0	0.8114	0.8080	0.0034	0.413
32.0	2000.0	0.7802	0.7804	-0.0002	-0.022
100.0	500.0	0.6793	0.6767	0.0026	0.383
100.0	1000.0	0.6940	0.6959	-0.0019	-0.277
100.0	1500.0	0.7067	0.7110	-0.0043	-0.608
100.0	2000.0	0.7174	0.7236	-0.0062	-0.870
130.0	500.0	0.6365	0.6307	0.0058	0.907
130.0	1250.0	0.6662	0.6701	-0.0039	-0.584
130.0	1500.0	0.6743	0.6795	-0.0052	-0.776
130.0	1750.0	0.6812	0.6879	-0.0067	-0.989
160.0	800.0	0.6031	0.5997	0.0034	0.559
160.0	1000.0	0.6146	0.6154	-0.0007	-0.119
160.0	1500.0	0.6382	0.6440	-0.0058	-0.908
160.0	2000.0	0.6566	0.6648	-0.0082	-1.250
220.0	500.0	0.1035	0.1025	0.0010	0.966
220.0	1500.0	0.5546	0.5546	0.0000	0.002
220.0	2000.0	0.5858	0.5929	-0.0070	-1.201
250.0	500.0	0.0901	0.0895	0.0006	0.689
250.0	1000.0	0.3893	0.3784	0.0109	2.790
250.0	1500.0	0.5061	0.4979	0.0082	1.615
250.0	2000.0	0.5470	0.5507	-0.0037	-0.678
302.0	425.7	0.0624	0.0622	0.0002	0.302
347.0	1180.1	0.2185	0.2196	-0.0011	-0.489
347.0	1406.8	0.2809	0.2817	-0.0008	-0.274
437.0	535.1	0.0624	0.0624	-0.0000	-0.044
437.0	2104.6	0.3121	0.3107	0.0014	0.446
482.0	3910.0	0.4370	0.4422	-0.0052	-1.201
527.0	605.9	0.0624	0.0625	-0.0001	-0.226
527.0	1132.8	0.1249	0.1255	-0.0006	-0.471
527.0	1872.0	0.2185	0.2198	-0.0013	-0.593
527.0	2404.9	0.2809	0.2823	-0.0014	-0.483

AVERAGE ABSOLUTE DEVIATION = 0.7434%

TABLE 27

COMPARISON OF PREDICTED DENSITIES USING THE OBWR EQUATION WITH EXPERIMENTAL VALUES FOR PROPANE

T (F)	PE (PSIA)	DE (LBMOLE/CF)	DC	DEV	%DEV
-250.0	14.7	0.9933	1.0935	-0.1002	-10.088
-220.0	14.7	0.9707	1.0347	-0.0640	-6.598
-190.0	14.7	0.9480	0.9851	-0.0371	-3.910
-160.0	14.7	0.9253	0.9419	-0.0166	-1.790
-130.0	14.7	0.8981	0.9033	-0.0052	-0.584
-148.0	1000.0	0.9218	0.9294	-0.0076	-0.826
-112.0	2000.0	0.9006	0.8911	0.0095	1.057
-76.0	1000.0	0.8610	0.8481	0.0129	1.503
-40.0	2000.0	0.8411	0.8199	0.0212	2.519
-4.0	1000.0	0.7986	0.7785	0.0201	2.521
-4.0	2000.0	0.8114	0.7881	0.0233	2.869
32.0	2000.0	0.7902	0.7574	0.0228	2.918
100.0	500.0	0.6793	0.6663	0.0130	1.917
100.0	1000.0	0.6940	0.6795	0.0145	2.088
100.0	1500.0	0.7067	0.6905	0.0162	2.297
100.0	2000.0	0.7174	0.7000	0.0174	2.422
130.0	500.0	0.6365	0.6280	0.0085	1.337
130.0	1250.0	0.6662	0.6547	0.0115	1.723
130.0	1500.0	0.6743	0.6616	0.0127	1.881
130.0	1750.0	0.6812	0.6679	0.0133	1.955
160.0	800.0	0.6031	0.5994	0.0037	0.615
160.0	1000.0	0.6146	0.6099	0.0047	0.765
160.0	1500.0	0.6382	0.6303	0.0079	1.234
160.0	2000.0	0.6566	0.6459	0.0107	1.629
220.0	500.0	0.1035	0.1038	-0.0003	-0.287
220.0	1500.0	0.5546	0.5539	0.0007	0.124
220.0	2000.0	0.5858	0.5833	0.0025	0.431
250.0	500.0	0.0901	0.0903	-0.0002	-0.221
250.0	1000.0	0.3893	0.3808	0.0085	2.189
250.0	1500.0	0.5061	0.5032	0.0029	0.579
250.0	2000.0	0.5470	0.5466	0.0004	0.080
302.0	425.7	0.0624	0.0625	-0.0001	-0.118
347.0	1180.1	0.2185	0.2197	-0.0012	-0.553
347.0	1406.8	0.2809	0.2814	-0.0005	-0.181
437.0	535.1	0.0624	0.0624	0.0000	0.034
437.0	2104.6	0.3121	0.3095	0.0026	0.837
482.0	3910.0	0.4370	0.4372	-0.0002	-0.038
527.0	605.9	0.0624	0.0623	0.0001	0.131
527.0	1132.8	0.1249	0.1246	0.0003	0.222
527.0	1872.0	0.2185	0.2176	0.0009	0.391
527.0	2404.9	0.2809	0.2795	0.0014	0.511

AVERAGE ABSOLUTE DEVIATION = 1.5602%

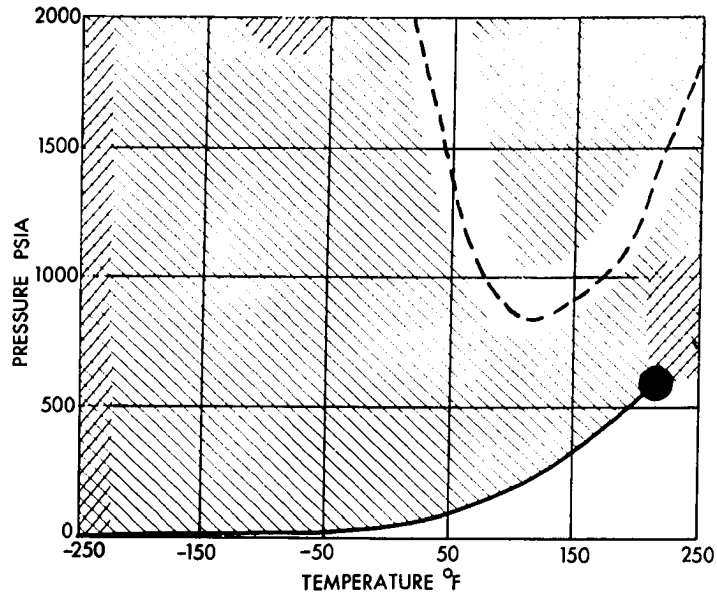


Figure 18. Comparison of Densities Calculated by the Modified BWR Equation with Experimental Values for Propane

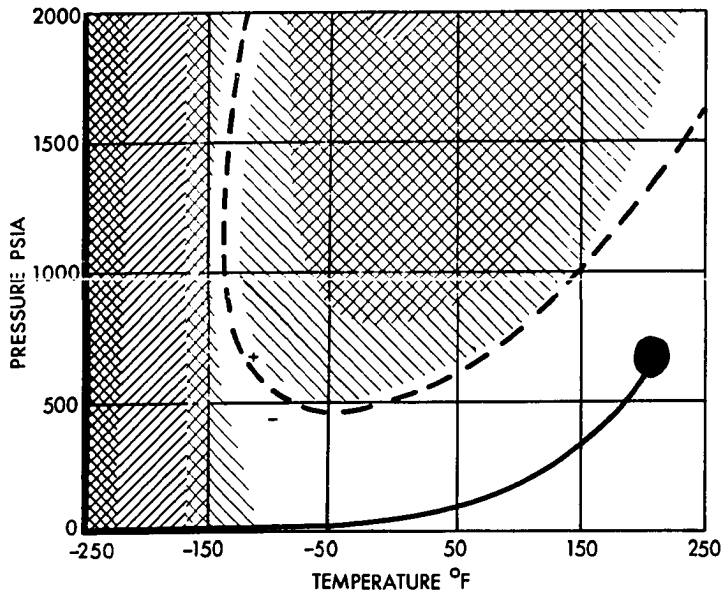


Figure 19. Comparison of Densities Calculated by the Original BWR Equation with Experimental Values for Propane

TABLE 28

COMPARISON OF PREDICTED ENTHALPY DEPARTURES USING THE MBWR EQUATION WITH EXPERIMENTAL VALUES FOR PROPANE.

T (F)	PF (PSIA)	HE (BTU/LBMOLE)	HC (BTU/LBMOLE)	DEV BTU/LB	%DEV
-250.0	500.0	-10071.07	-10123.38	1.19	-0.52
-250.0	1000.0	-9991.70	-10056.64	1.47	-0.65
-250.0	1500.0	-9916.74	-9990.02	1.66	-0.74
-250.0	2000.0	-9890.28	-9923.13	0.74	-0.33
-200.0	500.0	-9599.26	-9571.28	-0.63	0.29
-200.0	1000.0	-9519.89	-9501.89	-0.41	0.19
-200.0	1500.0	-9449.34	-9432.15	-0.39	0.18
-200.0	2000.0	-9414.07	-9362.13	-1.18	0.55
-150.0	500.0	-9131.86	-9120.67	-0.25	0.12
-150.0	1000.0	-9052.50	-9049.95	-0.06	0.03
-150.0	1500.0	-8981.95	-8978.62	-0.08	0.04
-150.0	2000.0	-8937.95	-8906.81	-0.70	0.35
-100.0	500.0	-8642.42	-8656.49	0.32	-0.16
-100.0	1000.0	-8602.73	-8586.40	-0.37	0.19
-100.0	1500.0	-8523.37	-8515.39	-0.18	0.09
-50.0	500.0	-8227.94	-8194.06	-0.77	0.41
-50.0	1000.0	-8152.98	-8127.70	-0.57	0.31
-50.0	1500.0	-8082.43	-8059.57	-0.52	0.28
-50.0	2000.0	-8038.33	-7989.97	-1.10	0.60
0.0	1000.0	-7712.04	-7678.99	-0.75	0.43
0.0	1500.0	-7650.30	-7617.64	-0.74	0.43
0.0	2000.0	-7610.62	-7553.54	-1.29	0.75
50.0	500.0	-7324.01	-7270.05	-1.22	0.74
50.0	1500.0	-7196.14	-7182.26	-0.31	0.19
50.0	2000.0	-7169.68	-7128.71	-0.93	0.57
100.0	500.0	-6794.88	-6755.67	-0.89	0.58
100.0	1500.0	-6733.15	-6735.56	0.05	-0.04
100.0	2000.0	-6719.92	-6701.56	-0.42	0.27
150.0	500.0	-6124.65	-6086.12	-0.87	0.63
150.0	1000.0	-6204.02	-6209.27	0.12	-0.08
150.0	1500.0	-6181.98	-6248.44	1.51	-1.08
200.0	500.0	-1843.13	-1835.50	-0.17	0.41
200.0	1000.0	-5494.11	-5472.55	-0.49	0.39
200.0	1500.0	-5670.48	-5673.45	0.07	-0.05
200.0	2000.0	-5745.45	-5752.43	0.16	-0.12
250.0	500.0	-1314.00	-1311.97	-0.05	0.15
250.0	1000.0	-4246.25	-4221.77	-0.56	0.58
250.0	1500.0	-4964.98	-4941.89	-0.52	0.46
250.0	2000.0	-5172.22	-5173.67	0.03	-0.03

AVERAGE ABSOLUTE DEVIATION = 0.3597%

AVERAGE ABSOLUTE DEVIATION IN BTU/LB = 0.61

TABLE 29

COMPARISON OF PREDICTED ENTHALPY DEPARTURES USING THE OBWR EQUATION WITH EXPERIMENTAL VALUES FOR PROPANE

T (F)	PF (PSIA)	HF (BTU/LBMOLE)	HC (BTU/LBMOLE)	DEV BTU/LB	%DEV
-250.0	500.0	-10071.07	-33234.57	525.32	-230.00
-250.0	1000.0	-9991.70	-33184.56	525.99	-232.12
-250.0	1500.0	-9916.74	-33134.59	526.55	-234.13
-250.0	2000.0	-9890.28	-33084.51	526.02	-234.52
-200.0	500.0	-9599.26	-20094.82	238.03	-109.34
-200.0	1000.0	-9519.89	-20040.68	238.60	-110.51
-200.0	1500.0	-9449.34	-19986.28	238.97	-111.51
-200.0	2000.0	-9414.07	-19931.74	238.53	-111.72
-150.0	500.0	-9131.86	-14101.30	112.70	-54.42
-150.0	1000.0	-9052.50	-14044.34	113.21	-55.14
-150.0	1500.0	-8981.95	-13986.95	113.51	-55.72
-150.0	2000.0	-8937.85	-13929.09	113.20	-55.84
-100.0	500.0	-8642.42	-10999.59	53.46	-27.27
-100.0	1000.0	-8602.73	-10941.42	53.04	-27.19
-100.0	1500.0	-8523.37	-10882.43	53.50	-27.68
-50.0	500.0	-8227.94	-9223.18	22.57	-12.10
-50.0	1000.0	-8152.98	-9166.14	22.98	-12.43
-50.0	1500.0	-8082.43	-9107.60	23.25	-12.68
-50.0	2000.0	-8038.33	-9047.74	22.89	-12.56
0.0	1000.0	-7712.04	-8051.92	7.71	-4.41
0.0	1500.0	-7650.30	-7996.89	7.86	-4.53
0.0	2000.0	-7610.62	-7939.49	7.46	-4.32
50.0	500.0	-7324.01	-7320.00	-0.09	0.05
50.0	1500.0	-7196.14	-7233.62	0.85	-0.52
50.0	2000.0	-7169.68	-7182.79	0.30	-0.18
100.0	500.0	-6794.88	-6688.92	-2.40	1.56
100.0	1500.0	-6733.15	-6649.69	-1.89	1.24
100.0	2000.0	-6719.92	-6612.55	-2.44	1.60
150.0	500.0	-6124.65	-6055.33	-1.57	1.13
150.0	1000.0	-6204.02	-6124.73	-1.80	1.28
150.0	1500.0	-6181.99	-6141.12	-0.93	0.66
200.0	500.0	-1843.13	-1891.93	1.11	-2.65
200.0	1000.0	-5494.11	-5479.57	-0.33	0.26
200.0	1500.0	-5670.48	-5621.94	-1.10	0.86
200.0	2000.0	-5745.45	-5671.59	-1.67	1.29
250.0	500.0	-1314.00	-1365.86	1.18	-3.95
250.0	1000.0	-4246.25	-4216.59	-0.67	0.70
250.0	1500.0	-4964.98	-4980.36	0.35	-0.31
250.0	2000.0	-5172.22	-5172.30	0.00	-0.00

AVERAGE ABSOLUTE DEVIATION = 45.0864%

AVERAGE ABSOLUTE DEVIATION IN BTU/LB = 97.54

Topographical plots of deviations are presented in Figures 20 and 21.

Vapor Pressures. A total of 19 points were taken from API Project 44[111] (-140°F to -60°F) and Canjar and Manning (-43.73°F to 206.26°F). The average absolute deviation was 0.48%. Original BWR equation predictions were compared with the same data set and the average absolute deviation was 10.47%. Predictions of fugacities along the vapor pressure curve using the modified and original BWR equations are presented in Tables 30 and 31.

n-Butane

Source of Data

Comprehensive compilations of the thermodynamic properties of n-butane have been presented by Prengle and coworkers[105], Sage[117] and Canjar and Manning[21].

Results from Regression Analysis

Densities. A total of 32 data points were taken from API Project 44[111] (-220.0°F to 20°F) and Sage and Lacey (100°F to 310°F). The average absolute deviation was 1.35%. Original BWR equation predictions were compared with the same data set, and the average absolute deviation was 1.93%. Comparisons of predicted experimental densities using the modified and original BWR equations are presented in Tables 32 and 33.

Enthalpy Departures. Thirty-nine derived enthalpy departure points were taken from Sage and Lacey (100°F to

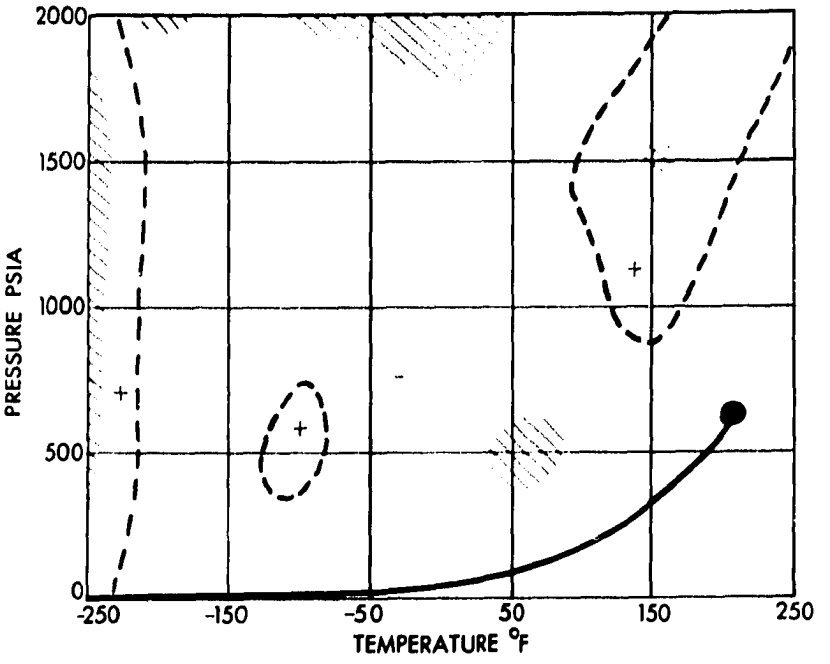


Figure 20. Comparison of Enthalpy Departures Calculated by the Modified BWR Equation with Experimental Values for Propane.

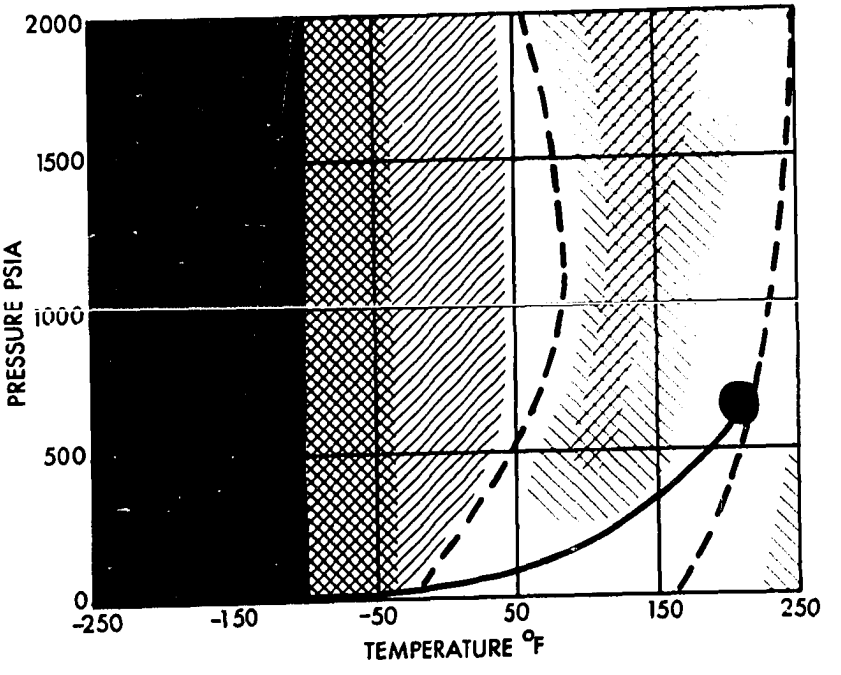


Figure 21. Comparison of Enthalpy Departures Calculated by the Original BWR Equation with Experimental Values for Propane.

TABLE 30

PREDICTION OF SATURATED VAPOR AND LIQUID FUGACITIES FOR PROPANE USING THE MBWR EQUATION

T (F)	PE (PSIA)	FUL (PSIA)	FUG (PSIA)	%DEV
-140.00	0.605	0.5900	0.6025	2.08
-130.00	0.932	0.9093	0.9267	1.88
-120.00	1.394	1.3605	1.3834	1.65
-110.00	2.030	1.9815	2.0096	1.40
-100.00	2.887	2.8159	2.8497	1.19
-90.00	4.017	3.9124	3.9515	0.99
-80.00	5.481	5.3257	5.3700	0.82
-60.00	9.680	9.3382	9.3907	0.56
-43.73	14.696	14.0585	14.1160	0.41
-30.00	20.338	19.2861	19.3459	0.31
-20.00	25.395	23.9158	23.9670	0.21
-10.00	31.376	29.3122	29.3598	0.16
0.0	38.371	35.5388	35.5767	0.11
10.00	46.470	42.6575	42.6654	0.02
20.00	55.807	50.7231	50.7047	-0.04
30.00	66.460	59.7892	59.7202	-0.12
40.00	78.577	69.9037	69.7883	-0.17
50.00	92.231	81.1072	80.9187	-0.23
60.00	107.590	93.4392	93.1876	-0.27
70.00	124.730	106.9264	106.5944	-0.31
80.00	143.820	121.5954	121.1990	-0.33
90.00	164.990	137.4636	137.0235	-0.32
100.00	188.320	154.5397	154.0500	-0.32
110.00	214.020	172.8301	172.3365	-0.29
120.00	242.190	192.3301	191.8605	-0.24
130.00	273.080	213.0353	212.6776	-0.17
140.00	306.760	234.9201	234.7252	-0.08
145.00	325.370	246.3418	246.5473	0.08
150.00	343.520	257.9700	258.0474	0.03
155.00	363.110	269.9216	270.1748	0.09
160.00	383.450	282.1445	282.5652	0.15
165.00	404.730	294.6460	295.2888	0.22
170.00	426.890	307.4185	308.2976	0.29
175.00	450.010	320.4580	321.6028	0.36
180.00	474.060	333.7585	335.1650	0.42
185.00	499.020	347.3115	348.9514	0.47
190.00	525.100	361.1375	363.0022	0.51
195.00	552.230	375.2344	377.2341	0.53
206.26	617.470	408.0886	408.0884	0.0

AVERAGE ABSOLUTE DEVIATION = 0.4567%

TABLE 31

PREDICTION OF SATURATED VAPOR AND LIQUID FUGACITIES FOR PROPANE USING THE OBWR EQUATION

T (F)	PF (PSIA)	FUL (PSIA)	FUG (PSIA)	%DEV
-140.00	0.605	0.2259	0.6025	62.51
-130.00	0.932	0.4210	0.9266	54.57
-120.00	1.394	0.7346	1.3932	46.89
-110.00	2.030	1.2120	2.0093	39.68
-100.00	2.887	1.9053	2.8491	33.13
-90.00	4.017	2.8729	3.9503	27.27
-80.00	5.481	4.1779	5.3679	22.17
-60.00	9.680	8.0653	9.3849	14.06
-43.73	14.696	12.7933	14.1035	9.29
-30.00	20.338	18.1048	19.3237	6.31
-20.00	25.395	22.8345	23.9341	4.59
-10.00	31.376	28.3578	29.3119	3.26
0.0	38.371	34.7279	35.5086	2.20
10.00	46.470	41.9978	42.5704	1.34
20.00	55.807	50.2124	50.5743	0.72
30.00	66.460	59.4151	59.5444	0.22
40.00	78.577	69.6405	69.5549	-0.12
50.00	92.231	80.9246	80.6134	-0.39
60.00	107.590	93.2962	92.7939	-0.54
70.00	124.730	106.7784	106.0933	-0.65
80.00	143.820	121.3926	120.5688	-0.68
90.00	164.990	137.1556	136.2401	-0.67
100.00	188.320	154.0817	153.0872	-0.65
110.00	214.020	172.1815	171.1653	-0.59
120.00	242.190	191.4619	190.4504	-0.53
130.00	273.080	211.9310	210.9959	-0.44
140.00	306.760	233.5859	232.7385	-0.36
145.00	325.370	244.8999	244.3886	-0.21
150.00	343.520	256.4329	255.7231	-0.28
155.00	363.110	268.3030	267.6697	-0.24
160.00	383.450	280.4614	279.8738	-0.21
165.00	404.730	292.9185	292.4038	-0.18
170.00	426.890	305.6660	305.2146	-0.15
175.00	450.010	318.7078	318.3186	-0.12
180.00	474.060	332.0332	331.6833	-0.11
185.00	499.020	345.6311	345.2805	-0.10
190.00	525.100	359.5081	359.1626	-0.10
195.00	552.230	373.6414	373.2737	-0.10
206.26	617.470	405.8464	405.8462	0.0

AVERAGE ABSOLUTE DEVIATION = 8.6053%

TABLE 32

COMPARISON OF PREDICTED DENSITIES USING THE MBWR EQUATION WITH EXPERIMENTAL VALUES FOR n-BUTANE

T (F)	PE (PSIA)	DE (LBMOLE/CF)	DC	DEV	%DEV
-220.0	14.7	0.7932	0.8056	-0.0124	-1.568
-200.0	14.7	0.7846	0.7904	-0.0058	-0.742
-180.0	14.7	0.7725	0.7762	-0.0037	-0.482
-160.0	14.7	0.7607	0.7629	-0.0022	-0.286
-140.0	14.7	0.7476	0.7502	-0.0026	-0.347
-120.0	14.7	0.7352	0.7380	-0.0028	-0.387
-100.0	14.7	0.7235	0.7263	-0.0028	-0.389
-80.0	14.7	0.7118	0.7149	-0.0031	-0.431
-60.0	14.7	0.7006	0.7036	-0.0030	-0.431
-40.0	14.7	0.6891	0.6925	-0.0034	-0.488
-20.0	14.7	0.6774	0.6813	-0.0039	-0.577
0.0	14.7	0.6653	0.6701	-0.0048	-0.715
20.0	14.7	0.6531	0.6586	-0.0055	-0.842
100.0	200.0	0.6010	0.6110	-0.0100	-1.666
100.0	1000.0	0.6127	0.6216	-0.0089	-1.455
100.0	2000.0	0.6246	0.6327	-0.0081	-1.291
100.0	5000.0	0.6494	0.6577	-0.0083	-1.284
160.0	80.0	0.0135	0.0136	-0.0001	-1.027
160.0	400.0	0.5583	0.5696	-0.0113	-2.031
160.0	1250.0	0.5754	0.5872	-0.0118	-2.045
160.0	1750.0	0.5838	0.5954	-0.0116	-1.988
160.0	3500.0	0.6061	0.6179	-0.0118	-1.939
160.0	7000.0	0.6369	0.6484	-0.0115	-1.812
220.0	100.0	0.0152	0.0154	-0.0002	-1.049
220.0	200.0	0.0353	0.0362	-0.0009	-2.527
220.0	400.0	0.5003	0.5048	-0.0045	-0.895
220.0	3000.0	0.5656	0.5794	-0.0138	-2.432
220.0	5000.0	0.5907	0.6061	-0.0154	-2.608
250.0	100.0	0.0144	0.0145	-0.0001	-0.400
250.0	1000.0	0.4948	0.5003	-0.0055	-1.115
250.0	2000.0	0.5266	0.5384	-0.0118	-2.235
280.0	100.0	0.0136	0.0137	-0.0001	-0.593
280.0	200.0	0.0299	0.0304	-0.0005	-1.517
280.0	1250.0	0.4757	0.4775	-0.0018	-0.387
280.0	2750.0	0.5238	0.5362	-0.0124	-2.368
280.0	7000.0	0.5848	0.6021	-0.0173	-2.961
310.0	2000.0	0.4803	0.4859	-0.0056	-1.157
310.0	3000.0	0.5094	0.5218	-0.0124	-2.431
400.0	200.0	0.0238	0.0240	-0.0002	-0.740
430.0	300.0	0.0356	0.0361	-0.0005	-1.381
430.0	400.0	0.0500	0.0509	-0.0009	-1.736

AVERAGE ABSOLUTE DEVIATION = 1.2867%

TABLE 33

COMPARISON OF PREDICTED DENSITIES USING THE OBWR EQUATION WITH EXPERIMENTAL VALUES FOR n-BUTANE

T (F)	PE (PSIA)	DE	DC (LBMOLE/CF)	DEV	%DEV
-220.0	14.7	0.7932	0.8806	-0.0874	-11.018
-200.0	14.7	0.7846	0.8522	-0.0676	-8.611
-180.0	14.7	0.7725	0.8266	-0.0541	-7.001
-160.0	14.7	0.7607	0.8033	-0.0426	-5.601
-140.0	14.7	0.7476	0.7819	-0.0343	-4.591
-120.0	14.7	0.7352	0.7621	-0.0269	-3.659
-100.0	14.7	0.7235	0.7436	-0.0201	-2.776
-80.0	14.7	0.7118	0.7261	-0.0143	-2.014
-60.0	14.7	0.7006	0.7096	-0.0090	-1.282
-40.0	14.7	0.6891	0.6938	-0.0047	-0.675
-20.0	14.7	0.6774	0.6785	-0.0011	-0.163
0.0	14.7	0.6653	0.6637	0.0016	0.241
20.0	14.7	0.6531	0.6492	0.0039	0.597
100.0	200.0	0.6010	0.5941	0.0069	1.145
100.0	1000.0	0.6127	0.6032	0.0095	1.545
100.0	2000.0	0.6246	0.6130	0.0116	1.862
100.0	5000.0	0.6494	0.6357	0.0137	2.111
160.0	80.0	0.0135	0.0135	-0.0000	-0.276
160.0	400.0	0.5583	0.5526	0.0057	1.014
160.0	1250.0	0.5754	0.5672	0.0082	1.431
160.0	1750.0	0.5838	0.5742	0.0096	1.639
160.0	3500.0	0.6061	0.5940	0.0121	1.988
160.0	7000.0	0.6369	0.6219	0.0150	2.350
220.0	100.0	0.0152	0.0152	-0.0000	-0.304
220.0	200.0	0.0353	0.0354	-0.0001	-0.191
220.0	400.0	0.5003	0.4993	0.0010	0.197
220.0	3000.0	0.5656	0.5567	0.0089	1.572
220.0	5000.0	0.5907	0.5802	0.0105	1.781
250.0	100.0	0.0144	0.0144	0.0000	0.240
250.0	1000.0	0.4948	0.4931	0.0017	0.335
250.0	2000.0	0.5266	0.5214	0.0052	0.992
280.0	100.0	0.0136	0.0136	-0.0000	-0.031
280.0	200.0	0.0299	0.0299	-0.0000	-0.077
280.0	1250.0	0.4757	0.4752	0.0005	0.106
280.0	2750.0	0.5238	0.5185	0.0053	1.018
280.0	7000.0	0.5848	0.5746	0.0102	1.739
310.0	2000.0	0.4803	0.4787	0.0016	0.329
310.0	3000.0	0.5094	0.5060	0.0034	0.665
400.0	200.0	0.0238	0.0238	0.0000	0.034
430.0	300.0	0.0356	0.0357	-0.0001	-0.278
430.0	400.0	0.0500	0.0501	-0.0001	-0.161

AVERAGE ABSOLUTE DEVIATION = 1.7962%

250°F). The average absolute deviation was 1.65%. Original BWR equation predictions were compared with the same data set, and the average absolute deviation was 2.0%. Seven points from the 130°F isotherm showed a relative deviation exceeding -5.0% using both the modified and original BWR equations. This tends to indicate inconsistency in the derived enthalpy departures at 130°F. Comparisons of predicted and derived enthalpy departures using the modified and original BWR equations are presented in Tables 34 and 35.

Vapor Pressures. A total of 25 points were taken from API Project 44[111] (-110°F to 25°F) and Canjar and Manning (31.1°F to 305.62°F). The average absolute deviation was 0.38%. Original BWR equation predictions were compared with the same data set, and the average absolute deviation was 13.7%. Predictions of fugacities along the vapor pressure curve using the modified and original BWR equations are presented in Tables 36 and 37.

n-Pentane

Source of Data

Comprehensive compilations of the thermodynamic properties of n-pentane have been presented by Sage and Lacey[112] and Canjar and Manning[21]. Limited experimental enthalpy data were reported by Gilliland[51].

TABLE 34

COMPARISON OF PREDICTED ENTHALPY DEPARTURE USING THE MBWR EQUATION WITH EXPERIMENTAL VALUES FOR n-BUTANE

T (F)	PE (PSIA)	HE (BTU/LBMOLE)	HC (BTU/LBMOLE)	DEV BTU/LB	%DEV
100.0	200.0	-8958.20	-8998.56	0.69	-0.45
100.0	600.0	-8915.19	-8950.16	0.60	-0.39
100.0	1000.0	-8868.49	-8897.14	0.49	-0.32
100.0	1500.0	-8799.88	-8825.89	0.45	-0.30
100.0	3000.0	-8593.59	-8588.30	-0.09	0.06
100.0	4000.0	-8438.50	-8416.34	-0.38	0.26
160.0	200.0	-8331.09	-8385.26	0.93	-0.65
160.0	400.0	-8329.90	-8382.51	0.91	-0.63
160.0	800.0	-8314.19	-8364.46	0.86	-0.60
160.0	1500.0	-8263.09	-8306.18	0.74	-0.52
160.0	3000.0	-8096.30	-8118.64	0.38	-0.28
160.0	5000.0	-7815.00	-7802.32	-0.22	0.16
190.0	600.0	-7972.49	-8051.39	1.36	-0.99
190.0	1250.0	-7963.70	-8048.09	1.45	-1.06
190.0	2000.0	-7914.89	-7996.92	1.41	-1.04
190.0	3000.0	-7816.10	-7887.36	1.23	-0.91
190.0	5000.0	-7555.79	-7596.11	0.69	-0.53
220.0	600.0	-7604.00	-7669.54	1.13	-0.86
220.0	1000.0	-7638.80	-7727.06	1.52	-1.16
220.0	3000.0	-7552.20	-7652.93	1.73	-1.33
220.0	5000.0	-7319.20	-7393.19	1.27	-1.01
250.0	800.0	-7251.79	-7272.51	0.36	-0.29
250.0	1500.0	-7337.20	-7425.46	1.52	-1.20
250.0	3000.0	-7297.09	-7411.53	1.97	-1.57
250.0	4000.0	-7209.39	-7316.93	1.85	-1.49
250.0	5000.0	-7094.30	-7191.11	1.67	-1.36
310.0	2000.0	-6780.40	-6800.00	0.34	-0.29
310.0	3000.0	-6817.09	-6894.35	1.33	-1.13
310.0	4000.0	-6777.00	-6866.01	1.53	-1.31
340.0	3000.0	-6560.70	-6613.79	0.91	-0.81
340.0	4000.0	-6554.30	-6629.39	1.29	-1.15
370.0	2000.0	-6114.30	-6018.34	-1.65	1.57
370.0	3000.0	-6304.40	-6318.20	0.24	-0.22
370.0	4000.0	-6333.39	-6384.40	0.88	-0.81
400.0	1000.0	-4007.40	-4033.20	0.44	-0.64
400.0	3000.0	-6065.20	-6010.60	-0.94	0.90
400.0	4000.0	-6109.09	-6131.60	0.39	-0.37
430.0	2000.0	-5355.79	-5194.32	-2.78	3.01
430.0	3000.0	-5726.59	-5696.77	-0.51	0.52

AVERAGE ABSOLUTE DEVIATION = 0.8249%

AVERAGE ABSOLUTE DEVIATION IN BTU/LB = 1.00

TABLE 35

COMPARISON OF PREDICTED ENTHALPY DEPARTURES USING THE OBWR EQUATION WITH DERIVED VALUES FOR n-BUTANE

T (F)	PF (PSIA)	HE (BTU/LBMOLE)	HC (BTU/LBMOLE)	DEV BTU/LB	%DEV
100.0	200.0	-8958.20	-9196.38	4.10	-2.66
100.0	600.0	-8915.19	-9153.68	4.10	-2.68
100.0	1000.0	-8868.49	-9106.94	4.10	-2.69
100.0	1500.0	-8799.88	-9043.79	4.20	-2.77
100.0	3000.0	-8593.59	-8831.55	4.09	-2.77
100.0	4000.0	-8438.50	-8676.48	4.09	-2.82
160.0	200.0	-8331.09	-8320.68	-0.18	0.12
160.0	400.0	-8329.90	-8314.06	-0.27	0.19
160.0	800.0	-8314.19	-8291.75	-0.39	0.27
160.0	1500.0	-8263.09	-8231.92	-0.54	0.38
160.0	3000.0	-8096.30	-8050.68	-0.78	0.56
160.0	5000.0	-7815.00	-7749.12	-1.13	0.84
190.0	600.0	-7972.49	-7924.77	-0.82	0.60
190.0	1250.0	-7963.70	-7903.46	-1.04	0.76
190.0	2000.0	-7914.89	-7843.91	-1.22	0.90
190.0	3000.0	-7816.10	-7731.17	-1.46	1.09
190.0	5000.0	-7555.79	-7443.40	-1.93	1.49
220.0	600.0	-7604.00	-7544.63	-1.02	0.78
220.0	1000.0	-7638.80	-7566.67	-1.24	0.94
220.0	3000.0	-7552.20	-7441.38	-1.91	1.47
220.0	5000.0	-7319.20	-7171.95	-2.53	2.01
250.0	800.0	-7251.79	-7178.99	-1.25	1.00
250.0	1500.0	-7337.20	-7242.89	-1.62	1.29
250.0	3000.0	-7297.09	-7171.72	-2.16	1.72
250.0	4000.0	-7209.39	-7061.41	-2.55	2.05
250.0	5000.0	-7094.30	-6925.97	-2.90	2.37
310.0	2000.0	-6780.40	-6648.45	-2.27	1.95
310.0	3000.0	-6817.09	-6663.55	-2.64	2.25
310.0	4000.0	-6777.00	-6594.90	-3.13	2.69
340.0	3000.0	-6560.70	-6413.75	-2.53	2.24
340.0	4000.0	-6554.30	-6373.53	-3.11	2.76
370.0	2000.0	-6114.30	-6003.35	-1.91	1.81
370.0	3000.0	-6304.40	-6161.10	-2.47	2.27
370.0	4000.0	-6333.39	-6155.21	-3.07	2.81
400.0	1000.0	-4007.40	-3972.11	-0.61	0.88
400.0	3000.0	-6065.20	-5902.86	-2.79	2.68
400.0	4000.0	-6109.09	-5937.40	-2.95	2.81
430.0	2000.0	-5355.79	-5265.45	-1.55	1.69
430.0	3000.0	-5726.59	-5637.73	-1.53	1.55

AVERAGE ABSOLUTE DEVIATION = 1.6822%

AVERAGE ABSOLUTE DEVIATION IN BTU/LB = 2.11

TABLE 36

PREDICTION OF SATURATED VAPOR AND LIQUID FUGACITIES FOR n-BUTANE USING THE MBWR EQUATION

T (F)	PE (PSIA)	FUL (PSIA)	FUG (PSIA)	%DEV
-110.00	0.176	0.1738	0.1757	1.11
-95.00	0.342	0.3401	0.3411	0.28
-85.00	0.515	0.5129	0.5131	0.04
-75.00	0.755	0.7532	0.7512	-0.27
-65.00	1.082	1.0799	1.0749	-0.46
-50.00	1.787	1.7800	1.7700	-0.57
-40.00	2.439	2.4237	2.4099	-0.58
-30.00	3.273	3.2425	3.2246	-0.56
-15.00	4.950	4.8683	4.8514	-0.35
0.0	7.250	7.0754	7.0609	-0.21
15.00	10.330	9.9890	9.9855	-0.04
25.00	12.900	12.3897	12.3991	0.08
31.10	14.696	14.0549	14.0726	0.13
40.00	17.620	16.7784	16.7763	-0.01
50.00	21.550	20.2896	20.3691	0.39
60.00	26.020	24.3154	24.4068	0.37
70.00	31.200	28.8969	29.0238	0.44
80.00	37.140	34.0721	34.2431	0.50
90.00	43.910	39.8803	40.1014	0.55
100.00	51.370	46.3523	46.4615	0.23
110.00	60.270	53.5313	53.9007	0.69
120.00	69.980	61.4407	61.8766	0.70
130.00	80.830	70.1117	70.6172	0.72
140.00	92.870	79.5679	80.1213	0.69
150.00	106.200	89.8335	90.4203	0.65
160.00	120.900	100.9270	101.5249	0.59
170.00	137.000	112.8578	113.4077	0.48
180.00	154.680	125.6405	126.1355	0.39
190.00	173.800	139.2703	139.5663	0.21
200.00	194.700	153.7557	153.8533	0.06
210.00	217.400	169.0780	168.9405	-0.08
220.00	241.600	185.1991	184.6048	-0.32
230.00	268.200	202.1209	201.2547	-0.43
240.00	297.200	219.7818	218.7764	-0.46
250.00	328.300	238.0542	236.9267	-0.48
260.00	361.900	256.7546	255.7754	-0.38
270.00	398.200	275.6321	275.2507	-0.14
280.00	437.300	294.8416	295.1619	0.11
305.62	550.700	348.1853	348.1853	0.0

AVERAGE ABSOLUTE DEVIATION = 0.3774%

TABLE 37

PREDICTION OF SATURATED VAPOR AND LIQUID FUGACITIES FOR n-BUTANE USING THE OBWR EQUATION

T (F)	PE (PSIA)	FUL (PSIA)	FUG (PSIA)	%DEV
-110.00	0.176	0.0478	0.1757	72.79
-95.00	0.342	0.1288	0.3411	62.23
-85.00	0.515	0.2302	0.5131	55.13
-75.00	0.755	0.3897	0.7513	48.13
-65.00	1.082	0.6292	1.0750	41.47
-50.00	1.787	1.1965	1.7702	32.41
-40.00	2.439	1.7582	2.4103	27.06
-30.00	3.273	2.5070	3.2254	22.27
-15.00	4.950	4.0636	4.8535	16.27
0.0	7.250	6.2603	7.0655	11.40
15.00	10.330	9.2372	9.9949	7.58
25.00	12.900	11.7246	12.4138	5.55
31.10	14.696	13.4604	14.0916	4.48
40.00	17.620	16.3127	16.8035	2.92
50.00	21.550	20.0018	20.4091	2.00
60.00	26.020	24.2392	24.4642	0.92
70.00	31.200	29.0608	29.1049	0.15
80.00	37.140	34.5019	34.3557	-0.43
90.00	43.910	40.5920	40.2554	-0.84
100.00	51.370	47.3603	46.6674	-1.48
110.00	60.270	54.8427	54.1771	-1.23
120.00	69.980	63.0538	62.2399	-1.31
130.00	80.830	72.0200	71.0894	-1.31
140.00	92.870	81.7596	80.7280	-1.28
150.00	106.200	92.2892	91.1922	-1.20
160.00	120.900	103.6291	102.4979	-1.10
170.00	137.000	115.7836	114.6228	-1.01
180.00	154.680	128.7728	127.6413	-0.89
190.00	173.800	142.5896	141.4147	-0.83
200.00	194.700	157.2556	156.1092	-0.73
210.00	217.400	172.7657	171.6768	-0.63
220.00	241.600	189.1027	187.8934	-0.64
230.00	268.200	206.3048	205.2023	-0.54
240.00	297.200	224.3662	223.5058	-0.38
250.00	328.300	243.2586	242.5661	-0.29
260.00	361.900	262.9841	262.4915	-0.19
270.00	398.200	283.5381	283.2634	-0.10
280.00	437.300	304.8879	304.7971	-0.03
305.62	550.700	362.5295	362.5295	0.0

AVERAGE ABSOLUTE DEVIATION = 11.0050%

Results from Regression Analysis

Densities. A total of 40 points were taken from API Project 44[111] (-200°F to 80°F) and Sage and Lacey (100°F to 460°F). The average absolute deviation was 0.59%. Original BWR equation predictions were compared with the same data set, and the average absolute deviation was 2.33%. Comparisons of predicted and experimental densities using the modified and original BWR equations are presented in Tables 38 and 39.

Enthalpy Departures. A total of 30 derived enthalpy departure points were taken from Sage and Lacey (100°F to 460°F) and Canjar and Manning (540°F to 800°F). The average absolute deviation was 0.88%. Original BWR equation predictions were compared with the same data set, and the average absolute deviation was 3.0%. Comparisons of predicted and derived enthalpy departures using the modified and original BWR equations are presented in Tables 40 and 41.

