MODIFIED BWR EQUATION FOR PROPANE FROM MULTIPROPERTY ANALYSIS OF PVT, ENTHALPY, AND VAPOR PRESSURE DATA

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Multiproperty analysis has been utilized to develop a modified BWR equation of state for propane which is accurate to lower reduced temperatures, $T_r = 0.32$, and higher reduced densities, $\rho_r = 3.2$, than any contemporary equation of state. Modification of the temperature dependence of the original BWR equation was selected by utilizing accurate enthalpy data in the temperature range from 250°F down to —250°F. To determine optimal values of the eleven parameters in the modified BWR equation, PVT, enthalpy, and vapor pressure data were used simultaneously in multiproperty analysis.

The objective of research reported in this paper was to apply the principles of multiproperty analysis to the development of an improved equation of state for propane. The goal sought for the equation was that it accurately represent propane behavior from —250°F to 250°F and from atmospheric pressure to 2000 psia. Accurate representation of propane behavior at the lower temperatures was realized to be a formidable task, since propane at —250°F is at a very low reduced temperature, $T_r = 0.32$. Virtually all existing equations of state are badly in error below $T_r < 0.5$. Besides the need for representing low temperature behavior, the problem of describing high density behavior was anticipated. At —250°F, propane in the liquid phase, at any pressure from 14.7 psia to 2000 psia, exists at a reduced density of approximately $\rho_r = 3.2$, while most existing equations of state are badly in error above $\rho_r = 2.5$. The BWR equation, for example, is generally inaccurate for $\rho_r > 2.0$.

Despite the fact that the cryogenic liquid region for propane extends to such low reduced temperatures and high reduced densities, it was anticipated that enthalpy behavior could be described quite accurately, using an equation of state, if some sacrifice were made in the accuracy of other properties. This belief was predicated on the basis of results obtained earlier from methane (1, 2). In this earlier work, a modified BWR equation for methane was developed which yielded highly accurate predictions of enthalpy behavior for $T_r > 0.58$, $\rho_r < 2.5$, even though predicted densities were low by 2 to 3 percent for $\rho_r > 2.0$. Because of these results for methane, initial steps in the work reported in this paper were carried out in a sequence which paralleled the early stages of the methane study.

As the first step in this sequence, the original BWR equation is used to calculate propane densities, enthalpy departures and vapor and liquid fugacities along the vapor pressure curve for comparison with available experimental data. These preliminary calculations serve to indicate the regions in which the original BWR equation becomes inaccurate. The second step in the sequence is the search for modifications to the BWR equation which will improve its predictive ability. The final step involves the simultaneous use of PVT, enthalpy and vapor pressure data in multiproperty regression to determine the optimal values of parameters in the new equation.

The general framework for multiproperty analysis has been presented previously (3). In the present application density, enthalpy departure and vapor and liquid fugacities along the vapor pressure curve are the properties of interest. Simultaneous treatment of these three types of thermodynamic data requires minimization of the following function to obtain optimal estimates of the parameters in an assumed equation of state,

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$$Q = \sum_{i} \left[1 - \frac{\rho C_i}{\rho E_i}\right]^2 \qquad \text{Eq. 1}$$

$$+ W_H \sum_{j} \left[1 - \frac{(HC - H^\circ)_j}{(HE - H^\circ)_j}\right]^2$$

$$+ W_f \sum_{k} \left[1 - \frac{f^L_k}{f^V_k}\right]^2$$

In Equation 1, ρE_i and ρC_i are the experimental and calculated densities, respectively, at the i^{th} PVT data point, $(HE\text{-}H^\circ)_j$ and $(HC\text{-}H^\circ)_j$ are the experimental and calculated enthalpy departures at the j_{th} enthalpy data point and f^V_k and f^L_k are the calculated vapor and liquid fugacities at the k^{th} vapor pressure data point. W_H and W_f are weighting factors for enthalpy and fugacity relative to density, which has an implied weighting factor of unity. The reasons for selecting the implicit function density as the dependent variable rather than compressibility factor or pressure in multiproperty analysis are discussed elsewhere (4, 5). For an equation of state such as the BWR equation, solution for the minimum in the regression function Q in Equation 1 requires a nonlinear regression procedure such as the Gauss-Newton linearization which has been discussed previously (3). The computer program required for multiproperty analysis is rather complex and therefore cannot be discussed here. Nevertheless, it should be mentioned that this program can be used for treating any individual property or any pair of properties in Equation 1 in addition to simultaneous treatment of all three properties.

