Isochoric $p-\rho-T$ Measurements on $\{(x)CO_2 + (1 - x)C_2H_6, x \approx 0.25, 0.49, 0.74\}$ from (220 to 400) K at Pressures to 35 MPa†

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The $p-\rho-T$ relationships were measured for binary hydrocarbon mixtures containing carbon dioxide (CO_2) and ethane (C_2H_6). Temperatures ranged from (220 to 400) K with pressures up to 35 MPa. Measurements of $p-\rho-T$ were conducted on compressed gaseous and liquid samples with the mole fraction compositions $\{(x)CO_2 + (1 - x)C_2H_6\}$ for $x = 0.251\,68$, 0.492 33, and 0.739 79. These mixtures were prepared gravimetrically to match, within 0.000 12 mole fraction, the compositions (0.251 66, 0.492 45, 0.739 78) of three mixtures which had been used by three laboratories for measurements of key thermophysical properties, including the density. For the $p-\rho-T$ apparatus used in this study, the uncertainty of the temperature is 0.03 K, and for pressure, it is 0.01% at $p > 3$ MPa and 0.05% at $p < 3$ MPa. The principal source of uncertainty in density is the cell volume (~28.5 cm^3), whose standard uncertainty is 0.003 cm^3. When all components of experimental uncertainty are considered, the expanded relative uncertainty (with a coverage factor $k = 2$ and thus a two-standard-deviation estimate) of the density measurements is estimated to be 0.05%.

Introduction

Mixtures of hydrocarbons and carbon dioxide are considered to be leading candidates to replace chlorofluorocarbon refrigerants, which are being phased out under the terms of the Montreal Protocol. Since mixtures containing sufficient amounts of carbon dioxide have acceptable flammability properties, they may find uses in refrigeration processes. Recently, Lemmon[1] analyzed the available data for numerous binary mixtures, including mixtures of carbon dioxide and ethane, and developed a Helmholtz mixture model[2] to represent these data. Lemmon noted that reliable published $p-\rho-T$ data were scarce for the saturated and compressed liquid phases of carbon dioxide + ethane mixtures, with much of the data exhibiting significant scatter from his mixture model. In an earlier study on carbon dioxide + ethane mixtures, carried out in the laboratories of NIST−Boulder, Texas A&M University, and NIST−Gaithersburg, heat capacities[3] C_v, densities,[4−6] and relative dielectric permittivities[6] ϵ_r were measured. Densities were reported from three different apparatus. Because the current work overlaps the ranges of temperature and pressure of the previous three studies, the present results will aid in estimating reasonable uncertainties for them.

In a recent bibliography, Diller and Magee[7] have documented reports of experimental studies of the density, enthalpy, viscosity, and thermal conductivity for this binary system. The total of all the published accurate thermophysical properties data for the $CO_2 + C_2H_6$ binary system makes it one of the most thoroughly studied for its properties. This conclusion is supported by the bibliographies in refs 1 and 7, which provide the number of data points and their ranges of temperatures and pressures.

Table 1. Mole Fraction Compositions and Molar Masses of $\{(x)CO_2 + (1 - x)C_2H_6\}$ Used in This Study

designation	x	molar mass/(g·mol^{-1})
NGAS1	0.492 33	36.933
NGAS2	0.251 68	33.578
NGAS3	0.739 79	46.228

Table 2. Expanded Uncertainties of the Measurements

temperature	0.03 K
pressure	
$p < 3$ MPa	0.05%
$p > 3$ MPa	0.01%
mass	0.002 g
volume	0.003 cm^3
composition, mole fraction	0.0002
density	0.05%

At the onset of this study, a decision was reached to match all three mixture compositions that were reported earlier in refs 4−6. Thus, more direct comparisons would become a possibility. If, after measurements, we compared densities from the three published sources and from this work, this would effectively constitute a round-robin study from which a consensus can be obtained for the recommended values of density for this important binary system. Thus, the chief goal of this work is to make benchmark measurements of densities for binary mixtures that supplement earlier $p-\rho-T$ data reported by this group on both pure carbon dioxide[8,9] and ethane.[10]

In this paper, new $p-\rho-T$ measurements for binary mixtures of carbon dioxide and ethane are reported for temperatures ranging from 220 K to a maximum temperature of 400 K, and at pressures up to 35 MPa.