Vapor Pressures. A total of 34 points were taken from API Project 44[111] (-50.0°F to 30°F) and Canjar and Manning (50°F to 385.9°F). The average absolute deviation was 0.35%. Original BWR equation predictions were compared with the same data set, and the average absolute deviation was 10.2%. Predictions of fugacities along the vapor pressure curve using the modified and original BWR equations are presented in Tables 42 and 43.

TABLE 38

COMPARISON OF PREDICTED DENSITIES USING THE MBWR EQUATION WITH EXPERIMENTAL VALUES FOR n-PENTANE

T (F)	PE (PSIA)	DE (LBMOLE/CF)	DC	DEV	%DEV
-200.0	14.7	0.6584	0.6669	-0.0085	-1.293
-160.0	14.7	0.6412	0.6437	-0.0025	-0.389
-120.0	14.7	0.6239	0.6231	0.0008	0.123
-60.0	14.7	0.5986	0.5955	0.0031	0.520
-10.0	14.7	0.5772	0.5741	0.0031	0.538
80.0	14.7	0.5359	0.5363	-0.0004	-0.070
100.0	150.0	0.5266	0.5286	-0.0020	-0.381
100.0	2000.0	0.5373	0.5409	-0.0036	-0.669
100.0	4000.0	0.5479	0.5517	-0.0038	-0.690
130.0	7000.0	0.5531	0.5566	-0.0035	-0.625
160.0	30.0	0.0048	0.0048	-0.0000	-0.327
160.0	400.0	0.4968	0.5039	-0.0071	-1.433
160.0	4000.0	0.5274	0.5321	-0.0047	-0.898
190.0	60.0	0.0097	0.0097	-0.0000	-0.012
190.0	1000.0	0.4883	0.4965	-0.0082	-1.687
190.0	10000.0	0.5525	0.5540	-0.0015	-0.265
220.0	40.0	0.0058	0.0058	-0.0000	-0.781
220.0	3000.0	0.4978	0.5040	-0.0062	-1.237
250.0	60.0	0.0086	0.0086	0.0000	0.252
250.0	8000.0	0.5236	0.5293	-0.0057	-1.086
280.0	100.0	0.0143	0.0144	-0.0001	-0.393
280.0	6000.0	0.5015	0.5081	-0.0066	-1.324
310.0	50.0	0.0064	0.0064	0.0000	0.393
310.0	200.0	0.0317	0.0317	-0.0000	-0.077
310.0	10000.0	0.5200	0.5253	-0.0053	-1.026
340.0	50.0	0.0061	0.0061	0.0000	0.082
340.0	300.0	0.0534	0.0534	0.0000	0.065
340.0	2500.0	0.4386	0.4472	-0.0086	-1.963
340.0	4500.0	0.4666	0.4751	-0.0085	-1.828
370.0	200.0	0.0270	0.0271	-0.0001	-0.432
370.0	400.0	0.0811	0.0811	0.0000	0.001
370.0	7000.0	0.4808	0.4894	-0.0086	-1.797
400.0	200.0	0.0253	0.0255	-0.0002	-0.649
400.0	500.0	0.1111	0.1124	-0.0013	-1.192
400.0	10000.0	0.4941	0.5036	-0.0095	-1.931
430.0	600.0	0.1314	0.1325	-0.0011	-0.842
430.0	3000.0	0.4039	0.4124	-0.0085	-2.101
430.0	8000.0	0.4706	0.4809	-0.0103	-2.186
460.0	200.0	0.0227	0.0229	-0.0002	-0.755
460.0	400.0	0.0531	0.0539	-0.0008	-1.535
460.0	2750.0	0.3808	0.3887	-0.0079	-2.075

AVERAGE ABSOLUTE DEVIATION = 0.8763%

TABLE 39

COMPARISON OF PREDICTED DENSITIES USING THE OBWR EQUATION WITH EXPERIMENTAL VALUES FOR n-PENTANE

T (F)	PE (PSIA)	DE (LBMOLE/CF)	DC	DEV	%DEV
-200.0	14.7	0.6584	0.7400	-0.0816	-12.392
-160.0	14.7	0.6412	0.6968	-0.0556	-8.664
-120.0	14.7	0.6239	0.6605	-0.0366	-5.869
-60.0	14.7	0.5986	0.6150	-0.0164	-2.733
-10.0	14.7	0.5772	0.5824	-0.0052	-0.901
80.0	14.7	0.5359	0.5308	0.0051	0.943
100.0	150.0	0.5266	0.5210	0.0056	1.070
100.0	2000.0	0.5373	0.5322	0.0051	0.955
100.0	4000.0	0.5479	0.5421	0.0058	1.065
130.0	7000.0	0.5531	0.5434	0.0097	1.746
160.0	30.0	0.0048	0.0048	-0.0000	-0.979
160.0	400.0	0.4968	0.4916	0.0052	1.046
160.0	4000.0	0.5274	0.5181	0.0093	1.762
190.0	60.0	0.0097	0.0098	-0.0001	-1.121
190.0	1000.0	0.4883	0.4826	0.0057	1.165
190.0	10000.0	0.5525	0.5366	0.0159	2.879
220.0	40.0	0.0058	0.0059	-0.0001	-1.245
220.0	3000.0	0.4978	0.4882	0.0096	1.932
250.0	60.0	0.0086	0.0086	-0.0000	-0.272
250.0	8000.0	0.5236	0.5107	0.0129	2.463
280.0	100.0	0.0143	0.0145	-0.0002	-1.091
280.0	6000.0	0.5015	0.4902	0.0113	2.261
310.0	50.0	0.0064	0.0064	0.0000	0.198
310.0	200.0	0.0317	0.0322	-0.0005	-1.468
310.0	10000.0	0.5200	0.5053	0.0147	2.830
340.0	50.0	0.0061	0.0061	-0.0000	-0.044
340.0	300.0	0.0534	0.0546	-0.0012	-2.163
340.0	2500.0	0.4386	0.4342	0.0044	1.005
340.0	4500.0	0.4666	0.4591	0.0075	1.614
370.0	200.0	0.0270	0.0272	-0.0002	-0.881
370.0	400.0	0.0811	0.0842	-0.0031	-3.766
370.0	7000.0	0.4908	0.4717	0.0091	1.900
400.0	200.0	0.0253	0.0255	-0.0002	-0.875
400.0	500.0	0.1111	0.1200	-0.0089	-7.998
400.0	10000.0	0.4941	0.4841	0.0100	2.019
430.0	600.0	0.1314	0.1415	-0.0101	-7.673
430.0	3000.0	0.4039	0.4050	-0.0011	-0.266
430.0	8000.0	0.4706	0.4637	0.0069	1.476
460.0	200.0	0.0227	0.0229	-0.0002	-0.727
460.0	400.0	0.0531	0.0540	-0.0009	-1.692
460.0	2750.0	0.3808	0.3859	-0.0051	-1.343

AVERAGE ABSOLUTE DEVIATION = 2.3047%

TABLE 40

COMPARISON OF PREDICTED ENTHALPY DEPARTURES USING THE MBWR EQUATION WITH DERIVED VALUES FOR n-PENTANE

T (F)	PF (PSIA)	HF (BTU/LBMOLE)	HC (BTU/LBMOLE)	DEV BTU/LB	%DEV
100.0	200.0	-11177.50	-11142.00	-0.49	0.32
100.0	2000.0	-10868.72	-10778.98	-1.24	0.83
100.0	4000.0	-10453.95	-10341.90	-1.55	1.07
100.0	10000.0	-9037.73	-8928.62	-1.51	1.21
130.0	5000.0	-9905.36	-9831.44	-1.02	0.75
130.0	6000.0	-9675.96	-9602.64	-1.02	0.76
130.0	9000.0	-8965.22	-8894.18	-0.98	0.79
160.0	400.0	-10433.82	-10479.29	0.63	-0.44
160.0	3000.0	-10000.95	-9997.40	-0.05	0.04
160.0	5000.0	-9584.66	-9568.00	-0.23	0.17
160.0	7000.0	-9130.87	-9112.48	-0.25	0.20
160.0	10000.0	-8426.72	-8400.18	-0.37	0.32
190.0	800.0	-10026.92	-10117.17	1.25	-0.90
190.0	1500.0	-9936.02	-10008.42	1.00	-0.73
190.0	3000.0	-9687.16	-9734.77	0.66	-0.49
190.0	5000.0	-9284.57	-9319.88	0.49	-0.38
190.0	7000.0	-8843.78	-8877.54	0.40	-0.33
220.0	2750.0	-9451.13	-9525.09	1.03	-0.78
250.0	3000.0	-9129.77	-9228.88	1.37	-1.09
250.0	5000.0	-8774.03	-8854.84	1.12	-0.92
250.0	8000.0	-8155.02	-8206.57	0.71	-0.63
280.0	2500.0	-8909.30	-9047.13	1.91	-1.55
280.0	5000.0	-8520.48	-8631.98	1.55	-1.31
280.0	7000.0	-8121.49	-8222.38	1.40	-1.24
310.0	200.0	-1219.99	-1238.32	0.25	-1.50
310.0	4000.0	-8392.16	-8582.68	2.64	-2.27
310.0	9000.0	-7473.24	-7587.37	1.58	-1.53
340.0	5000.0	-8091.03	-8193.64	1.42	-1.27
340.0	8000.0	-7557.39	-7616.29	0.82	-0.78
340.0	10000.0	-7156.09	-7179.86	0.33	-0.33
400.0	2000.0	-7818.59	-7836.68	0.25	-0.23
400.0	4000.0	-7859.59	-7865.77	0.09	-0.08
400.0	8000.0	-7316.54	-7242.59	-1.02	1.01
430.0	1500.0	-7188.77	-7182.31	-0.09	0.09
430.0	4500.0	-7531.75	-7579.46	0.66	-0.63
430.0	6000.0	-7384.39	-7397.39	0.18	-0.18
430.0	9000.0	-6911.15	-6864.13	-0.65	0.68
460.0	5000.0	-7222.89	-7300.85	1.08	-1.08
460.0	9000.0	-6710.88	-6688.21	-0.31	0.34

AVERAGE ABSOLUTE DEVIATION = 0.7493%

AVERAGE ABSOLUTE DEVIATION IN BTU/LB = 0.86

TABLE 41

COMPARISON OF PREDICTED ENTHALPY DEPARTURES USING THE OBWR EQUATION WITH DERIVED VALUES FOR n-PENTANE

T (F)	PE (PSIA)	HE (BTU/LBMOLE)	HC (BTU/LBMOLE)	DEV BTU/LB	%DEV
100.0	200.0	-11177.50	-11811.30	8.78	-5.67
100.0	2000.0	-10868.72	-11511.70	8.91	-5.92
100.0	4000.0	-10453.95	-11139.26	9.50	-6.56
100.0	10000.0	-9037.73	-9896.38	11.90	-9.50
130.0	500.0	-9905.36	-10307.60	5.58	-4.06
130.0	6000.0	-9675.96	-10103.67	5.93	-4.42
130.0	9000.0	-8965.22	-9465.27	6.93	-5.58
160.0	400.0	-10433.82	-10590.85	2.18	-1.50
160.0	3000.0	-10000.95	-10171.39	2.36	-1.70
160.0	5000.0	-9584.66	-9784.38	2.77	-2.08
160.0	7000.0	-9130.87	-9368.23	3.29	-2.60
160.0	10000.0	-8426.72	-8710.97	3.94	-3.37
190.0	800.0	-10026.92	-10073.06	0.64	-0.46
190.0	1500.0	-9936.02	-9976.99	0.57	-0.41
190.0	3000.0	-9687.16	-9728.76	0.58	-0.43
190.0	5000.0	-9284.57	-9345.43	0.84	-0.66
190.0	7000.0	-8843.78	-8927.89	1.17	-0.95
220.0	2750.0	-9451.13	-9389.95	-0.85	0.65
250.0	3000.0	-9129.77	-9011.20	-1.64	1.30
250.0	5000.0	-8774.03	-8644.54	-1.79	1.48
250.0	8000.0	-8155.02	-8011.55	-1.99	1.76
280.0	2500.0	-8909.30	-8781.31	-1.77	1.44
280.0	5000.0	-8520.48	-8355.83	-2.28	1.93
280.0	7000.0	-8121.49	-7945.69	-2.44	2.16
310.0	200.0	-1219.99	-1378.15	2.19	-12.96
310.0	4000.0	-8392.16	-8275.21	-1.62	1.39
310.0	9000.0	-7473.24	-7252.99	-3.05	2.95
340.0	5000.0	-8091.03	-7856.82	-3.25	2.89
340.0	8000.0	-7557.39	-7248.39	-4.28	4.09
340.0	10000.0	-7156.09	-6799.51	-4.94	4.98
400.0	2000.0	-7818.59	-7682.02	-1.89	1.75
400.0	4000.0	-7859.59	-7571.00	-4.00	3.67
400.0	8000.0	-7316.54	-6847.05	-6.51	6.42
430.0	1500.0	-7188.77	-7241.68	0.73	-0.74
430.0	4500.0	-7531.75	-7292.10	-3.32	3.18
430.0	6000.0	-7384.39	-7054.85	-4.57	4.46
430.0	9000.0	-6911.15	-6452.45	-6.36	6.64
460.0	5000.0	-7222.89	-7023.43	-2.76	2.76
460.0	9000.0	-6710.88	-6284.10	-5.92	6.36

AVERAGE ABSOLUTE DEVIATION = 3.3804%

AVERAGE ABSOLUTE DEVIATION IN BTU/LB = 3.69

TABLE 42

PREDICTION OF SATURATED VAPOR AND LIQUID FUGACITIES FOR n-PENTANE USING THE MBWR EQUATION

T (F)	PE (PSIA)	FUL (PSIA)	FUG (PSIA)	%DEV
-50.00	0.268	0.2654	0.2674	0.76
-40.00	0.392	0.3897	0.3909	0.31
-30.00	0.562	0.5594	0.5598	0.08
-20.00	0.789	0.7866	0.7850	-0.20
-10.00	1.088	1.0851	1.0810	-0.38
0.0	1.475	1.4708	1.4631	-0.53
10.00	1.970	1.9616	1.9503	-0.58
20.00	2.594	2.5772	2.5622	-0.59
30.00	3.370	3.3388	3.3199	-0.57
50.00	5.487	5.3953	5.3711	-0.45
70.00	8.559	8.3351	8.3114	-0.29
96.93	14.696	14.0836	14.0784	-0.04
100.00	15.570	14.8924	14.8895	-0.02
110.00	18.690	17.7690	17.7663	-0.02
120.00	22.300	21.0413	21.0598	0.09
130.00	26.420	24.7392	24.7765	0.15
140.00	31.110	28.8926	28.9566	0.22
150.00	36.400	33.5294	33.6115	0.24
160.00	42.370	38.6791	38.7931	0.29
170.00	49.050	44.3679	44.5076	0.31
180.00	56.490	50.6217	50.7761	0.30
190.00	64.770	57.4658	57.6404	0.30
200.00	73.890	64.9217	65.0761	0.24
210.00	83.940	73.0094	73.1271	0.16
220.00	94.990	81.7505	81.8169	0.08
230.00	107.100	91.1605	91.1577	-0.00
240.00	120.300	101.2542	101.1378	-0.12
250.00	134.700	112.0423	111.7974	-0.22
260.00	150.300	123.5337	123.0987	-0.35
270.00	167.300	135.7400	135.1291	-0.45
280.00	185.600	148.6555	147.7823	-0.59
290.00	205.400	162.2850	161.1332	-0.71
310.00	249.700	191.6504	189.8351	-0.96
330.00	300.700	223.6875	221.0711	-1.18
350.00	359.400	258.0273	254.8188	-1.26
370.00	426.800	290.8762	290.8762	0.0
385.92	489.500	321.5981	321.5977	-0.00

AVERAGE ABSOLUTE DEVIATION = 0.3525%

TABLE 43

PREDICTION OF SATURATED VAPOR AND LIQUID FUGACITIES FOR n-PENTANE USING THE OBWR EQUATION

T (F)	PE (PSIA)	FUL (PSIA)	FUG (PSIA)	%DEV
-50.00	0.268	0.1051	0.2673	60.69
-40.00	0.392	0.1795	0.3906	54.04
-30.00	0.562	0.2929	0.5594	47.64
-20.00	0.789	0.4588	0.7843	41.50
-10.00	1.088	0.6934	1.0798	35.79
0.0	1.475	1.0150	1.4611	30.53
10.00	1.970	1.4443	1.9470	25.82
20.00	2.594	2.0040	2.5571	21.63
30.00	3.370	2.7180	3.3122	17.94
50.00	5.487	4.7133	5.3545	11.97
70.00	8.559	7.6457	8.2786	7.64
96.93	14.696	13.4668	14.0051	3.84
100.00	15.570	14.2881	14.8098	3.52
110.00	18.690	17.2107	17.6626	2.56
120.00	22.300	20.5317	20.9265	1.89
130.00	26.420	24.2773	24.6076	1.34
140.00	31.110	28.4711	28.7451	0.95
150.00	36.400	33.1369	33.3501	0.64
160.00	42.370	38.2977	38.4734	0.46
170.00	49.050	43.9727	44.1211	0.34
180.00	56.490	50.1828	50.3139	0.26
190.00	64.770	56.9458	57.0927	0.26
200.00	73.890	64.2796	64.4343	0.24
210.00	83.940	72.1971	72.3818	0.26
220.00	94.990	80.7185	80.9590	0.30
230.00	107.100	89.8524	90.1786	0.36
240.00	120.300	99.6122	100.0302	0.42
250.00	134.700	110.0089	110.5543	0.49
260.00	150.300	121.0502	121.7155	0.55
270.00	167.300	132.7514	133.6003	0.64
280.00	185.600	145.1089	146.1070	0.68
290.00	205.400	158.1391	159.3104	0.74
310.00	249.700	186.2181	187.7235	0.80
330.00	300.700	217.0006	218.6906	0.77
350.00	359.400	250.4826	252.1774	0.67
370.00	426.800	286.5825	287.8687	0.45
385.92	489.500	317.1841	317.1838	0.0

AVERAGE ABSOLUTE DEVIATION = 10.2326%

n-Hexane

Source of Data

Literature sources for the thermodynamic properties of n-hexane are not extensive. PVT Data have been reported by Kelso and Felsing[69], Stewart and coworkers[121]. Save for a few measurements on liquid heat capacity[59] and latent heat of vaporization[60], calorimetric data are virtually nonexistent. Relying on PVT data and the BWR equation of state, Weber[135] derived enthalpy departures in the vapor phase (up to 520°F, 600 psia). Canjar and Manning's compilation[21] is based exclusively on the work by Weber. Because of the uncertainty and scarcity of the derived enthalpy departure data, this data type was not included in the n-hexane multiproperty regression calculations.

Results from Regression Analysis

Densities. A total of 38 points were taken from API Project 44[111] (-140°F to 140°F) and Stewart and coworkers (110°F to 340°F). The average absolute deviation was 1.05%. Original BWR equation predictions were compared with data set, and the average absolute deviation was 2.7%. Comparisons of predicted and experimental densities using the modified and original BWR equations are presented in Tables 44 and 45.

Vapor Pressures. A total of 30 points were taken from API Project 44[111] (-10°F to 30°F) and Canjar and Manning (32°F to 454.5°F). The average absolute deviation was 0.25%.

TABLE 44

COMPARISON OF PREDICTED DENSITIES USING THE MBWR EQUATION WITH EXPERIMENTAL VALUES FOR n-HEXANE

T (F)	PE (PSIA)	DE (LBMOLE/CF)	DC	DEV	%DEV
-140.0	14.7	0.5492	0.5618	-0.0126	-2.287
-130.0	14.7	0.5458	0.5563	-0.0105	-1.921
-120.0	14.7	0.5424	0.5510	-0.0086	-1.585
-110.0	14.7	0.5392	0.5459	-0.0067	-1.239
-100.0	14.7	0.5358	0.5409	-0.0051	-0.958
-90.0	14.7	0.5324	0.5361	-0.0037	-0.700
-80.0	14.7	0.5291	0.5315	-0.0024	-0.447
-70.0	14.7	0.5257	0.5269	-0.0012	-0.233
-60.0	14.7	0.5223	0.5225	-0.0002	-0.039
-50.0	14.7	0.5190	0.5182	0.0008	0.155
-40.0	14.7	0.5156	0.5140	0.0016	0.313
-20.0	14.7	0.5087	0.5058	0.0029	0.562
0.0	14.7	0.5018	0.4980	0.0038	0.754
20.0	14.7	0.4947	0.4905	0.0042	0.854
40.0	14.7	0.4875	0.4832	0.0043	0.889
60.0	14.7	0.4806	0.4761	0.0045	0.947
80.0	14.7	0.4732	0.4691	0.0041	0.867
100.0	14.7	0.4659	0.4623	0.0036	0.779
120.0	14.7	0.4583	0.4555	0.0028	0.602
140.0	14.7	0.4502	0.4489	0.0013	0.294
280.0	14.7	0.0019	0.0019	0.0000	0.387
100.0	108.4	0.4662	0.4626	0.0036	0.766
100.0	554.5	0.4688	0.4643	0.0045	0.961
100.0	848.3	0.4662	0.4654	0.0008	0.181
100.0	1813.0	0.4757	0.4687	0.0070	1.475
100.0	2909.0	0.4808	0.4722	0.0086	1.790
160.0	99.3	0.4439	0.4427	0.0012	0.276
160.0	438.6	0.4463	0.4444	0.0019	0.434
160.0	866.5	0.4498	0.4464	0.0034	0.753
160.0	2887.0	0.4625	0.4549	0.0076	1.636
160.0	3977.0	0.4682	0.4590	0.0092	1.974
220.0	96.3	0.4186	0.4228	-0.0042	-0.998
220.0	442.8	0.4225	0.4251	-0.0026	-0.615
220.0	844.6	0.4263	0.4276	-0.0013	-0.312
220.0	1961.0	0.4365	0.4340	0.0025	0.582
220.0	2956.0	0.4439	0.4389	0.0050	1.122
280.0	837.9	0.4023	0.4086	-0.0063	-1.556
280.0	1816.0	0.4137	0.4159	-0.0022	-0.525
280.0	2930.0	0.4244	0.4229	0.0015	0.354
340.0	1841.0	0.3912	0.3983	-0.0071	-1.824
340.0	2980.0	0.4054	0.4074	-0.0020	-0.485

AVERAGE ABSOLUTE DEVIATION = 0.8641%

TABLE 45

COMPARISON OF PREDICTED DENSITIES USING THE OBWR EQUATION WITH EXPERIMENTAL VALUES FOR n-HEXANE

T (F)	PE (PSIA)	DE (LBMOLE/CF)	DC	DEV	%DEV
-140.0	14.7	0.5492	0.5900	-0.0408	-7.429
-130.0	14.7	0.5453	0.5824	-0.0366	-6.711
-120.0	14.7	0.5424	0.5752	-0.0328	-6.039
-110.0	14.7	0.5392	0.5682	-0.0290	-5.369
-100.0	14.7	0.5358	0.5614	-0.0256	-4.777
-90.0	14.7	0.5324	0.5549	-0.0225	-4.221
-80.0	14.7	0.5291	0.5486	-0.0195	-3.678
-70.0	14.7	0.5257	0.5424	-0.0167	-3.186
-60.0	14.7	0.5223	0.5365	-0.0142	-2.722
-50.0	14.7	0.5190	0.5308	-0.0118	-2.266
-40.0	14.7	0.5156	0.5252	-0.0096	-1.854
-20.0	14.7	0.5087	0.5144	-0.0057	-1.119
0.0	14.7	0.5018	0.5041	-0.0023	-0.464
20.0	14.7	0.4947	0.4943	0.0004	0.080
40.0	14.7	0.4875	0.4849	0.0026	0.543
60.0	14.7	0.4806	0.4757	0.0049	1.017
80.0	14.7	0.4732	0.4668	0.0064	1.346
100.0	14.7	0.4659	0.4582	0.0077	1.661
120.0	14.7	0.4583	0.4496	0.0087	1.888
140.0	14.7	0.4502	0.4412	0.0090	1.990
280.0	14.7	0.0019	0.0019	0.0000	0.061
100.0	108.4	0.4662	0.4586	0.0076	1.635
100.0	554.5	0.4688	0.4605	0.0083	1.770
100.0	848.3	0.4662	0.4617	0.0045	0.960
100.0	1813.0	0.4757	0.4655	0.0102	2.140
100.0	2909.0	0.4808	0.4695	0.0113	2.353
160.0	99.3	0.4439	0.4334	0.0105	2.357
160.0	438.6	0.4463	0.4356	0.0107	2.408
160.0	868.5	0.4498	0.4381	0.0117	2.605
160.0	2887.0	0.4625	0.4483	0.0142	3.074
160.0	3977.0	0.4682	0.4530	0.0152	3.254
220.0	96.3	0.4186	0.4084	0.0102	2.437
220.0	442.8	0.4225	0.4116	0.0109	2.588
220.0	844.6	0.4263	0.4149	0.0114	2.666
220.0	1961.0	0.4365	0.4230	0.0135	3.086
220.0	2956.0	0.4439	0.4291	0.0148	3.328
280.0	837.9	0.4023	0.3915	0.0108	2.692
280.0	1816.0	0.4137	0.4014	0.0123	2.972
280.0	2930.0	0.4244	0.4104	0.0140	3.305
340.0	1841.0	0.3912	0.3807	0.0105	2.677
340.0	2980.0	0.4054	0.3926	0.0128	3.164

AVERAGE ABSOLUTE DEVIATION = 2.6803%

Original BWR equation predictions were compared with the same data set, and the average absolute deviation was 14.7%. Predictions of fugacities along the vapor pressure curve using the modified and original BWR equations are presented in Tables 46 and 47.

n-Heptane

Source of Data

Thermodynamic properties of n-heptane have been compiled by Stuart and co-workers[126]. Additional PVT data were measured by Nichols, Reamer and Sage[96]. Limited experimental enthalpy data on n-heptane were reported by Gilliland[51]. Vapor pressure data were reported by Young[144] and Kay[67].

Results from Regression Analysis

Densities. A total of 32 points were taken from API Project 44[111] (-130°F to -10°F) and Stuart and co-workers (40°F to 460°F). The average absolute deviation was 1.0%. Original BWR equation predictions were compared with the same data set, and the average absolute deviation was 2.8%. Comparisons of predicted and experimental densities using the modified and original BWR equations are presented in Tables 48 and 49.

Enthalpy Departures. Seventeen points were taken from Gilliland (512.3°F to 706.7°F). The average absolute deviation was 3.5%. Original BWR equation predictions

TABLE 46

PREDICTION OF SATURATED VAPOR AND LIQUID FUGACITIES FOR n-HEXANE USING THE MBWR EQUATION

T (F)	PF (PSIA)	FUL (PSIA)	FUG (PSIA)	%DEV
-10.00	0.217	0.2158	0.2166	0.36
-5.00	0.261	0.2593	0.2604	0.43
0.0	0.311	0.3100	0.3102	0.05
10.00	0.438	0.4368	0.4365	-0.07
15.00	0.517	0.5150	0.5150	0.01
20.00	0.606	0.6045	0.6033	-0.19
25.00	0.709	0.7066	0.7055	-0.16
30.00	0.825	0.8227	0.8204	-0.27
32.00	0.876	0.8733	0.8709	-0.27
40.00	1.107	1.1023	1.0994	-0.27
50.00	1.464	1.4561	1.4516	-0.31
70.00	2.464	2.4419	2.4334	-0.35
80.00	3.143	3.1058	3.0966	-0.30
90.00	3.966	3.9072	3.8969	-0.26
110.00	6.136	5.9989	5.9909	-0.13
120.00	7.531	7.3303	7.3261	-0.06
130.00	9.168	8.8810	8.8828	0.02
150.00	13.283	12.7311	12.7538	0.18
160.00	15.823	15.0775	15.1159	0.25
170.00	18.730	17.7362	17.7964	0.34
190.00	25.800	24.0864	24.2230	0.56
200.00	30.010	27.8251	27.9944	0.60
210.00	34.650	31.9713	32.1097	0.43
230.00	45.600	41.5764	41.6594	0.20
240.00	52.100	47.0833	47.2266	0.30
250.00	59.240	53.0860	53.2670	0.34
270.00	75.350	66.6581	66.6484	-0.01
280.00	84.930	74.2780	74.4304	0.20
290.00	95.050	82.4666	82.5520	0.10
310.00	118.200	100.6424	100.7146	0.07
320.00	131.300	110.6667	110.7611	0.09
330.00	145.100	121.3164	121.2097	-0.09
350.00	176.200	144.6092	144.1945	-0.29
360.00	193.600	157.2758	156.7445	-0.34
370.00	212.200	170.6354	169.9467	-0.41
390.00	253.800	199.5144	198.6824	-0.42
400.00	277.500	215.0997	214.5377	-0.26
410.00	301.300	231.3376	230.3485	-0.43
430.00	356.500	266.3108	265.6284	-0.26
454.50	439.700	314.0786	315.4614	0.44

AVERAGE ABSOLUTE DEVIATION = 0.2531%

TABLE 47

PREDICTION OF SATURATED VAPOR AND LIQUID FUGACITIES FOR n-HEXANE USING THE OBWR EQUATION

T (F)	PF (PSIA)	FUL (PSIA)	FUG (PSIA)	%DEV
-10.00	0.217	0.0853	0.2165	60.61
-5.00	0.261	0.1102	0.2603	57.66
0.0	0.311	0.1410	0.3101	54.54
10.00	0.438	0.2240	0.4363	48.66
15.00	0.517	0.2786	0.5147	45.87
20.00	0.606	0.3437	0.6030	43.00
25.00	0.709	0.4207	0.7051	40.34
30.00	0.825	0.5110	0.8199	37.67
32.00	0.876	0.5513	0.8703	36.65
40.00	1.107	0.7388	1.0984	32.74
50.00	1.464	1.0413	1.4500	28.19
70.00	2.464	1.9363	2.4297	20.31
80.00	3.143	2.5648	3.0909	17.02
90.00	3.966	3.3402	3.8884	14.10
110.00	6.136	5.4142	5.9732	9.36
120.00	7.531	6.7563	7.3009	7.46
130.00	9.168	8.3309	8.8477	5.84
150.00	13.283	12.2674	12.6880	3.32
160.00	15.823	14.6731	15.0275	2.36
170.00	18.730	17.3992	17.6788	1.58
190.00	25.800	23.8975	24.0211	0.51
200.00	30.010	27.7081	27.7340	0.09
210.00	34.650	31.9184	31.7783	-0.44
230.00	45.600	41.6116	41.1343	-1.16
240.00	52.100	47.1288	46.5696	-1.20
250.00	59.240	53.1105	52.4520	-1.26
270.00	75.350	66.5209	65.4305	-1.67
280.00	84.930	73.9864	72.9409	-1.43
290.00	95.050	81.9581	80.7543	-1.49
310.00	118.200	99.4910	98.1257	-1.39
320.00	131.300	109.0686	107.6740	-1.30
330.00	145.100	119.1792	117.5635	-1.37
350.00	176.200	141.0630	139.1511	-1.37
360.00	193.600	152.8429	150.8398	-1.33
370.00	212.200	165.1783	163.0611	-1.30
390.00	253.800	191.5411	189.3749	-1.14
400.00	277.500	205.6037	203.6985	-0.94
410.00	301.300	220.1055	217.9020	-1.01
430.00	356.500	250.8741	248.9955	-0.75
454.50	439.700	291.0593	291.0593	0.0

AVERAGE ABSOLUTE DEVIATION = 14.7108%

TABLE 48

COMPARISON OF PREDICTED DENSITIES USING THE MBWR EQUATION WITH EXPERIMENTAL VALUES FOR n-HEPTANE

T (F)	PR (PSIA)	DE (LBMOLE/CF)	DC	DEV	%DEV
-90.0	14.7	0.4712	0.4852	-0.0140	-2.979
-70.0	14.7	0.4657	0.4771	-0.0114	-2.452
-50.0	14.7	0.4601	0.4693	-0.0092	-1.993
-30.0	14.7	0.4544	0.4617	-0.0073	-1.601
-10.0	14.7	0.4487	0.4543	-0.0056	-1.250
40.0	25.2	0.4343	0.4367	-0.0024	-0.563
40.0	36.5	0.4344	0.4368	-0.0024	-0.545
40.0	913.8	0.4372	0.4387	-0.0015	-0.344
40.0	1911.5	0.4388	0.4408	-0.0020	-0.457
100.0	21.9	0.4169	0.4168	0.0001	0.035
100.0	36.7	0.4169	0.4168	0.0001	0.024
100.0	103.2	0.4174	0.4170	0.0004	0.096
100.0	868.5	0.4207	0.4192	0.0015	0.349
100.0	1964.5	0.4251	0.4222	0.0029	0.673
160.0	24.1	0.3987	0.3974	0.0013	0.332
160.0	34.4	0.3988	0.3974	0.0014	0.346
160.0	947.8	0.4035	0.4010	0.0025	0.628
160.0	2014.7	0.4089	0.4048	0.0041	1.014
220.0	25.9	0.3782	0.3779	0.0003	0.084
220.0	34.1	0.3784	0.3779	0.0005	0.124
220.0	978.9	0.3861	0.3829	0.0032	0.830
220.0	2012.3	0.3924	0.3877	0.0047	1.204
280.0	61.2	0.3572	0.3576	-0.0004	-0.124
280.0	122.9	0.3585	0.3581	0.0004	0.100
280.0	931.9	0.3679	0.3641	0.0038	1.039
280.0	3081.5	0.3849	0.3763	0.0086	2.224
340.0	132.0	0.3343	0.3356	-0.0013	-0.401
340.0	340.2	0.3384	0.3382	0.0002	0.069
340.0	884.5	0.3461	0.3439	0.0022	0.623
340.0	1962.7	0.3583	0.3531	0.0052	1.452
400.0	400.0	0.3115	0.3135	-0.0020	-0.637
400.0	1000.0	0.3247	0.3235	0.0012	0.368
400.0	1500.0	0.3333	0.3299	0.0034	1.012
400.0	2000.0	0.3396	0.3353	0.0043	1.260
400.0	2500.0	0.3454	0.3400	0.0054	1.561
400.0	3000.0	0.3501	0.3442	0.0059	1.693
460.0	600.0	0.2857	0.2862	-0.0005	-0.179
460.0	1000.0	0.2994	0.2981	0.0013	0.448
460.0	1500.0	0.3115	0.3082	0.0033	1.047
460.0	2000.0	0.3205	0.3160	0.0045	1.412
460.0	3000.0	0.3340	0.3277	0.0063	1.882

AVERAGE ABSOLUTE DEVIATION = 0.8647%

TABLE 49

COMPARISON OF PREDICTED DENSITIES USING THE OBWR EQUATION WITH EXPERIMENTAL VALUES FOR n-HEPTANE

T (F)	PE (PSIA)	DE (LBMOLE/CF)	DC	DEV	%DEV
-90.0	14.7	0.4712	0.4925	-0.0213	-4.511
-70.0	14.7	0.4657	0.4816	-0.0159	-3.407
-50.0	14.7	0.4601	0.4713	-0.0112	-2.444
-30.0	14.7	0.4544	0.4617	-0.0073	-1.607
-10.0	14.7	0.4487	0.4526	-0.0039	-0.862
40.0	25.2	0.4343	0.4315	0.0028	0.635
40.0	36.5	0.4344	0.4316	0.0028	0.652
40.0	913.8	0.4372	0.4335	0.0037	0.836
40.0	1911.5	0.4388	0.4357	0.0031	0.709
100.0	21.9	0.4169	0.4088	0.0081	1.952
100.0	36.7	0.4169	0.4088	0.0081	1.940
100.0	103.2	0.4174	0.4090	0.0084	2.006
100.0	868.5	0.4207	0.4114	0.0093	2.200
100.0	1964.5	0.4251	0.4147	0.0104	2.453
160.0	24.1	0.3987	0.3877	0.0110	2.768
160.0	34.4	0.3988	0.3877	0.0111	2.781
160.0	947.8	0.4035	0.3917	0.0118	2.921
160.0	2014.7	0.4089	0.3959	0.0130	3.176
220.0	25.9	0.3782	0.3672	0.0110	2.896
220.0	34.1	0.3784	0.3673	0.0111	2.933
220.0	978.9	0.3861	0.3731	0.0130	3.379
220.0	2012.3	0.3924	0.3784	0.0140	3.558
280.0	61.2	0.3572	0.3468	0.0104	2.920
280.0	122.9	0.3585	0.3474	0.0111	3.105
280.0	931.9	0.3679	0.3543	0.0136	3.692
280.0	1081.5	0.3849	0.3680	0.0169	4.394
340.0	132.0	0.3343	0.3253	0.0090	2.707
340.0	340.2	0.3384	0.3283	0.0101	2.996
340.0	884.5	0.3461	0.3349	0.0112	3.224
340.0	1962.7	0.3583	0.3451	0.0132	3.677
400.0	400.0	0.3115	0.3052	0.0063	2.031
400.0	1000.0	0.3247	0.3163	0.0084	2.586
400.0	1500.0	0.3333	0.3232	0.0101	3.020
400.0	2000.0	0.3396	0.3290	0.0106	3.131
400.0	2500.0	0.3454	0.3339	0.0115	3.330
400.0	3000.0	0.3501	0.3383	0.0118	3.384
460.0	600.0	0.2857	0.2819	0.0038	1.341
460.0	1000.0	0.2994	0.2938	0.0056	1.870
460.0	1500.0	0.3115	0.3041	0.0074	2.381
460.0	2000.0	0.3205	0.3119	0.0086	2.687
460.0	3000.0	0.3340	0.3237	0.0103	3.080

AVERAGE ABSOLUTE DEVIATION = 2.5898%

were compared with the same data set, and the average absolute deviation was 2.03%. The absolute overall experimental error was estimated by Gilliland to be approximately 3%. Comparisons of predicted and experimental enthalpy departures using the modified and original BWR equations are presented in Tables 50 and 51.

Vapor Pressures. A total of 18 points were taken from API Project 44[111] (70°F to 255°F) and Kay (296.0°F to 497.2°F). The average absolute deviation was 0.67%. Original BWR equation predictions were compared with the same data set, and the average absolute deviation was 5.11%. Predictions of fugacities along the vapor pressure curve using the modified and original BWR equations are presented in Tables 52 and 53.

Ethylene

Source of Data

Thermodynamic properties of ethylene have been compiled by Din[40] and Canjar and Manning[21].

Results from Regression Analysis

Densities. A total of 44 points were taken from API Project 44[111] (-250°F to -160°F) and Canjar and Manning (-140°F to 260°F). The average absolute deviation was 0.58%. Original BWR equation predictions were compared with the same data set, and the average absolute deviation was 0.62%. Comparisons of predicted and experimental densities using the modified and original BWR equations are presented in Tables 54 and 55.

