Densities of Carbon Dioxide + Methane Mixtures from 225 K to 350 K at Pressures up to 35 MPa

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This paper reports *PVT* measurements for five gravimetrically prepared $CO_2 + CH_4$ mixtures. A continuously-weighed, high-pressure pycnometer was used to measure densities at temperatures from 225 K to 350 K in 25 K increments and pressures to 35 MPa with one set of measurements to 69 MPa. A detailed error analysis indicates that the accuracy of the densities is better than ±0.1%.

Introduction

This paper reports experimental density measurements for $CO_2 + CH_4$ mixtures at temperatures from 225 K to 350 K and pressures up to 35 MPa (one isotherm up to 69 MPa). Brugge *et al.* (1989) report Burnett data and virial coefficients at 300 K and 320 K. Esper *et al.* (1989) report Burnett-isochoric measurements from 205 K to 320 K and pressures from 0.1 MPa to 48 MPa. Standard thermodynamic procedures permit evaluation of other properties from the densities. GPA/GRI Research Report RR-138 authored by Hwang *et al.* (1995) contains: energies (internal, Helmholtz, and Gibbs), enthalpies, and entropies obtained from the data reduction method described by Duarte-Garza *et al.* (1997); second and third virial coefficients for both the pure compounds and the mixture. Additional *PVT* data for $CO_2 + CH_4$ mixtures have been measured by Netherlandse Gasunie, and Ruhrgas as reported by Jaeschke and Humphreys (1990).

Experimental Section

Materials. The carbon dioxide was Ultra Pure grade from Scientific Gas Products, Inc., with a purity better than 99.995 mol % with 40 ppm nitrogen and 40 ppm oxygen maximum. The sample was degassed by pumping with a vacuum over a frozen sample for a least 30 min. The methane was Ultra Pure grade from Scientific Gas Products, Inc., with a specified purity of better than 99.995 mol % with nitrogen as the principal impurity. Additional purification was not attempted for the methane.

Measurements. The data were measured using a pycnometer that consisted of a sample cell of known volume suspended from an electronic balance described in detail by Lau (1986) and Lau *et al.* (1997). Pressures were measured using pressure transducers that were calibrated *in-situ* against an automatic dead-weight gauge pressure standard. The accuracy of the pressure measurements was estimated to be ±0.006 MPa. Temperatures were measured with a four-lead platinum resistance thermometer that was adjacent to the sample cell on the inside surface of the compartment. The temperature was controlled to ±0.002 K and measured to an accuracy of ±0.005 K on ITS-90; thus, the even values reported in the table are correct within experimental error. The mole fractions of the mixtures, which were prepared gravimetrically, were accurate to ±0.000 05 excluding any effects of sample impurity. The uncertainties in the pycnometric density measurements arose from the uncertainties in the mass determinations and from the cell volume calibration. The error in the cell volume calibrations was about ±0.04%, which includes random errors introduced by uncertainties in the temperature and pressure measurements, uncertainties from using a calibrating fluid, and errors associated with mass determinations. The estimated accuracy (at 95% confidence limit) provided by Lau *et al.* (1997) in the pycnometric density measurements is

$$\Delta\rho = \{(0.15)^2 + (0.0004\rho)^2\}^{1/2}; \quad \rho \text{ in kg·m}^{-3}$$

or

$$\Delta\rho/\rho = [\{0.15/\rho\}^2 + 1.6 \times 10^{-7}]^{1/2}; \quad \rho \text{ in kg·m}^{-3}$$

Results and Conclusions

Table 1 contains densities and derived compression factors for four $CO_2 + CH_4$ mixtures measured at temperatures from 225 K to 450 K at pressures up to 35 MPa (with one isotherm to 69 MPa). The experimental values are state-of-the-art and generally accurate within ±0.1%. These results are suitable for both stringent testing and development of models and correlations and formed a significant contribution to the development of the American Gas Association Standard AGA-8.