PRELIMINARY CALCULATIONS

To determine regions of temperature and pressure where the original BWR equation gives accurate predictions of propane behavior and where its accuracy should be improved, extensive calculations were made of density, enthalpy departure, and vapor and liquid fugacities along the vapor pressure curve. Density predictions were compared with the data reported by Sage and Lacey (6), Huang, Swift and Kurata (7) and Rossini (8). Enthalpy predictions were compared with the data reported by Yesavage (9). Calculated liquid fugacities were compared with calculated vapor fugacities along the vapor pressure curve reported by Rossini (8). These were also the sources of the data utilized in the regression calculations reported in this paper.

The original BWR expression for the pressure is

$$P = RT\rho + (B_oRT - A_o - \frac{C_o}{T^2})\,\rho^2 \qquad \text{Eq. 2}$$

$$+ (bRT - a)\,\rho^3 + a\alpha\rho^6$$

$$+ \frac{c}{T^2}\,\rho^3\,(1 + \gamma\rho^2)\,\exp\,(-\gamma\rho^2)$$

The density at a specified temperature-pressure condition is determined by the trial-and-error solution of this equation. The original BWR equation for enthalpy departure is

$$H - H^\circ = (B_oRT - 2A_o - \frac{4C_o}{T^2})\,\rho \qquad \text{Eq. 3}$$

$$+ \tfrac{1}{2}\,(2bRT - 3a)\,\rho^2 + \frac{6}{5}\,a\alpha\rho^5$$

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

$$- \frac{1}{2}\exp\,(-\gamma\rho^2) + \gamma\rho^2\exp\,(-\gamma\rho^2)]$$

To calculate the enthalpy departure at a specified temperature-pressure condition, Equation 2 first must be solved for the density for use in Equation 3. The original BWR equation for fugacity is given by the relation

$$RT\,\ln f = RT\,\ln(\rho RT) + 2\,(B_oRT - A_o - \frac{C_o}{T^2})\,\rho$$

$$+ \frac{3}{2}\,(bRT - a)\,\rho^2 + \frac{6}{5}\,a\alpha\rho^5 \qquad \text{Eq. 4}$$

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

For a given temperature-pressure condition along the vapor pressure curve, Equation 2 possesses multiple roots in density. The smallest root is the calculated saturated vapor density and the largest root is the calculated saturated liquid density. Use of these calculated saturated densities in Equation 4 yields calculated vapor and liquid fugacities for the specified point on the vapor pressure curve.

The eight original BWR parameters for propane reported by Benedict, Webb, and Rubin (10) are: B_o = 1.55884, A_o = 25915.4, C_o = 620993 x 10^4, b = 5.77355, a = 57248.0, α = 2.49577, c = 252478 x 10^5, γ = 5.64524. The units for these parameters correspond to pressure in psia, temperature in °R and density in lb-mole/cu ft. These parameter values were determined using 44.062 for the molecular weight of propane and R = 10.7335 for the gas constant.

Topographical plots of deviations given in Figures 2 and 3 summarize the results of the propane density and enthalpy departure predictions with the original BWR equation. The legend for the deviations shown in these plots is given in Figure 1.

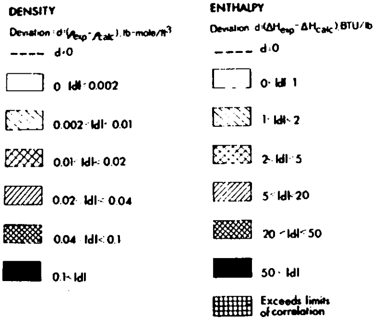

Figure 1. Legend for deviations presented in figures.

Table 1. *Prediction of saturated vapor and liquid fugacities for propane using the original BWR equation.*

T, °F	P, Psia	f^L, Psia	f^V, 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	1.3832	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%
% Dev. = $(1 - f^L/f^V)$ x 100%

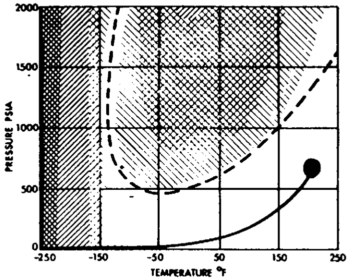

Figure 2. Comparison of densities calculated by the original BWR equation with experimental values for propane.