TABLE 50

COMPARISON OF PREDICTED ENTHALPY DEPARTURES USING THE MBWR EQUATION WITH EXPERIMENTAL VALUES FOR n-HEPTANE

T (F)	PE (PSIA)	HE (BTU/LBMOLE)	HC	DEV BTU/LB	%DEV
512.3	315.1	-2719.61	-2833.31	1.14	-4.18
512.3	590.8	-8741.62	-8491.06	-2.50	2.87
512.3	787.7	-9227.26	-8944.52	-2.82	3.06
609.5	78.8	-373.95	-395.04	0.21	-5.64
609.5	236.3	-1303.47	-1312.46	0.09	-0.69
609.5	315.1	-1901.78	-1865.68	-0.36	1.90
609.5	393.9	-2564.20	-2516.80	-0.47	1.85
609.5	787.7	-6410.51	-6040.20	-3.70	5.78
609.5	1181.6	-7478.93	-7325.79	-1.53	2.05
609.5	1575.4	-8013.14	-7888.54	-1.24	1.55
609.5	2363.1	-8440.52	-8334.92	-1.05	1.25
706.7	315.1	-1398.66	-1412.98	0.14	-1.02
706.7	393.9	-1748.32	-1833.34	0.85	-4.86
706.7	590.8	-2913.87	-3007.94	0.94	-3.23
706.7	787.7	-4195.98	-4164.23	-0.32	0.76
706.7	1575.4	-6760.18	-6348.66	-4.11	6.09
706.7	2363.1	-7459.51	-7087.14	-3.72	4.99

AVERAGE ABSOLUTE DEVIATION = 3.0453%

AVERAGE ABSOLUTE DEVIATION IN BTU/LB = 1.48

TABLE 51

COMPARISON OF PREDICTED ENTHALPY DEPARTURES USING THE OBWR EQUATION WITH EXPERIMENTAL VALUES FOR n-HEPTANE

T (F)	PE (PSIA)	HE (BTU/LBMOLE)	HC	DEV BTU/LB	%DEV
512.3	315.1	-2719.61	-2724.48	0.05	-0.18
512.3	590.8	-8741.62	-8843.99	1.02	-1.17
512.3	787.7	-9227.26	-9125.93	-1.01	1.10
609.5	78.8	-373.95	-393.31	0.19	-5.18
609.5	236.3	-1303.47	-1288.39	-0.15	1.16
609.5	315.1	-1901.78	-1813.15	-0.89	4.66
609.5	393.9	-2564.20	-2415.39	-1.49	5.80
609.5	787.7	-6410.51	-6421.76	0.11	-0.18
609.5	1181.6	-7478.93	-7756.77	2.77	-3.71
609.5	1575.4	-8013.14	-8182.34	1.69	-2.11
609.5	2363.1	-8440.52	-8464.34	0.24	-0.28
706.7	315.1	-1398.66	-1363.87	-0.35	2.49
706.7	393.9	-1748.32	-1758.80	0.10	-0.60
706.7	590.8	-2913.87	-2862.26	-0.52	1.77
706.7	787.7	-4195.98	-4069.20	-1.27	3.02
706.7	1575.4	-6760.18	-6730.70	-0.29	0.44
706.7	2363.1	-7459.51	-7405.14	-0.54	0.73

AVERAGE ABSOLUTE DEVIATION = 2.0338%

AVERAGE ABSOLUTE DEVIATION IN BTU/LB = 0.75

TABLE 52

PREDICTION OF SATURATED VAPOR AND LIQUID FUGACITIES FOR n-HEPTANE USING THE MBWR EQUATION

T (F)	PE (PSIA)	FUL (PSIA)	FUG (PSIA)	%DEV
70.00	0.726	0.7426	0.7222	-2.82
90.00	1.254	1.2619	1.2440	-1.44
110.00	2.069	2.0555	2.0449	-0.52
120.00	2.616	2.5849	2.5797	-0.20
130.00	3.276	3.2206	3.2223	0.05
140.00	4.065	3.9773	3.9869	0.24
150.00	5.002	4.8700	4.8902	0.41
160.00	6.106	5.9157	5.9483	0.55
170.00	7.398	7.1303	7.1788	0.68
180.00	8.899	8.5319	8.5984	0.77
190.00	10.633	10.1379	10.2259	0.86
200.00	12.623	11.9661	12.0783	0.93
210.00	14.897	14.0351	14.1763	1.00
220.00	17.480	16.3627	16.5367	1.05
230.00	20.400	18.9665	19.1775	1.10
240.00	23.680	21.8637	22.1116	1.12
250.00	27.360	25.0720	25.3651	1.16
255.00	29.350	26.7980	27.1086	1.15
280.00	40.960	36.7235	37.0771	0.95
296.00	50.000	44.2824	44.6208	0.76
340.00	83.200	70.3898	70.9157	0.74
358.00	100.000	83.4307	83.5468	0.14
399.50	150.000	118.9935	118.7000	-0.25
400.00	151.400	119.4983	119.5745	0.06
430.50	200.000	150.6062	150.6093	0.00
456.50	250.000	180.2038	179.8697	-0.19
460.00	257.800	184.4142	184.1484	-0.14
478.20	300.000	206.8715	206.3785	-0.24
497.20	350.000	230.0318	230.0317	0.0

AVERAGE ABSOLUTE DEVIATION = 0.6732%

TABLE 53

PREDICTION OF SATURATED VAPOR AND LIQUID FUGACITIES FOR n-HEPTANE USING THE OBWR EQUATION

T (F)	PE (PSIA)	FUL (PSIA)	FUG (PSIA)	%DEV
7C.00	C.726	0.4937	0.7218	31.61
9C.00	1.254	0.9628	1.2432	22.55
110.CC	2.069	1.7326	2.0432	15.21
12C.CC	2.616	2.2649	2.5774	12.12
130.00	3.276	2.9157	3.2191	9.42
14C.CC	4.065	3.7014	3.9826	7.06
150.CC	5.002	4.6387	4.8846	5.04
16C.CC	6.106	5.7445	5.9413	3.31
17C.CC	7.398	7.0365	7.1699	1.86
18C.00	8.899	8.5322	8.5875	0.64
19C.CC	10.633	10.2487	10.2129	-0.35
20C.00	12.623	12.2044	12.0632	-1.17
210.00	14.897	14.4150	14.1591	-1.81
22C.CC	17.480	16.8985	16.5177	-2.30
23C.CC	20.400	19.6712	19.1577	-2.68
240.00	23.680	22.7482	22.0920	-2.97
25C.CC	27.360	26.1447	25.3474	-3.15
255.CC	29.350	27.9674	27.0927	-3.23
28C.00	40.960	38.3950	37.0837	-3.54
29E.CC	50.000	46.2808	44.6593	-3.63
340.00	83.200	73.2596	71.1819	-2.92
358.00	10C.000	86.6378	83.9986	-3.14
399.50	150.000	122.9760	119.9732	-2.50
40C.CC	151.400	123.4932	120.8743	-2.17
43C.50	20C.000	155.3032	153.1128	-1.43
45E.5C	250.CCC	185.7807	184.0427	-0.94
46C.00	257.800	190.1450	188.6245	-0.81
47E.2C	3C0.000	213.6444	212.7261	-0.43
497.20	350.000	239.7234	239.3898	-0.14

AVERAGE ABSOLUTE DEVIATION = 5.1079%

TABLE 54

COMPARISON OF PREDICTED DENSITIES USING THE MBWR EQUATION WITH EXPERIMENTAL VALUES FOR ETHYLENE

T (F)	PE (PSIA)	DE (LBMOLE/CF)	DC	DEV	%DEV
-250.0	14.7	1.4261	1.4292	-0.0031	-0.217
-240.0	14.7	1.4091	1.4090	0.0001	0.008
-230.0	14.7	1.3927	1.3895	0.0032	0.227
-220.0	14.7	1.3756	1.3707	0.0049	0.353
-210.0	14.7	1.3588	1.3525	0.0063	0.462
-200.0	14.7	1.3421	1.3348	0.0073	0.546
-190.0	14.7	1.3253	1.3175	0.0078	0.592
-180.0	14.7	1.3096	1.3005	0.0091	0.698
-170.0	14.7	1.2918	1.2837	0.0081	0.623
-160.0	14.7	1.2747	1.2672	0.0075	0.585
-140.0	50.0	0.0165	0.0164	0.0001	0.388
-100.0	50.0	0.0140	0.0140	0.0000	0.001
-100.0	150.0	0.0540	0.0532	0.0008	1.496
-60.0	100.0	0.0262	0.0262	0.0000	0.037
-60.0	200.0	0.0625	0.0621	0.0004	0.650
-20.0	100.0	0.0230	0.0230	-0.0000	-0.050
-20.0	300.0	0.0890	0.0886	0.0004	0.486
20.0	50.0	0.0100	0.0100	-0.0000	-0.012
20.0	300.0	0.0724	0.0725	-0.0001	-0.173
60.0	50.0	0.0092	0.0092	0.0000	0.333
60.0	600.0	0.1619	0.1617	0.0002	0.128
100.0	500.0	0.1029	0.1034	-0.0005	-0.533
140.0	100.0	0.0160	0.0160	0.0000	0.054
140.0	500.0	0.0909	0.0914	-0.0005	-0.578
140.0	1000.0	0.2273	0.2278	-0.0005	-0.231
140.0	2000.0	0.6042	0.6064	-0.0022	-0.362
180.0	100.0	0.0149	0.0149	-0.0000	-0.052
180.0	500.0	0.0822	0.0826	-0.0004	-0.499
180.0	1000.0	0.1906	0.1918	-0.0012	-0.627
180.0	1500.0	0.3338	0.3312	0.0026	0.780
180.0	2000.0	0.4812	0.4735	0.0077	1.600
220.0	100.0	0.0139	0.0140	-0.0001	-0.505
220.0	500.0	0.0753	0.0757	-0.0004	-0.565
220.0	1000.0	0.1675	0.1687	-0.0012	-0.731
220.0	1500.0	0.2787	0.2790	-0.0003	-0.125
220.0	2000.0	0.3976	0.3937	0.0039	0.971
260.0	100.0	0.0131	0.0131	-0.0000	-0.377
260.0	500.0	0.0698	0.0701	-0.0003	-0.466
260.0	1000.0	0.1510	0.1521	-0.0011	-0.738
260.0	1500.0	0.2438	0.2448	-0.0010	-0.409
260.0	2000.0	0.3421	0.3408	0.0013	0.377

AVERAGE ABSOLUTE DEVIATION = 0.4548%

TABLE 55

COMPARISON OF PREDICTED DENSITIES USING THE OBWR EQUATION WITH EXPERIMENTAL VALUES FOR ETHYLENE

T (F)	PE (PSIA)	DE (LBMOLE/CF)	DC	DEV	%DEV
-250.0	14.7	1.4261	1.4939	-0.0678	-4.751
-240.0	14.7	1.4091	1.4643	-0.0552	-3.916
-230.0	14.7	1.3927	1.4362	-0.0435	-3.126
-220.0	14.7	1.3756	1.4095	-0.0339	-2.468
-210.0	14.7	1.3588	1.3840	-0.0252	-1.856
-200.0	14.7	1.3421	1.3595	-0.0174	-1.297
-190.0	14.7	1.3253	1.3359	-0.0106	-0.798
-180.0	14.7	1.3096	1.3130	-0.0034	-0.258
-170.0	14.7	1.2918	1.2907	0.0011	0.085
-160.0	14.7	1.2747	1.2689	0.0058	0.451
-140.0	50.0	0.0165	0.0165	-0.0000	-0.231
-100.0	50.0	0.0140	0.0140	-0.0000	-0.224
-100.0	150.0	0.0540	0.0542	-0.0002	-0.429
-60.0	100.0	0.0262	0.0262	-0.0000	-0.170
-60.0	200.0	0.0625	0.0627	-0.0002	-0.359
-20.0	100.0	0.0230	0.0230	-0.0000	-0.084
-20.0	300.0	0.0890	0.0893	-0.0003	-0.337
20.0	50.0	0.0100	0.0100	0.0000	0.010
20.0	300.0	0.0724	0.0725	-0.0001	-0.207
60.0	50.0	0.0092	0.0092	0.0000	0.369
60.0	600.0	0.1619	0.1625	-0.0006	-0.350
100.0	500.0	0.1029	0.1031	-0.0002	-0.209
140.0	100.0	0.0160	0.0160	0.0000	0.138
140.0	500.0	0.0909	0.0911	-0.0002	-0.184
140.0	1000.0	0.2273	0.2281	-0.0008	-0.370
140.0	2000.0	0.6042	0.6063	-0.0021	-0.356
180.0	100.0	0.0149	0.0149	0.0000	0.032
180.0	500.0	0.0822	0.0823	-0.0001	-0.099
180.0	1000.0	0.1906	0.1910	-0.0004	-0.233
180.0	1500.0	0.3338	0.3347	-0.0009	-0.281
180.0	2000.0	0.4812	0.4829	-0.0017	-0.355
220.0	100.0	0.0139	0.0140	-0.0001	-0.423
220.0	500.0	0.0753	0.0754	-0.0001	-0.179
220.0	1000.0	0.1675	0.1679	-0.0004	-0.211
220.0	1500.0	0.2787	0.2794	-0.0007	-0.249
220.0	2000.0	0.3976	0.3986	-0.0010	-0.259
260.0	100.0	0.0131	0.0131	-0.0000	-0.299
260.0	500.0	0.0698	0.0699	-0.0001	-0.103
260.0	1000.0	0.1510	0.1513	-0.0003	-0.201
260.0	1500.0	0.2438	0.2442	-0.0004	-0.179
260.0	2000.0	0.3421	0.3427	-0.0006	-0.176

AVERAGE ABSOLUTE DEVIATION = 0.6417%

Enthalpy Departures. Twenty-two points were taken from Canjar and Manning (-120°F to 260°F). The average absolute deviation was 1.59%. Original BWR equation predictions were compared with the same data set, and the average absolute deviation was 2.2%. Comparisons of predicted and experimental enthalpy departures using the modified and original BWR equations are presented in Tables 56 and 57.

Vapor Pressures. A total of 28 points were taken from API Project 44[111] (-220°F to -170°F) and Canjar and Manning (-154.66°F to 49.82°F). The average absolute deviation was 0.66%. Original BWR equation predictions were compared with the same data set, and the average absolute deviation was 15.9%. Predictions of fugacities along the vapor pressure curve using the modified and original BWR equations are presented in Tables 58 and 59.

TABLE 56

COMPARISON OF PREDICTED ENTHALPY DEPARTURES USING THE MBWR EQUATION WITH DERIVED VALUES FOR ETHYLENE

T (F)	PE (PSIA)	HE (BTU/LBMOLE)	HC (BTU/LBMOLE)	DEV BTU/LB	%DEV
-120.0	100.0	-437.64	-442.35	0.17	-1.08
-100.0	100.0	-418.00	-371.19	-1.67	11.20
-40.0	200.0	-524.61	-542.44	0.64	-3.40
0.0	400.0	-1021.16	-1023.66	0.09	-0.24
40.0	500.0	-1009.94	-1024.68	0.53	-1.46
80.0	500.0	-774.29	-793.39	0.68	-2.47
80.0	800.0	-1537.36	-1516.82	-0.73	1.34
100.0	1000.0	-1854.37	-1798.13	-2.00	3.03
100.0	1500.0	-3080.33	-3122.94	1.52	-1.38
120.0	500.0	-634.02	-649.92	0.57	-2.51
120.0	1000.0	-1548.58	-1539.81	-0.31	0.57
120.0	2000.0	-3156.07	-3227.33	2.54	-2.26
140.0	500.0	-580.72	-595.51	0.53	-2.55
140.0	1000.0	-1352.20	-1357.39	0.18	-0.38
140.0	2000.0	-2883.95	-2855.07	-1.03	1.00
160.0	500.0	-538.64	-548.96	0.37	-1.92
160.0	1000.0	-1192.29	-1217.92	0.91	-2.15
160.0	1500.0	-2000.25	-1951.42	-1.74	2.44
160.0	2000.0	-2606.22	-2542.38	-2.28	2.45
180.0	500.0	-502.17	-508.60	0.23	-1.28
180.0	1000.0	-1096.91	-1106.01	0.32	-0.83
180.0	1500.0	-1775.82	-1748.78	-0.96	1.52
180.0	2000.0	-2350.92	-2291.13	-2.13	2.54
200.0	500.0	-468.50	-473.22	0.17	-1.01
200.0	1000.0	-1007.14	-1013.27	0.22	-0.61
200.0	1500.0	-1601.88	-1584.60	-0.62	1.08
200.0	2000.0	-2137.71	-2083.29	-1.94	2.55
220.0	500.0	-440.45	-441.93	0.05	-0.34
220.0	1000.0	-931.39	-934.68	0.12	-0.35
220.0	1500.0	-1458.81	-1448.38	-0.37	0.71
220.0	2000.0	-1949.75	-1907.39	-1.51	2.17
240.0	500.0	-409.59	-414.04	0.16	-1.09
240.0	1000.0	-861.26	-866.94	0.20	-0.66
240.0	1500.0	-1338.17	-1333.20	-0.18	0.37
240.0	2000.0	-1787.04	-1756.36	-1.09	1.72
260.0	500.0	-378.73	-389.02	0.37	-2.72
260.0	1000.0	-796.73	-807.77	0.39	-1.39
260.0	1500.0	-1228.76	-1234.24	0.20	-0.45
260.0	2000.0	-1641.16	-1625.27	-0.57	0.97

AVERAGE ABSOLUTE DEVIATION = 1.7478%

AVERAGE ABSOLUTE DEVIATION IN BTU/LB = 0.78

TABLE 57

COMPARISON OF PREDICTED ENTHALPY DEPARTURES USING THE OBWR EQUATION WITH DERIVED VALUES FOR ETHYLENE

T (F)	PE (PSIA)	HE (BTU/LBMOLE)	HC (BTU/LBMOLE)	DEV BTU/LB	%DEV
-120.0	100.0	-437.64	-482.70	1.61	-10.30
-100.0	100.0	-418.00	-398.69	-0.69	4.62
-40.0	200.0	-524.61	-570.39	1.63	-8.73
0.0	400.0	-1021.16	-1081.05	2.13	-5.86
40.0	500.0	-1009.94	-1062.82	1.88	-5.24
80.0	500.0	-774.29	-808.26	1.21	-4.39
80.0	800.0	-1537.36	-1592.20	1.95	-3.57
100.0	1000.0	-1854.37	-1910.78	2.01	-3.04
100.0	1500.0	-3080.33	-3141.13	2.17	-1.97
120.0	500.0	-634.02	-655.38	0.76	-3.37
120.0	1000.0	-1548.58	-1592.63	1.57	-2.84
120.0	2000.0	-3156.07	-3201.00	1.60	-1.42
140.0	500.0	-580.72	-598.16	0.62	-3.00
140.0	1000.0	-1352.20	-1385.44	1.18	-2.46
140.0	2000.0	-2883.95	-2915.89	1.14	-1.11
160.0	500.0	-538.64	-549.50	0.39	-2.02
160.0	1000.0	-1192.29	-1232.86	1.45	-3.40
160.0	1500.0	-2000.25	-2032.12	1.14	-1.59
160.0	2000.0	-2606.22	-2634.94	1.02	-1.10
180.0	500.0	-502.17	-507.52	0.19	-1.07
180.0	1000.0	-1096.91	-1112.99	0.57	-1.47
180.0	1500.0	-1775.82	-1798.61	0.81	-1.28
180.0	2000.0	-2350.92	-2377.36	0.94	-1.12
200.0	500.0	-468.50	-470.90	0.09	-0.51
200.0	1000.0	-1007.14	-1015.01	0.28	-0.78
200.0	1500.0	-1601.88	-1614.36	0.44	-0.78
200.0	2000.0	-2137.71	-2151.33	0.49	-0.64
220.0	500.0	-440.45	-438.63	-0.06	0.41
220.0	1000.0	-931.39	-932.77	0.05	-0.15
220.0	1500.0	-1458.81	-1465.06	0.22	-0.43
220.0	2000.0	-1949.75	-1957.02	0.26	-0.37
240.0	500.0	-409.59	-409.98	0.01	-0.09
240.0	1000.0	-861.26	-862.42	0.04	-0.14
240.0	1500.0	-1338.17	-1341.00	0.10	-0.21
240.0	2000.0	-1787.04	-1790.62	0.13	-0.20
260.0	500.0	-378.73	-384.35	0.20	-1.48
260.0	1000.0	-796.73	-801.32	0.16	-0.58
260.0	1500.0	-1228.76	-1235.89	0.25	-0.58
260.0	2000.0	-1641.16	-1647.55	0.23	-0.39

AVERAGE ABSOLUTE DEVIATION = 2.1209%

AVERAGE ABSOLUTE DEVIATION IN BTU/LB = 0.81

TABLE 58

PREDICTION OF SATURATED VAPOR AND LIQUID FUGACITIES FOR ETHYLENE USING THE MBWR EQUATION

T (F)	PE (PSIA)	FUL (PSIA)	FUG (PSIA)	%DEV
-220.00	0.885	0.8764	0.8808	0.50
-215.00	1.167	1.1574	1.1602	0.24
-210.00	1.519	1.5082	1.5083	0.01
-205.00	1.953	1.9408	1.9365	-0.22
-200.00	2.484	2.4683	2.4589	-0.38
-195.00	3.127	3.1049	3.0897	-0.49
-190.00	3.899	3.8654	3.8444	-0.55
-185.00	4.816	4.7662	4.7377	-0.60
-180.00	5.899	5.8235	5.7883	-0.61
-175.00	7.168	7.0546	7.0138	-0.58
-170.00	8.640	8.4776	8.4284	-0.58
-160.00	12.310	11.9719	11.9257	-0.39
-165.00	10.350	10.1106	10.0629	-0.47
-154.66	14.696	14.2341	14.1791	-0.39
-150.00	17.150	16.4576	16.4801	0.14
-140.00	23.180	22.0852	22.0768	-0.04
-130.00	30.600	29.0059	28.8611	-0.50
-120.00	40.230	37.3707	37.5028	0.35
-110.00	52.150	47.3232	47.9795	1.37
-100.00	66.550	58.9969	60.3519	2.25
-90.00	83.210	72.5069	74.3435	2.47
-80.00	101.200	87.9480	89.1681	1.37
-70.00	122.600	105.4440	106.3623	0.86
-60.00	146.500	125.0572	125.1321	0.06
-50.00	173.300	146.8555	145.6855	-0.80
-40.00	206.200	170.9988	170.0269	-0.57
-30.00	244.500	197.5335	197.3541	-0.09
-20.00	285.000	226.3597	225.5102	-0.38
-10.00	332.500	257.7102	257.1763	-0.21
0.0	384.600	291.4839	290.7034	-0.27
10.00	442.700	327.7576	326.6150	-0.35
20.00	507.700	366.5845	365.0449	-0.42
30.00	578.500	407.8484	405.2502	-0.64
40.00	654.600	451.4050	446.9739	-0.99
49.82	742.100	497.0461	491.9553	-1.03

AVERAGE ABSOLUTE DEVIATION = 0.6052%

TABLE 59

PREDICTION OF SATURATED VAPOR AND LIQUID FUGACITIES FOR ETHYLENE USING THE OBWR EQUATION

T (F)	PE (PSIA)	FUL (PSIA)	FUG (PSIA)	%DEV
-220.00	0.885	0.3091	0.8805	64.90
-215.00	1.167	0.4663	1.1597	59.80
-210.00	1.519	0.6826	1.5075	54.72
-205.00	1.953	0.9727	1.9352	49.74
-200.00	2.484	1.3529	2.4571	44.94
-195.00	3.127	1.8409	3.0871	40.37
-190.00	3.899	2.4556	3.8409	36.07
-185.00	4.816	3.2172	4.7329	32.02
-180.00	5.899	4.1464	5.7818	28.29
-175.00	7.168	5.2642	7.0052	24.85
-170.00	8.640	6.5933	8.4172	21.67
-160.00	12.310	9.9699	11.9073	16.27
-165.00	10.350	8.1545	10.0484	18.85
-154.66	14.696	12.2140	14.1556	13.72
-150.00	17.150	14.4495	16.4511	12.17
-140.00	23.180	20.1972	22.0338	8.34
-130.00	30.600	27.3676	28.8002	4.97
-120.00	40.230	36.1074	37.4174	3.50
-110.00	52.150	46.5435	47.8631	2.76
-100.00	66.550	58.7894	60.1986	2.34
-90.00	83.210	72.9350	74.1503	1.64
-80.00	101.200	89.0333	88.9394	-0.11
-70.00	122.600	107.1744	106.0955	-1.02
-60.00	146.500	127.3799	124.8323	-2.04
-50.00	173.300	149.6779	145.3599	-2.97
-40.00	206.200	174.1910	169.6724	-2.66
-30.00	244.500	200.9235	196.9750	-2.00
-20.00	285.000	229.7262	225.1296	-2.04
-10.00	332.500	260.8027	256.7964	-1.56
0.0	384.600	294.0049	290.3350	-1.26
10.00	442.700	329.3669	326.2512	-0.95
20.00	507.700	366.9016	364.6387	-0.62
30.00	578.500	406.4158	404.6987	-0.42
40.00	654.600	447.6082	446.0579	-0.35
49.82	742.100	489.8892	489.8889	0.0

AVERAGE ABSOLUTE DEVIATION = 15.9977%

CHAPTER VIII

APPLICATION OF MULTIPROPERTY REGRESSION ANALYSIS TO NONHYDROCARBONS USING THE MODIFIED BWR EQUATION

To correlate the behavior of natural gas systems, the modified BWR equation of state is extended to some nonhydrocarbons. In most natural gas reservoirs, the most common nonhydrocarbons present are nitrogen, carbon dioxide and hydrogen sulfide. PVT, enthalpy departure and vapor pressure data were used simultaneously to determine the equation-of-state parameters for these nonhydrocarbons with the exception of hydrogen sulfide for which no experimental nor meaningful derived enthalpy values are available. Sets of parameters in British engineering units of the modified BWR equations are presented in Tables 60 and 61. Predictions of thermodynamic properties of the above nonhydrocarbons are discussed individually in the following sections.

Nitrogen

Nitrogen has been one of the most extensively studied materials because of its theoretical significance of being a simple molecule. Its extensive PVT, calorimetric and

TABLE 60

MODIFIED BWR EQUATION OF STATE PARAMETERS* FOR INDIVIDUAL NONHYDROCARBONS

	NITROGEN	CARBON DIOXIDE	HYDROGEN SULFIDE
B_o	0.575091E 00	0.394117E 00	0.297508E 00
A_o	0.374860E 04	0.659203E 04	0.105863E 05
C_o	0.165621E 09	0.295902E 10	0.211496E 10
γ	0.994303E 00	0.164916E 01	0.120447E 01
b	0.947657E 00	0.971443E 00	0.253315E 01
a	0.132506E 04	0.563285E 04	0.205110E 05
α	0.236954E 00	0.395525E 00	0.165961E 00
c	0.107004E 09	0.274668E 10	0.436132E 10
D_o	0.252022E 11	0.409151E 12	0.486518E 11
d	0.197227E 06	0.599297E 05	0.199731E 05
E_o	0.166844E 13	0.102898E 11	0.393226E 11

*These parameters are consistent with the following units: pressure in psia, volume in ft^3/lb mole temperature in °R. The gas constant used is 10.7335.

TABLE 61

ORIGINAL BWR EQUATION-OF-STATE PARAMETERS* FOR INDIVIDUAL NONHYDROCARBONS

	NITROGEN[123]	NITROGEN[30]	CARBON DIOXIDE[31]	HYDROGEN SULFIDE[49]
B_o	0.733549E 00	0.449796E 00	0.799496E 00	0.104473E 01
A_o	0.449557E 04	0.328183E 04	0.103228E 05	0.168733E 05
C_o	0.719313E 08	0.952712E 08	0.169301E 10	0.208416E 10
γ	0.192393E 01	0.115200E 01	0.138400E 01	0.149687E 01
b	0.508311E 00	0.828186E 00	0.105920E 01	0.720381E 00
a	0.110191E 03	0.188051E 04	0.826446E 04	0.474201E 04
α	0.119783E 01	0.290501E 00	0.348000E 00	0.587307E 00
c	0.107217E 09	0.106782E 09	0.291971E 10	0.413235E 10

*These parameters are consistent with the following units: pressure in psia, volume in ft^3/lb mole, temperature in °R. The gas constant used is 10.7335.

vapor pressure data allow a meaningful test for the validity of applying corresponding states principle to fluids composed of nonpolar molecules. Besides theoretical considerations, this wealth of experimental data have tempted the proposal of at least four empirical equations of state in the past thirty years.

Success of the original BWR equation on hydrocarbons prompted Stotler and Benedict[123] to extend its application to nitrogen. In 1953, a set of parameters for nitrogen was published by these investigators. The region extended from -267°F to 390°F with a reported average absolute deviation in pressure of 0.31%. Prior to this publication, Bloomer and Rao[16] modified the original BWR equation to predict PVT and vapor-liquid equilibrium behavior of nitrogen. The reported average absolute deviation in pressure was 0.36%. In 1961, Bubeck and Peck[19] proposed a thirteen-constant equation of state for nitrogen with special emphasis on vapor pressure prediction. The root-mean-square error in density was reported to be 0.7% to three times its critical density. To obtain more accurate predictions of PVT behavior, Strobridge[125] proposed a sixteen-constant equation of state for nitrogen. A root-mean-square error in compressibility factor of 0.87% was reported for densities up to three times the critical density. Recently, Crain and Sonntag[30] redetermined the original BWR equation of state parameters using

a nonlinear least squares method, and extended the range of density prediction to twice the critical density.

Source of Data

Comprehensive thermodynamic properties of nitrogen have been compiled by Sage and Lacey[112], Bloomer and Rao[16], Din[41] and Strobridge[125]. Recent contributions include PVT measurements by Crain and Sonntag[29] and Streett and Staveley[124]. Accurate enthalpy data were reported by Mage and co-workers[82]. A critical review of vapor pressures of liquid nitrogen was given by Edejer and Thodos[46].

Results from Regression Analysis

Densities. A total of 31 points were taken from Streett and Staveley (-320.5°F to -243.27°F) and Canjar and Manning (-220°F to 160°F). The average absolute deviation was 0.72%. Predictions using the original BWR equation with parameters determined by Stotler and Benedict as well as Crain and Sonntag were compared with the same data set, and the average absolute deviations were 7.73% and 1.04% respectively. Comparisons of predicted and experimental densities using the modified BWR equation and the original BWR equation with parameters determined by Stotler and Benedict, Crain and Sonntag are presented in Tables 62, 63 and 64. Topographical plots of deviations using the modified BWR equation and the original BWR equation with Crain and Sonntag's parameters are presented in Figures 22 and 23.

TABLE 62

COMPARISON OF PREDICTED DENSITIES USING THE MBWR EQUATION WITH EXPERIMENTAL VALUES FOR NITROGEN

T (F)	PE (PSIA)	DE (LBMOLE/CF)	DC	DEV	%DEV
-320.5	196.0	1.7967	1.7631	0.0336	1.870
-300.0	14.7	0.0088	0.0088	-0.0000	-0.286
-279.5	150.9	1.5333	1.5143	0.0190	1.238
-279.5	3028.8	1.7063	1.6892	0.0171	1.002
-279.5	6027.6	1.8076	1.7863	0.0213	1.179
-279.5	8031.8	1.8576	1.8346	0.0230	1.236
-261.7	1999.2	1.5660	1.5561	0.0099	0.634
-261.7	4998.0	1.7077	1.6982	0.0095	0.558
-261.7	8936.4	1.8203	1.8090	0.0113	0.620
-243.3	2498.9	1.5001	1.4950	0.0051	0.338
-243.3	4018.3	1.5911	1.5884	0.0027	0.172
-243.3	8016.8	1.7387	1.7361	0.0026	0.149
-220.0	100.0	0.0410	0.0414	-0.0004	-0.864
-180.0	150.0	0.0528	0.0529	-0.0001	-0.183
-180.0	350.0	0.1340	0.1345	-0.0005	-0.336
-140.0	200.0	0.0610	0.0612	-0.0002	-0.268
-140.0	400.0	0.1281	0.1285	-0.0004	-0.322
-100.0	500.0	0.1394	0.1396	-0.0002	-0.155
-100.0	900.0	0.2652	0.2632	0.0020	0.748
-60.0	700.0	0.1734	0.1736	-0.0002	-0.102
-20.0	800.0	0.1760	0.1765	-0.0005	-0.310
-20.0	1300.0	0.2904	0.2878	0.0026	0.909
0.0	560.0	0.1161	0.1164	-0.0003	-0.299
40.0	100.0	0.0187	0.0187	-0.0000	-0.083
40.0	500.0	0.0942	0.0945	-0.0003	-0.368
40.0	1000.0	0.1895	0.1893	0.0002	0.080
120.0	400.0	0.0642	0.0645	-0.0003	-0.401
120.0	800.0	0.1280	0.1285	-0.0005	-0.374
120.0	1300.0	0.2063	0.2063	0.0000	0.018
160.0	500.0	0.0748	0.0751	-0.0003	-0.372
160.0	1000.0	0.1482	0.1488	-0.0006	-0.380
160.0	1200.0	0.1772	0.1775	-0.0003	-0.164
180.0	500.0	0.0723	0.0726	-0.0003	-0.451
180.0	1000.0	0.1432	0.1438	-0.0006	-0.402
200.0	500.0	0.0701	0.0703	-0.0002	-0.337
200.0	1000.0	0.1389	0.1391	-0.0002	-0.172
220.0	500.0	0.0680	0.0682	-0.0002	-0.284
220.0	1000.0	0.1346	0.1348	-0.0002	-0.159
240.0	500.0	0.0660	0.0662	-0.0002	-0.275
240.0	750.0	0.0985	0.0987	-0.0002	-0.247
240.0	1000.0	0.1306	0.1308	-0.0002	-0.128

AVERAGE ABSOLUTE DEVIATION = 0.4506%

TABLE 63

COMPARISON OF PREDICTED DENSITIES USING THE OBWR EQUATION (STOTLER'S PARAMETERS) WITH EXPERIMENTAL VALUES FOR NITROGEN

T (F)	PE (PSIA)	CE (LBMOLE/CF)	DC	DEV	%DEV
-320.5	196.0	1.7967	2.4722	-0.6755	-37.597
-300.0	14.7	0.0088	0.0088	-0.0000	-0.511
-279.5	150.9	1.5333	2.0983	-0.5650	-36.851
-279.5	3028.8	1.7063	2.2029	-0.4966	-29.104
-279.5	6027.6	1.8076	2.2854	-0.4778	-26.434
-279.5	8031.8	1.8576	2.3317	-0.4741	-25.523
-261.7	1999.2	1.5660	2.0263	-0.4603	-29.396
-261.7	4998.0	1.7077	2.1425	-0.4348	-25.463
-261.7	8936.4	1.8203	2.2528	-0.4325	-23.759
-243.3	2498.9	1.5001	1.9021	-0.4020	-26.798
-243.3	4018.3	1.5911	1.9819	-0.3908	-24.561
-243.3	8016.8	1.7387	2.1299	-0.3912	-22.498
-220.0	100.0	0.0410	0.0414	-0.0004	-0.856
-180.0	150.0	0.0528	0.0528	-0.0000	-0.027
-180.0	350.0	0.1340	0.1334	0.0006	0.419
-140.0	200.0	0.0610	0.0610	-0.0000	-0.030
-140.0	400.0	0.1281	0.1277	0.0004	0.322
-100.0	500.0	0.1394	0.1387	0.0007	0.489
-100.0	900.0	0.2652	0.2598	0.0054	2.054
-60.0	700.0	0.1734	0.1724	0.0010	0.605
-20.0	800.0	0.1760	0.1754	0.0006	0.326
-20.0	1300.0	0.2904	0.2857	0.0047	1.606
0.0	560.0	0.1161	0.1159	0.0002	0.179
40.0	100.0	0.0187	0.0187	0.0000	0.019
40.0	500.0	0.0942	0.0942	0.0000	0.049
40.0	1000.0	0.1895	0.1883	0.0012	0.648
120.0	400.0	0.0642	0.0642	-0.0000	-0.062
120.0	800.0	0.1280	0.1278	0.0002	0.137
120.0	1300.0	0.2063	0.2052	0.0011	0.517
160.0	500.0	0.0748	0.0748	0.0000	0.022
160.0	1000.0	0.1482	0.1480	0.0002	0.156
160.0	1200.0	0.1772	0.1766	0.0006	0.364
180.0	500.0	0.0723	0.0723	-0.0000	-0.058
180.0	1000.0	0.1432	0.1430	0.0002	0.137
200.0	500.0	0.0701	0.0701	0.0000	0.053
200.0	1000.0	0.1389	0.1384	0.0005	0.369
220.0	500.0	0.0680	0.0679	0.0001	0.105
220.0	1000.0	0.1346	0.1341	0.0005	0.386
240.0	500.0	0.0660	0.0659	0.0001	0.113
240.0	750.0	0.0985	0.0983	0.0002	0.248
240.0	1000.0	0.1306	0.1301	0.0005	0.419

AVERAGE ABSOLUTE DEVIATION = 7.7870%

TABLE 64

COMPARISON OF PREDICTED DENSITIES USING THE OBWR EQUATION (CRAIN'S PARAMETER) WITH EXPERIMENTAL VALUES FOR NITROGEN

T (F)	PE (PSIA)	DE (LBMOLE/CF)	DC	DEV	%DEV
-320.5	196.0	1.7967	1.9044	-0.1077	-5.994
-300.0	14.7	0.0088	0.0089	-0.0001	-0.621
-279.5	150.9	1.5333	1.5953	-0.0620	-4.041
-279.5	3028.8	1.7063	1.7325	-0.0262	-1.534
-279.5	6027.6	1.8076	1.8185	-0.0109	-0.605
-279.5	8031.8	1.8576	1.8629	-0.0053	-0.285
-261.7	1999.2	1.5660	1.5885	-0.0225	-1.435
-261.7	4998.0	1.7077	1.7155	-0.0078	-0.454
-261.7	8936.4	1.8203	1.8190	0.0013	0.072
-243.3	2498.9	1.5001	1.5133	-0.0132	-0.877
-243.3	4018.3	1.5911	1.5982	-0.0071	-0.449
-243.3	8016.8	1.7387	1.7366	0.0021	0.123
-220.0	100.0	0.0410	0.0413	-0.0003	-0.787
-180.0	150.0	0.0528	0.0528	0.0000	0.012
-180.0	350.0	0.1340	0.1338	0.0002	0.153
-140.0	200.0	0.0610	0.0611	-0.0001	-0.088
-140.0	400.0	0.1281	0.1281	-0.0000	-0.013
-100.0	500.0	0.1394	0.1395	-0.0001	-0.076
-100.0	900.0	0.2652	0.2641	0.0011	0.421
-60.0	700.0	0.1734	0.1740	-0.0006	-0.375
-20.0	800.0	0.1760	0.1775	-0.0015	-0.841
-20.0	1300.0	0.2904	0.2916	-0.0012	-0.418
0.0	560.0	0.1161	0.1168	-0.0007	-0.609
40.0	100.0	0.0187	0.0187	-0.0000	-0.123
40.0	500.0	0.0942	0.0948	-0.0006	-0.688
40.0	1000.0	0.1895	0.1911	-0.0016	-0.831
120.0	400.0	0.0642	0.0646	-0.0004	-0.695
120.0	800.0	0.1280	0.1294	-0.0014	-1.084
120.0	1300.0	0.2063	0.2090	-0.0027	-1.330
160.0	500.0	0.0748	0.0754	-0.0006	-0.776
160.0	1000.0	0.1482	0.1502	-0.0020	-1.336
160.0	1200.0	0.1772	0.1796	-0.0024	-1.365
180.0	500.0	0.0723	0.0729	-0.0006	-0.861
180.0	1000.0	0.1432	0.1451	-0.0019	-1.355
200.0	500.0	0.0701	0.0706	-0.0005	-0.751
200.0	1000.0	0.1389	0.1405	-0.0016	-1.119
220.0	500.0	0.0680	0.0685	-0.0005	-0.700
220.0	1000.0	0.1346	0.1361	-0.0015	-1.100
240.0	500.0	0.0660	0.0665	-0.0005	-0.692
240.0	750.0	0.0985	0.0994	-0.0009	-0.913
240.0	1000.0	0.1306	0.1320	-0.0014	-1.063

AVERAGE ABSOLUTE DEVIATION = 0.9040%

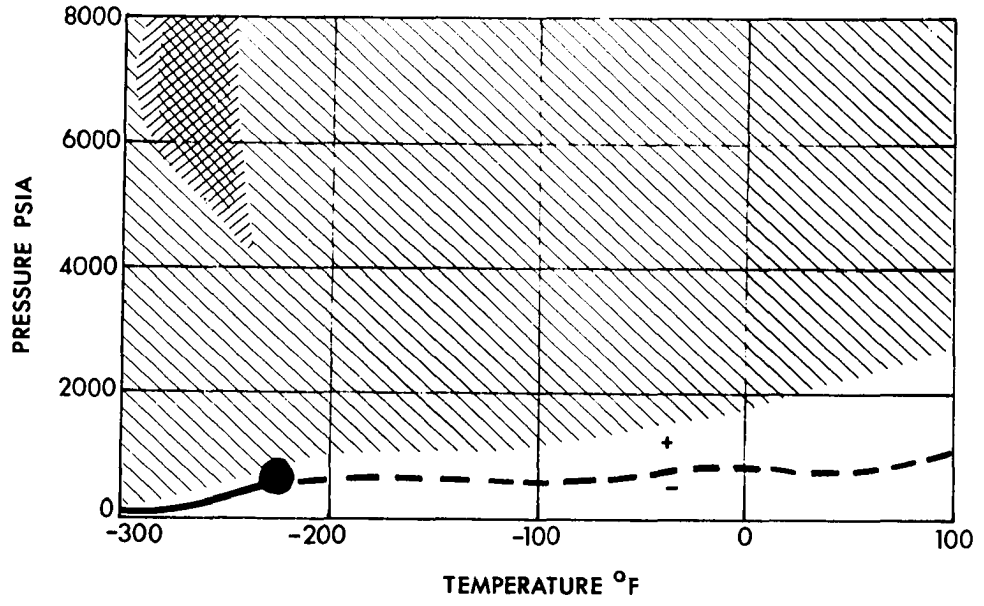


Figure 22. Comparison of Densities Calculated by the Modified BWR Equation with Experimental Values for Nitrogen.

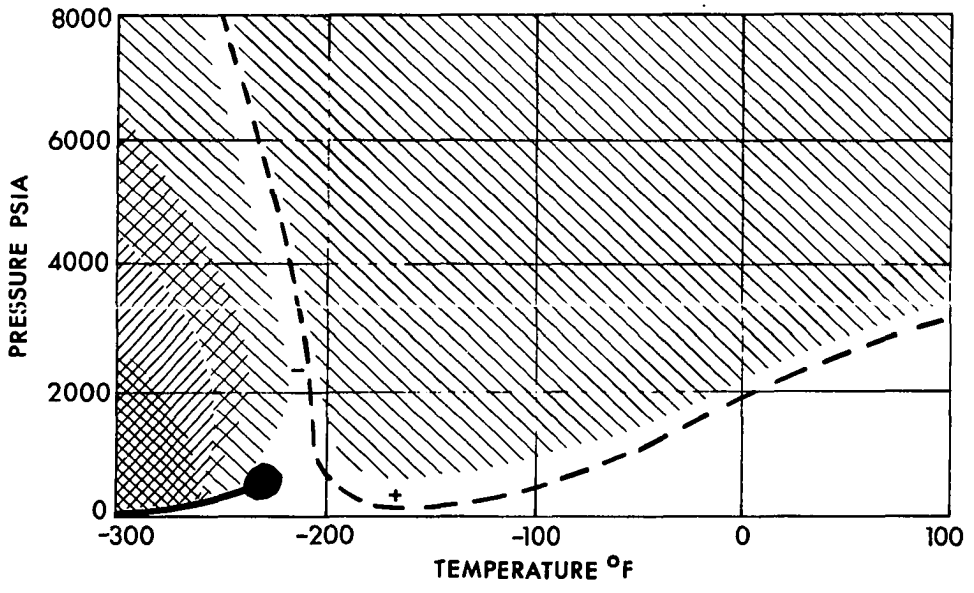


Figure 23. Comparison of Densities Calculated by the Original BWR Equation Using Crain and Sonntag's Parameters with Experimental Values for Nitrogen

Enthalpy Departures. Twenty-eight points were taken from Mage and co-workers (-330.0°F to -120°F). The average absolute deviation was 0.93%. Predictions using the original BWR equation with parameters determined by Stotler and Benedict, and Crain and Sonntag were compared with the same data set, and the average absolute deviations were 36.38% and 13.52% respectively. Comparisons of predicted and experimental enthalpy departures using the modified BWR equation and the original BWR equation with parameters determined by Stotler and Benedict, Crain and Sonntag are presented in Tables 65, 66 and 67. Topographical plots of deviations using the modified BWR equation and the original BWR equation with Crain and Sonntag's parameters are presented in Figures 24 and 25.

Vapor Pressures. Seventeen points were taken from Friedman and White[48]. The average absolute deviation was 0.8%. Prediction using the original BWR equation with parameters determined by Stotler and Benedict, and Crain and Sonntag were compared with the same data set with average absolute deviations of 25.66% and 13.64% respectively. Predictions of fugacities along the vapor pressure curve using the modified BWR equation and the original BWR equation with parameters determined by Stotler and Benedict and Crain and Sonntag are presented in Tables 68, 69 and 70.