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Table 1. Experimental *PVT* Values for CO_2 (A) + CH_4 (B) Mixtures Determined Using the Pycnometer. $M_{r,A}$ = 44.010, $M_{r,B}$ = 16.043

p/MPa	ρ/mol·m^{-3}	Z	p/MPa	ρ/mol·m^{-3}	Z	p/MPa	ρ/mol·m^{-3}	Z	p/MPa	ρ/mol·m^{-3}	Z
$x(CO_2)$ = 0.09826, M_r = 18.791											
T = 225.00 K											
32.234	19 839	0.8685	17.116	16 719	0.5472	8.504	9 586	0.4742	5.020	3 776	0.7107
27.431	19 121	0.7669	13.043	14 865	0.4691	6.785	6 208	0.5842	2.790	1 758	0.8486
21.910	18 061	0.6485	10.222	12 410	0.4403						
T = 250.00 K											
34.040	18 132	0.9032	19.265	14 369	0.6450	11.673	9 262	0.6063	6.150	3 843	0.7699
29.987	17 403	0.8290	16.544	13 039	0.6104	9.606	7 116	0.6494	4.067	2 306	0.8486
26.205	16 576	0.7606	13.751	11 138	0.5940	7.554	5 068	0.7171	1.827	941	0.9345
22.724	15 614	0.7002									
T = 275.00 K											
34.350	16 312	0.9210	22.103	12 940	0.7471	11.719	6 988	0.7335	6.206	3 230	0.8403
30.397	15 466	0.8596	17.963	11 029	0.7123	8.970	5 036	0.7789	4.132	2 024	0.8928
26.245	14 362	0.7992	14.546	8 970	0.7092						
T = 288.71 K											
69.471	19 899	1.4544	48.784	17 764	1.1440	28.093	13 844	0.8454	14.307	7 819	0.7623
62.575	19 291	1.3514	41.886	16 775	1.0402	21.203	11 408	0.7743	6.3116	3 040	0.8649
55.680	18 590	1.2478	34.793	15 520	0.9339						
T = 300.00 K											
34.350	14 607	0.9428	19.370	9 758	0.7958	11.789	5 793	0.8159	6.262	2 825	0.8886
30.414	13 653	0.8931	16.602	8 403	0.7921	9.714	4 645	0.8385	4.191	1 819	0.9238
26.275	12 441	0.8467	13.864	6 940	0.8009	7.645	3 536	0.8668	2.117	883	0.9615
22.818	11 220	0.8153									
T = 350.00 K											
32.059	11 300	0.9749	21.405	8 095	0.9087	12.479	4 728	0.9071	6.948	2 546	0.9379
28.363	10 308	0.9455	17.955	6 845	0.9014	9.727	3 634	0.9198	4.211	1 507	0.9606
24.851	9 247	0.9235	15.260	5 819	0.9011						
$x(CO_2)$ = 0.291 09, M_r = 24.184											
T = 225.00 K											
31.914	21 076	0.8094	22.054	19 724	0.5977	13.145	17 571	0.3999	9.946	16 016	0.3320
26.877	20 450	0.7025	17.116	18 729	0.4885						
T = 260.00 K											
34.401	18 686	0.8516	19.255	15 090	0.5903	11.706	9 984	0.5424	6.806	4 442	0.7088
30.357	18 015	0.7795	16.503	13 804	0.5530	9.970	7 939	0.5809	5.427	3 254	0.7716
26.142	17 155	0.7049	13.731	11 929	0.5325	8.216	5 878	0.6466	3.341	1 785	0.8659
22.697	16 260	0.6457									
T = 280.00 K											
34.339	17 122	0.8615	22.739	14 179	0.6889	13.787	9 257	0.6398	7.449	4 152	0.7707
30.391	16 333	0.7993	19.294	12 732	0.6509	11.722	7 571	0.6651	6.141	3 253	0.8110
26.178	15 285	0.7357	16.551	11 218	0.6338	9.636	5 831	0.7098	4.100	2 013	0.8750
T = 350.00 K											
34.545	12 590	0.9429	22.797	9 108	0.8601	11.812	4 633	0.8761	7.657	2 889	0.9109
30.402	11 532	0.9059	19.362	7 803	0.8527	9.703	3 738	0.8920	6.259	2 324	0.9254
26.263	10 297	0.8765	13.844	5 502	0.8647						
$x(CO_2)$ = 0.298 58, M_r = 24.393											
T = 300.00 K											
40.704	16 868	0.9674	27.606	14 021	0.7894	17.297	9 756	0.7108	7.557	3 661	0.8275
37.915	16 391	0.9274	24.151	12 892	0.7511	13.937	7 707	0.7250	5.557	2 554	0.8723
34.470	15 724	0.8789	20.733	11 503	0.7226	10.373	5 389	0.7716	3.323	1 441	0.9245
30.972	14 927	0.8318									
$x(CO_2)$ = 0.668 16, M_r = 34.729											
T = 225.00 K											
32.507	24 296	0.7152	22.569	23 585	0.5115	12.926	22 665	0.3049	6.866	21 883	0.1677
27.380	23 947	0.6112	16.979	23 089	0.3931	8.809	22 146	0.2126			
T = 250.00 K											
34.161	22 624	0.7264	24.745	21 712	0.5483	15.127	20 347	0.3577	8.886	18 760	0.2279
29.577	22 211	0.6406	19.956	21 114	0.4547	11.741	19 623	0.2879	7.507	18 165	0.1988
T = 275.00 K											
34.352	20 711	0.7254	19.974	18 402	0.4747	10.404	13 659	0.3331	8.702	10 303	0.3694
29.654	20 125	0.6444	15.885	17 215	0.4036	9.300	11 775	0.3454	8.016	8 331	0.4208
24.855	19 388	0.5607	12.466	15 564	0.3503						
T = 300.00 K											
34.390	18 667	0.7386	19.333	14 939	0.5188	11.783	9 088	0.5198	6.600	3 590	0.7371
30.405	17 997	0.6773	16.601	13 525	0.4921	10.076	6 975	0.5792	4.189	1 994	0.8424
26.238	17 122	0.6144	13.903	11 433	0.4875	8.364	5 124	0.6544	2.112	916	0.9244
22.749	16 183	0.5636									
T = 350.00 K											
34.268	14 789	0.7963	20.737	10 194	0.6990	11.797	5 270	0.7692	4.562	1 726	0.9081
29.650	13 586	0.7500	17.308	8 406	0.7076	9.153	3 853	0.8163	2.153	772	0.9579
24.834	11 968	0.7131	14.558	6 844	0.7310	6.975	2 789	0.8594			

