Table II. Parameters for the Redlich-Kwong and Deiters Equations of State

parameter	RK	D
T°_{11}/K	29.17581	33.35546
T°_{12}/K	66.32667	73.03337
T°_{22}/K	136.93072	132.65855
b_{11}/dm^3 mol^{-1}	0.0171576	0.0108770
b_{22}/dm^3 mol^{-1}	0.0290569	0.0218388
s_{11}		1.0
s_{22}		1.591521
s_{12}		1.244681

used in the calculations. The results for the molar volumes are shown in Figure 4. With respect to the expanded scale in Figure 5, both equations of state represent the experimental data quite well. In agreement with experiment, both equations predict an inflection point in the $V_m - x$ lines at lower pressure and high hydrogen concentration. The RK equation shows considerable deviations at high methane concentration, however, because it cannot fit *PVT* data and vapor pressure data well at the same time.

Registry No. H_2, 1333-74-0; CH_4, 74-82-8.

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Density Values of Carbon Dioxide and Nitrogen Mixtures from 500 to 2500 bar at 323 and 348 K

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The density of binary mixtures of carbon dioxide-nitrogen with mole fractions of 0.25, 0.5, and 0.74 were measured at 323 and 348 K and in a pressure range between 500 and 2500 bar. These results have been used for numerical calculations of the second and third virial coefficients of these mixtures.

Introduction

Experimental data for the densities of gas mixtures at high pressures and different temperatures are very useful to broaden our understanding of intermolecular forces. In particular, they allow the separation of density and temperature effects for spectroscopic studies. The paucity of these data in the literature (*1-4*), or rather their absence for the high-pressure range (>500 bar) for mixtures of carbon dioxide and nitrogen, initiated these measurements. The purpose of this paper is to present *unsmoothed P* vs ρ experimental data which have a very small interval between points. This will allow one to rather accurately calculate intermediate densities by interpolation.

Experimental Method

Materials. The nitrogen gas was obtained from Alphagaz Corp. and has minimum purity of 99.998%. The carbon dioxide "Precision Aquarator" grade used in this work was supplied by Linde-Union Carbide with reported minimum purity of 99.99% with O_2 < 7 ppm, CO < 7 ppm, and total hydrocarbons less then 7 ppm. These gases (with certified analyses) were used without further purifications. The composition analysis of mixtures were made by gas chromatography by direct comparison of the peak area ratio of the carbon dioxide signal to the nitrogen signal, with the maximum error limit being ±0.5%.

Apparatus. A schematic diagram of the *P-V-T* apparatus is shown in Figure 1. It was a small high-pressure system using an Omega Model 158 temperature controller which allows this system to achieve an accuracy of ±0.5 K. The main part of the system was a calibrated high-pressure hand pump with a screw-type positive displacement, nonrotating piston and CO_2 resistant seal produced by Nova-Swiss AG. No leaking was detected during the measurement. Using the calibrated vernier scale on the pump, we can control injection flow (e.g., changes of the initial volume of system) very accurately (±0.03 cm^3). The total volume of the high-pressure system was 31.9 cm^3. This value was chosen to obtain a reasonable change of pressure of our mixtures using the hand pump. The particular volumes of hand pump, connections, and gauge were 5.6, 12.3, and 14.0 ± 0.1 cm^3, respectively. The pressure measurements were made with a Heise 0-4000 bar gauge which has a precision of ±2.5 bar. The Heise gauge was calibrated at elevated temperature for "zero position" and the upper pressure limit variation is 1%/38 °C.

The density measuring principle simply used the experimental pressure-volume dependence along with a known constant mass of gas mixture inside the system at constant temperature. This mass was evaluated by using a medium pressure autoclave vessel (45.47 cm^3) and an electronic balance (Arbor Model 2007) with 0.001-g resolution and 2500-g capacity for

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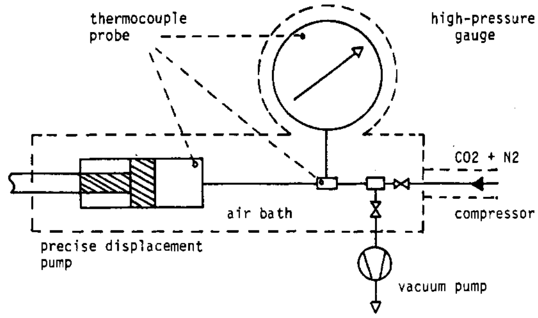

Figure 1. Schematic diagram of experimental apparatus.

