

# $(p, \rho, T)$ Behavior of Two Mixtures of Carbon Monoxide with Nitrogen in the Temperature Range from (250 to 400) K and Pressures up to 20 MPa

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**ABSTRACT:** The development of the current reference equation of state for natural gas and other related mixtures (GERG 2008) was based on a wide up-to-date database of experimental thermodynamic properties. This extensive data bank showed, however, a significant lack of data for many of the possible binary mixtures of natural gas components. In fact, density data for carbon monoxide–nitrogen mixtures were only available for one single composition (0.03 CO + 0.97 N<sub>2</sub>) and in a limited temperature range, (273 to 353) K. In this paper density data are presented for two new binary mixtures, (0.05 CO + 0.95 N<sub>2</sub>) and (0.10 CO + 0.90 N<sub>2</sub>), along seven isotherms between (250 and 400) K and pressures up to 20 MPa. These data allow the predictive capacity of the GERG model to be tested and, if necessary, to contribute to an improvement in its mixture parameters. The measurements were carried out using an accurate single sinker densimeter with magnetic suspension coupling to achieve the highest accuracy. Results showed very good agreement with the GERG model, since relative deviations in density between experimental and estimated values are within a 0.05 % band. Interaction second virial coefficients were fitted and reported.

## 1. INTRODUCTION

Gaseous mixtures containing significant amounts of nitrogen and carbon monoxide are present in several industrial processes, whether as a combustion byproduct in exhaust gases from coke ovens and blast furnaces or as a product of biomass pyrolysis and gasification. These mixtures are currently of great interest due to their potential use as alternative or renewable fuels. Thus, several projects, such as Marcogaz<sup>1</sup> and BONGO,<sup>2</sup> are currently analyzing the viability and feasibility of the injection of these fuel gases into the existing natural gas networks to contribute to the development of a more sustainable energy model. Accurate knowledge of the thermodynamic and chemical properties of these gases is essential to ensure the quality requirements of the final delivered gas.

The AGA8-DC92 equation of state is the current industry standard for natural gas mixtures<sup>3</sup> in the homogeneous gas region. However, new equations of state have been developed in the past few years to extend the range of application of the AGA8-DC92 and improve its accuracy. Thus, the GERG-2004 wide-range equation of state<sup>4</sup> was developed as an international reference equation of state for natural gases and similar mixtures consisting of up to 18 components.<sup>5</sup> A new version of this equation of state (GERG-2008)<sup>6</sup> has recently been developed as an extension of the first version, since it incorporates three new components (*n*-nonane, *n*-decane, and hydrogen sulfide). This new GERG-2008 equation of state is currently the most comprehensive and widely used model for the estimation of thermodynamic properties of natural gas mixtures and is under consideration to be adopted as an ISO Standard (ISO 20765-2 and ISO 20765-3). In this work we compare our experimental data with the GERG-2008 model, which is equivalent to the GERG-2004 model for the gas mixtures studied here, since they

do not contain any of the additional components covered by the GERG-2008 model.

The mentioned equations of state have an empirical basis and have been fitted to an extensive number of data sets of different thermodynamic properties and substances. Nevertheless, there is still a lack of reliable and accurate experimental data of thermodynamic properties for many of these substances, especially mixtures. To extend the scope of these correlations and to include the above-mentioned fuel gases as well as their mixtures with natural gas, accurate experimental measurements of mixtures containing their components are indispensable.

Despite the mentioned importance of carbon monoxide with nitrogen mixtures in these new alternative fuels, the study of their thermodynamic properties is comparatively poor. In fact, only density data for a single composition (0.03 CO + 0.97 N<sub>2</sub>) for a limited temperature range, (273 to 353) K, and pressures up to 30.1 MPa were reported by Jaeschke et al.<sup>7</sup> in 1997. These measurements were carried out using both Burnett apparatus and optical interferometry apparatus, with reported accuracies of 0.07 % and 0.08 %, respectively.

In view of the potential exploitation of the mentioned new gaseous fuels, which contain significant amounts of nitrogen and carbon monoxide, the study of the  $(p, \rho, T)$  behavior of binary mixtures containing these components is of great interest. Thus, a 98  $(p, \rho, T)$  data set of a (0.05 CO + 0.95 N<sub>2</sub>) mixture and a 125  $(p, \rho, T)$  data set of a (0.10 CO + 0.90 N<sub>2</sub>) mixture in the temperature range (250 to 400) K and pressures up to 20 MPa are presented in this work. Measurements were carried out with

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**Table 1. Molar Composition of the Gas Mixtures and Purity of Component Gases**

composition ( $x_{\text{CO}}$ )	specified purity of nitrogen ( $x_{\text{N}_2}$ )	specified purity of carbon monoxide ( $x_{\text{CO}}$ )
$0.04999 \pm 0.00001$	0.999995	0.999985
$0.10018 \pm 0.00002$	0.999995	0.999700

an accurate single sinker densimeter with magnetic suspension coupling to achieve the lowest uncertainties.

