New $P-\rho-T$ Data for Nitrogen at Temperatures from (265 to 400) K at Pressures up to 150 MPa†

Ivan D. Mantilla, Diego E. Cristancho, Saquib Ejaz, and Kenneth R. Hall*

Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, Texas 77843-3122

Mert Atilhan

Chemical Engineering Department, Qatar University, Doha, Qatar

Gustavo A. Iglesias-Silva

Departamento de Ingeniería Química, Instituto Tecnológico de Celaya, México

This paper reports $P-\rho-T$ data for pure nitrogen measured with a high-pressure, single-sinker magnetic suspension densimeter (MSD) at (265, 293, 298.15, 350, and 400) K. The MSD yields data with less than 0.03 % estimated error over the pressure range of (10 to 200) MPa. A comparison of the experimental data to the equation of state (EoS) developed by Span et al. indicates they are consistent at pressures below 30 MPa. The EoS has a relative uncertainty with respect to density of 0.02 % over this range. At higher pressures, the density predictions of this model agree with the experimental data reported in this paper within a 0.05 % deviation band.

Introduction

Nitrogen is an important reference fluid widely used for calibrating scientific equipment and testing physical models. Span et al.[1] developed the most recent reference equation of state (EoS) for nitrogen. The relative uncertainty of its density predictions apparently is better than 0.02 % between (240 and 523) K at pressures below 30 MPa. At higher pressures, the uncertainty of the EoS increases to 0.6 %. This uncertainty reflects a lack of high-accuracy data at high pressures during its development.

This paper provides new density data for pure nitrogen collected with a high-pressure single-sinker magnetic suspension densimeter (MSD). This apparatus uses the Archimedes principle and yields high-accuracy data, with estimated errors less than 0.05 %. Patil et al.[2] describe this specific MSD. The Experimental Section of this paper presents some details of the instrumentation, calibration data, and the methodology followed in collecting the data. Data tables and comparison plots appear in the Results Section.

Experimental Section

The isothermal density data for nitrogen reported here cover the range of temperatures of (265, 293, 298.15, 350, and 400) K up to 150 MPa. The nitrogen came from Scott Specialty Gases with a mole fraction purity of 0.999995. For the MSD, the mass of the titanium sinker, determined using the procedure described by McLinden and Splett,[3] was 30.39159 g with a volume of 6.741043 cm^3. A PRT (Minco Products model S1059PA5X6 platinum resistance thermometer) with fixed temperature points defined by ITS-90 and calibrated by a PRT traceable to the National Institute of Standards and Technology (NIST) provides temperature measurements with an uncertainty of 2.5 mK and a stability of 5 mK. The pressure measurement instruments are two Digiquartz transducers ((40 and 200) MPa) from Paroscientific, Inc. with uncertainties of ± 0.01 % of full scale.

The determination of the force transmission error (FTE), an inherent type of error resulting from forces altering the magnetic coupling within the apparatus, for this MSD system used the procedures suggested by McLinden et al.[4] The correction of this error applies a factor (φ) to the apparent sinker mass determined in each measurement cycle. This factor reflects the proportionality relation assumed between the force transmitted to the balance by the suspension coupling system and the suspended load. The comprehensive FTE analysis of the Texas A&M University (TAMU) instrument recently has appeared.[5]

The coupling factors, expressed as ($\varphi - 1$), applied to the density values reported here are $(193, 197, 207, 201, \text{and } 202)\cdot 10^{-6}$ for (265, 293, 298.15, 350, and 400) K, respectively. The reproducibility of these values was always better than $\pm 2\cdot 10^{-6}$ at each temperature.

Of particular importance are the high-pressure data (above 10 MPa) for which the total relative uncertainty is less than 0.03 %. That uncertainty increases to 0.05 % between (7 and 10) MPa and to more than 0.1 % below 5 MPa.

Results and Analysis

Table 1 contains the current isothermal data. Each (T, P) set results from several density measurement cycles (raw data). After adjusting these raw data to nominal temperatures and pressures, the mean density point is selected as the most likely value to report. The table also contains density values predicted

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* Corresponding author. E-mail: krhall@tamu.edu. Tel.: (979) 845 3357. Fax: (979) 845 6446.

