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Accurate $P\rho T$ Data for Ethane from (298 to 450) K up to 200 MPa

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This paper reports $P\rho T$ data measured with a high-pressure, single-sinker, magnetic-suspension densimeter (MSD) from (298 to 450) K up to 200 MPa. The MSD technique yields accurate data, with less than 0.05 % relative uncertainty, over the pressure range of (10 to 200) MPa. The Bücker and Wagner equation of state as implemented in RefProp 8.0 compares well to the experimental data. RefProp 8.0 has a relative uncertainty of (0.02 to 0.03) % up to 30 MPa. The equation predicts data with almost the same uncertainty as the experimental data up to 200 MPa. These $P\rho T$ data also allow reliable determination of both second and third virial coefficients.

Introduction

Ethane is the second-most abundant constituent of natural gas and an important raw material for many industrial processes and scientific applications. Accurate thermophysical property data for ethane are necessary for the design and evaluation of these processes. Bücker and Wagner[1] have made an extensive analysis of the thermodynamic data for ethane reported before 2006. On the basis of the uncertainty analysis of the data sources, they define three different groups of data: group 1 has the most consistent sets of data and lower experimental uncertainties, and the other two groups do not follow their predefined quality standards. They have developed an equation of state, using the group 1 data, on the basis of an explicit Helmholtz energy function with 44 coefficients. They claim a relative uncertainty in the density predictions of (0.02 to 0.03) % from the melting line up to temperatures of 520 K and pressures of 30 MPa.

Bücker and Wagner[1] provide a detailed description of the data used for fitting their equation of state. Two sets of data reside in group 1 for pressures greater than 30 MPa and less than 200 MPa: Pal et al.[2] at (0.52 to 73) MPa and Golovskii et al. at[3] (1.2 to 60) MPa. The estimated relative uncertainties by Bücker and Wagner[1] for the Pal et al.[2] and Golovskii et al[3] data are 0.40 % and 0.25 %, respectively. Byun et al[4] have published additional high-pressure data from (15 to 276) MPa; however, these data have high relative deviations (up to 7 %) compared to the Bücker and Wagner[1] equation of state. Therefore, these data do not appear in the current analysis. Any additional reliable data within the range of temperatures and pressures of concern to this publication are not readily available in the literature.

The Thermodynamics Laboratory at Texas A&M University has a state-of-the-art, high-pressure, high-temperature, single-sinker magnetic-suspension densimeter (MSD). The general features of this apparatus appear in refs 5 and 6, and the specific details of the present instrument appear in refs 7 to 10. Measurements of well-characterized pure fluids, including ethane, have validated the performance of our apparatus. These data and the equation developed by Bücker and Wagner[1] compare well. In the < 30 MPa region, it is reasonable to assume the equation of state is as good as the best available data. Above that pressure, the current data take precedence, but the equation of state is remarkably consistent with them.

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Experimental Section

This paper presents isothermal density data for ethane at (298, 350, 400, and 450) K up to 200 MPa. The ethane came from Matheson Tri Gas having a grade of ultra high purity (UHP) with a mole fraction of 99.95 % ethane. The titanium sinker mass and volume are 30.39159 g and 6.741043 cm^3, respectively, determined by using the apparatus and procedure described by McLinden and Splett.[11] Patil et al.[7,8] describe the single-sinker MSD, and additional modifications to expand the range of measured temperature appear in refs 9 and 10. The platinum resistance thermometer (PRT; Minco Products model S1059PA5 × 6) has calibration at fixed temperature points defined by ITS-90 and by a calibrated PRT traceable to the National Institute of Standards and Technology (NIST). The temperature stability is ± 5 mK for the measured data, and the uncertainty of the PRT is 2 mK with respect to the triple point of water.[9] Two Digiquartz transducers ((40 and 200) MPa) from Paroscientific, Inc., measure pressure. The uncertainty for these transducers is 0.01 % of the full scale.

An important part of the uncertainty for the MSD is the force transmission error (FTE). The analysis and quantification of the FTE for our MSD will appear in a future issue of *The International Journal of Thermophysics*. After compensation for the FTE in the raw data and on the basis of the assumption of

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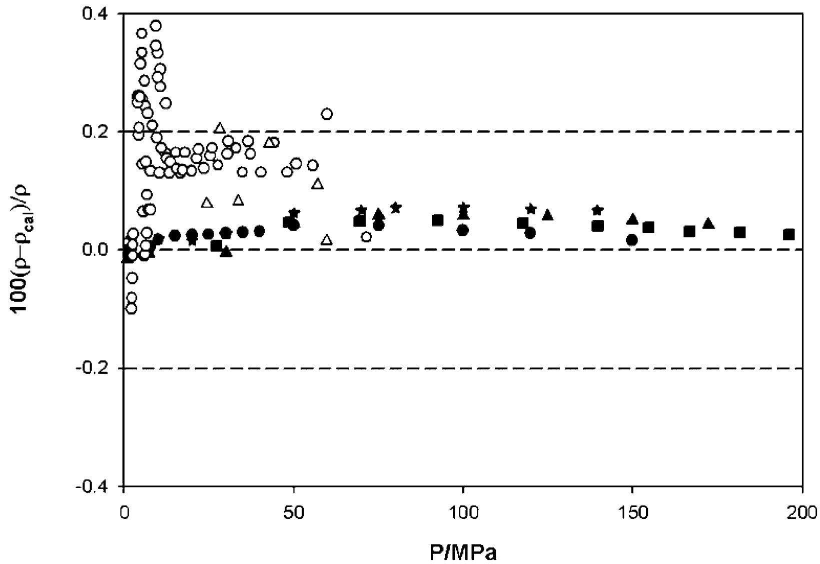