The experimental data reported here were compared with the densities calculated using the GERG-2008 equation of state to test its performance for these mixtures. Relative deviations in density of experimental data were listed and plotted for comparison with the literature data. Interaction second virial coefficients for binary mixtures of carbon monoxide and nitrogen were fitted with our experimental data and compared with the values reported by other authors.

## 2. EXPERIMENTAL SECTION

As mentioned above, measurements were carried out in a single sinker magnetic suspension densimeter. The apparatus, which was previously described by Chamorro et al.,<sup>8</sup> is based on the Archimedes' principle and yields high accuracy ( $p$ ,  $\rho$ ,  $T$ ) data in the temperature range (250 to 400) K and pressures up to 20 MPa. The density of the fluid is determined with the following equation

$$\rho = (m_{\text{SO}} - m_{\text{SF}})/V_{\text{s}}(T, p) \quad (1)$$

where ( $m_{\text{SO}} - m_{\text{SF}}$ ) refers to the buoyancy force, in kilograms, measured by a sinker immersed in the fluid, which is calculated as the difference between the sinker mass in a vacuum and the sinker mass in the pressurized fluid, while  $V_{\text{s}}(T, p)$  refers to the sinker volume, in  $\text{m}^3$ , as a function of the fluid temperature and pressure. The densimeter has recently been modified<sup>9</sup> to improve its measurement uncertainty. The uncertainty in density has been estimated to be less than 0.12 %, while uncertainties in temperature and pressure were evaluated to be less than 4 mK and 0.015 %, respectively ( $k = 2$ ). The pressure measurement instruments are two Digiquartz transducers (Paroscientific models 2300A-101 and 43KR-HHT-101) which cover pressure ranges up to (2 and 20) MPa, respectively. The temperature of the fluid is determined as the average of the measurements of two platinum resistance thermometers (PRTs) (model Minco S1059PJSX6).

The experimental data presented in this work were collected along seven isotherms at (250, 275, 300, 325, 350, 375, and 400) K at 11 pressure steps between (1 and 20) MPa. Several isotherms were measured twice at different pressure steps to analyze the repeatability of the apparatus. Furthermore, test measurements on nitrogen were carried out along five isotherms, in the whole range of the apparatus, before measuring each mixture to check the correct operation of the densimeter. Relative deviations of experimental densities of nitrogen from the densities calculated with the reference equation of state of Span et al.<sup>10</sup> were within a 0.02 % band. The force transmission error due to the magnetic characteristics of the apparatus is compensated for by using an appropriate measurement procedure, as described by Chamorro et al.<sup>8</sup> The minor contribution produced by the fluid specific effect, described by McLinden et al.<sup>11</sup> and calculated by Cristancho et al.<sup>12</sup> and Kano et al.,<sup>13</sup> was omitted, since the deviation which could be induced by the magnetic behavior of the fluid was estimated to be in the order of

**Table 2. Results of the ( $p$ ,  $\rho$ ,  $T$ ) Measurements for the (0.05 CO + 0.95 N<sub>2</sub>) Binary Mixture, Where  $T$  Is the Temperature (ITS-90),  $p$  the Pressure,  $\rho_{\text{exp}}$  the Experimental Density, and  $\rho_{\text{EoS}}$  the Density Calculated from the GERG-2008 Equation of State**