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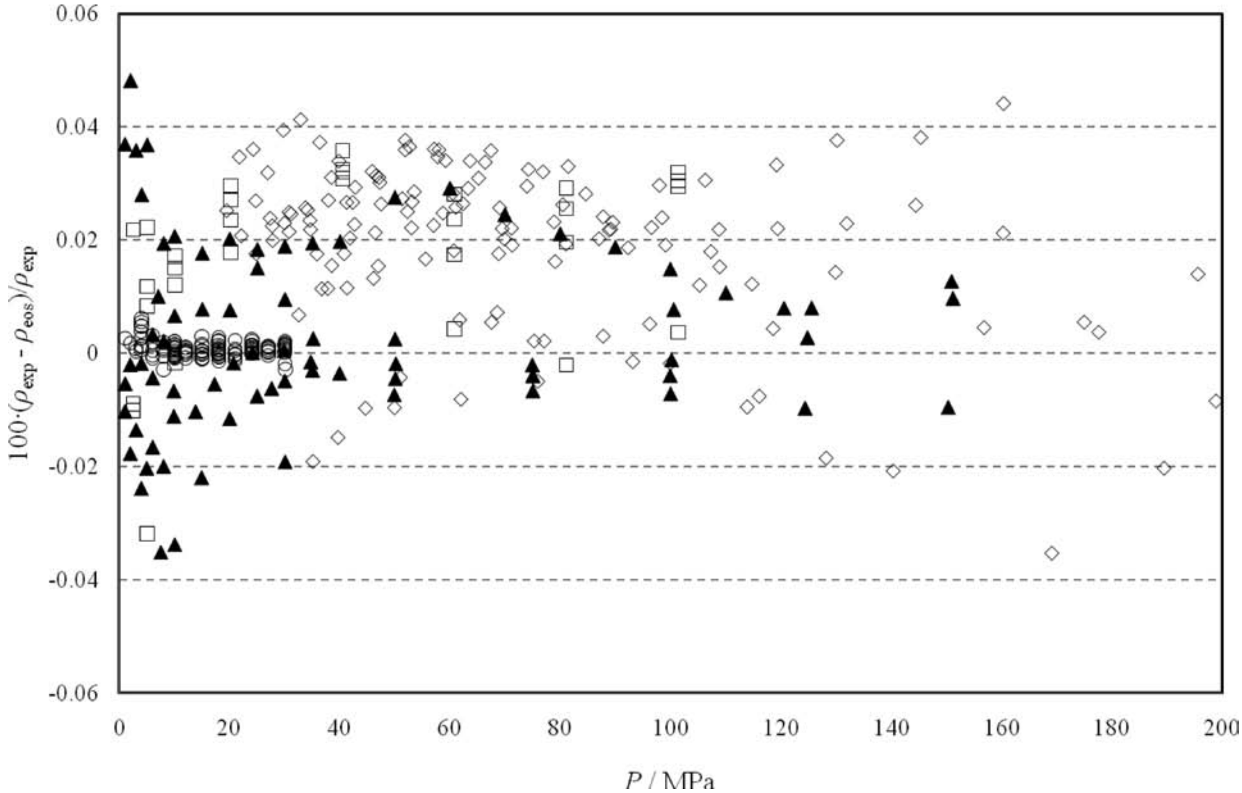

Figure 1. Percent deviation of experimental data using Span et al.[1] as the reference. ▲, this work; ○, Klimeck et al.;[7] ◇, Michels et al.;[8] □, Wiebe and Gaddy.[9]