Table 1. (Continued)

p/MPa	ρ/mol·m^{-3}	Z	p/MPa	ρ/mol·m^{-3}	Z	p/MPa	ρ/mol·m^{-3}	Z	p/MPa	ρ/mol·m^{-3}	Z
					$x(CO_2)$ = 0.901 12, M_r = 41.244						
					T = 225.00 K						
37.871	26 742	0.7570	22.618	26 077	0.4636	12.884	25 567	0.2694	6.194	25 149	0.1317
32.445	26 522	0.6539	17.680	25 829	0.3659	9.422	25 357	0.1986	3.211	24 942	0.0688
27.618	26 312	0.5611									
					T = 250.00 K						
31.317	24 701	0.6099	17.016	23 735	0.3449	9.831	23 083	0.2049	6.101	22 661	0.1295
26.251	24 393	0.5177	13.073	23 396	0.2688	7.873	22 869	0.1656	4.490	22 447	0.0962
21.472	24 070	0.4292									
					T = 275.00 K						
41.684	23 580	0.7731	24.576	22 232	0.4835	13.214	20 774	0.2782	7.659	19 520	0.1716
35.202	23 139	0.6654	20.383	21 784	0.4092	9.443	20 016	0.2063	6.233	19 009	0.1434
29.718	22 704	0.5725	16.736	21 323	0.3433						
					T = 300.00 K						
41.333	21 773	0.7611	21.973	19 382	0.4545	9.363	13 127	0.2860	7.357	5 660	0.5212
37.955	21 468	0.7088	17.911	18 513	0.3879	8.667	10 655	0.3261	6.771	4 621	0.5874
34.558	21 124	0.6559	13.751	17 139	0.3217	8.200	8 348	0.3938	5.726	3 379	0.6794
30.354	20 642	0.5895	10.916	15 402	0.2842	7.789	6 770	0.4613	4.024	2 028	0.7955
26.307	20 100	0.5247									
					T = 350.00 K						
44.924	18 656	0.8275	29.500	15 902	0.6375	15.418	9 094	0.5826	9.631	4 570	0.7242
39.439	17 877	0.7581	24.978	14 551	0.5899	13.568	7 558	0.6169	7.478	3 263	0.7876
34.474	17 013	0.6963	21.537	13 112	0.5645	11.381	5 816	0.6725	4.700	1 856	0.8704
29.632	15 941	0.6388	18.031	11 065	0.5600						

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