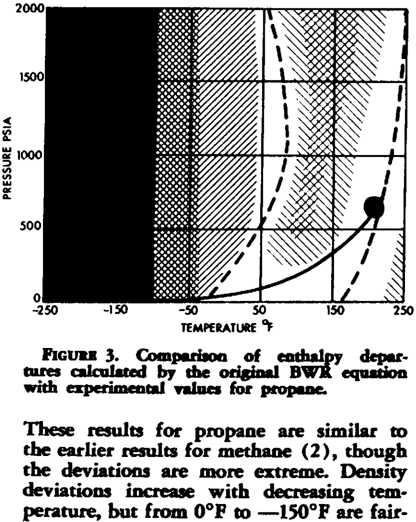

Figure 3. Comparison of enthalpy departures calculated by the original BWR equation with experimental values for propane.

These results for propane are similar to the earlier results for methane (2), though the deviations are more extreme. Density deviations increase with decreasing temperature, but from 0°F to —150°F are fairly uniform in the two to five per cent range (0.02 to 0.05 lb-mole/cu. ft.). Below —150°F, density deviations at 14.7 psia also are of this magnitude. Deviations of enthalpy departures increase much more rapidly than density as temperature is decreased and exceed 500% at —250°F. As has been explained in some detail previously (2), the fact that low temperature enthalpy departures are predicted much less accurately than densities implies that the temperature dependence of the BWR equation is in much greater need of modification than its density dependence.

Calculated vapor and liquid fugacities along the propane vapor pressure curve are given in Table 1, along with values of the relative deviation $(1 - f^L/f^V)$. Because of the thermodynamic requirement that $f^L = f^V$ for the coexisting equilibrium phases the relative deviation $(1 - f^L/f^V)$ is a measure of the thermodynamic inconsistency of the original BWR equation in describing phase behavior. At low pressures, where f^V should be quite accurately predicted by the original BWR equation, this relative deviation also is a measure of the error in calculated liquid fugacity. Thus, it can be concluded from the results in Table 1 that at the lower pressures, propane liquid fugacities predicted by the original BWR equation are severely in error. Because the vapor pressure is a function of temperature, it is possible to modify only the temperature dependence of the BWR equation to achieve equality of predicted liquid and vapor fugacities along the vapor pressure curve. However, because of the availability of extensive and highly accurate enthalpy data, the appropriate temperature modifications were sought from enthalpy data rather than vapor pressure data.

MODIFICATION OF BWR EQUATION

The calculations of the preceding section, as well as similar results of methane (2), show that it is possible to modify only the temperature dependence of the BWR equation to achieve improved predictions of low temperature fluid behavior. Enthalpy data provide significant information regarding the temperature dependence needed for the equation of state. Hence the extensive and highly accurate enthalpy data for propane recently obtained by Yesavage (9) were used to seek appropriate modifications of the BWR equation for propane. Initial regression calculations were made to determine the effect of treating the BWR parameter C_o as temperature-dependent using isothermal enthalpy data. As pointed out previously (2), if C_o in the expression for the Helmholtz free energy is considered to be temperature-dependent, then instead of C_o in Equation 3 for enthalpy departure one would have a quantity C_o^*,

$$C_o^* = C_o - \frac{T}{4}\frac{dC_o}{dT} \qquad \text{Eq. 5}$$

Regression calculations were performed to determine discrete values of C_0^* from propane enthalpy data for eleven isotherms from —250°F to 250°F with the results summarized in Table 2 and Figure 4. These results offer dramatic proof that modification of the temperature dependence of the BWR equation can greatly improve enthalpy predictions, especially in the cryogenic region. It can be noted in Table 2 that average absolute deviations of predicted enthalpy departures from 0°F to —250°F are less than 0.15%. These deviations can be compared with those obtained from the original BWR equation, which increase rapidly with decreasing temperature and exceed 100% below —200°F.