Figure 1. Percentage deviation of the experimental $P\rho T$ data from values calculated using the Bücker and Wagner[1] equation of state. This work: ●, 298.150 K; ▲, 350.000 K; ■, 400.000 K; ★, 450.000 K. Ref 2, ○, (290 to 345) K; ref 3, △, (255 to 270) K.

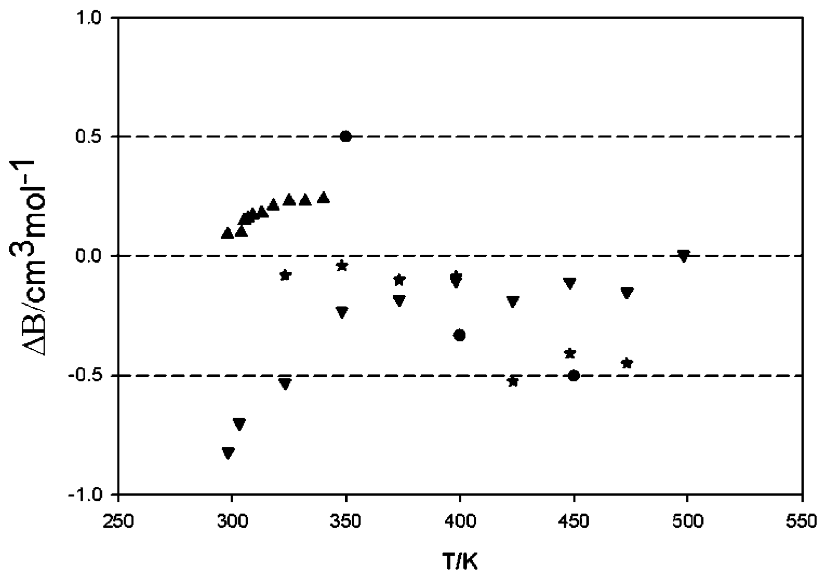

Figure 2. Absolute deviations for second virial coefficients from values calculated using the Bücker and Wagner[1] equation of state $\Delta B = (B_{\text{exp}} - B_{\text{calc}})$. ●, this work; ▲, ref 14; ▼, ref 15; ★, ref 16.

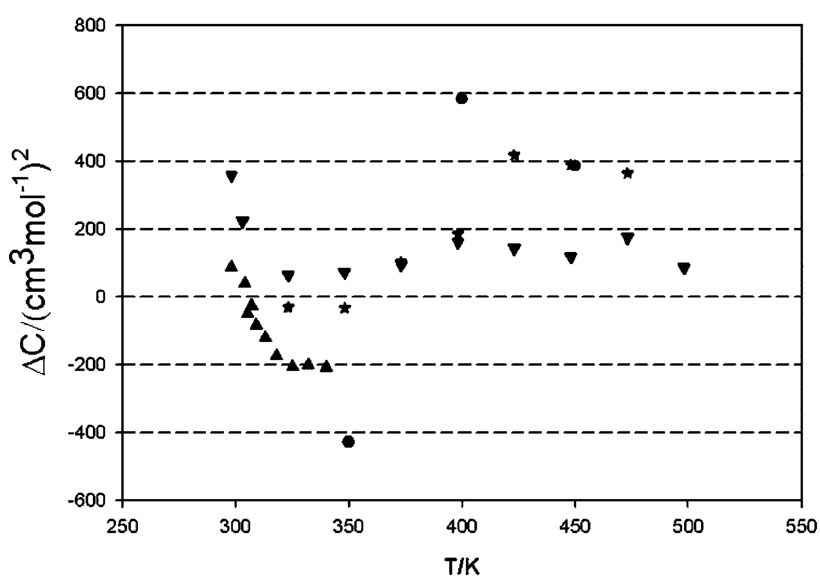

Figure 3. Absolute deviations for third virial coefficients from values calculated using the Bücker and Wagner[1] equation of state $\Delta C = (C_{\text{exp}} - C_{\text{calc}})$. ●, this work; ▲, ref 14; ▼, ref 15; ★, ref 16.

