P-ρ-T Data for Carbon Dioxide from (310 to 450) K up to 160 MPa

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This paper presents *P-ρ-T* data for pure carbon dioxide measured with a high-pressure single-sinker magnetic suspension densimeter (MSD). The data cover four isotherms (310, 350, 400, 450) K. The MSD technique yields data with less than 0.03 % relative uncertainty over the pressure range of (10 to 200) MPa. A comparison of the experimental data to the equation of state developed by Span and Wagner indicates that the equation and the data are consistent within the low range of pressure. The reference equation has a relative uncertainty of ± 0.03 % to ± 0.05 % below 30 MPa. At higher pressures, the density predictions of this model agree with the experimental data with a maximum relative deviation of 0.1 %.

Introduction

Carbon dioxide is the simplest and best known molecule with a strong quadrupole moment. It is an important reference and testing fluid for calibration purposes and for extending physical models beyond nonpolar frontiers. Span and Wagner[1] developed the most accurate reference equation of state (EOS) for carbon dioxide. The relative uncertainty of its density predictions ranges from ± 0.03 % to ± 0.05 % between (240 and 523) K at pressures up to 30 MPa. At higher pressures, up to 200 MPa, the EOS uncertainty increases to ± 0.1 %.

This work provides new density data for pure carbon dioxide measured with a single-sinker magnetic suspension densimeter (MSD) up to 160 MPa. Of particular importance are the high-pressure data (above 10 MPa) for which the total relative uncertainty is less than 0.03 %. The relative uncertainty increases to 0.05 % at lower pressures up to 7 MPa and greater than 0.1 % at the lowest pressures reported here.

Experimental Section

The reported data include isothermal density data for carbon dioxide at (310, 350, 400, 450) K up to 160 MPa. Matheson Tri-Gas provided the carbon dioxide with a mole fraction purity of 99.999 %. The mass and volume of the titanium sinker, determined using the procedure described by McLinden and Splett,[2] are 30.39159 g and 6.741043 cm^3, respectively. Patil et al.[3] provide a complete and detailed description of this specific MSD. A PRT (Minco Products model S1059PA5X6 Platinum Resistance Thermometer) calibrated at fixed temperature points defined by ITS-90 and by a calibrated PRT traceable to NIST provides temperatures with a readability of 2.5 mK and repeatability of 0.5 mK, for a total uncertainty of ± 3 mK. Pressure measurements use two Digiquartz transducers (40 and 200 MPa) from Paroscientific Inc. with uncertainties of ± 0.01 % full scale.

McLinden et al.[4] suggest a procedure to evaluate the force transmission error (FTE) in MSD systems. Using that work as a guide, a comprehensive FTE analysis of the TAMU instrument recently appeared.[5] The coupling factor ($\phi - 1$) for the MSD is (195, 189, 204, and 194) $\times 10^{-6}$ for (310, 350, 400, 450) K, respectively. The reproducibility of these values is less than ± 2×10^{-6} for each isotherm. The data reported here have these coupling factors applied.

Results and Analysis

Table 1 contains the four sets of isothermal data, each of which contains several density measurement cycles (raw data) at each pair of conditions (*T*, *P*). The raw data have been adjusted to nominal temperatures and pressures with the mean density point taken as the most likely value to report. The data compare well to values predicted by the Span and Wagner[1] reference equation of state as implemented in RefProp 8.0.[6] The last column in the table shows the percent deviation between data and the equation.

Figure 1 is a log−linear plot[7] (linear scale delimited by the ± 0.1 band and logarithmic scale beyond that) that compares these new data to other data used in developing the reference equation of state. The data by Michels et al.[8] range from (313 to 423) K in temperature and from (8 to 180) MPa in pressure. Likewise, the data by Juza et al.[9] range from (323.15 to 448.15) K and from (70 to 200) MPa. The data by Klimeck et al.[10] range from (313 to 430) K and from (4 to 30) MPa. And the data by Gokmenoglu et al.[11] range from (314 to 425) K in temperature and from (13 to 67) MPa in pressure. The development of the reference EOS excluded the latter data. The zero deviation line represents the prediction of the equation of state.

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Table 1. *P*, *ρ*, *T* Data Measured for Carbon Dioxide