TABLE 65

COMPARISON OF PREDICTED ENTHALPY DEPARTURES USING THE MBWR EQUATION WITH EXPERIMENTAL VALUES FOR NITROGEN

T (F)	PF (PSIA)	HE (BTU/LBMOLE)	HC (BTU/LBMOLE)	DEV BTU/LB	%DEV
-300.0	500.0	-2278.29	-2306.12	0.99	-1.22
-300.0	1000.0	-2258.68	-2277.87	0.69	-0.85
-300.0	1500.0	-2247.47	-2247.51	0.00	-0.00
-300.0	2000.0	-2227.86	-2215.58	-0.44	0.55
-300.0	2500.0	-2160.62	-2182.45	0.78	-1.01
-250.0	500.0	-1858.08	-1865.15	0.25	-0.38
-250.0	1000.0	-1897.30	-1904.72	0.26	-0.39
-250.0	1500.0	-1905.70	-1910.96	0.19	-0.28
-250.0	2000.0	-1897.30	-1903.22	0.21	-0.31
-250.0	2500.0	-1874.89	-1887.67	0.46	-0.68
-200.0	500.0	-455.51	-448.57	-0.25	1.52
-200.0	1000.0	-1155.91	-1141.34	-0.52	1.26
-200.0	1500.0	-1430.47	-1422.61	-0.28	0.55
-200.0	2000.0	-1525.72	-1523.30	-0.09	0.16
-200.0	2500.0	-1539.73	-1568.62	1.03	-1.88
-180.0	500.0	-350.59	-363.80	0.47	-3.77
-180.0	1000.0	-843.67	-838.01	-0.20	0.67
-180.0	1500.0	-1182.67	-1170.62	-0.43	1.02
-180.0	2000.0	-1353.56	-1324.26	-1.05	2.17
-180.0	2500.0	-1398.39	-1402.14	0.13	-0.27
-150.0	1000.0	-601.22	-602.27	0.04	-0.17
-150.0	1500.0	-898.19	-874.50	-0.85	2.64
-150.0	2000.0	-1077.49	-1049.29	-1.01	2.62
-150.0	2500.0	-1172.75	-1154.99	-0.63	1.51
-100.0	1000.0	-417.33	-409.63	-0.27	1.84
-100.0	1500.0	-610.64	-590.57	-0.72	3.29
-100.0	2000.0	-761.92	-730.90	-1.11	4.07
-100.0	2500.0	-854.38	-832.36	-0.79	2.58
0.0	1500.0	-347.93	-332.01	-0.57	4.58
-220.0	500.0	-608.31	-606.57	-0.06	0.29
-220.0	1000.0	-1563.66	-1539.11	-0.88	1.57
-220.0	1500.0	-1647.70	-1660.31	0.45	-0.76
-220.0	2000.0	-1689.73	-1702.40	0.45	-0.75
-220.0	2500.0	-1686.93	-1716.46	1.05	-1.75
-160.0	500.0	-296.30	-306.56	0.37	-3.46
-160.0	1000.0	-660.50	-663.75	0.12	-0.49
-160.0	1500.0	-979.89	-959.74	-0.72	2.06
-160.0	2000.0	-1161.99	-1134.42	-0.98	2.37
-160.0	2500.0	-1243.24	-1234.36	-0.32	0.71

AVERAGE ABSOLUTE DEVIATION = 1.4474%

AVERAGE ABSOLUTE DEVIATION IN BTU/LB = 0.52

TABLE 66

COMPARISON OF PREDICTED ENTHALPY DEPARTURES USING THE OBWR EQUATION (STOTLER'S PARAMETERS) WITH EXPERIMENTAL VALUES FOR NITROGEN

T (F)	PE (PSIA)	HE	HC (BTU/LBMOLE)	DEV BTU/LB	%DEV
-300.0	500.0	-2278.29	-4308.35	72.46	-89.10
-300.0	1000.0	-2258.68	-4292.33	72.59	-90.04
-300.0	1500.0	-2247.47	-4275.64	72.39	-90.24
-300.0	2000.0	-2227.86	-4258.32	72.48	-91.14
-300.0	2500.0	-2160.62	-4240.45	74.24	-96.26
-250.0	500.0	-1858.08	-2774.35	32.71	-49.31
-250.0	1000.0	-1897.30	-2785.22	31.69	-46.80
-250.0	1500.0	-1905.70	-2788.88	31.52	-46.34
-250.0	2000.0	-1897.30	-2787.52	31.78	-46.92
-250.0	2500.0	-1874.89	-2782.42	32.39	-48.40
-200.0	500.0	-455.51	-436.06	-0.69	4.27
-200.0	1000.0	-1155.91	-933.33	-7.94	19.26
-200.0	1500.0	-1430.47	-1514.71	3.01	-5.89
-200.0	2000.0	-1525.72	-1785.18	9.26	-17.01
-200.0	2500.0	-1539.73	-1875.84	12.00	-21.83
-180.0	500.0	-350.59	-356.51	0.21	-1.69
-180.0	1000.0	-843.67	-731.95	-3.99	13.24
-180.0	1500.0	-1182.67	-1029.59	-5.46	12.94
-180.0	2000.0	-1353.56	-1306.48	-1.68	3.48
-180.0	2500.0	-1398.39	-1504.48	3.79	-7.59
-150.0	1000.0	-601.22	-555.44	-1.63	7.61
-150.0	1500.0	-898.19	-775.16	-4.39	13.70
-150.0	2000.0	-1077.49	-943.60	-4.78	12.43
-150.0	2500.0	-1172.75	-1085.91	-3.10	7.40
-100.0	1000.0	-417.33	-390.48	-0.96	6.43
-100.0	1500.0	-610.64	-547.48	-2.25	10.34
-100.0	2000.0	-761.92	-668.38	-3.34	12.28
-100.0	2500.0	-854.38	-762.32	-3.29	10.77
0.0	1500.0	-347.93	-322.33	-0.91	7.36
-220.0	500.0	-608.31	-566.49	-1.49	6.88
-220.0	1000.0	-1563.66	-2045.69	17.21	-30.83
-220.0	1500.0	-1647.70	-2153.48	18.05	-30.70
-220.0	2000.0	-1689.73	-2201.29	18.26	-30.27
-220.0	2500.0	-1686.93	-2226.70	19.27	-32.00
-160.0	500.0	-296.30	-301.10	0.17	-1.62
-160.0	1000.0	-660.50	-604.37	-2.00	8.50
-160.0	1500.0	-979.89	-842.79	-4.89	13.99
-160.0	2000.0	-1161.99	-1031.20	-4.67	11.26
-160.0	2500.0	-1243.24	-1154.69	-1.73	3.90

AVERAGE ABSOLUTE DEVIATION = 27.1800%

AVERAGE ABSOLUTE DEVIATION IN BTU/LB = 17.56

TABLE 67

COMPARISON OF PREDICTED ENTHALPY DEPARTURES USING THE OBWR EQUATION (CRAIN'S PARAMETERS) WITH EXPERIMENTAL VALUES FOR NITROGEN

T (F)	PE (PSIA)	HE (BTU/LBMOLE)	HC (BTU/LBMOLE)	DEV BTU/LB	%DEV
-300.0	500.0	-2278.29	-3333.44	37.66	-46.31
-300.0	1000.0	-2258.68	-3313.37	37.65	-46.70
-300.0	1500.0	-2247.47	-3291.55	37.27	-46.46
-300.0	2000.0	-2227.86	-3268.31	37.14	-46.70
-300.0	2500.0	-2160.62	-3243.89	38.67	-50.14
-250.0	500.0	-1858.08	-2144.72	10.23	-15.43
-250.0	1000.0	-1897.30	-2177.29	9.99	-14.76
-250.0	1500.0	-1905.70	-2184.40	9.95	-14.62
-250.0	2000.0	-1897.30	-2179.45	10.07	-14.87
-250.0	2500.0	-1874.89	-2167.34	10.44	-15.60
-200.0	500.0	-455.51	-451.63	-0.14	0.85
-200.0	1000.0	-1155.91	-1159.74	0.14	-0.33
-200.0	1500.0	-1430.47	-1452.80	0.80	-1.56
-200.0	2000.0	-1525.72	-1543.74	0.64	-1.18
-200.0	2500.0	-1539.73	-1579.97	1.44	-2.61
-180.0	500.0	-350.59	-358.58	0.29	-2.28
-180.0	1000.0	-843.67	-825.63	-0.64	2.14
-180.0	1500.0	-1182.67	-1169.52	-0.47	1.11
-180.0	2000.0	-1353.56	-1318.60	-1.25	2.58
-180.0	2500.0	-1398.39	-1385.83	-0.45	0.90
-150.0	1000.0	-601.22	-580.45	-0.74	3.46
-150.0	1500.0	-898.19	-852.57	-1.63	5.08
-150.0	2000.0	-1077.49	-1027.39	-1.79	4.65
-150.0	2500.0	-1172.75	-1126.78	-1.64	3.92
-100.0	1000.0	-417.33	-386.55	-1.10	7.38
-100.0	1500.0	-610.64	-563.37	-1.69	7.74
-100.0	2000.0	-761.92	-703.51	-2.09	7.67
-100.0	2500.0	-854.38	-804.01	-1.80	5.89
0.0	1500.0	-347.93	-313.55	-1.23	9.88
-220.0	500.0	-608.31	-626.72	0.66	-3.03
-220.0	1000.0	-1563.66	-1635.40	2.56	-4.59
-220.0	1500.0	-1647.70	-1745.03	3.47	-5.91
-220.0	2000.0	-1689.73	-1780.79	3.25	-5.39
-220.0	2500.0	-1686.93	-1791.13	3.72	-6.18
-160.0	500.0	-296.30	-297.05	0.03	-0.25
-160.0	1000.0	-660.50	-643.65	-0.60	2.55
-160.0	1500.0	-979.89	-942.15	-1.35	3.85
-160.0	2000.0	-1161.99	-1116.21	-1.63	3.94
-160.0	2500.0	-1243.24	-1208.13	-1.25	2.82

AVERAGE ABSOLUTE DEVIATION = 10.8025%

AVERAGE ABSOLUTE DEVIATION IN BTU/LB = 7.12

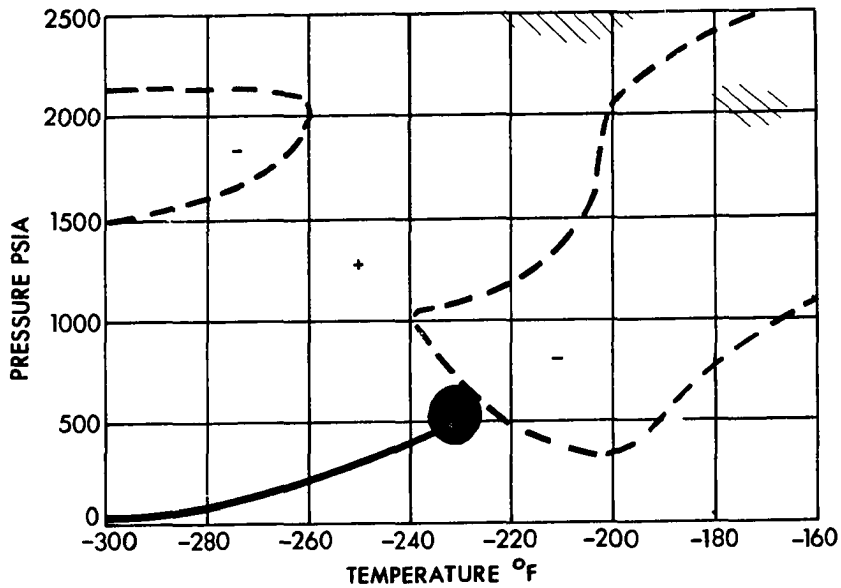


Figure 24. Comparison of Enthalpy Departures Calculated by the Modified BWR Equation with Experimental Values for Nitrogen

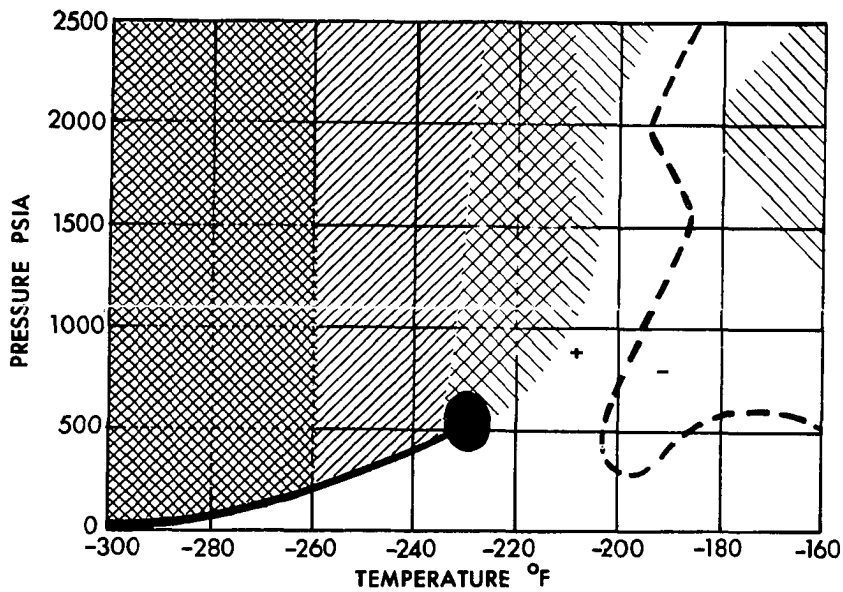


Figure 25. Comparison of Enthalpy Departures Calculated by the Original BWR Equation Using Crain and Sonntag's Parameters with Experimental Values for Nitrogen.

TABLE 68

PREDICTION OF SATURATED VAPOR AND LIQUID FUGACITIES FOR NITROGEN USING THE MBWR EQUATION

T (F)	PE (PSIA)	FUL (PSIA)	FUG (PSIA)	%DEV
-309.10	29.063	26.4377	27.1354	2.57
-303.36	39.322	35.7191	36.1761	1.26
-296.07	56.282	50.1817	50.6686	0.96
-288.60	78.653	68.3812	69.0645	0.99
-281.56	104.894	88.8907	89.7697	0.98
-276.05	129.547	107.3388	108.4694	1.04
-271.50	152.777	124.2245	125.5103	1.02
-267.61	175.051	139.8394	141.3497	1.07
-263.33	201.862	158.3021	159.8661	0.98
-260.16	223.511	172.8102	174.3922	0.91
-254.20	268.794	202.0422	203.6364	0.78
-250.40	300.808	221.9575	223.4700	0.68
-247.38	328.539	238.5321	240.0716	0.64
-243.44	367.140	260.9980	262.4324	0.55
-240.86	394.291	276.2031	277.5981	0.50
-238.04	425.578	293.3181	294.5757	0.43
-235.59	454.406	308.5366	309.6563	0.36
-233.74	475.511	320.0386	320.0386	0.0
-232.96	492.200	326.0747	326.0752	0.00

AVERAGE ABSOLUTE DEVIATION = 0.8275%

TABLE 69

PREDICTION OF SATURATED VAPOR AND LIQUID FUGACITIES FOR NITROGEN USING THE OBWR EQUATION WITH STOTLER'S PARAMETERS

T (F)	PE (PSIA)	FUL (PSIA)	FUG (PSIA)	%DEV
-305.10	29.063	5.6492	26.9803	79.06
-303.36	39.322	9.9827	35.9392	72.22
-296.07	56.292	18.6192	50.2893	67.98
-288.60	78.653	32.1022	68.5008	53.14
-281.56	104.894	49.9769	89.0140	43.86
-276.05	129.547	67.9131	107.5689	36.87
-271.50	152.777	85.5489	124.5149	31.29
-267.61	175.051	102.6988	140.3057	26.80
-263.33	201.862	123.8600	158.8310	22.02
-260.16	223.511	141.0524	173.4227	18.67
-254.20	268.794	176.9393	202.9992	12.84
-250.40	300.808	202.1989	223.2545	9.43
-247.38	328.539	223.6276	240.3667	6.96
-243.44	367.140	253.2314	263.7021	3.97
-240.86	394.291	273.5706	279.7671	2.21
-238.04	425.578	296.7610	298.0349	0.43
-235.59	454.406	317.5754	314.6001	-0.95
-233.74	475.511	333.6152	326.9070	-2.05
-232.96	492.200	341.0999	335.1052	-1.79

AVERAGE ABSOLUTE DEVIATION = 25.6594%

TABLE 70

PREDICTION OF SATURATED VAPOR AND LIQUID FUGACITIES FOR NITROGEN USING THE OBWR EQUATION WITH CRAIN'S PARAMETERS

T (F)	PE (PSIA)	FUL (PSIA)	FUG (PSIA)	%DEV
-309.10	29.063	12.8135	26.8871	52.34
-303.36	39.322	19.9479	35.8096	44.29
-296.07	56.282	32.4118	50.1029	35.31
-288.60	78.653	49.5927	68.2475	27.33
-281.56	104.894	70.1479	88.6912	20.91
-276.05	129.547	89.2752	107.1828	16.71
-271.50	152.777	107.1063	124.0654	13.67
-267.61	175.051	123.7662	139.7847	11.46
-263.33	201.862	143.6035	158.2055	9.23
-260.16	223.511	159.2558	172.6892	7.78
-254.20	268.794	190.8783	201.9435	5.48
-250.40	300.808	212.4515	221.8655	4.24
-247.38	328.539	230.4032	238.5904	3.43
-243.44	367.140	254.7395	261.2073	2.48
-240.86	394.291	271.1992	276.6055	1.95
-238.04	425.578	289.7251	293.9150	1.43
-235.59	454.406	306.1750	309.3606	1.03
-233.74	475.511	318.6370	318.6367	0.0
-232.96	492.200	324.9048	324.9043	-0.00

AVERAGE ABSOLUTE DEVIATION = 13.6354%

Carbon Dioxide

The original BWR equation has been successfully applied to carbon dioxide by Cullen and Kobe.[31] To describe the thermodynamic properties of carbon dioxide adequately, these authors proposed two sets of parameters. In this study, only the set which is capable of predicting fugacities along the vapor-pressure curve and pressures in the gaseous region is used for comparison.

Source of Data

Comprehensive compilations of the thermodynamic properties of carbon dioxide have been presented by Din[39], Canjar and Manning[21], Liley[81], Price[106], Koppel and Smith[73]. Recently, PVT measurements have been presented by Kennedy[71].

Results from Regression Study

Densities. Forty points were taken from Din's compilation (-22°F to 284°F). The average absolute deviation was 1.12%. Original BWR equation predictions were compared with the same data set, and the average absolute deviation was 2.83%. Comparisons of predicted and experimental densities using the modified and the original BWR equations are presented in Tables 71 and 72.

Enthalpy Departures. Thirty-nine derived enthalpy departure points were taken from Din's compilation (-22°F to 283.7°F). The average absolute deviation was 1.46%. Original BWR equation predictions were compared with the same data set, and the average absolute deviation was 2.9%.

TABLE 71

COMPARISON OF PREDICTED DENSITIES USING THE MBWR EQUATION WITH EXPERIMENTAL VALUES FOR CARBON DIOXIDE

T (F)	PE (PSIA)	DE (LBMOLE/CF)	DC	DEV	%DEV
-22.0	220.5	1.5246	1.5026	0.0220	1.444
-22.0	441.0	1.5312	1.5074	0.0238	1.553
-22.0	735.0	1.5390	1.5136	0.0254	1.647
-4.0	294.0	1.4616	1.4544	0.0072	0.490
-4.0	441.0	1.4678	1.4585	0.0093	0.635
-4.0	735.0	1.4789	1.4663	0.0126	0.855
-4.0	882.0	1.4840	1.4700	0.0140	0.944
14.0	441.0	1.3965	1.4039	-0.0074	-0.530
14.0	735.0	1.4132	1.4141	-0.0009	-0.061
14.0	882.0	1.4202	1.4189	0.0013	0.094
32.0	588.0	1.3272	1.3473	-0.0201	-1.512
32.0	1176.0	1.3708	1.3731	-0.0023	-0.168
32.0	2205.0	1.4259	1.4089	0.0170	1.191
32.0	4410.0	1.5046	1.4652	0.0394	2.619
68.0	4410.0	1.4062	1.3840	0.0222	1.581
86.0	2205.0	1.2065	1.2292	-0.0227	-1.883
86.0	5580.0	1.4076	1.3770	0.0306	2.174
104.0	294.0	0.0534	0.0537	-0.0003	-0.614
104.0	882.0	0.2170	0.2205	-0.0035	-1.622
104.0	2940.0	1.1923	1.2119	-0.0196	-1.642
104.0	4410.0	1.2993	1.2934	0.0059	0.457
140.0	294.0	0.0492	0.0495	-0.0003	-0.551
140.0	882.0	0.1806	0.1835	-0.0029	-1.632
140.0	1470.0	0.4194	0.4209	-0.0015	-0.348
140.0	2940.0	1.0274	1.0412	-0.0138	-1.346
140.0	4410.0	1.1833	1.1892	-0.0059	-0.501
176.0	294.0	0.0458	0.0460	-0.0002	-0.352
176.0	882.0	0.1591	0.1612	-0.0021	-1.343
176.0	4410.0	1.0628	1.0694	-0.0066	-0.626
212.0	294.0	0.0428	0.0430	-0.0002	-0.456
212.0	882.0	0.1437	0.1455	-0.0018	-1.248
212.0	2940.0	0.6951	0.6751	0.0200	2.973
212.0	4410.0	0.9459	0.9439	0.0020	0.214
248.0	294.0	0.0403	0.0404	-0.0001	-0.350
248.0	882.0	0.1318	0.1335	-0.0017	-1.262
248.0	2940.0	0.5781	0.5755	0.0026	0.453
248.0	4410.0	0.8395	0.8327	0.0068	0.813
284.0	294.0	0.0381	0.0382	-0.0001	-0.286
284.0	882.0	0.1223	0.1238	-0.0015	-1.233
284.0	1470.0	0.2189	0.2230	-0.0041	-1.880
284.0	4410.0	0.7467	0.7434	0.0033	0.444

AVERAGE ABSOLUTE DEVIATION = 1.0226%

TABLE 72

COMPARISON OF PREDICTED DENSITIES USING THE OBWR EQUATION WITH EXPERIMENTAL VALUES FOR CARBON DIOXIDE

T (F)	PE (PSIA)	DE (LBMOLE/CF)	DC	DEV	%DEV
-22.0	220.0	1.5246	1.4287	0.0959	6.291
-22.0	441.0	1.5312	1.4348	0.0964	6.293
-22.0	735.0	1.5390	1.4427	0.0963	6.260
-4.0	294.0	1.4616	1.3761	0.0855	5.847
-4.0	441.0	1.4678	1.3815	0.0863	5.880
-4.0	735.0	1.4789	1.3916	0.0873	5.905
-4.0	882.0	1.4840	1.3963	0.0877	5.907
14.0	441.0	1.3965	1.3216	0.0749	5.364
14.0	735.0	1.4132	1.3354	0.0778	5.508
14.0	882.0	1.4202	1.3417	0.0785	5.528
32.0	588.0	1.3272	1.2604	0.0668	5.035
32.0	1176.0	1.3708	1.2957	0.0751	5.478
32.0	2205.0	1.4259	1.3405	0.0854	5.988
32.0	4410.0	1.5046	1.4056	0.0990	6.579
68.0	4410.0	1.4062	1.3280	0.0782	5.559
86.0	2205.0	1.2065	1.1650	0.0415	3.437
86.0	5580.0	1.4076	1.3263	0.0813	5.773
104.0	294.0	0.0534	0.0535	-0.0001	-0.239
104.0	882.0	0.2170	0.2184	-0.0014	-0.628
104.0	2940.0	1.1923	1.1589	0.0334	2.799
104.0	4410.0	1.2993	1.2442	0.0551	4.240
140.0	294.0	0.0492	0.0493	-0.0001	-0.164
140.0	882.0	0.1806	0.1813	-0.0007	-0.404
140.0	1470.0	0.4194	0.4294	-0.0100	-2.386
140.0	2940.0	1.0274	1.0163	0.0111	1.084
140.0	4410.0	1.1833	1.1515	0.0318	2.690
176.0	294.0	0.0458	0.0458	0.0000	0.035
176.0	882.0	0.1591	0.1593	-0.0002	-0.107
176.0	4410.0	1.0628	1.0486	0.0142	1.332
212.0	294.0	0.0428	0.0428	-0.0000	-0.071
212.0	882.0	0.1437	0.1437	-0.0000	-0.034
212.0	2940.0	0.6951	0.6884	0.0067	0.958
212.0	4410.0	0.9459	0.9397	0.0062	0.657
248.0	294.0	0.0403	0.0403	0.0000	0.032
248.0	882.0	0.1318	0.1319	-0.0001	-0.070
248.0	2940.0	0.5781	0.5773	0.0008	0.133
248.0	4410.0	0.8395	0.8349	0.0046	0.549
284.0	294.0	0.0381	0.0381	0.0000	0.094
284.0	882.0	0.1223	0.1224	-0.0001	-0.060
284.0	1470.0	0.2189	0.2190	-0.0001	-0.049
284.0	4410.0	0.7467	0.7435	0.0032	0.433

AVERAGE ABSOLUTE DEVIATION = 2.8263%

Comparisons of predicted and derived enthalpy departures using the modified and the original BWR equations are presented in Tables 73 and 74.

Vapor Pressures. Thirty-three points were taken from Canjar and Manning (-69.90°F to 87.87°F). The average absolute deviation was 0.63%. Original BWR equation predictions were compared with the same data set, and the average absolute deviation was 0.53%. The modified BWR equation is more accurate below -50°F, while the original BWR equation excels above -50°F. Predictions of fugacities along the vapor pressure durve using the modified and original BWR equations are presented in Tables 75 and 76.

Hydrogen Sulfide

Application of the original BWR equation to hydrogen sulfide was first attempted by Simon and Briggs[115]. The set of parameters was obtained using mixture data for the hydrogen sulfide-methane system. It was not advised to be used to predict pure component hydrogen sulfide thermodynamic properties. Recent determination of BWR constants for hydrogen sulfide have been reported by Kate[65], Masuda and Yorizane[89] and Furr[49]. In this study, only Furr's constants are used for comparison.

Source of Data

Thermodynamic properties of hydrogen sulfide have been compiled by West[135]. However, at the time of West's

TABLE 73

COMPARISON OF PREDICTED ENTHALPY DEPARTURES USING THE MBWR EQUATION WITH DERIVED VALUES FOR CARBON DIOXIDE

T (F)	PR (PSIA)	HF (BTU/LBMOLE)	HC (BTU/LBMOLE)	DEV BTU/LB	%DEV
-22.0	441.0	-6294.69	-6205.43	-2.03	1.42
-4.0	735.0	-6083.18	-5999.41	-1.90	1.38
14.0	882.0	-5853.45	-5778.22	-1.71	1.29
32.0	882.0	-5595.20	-5533.48	-1.40	1.10
32.0	2205.0	-5660.15	-5548.97	-2.53	1.96
50.0	882.0	-5275.94	-5249.25	-0.61	0.51
50.0	1470.0	-5366.25	-5294.82	-1.62	1.33
50.0	2940.0	-5432.00	-5326.46	-2.40	1.94
68.0	1470.0	-5054.13	-5002.94	-1.16	1.01
68.0	2940.0	-5172.17	-5101.14	-1.61	1.37
68.0	4410.0	-5221.28	-5105.34	-2.63	2.22
86.0	2205.0	-4793.50	-4791.59	-0.04	0.04
86.0	4410.0	-4966.20	-4900.61	-1.49	1.32
86.0	5880.0	-4991.55	-4884.41	-2.43	2.15
104.0	735.0	-1006.87	-1029.35	0.51	-2.23
104.0	2940.0	-4527.33	-4597.07	1.58	-1.54
104.0	4410.0	-4690.52	-4690.19	-0.01	0.01
104.0	5880.0	-4749.14	-4696.30	-1.20	1.11
104.0	7350.0	-4755.48	-4664.30	-2.07	1.92
140.0	4410.0	-4162.13	-4247.71	1.94	-2.06
140.0	5880.0	-4293.63	-4317.25	0.54	-0.55
140.0	7350.0	-4343.54	-4317.45	-0.59	0.60
176.0	1470.0	-1665.17	-1630.37	-0.79	2.09
176.0	2940.0	-3224.98	-3208.84	-0.37	0.50
176.0	4410.0	-3726.43	-3773.87	1.08	-1.27
176.0	5880.0	-3923.68	-3934.85	0.25	-0.28
176.0	7350.0	-4007.66	-3977.41	-0.69	0.75
212.0	1470.0	-1334.83	-1339.89	0.12	-0.38
212.0	4410.0	-3336.68	-3298.39	-0.87	1.15
212.0	5880.0	-3588.59	-3554.52	-0.77	0.95
212.0	7350.0	-3709.80	-3645.96	-1.45	1.72
248.0	1470.0	-1109.05	-1137.64	0.65	-2.58
248.0	2940.0	-2299.71	-2245.68	-1.23	2.35
248.0	5880.0	-3261.42	-3190.80	-1.60	2.17
248.0	7350.0	-3419.06	-3327.32	-2.08	2.68
284.0	2940.0	-1907.58	-1936.16	0.65	-1.50
284.0	4410.0	-2592.02	-2530.34	-1.40	2.38
284.0	5880.0	-2926.33	-2860.08	-1.51	2.26
284.0	7350.0	-3116.45	-3027.80	-2.01	2.84

AVERAGE ABSOLUTE DEVIATION = 1.4595%

AVERAGE ABSOLUTE DEVIATION IN BTU/LB = 1.27

TABLE 74

COMPARISON OF PREDICTED ENTHALPY DEPARTURES USING THE OBWR EQUATION WITH DERIVED VALUES FOR CARBON DIOXIDE

T (F)	PE (PSIA)	HF (BTU/LBMOLE)	HC (BTU/LBMOLE)	DEV BTU/LB	%DEV
-22.0	441.0	-6294.69	-6264.67	-0.68	0.48
-4.0	735.0	-6083.18	-5954.51	-2.92	2.12
14.0	882.0	-5853.45	-5667.11	-4.23	3.18
32.0	882.0	-5595.20	-5381.66	-4.85	3.82
32.0	2205.0	-5660.15	-5417.43	-5.52	4.29
50.0	882.0	-5275.94	-5073.57	-4.60	3.84
50.0	1470.0	-5366.25	-5141.00	-5.12	4.20
50.0	2940.0	-5432.00	-5186.62	-5.58	4.52
68.0	1470.0	-5054.13	-4852.04	-4.59	4.00
68.0	2940.0	-5172.17	-4967.25	-4.66	3.96
68.0	4410.0	-5221.28	-4969.45	-5.72	4.82
86.0	2205.0	-4793.50	-4678.45	-2.61	2.40
86.0	4410.0	-4966.20	-4781.34	-4.20	3.72
86.0	5880.0	-4991.55	-4757.14	-5.33	4.70
104.0	735.0	-1006.87	-1044.34	0.85	-3.72
104.0	2940.0	-4527.33	-4519.21	-0.18	0.18
104.0	4410.0	-4690.52	-4597.44	-2.11	1.98
104.0	5880.0	-4749.14	-4591.95	-3.57	3.31
104.0	7350.0	-4755.48	-4549.74	-4.67	4.33
140.0	4410.0	-4162.13	-4229.98	1.54	-1.63
140.0	5880.0	-4293.63	-4275.88	-0.40	0.41
140.0	7350.0	-4343.54	-4260.57	-1.89	1.91
176.0	1470.0	-1665.17	-1662.91	-0.05	0.14
176.0	2940.0	-3224.98	-3407.62	4.15	-5.66
176.0	4410.0	-3726.43	-3848.46	2.77	-3.27
176.0	5880.0	-3923.68	-3967.19	0.99	-1.11
176.0	7350.0	-4007.66	-3987.69	-0.45	0.50
212.0	1470.0	-1334.83	-1354.33	0.44	-1.46
212.0	4410.0	-3336.68	-3451.85	2.62	-3.45
212.0	5880.0	-3588.59	-3658.06	1.58	-1.94
212.0	7350.0	-3709.80	-3722.50	0.29	-0.34
248.0	1470.0	-1109.05	-1146.09	0.84	-3.34
248.0	2940.0	-2299.71	-2373.59	1.68	-3.21
248.0	5880.0	-3261.42	-3348.91	1.99	-2.68
248.0	7350.0	-3419.06	-3460.97	0.95	-1.23
284.0	2940.0	-1907.58	-2023.73	2.64	-6.09
284.0	4410.0	-2592.02	-2706.41	2.60	-4.41
284.0	5880.0	-2926.33	-3047.31	2.75	-4.13
284.0	7350.0	-3116.45	-3203.39	1.98	-2.79

AVERAGE ABSOLUTE DEVIATION = 2.9042%

AVERAGE ABSOLUTE DEVIATION IN BTU/LB = 2.68

TABLE 75

PREDICTION OF SATURATED VAPOR AND LIQUID FUGACITIES FOR CARBON DIOXIDE USING THE MBWR EQUATION

T (F)	PF (PSIA)	FUL (PSIA)	FUG (PSIA)	%DEV
-69.90	75.146	69.6521	69.5365	-0.17
-60.00	94.500	86.2056	86.3107	0.12
-65.00	84.000	77.5151	77.2640	-0.33
-55.00	105.700	95.5811	95.8542	0.28
-50.00	118.000	105.6728	106.2036	0.50
-45.00	131.500	116.5058	117.4108	0.77
-40.00	145.900	128.0924	129.2136	0.87
-35.00	161.000	140.4489	141.4434	0.70
-30.00	177.300	153.6001	154.4646	0.56
-25.00	195.000	167.5634	168.3950	0.49
-20.00	214.500	182.3659	183.4830	0.61
-15.00	235.000	198.0000	199.1165	0.56
-10.00	257.300	214.4943	215.8242	0.62
-5.00	281.000	231.8469	233.2872	0.62
0.0	306.000	250.0621	251.4084	0.54
5.00	332.000	269.1274	269.9753	0.31
10.00	360.000	289.0830	289.5894	0.17
15.00	390.000	309.9331	310.1917	0.08
20.00	421.300	331.6431	331.3250	-0.10
25.00	454.000	354.2131	353.0278	-0.34
30.00	490.000	377.7310	376.2981	-0.38
35.00	527.300	402.0979	399.9778	-0.53
40.00	566.000	427.2952	424.1116	-0.75
45.00	608.000	453.4324	449.5908	-0.85
50.00	653.000	480.4871	476.1592	-0.91
55.00	703.000	508.6042	504.5720	-0.80
60.00	752.000	537.3325	532.1584	-0.97
65.00	801.000	566.6758	559.4829	-1.29
70.00	851.000	596.6526	587.0305	-1.64
75.00	905.000	627.4609	615.9048	-1.88
80.00	965.000	659.2412	646.6753	-1.94
85.00	1032.000	679.4680	679.4680	0.0
87.87	1070.000	698.0894	698.0894	0.0

AVERAGE ABSOLUTE DEVIATION = 0.6265%

TABLE 76

PREDICTION OF SATURATED VAPOR AND LIQUID FUGACITIES FOR CARBON DIOXIDE USING THE OBWR EQUATION

T (F)	PE (PSIA)	FUL (PSIA)	FUG (PSIA)	%DEV
-65.00	75.146	67.0657	69.3352	3.27
-60.00	94.500	84.5366	86.0724	1.78
-55.00	84.000	75.3781	77.0455	2.16
-55.00	105.700	94.3877	95.5988	1.27
-50.00	118.000	104.9515	105.9330	0.93
-45.00	131.500	116.2440	117.1277	0.75
-40.00	145.900	128.2717	128.9233	0.51
-35.00	161.000	141.0406	141.1535	0.08
-30.00	177.300	154.5687	154.1820	-0.25
-25.00	195.000	168.8679	168.1275	-0.44
-20.00	214.500	183.9566	183.2393	-0.39
-15.00	235.000	199.8215	198.9101	-0.46
-10.00	257.300	216.4870	215.6680	-0.38
-5.00	281.000	233.9456	233.1981	-0.32
0.0	306.000	252.1950	251.4055	-0.31
5.00	332.000	271.2219	270.0791	-0.42
10.00	360.000	291.0625	289.8218	-0.43
15.00	390.000	311.7222	310.5789	-0.37
20.00	421.300	333.1638	331.8936	-0.38
25.00	454.000	355.3835	353.8066	-0.45
30.00	490.000	378.4814	377.3208	-0.31
35.00	527.300	402.3459	401.2766	-0.27
40.00	566.000	426.9663	425.7190	-0.29
45.00	608.000	452.4619	451.5452	-0.20
50.00	653.000	478.8147	478.4951	-0.07
55.00	703.000	506.1841	507.3206	0.22
60.00	752.000	534.0925	535.3276	0.23
65.00	801.000	562.5593	563.0730	0.09
70.00	851.000	591.6077	591.0269	-0.10
75.00	905.000	621.4724	620.2603	-0.20
80.00	965.000	652.3545	651.2390	-0.17
85.00	1032.000	684.3740	683.8630	-0.07
87.87	1070.000	702.2419	702.2412	-0.00

AVERAGE ABSOLUTE DEVIATION = 0.5327%

compilation, only a limited amount of saturated liquid PVT data were available. The Beattie-Bridgeman equation was used to generate most of the thermodynamic properties including volumetric behavior of the superheated region. Recent contributions include PVT measurements by Reamer, Sage and Lacey[107] and Lewis and Fredericks[80]. Vapor pressure measurements have also been reported by Reamer, Sage and Lacey[107] and Kay and Rambosek[68].

Densities. Thirty-three points were taken from Reamer, Sage and Lacey (40.0°F to 340°F). The average absolute deviation was 0.86%. Original BWR equation predictions were compared with the same data set, and the average absolute deviation was 1.29%. Comparisons of predicted experimental densities using the modified and original BWR equations are presented in Tables 77 and 78.

Enthalpy Departures. No experimental nor meaningful derived enthalpy departures are available in literature. Hence no attempt was made to include enthalpy data in the regression analysis.

Vapor Pressures. A total of 24 points were taken from Weber (-76.4°F to 10°F) and Kay and Rambosek (30°F to 212.70°F). The average absolute deviation was 0.63%. Original BWR equation of state predictions were compared with the same data set, and the average absolute deviation was 1.49%. Predictions of fugacities along the vapor pressure curve using the modified and original BWR equations are presented in Tables 79 and 80.

TABLE 77

COMPARISON OF PREDICTED DENSITIES USING THE MBWR EQUATION WITH EXPERIMENTAL VALUES FOR HYDROGEN SULFIDE

T (F)	PE (PSIA)	DE (LBMOLE/CF)	DC	DEV	%DEV
40.0	100.0	0.0202	0.0199	0.0003	1.542
40.0	300.0	1.5151	1.5136	0.0015	0.102
40.0	500.0	1.5206	1.5169	0.0037	0.240
40.0	800.0	1.5286	1.5219	0.0067	0.439
40.0	1000.0	1.5335	1.5251	0.0084	0.548
40.0	1250.0	1.5389	1.5290	0.0099	0.642
40.0	1500.0	1.5446	1.5329	0.0117	0.761
40.0	2000.0	1.5552	1.5402	0.0150	0.962
100.0	100.0	0.0175	0.0174	0.0001	0.520
100.0	500.0	1.3715	1.3670	0.0045	0.329
100.0	800.0	1.3831	1.3763	0.0068	0.489
100.0	1000.0	1.3906	1.3822	0.0084	0.602
100.0	1250.0	1.3996	1.3893	0.0103	0.738
100.0	1500.0	1.4086	1.3960	0.0126	0.896
100.0	2000.0	1.4249	1.4085	0.0164	1.148
160.0	100.0	0.0155	0.0155	-0.0000	-0.224
160.0	300.0	0.0506	0.0502	0.0004	0.722
160.0	800.0	1.1677	1.1660	0.0017	0.148
160.0	1000.0	1.1870	1.1830	0.0040	0.338
160.0	1250.0	1.2098	1.2013	0.0085	0.702
160.0	1500.0	1.2286	1.2173	0.0113	0.922
160.0	2000.0	1.2643	1.2443	0.0200	1.579
220.0	100.0	0.0140	0.0141	-0.0001	-0.370
220.0	500.0	0.0793	0.0790	0.0003	0.345
220.0	800.0	0.1437	0.1424	0.0013	0.884
220.0	1000.0	0.2020	0.1984	0.0036	1.763
280.0	100.0	0.0128	0.0128	-0.0000	-0.328
280.0	500.0	0.0699	0.0700	-0.0001	-0.210
280.0	800.0	0.1209	0.1212	-0.0003	-0.264
280.0	1000.0	0.1607	0.1611	-0.0004	-0.246
280.0	1250.0	0.2208	0.2205	0.0003	0.128
280.0	1500.0	0.2967	0.2965	0.0002	0.058
280.0	2000.0	0.5420	0.5347	0.0073	1.348
340.0	100.0	0.0118	0.0118	-0.0000	-0.272
340.0	300.0	0.0365	0.0367	-0.0002	-0.455
340.0	500.0	0.0629	0.0633	-0.0004	-0.567
340.0	800.0	0.1062	0.1071	-0.0009	-0.821
340.0	1000.0	0.1379	0.1394	-0.0015	-1.111
340.0	1250.0	0.1818	0.1842	-0.0024	-1.334
340.0	1500.0	0.2314	0.2348	-0.0034	-1.480
340.0	2000.0	0.3547	0.3568	-0.0021	-0.602

AVERAGE ABSOLUTE DEVIATION = 0.6629%

TABLE 78

COMPARISON OF PREDICTED DENSITIES USING THE OBWR EQUATION WITH EXPERIMENTAL VALUES FOR HYDROGEN SULFIDE

T (F)	PC (PSIA)	DE (LBMOLE/CF)	DC	DEV	%DEV
40.0	100.0	0.0202	0.0201	0.0001	0.502
40.0	300.0	1.5151	1.4853	0.0298	1.966
40.0	500.0	1.5206	1.4892	0.0314	2.062
40.0	800.0	1.5286	1.4950	0.0336	2.200
40.0	1000.0	1.5335	1.4987	0.0348	2.271
40.0	1250.0	1.5389	1.5032	0.0357	2.322
40.0	1500.0	1.5446	1.5075	0.0371	2.399
40.0	2000.0	1.5552	1.5160	0.0392	2.523
100.0	100.0	0.0175	0.0175	-0.0000	-0.089
100.0	500.0	1.3715	1.3531	0.0184	1.341
100.0	800.0	1.3831	1.3638	0.0193	1.396
100.0	1000.0	1.3906	1.3705	0.0201	1.447
100.0	1250.0	1.3996	1.3784	0.0212	1.514
100.0	1500.0	1.4086	1.3859	0.0227	1.611
100.0	2000.0	1.4249	1.3998	0.0251	1.760
160.0	100.0	0.0155	0.0156	-0.0001	-0.575
160.0	300.0	0.0506	0.0509	-0.0003	-0.513
160.0	800.0	1.1677	1.1741	-0.0064	-0.551
160.0	1000.0	1.1870	1.1936	-0.0066	-0.554
160.0	1250.0	1.2098	1.2139	-0.0041	-0.336
160.0	1500.0	1.2286	1.2311	-0.0025	-0.207
160.0	2000.0	1.2643	1.2599	0.0044	0.351
220.0	100.0	0.0140	0.0141	-0.0001	-0.553
220.0	500.0	0.0793	0.0799	-0.0006	-0.788
220.0	800.0	0.1437	0.1457	-0.0020	-1.384
220.0	1000.0	0.2020	0.2054	-0.0034	-1.706
280.0	100.0	0.0128	0.0129	-0.0001	-0.396
280.0	500.0	0.0699	0.0703	-0.0004	-0.598
280.0	800.0	0.1209	0.1221	-0.0012	-0.953
280.0	1000.0	0.1607	0.1626	-0.0019	-1.165
280.0	1250.0	0.2208	0.2232	-0.0024	-1.097
280.0	1500.0	0.2967	0.3009	-0.0042	-1.405
280.0	2000.0	0.5420	0.5388	0.0032	0.585
340.0	100.0	0.0118	0.0118	-0.0000	-0.261
340.0	300.0	0.0365	0.0367	-0.0002	-0.420
340.0	500.0	0.0629	0.0632	-0.0003	-0.505
340.0	800.0	0.1062	0.1070	-0.0008	-0.711
340.0	1000.0	0.1379	0.1392	-0.0013	-0.966
340.0	1250.0	0.1818	0.1839	-0.0021	-1.143
340.0	1500.0	0.2314	0.2343	-0.0029	-1.249
340.0	2000.0	0.3547	0.3565	-0.0018	-0.496

AVERAGE ABSOLUTE DEVIATION = 1.0944%

TABLE 79

PREDICTION OF SATURATED VAPOR AND LIQUID FUGACITIES FOR HYDROGEN SULFIDE USING THE MBWR EQUATION

T (F)	PF (PSIA)	FUL (PSIA)	FUG (PSIA)	%DEV
-76.40	14.700	14.2573	14.4081	1.05
-30.00	45.570	44.1164	43.6181	-1.14
-10.00	69.090	65.8888	65.1978	-1.06
10.00	99.960	94.4543	92.8396	-1.74
30.00	145.500	130.7859	132.2285	1.09
40.00	170.100	152.0522	153.0461	0.65
50.00	198.800	175.5358	176.8667	0.75
60.00	230.100	201.2646	202.3937	0.56
70.00	265.200	229.3253	230.4503	0.49
80.00	304.200	259.7471	260.9727	0.47
90.00	347.300	292.5681	293.9622	0.47
100.00	394.600	327.7957	329.3386	0.47
110.00	446.500	365.4397	367.2114	0.48
120.00	503.000	405.4736	407.4067	0.47
130.00	564.600	447.8811	450.0540	0.48
140.00	631.600	492.6223	495.1221	0.50
150.00	703.500	539.5842	542.1260	0.47
160.00	781.600	588.7568	591.5522	0.47
170.00	865.600	639.9966	642.9802	0.46
180.00	956.400	693.2473	696.5601	0.48
190.00	1054.600	748.4133	752.1885	0.50
200.00	1160.500	805.3801	809.5300	0.51
212.00	1297.100	875.8325	879.4648	0.41
212.76	1306.000	880.0986	880.0977	-0.00

AVERAGE ABSOLUTE DEVIATION = 0.6330%

TABLE 80

PREDICTION OF SATURATED VAPOR AND LIQUID FUGACITIES FOR HYDROGEN SULFIDE USING THE OBWR EQUATION

T (F)	PE (PSIA)	FUL (PSIA)	FUG (PSIA)	%DEV
-76.40	14.700	11.8108	14.3589	17.75
-30.00	45.570	41.3512	43.2997	4.50
-10.00	69.090	63.1896	64.5772	2.15
10.00	99.960	91.7334	91.7362	-0.00
30.00	145.500	127.7769	130.2426	1.89
40.00	170.100	148.7315	150.5445	1.20
50.00	198.800	171.7624	173.7186	1.13
60.00	230.100	196.8900	198.5094	0.82
70.00	265.200	224.1765	225.7013	0.68
80.00	304.200	253.6597	255.2266	0.61
90.00	347.300	285.3684	287.0908	0.60
100.00	394.600	319.3257	321.1860	0.58
110.00	446.500	355.5547	357.6440	0.58
120.00	503.000	394.0579	396.2959	0.56
130.00	564.600	434.8501	437.2673	0.55
140.00	631.600	477.9402	480.5381	0.54
150.00	703.500	523.2708	525.6755	0.46
160.00	781.600	570.8870	573.1453	0.39
170.00	865.600	620.7163	622.5906	0.30
180.00	956.400	672.7559	674.1777	0.21
190.00	1054.600	726.9612	727.8582	0.12
200.00	1160.500	783.1748	783.4124	0.03
212.00	1297.100	852.0144	852.0139	0.0
212.70	1306.000	856.2297	856.2305	0.00

AVERAGE ABSOLUTE DEVIATION = 1.4859%

SUMMARY

For each of the eight hydrocarbons and three non-hydrocarbons studied, the modified BWR equation predicts thermodynamic properties with an average absolute deviation in the neighborhood of 1.0%. Improvements over the original BWR equation are most striking in predicting the low temperature enthalpy behavior of methane, propane, and nitrogen. Predictions of sub-atmospheric saturated vapor and liquid fugacities have also met with comparable success.

In the high temperature region, the modified BWR equation is slightly less accurate than the original BWR equation. This result originates principally from the use of density rather than compressibility factor or pressure as the dependent variable. Minimization of the relative deviation between experimental and calculated densities tends to weight high density points more heavily. Also, more liquid than gas phase data points were utilized.

These problems can be overcome by physically preparing a larger data deck with more high temperature points. However, it has not been economical to do so using the IBM 360/40. However, the accuracy with which the modified BWR equation predicts thermodynamic properties in high temperature region is adequate for engineering needs.