Table I. Raw Data. Density of Mixture 25.2 mol % Carbon Dioxide and 74.9 mol % Nitrogen at 323 K

press., bar	density, g/cm³	press., bar	density, g/cm³	press., bar	density, g/cm³
490	0.4743	737	0.5779	1254	0.7082
500	0.4791	755	0.5839	1295	0.7155
510	0.4840	774	0.5899	1338	0.7230
520	0.4890	794	0.5961	1382	0.7306
530.5	0.4942	815	0.6024	1429	0.7384
541	0.4994	836	0.6088	1478	0.7464
552	0.5047	860	0.6154	1529	0.7546
563.5	0.5101	884	0.6221	1584	0.7629
576	0.5157	909	0.6289	1647	0.7714
589	0.5214	936	0.6360	1709	0.7801
603	0.5272	965	0.6431	1774	0.7890
616	0.5332	992	0.6505	1843	0.7981
631	0.5392	1024	0.6580	1921	0.8074
647	0.5455	1059	0.6657	2000	0.8169
663	0.5518	1095	0.6735	2086	0.8267
680	0.5583	1132	0.6816	2178	0.8367
699	0.5650	1173	0.6898	2223	0.8418
717	0.5718	1195	0.6940		
728	0.5753	1217	0.7010		

Table II. Raw Data. Density of Mixture 25.2 mol % Carbon Dioxide and 74.9 mol % Nitrogen at 348 K

press., bar	density, g/cm³	press., bar	density, g/cm³	press., bar	density, g/cm³
511	0.4534	758.5	0.5571	1260	0.6826
520	0.4580	775	0.5628	1299	0.6897
530	0.4627	793	0.5686	1340	0.6969
540	0.4675	814	0.5745	1382	0.7042
550.5	0.4724	835	0.5806	1427	0.7117
561	0.4774	855	0.5868	1474	0.7194
572	0.4825	878	0.5931	1525	0.7273
583	0.4877	901	0.5996	1577	0.7353
596	0.4930	926.5	0.6062	1635	0.7435
608	0.4984	952	0.6130	1694	0.7519
621	0.5040	980	0.6199	1755	0.7604
634	0.5097	1008	0.6269	1824	0.7692
648	0.5155	1038	0.6342	1896	0.7782
663	0.5214	1072	0.6416	1973	0.7874
679	0.5275	1108	0.6492	2053	0.7969
695	0.5338	1143	0.6569	2140	0.8064
711	0.5401	1182	0.6649	2188	0.8113
730	0.5467	1202	0.6689		
740	0.5500	1225	0.6757		

one or two chosen pressures at constant temperature. This procedure allowed an absolute density to be evaluated.

Results

Pressure–density data for three carbon dioxide–nitrogen mixtures are listed in Tables I–VI. All data were obtained at constant temperature (either 323 or 348 K). In this study each state point (density) was measured six times at the same thermodynamic condition (three increasing in pressure and three decreasing pressure values) and each point shown in tables is an average of these six independent measurements. The temperature gradients in the high-pressure apparatus were eliminated by waiting (approximately 10 min) to obtain equilibrium thermodynamic conditions after each step (changing volume and pressure). A thermocouple (within ±0.1 K accu-

Table III. Raw Data. Density of Mixture 57.0 mol % Carbon Dioxide and 43.3 mol % Nitrogen at 323 K

press., bar	density, g/cm³	press., bar	density, g/cm³	press., bar	density, g/cm³
633	0.6476	897	0.7362	1411	0.8448
648	0.6542	929	0.7447	1467	0.8540
664	0.6609	961	0.7534	1528	0.8634
682	0.6677	1037	0.7714	1593	0.8731
700	0.6747	1078	0.7807	1662	0.8829
720	0.6818	1098	0.7855	1735	0.8930
741	0.6890	1132	0.7935	1813	0.9033
763	0.6965	1172	0.8016	1897	0.9246
787	0.7041	1213	0.8098	2082	0.9357
812	0.7119	1258	0.8184	2186	0.9470
839	0.7198	1306	0.8269	2242	0.9527
868	0.7279	1357	0.5358		

Table IV. Raw Data. Density of Mixture 57.0 mol % Carbon Dioxide and 43.3 mol % Nitrogen at 348 K

press., bar	density, g/cm³	press., bar	density, g/cm³	press., bar	density, g/cm³
656	0.6149	940	0.7072	1433	0.8109
671	0.6212	971	0.7154	1487	0.8199
688	0.6275	1005	0.7239	1545	0.8290
706	0.6340	1041	0.7325	1608	0.8384
724	0.6406	1079	0.7413	1673	0.8479
743	0.6474	1098	0.7459	1743	0.8577
763	0.6543	1130	0.7534	1816	0.8678
784	0.6614	1154	0.7611	1897	0.8780
806	0.6686	1204	0.7690	1982	0.8885
831	0.6760	1244	0.7771	2072	0.8992
856	0.6835	1288	0.7853	2122	0.9047
882	0.6912	1334	0.7936		
910	0.6991	1383	0.8022		

Table V. Raw Data. Density of Mixture 74.3 mol % Carbon Dioxide and 25.3 mol % Nitrogen at 323 K

press., bar	density, g/cm³	press., bar	density, g/cm³	press., bar	density, g/cm³
564	0.7535	918	0.8666	1645	0.9937
585	0.7612	960	0.8767	1730	1.0047
603	0.7612	1005	0.8870	1822	1.0159
623	0.7769	1055	0.8976	1918	1.0274
646	0.7850	1110	0.9085	2023	1.0391
668	0.7933	1139	0.9140	2135	1.0511
692	0.8018	1190	0.9232	2241	1.0633
718	0.8104	1241	0.9327	2370	1.0759
746	0.8193	1297	0.9423	2508	1.0887
775	0.8283	1359	0.9522	2658	1.1019
807	0.8376	1423	0.9623	2737	1.1086
842	0.8470	1492	0.9725		
879	0.8567	1566	0.9830		