$T$ K	$p$ MPa	$\rho_{\text{exp}}$ $\text{kg} \cdot \text{m}^{-3}$	$10^2(\rho_{\text{exp}} - \rho_{\text{EoS}})/\rho_{\text{EoS}}$
250.049	18.4739	250.840	0.014
250.049	17.9994	245.259	0.014
250.045	15.9997	220.890	0.012
250.047	14.0036	195.251	0.010
250.049	11.9985	168.354	0.008
250.051	9.99983	140.653	0.008
250.047	7.99853	112.326	0.002
250.045	6.01694	84.044	-0.003
250.044	4.00994	55.503	-0.012
250.043	1.99903	27.340	0.011
250.041	0.996970	13.537	0.000
275.023	19.9174	235.882	0.017
275.023	18.1977	218.123	0.015
275.021	15.9971	194.336	0.016
275.023	13.9973	171.740	0.015
275.023	11.9993	148.339	0.011
275.030	10.0622	124.995	0.006
275.029	8.03660	100.073	0.000
275.029	6.03862	75.170	-0.003
275.023	4.00007	49.643	-0.010
275.020	1.99595	24.643	0.013
275.020	0.990786	12.187	-0.002
299.978	19.9569	212.314	0.036
299.977	17.9967	193.879	0.021
299.977	15.9967	174.350	0.020
299.957	14.9541	163.889	0.015
299.980	13.9973	154.113	0.019
299.962	12.9975	143.747	0.013
299.975	11.8888	132.063	0.012
299.962	10.9995	122.587	0.018
299.972	10.0171	111.971	0.011
299.962	9.08652	101.826	0.010
299.974	8.02482	90.132	0.007
299.962	6.99826	78.744	0.009
299.972	6.02019	67.811	0.002
299.962	4.99795	56.340	0.002
299.972	3.97500	44.812	-0.008
299.961	2.98189	33.609	-0.006
299.971	1.99343	22.457	0.018
299.962	1.00376	11.294	0.011
299.971	0.986706	11.101	0.005
324.983	19.9309	193.033	0.018
324.983	17.9952	176.379	0.018
324.982	15.9569	158.239	0.025
324.985	14.1156	141.303	0.014
324.974	13.7432	137.825	0.010
324.975	12.9991	130.817	0.010
324.984	12.0000	121.293	0.011

Table 2. Continued

$T$	$p$	$\rho_{\text{exp}}$	$10^2(\rho_{\text{exp}} - \rho_{\text{EoS}})/\rho_{\text{EoS}}$
K	MPa	$\text{kg} \cdot \text{m}^{-3}$	
324.977	10.9966	111.619	0.019
324.983	10.0066	101.939	0.011
324.979	8.99869	91.988	0.010
324.984	7.99104	81.935	0.008
324.978	7.02577	72.228	0.009
324.983	5.96077	61.428	0.005
324.978	4.97996	51.417	0.002
324.984	4.00852	41.449	0.000
324.978	2.99127	30.967	-0.007
324.982	1.98129	20.531	0.009
324.984	0.996209	10.328	0.009
349.969	19.6554	175.420	0.022
349.969	17.9925	162.172	0.022
349.970	15.9944	145.784	0.021
349.970	13.9972	128.911	0.018
349.970	12.0181	111.731	0.015
349.970	10.0220	93.976	0.015
349.969	8.01856	75.757	0.010
349.968	5.99817	57.037	0.005
349.971	4.00481	38.283	0.003
349.970	1.95895	18.808	0.017
349.970	0.991177	9.530	0.004
374.959	19.8166	163.859	0.018
374.959	17.9875	150.312	0.017
374.959	15.9900	135.101	0.016
374.959	13.9946	119.477	0.013
374.959	11.9955	103.411	0.009
374.958	9.99598	86.957	0.010
374.960	7.99654	70.138	0.006
374.958	5.99791	52.996	-0.001
374.959	3.99850	35.556	-0.014
374.959	1.98927	17.794	0.013
374.959	0.991138	8.887	0.002
400.020	19.0266	147.507	0.015
400.019	17.9853	140.246	0.013
400.020	15.9860	126.014	0.012
400.019	13.9897	111.428	0.010
400.019	11.9915	96.459	0.007
400.019	9.97324	80.982	0.006
400.021	7.99662	65.491	0.001
400.019	5.99803	49.518	-0.008
400.020	3.98633	33.151	-0.020
400.020	1.93445	16.200	-0.006

0.006 %, which is much lower than the estimated uncertainty in density for the measurements reported in this work.

The two mixtures studied in this work were prepared gravimetrically in the Spanish National Metrology Institute (Centro Español de Metrología, CEM) and supplied in 10 dm<sup>3</sup> aluminum cylinders filled to a pressure of 7 MPa at room temperature. Mixture compositions and estimated uncertainties, together with the purities of the component gases, are given in Table 1.