In formulating the mathematical framework for multi-property regression analysis, no attempt was made to include critical property constraints. Hence application

of the modified BWR equation in the critical region may be expected to be less accurate than elsewhere.

This investigation shows that a comparatively simple modification of the BWR equation can be formulated to predict accurately all thermodynamic properties of light hydrocarbons and certain nonhydrocarbons in the vapor, liquid and coexisting phases. The simplicity of this modification of the BWR equation of state should facilitate its extension to other fluids.

CHAPTER IX

APPLICATION OF MULTIPROPERTY REGRESSION ANALYSIS TO GENERALIZE THE MODIFIED BWR EQUATION OF STATE

Methods for Generalization Using an Equation of State

To extend the usefulness of an equation of state, it is desirable to have available a practical means for generating parameters for other fluids of interest. One simple way is to rewrite the equation of state in reduced form based on the two-parameter corresponding states principle. Su and Viswanath[128] have defined a pseudo-critical volume in terms of critical temperature and pressure and applied this method to real gases using the reduced BWR equation. To improve the accuracy of predictions, some investigators have expressed reduced parameters as functions of acentric factor or critical compressibility factor. These generalizations based on the corresponding states principle have been applied with satisfactory results to predict the volumetric behavior of the vapor phase but become unreliable near the two phase region[66].

Another way to generalize is to correlate equation-of-state parameters as functions of some physical constants such as carbon number, acentric factor, and the critical constants. For example, Canjar and coworkers[20] have correlated the BWR constants for the hydrocarbon series in terms of critical temperature and carbon number.

Application of the Corresponding States Principle to the Modified BWR Equation

The eleven sets of modified BWR constants were used as the basis for generalization. To test the validity of using the three-parameter corresponding states principle, the reduced equation of state constants were plotted versus acentric factor after the manner of Edmister[47]. Two of the better "behaved" reduced parameters viz., a' and C_o', (reduced parameters are indicated by primes)

$$a' = \frac{aP_c^2}{R^3T_c^3} \tag{83}$$

$$C_o' = \frac{C_oP_c}{R^3T_c^4} \tag{84}$$

are shown in Figures 26 and 27. It can be seen that the wide scattering of the data points ruins any hope of proposing meaningful functionality between the reduced parameters and the acentric factor. The reason becomes obvious when the variances of the parameters are examined. In a multiparameter equation of state, it is inherent that

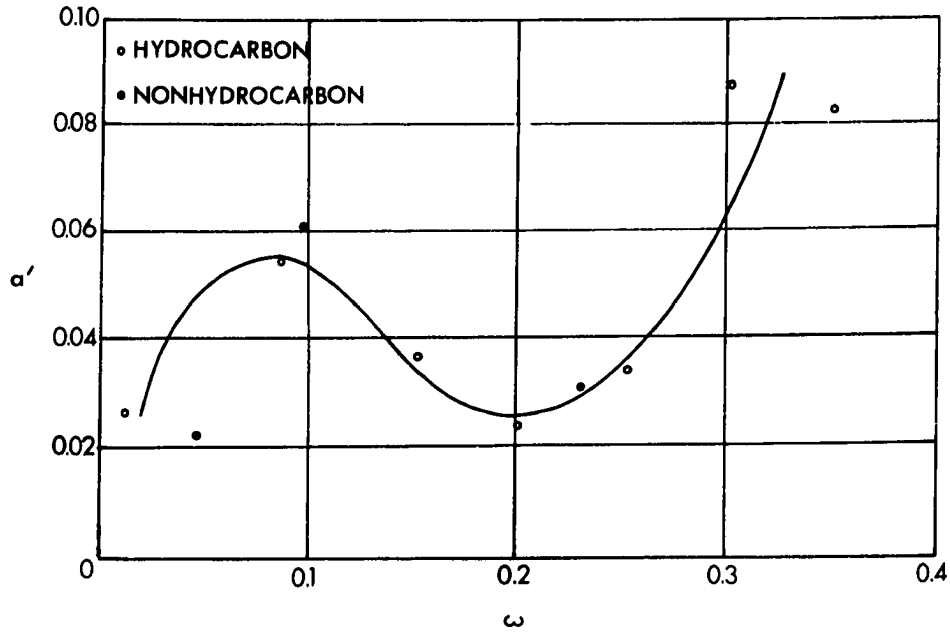


Figure 26. Variation of the Reduced Parameter a' with Acentric Factor

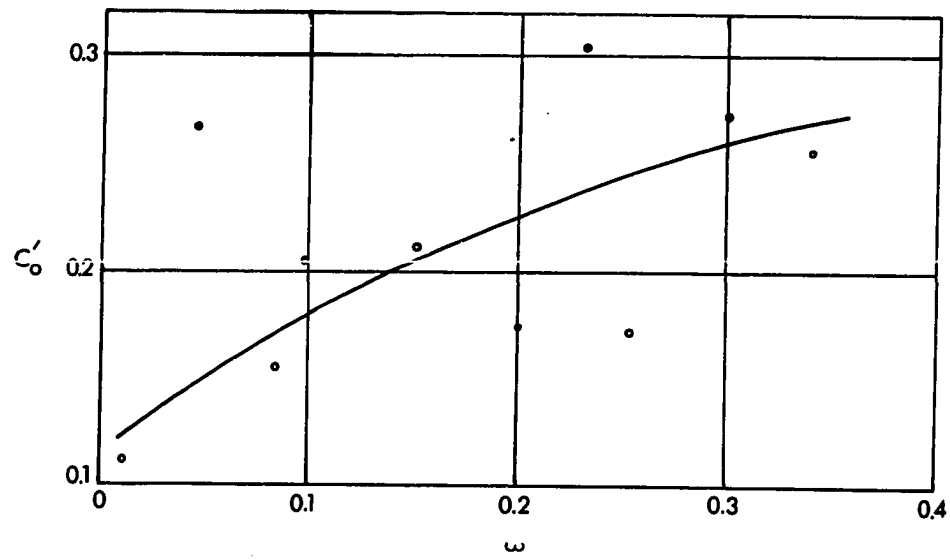


Figure 27. Variation of the Reduced Parameter C_o' with Acentric Factor.

some of the parameters will have large variances, which are measures of uncertainties. By transforming the parameters in reduced form, these uncertainties tend to be magnified when plotted, as in Figures 26 and 27. This finding does not repudiate the validity of the corresponding states principle. Rather it points out the inappropriateness of applying the corresponding states principle directly to the equation-of-state parameters.

Correlation of the Modified BWR Constants as Functions of Acentric Factor

For normal paraffins, it has been observed by Starling[117] that save for C_o, the roots of the original BWR parameters as indicated by their presence in the mixing rules assume a linear relationship with carbon number, e.g.

$$\gamma_i^{\frac{1}{2}} = a + bN_i \tag{85}$$

where a and b are constants and N_i is the carbon number for the i^{th} component. In this study, the same approach was applied to the modified BWR parameters. The acentric factor was preferred over carbon number because it offered a smoother correlation. Figure 28 depicts the relatively well behaved quadratic functionality between the roots of the modified BWR constants and acentric factors, for example,

$$\gamma_i^{\frac{1}{2}} = a + b\omega_i + c\omega_i^2 \tag{86}$$

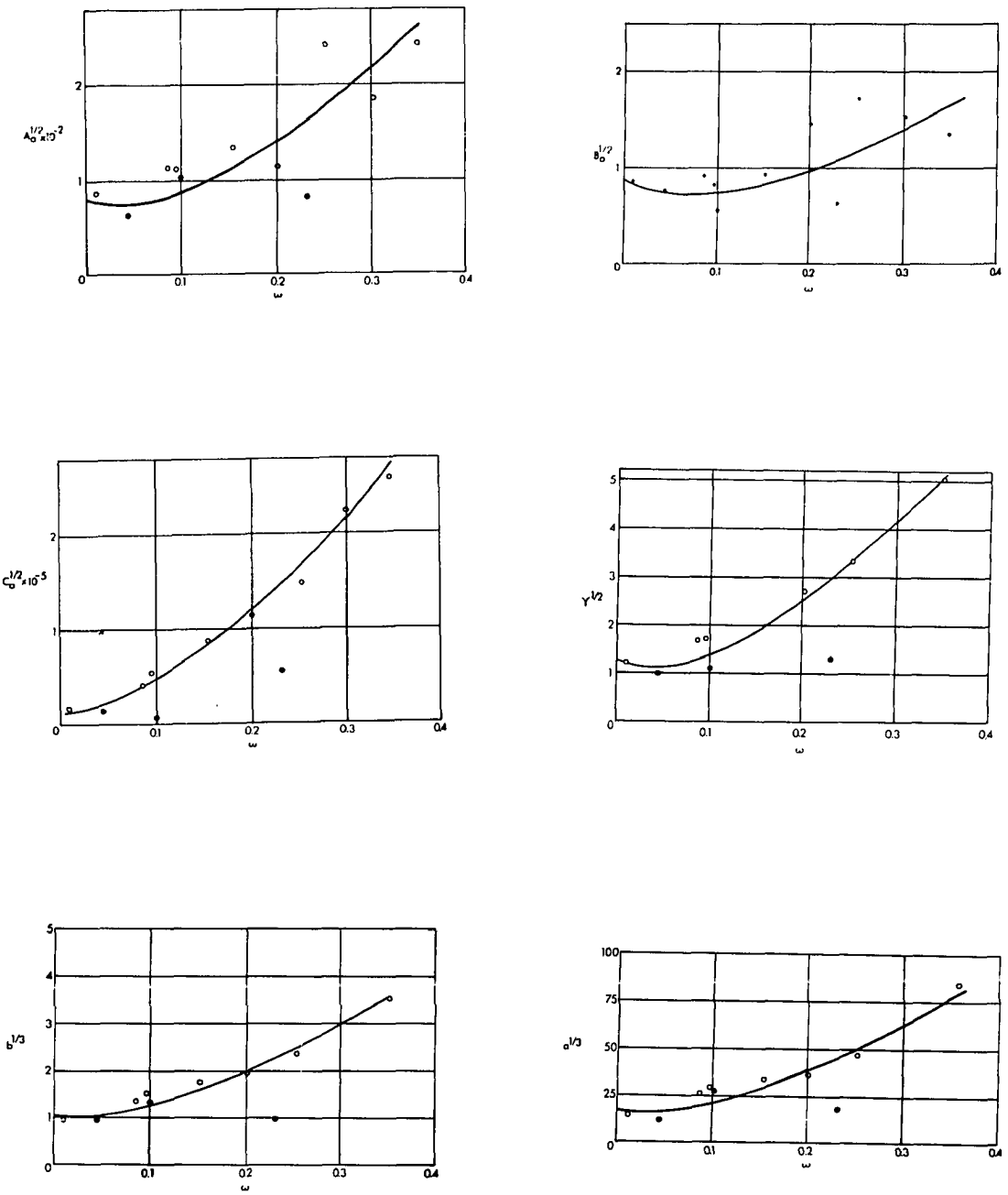


Figure 28. Variation of the Roots of the Modified BWR Equation Parameters with Acentric Factor.

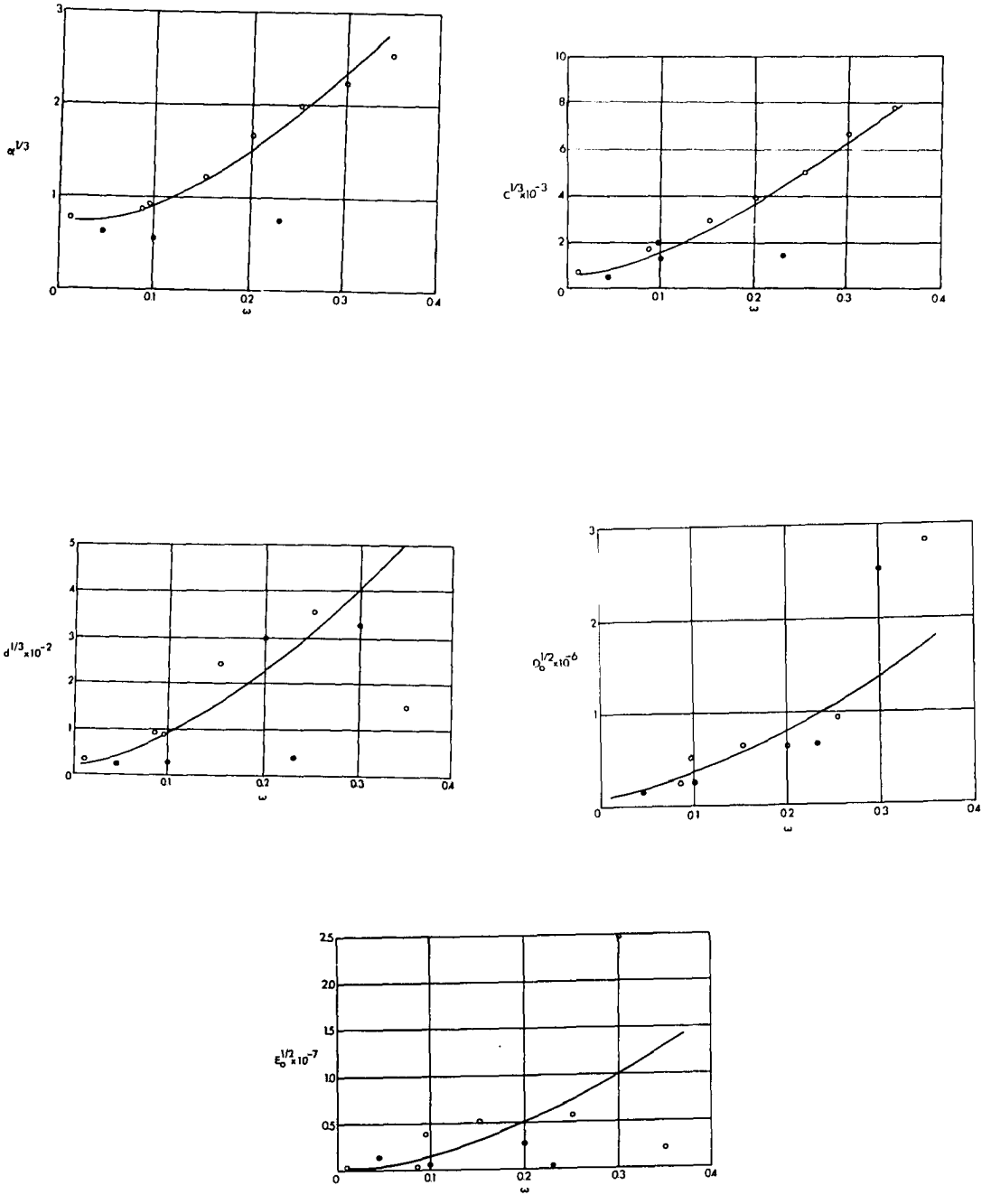


Figure 28. Continued.

This is not surprising because of the fact that taking the roots of the parameters has the effect of minimizing their apparent uncertainties when plotted, as in Figure 28.

The high interdependence among the parameters of a given fluid suggests the feasibility of determining an aggregate set of parameters for several fluids such that they do conform to the proposed quadratic functionality with acentric factor. Of more importance, it is hoped that the set of generalized parameters may be used to predict several thermodynamic properties instead of just volumetric behavior as is traditionally the case.

To this end, multiproperty regression analysis was used to determine the generalized parameters in Equation (86). Because of limitations in available computer core storage and execution time, only the first five normal paraffins (methane through n-pentane) were used to generate the coefficients in the expressions for the parametric relations as indicated in Equation (86).

Results Using the Generalized Parameters of the Modified BWR Equation of State for Methane through n-Pentane

PVT, enthalpy and vapor pressure data for methane, ethane, propane, n-butane and n-pentane were used simultaneously to determine the following set of generalized parameters:

$$B_o^{1/2} = 0.933417 - 5.48353*\omega + 31.6704*\omega^2$$

$$A_o^{1/2} = 90.3538 - 94.4834*\omega + 2295.11*\omega^2$$

$$C_o^{1/2} = 10325.5 + 455601*\omega + 279126.0*\omega^2$$

$$\gamma^{1/2} = 1.24601 + 0.420928*\omega + 27.9750*\omega^2$$

$$b^{1/3} = 0.957541 + 5.47550*\omega + 1.78745*\omega^2 \qquad (87)$$

$$a^{1/3} = 12.6896 + 157.121*\omega - 18.2303*\omega^2$$

$$\alpha^{1/3} = 0.756805 - 0.213250*\omega + 18.5870*\omega^2$$

$$c^{1/3} = 636.089 + 10663.0*\omega + 21817.5*\omega^2$$

$$D_o^{1/2} = 36948.9 + 50533.1*10^2*\omega - 13678.5*10^2*\omega^2$$

$$d^{1/3} = 4.80701 + 1045.53*\omega + 1868.43*\omega^2$$

$$E_o^{1/2} = 6547.80 + 25062.0*10^3*\omega + 11090.6*10^4*\omega^2$$

Table 81 summarizes the results of using the generalized parameters in predicting the thermodynamic behavior of methane through n-pentane.

Use of the Generalized Parameters to Predict Behavior of n-Hexane

As a check for its validity, generalized parameters of the modified BWR equation was applied to n-hexane. An acentric factor of 0.3007 for n-hexane was selected from literature[1]. Comparisons were made on the same PVT and

TABLE 81

PREDICTION OF THE THERMODYNAMIC BEHAVIOR OF METHANE THROUGH N-PENTANE

USING THE GENERALIZED PARAMETERS OF THE MODIFIED BWR EQUATION

COMPONENT	ACENTRC FACTOR*	PVT			ENTHALPY DEPARTURE			SATURATED FUGACITY		
		NO. OF POINTS	TEMPERATURE RANGE (°F)	AVG. ABS. DEV. %	NO. OF POINTS	TEMPERATURE RANGE (°F)	AVG. ABS. DEV. %	NO. OF POINTS	TEMPERATURE RANGE (°F)	AVG. ABS. DEV. %
METHANE	0.0104	30	-253 to 257	0.471	28	-250 to 50	1.806	18	-259 to -116	0.414
ETHANE	0.0986	27	-250 to 310	3.279	30	100 to 310	2.99	23	-190 to 90	1.085
PROPANE	0.1524	30	-250 to 527	2.956	30	-250 to 250	1.07	19	-140 to 206	0.347
N-BUTANE	0.2010	29	-220 to 280	2.269	26	100 to 250	0.415	15	31.1 to 305	3.819
N-PENTANE	0.2539	30	-200 to 430	3.803	26	100 to 460	1.464	24	30 to 385.9	0.25

* Values of acentric factors are taken from reference 1.

vapor pressure data sets previously described in Chapter VI. Using this method, the average absolute deviation was 9.4% for density at 41 points and 10.2% for fugacities of the coexisting vapor and liquid phases at 40 vapor pressure points.

To compare with the two-parameter corresponding states principle, a set of n-hexane parameters of the modified BWR equation was generated from the set of n-pentane parameters in the same manner previously described in Chapter V. The values of the resulting n-hexane parameters are: B_o = 0.358221E+01, A_o = 0.755694E+05, C_o = 0.313707E+11, γ = 0.169689E+02, b = 0.193062E+02, a = 0.169175E+06, α = 0.135000E+02, D_o = 0.124900E+12, d = 0.806872E+08, E_o = 0.575413E+14. Comparisons using the above parameter values were made on the same PVT and vapor pressure data sets. The average absolute deviation was 1.7% for density at 41 points and 75.1% for fugacities of the coexisting vapor and liquid phases at 40 vapor pressure points.

Comparisons of predicted and experimental densities using the simple corresponding states parameters of the modified BWR equation are presented in Table 82. Predictions of fugacities along the vapor pressure curve using the simple corresponding states parameters are presented in Table 83.

The most interesting observation from Tables 82 and 83 is the contrasting accuracies in predicting

TABLE 82

COMPARISON OF PREDICTED DENSITIES USING THE MBWR EQUATION-OF-STATE PARAMETERS OBTAINED FROM SIMPLE CSP FOR n-HEXANE

T (F)	PL (PSIA)	DE (LBMOLE/CF)	DC	DEV	%DEV
-140.0	14.7	0.5492	0.5426	0.0066	1.204
-130.0	14.7	0.5459	0.5389	0.0069	1.273
-120.0	14.7	0.5424	0.5352	0.0072	1.323
-110.0	14.7	0.5392	0.5317	0.0075	1.392
-100.0	14.7	0.5358	0.5283	0.0075	1.400
-90.0	14.7	0.5324	0.5249	0.0075	1.411
-80.0	14.7	0.5291	0.5216	0.0075	1.417
-70.0	14.7	0.5257	0.5184	0.0073	1.391
-60.0	14.7	0.5223	0.5152	0.0071	1.353
-50.0	14.7	0.5190	0.5121	0.0069	1.323
-40.0	14.7	0.5156	0.5091	0.0065	1.263
-20.0	14.7	0.5087	0.5031	0.0056	1.093
0.0	14.7	0.5018	0.4973	0.0045	0.889
20.0	14.7	0.4947	0.4917	0.0030	0.613
40.0	14.7	0.4875	0.4861	0.0014	0.289
60.0	14.7	0.4806	0.4806	0.0000	0.002
80.0	14.7	0.4732	0.4751	-0.0019	-0.409
100.0	14.7	0.4659	0.4697	-0.0038	-0.815
120.0	14.7	0.4583	0.4643	-0.0060	-1.303
140.0	14.7	0.4502	0.4588	-0.0086	-1.916
280.0	14.7	0.0019	0.0019	0.0000	0.168
100.0	108.4	0.4662	0.4700	-0.0038	-0.820
100.0	554.5	0.4688	0.4715	-0.0027	-0.584
100.0	848.3	0.4662	0.4725	-0.0063	-1.354
100.0	1813.0	0.4757	0.4756	0.0001	0.021
100.0	2903.0	0.4809	0.4749	0.0019	0.391
160.0	99.3	0.4439	0.4537	-0.0098	-2.212
160.0	438.6	0.4463	0.4552	-0.0089	-1.990
160.0	868.5	0.4493	0.4570	-0.0077	-1.696
160.0	2887.0	0.4625	0.4647	-0.0022	-0.478
160.0	3977.0	0.4682	0.4685	-0.0003	-0.062
220.0	96.3	0.4186	0.4369	-0.0183	-4.383
220.0	442.8	0.4225	0.4388	-0.0163	-3.869
220.0	844.6	0.4263	0.4410	-0.0147	-3.441
220.0	1961.0	0.4365	0.4465	-0.0100	-2.280
220.0	2956.0	0.4439	0.4509	-0.0070	-1.581
280.0	837.9	0.4023	0.4243	-0.0220	-5.459
280.0	1816.0	0.4137	0.4303	-0.0166	-4.021
280.0	2930.0	0.4244	0.4365	-0.0121	-2.850
340.0	1841.0	0.3912	0.4142	-0.0230	-5.890
340.0	2980.0	0.4054	0.4220	-0.0166	-4.091

AVERAGE ABSOLUTE DEVIATION = 1.6032%

TABLE 83

PREDICTION OF SATURATED VAPOR AND LIQUID FUGACITIES FOR n-HEXANE USING THE MBWR EQUATION-OF-STATE PARAMETERS OBTAINED FROM SIMPLE CSP

T (F)	PF (PSIA)	FUL (PSIA)	FUG (PSIA)	%DEV
-10.00	0.217	0.0007	0.2166	99.66
-5.00	0.261	0.0011	0.2604	99.57
0.0	0.311	0.0015	0.3102	99.51
10.00	0.438	0.0030	0.4366	99.30
15.00	0.517	0.0042	0.5151	99.18
20.00	0.606	0.0058	0.6035	99.04
25.00	0.709	0.0078	0.7057	98.89
30.00	0.825	0.0105	0.8206	98.72
32.00	0.876	0.0117	0.8712	98.66
40.00	1.107	0.0183	1.0997	98.34
50.00	1.464	0.0303	1.4520	97.88
70.00	2.464	0.0798	2.4342	96.72
80.00	3.143	0.1231	3.0975	96.02
90.00	3.966	0.1853	3.8990	95.25
110.00	6.136	0.3920	5.9916	93.46
120.00	7.531	0.5531	7.3259	92.45
130.00	9.168	0.7663	8.8810	91.37
150.00	13.283	1.3990	12.7442	89.02
160.00	15.823	1.9409	15.0989	87.75
170.00	18.730	2.4114	17.7682	86.43
190.00	25.800	3.9474	24.1556	83.66
200.00	30.010	4.9651	27.8953	82.20
210.00	34.650	6.1802	31.9682	80.67
230.00	45.600	9.3049	41.3867	77.52
240.00	52.100	11.2684	46.8553	75.95
250.00	59.240	13.5362	52.7691	74.35
270.00	75.350	19.0999	65.7948	70.97
280.00	84.930	22.4572	73.3190	69.37
290.00	95.050	26.2348	81.1302	67.66
310.00	118.200	35.1786	98.4341	64.26
320.00	131.300	40.4045	107.9011	62.55
330.00	145.100	46.1576	117.6657	60.76
350.00	176.200	59.4333	138.2150	57.19
360.00	193.600	66.9938	150.1491	55.38
370.00	212.200	75.2078	161.8876	53.54
390.00	253.800	93.7184	186.5939	49.77
400.00	277.500	104.0878	104.0878	0.0
410.00	301.300	115.1787	115.1784	-0.00
430.00	356.500	139.8550	139.8550	0.0
454.50	439.700	175.0400	175.0400	0.0

AVERAGE ABSOLUTE DEVIATION = 75.0759%

density and fugacity along the vapor pressure curve using the simple corresponding states parameters. Comparatively accurate predictions in densities may still yield large deviations in describing phase equilibrium behavior. Extension of the generalized parameters in n-hexane results in an error of about 10% in both density and fugacity predictions. The results undoubtedly disqualify the use of the generalized parameters with acentric factors reported in literature as a direct means to correlate thermodynamic behavior of fluids other than the first five hydrocarbons of the normal paraffins. However, one is at liberty to adjust the value used for the acentric factor in the generalized expressions for parameters. In view of this fact, the generalized parameters of the modified BWR equation provide yet another method of correlating fluid behavior through an "effective" acentric factor.

Use of an "Effective" Acentric Factor to Correlate the Thermodynamic Behavior of iso-Pentane

In applying the generalized parameters of the modified BWR equation to n-hexane, a value of acentric factor was obtained from literature. The acentric factor, as first introduced by Pitzer[101], is evaluated empirically according to the following relationship

$$\omega = \left[-1 - \log_{10}(P_r)\right]_{T_r=0.7} \qquad (88)$$

where P_r is the reduced vapor pressure.

However, if one is willing to make the bold assumption that the coefficient in Equation (87) are universal constants, then it seems probable that there exists a value of ω such that when substituted in Equation (87), it will yield the predicted properties of a fluid within a reasonable degree of uncertainty. This value of ω, for lack of a better name, is termed the "effective " acentric factor.

To prove the above concept, i-pentane was chosen for study. A total of 41 PVT points (-60°F to 392°F) were chosen from API Project 44[111] and Silberberg and coworkers[114]. Using a value of 0.2223 for the acentric factor[1], the generalized parameters yielded an average absolute deviation of 9.8% for densities. By a trial and error procedure, an "effective" acentric factor of 0.2420 was found which improved the average absolute deviation to 3.9%. A total of 17 vapor pressure points were taken from API Project 44[111] and Canjar and Manning's[21] compilation (0°F to 346.98°F). Prediction of saturated vapor and liquid fugacities using the acentric factor defined by Equation (88) yielded an average absolute deviation of 55%. Use of the "effective" acentric factor reduced the average absolute deviation to 2.1%.

The above results clearly show that appreciable improvement in the predictive ability of the generalized

parameters can be effected simply by adjusting just one variable, viz., the acentric factor. The relatively large deviation in the predicted properties of isopentane using the "effective" acentric factor indicate the inadequacy of treating the coefficients of the generalized parameters as universal constants. This inadequacy may be greatly overcome when a much larger sample of representative fluids can be used in the above correlation scheme. Unfortunately, the present limited resources in computer core storage and running time do not permit such an undertaking.

Prediction of Natural Gas Behavior at Cryogenic Conditions Using the Generalized Parameters

Usually, over 90% of natural gas is methane, with the remaining fraction composed of heavier normal paraffins and isomers and some nonhydrocarbons, notably nitrogen, carbon dioxide and hydrogen sulfide. With increasing interest in processing natural gas at cryogenic conditions, it is desirable to develop a simple means to correlate natural gas behavior. Use of the generalized parameters of the modified BWR equation to predict thermodynamic properties of natural gas offers the following advantages:

1. The generalized parameters were developed from the light normal paraffins (methane through n-pentane) which represent the bulk of the constituents present in natural gas.

2. For constituents other than the above five hydrocarbons, parameters can be generated very simply by the use of acentric factors as reported in literature. Since these constituents usually occur only in small amounts, their presence should not impair the overall accuracy of prediction to any appreciable extent.

3. The high accuracy with which the generalized parameters predict methane behavior ensures the applicability in correlating the behavior of natural gas because of its predominant methane content.

4. The generalized parameters were developed from considering PVT, enthalpy and phase equilibrium behavior of methane through n-pentane. The temperature range of the above properties lies between -250°F to 250°F. Thus, the generalized parameters should be applicable to predict behavior of natural gas over the same temperature range.

Recently, cryogenic PVT, and enthalpy measurements of several "synthesized" natural gas samples have been reported by Subramaniam and coworkers[129]. While the accuracy of the above measurements has not been established, this work represents one of the few sources of data on natural gas at cryogenic conditions. Hence, they are used in this study only for comparison purposes.

Mixture No. 4 from Subramaniam and coworkers' PVT measurements was selected to test the ability of the

generalized parameters of the modified BWR equation in predicting volumetric behavior of natural gas. The composition of this mixture is 1.24 mole % nitrogen, 94.75% methane, 2.83% ethane, 0.45% propane, 0.45% n-butane, 0.11% n-pentane and 0.17% n-hexane. The average absolute deviation in density was 3.58% for 36 points (-240°F to 100°F).

Mixture No. 4 from Subramaniam and coworkers' enthalpy measurements was selected to test the ability of the generalized parameters of the modified BWR equation in predicting enthalpy behavior of natural gas. The composition of this mixture is 0.9 mole % nitrogen, 95.02% methane, 3.00% ethane, 0.35% propane, 0.48% n-butane, 0.07% n-pentane and 0.18% n-hexane. The average absolute deviation in enthalpy departure was 16% (4.25 Btu/lb) for 41 points (-200°F to 200°F).

In view of the fact that (1) the average absolute deviation in density of pure methane is 0.5% for 30 points (-253°F to 257°F), (2) the average absolute deviation in enthalpy departure of pure methane is 1.8% for 28 points (-250°F to 50°F), (3) the methane content of the two natural gas mixtures is near 95%, it is possible that the large deviations in the predicted properties of natural gas are due to inaccurate experimental values rather than to the inadequacy of using the generalized parameters to correlate natural gas behavior.

Summary

There are three basic factors which hinder application of the corresponding states principle or the generalized correlating scheme described in this chapter to the parameters of the modified BWR equation of state as a direct means to predict thermodynamic properties.

1. The additional parameters d, D_o and E_o, are designed for low temperature correlation (to reduced temperatures as low as 0.3 for propane). Experimental data for the eleven fluids thus far determined do not extend to the same low reduced temperature. Hence it can be expected that the parameters d, D_o and E_o cannot be equally well defined for all fluids.

2. The eleven sets of modified BWR constants were determined from multiproperty regression analysis. However, only methane, propane, and nitrogen have extensive low temperature enthalpy data. Hence, the sets of constants for these three fluids are much better defined than the remaining eight fluids.

3. Multiproperty regression analysis can be used to partially offset the handicaps listed in (1) and (2) by capitalizing on the high interdependence among parameters of a given fluid. But, the accuracy of prediction using an empirical equation of state is highly sensitive to the numerical values of its parameters. Experience has shown that a slight change in the numerical value of any one of the parameters may cause errors

of several orders of magnitude in predicted properties, especially enthalpy departures and fugacities along the vapor pressure curve.

Despite these difficulties, there remains the urgent need to provide a way whereby equation of state parameters for other fluids can be readily determined. Successful use of multiproperty regression analysis with the Gauss-Newton linearization scheme requires the availability of initial estimates of parameters that are reasonably close to the optimum values. Of course, more sophisticated schemes such as Marquardt's compromise[84] may be used to minimize the number of iterations required for convergence. However, the need for "reasonable" initial estimates remains for any nonlinear regression scheme.

The proposed generalized parameters serve the purpose of generating reasonable initial estimates for parameters of normal fluids (with acentric factors, not exceeding 0.35) in the following way. To determine the parameters of a fluid of interest, the coefficients in Equation (87) are assumed to be universal constants. By regression analysis or a trial and error procedure, an "effective" acentric factor is determined such that the average absolute deviation in predicted properties of the fluid of interest is a minimum. This minimum may or may not fall within tolerable uncertainty for

engineering design purposes (say 1 or 2%). In the latter case, the parameters generated from Equation (87) using the "effective" acentric factor may then be used as input values in the multiproperty regression analysis.

The original BWR equation has been applied to well over thirty materials including aromatic and polar fluids. Use of "effective" acentric factor in conjunction with the generalized parameters of the modified BWR equation can be rapidly applied to generate parameters for both aromatic and polar fluids. When a representative sample or materials with different characteristics have been correlated with their "effective" acentric factors, the coefficients appearing in the generalized parameters may then be redetermined using multiproperty regression analysis. The resulting coefficients then should approximate to a much better degree, universal constants.

Completion of the above scheme lies beyond the scope of this research and therefore was not attempted.

Use of the generalized parameters of the modified BWR equation of state to predict natural gas behavior has been successfully demonstrated, although its true merit cannot be assessed until undisputably accurate experimental values are available.

CHAPTER X

APPLICATION OF THE MODIFIED BWR EQUATION OF STATE TO THE METHANE-PROPANE SYSTEM

Mixing Rules for the Modified BWR Equation

For a chemically noninteracting system, it is well known that the thermodynamic behavior of a mixture may be predicted using the same equation of state applicable to its pure components provided an "appropriate" set of mixing rules can be formulated for the equation's parameters. From statistical mechanics, Mayer[92] derived a general form for the composition dependence of coefficients in the virial equation of state.

Specifically, Mayer[92] has shown that the residual work content of a mixture may be expressed as a power series in molal density

$$\tilde{A} = \rho \sum_i \sum_j x_i x_j Q'_{ij} + \rho^2 \sum_i \sum_j \sum_k x_i x_j x_k Q''_{ijk} + \cdots \qquad (89)$$

where Q'_{ij} and Q''_{ijk} are functions of temperature. Since the pressure of a mixture is related to the residual work content by the thermodynamic relationship

$$P = RT\rho + \rho^2 \left(\frac{\partial \tilde{A}}{\partial \rho}\right)_{T,x} \tag{90}$$

it can be seen that the parameters associated with the second virial coefficient B may be expressed, in general, as

$$B = \sum_i \sum_j x_i x_j B_{ij} \tag{91}$$

where B_{ii} is the second virial coefficient for i^{th} component parameter and B_{ij} $(i \neq j)$ is the so-called unlike interaction parameter. Similarly, mixture parameters associated with the third virial coefficient C, may be expressed, in general, as

$$C = \sum_i \sum_j \sum_k x_i x_j x_k C_{ijk} \tag{92}$$

where C_{iii} is the third virial coefficient for the i^{th} component and C_{ijk} (with two or three differing subscripts) is an unlike interaction parameter.

The unlike interaction parameters (B_{ij} and C_{ijk}), may be determined empirically from experimental data. However, when the number of parameters of an equation of state is large, the determination of many two-body and three-body unlike interaction parameters becomes difficult because of the need for such a large amount of accurate binary, ternary, etc. data to determine the large number of parameters. It becomes desirable then,

to be able to predict the thermodynamic behavior of a mixture from knowledge of the pure component behavior of its constituents.

To this end, Benedict and coworkers[10], using the results by Mayer, chose to define unlike interaction parameters to be arithmetic and geometric averages of the corresponding pure component parameters. For example, defining the unlike interaction parameter B_{ij}, to be the arithmetic average of B_i and B_j, i.e.,

$$B_{ij} = \frac{1}{2} (B_i + B_j) \tag{93}$$

leads to

$$B = \sum_i x_i B_i \tag{94}$$

Similarly, using geometric averages such as

$$B_{ij} = B_{ii}^{\frac{1}{2}} B_{jj}^{\frac{1}{2}} \tag{95}$$

and

$$C_{ijk} = C_i^{1/3} C_j^{1/3} C_k^{1/3} \tag{96}$$

reduces Equations (91) and (92) to

$$B^{\frac{1}{2}} = \sum_i x_i B_i^{\frac{1}{2}} \tag{97}$$

$$C^{1/3} = \sum_i x_i C_i^{1/3} \tag{98}$$

Benedict, Webb and Rubin[10] used the linear mixing rule for B_o and geometric mixing rules for the remainder of the parameters in the BWR equation. These simple mixing rules are retained in this work. Geometric mixing rules are chosen for the new parameters d, D_o, E_o in the modified BWR equation. Accordingly, the mixture parameters for the modified BWR equation are as follows:

$$
\begin{aligned}
B_o &= \sum_i x_i B_{o_i} & b^{1/3} &= \sum_i x_i b_i^{1/3} \\
A_o^{1/2} &= \sum_i x_i A_{o_i}^{1/2} & a^{1/3} &= \sum_i x_i a_i^{1/3} \\
C_o^{1/2} &= \sum_i x_i C_{o_i}^{1/2} & \alpha^{1/3} &= \sum_i x_i \alpha_i^{1/3} \\
\gamma^{1/2} &= \sum_i x_i \gamma_i^{1/2} & c^{1/3} &= \sum_i x_i c_i^{1/3} \\
D_o^{1/2} &= \sum_i x_i D_{o_i}^{1/2} & d^{1/3} &= \sum_i x_i d_i^{1/3} \\
E_o^{1/2} &= \sum_i x_i E_{o_i}^{1/2}
\end{aligned}
\qquad (99)
$$

Thermodynamic-Property Equations for Mixtures Using the Modified BWR Equation

Pressure Equation for a Mixture

The pressure equation of a mixture is the same as that of a pure component, viz.

$$P = \rho RT + \left(B_o RT - A_o - \frac{C_o}{T^2} + \frac{D_o}{T^3} - \frac{E_o}{T^4}\right)\rho^2 + \left(bRT - a - \frac{d}{T}\right)\rho^3 + \alpha\left(a + \frac{d}{T}\right)\rho^6 + \frac{c\rho^3}{T^2}\left(1 + \gamma\rho^2\right)\exp\left(-\gamma\rho^2\right). \quad (100)$$

Detailed derivation of the Helmholtz free energy after the manner of Wolfe[140] is presented in Appendix C. Hence, only the final form of the Helmholtz free energy using the modified BWR equation and its related thermodynamic functions are presented here.

Helmholtz Free Energy Equation of a Mixture

$$A = \sum_i x_i\left[RT\ell n(RT\rho x_i) + E_i^\circ - TS_i^\circ\right] + \left(B_o RT - A_o - \frac{C_o}{T^2} + \frac{D_o}{T^3} - \frac{E_o}{T^4}\right)\rho + \left(bRT - a - \frac{d}{T}\right)\frac{\rho^2}{2} + \left(a + \frac{d}{T}\right)\frac{\alpha\rho^5}{5} + \frac{c\rho^2}{T^2}\left[\frac{1 - \exp(-\gamma\rho^2)}{\gamma\rho^2} - \frac{\exp(-\gamma\rho^2)}{2}\right] \quad (101)$$

where E_i° and S_i° are the internal energy and entropy of the i^{th} component at unit pressure.

Enthalpy Equation of a Mixture

$$H = \sum_i x_i H_i^\circ + \left(B_o RT - 2A_o - \frac{4C_o}{T^2} + \frac{5D_o}{T^3} - \frac{6E_o}{T^4} \right) \rho$$

$$+ \frac{1}{2} \left(2bRT - 3a - \frac{4d}{T} \right) \rho^2 + \frac{1}{5} \alpha \left(6a + \frac{7d}{T} \right) \rho^5 \qquad (102)$$

$$+ \frac{c}{\gamma T^2} \left[3 - \left(3 + \frac{1}{2} \gamma\rho^2 - \gamma^2\rho^4 \right) \exp\left(-\gamma\rho^2 \right) \right].$$

where H_i° is the enthalpy of i^{th} component at unit pressure.

Entropy Equation of Mixture

$$S = \sum_i x_i \left[S_i^\circ - R\ell n \ (RT\rho x_i) \right]$$

$$- \left(B_o R + \frac{2C_o}{T^3} - \frac{3D_o}{T^4} + \frac{4E_o}{T^5} \right) \rho \qquad (103)$$

$$- \frac{1}{2} \left(bR + \frac{d}{T^2} \right) \rho^2 + \frac{\alpha d \rho^5}{5T^2}$$

$$+ \frac{2c}{\gamma T^3} \left[1 - \left(1 + \frac{1}{2} \gamma\rho^2 \right) \exp \ (- \gamma\rho^2) \right]$$

Fugacity Equation of the i^{th} Component in a Mixture

$$
\begin{aligned}
RT\ell n f_i = {} & RT\ell n(\rho RTx_i) + \\
& \rho\left[\left(B_o+B_{o_i}\right)RT - 2\left(A_oA_{o_i}\right)^{\frac{1}{2}} - \frac{2\,C_oC_{o_i}^{\frac{1}{2}}}{T^2}\right] \\
& + \rho\left[\frac{2\left(D_oD_{o_i}\right)^{\frac{1}{2}}}{T^3} - \frac{2\left(E_oE_{o_i}\right)^{\frac{1}{2}}}{T^4}\right] \\
& + \frac{\rho^2}{2}\left[3(b^2b_i)^{1/3}\,RT - 3(a^2a_i)^{1/3} - \frac{3(d^2d_i)^{1/3}}{T}\right] \\
& + \frac{\alpha\rho^5}{5}\left[3(a^2a_i)^{1/3} + \frac{3(d^2d_i)^{1/3}}{T}\right] \\
& + \frac{3\rho^5}{5}\left(a + \frac{d}{T}\right)(\alpha^2\alpha_i)^{1/3} \qquad (104) \\
& + \frac{3(c^2c_i)^{1/3}\rho^2}{T^2}\left[\frac{1-\exp(-\gamma\rho^2)}{\gamma\rho^2} - \frac{\exp(-\gamma\rho^2)}{2}\right] \\
& - \frac{2c}{\gamma T^2}\left(\frac{\gamma_i}{\gamma}\right)^{\frac{1}{2}}\left\{1-\exp(-\gamma\rho^2)\left[1+\gamma\rho^2+\tfrac{1}{2}\gamma^2\rho^4\right]\right\}
\end{aligned}
$$

Prediction of Methane-Propane Behavior Using the Modified BWR Equation with Parameters Determined from Pure-Component Data

To test the validity of the proposed mixing rules, the modified BWR equation was applied to the methane-propane system.

Sources of Data

The methane-propane system was chosen for study because of the availability of extensive data for both the mixture and its pure components, including the vapor, liquid and coexisting phases. Sources of calorimetric data have been tabulated by Mather[90]. Cryogenic PVT behavior of three methane-propane mixtures were measured by Huang[58]. Extensive enthalpy data for the methane-propane mixtures were reported by Manker[83], Mather[90] and Yesavage[141]. Phase equilibrium data of the methane-propane system have been smoothed by Powers, et al.[104] using existing literature data. Pure component data for methane and propane have been reviewed in Chapters II and VI respectively.

Predictions of Methane-Propane System Behavior

The methane and propane parameters determined from pure-component data (herein known as set II) and the proposed mixing rules were used to calculate densities, enthalpy departures and phase equilibria. (Note: Methane-propane parameters designated as set I have appeared elsewhere[120]. Since the set is valid for predicting enthalpy of mixtures only, it is not included in the following discussions.) The results are presented below.

Densities. Seventy-six mixture PVT points in the temperature range from -238°F to 32°F were chosen for study from Huang's data. The average absolute deviation

was 0.88%, with a maximum deviation of 4% at two data points viz., 32°F, 2000 psia (24.7 mole percent propane mixture) and -40°F, 1000 psia (50 mole percent propane mixture). The deviations of predicted densities from experimental values are surprisingly close to the experimental uncertainty of 0.8% reported by Huang[56].