P	*ρ* (exp)	*ρ* (EOS)	
MPa	$kg \cdot m^{-3}$	$kg \cdot m^{-3}$	$100 \cdot (\rho_{exp} - \rho_{EoS})/\rho_{exp}$
		$T = 310$ K	
1.998	37.614	37.603	0.029
5.002	116.171	116.197	–0.022
10.014	686.160	686.431	–0.039
19.987	856.152	856.161	–0.001
29.966	921.817	921.860	–0.005
49.929	999.875	1000.131	–0.026
75.042	1062.566	1063.061	–0.047
100.055	1108.290	1108.777	–0.044
125.012	1144.813	1145.222	–0.036
139.289	1162.991	1163.314	–0.028
149.970	1175.569	1175.839	–0.023
159.844	1186.558	1186.760	–0.017
		$T = 350$ K	
2.011	32.349	32.353	–0.014
5.001	89.638	89.641	–0.003
9.986	228.244	228.298	–0.024
19.981	613.586	613.738	–0.025
30.013	758.897	759.108	–0.028
50.017	884.809	884.832	–0.003
74.904	969.636	969.722	–0.009
99.977	1027.564	1027.687	–0.012
124.895	1071.804	1071.896	–0.009
		$T = 400$ K	
0.999	13.455	13.464	–0.062
1.998	27.430	27.436	–0.022
4.998	72.779	72.772	0.010
10.021	161.960	161.938	0.014
14.986	267.104	267.101	0.001
20.028	381.082	381.115	–0.009
25.054	482.518	482.526	–0.002
29.994	561.435	561.412	0.004
35.005	623.368	623.290	0.012
39.985	672.037	671.953	0.012
49.967	745.445	745.244	0.027
59.920	799.163	798.946	0.027
69.997	842.031	841.747	0.034
79.880	876.766	876.413	0.040
89.950	906.957	906.558	0.044
99.838	932.857	932.415	0.047
109.931	956.349	955.880	0.049
120.079	977.599	977.117	0.049
126.010	989.102	988.620	0.049
139.527	1013.251	1012.762	0.048
		$T = 450$ K	
4.998	62.269	62.269	0.000
9.998	131.635	131.605	0.023
19.983	284.802	284.880	–0.027
29.992	430.142	430.143	0.000
49.933	626.132	625.718	0.066
75.024	762.158	761.715	0.058
99.833	847.163	846.528	0.075
122.193	903.768	902.952	0.090

Table 2. Second and Third Virial Coefficients for CO_2

T	*B*	*C*
K	$cm^3 \cdot mol^{-1}$	$(cm^3 \cdot mol^{-1})^2$
310	–111.85	4133
350	–83.70	3464
400	–59.70	2838
450	–43.10	2515

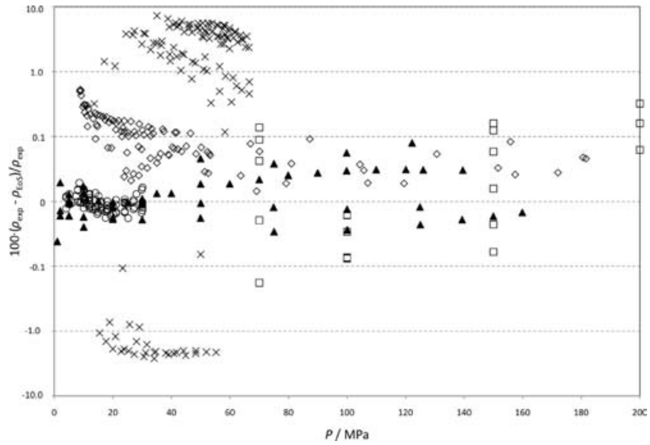

Figure 1. Percent deviation of experimental data compared to Span and Wagner equation of state. ▲, This work; ○, Klimeck;[10] ◇, Michels;[8] □, Juza;[9] ×, Gokmenoglu.[11]

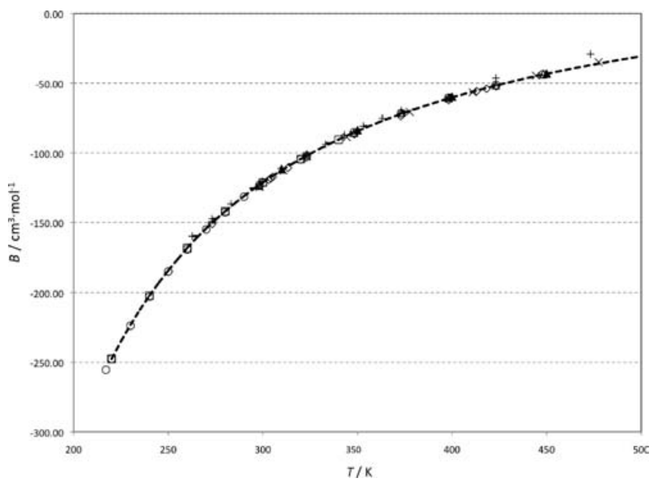

Figure 2. Second virial coefficients for CO_2. ▲, This work; ○, Holste;[12] □, Duschek;[13] Δ, Patel;[14] +, Butcher;[15] -, Dadson;[16] ×, Huff;[17] ◇, Michels;[18] *, Waxman;[19] ---, EOS prediction.[1]