Thus, it is established that the BWR parameter C_0 can profitably be treated as temperature-dependent. The remaining task is to seek an analytic temperature-dependent form for C_0 to describe the enthalpy behavior of propane in the compressed liquid region. It should be noted that if the quantity C_0^* defined in Equation 5 can be represented by an expansion in 1/T, then C_0 also can be represented by a reciprocal temperature expansion. The use of this temperature dependence for C_0 is in accord with the perturbation theory of statistical mechanics (11), which indicates that all virial coefficients can be expressed as expansions in 1/T. For methane (2), it was found that C_0^*, and therefore C_0, can be represented as a linear function of 1/T for reduced temperatures from $T_r = 0.97$ to $T_r = 0.58$ (—250°F). However, it is evident from the plot of C_0^* versus 1/T in Figure 4 that C_0^* for propane cannot be represented adequately as a linear function of 1/T at the reduced temperatures below $T_r = 0.8$. This is not surprising because at —250°F, the corresponding reduced temperature for propane is 0.32, which is much lower than the corresponding reduced temperature for methane (0.61).

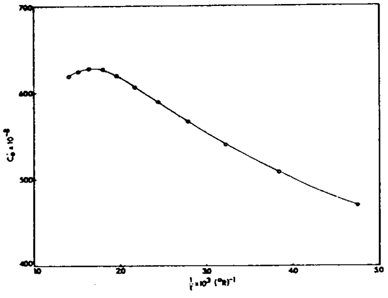

FIGURE 4. Temperature dependence of C_0^* for propane determined from regression on isothermal enthalpy data.

To arrive at an adequate form for C_0, the entire BWR term ($B_0 - A_0/RT - C_0/RT^3$), which will be referred to as the BWR second virial coefficient, was replaced by trial expansions in 1/T. The propane enthalpy data for the eleven isotherms referred to in Table 2 were then used simultaneously in regression calculations to determine the coefficients in these trial expansions. It was determined that the expansion ($B_0 - A_0/RT - C_0/RT^3 + D_0/RT^4 - E_0/RT^5$) for the BWR second virial coefficient is the most concise expansion which is capable of representing low temperature propane enthalpy behavior within twice the uncertainty of the data. Including a term in $1/T^2$ or terms in reciprocal temperature to the sixth or higher powers did not significantly improve enthalpy predictions.

One additional modification of the BWR

TABLE 2. *Variation of C_0^* with temperature.*

Temp., °F	Estimated $C_0^* \times 10^{-8}$	Std. Dev. of $C_0^* \times 10^{-8}$	Avg. Abs. Dev. of (H-H°), %
—250	469.357	0.006	0.12
—200	506.788	0.007	0.11
—150	538.785	0.010	0.11
—100	565.889	0.015	0.14
—50	588.682	0.017	0.10
0	606.789	0.016	0.09
50	619.237	0.073	0.33
100	626.826	0.042	0.17
150	626.549	0.136	0.39
200	624.453	0.139	0.34
250	617.796	0.873	1.56

equation for propane was considered appropriate on the basis of the results given in Table 2 and earlier experience in modifying the BWR equation for the description of methane enthalpy behavior (1, 2). In the methane study it was noted that modifications of C_0 alone were insufficient to provide an adequate representation of methane enthalpy behavior at temperatures near the critical temperature. A corresponding result can be noted for propane. The results in Table 2 represent the most accurate calculations of propane enthalpy departures which can be attained merely by treating C_0 as temperature-dependent. It may be noted in Table 2 that the enthalpy isotherms having larger average deviations bracket the propane critical temperature, 206.6°F, a result which is analogous to that obtained for methane. As has been discussed (2), in relation to methane behavior, these results indicate the need for modification of terms in the BWR equation of higher order in density than the term involving C_0. For methane, the BWR parameter a was replaced by the linear function (a + d/T) to achieve improved enthalpy predictions in the critical region. Because of the successful use of this relation for methane, this change was also incorporated in the modified BWR equation for propane.

As has been pointed out previously (3), it is now well understood that an equation of state cannot be accurately defined using data for only one thermodynamic property. Obviously, the above use of enthalpy data serves to suggest changes in the temperature dependence of the BWR equation

Table 3. *Prediction of saturated vapor and liquid fugacities for propane using the modified BWR equation.*

T, °F	P, Psia	f^L, Psia	f^V, 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%

% Dev. = $(1 - f^L/f^V) \times 100\%$

which can improve its predictive ability. But to insure that thermodynamic consistency between different predicted properties will result when the equation of state is used, one really must apply multiproperty analysis in some form in developing the equation. At the very least, multiproperty regression should be used to determine the parameters in an assumed equation.