Enthalpy Departures. A total of 115 mixture enthalpy departure points were chosen from data of Manker, Mather and Yesavage with temperatures for each mixture ranging from -250°F to 250°F. The average absolute deviation was 5.6% with a maximum deviation of 35% at -250°F, 2000 psia (50.6 mole percent propane mixture).

Phase Equilibrium Behavior. Twenty-eight phase equilibrium points for the methane-propane system were chosen from Powers' compilation. These data cover the temperature range from -160°F to 160°F. The average absolute deviation for propane K values was 7.3% with a maximum deviation of 57.9% at -160°F, 250 psia. The average absolute deviation for methane K values was 4.5% with a maximum deviation of 13% at 160°F, 800 psia. Comparisons of predicted and experimental K-values for the methane-propane system at -120°F using the modified and original BWR equations are presented in Table 84.

Summary

The accuracy with which the modified BWR equation can predict densities of the methane-propane system

TABLE 84

COMPARISON OF PREDICTED AND EXPERIMENTAL K-VALUES

FOR THE METHANE-PROPANE SYSTEM AT -120°F

	METHANE K-VALUES			PROPANE K-VALUES		
PRESSURE PSIA	EXPTL.	MBWR	BWR	EXPTL.	MBWR	BWR
50	8.571	9.185	13.531	0.368	0.031	0.017
100	6.355	5.035	6.823	0.018	0.018	0.010
150	4.151	3.614	4.580	0.016	0.014	0.008
200	3.194	2.880	3.453	0.014	0.012	0.007
250	2.537	2.421	2.769	0.013	0.011	0.007
300	2.088	2.099	2.306	0.015	0.011	0.007
400	1.524	1.655	1.700	0.014	0.013	0.009
500	1.183	1.293	1.285	0.037	0.021	0.016
600	1.030	1.011	1.032	0.033	0.172	0.076

approaches the experimental uncertainty. However, below -150°F, predicted enthalpy departures show consistently large negative deviations from experimental values. For the -150°F isotherm, the absolute deviations range from 5 Btu/lb to 20Btu/lb for the five mixtures of Manker[83], Mather[90] and Yesavage[141], compared to 10 Btu/lb to 98 Btu/lb using the original BWR equation. Methane K-values are predicted reliably. So are the propane K-values except at temperatures below -150°F.

These results tend to indicate that while the density and temperature dependence of the modified BWR equation may be adequate (attested by its ability to predict pure component behavior), its composition dependence may not be properly expressed by the mixing rules used in the above calculations. Before delving further into solution nonideality, it may be remarked that the modified BWR equation with parameters determined from pure component data and the proposed mixing rules offers appreciable improvement over the original BWR equation, especially down to -150°F. Since most cryogenic processes seldom operate at temperatures below -150°F, the modified BWR equation provides an accurate means of correlating the thermodynamic behavior of the methane-propane system and offers the possibility of correlating multicomponent systems of industrial interest.

CHAPTER XI

EXTENSION OF MULTIPROPERTY REGRESSION ANALYSIS TO INCLUDE MIXTURE DATA IN DETERMINING EQUATION OF STATE PARAMETERS

Use of Empirical Unlike Interaction Parameters in Correlating Mixture Behavior

Unlike interaction parameters appearing in Equations (91), (92) arise from consideration of intermolecular forces. If the intermolecular forces are the same for both like and unlike molecular interactions, the solution is said to be ideal.[116] Any dissimilarity in intermolecular forces gives rise to solution nonideality. Also, the effects of intermolecular forces increase with increasing density. Thus, nonideal solution behavior may owe its origin to

(1) unlike molecules in both type and size

(2) low temperature and high pressure effects

or both.

To correlate mixture behavior then, molecular dissimilarities must be fully understood and accounted for. Unfortunately, the present knowledge of the liquid state does not permit a theoretical evaluation of unlike

interaction parameters. Resort has been made to defining unlike interaction parameters in terms of mixture constituent pure-component parameters using arithmetic and geometric averages. It is obvious that such definitions are at best empirical approximations.

Stotler and Benedict[123] found that it is not possible to apply geometric mixing rules to the original BWR equation for predicting phase equilibrium behavior of the methane-nitrogen system. To account for the dissimilarity in molecular type, these investigators introduced an empirical unlike interaction parameter, U_{ij}, in the mixing rule for A_o of Equation (94), viz.,

$$A_o = \sum_i x_i^2 A_{o_i} + \sum_i \sum_j U_{ij} x_i x_j A_{o_i}^{\frac{1}{2}} A_{o_j}^{\frac{1}{2}} \qquad (105)$$

More recently, Orye[99] and Furr[49] have made more extensive studies of the use of Equation (105) in the original BWR equation for predicting phase equilibrium behavior of eleven binary systems.

Disadvantages of Using Unlike Interaction Parameters

Although the introduction of an empirical parameter, U_{ij}, improves appreciably the correlation of phase equilibria of binary mixtures, its use can hardly be popularized, by virtue of the following reasons.

(1) The number of distinct two-body unlike interaction parameters is $\frac{N}{2}(N-1)$ where N is the number of

components in the mixture. It is obvious that even for a ternary system, the determination of three unlike interaction parameters is not a trivial problem.

(2) There is no a priori knowledge as to which mixture parameter requires empirical unlike interaction parameters to achieve optimum representation of experimental data. Nor indeed is there a priori knowledge as to the number of mixture parameters requiring empirical interaction parameters. It can be seen that for an equation of state with eleven parameters, the use of unlike interaction parameters in correlating mixture behavior can require a tremendous amount of effort for its development.

(3) Unlike interaction parameters traditionally have been determined from phase equilibrium data only. Application to other thermodynamic properties may decrease their accuracy. Therefore, multiproperty analysis would be required, creating a larger computational problem.

Use of Mixture Data to Determine Equation of State Parameters

The mathematical framework of multicomponent, multiproperty regression analysis discussed in Chapter III provides a unified approach for correlating thermodynamic behavior of any particular system. By this method, parameters are determined such that the equation of state

approaches, to the best degree possible, the condition of thermodynamic consistency, namely that the sets of parameters determined will be capable of adequately representing all thermodynamic properties of the pure components and the mixture.

It has been established that the application of multiproperty regression analysis successfully removes some degree of interdependence among the parameters by forcing the equation of state to simultaneously fit several properties of a fluid. It becomes logical that there is a possibility of removing further degrees of interdependence among the parameters by demanding satisfactory representation of both pure-component and mixture behaviors.

To this end, multiproperty regression analysis was extended to include mixture density, enthalpy departure and phase equilibrium data. This general regression analysis method was then applied to determine methane and propane modified BWR parameters simultaneously using pure-component and mixture PVT, enthalpy departure and phase equilibrium data. This aggregate data set is the same as the set previously used in Chapter X. Their type, distribution and temperature range are summarized in Table 85.

TABLE 85

DISTRIBUTION AND TEMPERATURE RANGE OF A SET OF REGRESSION DATA

FOR THE METHANE-PROPANE SYSTEM

COMPOSITION		NO. OF DATA POINTS			TEMPERATURE RANGE (°F)		
METHANE	PROPANE	PVT	ΔH	PHASE	PVT	ΔH	PHASE
1	0	40	55	18	-253.5, 257	-250, 50	-258.7, -116.5
0	1	45	53	19	-250 , 527	-250, 250	-140 , 206.3
0.753	0.247	24			-238 , 32		
0.5	0.5	27			-184 , 32		
0.221	0.779	25			-184 , 32		
0.948	0.052		25			-250, 250	
0.883	0.117		22			-250, 250	
0.720	0.28		21			-250, 250	
0.494	0.506		25			-250, 250	
0.234	0.766		22			-250, 250	
BINARY MIXTURE				26			-160 , 160
TOTAL		161	223	63			

Prediction of Methane-Propane System Behavior Using the Modified BWR Equation with Parameters Determined from Multicomponent, Multiproperty Analysis

The general regression analysis program successfully produced sets of methane and propane parameters (herein known as set III) capable of predicting pure-component and mixture thermodynamic properties with an accuracy acceptable for engineering design. These parameters (in British engineering units), which differ appreciably from set II are presented in Table 86.

TABLE 86

PARAMETERS OF METHANE AND PROPANE (SET III)

	METHANE	PROPANE
B_o	0.560516E + 00	0.101258E + 01
A_o	0.609816E + 04	0.202061E + 05
C_o	0.375547E + 09	0.732631E + 10
γ	0.110810E + 01	0.398893E + 01
b	0.798362E + 00	0.550211E + 01
a	0.245005E + 04	0.348873E + 05
α	0.418932E + 00	0.173835E + 01
c	0.437222E + 09	0.244356E + 11
D_o	0.185578E + 11	0.391972E + 12
d	0.805271E + 05	0.148511E + 08
E_o	0.210409E + 10	0.257321E + 14

The results using set III parameters to predict mixture and pure-component behaviors of the methane-propane system are discussed individually. The average absolute

deviation of a thermodynamic property was calculated with reference to the data set described in Table 85.

Methane-Propane Mixture

Densities. The average absolute deviation was 1.13%. The maximum deviation was 2.3% at -40°F, 1000 psia (50 mole percent propane mixture). Original BWR equation predictions were compared with the same data set with an average absolute deviation of 1.4%. Comparisons of predicted and experimental densities using the modified BWR equation with the parameter set III, and the original BWR equation are presented in Tables 87 through 92 for three mixtures. Topographical plots of deviations for the 50 mole percent propane mixture[58] are presented in Figures 29 and 30.

Enthalpy Departures. The average absolute deviation was 1.8%. The maximum deviation was 5.6% at -250°F, 2000 psia (50.6 mole per cent propane mixture). Original BWR equation predictions were compared with an average absolute deviation of 19.8%. Comparisons of predicted and experimental enthalpy departures using the modified BWR equation with parameter set III and the original BWR equation are presented in Tables 93 through 102 for five mixtures. Topographical plots of deviations for the 50 mole per cent propane mixture[141] are presented in Figures 31 and 32.

Phase Equilibria. The average absolute deviation for methane K values was 6.34% with a maximum deviation of

TABLE 87

COMPARISON OF PREDICTED DENSITIES USING SET III PARAMETERS IN THE MBWR EQUATION WITH EXPERIMENTAL VALUES FOR THE 77.9 MOLE % PROPANE MIXTURE

T (F)	PP (PSIA)	DE	DC (LBMOLE/CF)	DEV	%DEV
32.0	1000.0	0.7938	0.8004	-0.0066	-0.827
32.0	2000.0	0.8235	0.8296	-0.0061	-0.739
32.0	3000.0	0.8432	0.8514	-0.0082	-0.972
32.0	4000.0	0.8551	0.8661	-0.0110	-1.283
32.0	5000.0	0.8729	0.8841	-0.0112	-1.288
-4.0	500.0	0.8235	0.8344	-0.0109	-1.324
-4.0	1000.0	0.8400	0.8475	-0.0075	-0.905
-4.0	2000.0	0.8647	0.8687	-0.0040	-0.465
-4.0	3000.0	0.8811	0.8858	-0.0047	-0.532
-4.0	4000.0	0.8927	0.9002	-0.0075	-0.842
-4.0	5000.0	0.9042	0.9128	-0.0086	-0.952
-40.0	500.0	0.8680	0.8801	-0.0121	-1.392
-40.0	1000.0	0.8811	0.8894	-0.0083	-0.938
-40.0	2000.0	0.9025	0.9053	-0.0028	-0.313
-40.0	3000.0	0.9158	0.9188	-0.0030	-0.332
-40.0	4000.0	0.9273	0.9306	-0.0033	-0.360
-40.0	5000.0	0.9371	0.9412	-0.0041	-0.435
-76.0	500.0	0.9124	0.9215	-0.0091	-0.996
-76.0	1000.0	0.9223	0.9283	-0.0060	-0.655
-76.0	2000.0	0.9405	0.9406	-0.0001	-0.007
-76.0	3000.0	0.9503	0.9513	-0.0010	-0.108
-76.0	4000.0	0.9602	0.9610	-0.0008	-0.080
-76.0	5000.0	0.9684	0.9697	-0.0013	-0.139
-112.0	500.0	0.9553	0.9610	-0.0057	-0.599
-112.0	1000.0	0.9635	0.9661	-0.0026	-0.275
-112.0	2000.0	0.9767	0.9756	0.0011	0.115
-112.0	3000.0	0.9849	0.9841	0.0008	0.079
-112.0	4000.0	0.9964	0.9919	0.0045	0.447
-112.0	5000.0	1.0030	0.9992	0.0038	0.381
-148.0	500.0	0.9948	1.0005	-0.0057	-0.574
-148.0	1000.0	1.0014	1.0044	-0.0030	-0.295
-148.0	2000.0	1.0145	1.0116	0.0029	0.288
-148.0	3000.0	1.0211	1.0183	0.0028	0.277
-148.0	4000.0	1.0293	1.0245	0.0048	0.464
-148.0	5000.0	1.0359	1.0304	0.0055	0.532
-184.0	500.0	1.0343	1.0418	-0.0075	-0.721
-184.0	1000.0	1.0393	1.0446	-0.0053	-0.509
-184.0	2000.0	1.0491	1.0500	-0.0009	-0.087
-184.0	3000.0	1.0557	1.0551	0.0006	0.054
-184.0	4000.0	1.0607	1.0600	0.0007	0.067
-184.0	5000.0	1.0689	1.0646	0.0043	0.400

AVERAGE ABSOLUTE DEVIATION = 0.53787

TABLE 88

COMPARISON OF PREDICTED DENSITIES USING THE OBWR EQUATION WITH EXPERIMENTAL VALUES FOR THE 77.9 MOLE % PROPANE MIXTURE

T (F)	PE (PSIA)	DE	DC (LBMOLE/CF)	DEV	%DEV
32.0	100.0	0.7938	0.7851	0.0087	1.097
32.0	200.0	0.8235	0.8056	0.0179	2.174
32.0	300.0	0.8432	0.8221	0.0211	2.507
32.0	400.0	0.8581	0.8360	0.0221	2.579
32.0	500.0	0.8729	0.8481	0.0248	2.840
-4.0	50.0	0.8235	0.8208	0.0027	0.323
-4.0	100.0	0.8400	0.8295	0.0105	1.246
-4.0	200.0	0.8647	0.8446	0.0201	2.329
-4.0	300.0	0.8811	0.8574	0.0237	2.692
-4.0	400.0	0.8927	0.8686	0.0241	2.696
-4.0	500.0	0.9042	0.8787	0.0255	2.819
-40.0	50.0	0.8680	0.8662	0.0018	0.205
-40.0	100.0	0.8811	0.8724	0.0087	0.983
-40.0	200.0	0.9025	0.8837	0.0188	2.085
-40.0	300.0	0.9158	0.8937	0.0221	2.414
-40.0	400.0	0.9273	0.9027	0.0246	2.648
-40.0	500.0	0.9371	0.9110	0.0261	2.781
-76.0	50.0	0.9124	0.9112	0.0012	0.130
-76.0	100.0	0.9223	0.9158	0.0065	0.709
-76.0	200.0	0.9405	0.9242	0.0163	1.730
-76.0	300.0	0.9503	0.9320	0.0183	1.925
-76.0	400.0	0.9602	0.9392	0.0210	2.185
-76.0	500.0	0.9684	0.9460	0.0224	2.317
-112.0	50.0	0.9553	0.9579	-0.0026	-0.270
-112.0	100.0	0.9635	0.9612	0.0023	0.237
-112.0	200.0	0.9767	0.9676	0.0091	0.934
-112.0	300.0	0.9849	0.9736	0.0113	1.152
-112.0	400.0	0.9964	0.9792	0.0172	1.725
-112.0	500.0	1.0030	0.9846	0.0184	1.836
-148.0	50.0	0.9948	1.0082	-0.0134	-1.350
-148.0	100.0	1.0014	1.0107	-0.0093	-0.925
-148.0	200.0	1.0145	1.0154	-0.0009	-0.086
-148.0	300.0	1.0211	1.0199	0.0012	0.119
-148.0	400.0	1.0293	1.0242	0.0051	0.494
-148.0	500.0	1.0359	1.0284	0.0075	0.725
-184.0	50.0	1.0343	1.0646	-0.0303	-2.928
-184.0	100.0	1.0393	1.0663	-0.0270	-2.600
-184.0	200.0	1.0491	1.0697	-0.0206	-1.967
-184.0	300.0	1.0557	1.0730	-0.0173	-1.643
-184.0	400.0	1.0607	1.0763	-0.0156	-1.468
-184.0	500.0	1.0685	1.0794	-0.0105	-0.984

AVERAGE ABSOLUTE DEVIATION = 1.58199

TABLE 89

COMPARISON OF PREDICTED DENSITIES USING SET III PARAMETER WITH EXPERIMENTAL VALUES FOR THE 50 MOLE % PROPANE MIXTURE

T (F)	PE (PSIA)	DE (LBMOLE/CF)	DC	DEV	%DEV
32.0	2000.0	0.8346	0.8423	-0.0057	-0.687
32.0	3000.0	0.8864	0.8953	-0.0089	-1.005
32.0	4000.0	0.9238	0.9319	-0.0081	-0.878
32.0	5000.0	0.9508	0.9602	-0.0094	-0.993
-4.0	1000.0	0.8304	0.8512	-0.0208	-2.509
-4.0	2000.0	0.9031	0.9120	-0.0089	-0.982
-4.0	3000.0	0.9405	0.9502	-0.0097	-1.036
-4.0	4000.0	0.9695	0.9789	-0.0094	-0.968
-4.0	5000.0	0.9924	1.0021	-0.0097	-0.973
-40.0	1000.0	0.9134	0.9343	-0.0209	-2.290
-40.0	2000.0	0.9643	0.9732	-0.0089	-1.029
-40.0	3000.0	0.9924	1.0014	-0.0090	-0.909
-40.0	4000.0	1.0172	1.0239	-0.0067	-0.661
-40.0	5000.0	1.0359	1.0428	-0.0069	-0.670
-76.0	1000.0	0.9903	1.0023	-0.0120	-1.207
-76.0	2000.0	1.0213	1.0289	-0.0076	-0.740
-76.0	3000.0	1.0443	1.0500	-0.0057	-0.547
-76.0	4000.0	1.0629	1.0678	-0.0049	-0.457
-76.0	5000.0	1.0796	1.0832	-0.0036	-0.330
-112.0	500.0	1.0380	1.0514	-0.0134	-1.293
-112.0	1000.0	1.0525	1.0625	-0.0100	-0.946
-112.0	2000.0	1.0754	1.0814	-0.0060	-0.556
-112.0	3000.0	1.0941	1.0974	-0.0033	-0.301
-112.0	4000.0	1.1106	1.1114	-0.0008	-0.070
-112.0	5000.0	1.1231	1.1238	-0.0007	-0.066
-148.0	500.0	1.1045	1.1117	-0.0072	-0.652
-148.0	1000.0	1.1148	1.1193	-0.0045	-0.404
-148.0	2000.0	1.1315	1.1330	-0.0015	-0.131
-148.0	3000.0	1.1418	1.1451	-0.0033	-0.288
-148.0	4000.0	1.1563	1.1560	0.0003	0.026
-148.0	5000.0	1.1667	1.1660	0.0007	0.062
-184.0	500.0	1.1625	1.1707	-0.0082	-0.709
-184.0	1000.0	1.1667	1.1760	-0.0093	-0.800
-184.0	2000.0	1.1791	1.1859	-0.0068	-0.576
-184.0	3000.0	1.1895	1.1949	-0.0054	-0.455
-184.0	4000.0	1.1999	1.2033	-0.0034	-0.280
-184.0	5000.0	1.2082	1.2110	-0.0028	-0.235

AVERAGE ABSOLUTE DEVIATION = 0.7221%

TABLE 90

COMPARISON OF PREDICTED DENSITIES USING THE OBWR EQUATION WITH EXPERIMENTAL VALUES FOR THE 50 MOLE % PROPANE MIXTURE

T (F)	P (PSIA)	DE (LBMOLE/CF)	DC	DEV	%DEV
32.0	2000.0	0.8361	0.8442	-0.0076	-0.903
32.0	3000.0	0.8804	0.8816	0.0048	0.537
32.0	4000.0	0.9238	0.9091	0.0147	1.587
32.0	5000.0	0.9508	0.9312	0.0196	2.058
-4.0	1000.0	0.8304	0.8700	-0.0396	-4.765
-4.0	2000.0	0.9031	0.9068	-0.0037	-0.406
-4.0	3000.0	0.9405	0.9333	0.0072	0.769
-4.0	4000.0	0.9695	0.9544	0.0151	1.554
-4.0	5000.0	0.9924	0.9722	0.0202	2.031
-40.0	1000.0	0.9134	0.9403	-0.0269	-2.949
-40.0	2000.0	0.9633	0.9642	-0.0009	-0.097
-40.0	3000.0	0.9924	0.9835	0.0089	0.894
-40.0	4000.0	1.0172	0.9999	0.0173	1.702
-40.0	5000.0	1.0359	1.0142	0.0217	2.094
-76.0	1000.0	0.9903	1.0033	-0.0130	-1.313
-76.0	2000.0	1.0213	1.0198	0.0015	0.148
-76.0	3000.0	1.0443	1.0340	0.0103	0.992
-76.0	4000.0	1.0629	1.0467	0.0162	1.525
-76.0	5000.0	1.0796	1.0581	0.0215	1.991
-112.0	500.0	1.0380	1.0580	-0.0200	-1.927
-112.0	1000.0	1.0525	1.0644	-0.0119	-1.126
-112.0	2000.0	1.0754	1.0760	-0.0006	-0.058
-112.0	3000.0	1.0941	1.0866	0.0075	0.686
-112.0	4000.0	1.1106	1.0963	0.0143	1.288
-112.0	5000.0	1.1231	1.1053	0.0178	1.587
-148.0	500.0	1.1045	1.1227	-0.0182	-1.651
-148.0	1000.0	1.1149	1.1271	-0.0123	-1.106
-148.0	2000.0	1.1315	1.1354	-0.0040	-0.349
-148.0	3000.0	1.1418	1.1432	-0.0014	-0.125
-148.0	4000.0	1.1563	1.1505	0.0059	0.497
-148.0	5000.0	1.1667	1.1575	0.0092	0.791
-184.0	500.0	1.1625	1.1920	-0.0295	-2.538
-184.0	1000.0	1.1667	1.1950	-0.0283	-2.429
-184.0	2000.0	1.1791	1.2009	-0.0218	-1.849
-184.0	3000.0	1.1895	1.2065	-0.0170	-1.431
-184.0	4000.0	1.1990	1.2119	-0.0130	-1.091
-184.0	5000.0	1.2082	1.2171	-0.0089	-0.736

AVERAGE ABSOLUTE DEVIATION = 1.33739

TABLE 91

COMPARISON OF PREDICTED DENSITIES USING SET III PARAMETERS WITH EXPERIMENTAL VALUES FOR THE 24.7 MOLE % PROPANE MIXTURE

T (F)	PE (PSIA)	DE (LBMOLE/CF)	DC	DEV	%DEV
32.0	2000.0	0.7529	0.7420	0.0109	1.448
32.0	3000.0	0.8943	0.8817	0.0126	1.403
32.0	4000.0	0.9676	0.9616	0.0060	0.622
-4.0	2000.0	0.8833	0.8711	0.0122	1.379
-4.0	3000.0	0.9893	0.9722	0.0171	1.733
-4.0	4000.0	1.0410	1.0345	0.0065	0.620
-40.0	2000.0	1.0002	0.9871	0.0131	1.312
-40.0	3000.0	1.0681	1.0570	0.0111	1.040
-40.0	4000.0	1.1085	1.1046	0.0043	0.389
-76.0	1000.0	1.0328	1.0096	0.0232	2.245
-76.0	2000.0	1.0981	1.0871	0.0110	1.004
-76.0	3000.0	1.1443	1.1355	0.0088	0.770
-76.0	4000.0	1.1769	1.1716	0.0053	0.450
-76.0	5000.0	1.2068	1.2007	0.0062	0.511
-112.0	500.0	1.1143	1.0952	0.0191	1.712
-112.0	1000.0	1.1471	1.1291	0.0180	1.569
-112.0	2000.0	1.1878	1.1743	0.0135	1.096
-112.0	3000.0	1.2177	1.2090	0.0087	0.715
-112.0	4000.0	1.2449	1.2364	0.0085	0.680
-112.0	5000.0	1.2694	1.2596	0.0099	0.774
-148.0	500.0	1.2204	1.2061	0.0143	1.171
-148.0	1000.0	1.2367	1.2249	0.0118	0.955
-148.0	2000.0	1.2694	1.2551	0.0143	1.123
-148.0	3000.0	1.2883	1.2797	0.0086	0.666
-148.0	4000.0	1.3101	1.3006	0.0095	0.727
-148.0	5000.0	1.3317	1.3188	0.0129	0.968
-184.0	500.0	1.3101	1.3004	0.0097	0.740
-184.0	1000.0	1.3236	1.3121	0.0115	0.869
-184.0	2000.0	1.3454	1.3326	0.0128	0.950
-184.0	3000.0	1.3591	1.3503	0.0088	0.645
-184.0	4000.0	1.3752	1.3660	0.0092	0.673
-184.0	5000.0	1.3943	1.3802	0.0141	1.011
-220.0	500.0	1.3862	1.3898	-0.0036	-0.259
-220.0	1000.0	1.3970	1.3974	-0.0004	-0.025
-220.0	2000.0	1.4134	1.4113	0.0021	0.149
-220.0	3000.0	1.4269	1.4239	0.0030	0.210
-220.0	4000.0	1.4405	1.4355	0.0050	0.349
-220.0	5000.0	1.4541	1.4462	0.0079	0.544
-238.0	500.0	1.4296	1.4349	-0.0053	-0.369
-238.0	1000.0	1.4378	1.4410	-0.0032	-0.221
-238.0	2000.0	1.4496	1.4524	-0.0028	-0.192

AVERAGE RESULTANT DEVIATION = 0.8377%

TABLE 92

COMPARISON OF PREDICTED DENSITIES USING THE OBWR EQUATION WITH EXPERIMENTAL VALUES FOR THE 24.7 MOLE % PROPANE MIXTURE

T (F)	P (PSIA)	D (LBMOLES/CF)	DC	DEV	%DEV
32.C	200C.C	C.7529	C.7509	C.0020	C.269
32.C	300C.C	C.8942	C.8797	C.0145	1.625
32.C	400C.C	C.9676	C.9477	C.0199	2.058
-4.C	200C.C	C.8833	C.8867	-C.0034	-C.389
-4.C	300C.C	C.9893	C.9672	C.0221	2.237
-4.C	400C.C	1.0410	1.0168	C.0242	2.323
-40.C	200C.C	1.0002	C.9967	C.0035	C.345
-40.C	300C.C	1.0681	1.0471	C.0210	1.962
-40.C	400C.C	1.1089	1.0833	C.0256	2.311
-76.C	100C.C	1.0328	1.0417	-C.0089	-C.859
-76.C	200C.C	1.0691	1.0593	C.0098	C.924
-76.C	300C.C	1.1443	1.1216	C.0227	1.991
-76.C	400C.C	1.1769	1.1482	C.0287	2.442
-76.C	500C.C	1.2065	1.1704	C.0361	3.021
-112.C	50C.C	1.1143	1.1254	-C.0111	-C.999
-112.C	100C.C	1.1471	1.1426	C.0045	C.395
-112.C	200C.C	1.1878	1.1707	C.0171	1.439
-112.C	300C.C	1.2177	1.1937	C.0240	1.972
-112.C	400C.C	1.2449	1.2133	C.0316	2.538
-112.C	500C.C	1.2694	1.2305	C.0389	3.061
-148.C	50C.C	1.2204	1.2218	-C.0014	-C.118
-148.C	100C.C	1.2367	1.2321	C.0046	C.371
-148.C	200C.C	1.2694	1.2505	C.0189	1.491
-148.C	300C.C	1.2883	1.2666	C.0217	1.683
-148.C	400C.C	1.3101	1.2811	C.0290	2.214
-148.C	500C.C	1.3317	1.2943	C.0374	2.811
-184.C	50C.C	1.3101	1.3138	-C.0037	-C.286
-184.C	100C.C	1.3236	1.3204	C.0032	C.239
-184.C	200C.C	1.3454	1.3327	C.0127	C.941
-184.C	300C.C	1.3591	1.3441	C.0150	1.105
-184.C	400C.C	1.3753	1.3546	C.0207	1.504
-184.C	500C.C	1.3943	1.3645	C.0298	2.139
-220.C	50C.C	1.3862	1.4103	-C.0241	-1.741
-220.C	100C.C	1.3970	1.4146	-C.0176	-1.261
-220.C	200C.C	1.4134	1.4228	-C.0094	-C.668
-220.C	300C.C	1.4265	1.4307	-C.0038	-C.264
-220.C	400C.C	1.4405	1.4381	C.0024	C.165
-220.C	500C.C	1.4541	1.4453	C.0088	C.609
-238.C	50C.C	1.4296	1.4628	-C.0332	-2.320
-238.C	100C.C	1.4378	1.4662	-C.0284	-1.976
-238.C	200C.C	1.4486	1.4729	-C.0243	-1.676

AVERAGE ABSOLUTE DEVIATION = 1.4219%

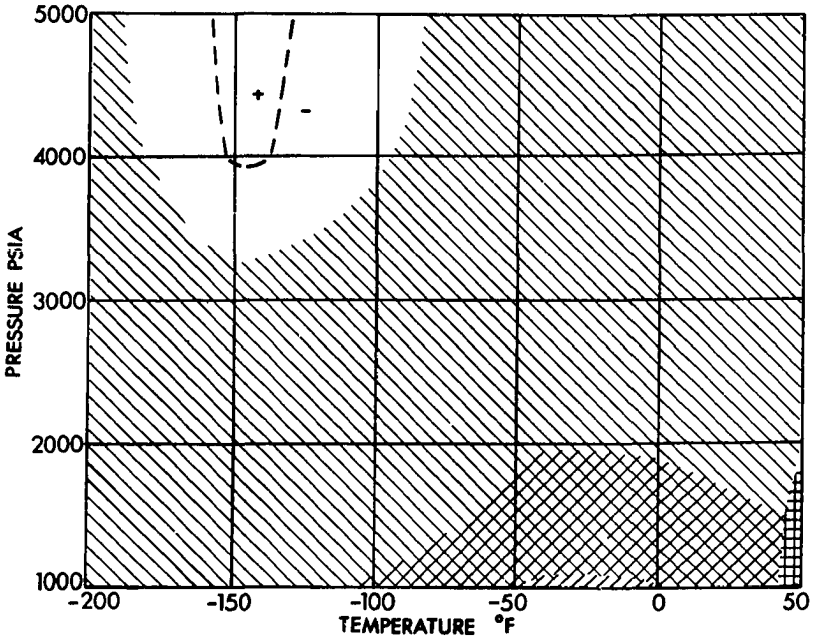


Figure 29. Comparison of Densities Calculated by the Modified BWR Equation Using Set III Parameters with Experimental Values for the 50 Mole % Propane Mixture

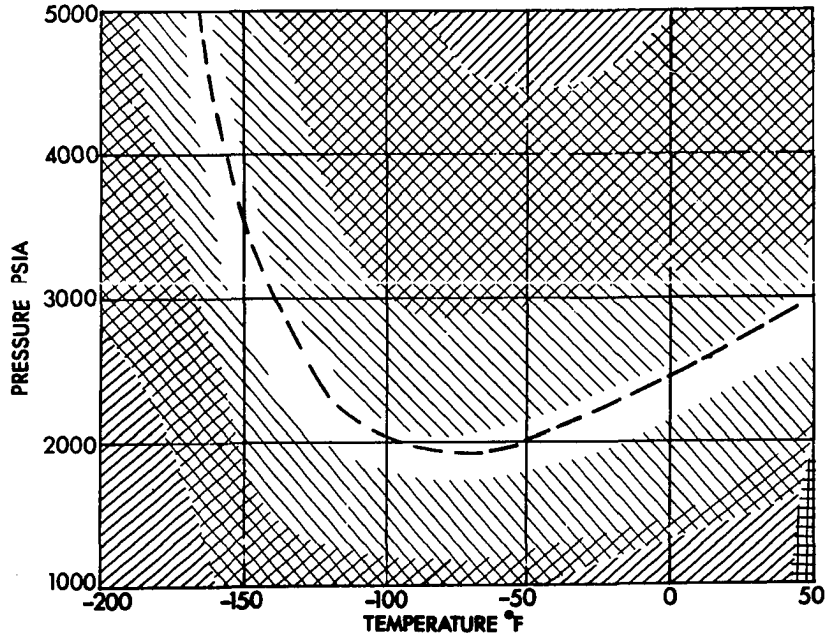


Figure 30. Comparison of Densities Calculated by the Original BWR Equation with Experimental Values for the 50 Mole % Propane Mixture

TABLE 93

COMPARISON OF PREDICTED ENTHALPY DEPARTURES USING SET III PARAMETERS WITH EXPERIMENTAL VALUES FOR THE 76.6 MOLE % PROPANE MIXTURE

T (F)	PE (PSIA)	HE (BTU/LBMOLE)	HC (BTU/LBMOLE)	DEV BTU/LB	%DEV
-200.0	500.0	-8073.24	-8102.54	0.78	-0.36
-200.0	1000.0	-7998.17	-8042.16	1.17	-0.55
-200.0	1500.0	-7930.61	-7981.36	1.35	-0.64
-200.0	2000.0	-7863.06	-7920.16	1.52	-0.73
-150.0	500.0	-7645.37	-7629.75	-0.42	0.20
-150.0	1000.0	-7577.81	-7569.51	-0.22	0.11
-150.0	1250.0	-7547.79	-7539.05	-0.23	0.12
-150.0	1500.0	-7517.76	-7508.47	-0.25	0.12
-150.0	2000.0	-7457.71	-7446.79	-0.29	0.15
-100.0	500.0	-7232.51	-7194.77	-1.01	0.52
-100.0	750.0	-7191.23	-7166.41	-0.66	0.35
-100.0	1000.0	-7164.95	-7137.61	-0.73	0.38
-100.0	1500.0	-7082.38	-7078.96	-0.09	0.05
-100.0	2000.0	-7063.61	-7019.07	-1.19	0.63
-50.0	500.0	-6804.64	-6772.18	-0.86	0.48
-50.0	1000.0	-6759.60	-6723.41	-0.96	0.54
-50.0	1500.0	-6703.30	-6671.38	-0.85	0.48
-50.0	2000.0	-6673.28	-6616.76	-1.51	0.85
0.0	500.0	-6358.00	-6334.89	-0.62	0.36
0.0	1000.0	-6354.25	-6305.98	-1.29	0.76
0.0	1500.0	-6286.69	-6268.57	-0.48	0.29
0.0	2000.0	-6256.66	-6225.21	-0.84	0.50
50.0	750.0	-5896.36	-5841.39	-1.46	0.93
50.0	1000.0	-5877.59	-5848.86	-0.77	0.49
50.0	1500.0	-5840.05	-5844.64	0.12	-0.08
50.0	2000.0	-5832.55	-5824.24	-0.22	0.14
100.0	1000.0	-5322.11	-5273.61	-1.29	0.91
100.0	1250.0	-5344.63	-5325.70	-0.50	0.35
100.0	1500.0	-5359.64	-5357.44	-0.06	0.04
100.0	2000.0	-5389.66	-5386.07	-0.10	0.07
150.0	1000.0	-4485.13	-4382.64	-2.73	2.29
150.0	1500.0	-4755.37	-4740.21	-0.40	0.32
150.0	2000.0	-4882.98	-4875.94	-0.19	0.14
200.0	500.0	-1047.16	-1063.67	0.44	-1.58
200.0	1000.0	-2893.76	-2964.98	1.90	-2.46
200.0	1500.0	-4000.96	-3948.98	-1.39	1.30
200.0	2000.0	-4304.98	-4272.52	-0.86	0.75
250.0	1000.0	-1974.21	-2002.70	0.76	-1.44
250.0	2000.0	-3633.15	-3615.13	-0.48	0.50

AVERAGE ABSOLUTE DEVIATION = 0.5884%

AVERAGE ABSOLUTE DEVIATION IN BTU/LB = 0.79

TABLE 94

COMPARISON OF PREDICTED ENTHALPY DEPARTURES USING THE OBWR EQUATION WITH EXPERIMENTAL VALUES FOR THE 76.6 MOLE % PROPANE MIXTURE

T (F)	PR (PSIA)	HE (BTU/LBMOLE)	HC	DEV BTU/LB	%DEV
-200.0	500.0	-8073.24	-15834.47	206.79	-96.14
-200.0	1000.0	-7998.17	-15786.18	207.50	-97.37
-200.0	1500.0	-7930.61	-15737.57	208.01	-98.44
-200.0	2000.0	-7863.06	-15688.66	208.50	-99.52
-150.0	500.0	-7645.37	-11324.74	98.03	-48.13
-150.0	1000.0	-7577.81	-11274.81	98.50	-49.79
-150.0	1250.0	-7547.79	-11249.61	98.63	-49.05
-150.0	1500.0	-7517.76	-11224.30	98.76	-49.30
-150.0	2000.0	-7457.71	-11173.23	98.99	-49.82
-100.0	500.0	-7232.51	-8960.06	46.03	-23.89
-100.0	750.0	-7191.23	-8935.57	46.48	-24.26
-100.0	1000.0	-7164.95	-8910.80	46.52	-24.37
-100.0	1500.0	-7082.38	-8860.39	47.37	-25.10
-100.0	2000.0	-7063.61	-8808.95	46.50	-24.71
-50.0	500.0	-6804.64	-7573.25	20.48	-11.30
-50.0	1000.0	-6759.60	-7528.55	20.49	-11.38
-50.0	1500.0	-6703.30	-7481.45	20.73	-11.61
-50.0	2000.0	-6673.28	-7432.30	20.22	-11.37
0.0	500.0	-6358.00	-6657.70	7.98	-4.71
0.0	1000.0	-6354.25	-6625.47	7.23	-4.27
0.0	1500.0	-6286.69	-6587.53	8.02	-4.70
0.0	2000.0	-6256.66	-6545.20	7.69	-4.61
50.0	750.0	-5896.36	-5951.36	1.47	-0.93
50.0	1000.0	-5877.59	-5949.20	1.91	-1.22
50.0	1500.0	-5840.05	-5933.27	2.48	-1.60
50.0	2000.0	-5832.55	-5906.36	1.97	-1.27
100.0	1000.0	-5322.11	-5329.84	0.21	-0.15
100.0	1250.0	-5344.63	-5357.93	0.35	-0.25
100.0	1500.0	-5359.64	-5373.49	0.37	-0.26
100.0	2000.0	-5389.66	-5381.36	-0.22	0.15
150.0	1000.0	-4485.13	-4475.20	-0.26	0.22
150.0	1500.0	-4755.37	-4781.00	0.68	-0.54
150.0	2000.0	-4882.98	-4877.06	-0.16	0.12
200.0	500.0	-1047.16	-1086.69	1.05	-3.78
200.0	1000.0	-2893.76	-2888.44	-0.14	0.18
200.0	1500.0	-4000.96	-3986.07	-0.40	0.37
200.0	2000.0	-4304.98	-4311.91	0.18	-0.16
250.0	1000.0	-1974.21	-2017.52	1.15	-2.19
250.0	2000.0	-3633.15	-3661.47	0.75	-0.78

AVERAGE ABSOLUTE DEVIATION = 21.4634%

AVERAGE ABSOLUTE DEVIATION IN BTU/LB = 43.16

TABLE 95

COMPARISON OF PREDICTED ENTHALPY DEPARTURES USING SET III PARAMETERS WITH EXPERIMENTAL VALUES FOR THE 50.6 MOLE % PROPANE MIXTURE

T (F)	PE (PSIA)	HE (BTU/LBMOLE)	HC	DEV BTU/LB	%DEV
-200.0	500.0	-6434.72	-6625.29	6.30	-2.96
-150.0	500.0	-6065.82	-6130.23	2.13	-1.06
-100.0	500.0	-5687.84	-5666.42	-0.71	0.38
150.0	500.0	-771.08	-750.84	-0.67	2.62
200.0	500.0	-625.93	-602.95	-0.76	3.67
250.0	500.0	-520.10	-499.68	-0.68	3.93
-200.0	1000.0	-6383.32	-6575.77	6.36	-3.01
-150.0	1000.0	-6017.44	-6083.81	2.19	-1.10
-120.0	1000.0	-5793.68	-5807.81	0.47	-0.24
-100.0	1000.0	-5645.51	-5629.57	-0.53	0.28
-80.0	1000.0	-5488.27	-5453.41	-1.15	0.64
-50.0	1000.0	-5246.36	-5186.45	-1.98	1.14
0.0	1000.0	-4795.81	-4693.79	-3.37	2.13
50.0	1000.0	-4015.66	-4006.98	-0.29	0.22
150.0	1000.0	-1805.23	-1790.94	-0.47	0.79
200.0	1000.0	-1357.70	-1324.25	-1.11	2.46
250.0	1000.0	-1100.68	-1054.56	-1.53	4.19
-200.0	1500.0	-6331.92	-6525.58	6.40	-3.06
-150.0	1500.0	-5969.06	-6035.98	2.21	-1.12
-120.0	1500.0	-5748.32	-5783.40	0.50	-0.26
-100.0	1500.0	-5603.17	-5588.87	-0.47	0.26
-80.0	1500.0	-5455.00	-5419.11	-1.22	0.69
-50.0	1500.0	-5222.17	-5164.13	-1.92	1.11
0.0	1500.0	-4801.86	-4721.47	-2.66	1.67
50.0	1500.0	-4299.90	-4196.29	-3.43	2.41
150.0	1500.0	-2772.86	-2729.75	-1.43	1.55
200.0	1500.0	-2095.52	-2058.84	-1.21	1.75
250.0	1500.0	-1666.14	-1614.17	-1.72	3.12
-200.0	2000.0	-6277.49	-6474.81	6.53	-3.14
-150.0	2000.0	-5917.65	-5986.72	2.28	-1.17
-120.0	2000.0	-5699.94	-5716.92	0.56	-0.30
-100.0	2000.0	-5554.79	-5545.30	-0.31	0.17
-80.0	2000.0	-5406.63	-5379.58	-0.93	0.52
-50.0	2000.0	-5182.86	-5133.83	-1.62	0.95
0.0	2000.0	-4792.79	-4721.82	-2.35	1.48
50.0	2000.0	-4351.30	-4269.21	-2.71	1.89
150.0	2000.0	-3289.94	-3142.17	-4.89	4.49
200.0	2000.0	-2627.72	-2557.43	-2.32	2.67
250.0	2000.0	-2149.95	-2071.72	-2.59	3.64

AVERAGE ABSOLUTE DEVIATION = 1.74979%

AVERAGE ABSOLUTE DEVIATION IN BTU/LB = 2.08

TABLE 96

COMPARISON OF PREDICTED ENTHALPY DEPARTURES USING THE OBWR EQUATION WITH EXPERIMENTAL VALUES FOR THE 50.6 MOLE % PROPANE MIXTURE