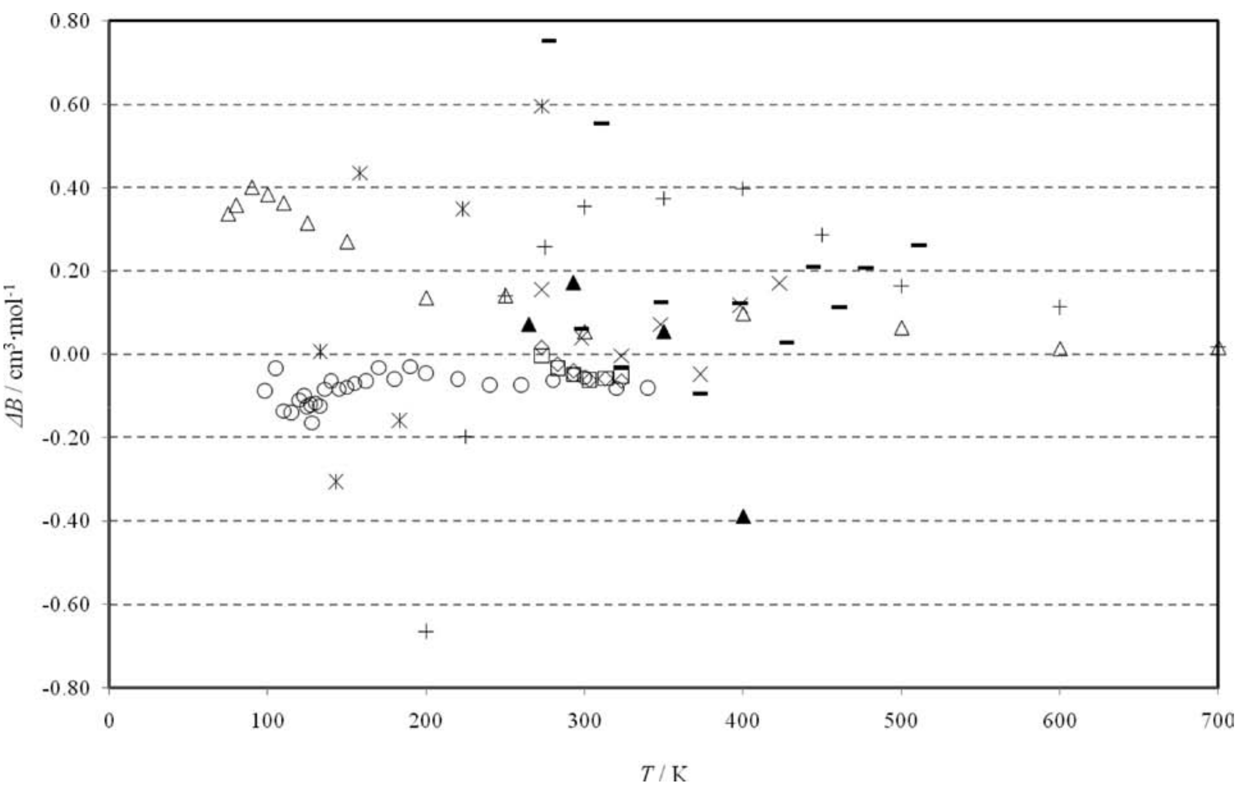

Figure 2. Absolute deviations of second virial coefficients using Span et al.[1] as the reference. $\Delta B = B_{exp} - B_{eos}$. ▲, this work; ○, Nowak et al.;[13] ◇, Duschek et al.;[10] □, Pieperbeck et al.;[11] △, Ewing and Trusler;[12] −, Huff and Reed;[15] ×, Otto and Wouters;[16] ∗, Canfield et al.;[17,18] +, Pocock and Wormald.[19]

by Span et al.[1] as implemented in REFPROP 8.0.[6] The last column in the table is the percent difference between the data and the equation. Figure 1 depicts those relative deviations from Table 1 along with other sets of data used in the development of the reference EoS.[7−9]

It is clear that the density predictions of REFPROP 8.0 agree with the current experimental data within the uncertainties claimed for the reference EoS[1] at low pressures (up to 30 MPa). Figure 1 shows that the predictions at pressures greater than 30 MPa also have an uncertainty of 0.03 %, which means that, at