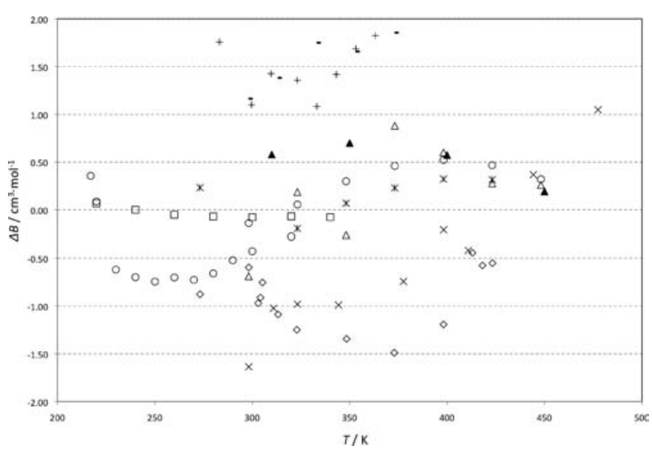

Figure 3. Absolute deviations of second virial coefficients from values predicted by the Span et al. equation of state $\Delta B = B_{exp} - B_{EoS}$. ▲, This work; ○, Holste;[12] □, Duschek;[13] Δ, Patel;[14] +, Butcher;[15] -, Dadson;[16] ×, Huff;[17] ◇, Michels;[18] *, Waxman.[19]

The predictions are consistent with current experimental densities within the relative uncertainties claimed for the reference EOS over the whole range of pressures studied, namely, ± 0.03 % to ± 0.05 % below 30 MPa and ± 0.1 % beyond that. However, in the high-pressure region the current uncertainties are lower than those of the data used to develop the EOS. It is possible that a refit using the data reported here would improve the predictive capabilities of the EOS at high pressures.

The linear behavior of the compressibility factor of carbon dioxide at low pressures was used to determine the second and third virial coefficients with an uncertainty of 2.5 $cm^3 \cdot mol$ and

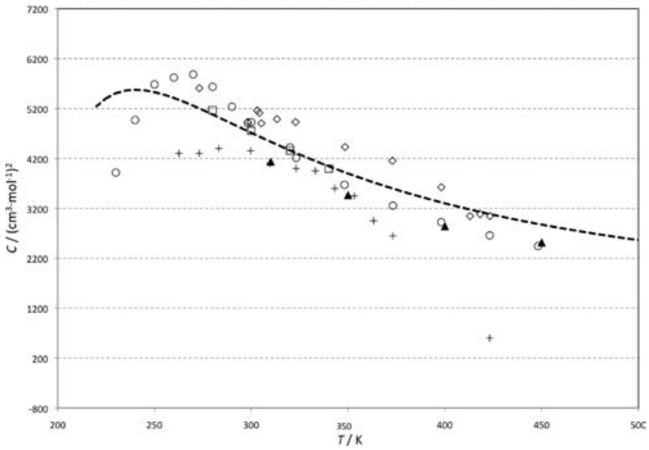

Figure 4. Third virial coefficients for CO_2. ▲, This work; ○, Holste;[12] □, Duschek;[13] ◇, Michels;[18] +, Butcher;[15] ---, EOS prediction.[1]

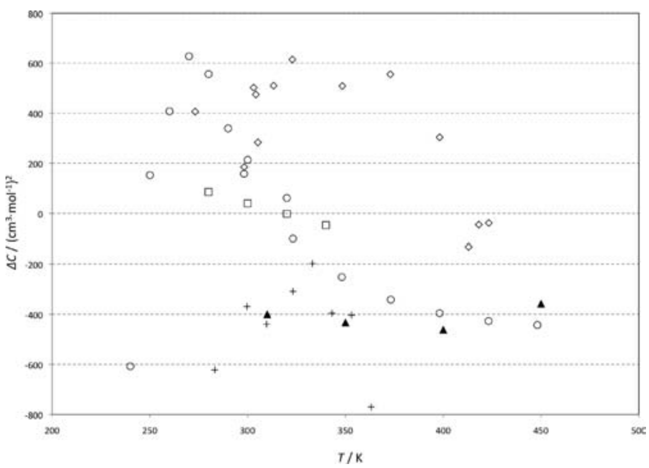

Figure 5. Absolute deviations of third virial coefficients from values predicted by the Span et al. equation of state $\Delta C = C_{exp} - C_{EoS}$. ▲, This work; ○, Holste;[12] □, Duschek;[13] ◇, Michels;[18] +, Butcher.[15]

250 $(cm^3 \cdot mol)^2$, respectively. These values appear in Table 2. Figures 2 and 3 present the second virials and their deviations using Span and Wagner[1] as the reference. Figures 4 and 5 present the same information for the third virials. The current values are consistent with previous ones generated using low-pressure experiments (lower uncertainty), and their trends with temperature follow the equation of state predictions.

Conclusions

This paper presents accurate $P\rho T$ data for carbon dioxide using a high-pressure single-sinker MSD within an experimental uncertainty of 3×10^{-4} $kg \cdot m^3$ in density for pressures greater than 7 MPa and up to 5×10^{-4} $kg \cdot m^3$ for pressures between 5 and 7 MPa. The Span and Wagner[1] EOS agrees well with the data up to 160 MPa.

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