T (F)	PF (PSIA)	HF (BTU/LBMOLE)	HC	DEV BTU/LB	%DEV
-200.0	500.0	-7434.73	-11225.44	158.43	-74.45
-150.0	500.0	-6065.82	-8283.53	73.34	-36.56
-100.0	500.0	-5687.84	-6695.41	33.32	-17.71
150.0	500.0	-771.08	-764.87	-0.21	0.80
200.0	500.0	-625.93	-616.56	-0.31	1.50
250.0	500.0	-520.10	-512.52	-0.25	1.46
-200.0	1000.0	-6283.32	-11183.84	158.76	-75.20
-150.0	1000.0	-6017.44	-8242.44	73.58	-36.59
-120.0	1000.0	-5793.68	-7191.64	46.23	-24.13
-100.0	1000.0	-5645.51	-6659.29	33.53	-17.96
-80.0	1000.0	-5488.27	-6219.79	24.19	-13.23
-50.0	1000.0	-5246.36	-5681.19	14.38	-8.20
0.0	1000.0	-4795.81	-4958.55	5.38	-3.39
50.0	1000.0	-4015.66	-4210.58	6.45	-4.85
150.0	1000.0	-1805.23	-1781.31	-0.79	1.33
200.0	1000.0	-1357.70	-1338.24	-0.64	1.43
250.0	1000.0	-1100.68	-1073.57	-0.90	2.46
-200.0	1500.0	-6331.52	-11141.84	159.07	-75.56
-150.0	1500.0	-5969.06	-8300.44	73.79	-37.28
-120.0	1500.0	-5748.32	-7151.23	46.40	-24.41
-100.0	1500.0	-5603.17	-6620.94	33.66	-18.16
-80.0	1500.0	-5455.00	-6184.66	24.13	-13.38
-50.0	1500.0	-5222.17	-5654.09	14.28	-8.27
0.0	1500.0	-4801.86	-4963.61	5.35	-3.37
50.0	1500.0	-4299.90	-4348.21	1.60	-1.12
150.0	1500.0	-2772.86	-2704.87	-2.25	2.45
200.0	1500.0	-2095.52	-2057.44	-1.26	1.82
250.0	1500.0	-1666.14	-1631.31	-1.15	2.09
-200.0	2000.0	-6277.49	-11099.47	159.47	-76.81
-150.0	2000.0	-5917.65	-8157.59	74.08	-37.85
-120.0	2000.0	-5699.94	-7109.45	46.61	-24.73
-100.0	2000.0	-5554.79	-6580.71	33.93	-18.47
-80.0	2000.0	-5406.63	-6146.83	24.48	-13.69
-50.0	2000.0	-5182.86	-5622.22	14.53	-8.48
0.0	2000.0	-4792.79	-4952.98	5.30	-3.34
50.0	2000.0	-4351.30	-4396.46	1.49	-1.04
150.0	2000.0	-3289.94	-3173.19	-3.86	3.55
200.0	2000.0	-2627.72	-2567.50	-1.99	2.29
250.0	2000.0	-2149.95	-2091.06	-1.95	2.74

AVERAGE ABSOLUTE DEVIATION = 18.0317%

AVERAGE ABSOLUTE DEVIATION IN BTU/LB = 34.91

TABLE 97

COMPARISON OF PREDICTED ENTHALPY DEPARTURES USING SET III PARAMETERS WITH EXPERIMENTAL VALUES FOR THE 28 MOLE % PROPANE MIXTURE

T (F)	PP (PSIA)	HP (BTU/LBMOLE)	HC	DEV BTU/LB	%DEV
-200.0	500.0	-4994.71	-5159.47	6.80	-3.30
-200.0	1000.0	-4942.14	-5120.95	7.48	-3.62
-200.0	1500.0	-4891.55	-5081.24	7.92	-3.87
-200.0	2000.0	-4841.77	-5040.49	8.31	-4.10
-150.0	500.0	-4846.55	-4982.07	5.67	-2.80
-150.0	1000.0	-4803.53	-4946.14	5.97	-2.97
-150.0	1500.0	-4765.20	-4908.38	6.09	-3.00
-150.0	2000.0	-4724.66	-4869.05	6.04	-3.06
-100.0	500.0	-4621.00	-4711.18	3.74	-1.93
-100.0	1000.0	-4595.61	-4682.24	3.62	-1.88
-100.0	1500.0	-4562.16	-4649.41	3.66	-1.92
-100.0	2000.0	-4531.09	-4614.22	3.48	-1.83
-100.0	350.0	-4232.36	-4239.87	0.31	-0.18
-100.0	1000.0	-4229.97	-4238.92	0.37	-0.21
-100.0	1500.0	-4218.02	-4226.84	0.37	-0.21
-100.0	2000.0	-4210.66	-4205.80	-0.21	0.12
-50.0	1000.0	-3768.74	-3724.44	-1.85	1.18
-50.0	1250.0	-3811.76	-3759.33	-2.19	1.38
-50.0	1500.0	-3828.45	-3776.78	-2.04	1.37
-50.0	2000.0	-3836.66	-3756.19	-1.65	1.03
0.0	1500.0	-3283.61	-3224.23	-2.48	1.81
0.0	1750.0	-3352.91	-3292.84	-2.51	1.79
0.0	2000.0	-3391.15	-3337.80	-2.23	1.57
50.0	1500.0	-2504.53	-2498.99	-0.23	0.22
50.0	1750.0	-2674.20	-2679.84	0.24	-0.21
50.0	2000.0	-2841.49	-2797.53	-1.84	1.55
100.0	500.0	-528.15	-518.88	-0.39	1.75
100.0	1000.0	-1163.84	-1149.65	-0.59	1.22
100.0	1500.0	-1811.48	-1801.31	-0.43	0.56
100.0	2000.0	-2253.60	-2227.58	-1.07	1.14
150.0	500.0	-430.17	-418.19	-0.50	2.78
150.0	1000.0	-905.74	-882.54	-0.95	2.52
150.0	1500.0	-1364.58	-1356.10	-0.36	0.62
150.0	2000.0	-1780.41	-1748.49	-1.34	1.79
200.0	500.0	-358.47	-346.76	-0.49	3.27
200.0	1000.0	-738.45	-713.40	-1.05	3.39
200.0	1500.0	-1099.76	-1077.72	-0.90	1.10
200.0	2000.0	-1421.54	-1401.41	-0.86	1.44
250.0	2000.0	-1166.23	-1152.71	-0.52	1.07

AVERAGE ABSOLUTE DEVIATION = 1.78659

AVERAGE ABSOLUTE DEVIATION IN BTU/LB = 2.47

TABLE 98

COMPARISON OF PREDICTED ENTHALPY DEPARTURES USING THE OBWR EQUATION WITH EXPERIMENTAL VALUES FOR THE 28 MOLE % PROPANE MIXTURE

T (F)	P (PSIA)	H-H (BTU/LB-MOLE)	H-C	DEV BTU/LB	%DEV
-200.0	500.0	-4994.71	-7428.11	102.24	-48.92
-200.0	1000.0	-4942.14	-7403.09	102.98	-49.80
-200.0	1500.0	-4891.96	-7381.35	103.58	-50.60
-200.0	2000.0	-4841.77	-7370.93	104.16	-51.41
-100.0	500.0	-4846.55	-6621.66	74.28	-36.67
-100.0	1000.0	-4803.53	-6587.71	74.66	-37.14
-100.0	1500.0	-4765.29	-6552.72	74.79	-37.51
-100.0	2000.0	-4724.66	-6516.79	74.99	-37.93
-50.0	500.0	-4621.50	-5729.10	46.33	-23.56
-50.0	1000.0	-4595.61	-5695.85	46.16	-24.01
-50.0	1500.0	-4562.16	-5666.62	46.22	-24.21
-50.0	2000.0	-4521.69	-5632.70	46.10	-24.31
-100.0	750.0	-4232.36	-4725.51	20.64	-11.65
-100.0	1000.0	-4229.97	-4718.41	20.44	-11.55
-100.0	1500.0	-4218.02	-4699.09	20.13	-11.40
-100.0	2000.0	-4210.61	-4674.51	19.40	-11.01
-50.0	1000.0	-3768.74	-3995.04	9.47	-6.00
-50.0	1250.0	-3811.76	-4012.43	8.40	-5.26
-50.0	1500.0	-3828.49	-4021.88	8.09	-5.06
-50.0	2000.0	-3835.66	-4025.53	7.55	-4.55
0.0	1500.0	-3283.61	-3360.60	3.22	-2.34
0.0	1750.0	-3352.91	-3429.13	3.02	-2.19
0.0	2000.0	-3391.15	-3464.58	3.09	-2.18
50.0	1500.0	-2504.52	-2482.49	-0.52	0.88
50.0	1750.0	-2674.20	-2701.22	1.13	-1.01
50.0	2000.0	-2841.49	-2842.75	0.05	-0.04
100.0	500.0	-528.19	-527.71	-0.02	0.08
100.0	1000.0	-1162.84	-1154.92	-0.37	0.77
100.0	1500.0	-1811.45	-1786.35	-1.05	1.39
100.0	2000.0	-2453.60	-2424.16	-1.23	1.21
150.0	500.0	-430.17	-426.60	-0.15	0.83
150.0	1000.0	-905.74	-894.13	-0.49	1.28
150.0	1500.0	-1364.58	-1361.77	-0.12	0.21
150.0	2000.0	-1780.41	-1750.87	-1.24	1.66
200.0	500.0	-358.47	-354.62	-0.16	1.07
200.0	1000.0	-738.45	-729.88	-0.53	1.70
200.0	1500.0	-1089.76	-1090.72	0.04	-0.09
200.0	2000.0	-1421.94	-1413.69	-0.35	0.58
250.0	2000.0	-1166.23	-1170.54	0.18	-0.37

AVERAGE ABSOLUTE DEVIATION = 13.67293

AVERAGE ABSOLUTE DEVIATION IN BTU/LB = 26.37

TABLE 99

COMPARISON OF PREDICTED ENTHALPY DEPARTURES USING USING SET III PARAMETERS WITH EXPERIMENTAL VALUES FOR THE 11.7 MOLE % PROPANE MIXTURE

T (F)	PF (PSIA)	HF (BTU/LBMOLE)	HC	DEV BTU/LB	%DEV
-250.0	500.0	-4270.90	-4251.48	-1.00	0.45
-250.0	1000.0	-4214.85	-4216.45	0.08	-0.04
-250.0	1500.0	-4160.74	-4180.67	1.03	-0.48
-250.0	2000.0	-4108.56	-4144.27	1.85	-0.87
-200.0	500.0	-3975.22	-3994.79	1.12	-0.54
-200.0	1000.0	-3924.97	-3968.22	2.24	-1.10
-200.0	1500.0	-3874.73	-3937.32	3.24	-1.62
-200.0	2000.0	-3826.42	-3904.61	4.05	-2.04
-150.0	500.0	-3621.57	-3600.81	-1.07	0.57
-150.0	1000.0	-3586.79	-3595.62	0.46	-0.25
-150.0	1500.0	-3552.00	-3580.38	1.47	-0.80
-150.0	2000.0	-3521.08	-3558.88	1.96	-1.07
-100.0	1000.0	-3165.49	-3137.80	-1.43	0.87
-100.0	1250.0	-3180.55	-3164.44	-0.85	0.52
-100.0	1500.0	-3188.68	-3179.75	-0.46	0.28
-100.0	2000.0	-3196.41	-3190.78	-0.29	0.18
-50.0	1250.0	-2572.20	-2534.84	-1.93	1.45
-50.0	1500.0	-2661.10	-2651.67	-0.49	0.35
-50.0	1750.0	-2719.07	-2720.08	0.05	-0.04
-50.0	2000.0	-2775.12	-2763.84	-0.58	0.41
0.0	1250.0	-1619.46	-1594.45	-1.29	1.54
0.0	1500.0	-1884.22	-1906.83	1.17	-1.20
0.0	1750.0	-2071.68	-2105.46	1.75	-1.63
0.0	2000.0	-2226.28	-2233.37	0.37	-0.32
50.0	500.0	-380.71	-387.53	0.35	-1.79
50.0	1000.0	-834.85	-838.08	0.17	-0.39
50.0	1500.0	-1316.05	-1316.13	0.00	-0.01
50.0	2000.0	-1692.90	-1693.76	0.04	-0.05
100.0	500.0	-320.80	-311.50	-0.48	2.90
100.0	1000.0	-660.93	-648.05	-0.67	1.95
100.0	1500.0	-1006.85	-990.54	-0.84	1.62
100.0	2000.0	-1310.26	-1296.88	-0.69	1.02
150.0	500.0	-264.76	-257.63	-0.37	2.69
150.0	1000.0	-539.18	-524.61	-0.75	2.70
150.0	1500.0	-807.80	-788.93	-0.98	2.34
150.0	2000.0	-1051.30	-1031.90	-1.00	1.85
200.0	500.0	-224.17	-217.49	-0.35	2.99
200.0	1000.0	-450.29	-436.82	-0.70	2.99
200.0	1500.0	-666.72	-650.08	-0.86	2.50

AVERAGE ABSOLUTE DEVIATION = 1.1896%

AVERAGE ABSOLUTE DEVIATION IN BTU/LB = 0.99

TABLE 100

COMPARISON OF PREDICTED ENTHALPY DEPARTURES USING THE OBWR EQUATION WITH EXPERIMENTAL VALUES FOR THE 11.7 MOLE % PROPANE MIXTURE

T (F)	P (PSIA)	H (BTU/LBMOLE)	HC	DEV BTU/LB	%DEV
-250.0	500.0	-4270.90	-6830.82	132.46	-60.54
-250.0	1000.0	-4214.85	-6799.27	133.73	-61.32
-250.0	1500.0	-4160.74	-6767.21	134.97	-62.04
-250.0	2000.0	-4108.56	-6734.72	135.89	-63.53
-200.0	500.0	-3975.22	-4959.34	50.92	-24.76
-200.0	1000.0	-3924.57	-4930.72	52.04	-25.62
-200.0	1500.0	-3874.13	-4900.61	53.08	-26.48
-200.0	2000.0	-3826.42	-4869.27	53.96	-27.25
-150.0	500.0	-3621.57	-3940.65	19.10	-10.19
-150.0	1000.0	-3586.78	-3917.09	20.20	-10.98
-150.0	1500.0	-3552.00	-3893.76	21.09	-11.42
-150.0	2000.0	-3521.08	-3874.23	21.38	-11.73
-100.0	1000.0	-3165.49	-3311.81	7.57	-4.62
-100.0	1250.0	-3180.95	-3328.34	7.63	-4.63
-100.0	1500.0	-3188.68	-3337.22	7.69	-4.66
-100.0	2000.0	-3196.41	-3340.64	7.46	-4.51
-50.0	1250.0	-2572.20	-2573.74	0.08	-0.06
-50.0	1500.0	-2661.10	-2709.67	2.51	-1.82
-50.0	1750.0	-2719.07	-2781.43	3.23	-2.29
-50.0	2000.0	-2775.12	-2824.81	2.57	-1.79
0.0	1250.0	-1619.46	-1558.20	-3.17	3.78
0.0	1500.0	-1884.22	-1866.44	-0.92	0.94
0.0	1750.0	-2071.68	-2082.42	0.56	-0.52
0.0	2000.0	-2226.28	-2228.01	0.09	-0.08
50.0	500.0	-380.71	-393.49	0.66	-3.36
50.0	1000.0	-834.85	-843.37	0.44	-1.02
50.0	1500.0	-1316.05	-1307.51	-0.44	0.65
50.0	2000.0	-1692.90	-1677.13	-0.82	0.93
100.0	500.0	-320.80	-317.31	-0.18	1.09
100.0	1000.0	-660.93	-656.41	-0.23	0.68
100.0	1500.0	-1006.85	-995.53	-0.57	1.08
100.0	2000.0	-1310.26	-1296.37	-0.72	1.06
150.0	500.0	-264.76	-263.17	-0.08	0.60
150.0	1000.0	-539.18	-533.67	-0.28	1.02
150.0	1500.0	-807.80	-798.66	-0.47	1.13
150.0	2000.0	-1051.30	-1040.03	-0.58	1.07
200.0	500.0	-224.17	-222.65	-0.08	0.68
200.0	1000.0	-450.28	-445.73	-0.24	1.01
200.0	1500.0	-666.72	-660.98	-0.30	0.86

AVERAGE ABSOLUTE DEVIATION = 11.33659

AVERAGE ABSOLUTE DEVIATION IN BTU/LB = 22.52

TABLE 101

COMPARISON OF PREDICTED ENTHALPY DEPARTURES USING SET III PARAMETERS WITH EXPERIMENTAL VALUES FOR THE 5.2 MOLE % PROPANE MIXTURE

T (F)	PP (PSIA)	HE	HC	DEV BTU/LB	%DEV
		(BTU/LBMOLE)			
-25C.C	5CC.C	-3731.36	-3761.22	1.70	-0.80
-2CC.C	5CC.C	-3446.11	-3525.88	4.56	-2.31
-15C.C	5CC.C	-3110.07	-3136.44	1.51	-0.85
C.C	5CC.C	-303.79	-288.97	-0.28	1.03
5C.C	5CC.C	-317.28	-305.80	-0.43	2.35
1CC.C	5CC.C	-257.28	-249.15	-0.46	3.16
15C.C	5CC.C	-215.27	-208.01	-0.42	3.37
-25C.C	1CCC.C	-3706.88	-3728.67	1.24	-0.59
-2CC.C	1CCC.C	-3421.60	-3502.29	4.61	-2.36
-15C.C	1CCC.C	-3115.32	-3149.94	1.58	-1.11
-1CC.C	1CCC.C	-2621.77	-2639.45	1.01	-0.67
-5C.C	1CCC.C	-1345.85	-1395.13	2.81	-3.66
C.C	1CCC.C	-861.09	-866.20	0.29	-0.59
5C.C	1CCC.C	-652.82	-644.44	-0.48	1.28
1CC.C	1CCC.C	-521.55	-510.89	-0.61	2.05
15C.C	1CCC.C	-430.54	-419.59	-0.62	2.54
2CC.C	1CCC.C	-364.04	-352.71	-0.65	3.11
25C.C	1CCC.C	-311.53	-301.44	-0.58	3.24
-25C.C	15CC.C	-3678.88	-3695.20	0.93	-0.44
-2CC.C	15CC.C	-3400.60	-3475.48	4.28	-2.20
-15C.C	15CC.C	-3109.32	-3145.73	2.14	-1.20
-1CC.C	15CC.C	-2719.78	-2739.55	1.13	-0.73
-5C.C	15CC.C	-2070.46	-2115.95	2.83	-2.30
C.C	15CC.C	-1358.14	-1395.54	2.14	-2.75
5C.C	15CC.C	-994.10	-997.84	0.21	-0.38
1CC.C	15CC.C	-784.08	-773.74	-0.59	1.32
15C.C	15CC.C	-638.82	-627.17	-0.67	1.82
2CC.C	15CC.C	-537.81	-522.61	-0.64	2.10
25C.C	15CC.C	-456.80	-443.75	-0.74	2.85
-25C.C	2CCC.C	-3649.13	-3660.97	0.68	-0.32
-2CC.C	2CCC.C	-3379.60	-3446.29	3.81	-1.97
-15C.C	2CCC.C	-3094.32	-3131.92	2.15	-1.22
-1CC.C	2CCC.C	-2747.78	-2774.88	1.55	-0.99
-5C.C	2CCC.C	-2285.24	-2322.31	1.85	-1.44
-1C.C	2CCC.C	-1839.44	-1879.40	2.28	-2.17
5C.C	2CCC.C	-1295.13	-1312.62	1.00	-1.35
1CC.C	2CCC.C	-1020.36	-1017.08	-0.19	0.32
15C.C	2CCC.C	-829.59	-820.50	-0.52	1.10
2CC.C	2CCC.C	-691.32	-680.66	-0.61	1.54

AVERAGE RESULTANT DEVIATION = 1.69039

AVERAGE RESULTANT DEVIATION IN BTU/LB = 1.42

TABLE 102

COMPARISON OF PREDICTED ENTHALPY DEPARTURES USING THE OBWR EQUATION WITH EXPERIMENTAL VALUES FOR THE 5.2 MOLE % PROPANE MIXTURE

T (F)	PP (PSIA)	HP (BTU/LBMOLE)	HC	DEV BTU/LB	%DEV
-250.0	500.0	-3731.39	-5379.50	94.11	-44.14
-200.0	500.0	-3446.11	-4068.40	35.56	-18.06
-150.0	500.0	-3110.07	-3329.27	12.53	-7.05
0.0	500.0	-393.79	-393.69	-0.01	0.03
50.0	500.0	-313.28	-310.73	-0.15	0.81
100.0	500.0	-257.28	-254.07	-0.18	1.25
150.0	500.0	-215.27	-212.75	-0.14	1.17
-250.0	1000.0	-3706.88	-5348.31	93.79	-44.29
-200.0	1000.0	-3421.60	-4043.65	35.54	-18.18
-150.0	1000.0	-3115.32	-3332.05	12.38	-6.56
-100.0	1000.0	-2621.77	-2659.54	4.44	-2.97
-50.0	1000.0	-1345.89	-1347.08	0.07	-0.09
0.0	1000.0	-861.09	-866.26	0.30	-0.60
50.0	1000.0	-652.82	-650.48	-0.13	0.36
100.0	1000.0	-521.55	-519.56	-0.17	0.37
150.0	1000.0	-430.54	-427.60	-0.17	0.68
200.0	1000.0	-364.04	-360.47	-0.20	0.98
250.0	1000.0	-311.53	-308.64	-0.17	0.93
-250.0	1500.0	-3679.88	-5317.46	93.62	-44.54
-200.0	1500.0	-3400.60	-4016.64	35.20	-18.12
-150.0	1500.0	-3108.32	-3322.92	12.26	-6.90
-100.0	1500.0	-2719.78	-2791.69	4.11	-2.64
-50.0	1500.0	-2070.46	-2079.11	0.49	-0.42
0.0	1500.0	-1358.14	-1365.03	0.62	-0.80
50.0	1500.0	-994.10	-997.22	0.18	-0.31
100.0	1500.0	-784.09	-780.58	-0.20	0.45
150.0	1500.0	-638.82	-636.38	-0.14	0.38
200.0	1500.0	-533.81	-532.30	-0.09	0.28
250.0	1500.0	-456.80	-455.11	-0.21	0.81
-250.0	2000.0	-3649.13	-5286.01	93.53	-44.66
-200.0	2000.0	-3379.60	-3987.83	34.75	-18.00
-150.0	2000.0	-3094.32	-3306.51	12.12	-6.86
-100.0	2000.0	-2747.78	-2822.10	4.25	-2.70
-50.0	2000.0	-2289.24	-2314.65	1.45	-1.11
-10.0	2000.0	-1839.44	-1844.91	0.31	-0.30
50.0	2000.0	-1295.13	-1301.19	0.35	-0.47
100.0	2000.0	-1020.36	-1019.80	-0.03	0.05
150.0	2000.0	-829.59	-828.86	-0.04	0.09
200.0	2000.0	-691.32	-690.95	-0.02	0.05

AVERAGE ABSOLUTE DEVIATION = 7.6725%

AVERAGE ABSOLUTE DEVIATION IN BTU/LB = 14.97

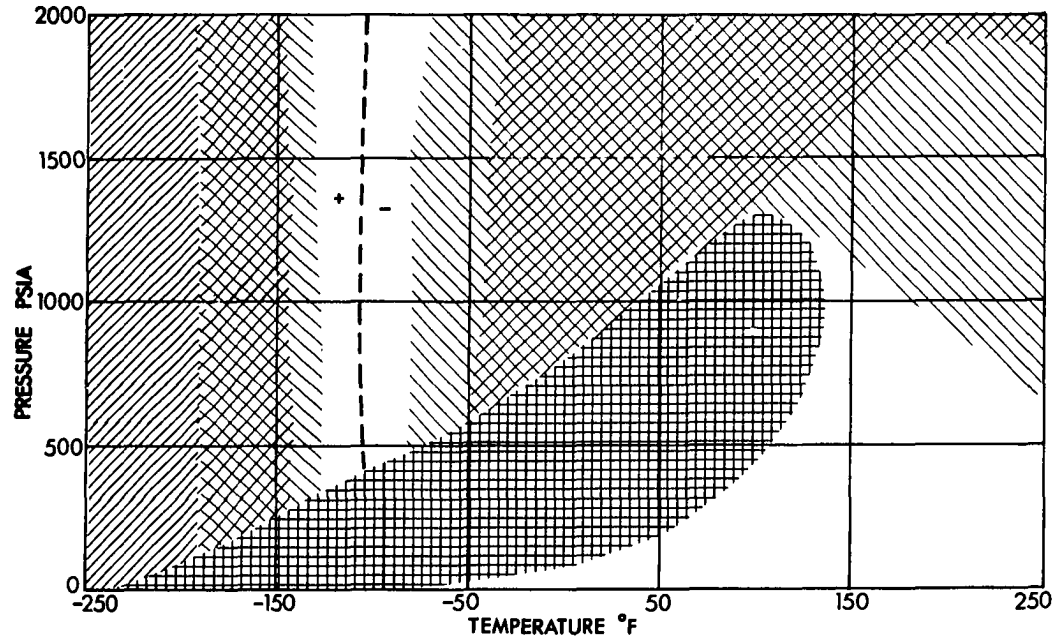


Figure 31. Comparison of Enthalpy Departures Calculated by the Modified BWR Equation Using Set III Parameters with Experimental Values for the 50.6 Mole % Propane Mixture.

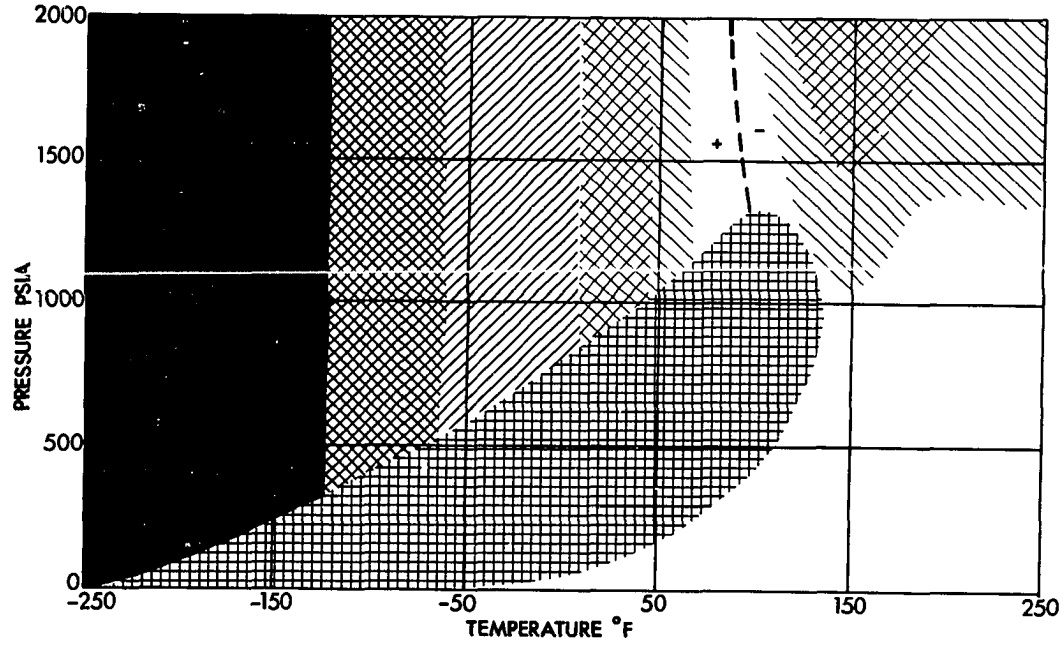


Figure 32. Comparison of Enthalpy Departures Calculated by the Original BWR Equation with Experimental Values for the 50.6 Mole % Propane Mixture

19.8% at 160°F, 800 psia. The average absolute deviation for propane K values was 10.5% with a maximum deviation of -19.3% at -100°F, 400 psia. Original BWR equation predictions were compared with the same data set. The average absolute deviation for methane K values was 4.9% with a maximum deviation of -18.6% at -100°F, 250 psia. The average absolute deviation for propane K values was 13.6% with a maximum of 82.3% at -160°F, 250 psia. Comparisons of predicted and experimental K values for methane and propane using the modified BWR equation with the set III parameters and the original BWR equation are presented in Tables 103 through 106. Figure 33 shows graphically the improvement of predicting methane and propane K values at -120°F using the modified BWR equation with set III parameters.

Pure Component

To preserve internal consistency, the set III parameters must be able to predict pure component behavior. The results on pure component data described in Table 85 are as follows:

Methane. The average absolute deviations were 0.82% for densities, 1.35% for enthalpy departures and 1.01% for saturated fugacities. Comparisons using the original BWR equation yielded average absolute deviations of 1.16% for densities, 7.14% for enthalpy departures and 5.50% for saturated fugacities.

TABLE 103

COMPARISON OF PREDICTED K-VALUES OF METHANE USING SET III PARAMETERS WITH EXPERIMENTAL VALUES FOR THE METHANE-PROPANE SYSTEM

T (F)	PE (PSIA)	KE	KC	%DEV
-160.00	250.000	1.1920	1.1714	1.74
-140.00	200.000	2.3440	2.2503	3.98
-120.00	300.000	2.0880	2.0146	3.53
-100.00	400.000	2.0060	1.9507	2.75
-80.00	250.000	4.0710	4.2507	-4.40
-60.00	300.000	4.0940	4.2303	-3.32
-60.00	600.000	2.0420	1.9357	5.22
-40.00	300.000	4.7060	4.9620	-5.45
-40.00	600.000	1.7500	1.6402	6.25
-20.00	400.000	3.9430	4.1431	-5.06
-20.00	600.000	1.7510	1.6314	6.85
0.0	200.000	8.8070	9.5147	-8.04
0.0	500.000	3.5180	3.6138	-2.73
0.0	1000.000	1.7140	1.5853	7.52
20.00	300.000	6.3140	6.7594	-7.05
40.00	400.000	5.1530	5.3015	-2.89
60.00	600.000	3.5190	3.5518	-0.92
60.00	1050.000	1.9380	1.7343	10.51
80.00	500.000	4.4140	4.4169	-0.06
80.00	1100.000	1.8480	1.5741	14.74
100.00	400.000	5.4570	5.5604	-1.90
100.00	1000.000	2.0700	1.7824	13.88
120.00	600.000	3.5980	3.4363	3.42
120.00	800.000	2.6720	2.3677	11.37
140.00	700.000	2.9250	2.5984	11.48
160.00	800.000	2.2110	1.7733	19.78

AVERAGE RESULTE DEVIATION = 6.2400%

TABLE 104

COMPARISON OF PREDICTED K-VALUES OF METHANE USING THE OBWR EQUATION WITH EXPERIMENTAL VALUES FOR THE METHANE-PROPANE SYSTEM

T (F)	PE (PSIA)	KE	KC	%DEV
-100.00	250.000	1.1920	1.4144	-18.64
-140.00	200.000	2.3440	2.7218	-16.57
-120.00	300.000	2.0880	2.3057	-10.40
-100.00	400.000	2.0060	2.1448	-6.91
-80.00	250.000	4.0710	4.0196	1.27
-60.00	300.000	4.0940	3.9185	4.30
-60.00	400.000	2.0420	2.0380	0.21
-40.00	300.000	4.7060	4.4603	5.21
-40.00	400.000	1.7500	1.7725	-1.31
-20.00	400.000	3.5420	3.7917	-3.85
-20.00	500.000	1.7510	1.7662	-0.84
0.0	200.000	8.8070	8.1247	7.75
0.0	300.000	3.5180	3.3717	4.15
0.0	1000.000	1.7140	1.7393	-1.46
20.00	300.000	6.3140	5.9500	5.77
40.00	400.000	5.1530	4.8099	6.65
60.00	600.000	3.5190	3.4051	3.24
60.00	1050.000	1.9380	1.9202	0.92
80.00	500.000	4.4140	4.1854	5.18
80.00	1100.000	1.8460	1.8274	1.02
100.00	400.000	5.4570	5.2402	3.97
100.00	1000.000	2.0700	2.0236	2.23
120.00	600.000	3.5580	3.4705	2.46
120.00	800.000	2.6720	2.5509	4.52
140.00	700.000	2.9350	2.8029	4.51
160.00	800.000	2.2110	2.1010	4.96

AVERAGE ABSOLUTE DEVIATION = 4.53462

TABLE 105

COMPARISON OF PREDICTED K-VALUES OF PROPANE USING SET III PARAMETERS WITH EXPERIMENTAL VALUES FOR THE METHANE-PROPANE SYSTEM

T (F)	P (PSIA)	KE	KC	%DEV
-100.00	250.000	0.0060	0.0054	11.76
-140.00	200.000	0.0070	0.0072	-4.03
-120.00	300.000	0.0150	0.0142	6.71
-100.00	400.000	0.0220	0.0259	-15.27
-80.00	250.000	0.0410	0.0388	4.53
-60.00	300.000	0.0600	0.0585	2.50
-60.00	600.000	0.0980	0.0981	0.13
-40.00	300.000	0.0910	0.0890	2.07
-40.00	600.000	0.1050	0.1242	-13.54
-20.00	400.000	0.1210	0.1177	2.54
-20.00	900.000	0.1450	0.1762	-18.04
0.0	200.000	0.2470	0.2417	2.02
0.0	500.000	0.1470	0.1558	-5.82
0.0	1000.000	0.2110	0.2462	-16.54
20.00	300.000	0.2980	0.2994	3.40
40.00	400.000	0.3010	0.2985	0.95
60.00	600.000	0.3360	0.3357	0.78
60.00	1050.000	0.3670	0.4199	-14.46
80.00	500.000	0.4440	0.4434	0.17
80.00	1100.000	0.4590	0.5357	-17.57
100.00	400.000	0.6070	0.6071	0.01
100.00	1000.000	0.5060	0.5672	-12.13
120.00	600.000	0.6210	0.6168	0.70
120.00	800.000	0.5720	0.6023	-5.37
140.00	700.000	0.6880	0.7046	-2.47
160.00	800.000	0.7830	0.8227	-5.07

AVERAGE ABSOLUTE DEVIATION = 10.506%

TABLE 106

COMPARISON OF PREDICTED K-VALUES OF PROPANE USING THE OBWR EQUATION WITH EXPERIMENTAL VALUES FOR THE METHANE-PROPANE SYSTEM

T (F)	PE (PSIA)	KE	KC	%DEV
-100.00	250.000	0.0060	0.0011	82.32
-140.00	200.000	0.0070	0.0026	63.34
-120.00	300.000	0.0150	0.0070	53.95
-100.00	400.000	0.0220	0.0160	26.42
-80.00	250.000	0.0410	0.0302	25.66
-60.00	300.000	0.0600	0.0503	16.19
-60.00	600.000	0.0680	0.0536	21.37
-40.00	300.000	0.0910	0.0822	9.56
-40.00	600.000	0.1090	0.0980	10.56
-20.00	400.000	0.1210	0.1127	6.67
-20.00	500.000	0.1490	0.1438	3.68
0.0	200.000	0.2470	0.2411	2.26
0.0	500.000	0.1470	0.1523	-3.40
0.0	1000.000	0.2110	0.2025	3.81
20.00	300.000	0.2680	0.2618	2.48
40.00	400.000	0.3010	0.3026	-0.38
60.00	600.000	0.3380	0.3374	0.30
60.00	1050.000	0.3670	0.3771	-2.80
80.00	500.000	0.4440	0.4492	-1.13
80.00	1100.000	0.4590	0.4727	-2.99
100.00	400.000	0.6070	0.6161	-1.47
100.00	1000.000	0.5060	0.5264	-4.06
120.00	600.000	0.6210	0.6195	0.26
120.00	800.000	0.5720	0.5909	-3.38
140.00	700.000	0.6880	0.6956	-1.75
160.00	800.000	0.7830	0.8011	-2.30

AVERAGE ABSOLUTE DEVIATION = 13.5650%

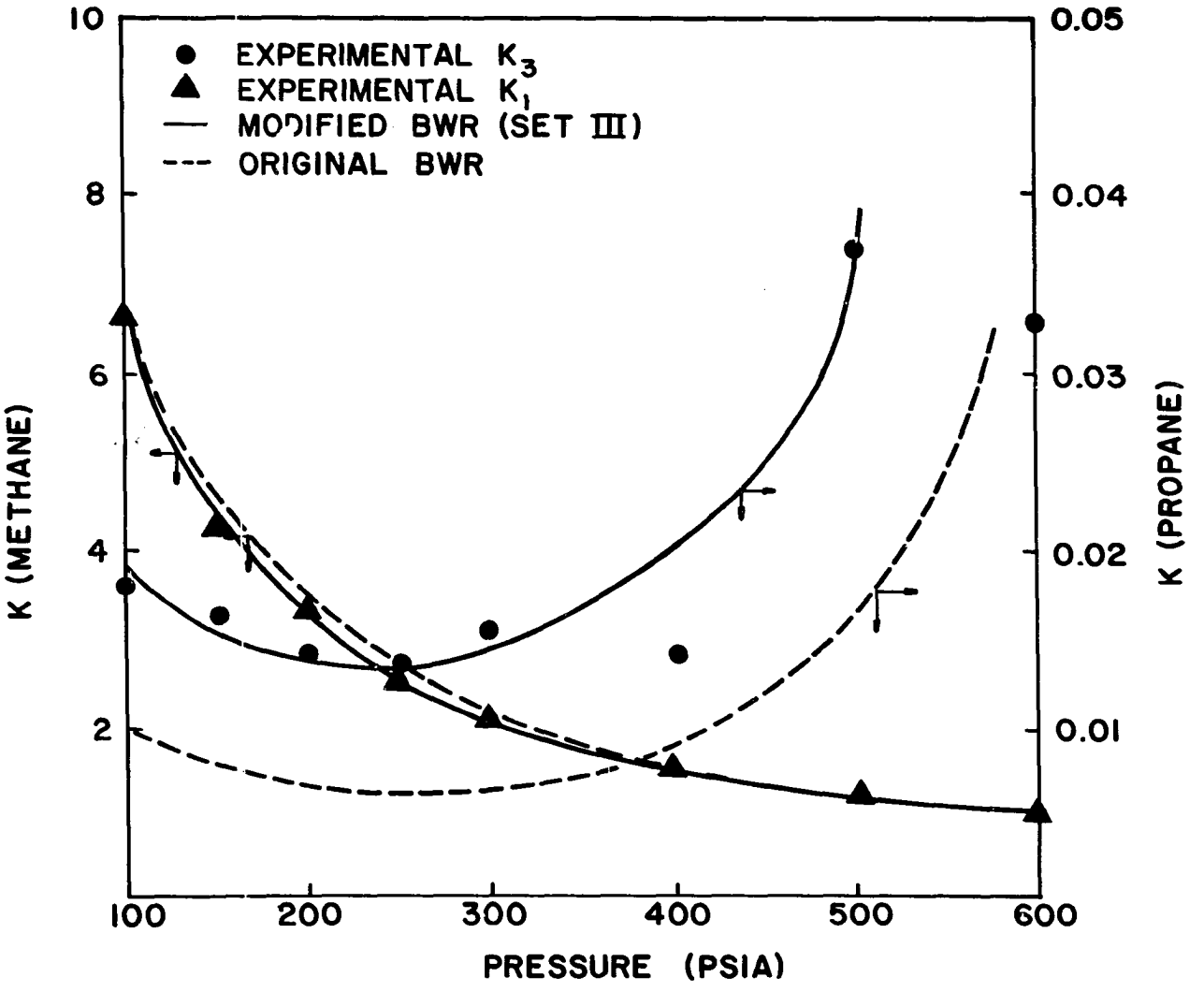


Figure 33. Comparison of Predicted K-values for Methane and Propane Using the Modified and Original BWR Equation with Experimental Values.

Propane. The average absolute deviations were 1.07% for densities, 1.26% for enthalpy departures and 1.09 for saturated fugacities. Comparisons using the original BWR equation yielded average absolute deviations of 1.46% for densities, 39.37% for enthalpy departures and 7.18% for saturated fugacities.

It can be seen that results using the set III parameters to predict pure-component behavior are not as accuate as those predicted by set II. Nonetheless, the 1 to 2% uncertainty in predicted property values using set III parameters still show appreciable improvement over the original BWR equation. Thus, the set III parameters are preferred to describe the thermodynamic behavior of the methane-propane system.

Summary

The feasibility of simultaneously using mixture and pure-component PVT, enthalpy departure and phase equilibrium data in equation of state development has been successfully demonstrated. The multicomponent, multiproperty regression analysis method developed in this research allows the mixing rules of an equation of state to remain fixed while "absorbing" solution nonideality into the pure component parameters. Of more significance, application of this general method of regression analysis results in an equation of state for the methane-propane system which for the first time satisfied all aspects

of thermodynamic consistency. Extension to ternary system simply entails the use of ternary with binary and pure component data. The possible difficulties appear in computer core storage to house a large number of data and in computer executing time. With the availability of large and fast computers, such problems can be alleviated appreciably.

CHAPTER XII

CORRESPONDING STATES PRINCIPLE

Two-Parameter Corresponding States Principle

The corresponding states principle (for brevity, herein referred to as CSP), as introduced by van der Waals[130], states that all fluids behave identically at the same reduced temperature and pressure, i.e.,

$$Z = f(T_r, P_r) \tag{106}$$

where Z is compressibility factor, T_r is reduced temperature and P_r is the reduced pressure.

Through the corresponding states principle, properties of materials whose behavior is unknown may be predicted from the known behavior of a reference fluid. Since van der Waals' enunciation of the law, countless efforts have been contributed to its further development and refinement. At the risk of doing injustice to the subject, only a brief discussion leading to the use of an equation of state in CSP applications will be given here. Excellent articles on the theoretical developments and empirical applications of CSP can be found in the literature[77,78,52,101,122].

The empirical statement of the simple CSP was put on a firm theoretical foundation by Pitzer[101], who elucidated the molecular requirements for simple fluids obeying the two-parameter CSP. These molecular requirements limit the fluids to simple spherical molecules with no hydrogen bonding, polarity or quantum effects.

Three-Parameter Corresponding States Principle

For a wider class of asymmetric molecules collectively known as "normal fluids", Pitzer introduced a third parameter to account for the deviations from the simple CSP. Equation (106) becomes

$$Z = f(T_r, P_r, \omega) \tag{107}$$

where ω is the acentric factor defined by

$$\omega = \left[- 1 - \log_{10} (P_r) \right]_{T_r=0.7} \tag{108}$$

where P_r is the reduced pressure. Of course, the choice of a third parameter is by no means unique. Comparable success has been enjoyed using the critical compressibility factor[56] and the Riedel factor[110] as the third parameter in CSP. Recently, Leach and Leland[76] introduced the so-called shape factor to correlate fluids with moderate polarity.

Hydrocarbons fall within the definition of "normal fluids", and it has been observed by Curl and Pitzer[32]

that reduced enthalpy departures $\frac{H-H^\circ}{RT_c}$ of normal fluids can be correlated as linear functions of acentric factor. These investigators chose to correlate properties of normal fluids by measuring their departures from simple CSP, viz.,

$$\frac{H^\circ-H}{RT_c} = \left[\frac{H^\circ-H}{RT_c}\right]_o + \omega\left[\frac{H^\circ-H}{RT_c}\right]_1 \qquad (109)$$

where subscript 0 and 1 denote zero and first order approximations in acentric factor.

Two-Fluid Model Corresponding States Principle

Recently Yesavage[141], utilizing accurate and extensive enthalpy data for the methane-propane system, capitalized on the linear functionality between reduced enthalpy departures and acentric factors, and proposed the following interpolation scheme to predict enthalpy departures,

$$\frac{H-H^\circ}{RT_c} = \left[\frac{H^\circ-H}{RT_c}\right]_1 W_1 + \left[\frac{H^\circ-H}{RT_c}\right]_2 W_2 \qquad (110)$$

where subscripts 1 and 2 refer to reference fluids (methane and propane in this case). W_1 and W_2 are weighting factors given by

$$W_1 = \frac{\omega_2-\omega}{\omega_2-\omega_1} \qquad (111)$$

$$W_2 = \frac{\omega-\omega_1}{\omega_2-\omega_1} \tag{112}$$

For hydrocarbons, with the exception of methane, the carbon numbers and acentric factors fall on the same scale. Using the carbon number as a reference scale, Equation (110) is valid provided that the unknown fluid of interest has an acentric factor lying in between two reference fluids whose carbon numbers do not differ by more than two.