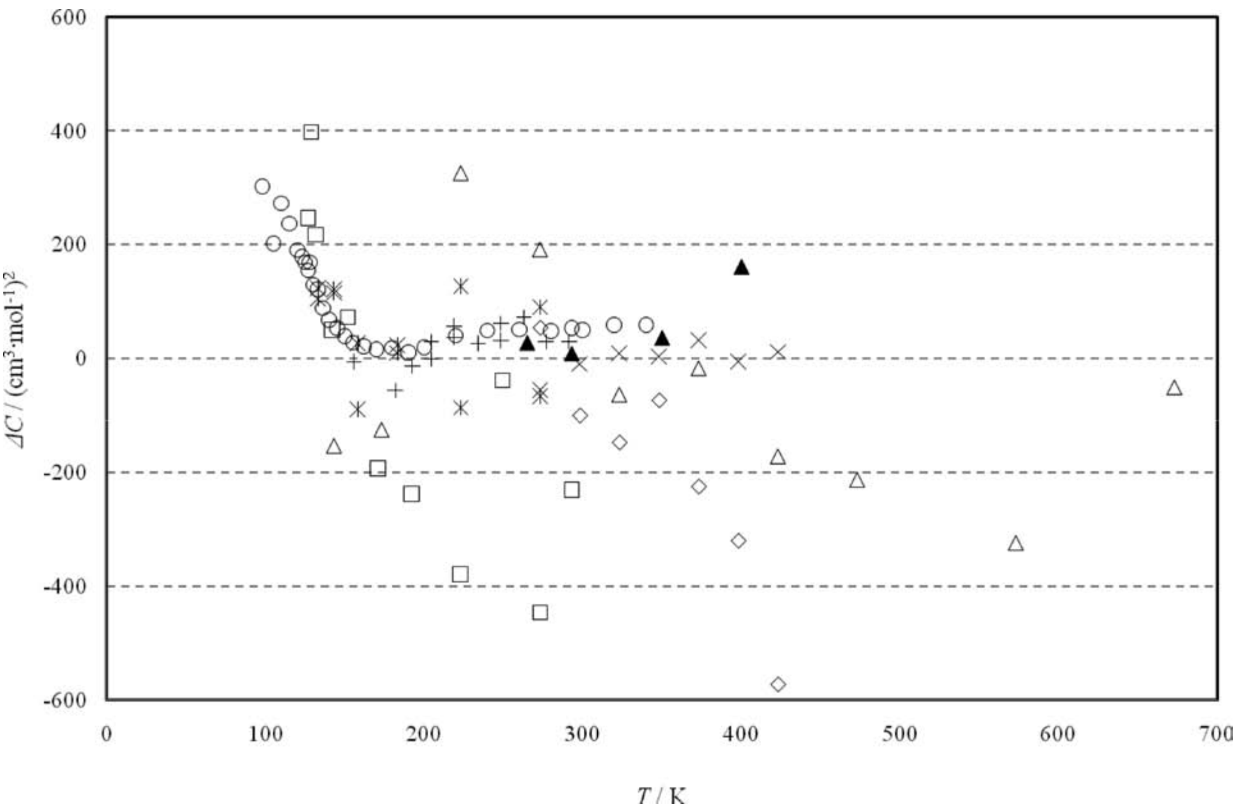

Figure 3. Absolute deviations of third virial coefficients using Span et al.[1] as the reference. $\Delta C = (C_{exp} - C_{eos})$. ▲, this work; ○, Nowak et al.;[13] △, Holborn and Otto;[20] □, Kamerlingh and Urk;[21] ◇, Michels et al.;[8] ×, Otto and Wouters;[16] ∗, Canfield et al.;[17,18] +, Roe and Saville.[22]

Table 1. New $P-\rho-T$ Data Obtained for Nitrogen

P / MPa	ρ (exp) / $kg\cdot m^{-3}$	ρ (EoS) / $kg\cdot m^{-3}$	$100\cdot(\rho_{exp} - \rho_{eos})/\rho_{exp}$
		T/K = 265.000	
0.967	12.355	12.357	−0.010
1.937	24.865	24.865	−0.002
3.929	50.840	50.841	−0.002
5.996	77.972	77.976	−0.004
7.985	104.063	104.061	0.002
9.835	128.039	128.053	−0.011
15.014	192.346	192.331	0.008
20.022	248.359	248.340	0.008
25.019	297.183	297.138	0.015
30.006	339.165	339.133	0.009
35.119	376.198	376.188	0.003
50.041	459.104	459.125	−0.005
74.887	549.760	549.772	−0.002
100.559	613.291	613.244	0.008
		T/K = 293.000	
0.965	11.119	11.115	0.037
1.933	22.306	22.310	−0.018
3.923	45.361	45.371	−0.024
5.988	69.244	69.255	−0.017
7.971	91.982	92.001	−0.020
9.822	112.910	112.918	−0.007
14.872	167.663	167.699	−0.022
19.976	218.428	218.453	−0.012
24.948	262.722	262.742	−0.008
29.965	302.337	302.352	−0.005
34.993	337.389	337.399	−0.003
39.916	367.801	367.814	−0.004
50.130	421.000	421.008	−0.002
74.957	513.932	513.952	−0.004
99.903	578.472	578.495	−0.004
125.585	628.863	628.813	0.008
150.976	668.880	668.795	0.013
		T/K = 298.150	
10.005	112.564	112.602	−0.034
30.026	296.940	296.997	−0.019
49.844	413.221	413.252	−0.007
74.988	507.852	507.886	−0.007
100.175	573.318	573.325	−0.001
124.825	622.069	622.052	0.003
151.239	664.101	664.037	0.010

