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Accurate $P\rho T$ Data for Methane from (300 to 450) K up to 180 MPa

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This paper reports $P\rho T$ data measured with a high-pressure, single-sinker, magnetic-suspension densimeter (MSD) from (300 to 450) K up to 180 MPa. Our MSD technique yields accurate data, with less than 0.05 % relative uncertainty, over the pressure range of (10 to 200) MPa. The experimental data compare well to the Setzmann and Wagner equation of state as implemented in RefProp 8.0. These methane density data are consistent with the low range of pressure predicted by RefProp 8.0 that has a relative uncertainty of 0.03 % up to 12 MPa and 0.07 % up to 50 MPa. The density predictions of this model agree well with previous data at higher pressures. The equation predicts data with almost the same uncertainty as the experimental data up to 180 MPa. These $P\rho T$ data also allow reliable determination of both second and third virial coefficients.

Introduction

Methane is the principal constituent of natural gas and an important raw material for many industrial processes. Accurate thermophysical property data for methane are necessary for design and evaluation of these processes. Setzmann and Wagner[1] made an extensive analysis of the thermodynamic data for methane reported before of 1991. 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 40 coefficients. They claim a relative uncertainty in the density predictions of 0.03 % up to 12 MPa and from 0.03 % to 0.15 % for higher pressures.

Setzmann and Wagner[1] provide a detailed description of the data used for fitting their equation of state. Four sets of data reside in group 1 for pressures greater than 35 MPa: Trappeniers et al.,[2] (2 to 260) MPa; Morris,[3] (130 to 690) MPa; Mollerup,[4] (0.2 to 72) MPa; and Kortbeek and Schouten,[5] (150 to 1000) MPa. Mollerup[4] reports an uncertainty in density of $10^{-3}\ \rho$, and Setzman and Wagner estimate the uncertainties for Kortbeek and Schouten[5] at $10^{-3}\ \rho$ with Trappeniers et al.[2] and Morris[3] at $5\cdot10^{-4}\ \rho$.

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 6 and 7, and the specific details of the present instrument appear in refs 8 to 11. Measurements of well-characterized pure fluids, including methane, have validated the performance of our apparatus. These data compare well to the predictions of the equation developed by Setzmann and Wagner.[1]

Experimental Section

This paper presents isothermal density data for methane at (298, 305, 338, 400, and 450) K up to 180 MPa. The methane came from Scott Specialty Gases having a grade of ultra high purity with a mole fraction of 99.99 % methane. 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.[12] Patil et al.[8,9] describe the single-sinker MSD, and additional modifications to expand the range of measured temperature appear in refs 10 and 11. 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 NIST. The temperature stability was ± 5 mK, and the uncertainty of the PRT was 2 mK with respect to the triple point of water.[13] 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 uncorrelated errors for the different sources of error such as temperature and pressure, the uncertainty for our data is $3\cdot10^{-4}\ \rho$ for pressures greater than 7 MPa and up to $5\cdot10^{-4}\ \rho$ for pressures between (5 and 7) MPa. The two reported uncertainties exist because our MSD uses two different pressure transducers (40 and 200 MPa), and they do not produce a uniform uncertainty across the entire range of pressures.[12−14]

Results and Analysis

The five sets of isothermal data appear in Table 1, along with the predicted densities obtained from RefProp 8.0.[13] The last

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Table 1. Measured Density Values for Methane