MULTIPROPERTY ANALYSIS

PVT, enthalpy and vapor pressure data were used simultaneously to determine parameters for propane in the modified BWR equation resulting from the study of propane enthalpy behavior. The expressions for pressure, enthalpy departure and fugacity for the modified BWR equation are

$$H-H^{\circ} = \left(B_oRT - 2A_o - \frac{4C_o}{T^2} + \frac{5D_o}{T^3} - \frac{6E_o}{T^4}\right)\rho + \frac{1}{2}\left(2bRT - 3a - \frac{4d}{T}\right)\rho^2 + \frac{1}{5}\alpha\left(6a + \frac{7d}{T}\right)\rho^5 + \frac{c}{\gamma T^2}\left[3 - \left(3 - \frac{1}{2}\gamma\rho^2 - \gamma^2\rho^4\right)\exp\left(-\gamma\rho^2\right)\right] \qquad \text{Eq. 6'}$$

$$P = \rho RT + \left(B_oRT - A_o - \frac{C_o}{T^2} + \frac{D_o}{T^3} - \frac{E_o}{T^4}\right)\rho^2 + \left(bRT - a - \frac{d}{T}\right)\rho^3 + \alpha\left(a + \frac{d}{T}\right)\rho^6 + \frac{c\rho^3}{T^2}\left(1 + \gamma\rho^2\right)\exp\left(-\gamma\rho^2\right) \qquad \text{Eq. 7}$$

$$RT \ln f = RT \ln(\rho RT) + 2\left(B_oRT - A_o - \frac{C_o}{T^2} + \frac{D_o}{T^3} - \frac{E_o}{T^4}\right)\rho + \frac{3}{2}\left(bRT - a - \frac{d}{T}\right)\rho^2 + \frac{6\alpha}{5}\left(a + \frac{d}{T}\right)\rho^5 + \frac{c}{\gamma T^2}\left[1 - \left(1 - \frac{1}{2}\gamma\rho^2 - \gamma^2\rho^4\right)\exp\left(-\gamma\rho^2\right)\right] \qquad \text{Eq. 8}$$

Initial and final calculations in this study spanned more than a year because the vapor pressure portion of the multiproperty program had not been written at the time of initial calculations. Initial calculations also attempted to preserve as many as possible of the original BWR parameters at the values originally reported (10), while emphasizing the accurate prediction of enthalpy behavior. The parameters b, α, c and γ were retained intact in these initial calculations (3), which were performed in 1968. In these calculations (12), 84 enthalpy and 36 density data points were utilized simultaneously to determine the values: $B_o = 1.17001$; $A_o = 21293.3$; $C_o = 827999 \times 10^4$; $D_o = 888011 \times 10^6$; $E_o = 589916 \times 10^8$; $a = 48303.6$; $d = 564493 \times 10$. The resultant average deviation for enthalpy departures was 0.55%. The corresponding average deviation for enthalpy, 0.85 Btu/lb, is roughly twice the probable experimental uncertainty. For density predictions, an average deviation of 0.43% was obtained for densities below twice the critical density, but for larger densities the average deviation was 2.73%. Accurate calculations of fugacity and entropy at high densities obviously could not be expected from the resultant equation of state.

To obtain an improved description of density and fugacity behavior, PVT, enthalpy and vapor pressure data were utilized simultaneously in 1969 to determine all eleven parameters in the modified BWR equation. The resultant parameter values are: $B_o = 0.850969$; $A_o = 17859.7$; $C_o = 772153 \times 10^4$; $D_o = 421549 \times 10^6$; $E_o = 250712 \times 10^8$; $b = 5.26635$; $a = 34833.9$; $d = 148572 \times 10^2$; $\alpha = 1.78868$; $c = 244356 \times 10^5$; $\gamma = 3.91196$. Using these parameter values, the modified BWR equation predicts densities with an average deviation of 1.16% and enthalpy departures with an average deviation of 0.40%. To summarize the results graphically, topographical plots of these deviations are given in Figures 5 and 6. These figures can be compared

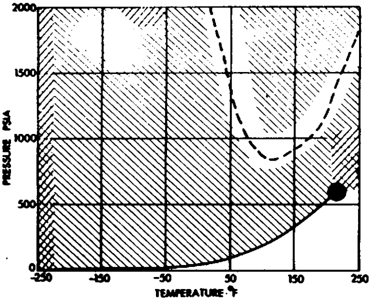

FIGURE 5. Comparison of densities calculated by the modified BWR equation with experimental values for propane.

