Densities of Carbon Dioxide + Ethane Mixtures from 240 K to 450 K at Pressures up to 35 MPa

W-W. R. Lau, Chih-An Hwang, James C. Holste, and Kenneth R. Hall*

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

Bruce E. Gammon and Kenneth N. Marsh†

Thermodynamics Research Center, Texas Engineering Experiment Station, College Station, Texas 77843-3111

This paper reports density measurements for CO_2, C_2H_6, and four gravimetrically prepared mixtures of CO_2 + C_2H_6. These results have been determined using a continuously-weighed pycnometer at temperatures from 240 K to 450 K at pressures up to 35 MPa. A detailed error analysis indicates that the accuracy of the densities is better than ± 0.1%.

Introduction

This paper contains experimental measurements of densities for $CO_2 + C_2H_6$ mixtures from 240 K to 450 K at pressures up to 35 MPa made with a continuously-weighed pycnometer. The results obtained for this system using a Burnett apparatus and the derived virial coefficients at 300 K and 320 K have been reported previously by Brugge *et al.* (1989). Enthalpy increments, measured with an enthalpy difference calorimeter, have been reported by Möller *et al.* (1993). Standard thermodynamic procedures permit the evaluation of other properties from these densities and other related data. GPA/GRI Research Report RR-139 authored by Lau *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 $CO_2 + C_2H_6$ mixtures have been reported by Jaeschke and Humphreys (1990) and Weber (1992).

Experimental Details

Materials. The carbon dioxide was Ultra Pure grade from Scientific Gas Products, Inc., with a purity exceeding 99.995 mol % with 40 ppm nitrogen and 40 ppm oxygen maximum contaminant concentrations. The sample was degassed by evacuating a frozen sample for a least 30 min. The ethane was Research Grade from Phillips Petroleum Company with a specified purity of better than 99.5 mol %. Gas chromatography analysis gave a purity of 99.6 mol %. The sample was purified by passing it through 3 Å molecular sieves. The final purity of the sample, determined chromatographically, was 99.995 mol %.

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

$$\sigma(\rho) = \{(0.15)^2 + (0.0004\rho)^2\}^{1/2}$$

or

$$\frac{\sigma(\rho)}{\rho} = \left\{\left(\frac{0.15}{\rho}\right)^2 + 1.6 \times 10^{-7}\right\}^{1/2}$$

where ρ has units of kg·m^{-3}.

Results and Conclusions

Table 1 contains the densities measured with the pycnometer and the derived compressibility factors for CO_2, C_2H_6, and the four $CO_2 + C_2H_6$ mixtures. The experimental *PVT* results reported here are state-of-the-art measurements and generally are accurate within ±0.1%. These results are suitable for the stringent testing and development of models and correlations. These results formed a significant contribution to the development of the American Gas Association Standard AGA-8.

* Corresponding author.
† Present address: Department of Chemical and Process Engineering, University of Canterbury, Private Bag 4800, Christchurch, New Zealand.

S0021-9568(97)00043-5 CCC: $14.00

Table 1. Experimental Densities and Derived Compressibility Factors for CO_2 (A) + C_2H_6 (B)