T / K	P / MPa	ρ / kg·m^{-3}	ρ / kg·m^{-3} (RefProp 8.0)	$100(\rho - \rho_{\mathrm{RefProp}})/\rho$	T / K	P / MPa	ρ / kg·m^{-3}	ρ / kg·m^{-3} (RefProp 8.0)	$100(\rho - \rho_{\mathrm{RefProp}})/\rho$
					$T = 298.15$ K				
298.156	1.012	6.665	6.665	−0.001	298.150	79.980	321.098	321.030	0.021
298.189	5.009	35.316	35.329	−0.039	298.144	99.874	342.269	342.183	0.025
298.149	10.010	76.080	76.078	0.003	298.138	124.934	363.139	363.026	0.031
298.249	14.994	118.506	118.512	−0.005	298.141	150.062	380.039	379.913	0.033
298.145	20.012	157.172	157.183	−0.007	298.138	159.617	385.731	385.591	0.036
298.138	29.958	212.508	212.485	0.011	298.142	170.054	391.531	391.416	0.029
298.144	35.056	232.422	232.377	0.019	298.143	185.333	399.489	399.340	0.037
298.139	49.959	273.189	273.169	0.007	298.145	186.931	400.257	400.131	0.032
298.157	66.961	303.605	303.563	0.014	298.142	188.059	400.837	400.688	0.037
					$T = 305.24$ K				
305.236	5.001	34.173	34.175	−0.007	305.230	49.968	267.232	267.252	−0.008
305.235	6.897	48.435	48.438	−0.006	305.233	60.012	287.019	287.012	0.002
305.231	9.993	72.932	72.931	0.002	305.239	69.988	302.917	302.884	0.011
305.240	15.006	113.440	113.440	0.000	305.227	79.855	316.163	316.098	0.020
305.242	20.696	155.024	155.030	−0.004	305.234	99.904	337.939	337.879	0.018
305.239	29.976	205.443	205.430	0.006	305.233	124.930	359.159	359.090	0.019
305.239	34.563	223.779	223.755	0.011	305.225	149.862	376.248	376.153	0.025
					$T = 338$ K				
338.049	5.000	29.983	29.986	−0.009	338.079	59.971	263.229	263.250	−0.008
338.037	6.905	42.093	42.086	0.017	338.063	70.001	280.639	280.679	−0.014
338.103	9.969	62.054	62.044	0.016	338.103	80.310	295.610	295.648	−0.013
338.079	15.026	95.246	95.243	0.003	338.112	99.908	318.744	318.719	0.008
338.082	20.687	130.132	130.139	−0.005	338.068	124.895	341.685	341.626	0.017
338.080	30.005	177.380	177.371	0.005	338.066	149.542	359.787	359.752	0.010
338.048	34.473	195.446	195.453	−0.004	338.094	164.905	369.665	369.505	0.043
338.083	50.031	241.969	242.001	−0.013	338.121	179.829	378.164	378.121	0.011
					$T = 400$ K				
400.068	5.005	24.610	24.618	−0.031	400.001	50.037	203.469	203.518	−0.024
400.013	6.915	34.195	34.199	−0.011	399.967	59.973	225.951	225.977	−0.011
400.015	10.002	49.746	49.744	0.005	400.042	69.978	244.725	244.750	−0.011
400.029	13.795	68.723	68.704	0.027	400.003	79.920	260.652	260.674	−0.009
399.988	15.027	74.789	74.786	0.005	399.943	89.964	274.637	274.631	0.002
400.025	20.675	101.642	101.644	−0.002	400.089	99.984	286.800	286.796	0.001
399.984	30.014	141.158	141.137	0.015	400.022	124.882	312.062	312.064	−0.001
400.036	34.510	157.640	157.611	0.019	400.023	149.627	332.136	332.150	−0.004
					$T = 450$ K				
450.091	6.886	29.741	29.747	−0.022	450.064	69.966	221.073	221.139	−0.030
450.010	20.697	87.478	87.464	0.016	450.083	80.008	237.571	237.606	−0.015
450.048	30.002	121.791	121.792	−0.001	450.025	89.981	251.923	251.957	−0.013
450.115	34.492	136.647	136.635	0.009	450.011	99.932	264.608	264.645	−0.014
450.057	50.036	179.955	179.987	−0.018	450.018	119.918	286.376	286.412	−0.013
450.027	59.975	202.137	202.170	−0.017	450.034	139.476	304.187	304.188	0.000

column in the table contains the deviations with respect to the experimental data. Figure 1 shows a comparison between our experimental data and the data of Trappeniers et al.,[2] Mollerup,[4] and Kortbeek and Schouten[5] based upon RefProp 8.0 predic-