Table 3. Results of the ( $p$ ,  $\rho$ ,  $T$ ) Measurements for the (0.10 CO<sub>2</sub> + 0.90 N<sub>2</sub>) Binary Mixture, Where  $T$  Is the Temperature (ITS-90),  $p$  the Pressure,  $\rho_{\text{exp}}$  the Experimental Density, and  $\rho_{\text{EoS}}$  the Density Calculated from the GERG-2008 Equation of State

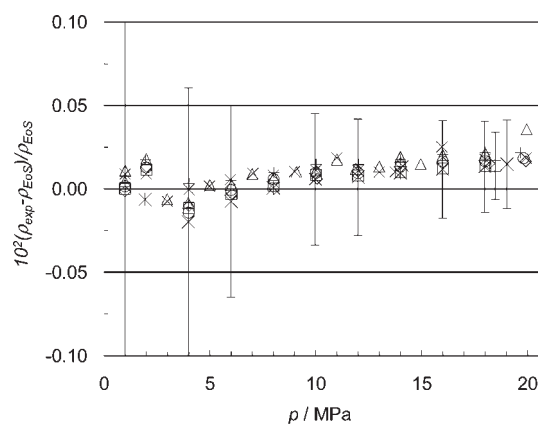
$T$	$p$	$\rho_{\text{exp}}$	$10^2(\rho_{\text{exp}} - \rho_{\text{EoS}})/\rho_{\text{EoS}}$
K	MPa	$\text{kg} \cdot \text{m}^{-3}$	
250.060	19.9624	268.002	0.016
250.060	17.9996	245.432	0.015
250.055	16.7064	229.835	0.019
250.059	15.9987	221.035	0.014
250.051	15.0030	208.407	0.016
250.061	13.9985	195.325	0.014
250.053	13.0333	182.506	0.014
250.063	11.9982	168.471	0.014
250.051	11.0009	154.742	0.017
250.056	9.99883	140.734	0.013
250.050	8.99903	126.622	0.009
250.055	7.99832	112.391	0.010
250.057	6.99906	98.128	0.015
250.056	5.99926	83.836	0.012
250.056	5.04318	70.198	0.011
250.054	3.99885	55.373	0.010
250.056	3.03294	41.760	0.002
250.053	2.00426	27.416	0.013
250.053	0.999785	13.577	0.010
250.051	0.969128	13.157	0.002
275.024	19.8876	235.720	0.023
275.024	17.9971	216.135	0.022
275.024	15.9977	194.459	0.022
275.022	14.0007	171.880	0.020
275.019	12.0042	148.483	0.017
275.018	9.99954	124.305	0.016
275.015	7.99941	99.667	0.012
275.014	5.99890	74.708	0.009
275.012	3.99849	49.641	0.001
275.012	1.98443	24.502	0.011
275.011	0.997907	12.276	-0.001
299.977	19.8296	211.228	0.036
299.976	17.9986	193.977	0.022
299.975	16.1086	175.535	0.022
299.974	15.3704	168.159	0.024
299.973	14.8070	162.461	0.023
299.972	13.9972	154.176	0.021
299.972	13.0026	143.858	0.022
299.972	11.9990	133.290	0.020
299.972	11.0075	122.717	0.026
299.973	9.99714	111.800	0.023
299.969	9.07366	101.718	0.018
299.976	7.99752	89.866	0.024
299.971	7.03398	79.163	0.018
299.974	5.99923	67.600	0.019
299.969	5.02084	56.608	0.007
299.972	3.99843	45.092	0.013
299.969	2.99357	33.744	-0.005

Table 3. Continued

$T$	$p$	$\rho_{\text{exp}}$	$10^2(\rho_{\text{exp}} - \rho_{\text{EoS}})/\rho_{\text{EoS}}$
K	MPa	$\text{kg} \cdot \text{m}^{-3}$	
299.972	1.98975	22.417	0.022
299.972	1.00194	11.274	0.016
299.971	0.992979	11.173	0.011
324.978	19.9475	193.262	0.033
324.977	17.9956	176.463	0.033
324.978	15.9946	158.639	0.033
324.977	13.9961	140.254	0.032
324.977	11.9970	121.320	0.031
324.978	9.99872	101.905	0.032
324.976	7.99937	82.050	0.028
324.977	5.99998	61.847	0.025
324.976	3.99850	41.357	0.017
324.976	1.97022	20.421	0.022
324.977	0.997476	10.342	0.013
349.966	19.9592	177.859	0.032
349.964	18.2140	164.000	0.027
349.966	17.9917	162.217	0.033
349.965	16.9943	154.090	0.028
349.968	15.9939	145.829	0.035
349.965	14.9956	137.446	0.028
349.968	13.9949	128.938	0.037
349.965	12.9990	120.335	0.026
349.968	11.9970	111.586	0.035
349.963	10.9983	102.742	0.029
349.969	9.99826	93.794	0.036
349.963	8.99760	84.725	0.021
349.968	7.99894	75.601	0.031
349.963	6.99788	66.355	0.019
349.968	5.99772	57.048	0.024
349.962	4.99789	47.663	0.005
349.967	3.92247	37.508	0.011
349.964	2.99918	28.731	-0.012
349.967	1.97883	18.999	0.020
349.967	0.993387	9.551	-0.004
349.963	0.991956	9.538	0.009
374.957	19.9713	165.047	0.039
374.954	19.9666	165.012	0.038
374.956	18.9875	157.820	0.038
374.956	17.9867	150.362	0.040
374.955	16.9904	142.823	0.038
374.957	15.9904	135.151	0.039
374.955	15.0159	127.569	0.037
374.957	13.9926	119.504	0.039
374.954	12.9938	111.524	0.036
374.957	11.9876	103.381	0.034
374.955	10.9952	95.265	0.040
374.957	9.99790	86.999	0.032
374.955	8.99739	78.624	0.031
374.956	8.02423	70.391	0.026
374.955	6.99762	61.627	0.027
374.958	5.99898	53.019	0.021
374.955	4.98094	44.170	0.014