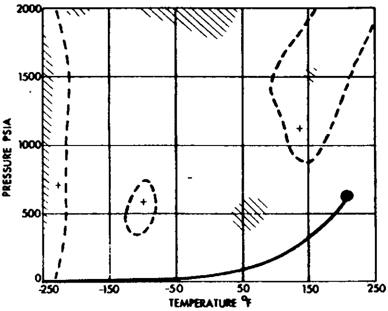

Figure 6. Comparison of enthalpy departures calculated by the modified BWR equation with experimental values for propane.

with the corresponding plots, Figures 2 and 3, to determine regions of improved predictions. The average deviation of liquid fugacities from vapor fugacities using the modified BWR equation is 0.48% for 19 points along the vapor pressure curve from 0.6 psia to the critical pressure (617.4 psia). Deviations of predicted vapor and liquid fugacities are given in Table 3. The results for each property must be considered to be excellent because of the fact that the low temperature density data have a reported probable uncertainty of 0.5%. Obviously, the eleven modified BWR equation parameters for propane could be defined more precisely if more accurate (and extensive) PVT data for propane in the compressed liquid region were available. Nevertheless, the fact that densities, enthalpies and fugacities are described with thermodynamic consistency proves that the need for highly accurate PVT data is diminished by the use of multiproperty analysis. A dividend of thermodynamic consistency is the assurance that the entropy of propane will be accurately calculated using the modified BWR equation of state. The entropy departure expressed as the entropy, S, relative to the entropy of an ideal gas at unit pressure (in the units employed), S°, is given by the thermodynamic relation

$$S - S^{O} = (H - H^{O})/T - R \ln f \quad \text{Eq. 9}$$

Since the saturated fugacities along the vapor pressure curve agree within 0.48% and enthalpy departures agree with experimental values within 0.40%, it follows that the uncertainty in predicted entropy departures should be near 0.5%. The average uncertainty in predicted entropy departures certainly would not be expected to exceed the average uncertainty in density, 1.16%.

CONCLUSIONS

The major conclusion is the confirmation that multiproperty analysis is a very powerful tool in equation of state development when it is required that all thermodynamic properties be predicted with consistency. Multiproperty analysis becomes especially valuable when data for one property are of lower accuracy or less complete than data for another property. In the study reported, extensive and highly accurate propane enthalpy data were available, but only incomplete PVT data existed. To develop an equation of state for propane of high accuracy in the low temperature region (—250°F to 0°F) would be impossible using only available PVT data. However, simultaneous use of PVT, enthalpy and vapor pressure data have led here to an accurate and thermodynamically consistent equation of state for propane. Through rigorous thermodynamic relationships, derived properties such as entropy therefore also will be accurately predicted.

It should be noted that enthalpy data have been used to advantage in this study to determine suitable modifications to the temperature dependence of the BWR equation of state. The resultant eleven parameter modified BWR equation is capable of accurately predicting fluid behavior at reduced temperatures as low as $T_r = 0.32$ and reduced densities as large as $\rho_r = 3.2$. It is doubtful that many fluid systems will ever be encountered industrially at such low temperatures or large reduced densities. Therefore, it can be anticipated that the modified BWR equation which has been developed in this study will be adequate in form to describe thermodynamic behavior for virtually any nonpolar or slightly polar fluid at conditions of industrial interest.

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NOMENCLATURE

A_o, B_o, C_o, b, a, c, α, γ	Parameters in BWR equation
D_o, E_o, d	Parameters in modified BWR equation
f^L	Fugacity in liquid phase
f^V	Fugacity in vapor phase
H	Enthalpy
H°	Enthalpy of ideal gas
HC	Calculated enthalpy
HE	Experimental enthalpy
P	Pressure
Q	Regression function
R	Universal gas constant
ρ C	Calculated molar density
ρ E	Experimental molar density
S	Entropy
S°	Entropy of ideal gas at unit pressure
T	Absolute temperature
W	Statistical weighting function

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