Table 1. Measured Density Values for Ethane

P	ρ	ρ (RefProp 8.0)	
MPa	$kg \cdot m^{-3}$	$kg \cdot m^{-3}$	$100(\rho - \rho_{RefProp})/\rho$
		$T = 298.150$ K	
2.000	29.226	29.228	−0.004
5.987	352.999	353.033	−0.010
7.909	371.593	371.571	0.006
10.071	385.867	385.799	0.018
14.959	407.911	407.811	0.024
20.004	423.934	423.827	0.025
24.927	436.235	436.121	0.026
29.893	446.599	446.474	0.028
35.020	455.820	455.683	0.030
39.905	463.582	463.434	0.032
49.977	477.362	477.162	0.042
75.091	503.592	503.383	0.041
99.827	523.125	522.954	0.033
119.760	536.225	536.070	0.029
149.807	552.995	552.905	0.016
		$T = 350.000$ K	
1.999	22.819	22.814	0.024
29.974	384.889	384.905	−0.004
49.928	430.315	430.124	0.044
74.959	464.696	464.424	0.058
100.019	489.111	488.825	0.058
124.863	508.192	507.902	0.057
149.906	524.195	523.931	0.050
172.157	536.528	536.301	0.042
		$T = 400.000$ K	
0.805	7.452	7.453	−0.016
7.325	84.481	84.487	−0.006
27.286	311.921	311.899	0.007
48.575	383.533	383.354	0.047
69.346	421.214	421.012	0.048
92.289	450.020	449.796	0.050
117.459	473.901	473.683	0.046
139.686	491.026	490.822	0.041
154.657	501.119	500.927	0.038
166.558	508.474	508.315	0.031
181.565	517.111	516.954	0.030
196.062	524.823	524.691	0.025
		$T = 450.000$ K	
1.998	16.685	16.685	0.002
5.021	44.467	44.464	0.007
10.001	96.599	96.581	0.019
20.005	202.282	202.249	0.016
30.018	272.417	272.340	0.028
49.974	346.238	346.020	0.063
69.967	388.105	387.843	0.068
79.928	403.693	403.405	0.072
99.962	429.113	428.804	0.072
119.860	449.290	448.977	0.070
139.478	465.963	465.650	0.067

uncorrelated errors for the different sources of error such as temperature and pressure, the expanded combined uncertainty for the current data is $3 \cdot 10^{-4}\ \rho$ for pressures greater than 7 MPa and up to $5 \cdot 10^{-4}\ \rho$ for pressures between (5 and 7) MPa. The two reported uncertainties exist because the MSD uses two different pressure transducers ((40 and 200) MPa), and they do not produce a uniform uncertainty across the entire range of pressures.[8−10] Uncertainties below 5 MPa are about $1 \cdot 10^{-3}\ \rho$ or higher on the basis of the fluid density. Because the densimeter has a high-pressure design, it is not suitable for measurements at pressures below 5 MPa.

Results and Analysis

The four sets of isothermal data appear in Table 1, along with the predicted densities obtained from the Bücker and Wagner[1] equation of state as implemented in RefProp 8.0.[12] The last column in the table contains the deviations with respect to the experimental data. Figure 1 is a comparison among the current experimental data, those of Pal et al.,[2] and those of Golovskii et al.[3] using RefProp 8.0 predictions as the baseline. It is clear that the calculations from the Bücker and Wagner equation of state are in excellent agreement with the current experimental data and that the predictions from the equation are better than expected for pressures greater than 30 MPa.

Second and third virial coefficients determined from the $P\rho T$ data indicate that extrapolation of the data into the low pressure range is reliable. Cristancho et al.[13] describe the technique used to determine the second and third virial coefficients. No virial coefficients appear for the 298.150 K isotherm because only one vapor datum is available for the extrapolation. Figures 2 and 3 present a comparison of experimental literature data[14−16] along with the current measurements using the Bücker and Wagner equation as the baseline. Most of these data lie in a band with an absolute deviation of 0.5 $cm^3 \cdot mol^{-1}$ for the second virial coefficient and of 500 $(cm^3 \cdot mol^{-1})^2$ for the third virial coefficient. The estimated uncertainty for the second and the third virial coefficients are respectively 0.57 $cm^3 \cdot mol^{-1}$ and 270 $(cm^3 \cdot mol^{-1})^2$. These uncertainties result from statistical analysis of the extrapolation procedure based upon the experimental data. Therefore, it appears that the apparatus can determine second and third virial coefficients. The second and third virial coefficient values appear in Table 2.

Table 2. Second and Third Virial Coefficients for Ethane

T	B	C
K	$cm^3 \cdot mol^{-1}$	$(cm^3 \cdot mol^{-1})^2$
350.000	−130.71	8084
400.000	−96.43	7327
450.000	−71.29	5912

Conclusions

This paper reports accurate experimental $P\rho T$ data for ethane using a high-pressure, single-sinker MSD within an experimental uncertainty of $3 \cdot 10^{-4}\ \rho$ in density for pressures greater than 7 MPa and up to $5 \cdot 10^{-4}\ \rho$ for pressures between (5 and 7) MPa. The data validate the performance of the equation of state developed by Bücker and Wagner[1] up to 200 MPa with better predictive capabilities than expected. The second and third virial coefficients determined from the data appear to be reliable when compared to the Bücker and Wagner[1] equation of state.

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