Table 3. Continued

$T$	$p$	$\rho_{\text{exp}}$	$10^2(\rho_{\text{exp}} - \rho_{\text{EoS}})/\rho_{\text{EoS}}$
K	MPa	$\text{kg} \cdot \text{m}^{-3}$	
374.956	4.00484	35.621	0.009
374.955	2.99823	26.743	-0.005
374.955	1.99501	17.848	0.028
374.957	0.993407	8.908	0.012
400.031	18.4582	143.591	0.032
400.021	17.9819	140.257	0.030
400.020	16.2271	127.785	0.032
400.022	15.9860	126.048	0.032
400.020	14.9879	118.800	0.032
400.019	13.9901	111.464	0.034
400.019	12.9907	104.017	0.030
400.022	11.9942	96.505	0.030
400.019	11.0249	89.118	0.033
400.021	9.89549	80.402	0.031
400.018	8.98697	73.307	0.021
400.018	7.99464	65.495	0.028
400.020	7.00550	57.622	0.020
400.017	5.99615	49.523	0.032
400.021	4.99706	41.415	0.004
400.019	3.99728	33.254	0.019
400.020	2.99426	24.985	-0.020
400.020	1.97547	16.545	0.022
400.017	0.997158	8.375	0.008
400.020	0.984405	8.268	-0.005



**Figure 1.** Percentage density deviations of experimental ( $p, \rho, T$ ) data of the (0.05 CO + 0.95 N<sub>2</sub>) binary mixture from density values  $\rho_{\text{EoS}}$  calculated from the GERG-2008 equation of state versus pressure:  $\square$ , 250 K;  $\diamond$ , 275 K;  $\triangle$ , 300 K;  $\times$ , 325 K;  $+$ , 350 K;  $\circ$ , 375 K;  $*$ , 400 K. The error bars represent expanded uncertainties in density ( $k = 2$ ) of the experimental data.

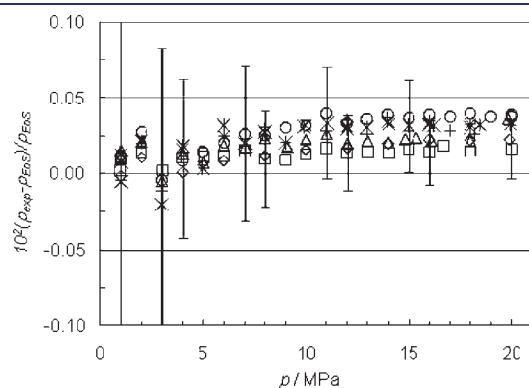
Nitrogen used for test measurements was supplied by Alphagaz (Air Liquid) with a certified mole fraction purity of 0.999999.

### 3. RESULTS AND DISCUSSION

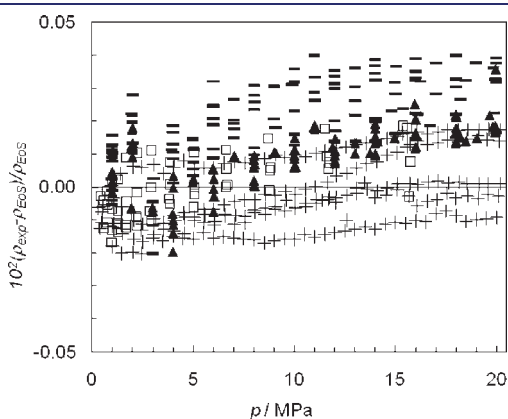
Experimental ( $p, \rho, T$ ) data, together with their relative deviations in density from the GERG-2008 equation of state,

are presented in Tables 2 and 3 for the  $x_{\text{CO}} = 0.05$  and  $x_{\text{CO}} = 0.10$  mixtures, respectively. Each magnitude value was obtained as the average of the last 10 values of the 30 replicate measurements of each pressure step.