This fact is vividly illustrated in Figure 34 where experimental or derived reduced enthalpy departures of methane, propane, n-pentane and n-heptane are shown at four reduced conditions covering both the vapor and liquid phases. Incidentally, although the modified BWR equation is accurate in predicting enthalpy departures at the conditions presented in Figure 34, experimental values are used where possible, to show the inappropriateness of using methane and propane as reference materials to predict enthalpy departures of n-pentane

As a numerical example, at the reduced condition $T_r = 0.66$, $P_r = 0.405$, experimental reduced enthalpy departures of methane and propane are -4.97 and -6.0214 respectively. To estimate the reduced enthalpy departure of n-pentane at the same reduced condition, a straight line was passed through the above two points, and a value

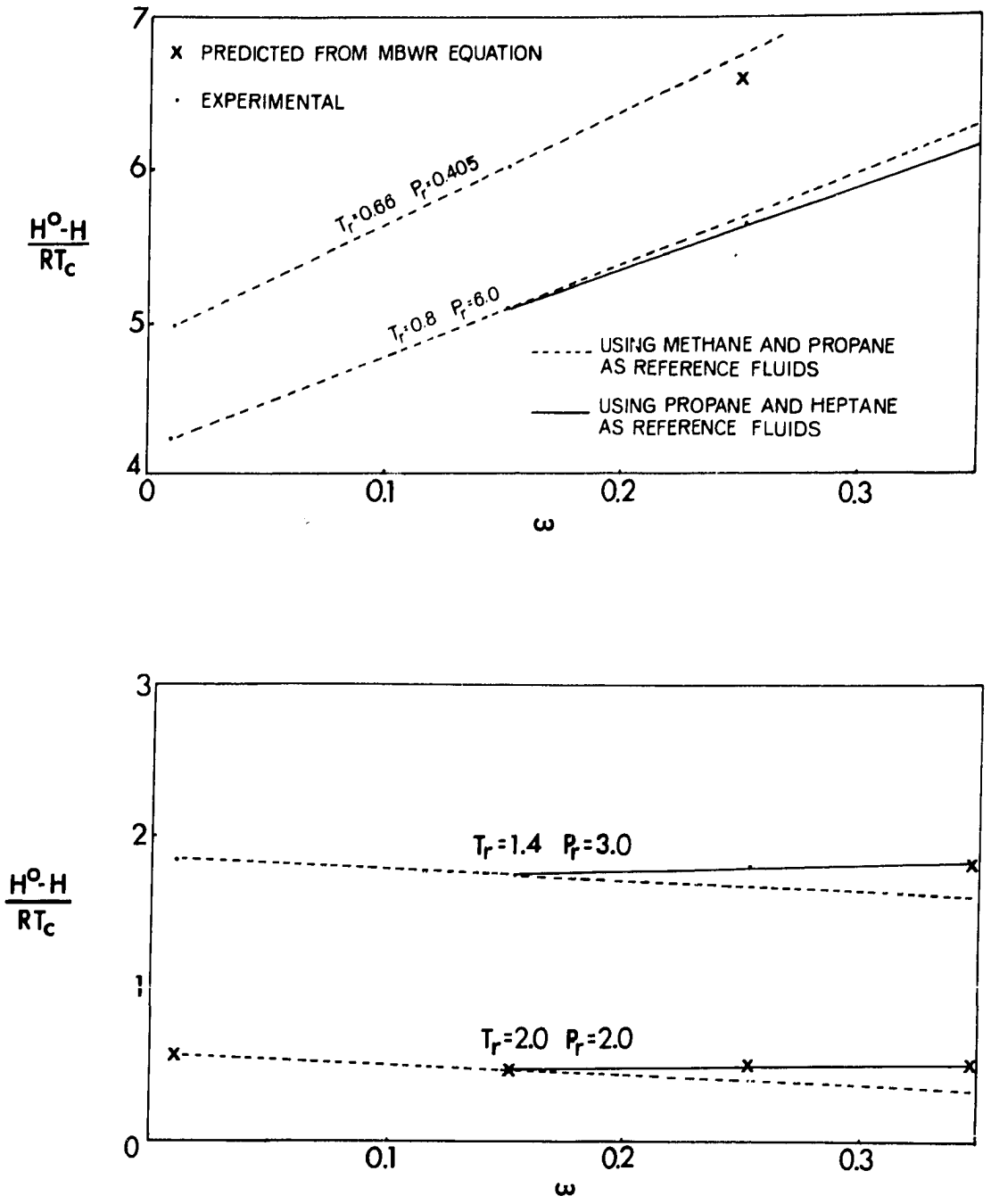


Figure 34. Variation of Reduced Enthalpy Departure with Acentric Factor.

of -6.78 was read from Figure 34. In terms of the unreduced coordinates, this linear correlation yields -159 Btu/lb as the enthalpy departure of n-pentane at 100°F and 200 psia. The predicted enthalpy departure from the modified BWR equation at the same condition is -154.5 Btu/lb. (The derived enthalpy departure from PVT data by Sage and Lacey[112] at the same condition is also -154.5 Btu/lb.)

Thus, use of methane and propane as reference fluids in Equation (110) to predict enthalpy departure of n-pentane is inadequate. However, it can be seen graphically from Figure 34 that enthalpy departures of n-pentane can be predicted accurately using propane and n-heptane as reference materials.

Development of a Three-Parameter Corresponding States Chart Using the Modified BWR Equation

In CSP applications, it is in predicting the behavior of reference fluids that the modified BWR equation can make its contribution. Because of the proven high accuracy with which the modified BWR equation can predict thermodynamic properties of methane, propane, n-pentane and n-heptane, it becomes possible to use these materials as reference fluids. For example, to predict enthalpy departures of n-hexane where no experimental values are available, Equation (110) may be employed using n-pentane and n-heptane as the reference fluids.

Although the modified BWR equation can be used repeatedly to calculate reduced enthalpy departures of the reference fluids at the reduced conditions of interest, it is desirable to have available a set of charts or better still, a single chart whereby estimation of enthalpy departures requires only interpolation. To correlate K-values of hydrocarbons, DePriester[36] successfully condensed a large number of charts with three parameters into a single chart with four parameters. It was found that the reduced enthalpy departures of hydrocarbons in the liquid phase ($0.3 \leq T_r \leq 0.85$) also can be summarized in a single chart using four parameters, viz., reduced temperature T_r, pressure P_r, enthalpy departure $\frac{H-H^\circ}{RT_c}$ and acentric factor ω.

To estimate liquid phase reduced enthalpy departures for normal fluids with acentric factors of less than 0.35, a generalized chart was prepared using four reference fluids, viz., methane, propane, n-pentane and n-heptane. Reduced enthalpy departures of these hydrocarbons at various reduced conditions were calculated using the modified BWR equation. The results were then plotted as shown in Figure 35. The actual size of the chart is 14 x 19 inches.

If the reduced enthalpy departures were indeed linear functions of acentric factor as demanded by Equation (110) using a two fluid model, the parametric lines of reduced

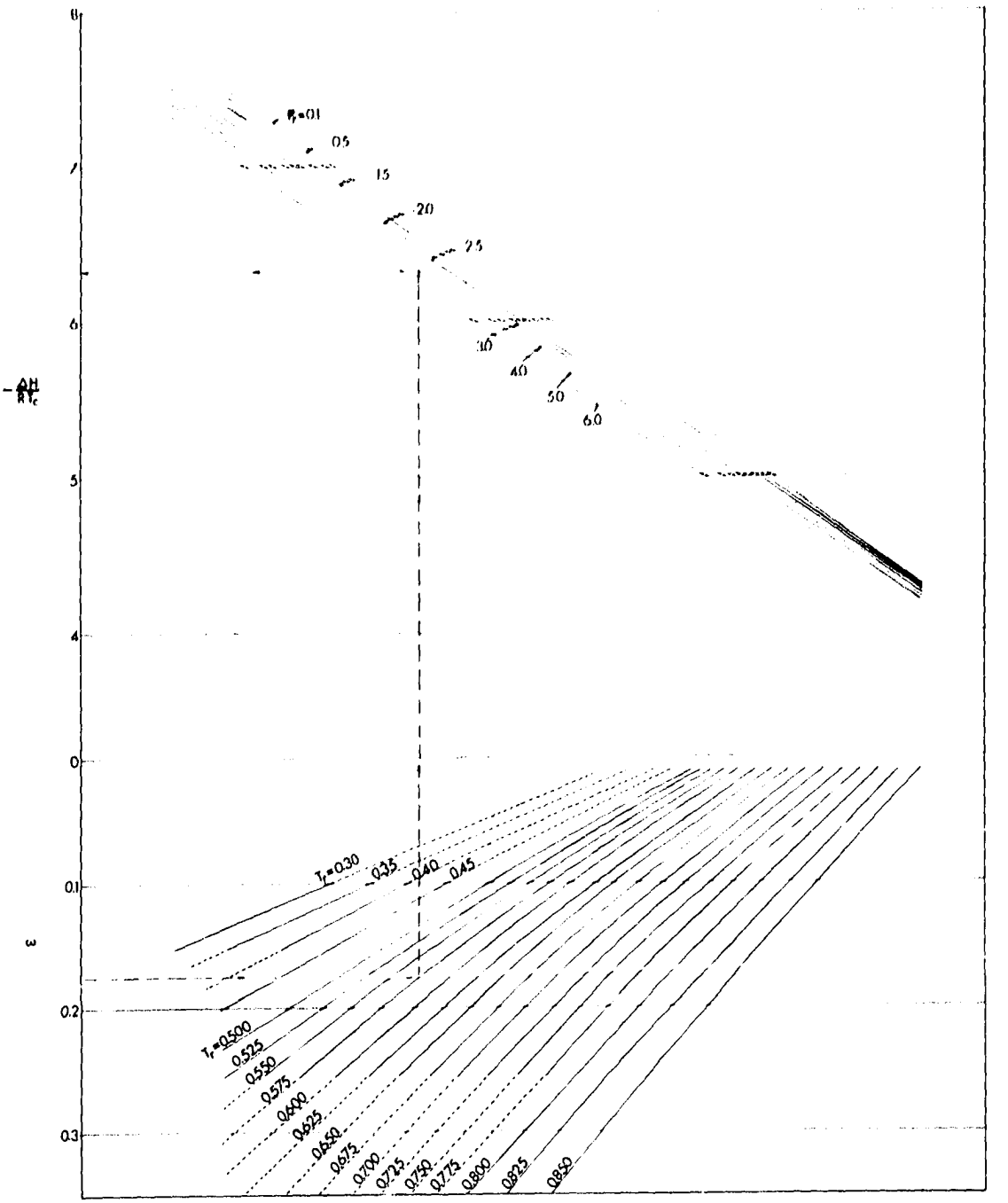


Figure 35. Corresponding States Correlation of Liquid Enthalpy Departures for Normal Fluids.

temperature and pressure should be straight lines. From Figure 35, it can be seen that the parametric lines of reduced temperature are not linear. This fact reveals the desirability of using more than two reference fluids to ascertain the functionality between reduced enthalpy departures and acentric factor.

Deviations of the predicted liquid enthalpy departures for normal fluids from experimental and derived values using the generalized chart developed in this chapter were compared with the generalized charts of Yen and Alexander[142] and Yarborough[143]. The average absolute deviations in Btu/lb using eight normal fluids were 1.7, 12.67 and 2.67 for the above three generalized charts respectively. These results are presented in Table 107.

Prediction of Liquid Enthalpy Departures of Mixtures Using Kay's Rule and the Three-Parameter Corresponding States Chart

It is of interest to test the capability of the generalized corresponding chart developed in this chapter for predicting liquid enthalpy departures of mixtures. To this end, the simple and widely used mixing rules of Kay[67] were employed to calculate the pseudo-critical constants and ω, (pseudo-properties are denoted by double primes)

$$T_c'' = \Sigma x_i T_{c_i} \qquad (113)$$

TABLE 107

COMPARISON OF PREDICTED LIQUID ENTHALPY DEPARTURE USING THE CORRESPONDING STATES CHARTS WITH LITERATURE VALUES

COMPOUND	T_R	P_R	LITERATURE (BTU/LB)	THIS CHART	YEN AND ALEXANDER	YARBOROUGH	REF.
METHANE	0.55	0.52	-225.0	-225.0	-234.2	-226.0	141
NITROGEN	0.705	3.06	-80.6	-80.9	-84.9	-78.8	82
PROPANE	0.299	0.57	-230.5	-233.0	———	———	
	0.705	2.02	-172.0	-171.5	-185.3	-169.6	141
I-BUTANE	0.76	0.946	-140.5	-143.5	-127.6	-137.8	21
N-BUTANE	0.732	1.82	-152.6	-153.1	-147.5	-152.5	112
CARBON DIOXIDE	0.8	0.41	-143.0	-137.0	-142.0	-156.7	39
PENTANE	0.66	4.05	-150.6	-150.1	-185.5	-149.0	
	0.8	2.0	-138.0	-135.0	-166.3	-135.5	51
N-HEPTANE	0.8	0.8	-120.5	-122.0	-110.8	-122.8	
	0.8	4.0	-119.9	-119.0	-108.5	-120.5	51
AVG. ABS. DEVIATION (BTU/LB)				1.7	12.67	2.67	

$$P''_c = \Sigma x_i P_{c_i} \quad (114)$$

$$Z''_c = \Sigma x_i Z_{c_i} \quad (115)$$

$$\omega'' = \Sigma x_i \omega_i \quad (116)$$

Experimental liquid enthalpy departures of five methane-propane mixtures from the University of Michigan[83,90,141] and one natural gas mixture from the Institute of Gas Technology[129] were used as the basis for comparison. Predictions using the generalized correlations of Yen and Alexander[142] and Yarborough[143] were also carried out. The results are summarized in Tables 108 and 109.

In predicting the liquid enthalpy departures of the methane-propane system and the natural gas sample, the three-parameter corresponding states chart proved to be more accurate than the correlations of Yen and Alexander[142] and Yarborough[143]. Of more importance, this generalized chart extends the correlation of cryogenic enthalpy departures to reduced temperatures as low as 0.3.

Summary

In today's cryogenic processing of natural gas it is imperative to have available, a method whereby liquid enthalpy departures can be accurately and easily estimated. Virtually all the constituents present in natural gas are

TABLE 108

COMPARISON OF PREDICTED LIQUID ENTHALPY DEPARTURES WITH

EXPERIMENTAL VALUES FOR THE METHANE-PROPANE SYSTEM

MOLE FRACTION CH_4	MOLE FRACTION C_3H_8	T_R	P_R	EXPTL. (BTU/LB)	THIS CHART	YEN AND ALEXANDER	YARBOROUGH	REF.
0.948	0.052	0.58	1.87	-210.9	-216.0	-220.0	-214.0	83
		0.721	1.87	-194.9	-198.5	-216.0	-197.0	
		0.86	1.87	-178.0	-178.0	-202.0	-177.4	
0.883	0.117	0.55	1.88	-216.7	-212.0	-214.0	-212.5	90
		0.68	1.88	-201.9	-186.5	-202.0	-194.4	
		0.81	1.88	-185.3	-179.0	-198.5	-178.1	
0.72	0.28	0.484	2.28	-217.6	-210.0	-206.0	-201.0	90
		0.599	2.28	-204.7	-196.8	-197.0	-192.5	
		0.714	2.28	-190.9	-187.5	-191.5	-179.5	
		0.83	2.28	-176.5	-164.0	-182.5	-166.0	
0.506	0.494	0.416	1.94	-222.1	-213.0	———	———	141
		0.515	1.94	-210.3	-203.0	-188.5	-194.5	
		0.614	1.94	-198.2	-191.5	-180.0	-185.0	
		0.713	1.94	-183.9	-178.5	-176.5	-173.5	
		0.812	1.94	-173.3	-164.5	-170.5	-166.0	

TABLE 108 - CONTINUED

MOLE FRACTION CH_4	MOLE FRACTION C_3H_8	T_R	P_R	EXPTL. (BTU/LB)	THIS CHART	YEN AND ALEXANDER	YARBOROUGH	REF.
0.234	0.766	0.356	1.98	-223.1	-209.0	———	———	141
		0.440	1.98	-212.2	-199.0	———	———	
		0.525	1.98	-201.1	-190.0	-241.0	-184.5	
		0.610	1.98	-190.1	-180.0	-214.1	-181.5	
		0.695	1.98	-179.3	-169.0	-197.5	-167.3	
		0.778	1.98	-168.5	-159.0	-184.5	-159.0	
AVG. ABS. DEV. (BTU/LB)					6.84	13.30	9.84	

TABLE 109

COMPARISON OF PREDICTED LIQUID ENTHALPY DEPARTURES WITH EXPERIMENTAL VALUES FOR A NATURAL GAS SAMPLE (MIXTURE NO. 4 FROM IGT[129])

TEMPERATURE °F	PRESSURE PSIA	EXPERIMENTAL (BTU/LB)	THIS CHART	YEN AND ALEXANDER	YARBOROUGH
-200.0	1606.5	-200.99	-199.0	-221.5	-194.0
-150.0	719.3	-187.56	-182.0	-198.5	-182.0
-150.0	1133.2	-188.46	-179.5	-205.0	-182.0
-150.0	1444.3	-184.77	-179.0	-207.0	-180.0
-150.0	1664.2	-183.24	-178.0	-209.0	-179.0
AVG. ABS. DEV.			5.5	19.2	5.6

The composition of this mixture is 0.9 mole % N_2, 95.02% CH_4, 3.0% C_2H_6, 0.35% C_eH_8, 0.48% n-C_4H_{10}, 0.07% n-C_5H_{12}, 0.18% C_6H_{14}.

normal fluids, conformal to the three-parameter corresponding states principle. Generalized charts of the type prepared by Yen and Alexander[142] and Yarborough[143] provide a rapid means for predicting enthalpy departures of normal fluids. However, correlation of liquid enthalpy departures from these charts is limited to reduced temperatures no smaller than 0.5.

The generalized chart developed in this chapter extends the correlation of liquid enthalpy departures to reduced temperatures as low as 0.3. This chart was constructed using four reference fluids, viz., methane, propane, n-pentane and n-heptane whose reduced enthalpy departures were calculated from the modified BWR equation. The conciseness and accuracy of this chart offers a simple and direct means for estimating enthalpy departures of normal fluids and their mixtures with ω less than 0.35 in the liquid phase ($0.3 \leq T_r \leq 0.85$). The success of this chart as a means for generalized correlation reaffirms the usefulness of the modified BWR equation in corresponding states applications.

CHAPTER XIII

CONCLUSIONS

The main objective of this research has been to correlate the thermodynamic behavior of fluids at low temperatures. To accomplish this objective, a new equation of state has been developed from a careful study of isochoric data of methane. This equation is capable of predicting all thermodynamic properties of methane and propane with an uncertainty of 1.0% to reduced temperatures as low as 0.3. Its temperature dependence, expressed by a polynomial series in reciprocal temperature, was proven to be preferred over the mathematically more complex exponential functions.

To provide a uniform approach for determining a set of self-consistent equation-of-state parameters, a general multicomponent, multiproperty nonlinear regression program has been developed. This program can treat PVT, enthalpy departure, vapor pressure and K-values of pure components and mixtures selectively and/or simultaneously.

From the standpoint of economizing resources, it was decided to pursue the objective of correlating the

thermodynamic behavior of fluids at cryogenic conditions with the modified BWR equation of state. This modified BWR equation has been successfully applied to methane, ethane, propane, n-butane, n-pentane, n-hexane, n-heptane, ethylene, nitrogen, carbon dioxide and hydrogen sulfide. When compared with the original BWR equation, the modified BWR equation shows marked improvement in predicting the thermodynamic behavior of the above materials.

A set of generalized parameters for the modified BWR equation has been developed from methane, ethane, propane, n-butane, and n-pentane data using acentric factor as the correlating parameter. This set of generalized parameters has been shown to be capable of predicting the volumetric and enthalpy behavior of natural gas mixtures. Use of an "effective" acentric factor in the generalized parameter relations offers a very simple way to generate equation of state parameters for additional materials.

Incidentally, the generalized parameters of the modified BWR equation of state may be used as defining equations for a more general characterization parameter, the "effective" acentric factor, provided that the coefficients appearing in Equation (87) can approximate, to a good degree, universal constants. The original BWR equation has been applied to such diversified materials as benzene and pentafluormonochloroethane.[26] It is highly

plausible that the modified BWR equation may be applied to aromatic and polar fluids. If a reasonably large sample of representative fluids can be correlated using the "effective" acentric factor and the generalized parameters, the condition that the coefficients in Equation (87) be universal constants, may indeed be realized.

Correlation of a new fluid, then, involves simply the determination of an "effective" acentric factor for the fluid of interest using the generalized parameters. Deviations of the fluid of interest from the simple fluid model due to aromaticity, polarity and quantum effects, etc. may be looked upon as being "lumped" into the "effective" acentric factor. It is within this context that the "effective" acentric factor becomes a more general characterization parameter. However, this worthwhile undertaking lies beyond the scope of this research.

To correlate the thermodynamic behavior of mixtures at cryogenic conditions, the method of multicomponent, multiproperty regression analysis has been applied to the methane-propane system using the modified BWR equation. This general regression analysis method has successfully produced sets of methane and propane parameters capable of predicting the thermodynamic behavior of the mixture and its constituents to the low temperature of -250°F with an accuracy approaching experimental uncertainty.

Extension to a ternary system simply entails addition of ternary and additional binary experimental mixture data in the general regression calculation. This approach avoids the cumbersome task of introducing and evaluating the many two-body and three-body unlike interaction parameters in a multi-parameter equation of state.

Finally, a generalized reduced enthalpy departure chart, based on the three-parameter corresponding states principle, has been constructed using four reference fluids, viz., methane, propane, n-pentane and n-heptane. This chart was developed for estimating enthalpy departures of normal fluids and their mixtures with ω less than 0.35 in the liquid phase ($0.3 \leq T_r \leq 0.85$). This graphical correlating scheme has been shown to be more accurate than the correlations of Yen and Alexander[142] and Yarborough[143] in the region applicable.

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NOMENCLATURE

A,B,C,D,E,F,G,K	Equation of state parameters
A_o,B_o,C_o	Equation of state parameters
A',B',C',D'	Constants used in Equation (22)
A',B',C',D'	Reduced parameters used in Equation (73)
a,b,c,d,k,T_o	Equation of state parameters
A	Helmholtz free energy
$\tilde{A}$	Residual Helmholtz free energy
$\underline{A}$	Coefficient matrix
$\underline{A}^{-1}$	Inverse of $\underline{A}$
A_{gh}	Elements of $\underline{A}$
$[A]$	A set of true-valued mixture parameters
$\Delta\bar{A}_{rs}$	Difference between $\bar{A}_{rs}$ and $\bar{A}_{rs_o}$
$\underline{B}$	Column matrix
B_h	Elements of $\underline{B}$
B	Second virial coefficient
B_{ij}	Second interaction virial coefficients
$\underline{C}$	Augmented matrix
C_g	Elements of $\underline{C}$

C	Third virial coefficient
C_p	Heat capacity at constant pressure
C_{ijk}	Third interaction virial coefficients
d	Reduced molal density used in Equation (73)
d	Differential operator
f	Fugacity (psia)
f	Symbol for a functional relationship
G	Gibbs free energy
H	Enthalpy (Btu/lb mole)
H°	Enthalpy in ideal gas state
ΔH	H-H°
K	Vapor-liquid equilibrium ratio
ln	Natural logarithm
M	Number of regression parameters
N	Total number of data point used in regression analysis
N	Total number of moles in a mixture
n_i	Number of moles of the i^{th} component in a mixture
NC	Number of components in a mixture
NP	Number of data points for each property
P	Pressure (psia)
PDF	Probability distribution function
Q	Regression function
R	Universal gas constant $\left(\frac{\text{Btu}}{\text{lb mole}^\circ\text{R}}\right)$
R	Thermodynamic property

S	Entropy (Btu/lb mole °R)
$S°$	Entropy in ideal gas state
ΔS	$S-S°$
T	Temperature (°R)
U	Internal energy
U_{ij}	Empirical unlike interaction parameters
V	Molal volume (ft^3/lb mole)
W	Weighting function
x_i	Mole fraction of the i^{th} component in general
x_i	Mole fraction of the i^{th} component in the liquid phase
Y	Observed response
y	Calculated response
y_i	Mole fraction of the i^{th} component in the gas phase
Z	Compressibility factor

Greek Letters

α, γ, ρ_o	Equation of state parameters
β	Proportionality constant used in Equation (37)
δ	Kronecker delta
Δ	Difference operator
ϵ	Least squares error
η	Calculated property using an equation of state
θ	Reduced temperature
$\mu(R)$	Expected value of thermodynamic property R

μ_i	Chemical potential of the i^{th} component in a mixture
Π	Reduced pressure
σ^2 (R)	Variance of thermodynamic property R
ω	Acentric factor

Subscripts

c	Critical property
g	Row index in the regression matrix
h	Column index in the regression matrix
i,m,r	Component index
j,k	Thermodynamic state index
n,s	Parameter index
o	Guessed value in least squares formalism
r	Reduced property
_	Indicating partial molal quantity

Superscripts

g	Gas phase
l	Liquid phase
°	Ideal gas state
-	Indicating least squares estimate
"	Indicating pseudo-property

Abbreviations

AVG. ABS. DEV. Average absolute deviation

$$\frac{1}{NP}\sum\frac{R_j-\bar{R}_j}{R_j}$$

Btu	British thermal unit
CF, ft^3	Cubic foot
DE	Experimental density
DC	Calculated density
DEV	Deviation, $R_j - \overline{R}_j$
% DEV	Percent Deviation $\frac{R_j - \overline{R}_j}{R_j} \times 100\%$
exp	Exponential function
Exptl	Experimental
°F	Degree Fahrenheit
HE	Experimental enthalpy departure (Btu/lb)
HC	Calculated enthalpy departure (Btu/lb)
FUL	Calculated liquid fugacity
FUG	Calculated gas fugacity
lb	Pound
lb_f	Pound-force
MBWR	Modified BWR equation of state
OBWR	Original BWR equation of state
psia	Absolute pound-force per square inch
°R	Degree Rankine
Ref	Reference

APPENDIX A

COMPUTATIONAL PROCEDURES FOR THE MULTICOMPONENT MULTIPROPERTY NONLINEAR REGRESSION PROGRAM

Main Program

The main program serves as the controller for all the subprograms and subroutines in the nonlinear regression analysis. To preserve generality, the main program is structured such that the incorporation of any additional thermodynamic subprogram entails only the addition of a regression matrix for the property of interest, an "if" statement to tests its presence and a "call" statement for the subprogram. The subprogram must then be a separate entity whose incorporation into the regression program becomes physical. This can be achieved by including thermodynamic property input and output information within the subprogram. The necessary input and output control is performed by the "input-convergence counter". The input-convergence counter (ICC) assumes the values of zero (0), minus (-1) and plus one (+1). It works as follows:

1. When ICC is set equal to zero, the subprogram reads in thermodynamic property data.
2. When ICC is set equal to minus one, convergence in correction terms $(\bar{A}_{rs} - \bar{A}_{rs_o})$ has not been attained. The main program proceeds to call on subroutine NEQSP to calculate new parameter values and no output is effected.
3. When ICC is set equal to plus one, convergence in $(\bar{A}_{rs} - \bar{A}_{rs_o})$ has been attained or the last

iteration has been reached, the main program calls on subprograms for output information and statistical summary.

To control the amount of computer output, the following device is used:

1. SLON (1) = 0, print input information
2. SLON (2) = 0, print relative deviation of each data point
3. SLON (3) = 0, print output information
4. SLON (4) = 0, Calculate statistics on regression parameters.

The input quantities of the main program are

1. Q, M, WTFH, WTFK, WTFKZ, ITNM, IK
2. II(I), I = 1, M; IJ(I), I = 1,2
3. NC, NPVTP, NHP, NPP, CMW(I), I = 1, NC
4. VMINI, SLON(I), I = 1, 4

Computational procedures

Step 1. Read and write input data

Step 2. Initialize

a) the iteration counter, set ITN = 0

b) the input-convergence ounter, set ICC = 0.

Step 3. Initialize the size of regression matrix

Step 4. Initialize regression matrix W(K,L) for PVT subprogram. W(K,L) is also used as

the resultant regression matrix for all thermodynamic properties. Restore ICC in situ.

Step 5. Perform regression on PVT data if NPVTP is positive by calling subprogram TPVT. If NPVTP is zero, go to step 6.

Step 6. Initialize the regression matrix U(K,L) for the enthalpy subprogram. Perform regression on enthalpy data if NHP is positive by calling subprogram TENTHA. If NHP is zero, go to step 7.

Step 7. Initialize the regression matrix UK(K,L) for the enthalpy section. Perform regression on phase equilibrium data if NPP is positive. Go to step 8. (Note: If NPVTP, NHP and NPP are all zero, the problem is trivial.)

Step 8. Test for the input-convergence counter. If ICC = 0 or -1, convergence in $\Delta\bar{A}_{rs}$ has not been attained; go to step 9. Otherwise go to step 16.

Step 9. Set up the resultant regression matrix for properties of interest.

Step 10. Invert the regression matrix to solve for $\Delta\bar{A}_{rs}$ by calling subroutine MATINV.

Step 11. Test for convergence in $\Delta\bar{A}_{rs}$. When convergence is encountered, go to step 15. Otherwise go to step 12.

Step 12. Set ICC = -1. Update iteration counter by one. Calculate new parameters by calling subroutine NEQSP. Go to step 13.

Step 13. Test for iteration counter. If ITN exceeds ITNM, go to step 14, otherwise go to step 4.

Step 14. Write "Did not converge". Set ICC = 1, and go to step 5 to effect output summaries from the subprograms.

Step 15. Test ICC. If ICC = 0 or -1, set ICC = 1, and go to 5. If ICC = 1, go to step 16.

Step 16. Either convergence in $\Delta\bar{A}_{rs}$ has been attained or the last iteration has been reached. Calculate statistical summary by calling subroutine STATSUM.

Step 17. End of program.

PVT Subprogram

Subprogram TPVT reads in PVT data and calls on subroutine PVTD to calculate both the compressibility factors and densities by an equation of state. Subroutine PVTD also forms a set of linearized normal

equations using density as the dependent variable. Average absolute deviations between experimental and calculated densities and compressibility factors are computed by subroutine AVDEVI in each pass.

Computational Procedures

Step 1. Test the input-convergence counter. If ICC equals zero, go to step 2. If ICC equals negative one, go to step 4. Otherwise go to step 8.

Step 2. Read and write input data which include temperatures, pressures, experimental densities, density keys and mole fractions.

Step 3. Convert data to proper units, e.g., temperature in degree Fahrenheit to degree Rankine.

Step 4. Calculate mixture equation-of-state parameters if necessary by calling subroutine BWRC.

Step 5. Calculate densities using an equation of state by calling subroutine DENNR.

Step 6. Form the set of linearized normal equations using density as the dependent variable by calling subroutine PVTD.

Step 7. Calculate average absolute deviations

in both compressibility factors and densities. Return to main program.

Step 8. Write output summary for PVT section. This includes temperatures, pressures, experimental and calculated compressibility factors, experimental and calculated densities and the relative deviations of densities.

Step 9. Return to main program.

Enthalpy Departure Subprogram

Subprogram TENTHA reads in enthalpy departure data and calls on subroutine ENTHAL to calculate enthalpy departure by an equation of state and form the set of linearized normal equations. Absolute average deviations between experimental and calculated enthalpy departures are calculated in each pass.

Computational procedures

Step 1. Test input-convergence counter. If ICC equals zero, go to step 2. If ICC equal negative one, go to step 4. Otherwise go to step 8.

Step 2. Read and write input data which include temperatures, pressures, enthalpy departures, density keys and mole fractions.

Step 3. Convert input data to proper units; temperatures from degrees Fahrenheit to

degrees Rankine, specific enthalpy departures (Btu/lb) to molar enthalpy departures (Btu/lb mole)

Step 4. Calculate mixture equation of state parameters if necessary by calling subrouting BWRC

Step 5. Calculate densities using an equation of state by calling subrouting DENNR

Step 6. Calculate enthalpy departures using an equation of state and form the set of linearized normal equations by calling subrouting ENTHAL.

Step 7. Calculate average absolute deviation of enthalpy departures and return to main program.

Step 8. Write output summary. This includes temperatures, pressures, calculated densities, experimental and calculated enthalpy departures and their relative deviations.

Step 9. Return to main program.

Phase Equilibrium Subprogram

Subprogram PHASE reads in phase equilibrium data and calls on subroutine FLASH to perform an interval flash calculation when the feed is a mixture. It relies on subroutine PKWA for the set of linearized

normal equations using K- values as the dependent variable. Average absolute deviations on component K- values are calculated in each pass.

There are two distinguishable features in the phase equilibrium regression subprogram that need to be elucidated.

1. The data points in subprograms TPVT and TENTHA discussed so far are single phase values. The phase equilibrium subprogram deals with the two-phase region. For each data point, one has to calculate mixture equation-of-state parameters, density and fugacity of both the vapor and liquid phases. In order to have common access to the subroutines for all thermodynamic property calculations, the initial value and test value of their "DO" loops are written in variable names rather than integer values. By forcing their initial and test values to take on the same values as the phase equilibrium data point and by proper choice of the density key and mole fraction, one can use the same subroutines that are written for single phase region to calculate thermodynamic properties in the two-phase region.

2. Because of the dual functionality of K- values in a mixture with respect to pure-component and mixture parameters, in principle, it is possible to determine parameters of either component 1 or 2 from K- values

of either component 1 or 2 from K- values of either component 1 or 2 or both. Taking this possibility into consideration, a control key IK is introduced which assumes values of -1,0, and 1. For the case of binary mixtures it works as follows:

1. When IK = -1, parameter values of either component 1 or 2 are determined from K_1.

2. When IK = 0, parameter values of either component 1 or 2 are determined from K_2.

3. When IK = 1, parameter values of either component 1 or 2 are determined from both K_1 and K_2.

Computational Procedure

Step 1. Test input-convergence counter. If ICC = 0, go to step 2. If ICC = -1, go to step 7. If ICC = 1, go to step 21.

Step 2. Read and write input data which include temperature, pressure, mole fractions of liquid and vapor phases, component key.

Step 3. Initialize and set the following quantities to zero: AK(I,L), AKE(I,L) RFK(I,L), FUL(I,L), FUG(I,L), X(I,L), Y(I,L), Z(I,L)

Step 4. Convert temperature from degree Fahrenheit to Rankine and calculate experiment K-values.

Step 5. Calculate the feed composition

Step 6. Set ITN = 0

Step 7. Test for pure material or mixture. If NCK(L)-1 = 0, go to step 9. Otherwise go to step 8.

Step 8. Perform an equilibrium flash calculation.

Step 9. Calculate liquid phase equation-of-state parameters, densities and fugacities.

Step 10. Calculate vapor phase equation-of-state parameters, densities and fugacities.

Step 11. Compute calculated K-values

Step 12. Test for pure material or mixture, If NCK(L)-1 = 0, skip iteration on K values and proceed to step 18. Otherwise go to step 13.

Step 13. Test if fugacities in both liquid and vapor phases are equal. If $|\underline{f}_i^{\ell}/\underline{f}_i^{g}|-0.001 = 0$, go to step 14. Otherwise go to step 15.

Step 14. Print K-values and go to step 18.

Step 15. Update iteration counter. Set ITN = ITN + 1

Step 16. Test if ITN exceeds ITNM. If (ITNM - ITN) $\geq$ 0, go to step 8. Otherwise go to step 17.

Step 17. Print "Failed to Converge"

Step 18. Calculate ratio of experimental and calculated K-values.

Step 19. Calls subroutine PKWA to form the set of linearized normal equations.

Step 20. Calculate average deviation of component K values

Step 21. Requests output summary and return to the main program.

Step 22. Return to main program

APPENDIX B

NOMENCLATURE FOR THE MULTICOMPONENT MULTIPROPERTY NONLINEAR REGRESSION PROGRAM

Program Nomenclature

A	Input modified BWR parameters.
AK	Calculated component K-values.
AKE	Experimental component K-values.
AL	Mixture modified BWR parameters.
AVDEVD	Average absolute deviation of densities.
AVDEVH	Average absolute deviation of enthalpy departures.
AVDEVK	Average absolute deviation of component K-values.
CMW	Component molecular weight in lb/lb mole.
CONVR	Conversion factor 0.185057 $(in^2\text{-Btu})/ft^2\text{-}lb_f\text{-ft.})$
CORR	Correlation Coefficient.
D	Derivatives of dependent variable in a regression analysis with respect to equation-of-state parameters.
DB	Derivatives of dependent variable with respect to the regression parameters.
DE	Experimental density in lb mole/ft^3.
DEV	Relative deviation of calculated property from the experimental value.
DZD	Derivative of compressibility factor with respect to density.
FL	Liquid fraction.
FU	Fugacity in general.
FUG	Vapor fugacity.
FUL	Liquid fugacity.
FVA	$\Sigma \frac{Z(L - 1)}{V(K - 1) + 1}$
FVAD	Derivative of FVA with respect to volume.

HC	Calculated enthalpy departures in Btu/lb mole.
HE	Experimental enthalpy departures in Btu/lb mole.
ICC	Input convergence counter.
II	Regression parameters index.
IJ	Component index.
IK	Control key for phase equilibrium subprogram.
ITN	Iteration counter.
ITNM	Maximum number of iterations.
J	Data point index.
K	Parameter index.
M	Number of parameters determined in the regression.
MD	Density key.
MMC	Number of rows in the regression matrix.
MMNC	Number of columns in the regression matrix.
MMW	Mixture molecular weight in lb/lb mole.
NBP	Initial data point of a given property when used in a "DO LOOP".
NC	Number of components.
NCK	Number-of-component key.
NEP	Test data point of a given property when used in a "DO LOOP".
NHP	Number of enthalpy departure points.
NP	Number of data points for a given property in general.
NPVTP	Number of PVT points.
NPP	Number of phase equilibrium points.

NTP	Total number of data points.
PE	Experimental pressure in psia.
Q	Regression convergence criterion.
R	Gas constant in psia-ft^3/(lb mole °R)
RF	Ratio of the calculated property to the experimental value.
RFK	Ratio of the calculated component K-value to the experimental value.
SGMAX	Maximum standard deviation of data points.
SIGMA	Standard deviation of the data points.
SLON	Computer output control key.
T	Temperature in °R.
U	Regression matrix for enthalpy departures.
UK	Regression matrix for phase equilibrium points.
UK1	Regression matrix for the K values of component 1.
UK2	Regression matrix for the K values of component 2.
V	Vapor fraction.
VAR	Variance of regression parameters.
VMIN	Fraction of the regression delta added to the parameter.
VMINI	Initial step size of the regression delta.
W	Regression matrix for densities and/or composite thermodynamic properties.
WTF	Weighting function in general.
WTFH	Weighting function for enthalpy departures.
WTFK	Weighting function for phase equilibrium points.

WTFK2	Weighting function for component 2 K values with respect to component 1.
X	Calculated liquid mole fraction.
XE	Experimental liquid mole fraction.
XL	Component mole fraction in general.
Y	Calculated vapor mole fraction.
YE	Experimental vapor mole fraction.
Z	Feed composition in flash calculation.
ZC	Calculated compressibility factors.
ZE	Experimental compressibility factors.

APPENDIX C

DERIVATION OF THE MIXTURE HELMHOLTZ FREE ENERGY AND RELATED THERMODYNAMIC FUNCTIONS

Derivation of the Mixture Helmholtz Free Energy

The Helmholtz free energy or work content of a mixture per mole may be written as

$$A_T = A_T^\circ + (A^* - A^\circ)_T + (A - A^*)_T \qquad \text{(C-1)}$$

where the superscript ° denotes an ideal gas state at unit pressure and system temperature, and the superscript asterisk * denotes the hypothetical ideal gas state at the system pressure and temperature.

By definition

$$A_T^\circ = \sum_i x_i \, (\underline{U}_i^\circ - T\underline{S}_i^\circ) \qquad \text{(C-2)}$$

and $\underline{U}_i^\circ$ and $\underline{S}_i^\circ$ are the partial molal internal energy and entropy of the i^{th} component in a mixture at the ideal gas state.

In an ideal gas state, the molal entropy of mixing is simply

$$\sum x_i \, (\underline{S}_i^\circ - S_i^\circ) = - R \sum x_i \ell n \, x_i \qquad \text{(C-3)}$$

where R is the universal gas constant.

Hence Equation (C-2) can be written as

$$A_T^\circ = \sum_i x_i \, (U_i^\circ - TS_i^\circ + RT \, \ell n \, x_i) \qquad \text{(C-4)}$$

The second term in Equation (C-1) may be expressed as an integral along an isothermal path in an ideal gas state, i.e.,

$$(A^* - A^\circ)_T = \int_{A^\circ}^{A^*} dA \qquad \text{(C-5)}$$

For a closed system in an equilibrium state, the differential work function is

$$dA = -SdT - PdV \qquad \text{(C-6)}$$

Invoking the conditions of constant temperature and ideal gas state, and changing the integration variable from molal volume to molal density, Equation (C-6) becomes

$$dA = \frac{RTd\rho}{\rho} \qquad \text{(C-7)}$$

Substituting Equation (C-7) into Equation (C-5) yields

$$\begin{aligned}(A^* - A^\circ)_T &= \int_{\rho^\circ}^{\rho^*} \frac{RTd\rho}{\rho} \\ &= RT \ \ell n \left(\frac{\rho^*}{\rho^\circ}\right)\end{aligned} \qquad \text{(C-8)}$$

By definition $\rho = \rho^*$ and $\rho^\circ = \frac{P}{RT}$. At unit pressure, Equation (C-8) becomes

$$(A^* - A^\circ)_T = \sum_i x_i \ RT \ \ell n \ RT\rho \qquad \text{(C-9)}$$

Similarly, the third term in Equation (C-1) may be expressed as an isothermal integral in terms of molal density

$$(A - A^*)_T = \int_{\rho^*}^{\rho} \frac{P d\rho}{\rho^2} \qquad \text{(C-10)}$$

$$= \int_{\rho^*}^{o} \frac{P d\rho}{\rho^2} + \int_{o}^{\rho} \frac{P d\rho}{\rho^2}$$

Substituting the ideal gas law in the first term in Equation (C-10) results in

$$(A - A^*)_T = \int_{o}^{\rho} \left(\frac{P - RT\rho}{\rho^2} \right) d\rho \qquad \text{(C-11)}$$

Combining Equations (C-4), (C-9) and (C-11), Equation (C-1) becomes

$$A = \sum_i x_i \left(RT \ln (RT\rho x_i) + U_i^o - TS_i^o \right) \qquad \text{(C-12)}$$

$$+ \int_{o}^{\rho} \left(\frac{P - RT\rho}{\rho^2} \right) d\rho$$

which is the desired expression for the work content of one mole of mixture. The first term in Equation (C-12) denotes the part of Helmholtz free energy "which may be evaluated from properties of the pure components at low pressure"[10]. The second term in Equation (C-12) defines what is commonly known as the residual work content $\tilde{A}$.

It is "the difference between the actual work content of one mole of the mixture, and the work content of one mole of the mixture in the hypothetical ideal gas state at the same temperature, density and composition."[10]

In terms of residual work content, Equation (C-12) becomes

$$A = \sum_i x_i \left(RT \ell n (RT\rho x_i) + U_i^\circ - TS_i^\circ \right) + \tilde{A} \qquad \text{(C-13)}$$

Pressure

From the definition of the residual work content $\tilde{A}$ (Equation (C-11)), pressure of one mole of mixture may be expressed as

$$P = RT\rho + \rho^2 \left(\frac{\partial \tilde{A}}{\partial \rho} \right)_{T,x} \qquad \text{(C-14)}$$

Enthalpy

From Equation (C-6), entropy of one mole of mixture may be expressed as

$$S = - \left(\frac{\partial A}{\partial T} \right)_{\rho,x} \qquad \text{(C-15)}$$

Using Equation (C-15) and the following thermodynamic relationships

$$C_{V_i}^\circ = \left(\frac{\partial E_i^\circ}{\partial T} \right)_\rho \qquad \text{(C-16)}$$

$$C^{\circ}_{P_i} = T\left(\frac{\partial S^{\circ}_i}{\partial T}\right)_P \qquad \text{(C-17)}$$

and

$$C^{\circ}_{P_i} - C^{\circ}_{V_i} = R \qquad \text{(C-18)}$$

Equation (C-15) becomes

$$S = \sum x_i \left[S^{\circ}_i - R \ln RT\rho x_i\right] - \left(\frac{\partial \tilde{A}}{\partial T}\right)_{\rho,x} \qquad \text{(C-19)}$$

Internal Energy

Internal energy of one mole is related to the work content by the following fundamental relationship

$$U = A + TS \qquad \text{(C-20)}$$

Enthalpy

Enthalpy of one mole of mixture is given by the following fundamental relationship

$$H = U + PV \qquad \text{(C-21)}$$

Gibbs Free Energy

Gibbs free energy of one mole of mixture is given by the following fundamental relationship

$$G = H - TS \qquad \text{(C-22)}$$

Chemical Potential of the i^{th} Component

Chemical potential of the i^{th} component in a mixture is related to the Helmholtz free energy by the following relationship

$$\mu_i = \left(\frac{\partial NA}{\partial n_i}\right)_{T,V,n_j} \qquad \text{(C-23)}$$

where n_i is the number of moles of the i^{th} component and N is the total number of moles in a mixture $\left(\sum_i n_i\right)$.

Fugacity of the i^{th} Component

Fugacity of the i^{th} component in a mixture is given by the following relationship

$$RT \ln f_i = \left(\frac{\partial NA}{\partial n_i}\right)_{T,V,n_j} - U_i^\circ + TS_i^\circ - RT \qquad \text{(C-24)}$$