Experimental Section

The $p-\rho-T$ apparatus used in this work has been used for studies of both pure fluids and mixtures. Details of the

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Table 3. Experimental Densities (ρ) for $\{(x)CO_2 + (1 - x)C_2H_6\}$ as a Function of Temperature (T, ITS-90) and Pressure (p)

T/K	p/MPa	ρ/(mol·dm^{-3})	T/K	p/MPa	ρ/(mol·dm^{-3})	T/K	p/MPa	ρ/(mol·dm^{-3})	T/K	p/MPa	ρ/(mol·dm^{-3})
					$x = 0.492\ 33$						
220.001	7.0743	19.7702	251.001	7.6962	17.7007	315.999	29.9507	15.8235	330.000	17.5148	12.5580
220.001	7.0736	19.7702	252.001	8.3768	17.6966	320.000	31.9430	15.8178	340.000	20.3345	12.5457
220.002	7.0726	19.7702	253.000	9.0526	17.6922	324.000	33.9290	15.8122	349.999	23.1568	12.5340
220.000	7.0735	19.7702	254.002	9.7237	17.6877	280.000	7.1126	14.7875	359.999	25.9776	12.5228
221.001	8.0431	19.7649	256.000	11.0621	17.6785	281.000	7.5169	14.7850	370.001	28.7913	12.5119
222.000	9.0025	19.7591	258.001	12.4112	17.6704	281.999	7.9206	14.7823	380.002	31.5952	12.5010
223.000	9.9470	19.7530	260.001	13.7693	17.6636	282.999	8.3253	14.7796	390.001	34.3859	12.4902
224.002	10.8945	19.7468	264.000	16.5061	17.6525	283.999	8.7282	14.7768	320.001	11.5740	10.8349
226.000	12.8035	19.7360	268.000	19.2554	17.6434	286.000	9.5351	14.7709	330.002	13.6312	10.8210
228.001	14.7557	19.7276	272.000	22.0020	17.6353	288.002	10.3431	14.7649	339.998	15.6997	10.8089
230.000	16.7289	19.7208	275.999	24.7499	17.6279	292.000	11.9624	14.7534	349.999	17.7748	10.7980
232.000	18.7114	19.7148	280.001	27.4856	17.6208	295.999	13.5889	14.7440	360.002	19.8520	10.7878
236.000	22.6761	19.7046	284.000	30.2160	17.6140	300.000	15.2238	14.7359	370.000	21.9275	10.7780
239.999	26.6404	19.6955	260.001	6.9857	16.8741	303.999	16.8640	14.7287	380.000	23.9996	10.7684
244.001	30.5875	19.6870	261.000	7.5734	16.8708	307.999	18.5097	14.7222	390.001	26.0682	10.7589
248.001	34.5153	19.6790	261.999	8.1614	16.8672	312.000	20.1537	14.7161	399.998	28.1298	10.7495
230.000	7.1301	19.1366	262.999	8.7475	16.8634	316.000	21.7986	14.7103	320.001	8.6235	6.8540
230.999	7.9999	19.1318	264.001	9.3315	16.8594	320.001	23.4425	14.7046	320.000	8.6237	6.8540
232.002	8.8623	19.1266	266.000	10.4944	16.8512	329.999	27.5500	14.6911	330.000	9.6275	6.8447
233.001	9.7135	19.1210	268.000	11.6577	16.8435	339.999	31.6411	14.6780	340.000	10.6236	6.8352
233.999	10.5682	19.1153	272.001	14.0100	16.8308	290.002	9.3301	14.2151	350.001	11.6139	6.8262
235.998	12.2783	19.1050	276.000	16.3733	16.8209	292.001	10.0612	14.2096	359.999	12.5977	6.8178
238.000	14.0205	19.0967	279.999	18.7451	16.8126	295.999	11.5256	14.1987	370.001	13.5760	6.8101