Figures 1 and 2 represent the relative deviations in density of the experimental data from the GERG-2008 equation of state versus pressure. As can be observed, both mixtures show very good agreement with the density values predicted by the equation of state, since the relative deviations in density are within a 0.05 % band and the estimated uncertainty of the



**Figure 2.** Percentage density deviations of experimental ( $p, \rho, T$ ) data of the (0.10 CO + 0.90 N<sub>2</sub>) binary mixture from density values  $\rho_{\text{EoS}}$  calculated from the GERG-2008 equation of state versus pressure:  $\square$ , 250 K;  $\diamond$ , 275 K;  $\triangle$ , 300 K;  $\times$ , 325 K;  $+$ , 350 K;  $\circ$ , 375 K;  $*$ , 400 K. The error bars represent expanded uncertainties in density ( $k = 2$ ) of the experimental data.



**Figure 3.** Percentage density deviations of experimental ( $p, \rho, T$ ) data of CO/N<sub>2</sub> binary mixtures from density values  $\rho_{\text{EoS}}$  calculated from the GERG-2008 equation of state versus pressure, for CO molar compositions between 0.03 and 0.10 in the temperature range (250 to 400) K and pressures up to 20 MPa:  $\blacktriangle$ , this work ( $x_{\text{CO}} = 0.05$ );  $-$ , this work ( $x_{\text{CO}} = 0.10$ );  $\square$ , Jaeschke et al. (Burnett apparatus);  $+$ , Jaeschke et al. (optical interferometer).

equation is 0.1 %. The error bars, which represent the expanded uncertainties ( $k = 2$ ) in density of the experimental values, were plotted only for some data points of the (250 and 400) K isotherms to show the uncertainty as a function of the density value.

The percentage deviations of the experimental data reported in this work from the equation of state, together with the data reported by Jaeschke et al.<sup>7</sup> for a  $x_{\text{CO}} = 0.03$  mixture, are shown in Figure 3. It can be seen that relative deviations are slightly larger for the mixtures with a higher carbon monoxide molar fraction. However, since these observed differences are much lower than the estimated uncertainty of the density data, it is not possible to confirm whether this can mean a worse agreement of the experimental data with the GERG-2008 equation of state for mixtures with a high carbon monoxide molar composition. This trend is also found in the statistical comparison given in Table 4, where  $n$  is the number of data points, AAD is the average absolute deviation defined in eq 2, RMS refers to the root mean squared defined in eq 3, and MaxD represents the maximum relative deviation in the considered data set

$$\text{AAD} = \frac{1}{n} \sum_{i=1}^n \left| 10^2 \frac{\rho_{i,\text{exp}} - \rho_{i,\text{EoS}}}{\rho_{i,\text{EoS}}} \right| \quad (2)$$

$$\text{RMS} = \sqrt{\frac{1}{n} \sum_{i=1}^n \left( \frac{\rho_{i,\text{exp}} - \rho_{i,\text{EoS}}}{\rho_{i,\text{EoS}}} \right)^2} \quad (3)$$

To determine the interaction second virial coefficient  $B_{12}$  for mixtures of carbon monoxide and nitrogen, the experimental data of the two mixtures measured in this work were fitted to a second-order virial equation of state, as indicated in eq 4.

$$\begin{aligned} \frac{Z-1}{\rho} &= B + C\rho \\ &= (B_{11}x_1^2 + B_{22}x_2^2 + 2B_{12}x_1x_2) + C\rho \end{aligned} \quad (4)$$

Here,  $Z$  is the experimental compressibility factor,  $\rho$  is the experimental density,  $B$  and  $C$  are the second and third virial coefficients,  $x_1$  and  $x_2$  are the molar fraction of nitrogen and carbon monoxide, and  $B_{11}$  and  $B_{22}$  are the pure-component virial coefficients of nitrogen and carbon monoxide, which were calculated from the equations of state of Span et al.<sup>10</sup> and Lemmon and Span,<sup>14</sup> respectively.