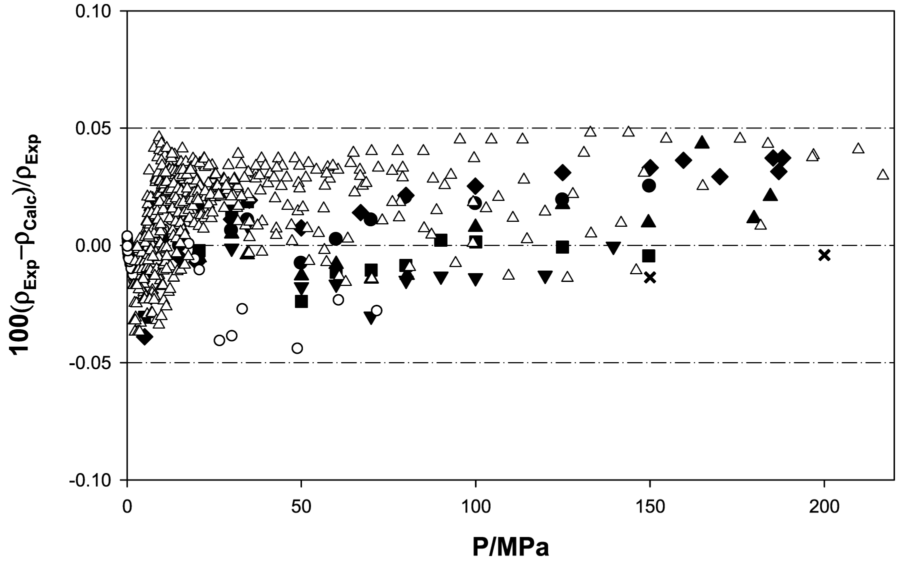

Figure 1. Percentage deviation of the experimental $P\rho T$ data from values calculated using the Setzmann and Wagner[1] equation of state. This work: ♦, 298 K; ●, 305 K; ▲, 338 K; ■, 400 K; ▼, 450 K; ref 2, Δ, (273.25 to 423.25) K; ref 4, ○, 310 K: ref 5, ×, 298.15 K.

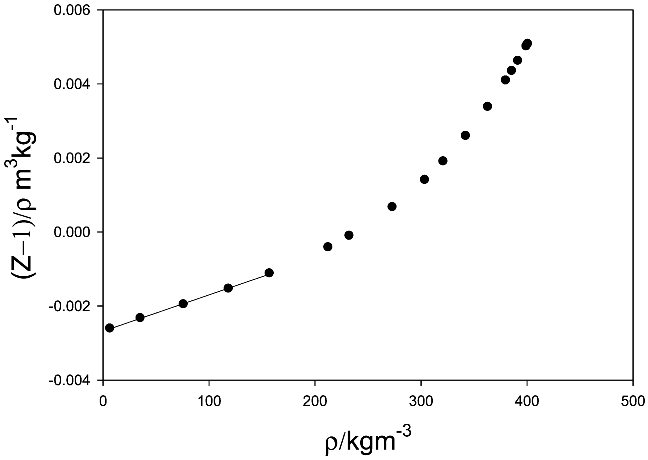

Figure 2. Procedure for the determination of the second virial coefficient using 298 K data. The intercept value, determined by mean square regression, is -0.002681 m^3·kg^{-1}, the slope $9.82 \cdot 10^{-6}$ (m^3·kg^{-1})^2, and the correlation coefficient R^2 0.999.