Table VI. Raw Data. Density of Mixture 74.3 mol % Carbon Dioxide and 25.3 mol % Nitrogen at 348 K

press., bar	density, g/cm³	press., bar	density, g/cm³	press., bar	density, g/cm³
606	0.7224	941	0.8307	1580	0.9526
624	0.7297	979	0.8404	1655	0.9631
643	0.7371	1020	0.8503	1733	0.9739
663	0.7448	1066	0.8604	1817	0.9848
682	0.7525	1113	0.8709	1907	0.9961
704	0.7605	1139	0.8762	2002	1.0076
723	0.7686	1180	0.8850	2107	1.0193
752	0.7769	1227	0.8941	2219	1.0313
779	0.7854	1277	0.9033	2338	1.0437
807	0.7940	1329	0.9128	2463	1.0563
838	0.8029	1387	0.9224	2527	1.0627
868	0.8119	1447	0.9323		
903	0.8212	1512	0.9423		

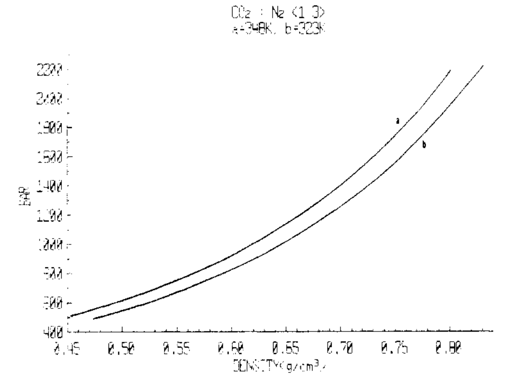

Figure 2. Pressure dependence vs density for a mixture 25.2 mol % carbon dioxide and 74.9 mol % nitrogen at (a) 348 K and (b) 323 K.

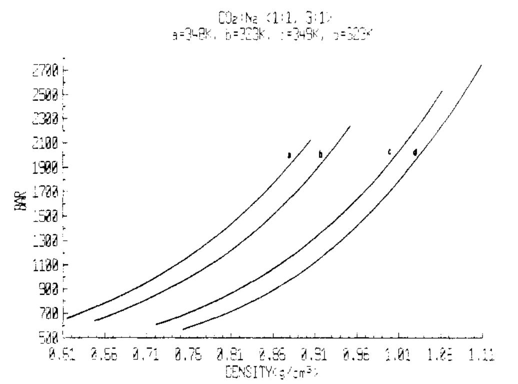

Figure 3. Pressure dependence of density for the following mixtures: (a) 57.0 mol % CO_2 and 43.3 mol % N_2 at 348 K; (b) 57.0 mol % CO_2 and 43.3 mol % N_2 at 323 K; (c) 74.3 mol % CO_2 and 25.3 mol % N_2 at 348 K; (d) 74.3 mol % CO_2 and 25.3 mol % N_2 at 323 K.

racy) and temperature controller were used to establish this time criteria. The same unsmoothed data was used to prepare graphs shown in Figures 2 and 3, which reflect the character of the pressure–density dependence of the gas mixtures. The density uncertainties increase from approximately 0.5% of density for low pressure (about 500 bar) to approximately 1% for high pressure (about 2000 bar). Comparison with literature data shows good conformity with the measurements of Haney and Bliss (*2*) for the low-pressure range. For the isotherms on

Table VII. Experimental Virial Coefficients for Mixtures of Carbon Dioxide and Nitrogen

mixture, mol %	T, K	B_m, cm^3/mol	C_m, cm^6/mol^2
CO_2:N_2 = 25.2:74.9	323	21.62	2121
CO_2:N_2 = 25.2:74.9	348	13.84	2062

Figures 2 and 3 polynomials up to order 20 were fitted and the second and third virial coefficients were found. The "best fit", with correct signs and values of the first and second virial coefficients, were obtained for polynomial order 18. The numerical values for this fit of the measurements for the mixture 25.2 mol % carbon dioxide and 74.9 mol % nitrogen are presented in Table VII. The values of the virial coefficients were obtained from the low-pressure data of Haney (*2*) and our high-pressure measurements.

The results from the B_m coefficient for the 1:3 mixture were compared with Gunn's data (*4*) and show about a 10% difference. The uncertainty of C_m coefficients is probably higher. The size of these errors is not suprising. The agreement between all experimental data and the polynomial fit is quite precise and very accurate within experimental uncertainty. For the other mixtures (1:1 and 3:1 at 323 and 348 K), accurate determination of the virial coefficients requires measurements down to at least a few bars (*2–5*). We do not have low-pressure data for these mixtures and therefore we have not included the values of the second and third virial coefficients for the other mixtures.

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Registry No. CO_2, 124-38-9; N_2, 7727-37-9.

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