The fitted interaction second virial coefficients  $B_{12}$  are listed in Table 5, together with the  $B_{12}$  values and pure component second virial coefficients  $B_{11}$  and  $B_{22}$ , calculated from the GERG model. The uncertainty of the fitted  $B_{12}$  coefficients was calculated following the law of propagation of uncertainties (GUM)<sup>15</sup> and is estimated to be less than  $2.7 \text{ cm}^3 \cdot \text{mol}^{-1}$ . These values were compared with the measured values of McElroy and Buchanan<sup>16</sup> and with the GERG-2008 equation of state in Figure 4. As can be observed, there is a good agreement between

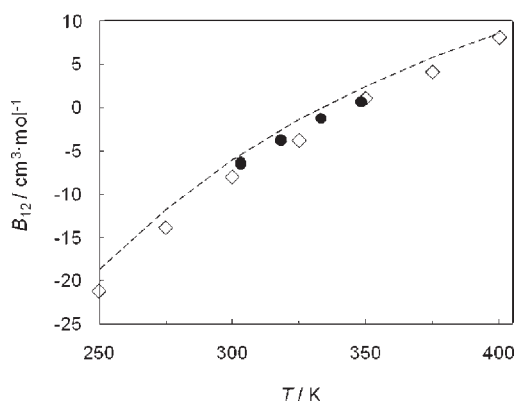
**Table 4.** Statistical Comparison of the Experimental Density Measurements Plotted in Figure 3 Respect to the GERG Model

source	year	experimental technique	$x_{\text{CO}}$	$n$	$10^2$ AAD	$10^2$ RMS	$10^2$ MaxD
Jaeschke et al. <sup>5</sup>	1997	Burnett apparatus	0.03	56	0.009	0.012	-0.052
Jaeschke et al. <sup>5</sup>	1997	optical interferometer	0.03	287	0.009	0.011	-0.023
this work	2011	single sinker densimeter	0.05	99	0.011	0.014	0.036
this work	2011	single sinker densimeter	0.10	125	0.022	0.024	0.040



**Table 5. Interaction ( $B_{12}$ ) Second Virial Coefficients Obtained from Experimental Data Together with the Interaction and Pure Component ( $B_{12\text{-GERG}}$ ,  $B_{11\text{-GERG}}$ ,  $B_{22\text{-GERG}}$ ) Second Virial Coefficients from the GERG Model for Mixtures of Carbon Monoxide with Nitrogen**

$T$ K	$B_{12}$ $\text{cm}^3 \cdot \text{mol}^{-1}$	$B_{12\text{-GERG}}$ $\text{cm}^3 \cdot \text{mol}^{-1}$	$B_{11\text{-GERG}}$ $\text{cm}^3 \cdot \text{mol}^{-1}$	$B_{22\text{-GERG}}$ $\text{cm}^3 \cdot \text{mol}^{-1}$
250	-21.21	-18.67	-16.44	-21.91
275	-13.90	-11.68	-9.86	-14.48
300	-8.02	-6.03	-4.55	-8.47
325	-3.80	-1.39	-0.20	-3.52
350	1.08	2.49	3.43	0.63
375	4.12	5.76	6.49	4.13
400	8.11	8.55	9.10	7.13



**Figure 4.** Interaction second virial coefficients of carbon monoxide with nitrogen mixtures.  $\diamond$ , this work;  $\bullet$ , McElroy and Buchanan; ---, GERG 2008 equation of state.

the fitted coefficients and the coefficients calculated from the equation of state. Major deviations occur at low temperatures, where the difference between the fitted and calculated coefficients reaches  $2.5 \text{ cm}^3 \cdot \text{mol}^{-1}$ .

#### 4. CONCLUSION

Density data for two binary mixtures of carbon monoxide and nitrogen with molar compositions  $x_{\text{CO}} = (0.05, 0.10)$  in the temperature range (250 to 400) K and pressures up to 20 MPa are reported in this paper. The measurements were carried out using a single sinker densimeter with magnetic suspension coupling to achieve high accuracy determinations.

Experimental densities were compared with those calculated from the GERG-2008 equation of state showing a very good agreement within a 0.05 % deviation band, which is less than the 0.10 % estimated uncertainty of the equation of state for these mixtures. Plots for each mixture revealed deviations were independent from the temperature. Though the deviations showed a slight increase with the carbon monoxide molar fraction, a relation between the agreement of the equation of state and the carbon monoxide composition cannot be concluded, due to the uncertainty in density of the experimental values.

These new, accurate ( $p, \rho, T$ ) data for carbon monoxide with nitrogen mixtures are a contribution to the few previously existing data, as they cover two additional compositions and a wider temperature range.