Table 1. Continued

P / MPa	ρ (exp) / $kg\cdot m^{-3}$	ρ (EoS) / $kg\cdot m^{-3}$	$100\cdot(\rho_{exp} - \rho_{eos})/\rho_{exp}$
		T/K = 350.000	
2.974	28.486	28.490	−0.014
4.917	46.878	46.888	−0.020
5.971	56.772	56.770	0.003
7.481	70.762	70.787	−0.035
9.976	93.531	93.525	0.007
13.786	127.029	127.042	−0.010
17.230	155.891	155.899	−0.006
20.677	183.287	183.290	−0.002
24.132	209.197	209.197	0.000
27.582	233.510	233.524	−0.006
29.848	248.687	248.686	0.000
34.691	279.018	279.022	−0.002
49.978	358.872	358.864	0.002
74.999	452.980	452.998	−0.004
99.994	520.331	520.368	−0.007
124.395	571.157	571.212	−0.010
150.364	614.997	615.056	−0.010
		T/K = 400.000	
1.004	8.432	8.433	−0.005
1.999	16.747	16.739	0.048
2.999	25.040	25.031	0.036
4.000	33.281	33.272	0.028
5.001	41.463	41.448	0.037
7.000	57.573	57.567	0.010
8.004	65.564	65.551	0.019
10.000	81.202	81.186	0.021
14.997	118.841	118.820	0.018
19.991	154.143	154.112	0.020
24.998	187.116	187.081	0.018
29.991	217.621	217.580	0.019
35.015	246.029	245.981	0.019
40.004	272.126	272.072	0.020
49.964	318.659	318.571	0.028
59.948	358.969	358.864	0.029
69.931	394.143	394.046	0.025
79.958	425.322	425.232	0.021
89.963	453.061	452.976	0.019
99.951	477.982	477.911	0.015
110.031	500.804	500.751	0.011
120.573	522.585	522.543	0.008

Table 2. Second and Third Virial Coefficients for Nitrogen

T/K	B/$cm^3 \cdot mol^{-1}$	C/$(cm^3 \cdot mol^{-1})^2$
265.00	−12.24	1538
293.00	−5.76	1435
350.00	3.48	1364
400.00	8.71	1442

least for the temperature range studied here, the EoS has better predictive capabilities than originally claimed at these high pressures.

Extrapolation and analysis of the linear behavior of the $(Z - 1)/\rho$ function to zero pressure determines the second and third virial coefficients as the intercept and slope, respectively. The procedure yields uncertainties less than 0.28 $cm^3 \cdot mol^{-1}$ and 200 $(cm^3 \cdot mol^{-1})^2$ for B and C, respectively. These values appear in Table 2.

Figure 2 presents the absolute deviation of second virial coefficients presented in Table 2 along with other sets of data from the literature.[10−14] Figure 3 is a similar plot for the third virial coefficients. Although the reference equation does not include fits of virial coefficients, the current data agree with the EoS and other data within the experimental uncertainties quoted above.

Conclusions

This paper contains new, accurate $P-\rho-T$ data for nitrogen measured using a high-pressure single-sinker MSD apparatus that yields an experimental uncertainty of $\pm 3 \cdot 10^{-4}$ in density for pressures greater than 7 MPa and up to $\pm 5 \cdot 10^{-4}$ for pressures between (5 and 7) MPa. The data validate the performance of the EoS developed by Span et al.[1] up to 150 MPa with better predictive capabilities than expected.

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