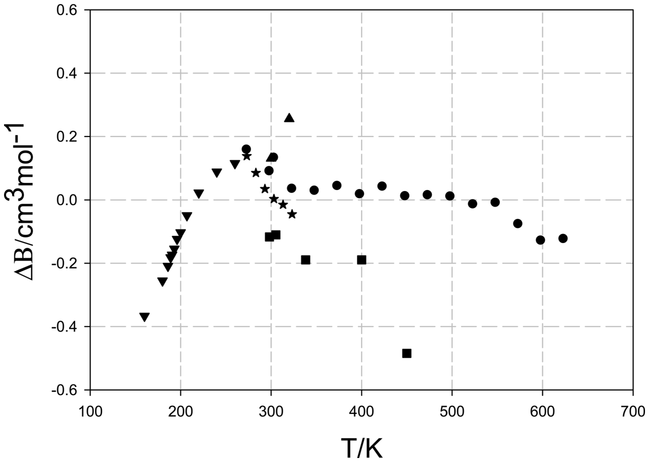

Figure 3. Absolute deviations for the second virial coefficient from values calculated using the Setzmann and Wagner[1] equation of state $\Delta B = (B_{\mathrm{exp}} - B_{\mathrm{calc}})$. ■, this work; ●, ref 14; ★, ref 15; ▲, ref 16; ▼, ref 17.

tions. Figure 1 demonstrates the deviations compared to our experimental data. It is clear that the calculations from the Setzmann and Wagner equation of state are in excellent agreement with our experimental data and that the predictions from the equation are better than expected for pressures greater than 12 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. Figure 2 presents the methodology to evaluate the second and third virial coefficient at 298 K. The selected low-density data both exhibit a linear trend and have a good correlation coefficient. Figures 3 and 4 present a comparison of experimental literature data[14−17] along with the current predictions based upon the Setzmann and Wagner equation. Most of these data lie in a band with an absolute deviation of 0.2 cm^3·mol^{-1} for the second virial coefficient and 150 (cm^3·mol^{-1})^2 for the third virial coefficient. The estimated uncertainty for the second and the third virial coefficients are 0.57 cm^3·mol^{-1} and 125 (cm^3·mol^{-1})^2, respectively. The current values for the 450 K virial coefficients have a higher absolute deviation of 0.48 cm^3·mol^{-1} and 301.2 (cm^3·mol^{-1})^2, which is a reflection of fewer low-density data taken for this isotherm. However, it appears that our apparatus is capable of determining second and third virial coefficients. The second and third virial coefficient values appear in Table 2.

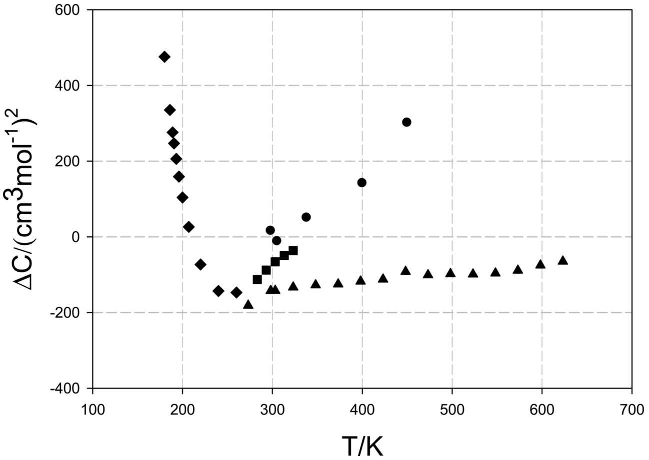

Figure 4. Absolute deviations for the third virial coefficient from values calculated using the Setzmann and Wagner[1] equation of state $\Delta C = (C_{\mathrm{exp}} - C_{\mathrm{calc}})$. ●, this work; ▲, ref 14; ■, ref 15; ♦, ref 17.

Table 2. Second and Third Virial Coefficients for Methane

T K	B cm^3·mol^{-1}	C (cm^3·mol^{-1})^2
298.190	−43.01	2527.8
305.235	−40.40	2430.1
338.092	−30.01	2220.5
400.017	−15.72	1978.8
450.038	−7.78	1973.2

Conclusions

This paper reports accurate experimental $P\rho T$ data for methane using a high-pressure, single-sinker MSD within an experimental uncertainty of $3 \cdot 10^{-4}$ ρ in density for pressures greater than 7 MPa and up to $5 \cdot 10^{-4}$ ρ for pressures between (5 and 7) MPa. The data validate the performance of the equation of state developed by Setzmann and Wagner up to 180 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 Setzmann and Wagner equation of state.

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