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#### REFERENCES

- (1) Marcogaz Final Recommendation. *Injection of Gases from Non-Conventional Sources into Gas Networks*, 2006. <http://www.marcogaz.org/membernet/show.asp?wat=WG-Biogaz-06-18%20D497%20Final%20Recommendationm.pdf>.
- (2) Florrisson, O.; Pinchbeck, D. In *Biogas and others in natural gas operations (BONGO): a project under development*; 23rd World Gas Conference, Amsterdam, The Netherlands, June 5–9, 2006.
- (3) Starling K. E.; Savidge J. L. *Compressibility factors of natural gas and other related hydrocarbon gases*; AGA Transmission Measurement Committee Report 8; American Gas Association (AGA): Washington, DC, 1992.
- (4) Kunz, O.; Klimeck, R.; Wagner, W.; Jaeschke, M. *The GERG-2004 Wide-Range Reference Equation of State for Natural Gases and Other Mixtures*. *GERG Tech. Monogr. Fortsch. 15*; VDI-Verlag: Düsseldorf, Germany, 2007.
- (5) Jaeschke, M.; Benito, A.; Fredheim, A.; Henault, J.-M.; Sangalli, M.; Wesenbeeck, P. V.; Klimeck, R.; Kunz, O.; Span, R.; Wagner, W. In *GERG project: Wide-range reference equation of state for natural gases*; International Gas Research Conference Proceedings, Amsterdam, November 2001; p 11.
- (6) Kunz, O.; Wagner, W. *The GERG-2008 Wide-Range Equation of State for Natural Gases and Other Mixtures: An Expansion of GERG-2004*. *J. Chem. Eng. Data*, to be submitted.
- (7) Jaeschke, M.; Humphreys, A. E.; Van Caneghem, P.; Fauveau, M.; Janssen-van Rosmalen, R.; Pellei, Q. *The GERG Databank of High Accuracy Compressibility Factor Measurements*, GERG Technical Monograph, 1997; Vol. 4.
- (8) Chamorro, C. R.; Segovia, J. J.; Martin, M. C.; Villamanan, M. A.; Estela-Urbe, J. F.; Trusler, J. P. M. Measurement of the (pressure, density, temperature) relation of two (methane plus nitrogen) gas mixtures at temperatures between 240 and 400 K and pressures up to 20 MPa using an accurate single-sinker densimeter. *J. Chem. Thermodyn.* **2006**, *7*, 916–922.
- (9) Mondéjar, M. E.; Segovia, J. J.; Chamorro, C. R. Improvement of the measurement uncertainty of a high accuracy single sinker densimeter via setup modifications based on a state point uncertainty analysis. *Measurement* **2011**, *44*, 1768–1780.
- (10) Span, R.; Lemmon, E. W.; Jacobsen, R. T.; Wagner, W.; Yokozeki, A. A reference equation of state for the thermodynamic properties of nitrogen for temperatures from 63.151 to 1000 K and pressures to 2200 MPa. *J. Phys. Chem. Ref. Data* **2000**, *6*, 1361–1401.

(11) McLinden, M. O.; Kleinrahm, R.; Wagner, W. Force transmission errors in magnetic suspension densimeters. *Int. J. Thermophys.* **2007**, *2*, 429–448.

(12) Cristancho, D. E.; Mantilla, I. D.; Ejaz, S.; Hall, K. R.; Iglesias-Silva, G. A.; Atilhan, M. Force transmission error analysis for a high-pressure single-sinker magnetic suspension densimeter. *Int. J. Thermophys.* **2010**, *4–5*, 698–709.

(13) Kano, Y.; Kayukawa, Y.; Fujii, K.; Sato, H. A new method for correcting a force transmission error due to magnetic effects in a magnetic levitation densimeter. *Meas. Sci. Technol.* **2007**, *3*, 659–666.

(14) Lemmon, E. W.; Span, R. Short fundamental equations of state for 20 industrial fluids. *J. Chem. Eng. Data* **2006**, *3*, 785–850.

(15) *BIPM, IEC, IFCC, ISO, IUPAC, IUPAP and OIML Guide to the Expression of Uncertainty in Measurement*; International Organization for Standardization: Geneva, Switzerland, 1995.

(16) Mcelroy, P. J.; Buchanan, S. Second virial coefficients of fuel-gas components: (carbon monoxide + nitrogen) and (carbon monoxide + ethene). *J. Chem. Thermodyn.* **1995**, *7*, 755–761.