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
$x_A = 0.0$, $M_r = 30.0701$											
$T = 240.00$ K											
34.300	17 149	1.002 33	19.993	16 593	0.603 82	9.961	16 091	0.310 22	2.013	15 568	0.064 80
29.603	16 978	0.873 78	14.812	16 353	0.453 91	5.014	15 785	0.159 18	1.124	15 496	0.036 35
24.925	16 798	0.743 59									
$T = 260.00$ K											
34.298	16 461	0.963 84	24.809	16 037	0.715 61	14.965	15 482	0.447 14	4.955	14 666	0.156 29
29.829	16 271	0.848 04	19.969	15 783	0.585 27	10.153	15 138	0.310 25	2.012	14 316	0.065 01
$T = 280.00$ K											
34.296	15 772	0.934 04	24.981	15 268	0.702 80	14.424	14 483	0.427 79	7.067	13 621	0.222 86
29.575	15 530	0.818 01	19.636	14 908	0.565 77	10.180	14 041	0.311 43	4.282	13 101	0.140 39
$T = 300.00$ K											
33.955	15 032	0.905 59	24.179	14 365	0.674 80	15.682	13 532	0.464 60	6.799	11 759	0.231 80
31.087	14 857	0.838 86	20.035	14 002	0.573 64	11.547	12 932	0.357 97	4.636	10 266	0.181 04
27.632	14 625	0.757 46									
$T = 350.00$ K											
34.300	13 224	0.891 31	19.821	11 385	0.598 26	10.854	7 980	0.467 39	7.272	4 162	0.600 41
30.066	12 823	0.805 72	15.685	10 374	0.519 56	9.477	6 656	0.489 28	6.032	3 044	0.680 95
25.340	12 269	0.709 73	12.923	9 296	0.477 71	8.376	5 376	0.535 39	4.654	2 087	0.766 30
$x_A = 0.251\ 66$, $M_r = 33.5782$											
$T = 240.00$ K											
34.489	18 422	0.938 20	24.948	18 010	0.694 19	14.978	17 492	0.429 11	5.062	16 802	0.150 98
30.010	18 236	0.824 69	19.979	17 767	0.563 53	9.991	17 176	0.291 50	1.567	16 478	0.047 66
$T = 260.00$ K											
34.499	17 599	0.906 80	25.033	17 105	0.676 99	14.993	16 425	0.422 25	5.028	15 378	0.151 25
30.029	17 377	0.799 39	19.974	16 789	0.550 34	10.042	15 978	0.290 73	2.822	15 023	0.086 89
$T = 280.00$ K											
34.266	16 753	0.878 57	25.004	16 150	0.665 03	15.000	15 236	0.422 89	6.288	13 780	0.196 01
29.923	16 488	0.779 55	19.976	15 740	0.545 14	10.154	14 576	0.299 23	4.535	13 188	0.147 71
$T = 300.00$ K											
33.955	15 894	0.856 47	24.179	15 090	0.642 38	11.549	13 196	0.350 87	6.985	11 148	0.251 20
31.087	15 687	0.794 48	20.035	14 637	0.548 76	8.794	12 290	0.286 87	6.294	10 183	0.247 80
27.632	15 407	0.719 01	15.687	14 027	0.448 35						
$T = 350.00$ K											
34.520	13 767	0.861 64	16.645	10 384	0.550 83	9.824	5 858	0.576 28	5.687	2 575	0.758 93
29.860	13 218	0.776 28	14.162	9 244	0.526 46	8.639	4 773	0.621 97	4.257	1 774	0.824 61
24.953	12 480	0.687 08	12.435	8 127	0.525 79	7.107	3 531	0.691 65	2.913	1 131	0.885 06
20.114	11 465	0.602 87	11.097	7 034	0.542 13						
$x_A = 0.492\ 45$, $M_r = 36.9357$											
$T = 240.00$ K											
34.466	20 085	0.859 95	24.957	19 639	0.636 83	15.048	19 073	0.395 38	4.996	18 298	0.136 83
29.954	19 880	0.755 08	19.993	19 371	0.517 23	10.016	18 719	0.268 14	1.611	17 954	0.044 97
$T = 260.00$ K											
34.215	19 088	0.829 18	25.024	18 556	0.623 83	15.215	17 807	0.395 25	5.092	16 599	0.141 91
29.996	18 855	0.735 92	20.076	18 211	0.509 96	9.964	17 274	0.266 83	2.815	16 160	0.080 58
$T = 280.00$ K											
34.251	18 117	0.812 07	25.062	17 437	0.617 38	15.029	16 374	0.394 26	6.374	14 549	0.188 19
29.962	17 825	0.722 02	20.111	16 973	0.508 96	9.942	15 525	0.275 07	4.517	13 538	0.143 32
$T = 300.00$ K											
33.955	17 096	0.796 26	24.179	16 151	0.600 18	11.550	13 766	0.336 37	7.595	11 008	0.276 61
31.087	16 853	0.739 51	20.036	15 609	0.514 61	8.793	12 377	0.284 82	6.867	8 585	0.320 68
27.633	16 527	0.670 31	15.687	14 861	0.423 19						
$T = 350.00$ K											
34.641	14 555	0.817 85	20.370	11 765	0.594 97	13.020	7 980	0.560 67	7.790	3 759	0.712 13
30.035	13 906	0.742 20	17.236	10 563	0.560 72	11.030	6 320	0.599 73	5.922	2 591	0.785 41
25.004	12 977	0.662 11	14.942	9 332	0.550 21	9.570	5 099	0.644 95	4.164	1 678	0.852 74
$x_A = 0.739\ 78$, $M_r = 40.3874$											
$T = 240.00$ K											
34.457	22 551	0.765 71	24.990	22 097	0.566 74	15.001	21 519	0.349 34	4.954	20 761	0.119 58
29.937	22 343	0.671 46	19.987	21 825	0.458 93	10.060	21 178	0.238 05	1.708	20 452	0.041 85
$T = 260.00$ K											
34.250	21 380	0.741 04	25.148	20 826	0.558 58	14.959	20 022	0.345 61	5.040	18 841	0.123 74
29.823	21 124	0.653 08	19.999	20 450	0.452 38	9.959	19 503	0.236 21	2.984	18 475	0.074 71
$T = 280.00$ K											
34.153	20 198	0.726 32	25.074	19 478	0.552 95	15.072	18 356	0.352 70	6.894	16 643	0.177 93
30.059	19 897	0.648 92	20.114	18 985	0.455 09	9.962	17 465	0.245 01	4.716	15 630	0.129 60

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
					T = 300.00 K						
33.955	18 977	0.717 33	24.179	17 943	0.540 24	15.681	16 493	0.381 17	8.795	13 550	0.260 22
31.087	18 714	0.665 97	20.036	17 333	0.463 43	10.862	14 954	0.291 20	7.243	8 930	0.325 17
27.633	18 358	0.603 46									
					T = 350.00 K						
34.400	15 789	0.748 69	17.724	11 190	0.544 29	10.584	5 677	0.640 66	4.870	1 998	0.837 59
30.006	15 049	0.685 17	15.524	9 805	0.544 07	8.770	4 291	0.702 32	3.075	1 182	0.893 97
25.050	13 952	0.616 98	13.818	8 468	0.560 74	6.900	3 086	0.768 33	1.476	541	0.937 53
20.706	12 567	0.566 19	12.215	7 080	0.592 87						
					$x_A = 0.903\ 67$, $M_r = 42.6670$						
					T = 240.00 K						
34.512	24 848	0.696 04	25.032	24 406	0.513 99	15.283	23 873	0.320 82	5.013	23 174	0.108 41
29.826	24 636	0.606 71	19.938	24 141	0.413 89	10.066	23 540	0.214 29	1.684	22 893	0.036 86
					T = 260.00 K						
34.509	23 563	0.677 48	25.052	22 996	0.503 94	15.200	22 257	0.315 91	5.003	21 171	0.109 32
30.028	23 308	0.595 95	20.087	22 648	0.410 28	10.041	21 766	0.213 40	2.895	20 855	0.064 21
					T = 280.00 K						
34.300	22 208	0.663 42	25.439	21 509	0.508 03	15.065	20 382	0.317 49	6.883	18 863	0.156 74
30.103	21 896	0.590 54	20.215	21 001	0.413 47	10.058	19 582	0.220 63	4.834	18 184	0.114 19
					T = 300.00 K						
33.956	20 717	0.657 10	24.179	19 653	0.493 23	11.550	16 998	0.272 41	7.618	13 757	0.222 00
31.088	20 445	0.609 61	20.036	19 044	0.421 79	8.795	15 443	0.228 32	7.253	11 593	0.250 82
27.633	20 075	0.551 84	15.688	18 208	0.345 42						
					T = 350.00 K						
34.439	17 065	0.693 49	18.048	12 000	0.516 83	13.001	7 819	0.571 38	7.759	3 575	0.745 81
30.146	16 271	0.636 67	16.097	10 620	0.520 86	11.676	6 572	0.610 51	5.920	2 514	0.809 20
25.072	14 998	0.574 45	14.427	9 174	0.540 40	9.837	5 012	0.674 45	4.209	1 667	0.867 64
20.747	13 431	0.530 82									
					$x_A = 1.0$, $M_r = 44.0098$						
					T = 240.00 K						
34.452	26 559	0.650 06	25.064	26 148	0.480 36	15.081	25 644	0.294 71	5.095	25 029	0.102 01
29.992	26 370	0.569 97	20.050	25 906	0.387 85	10.072	25 355	0.199 07	1.592	24 778	0.032 20
					T = 260.00 K						
34.464	25 179	0.633 17	24.887	24 638	0.467 26	14.976	23 948	0.289 28	4.994	23 017	0.100 37
28.923	24 876	0.537 84	20.805	24 372	0.394 88	9.895	23 516	0.194 65	2.656	22 738	0.054 03
					T = 280.00 K						
34.048	23 730	0.616 31	20.046	22 588	0.381 20	10.174	21 359	0.204 61	4.537	20 208	0.096 44
30.132	23 450	0.551 94	14.855	22 017	0.289 82	6.241	20 625	0.129 98	4.170	20 077	0.089 22
25.063	23 049	0.467 08									
					T = 300.00 K						
33.956	22 203	0.613 12	27.633	21 582	0.513 31	20.036	20 606	0.389 82	11.554	18 803	0.246 35
31.088	21 936	0.568 17	24.180	21 180	0.457 69	15.689	19 846	0.316 93	7.418	16 615	0.178 99
					T = 350.00 K						
34.322	18 104	0.651 47	17.982	12 762	0.484 19	13.191	8 301	0.546 06	8.617	4 163	0.711 29
30.092	17 295	0.597 90	16.024	11 205	0.491 42	11.903	6 953	0.588 28	6.674	2 933	0.781 94
25.101	16 013	0.538 66	14.461	9 663	0.514 26	10.282	5 448	0.648 54	4.208	1 674	0.863 81
20.785	14 370	0.497 04									

Literature Cited

Brugge, H. B.; Hwang, C.-A.; Rogers, W. Holste; J. C.; Hall, K. R.; Lemming, W.; Esper, G. J.; Marsh, K. N.; Gammon, B. E. Experimental cross virial coefficients for binary mixtures of carbon dioxide with nitrogen, methane, and ethane at 300 and 320 K. *Physica* **1989**, *A156*, 382−416.

Duarte-Garza, H. A.; Hwang, C.-A.; Kidd, M. W.; Lau, W.-W. R.; Möller, D.; Eubank, P. T.; Holste, J. C.; Hall, K. R.; Gammon, B. E.; Marsh, K. N. Thermodynamic Properties of CO_2 + C_2H_6 Mixtures. GPA/GRI Report RR-139, 1995.

Jaeschke, M.; Humphreys, A. E. *GERG Technical Monograph 4, The GERG Databank of High Accuracy Compressibility Factor Measurements*; Verlag des Vereins Deutscher Ingenieure: Dusseldorf, Germany, 1990.

Lau, W.-W. R. A Continuously Weighed Pycnometer Providing Densities for Carbon Dioxide + Ethane Mixtures Between 240 and 350 K at Pressures Up to 35 MPa. Ph.D. Dissertation, Texas A&M University, College Station, TX 1986.

Lau, W.-W. R.; Hwang, C.-A.; Brugge, H. B.; Iglesias-Silva, G. A.; Duarte-Garza, H. A.; Rogers, W. J.; Hall, K. R.; Holste, J. C.; Gammon, B. E.; Marsh, K. N. A continuously weighed pycnometer for measuring fluid properties. *J. Chem. Eng. Data* **1997**, 42, 738−744.

Möller, D.; Gammon, B. E.; Marsh, K. N.; Hall, K. R.; Holste, J. C. Enthalpy increment measurements from flow calorimetry of CO_2 and of $\{xCO_2 + (1-x)C_2H_6\}$ from pressures of 15 MPa to 18 MPa between the temperatures 230 K and 350 K. *J. Chem. Thermodyn.* **1993**, *25*, 1273−1279.

Weber, L. A. Measurements of the virial coefficients and equation of state of the carbon dioxide + ethane system in the supercritical region. *Int. J. Thermophys.* **1992**, *13*, 1011−1032.

Received for review February 16, 1997. Accepted May 21, 1997.[⊗] The authors appreciate financial support from the Gas Research Institute, the Gas Processors Association and the Texas Engineering Experiment Station.

JE9700434

[⊗] Abstract published in *Advance ACS Abstracts,* July 1, 1997.