239.999	15.7780	19.0898	283.999	21.1113	16.8051	300.002	12.9975	14.1893	380.000	14.5483	6.8029
244.001	19.3187	19.0787	288.001	23.4851	16.7980	304.000	14.4772	14.1813	389.999	15.5175	6.7960
248.000	22.8627	19.0694	291.999	25.8526	16.7913	308.000	15.9627	14.1743	400.000	16.4816	6.7893
252.001	26.4042	19.0609	296.000	28.2134	16.7849	311.999	17.4511	14.1678	320.001	6.2069	3.5565
256.000	29.9259	19.0530	300.000	30.5691	16.7786	315.999	18.9425	14.1618	330.000	6.6339	3.5529
260.001	33.4348	19.0454	304.000	32.9261	16.7724	320.001	20.4362	14.1568	340.001	7.0545	3.5492
240.000	6.9935	18.4444	306.001	34.0962	16.7694	330.000	24.1685	14.1432	349.999	7.4699	3.5453
241.001	7.7689	18.4401	270.001	6.9955	15.9221	340.000	27.8937	14.1304	359.999	7.8802	3.5414
241.999	8.5389	18.4355	271.001	7.4927	15.9191	350.001	31.6079	14.1179	369.998	8.2865	3.5373
243.000	9.3016	18.4305	272.000	7.9887	15.9161	300.000	10.8992	13.4911	379.998	8.6885	3.5331
243.999	10.0612	18.4254	273.000	8.4860	15.9128	302.001	11.5464	13.4864	390.001	9.0868	3.5288
245.999	11.5839	18.4155	274.000	8.9785	15.9094	304.000	12.1955	13.4820	399.999	9.4815	3.5244
248.000	13.1180	18.4071	276.001	9.9653	15.9024	308.001	13.4968	13.4739	320.002	3.1895	1.4217
249.998	14.6708	18.4002	279.998	11.9411	15.8888	312.000	14.8054	13.4669	329.999	3.3290	1.4205
252.002	16.2301	18.3943	284.000	13.9302	15.8778	316.001	16.1168	13.4605	340.000	3.4671	1.4193
255.999	19.3594	18.3843	288.000	15.9289	15.8689	320.000	17.4320	13.4546	349.999	3.6044	1.4181
260.000	22.4931	18.3756	292.000	17.9344	15.8611	329.999	20.7258	13.4411	359.998	3.7405	1.4169
264.000	25.6203	18.3677	295.999	19.9400	15.8541	340.001	24.0135	13.4292	370.001	3.8755	1.4157
268.000	28.7373	18.3602	300.000	21.9491	15.8475	350.002	27.3044	13.4172	380.001	4.0101	1.4144
272.000	31.8474	18.3529	304.001	23.9538	15.8413	360.000	30.5842	13.4052	390.000	4.1438	1.4131
273.999	33.3949	18.3494	308.001	25.9567	15.8352	370.000	33.8559	13.3936	399.999	4.2767	1.4118
250.002	7.0188	17.7046	312.001	27.9569	15.8293	320.000	14.7051	12.5719			
					$x = 0.251\ 68$						
220.000	6.8095	17.9971	272.000	29.6856	16.8011	324.002	32.6338	14.7039	308.001	8.5827	10.9408
220.999	7.6680	17.9917	276.001	32.5393	16.7949	328.000	34.5346	14.6988	312.000	9.4721	10.9330
222.001	8.5137	17.9858	279.999	35.3773	16.7888	280.000	6.7941	13.8891	316.000	10.3670	10.9257
223.001	9.3539	17.9798	250.001	6.8184	16.2596	281.999	7.5855	13.8836	319.999	11.2681	10.9192
224.001	10.2032	17.9741	252.001	8.0628	16.2512	284.001	8.3746	13.8776	330.000	13.5390	10.9057
226.002	11.9390	17.9650	254.001	9.2976	16.2420	285.999	9.1633	13.8712	340.002	15.8178	10.8953
228.000	13.7116	17.9580	256.000	10.5382	16.2335	288.000	9.9518	13.8658	350.000	18.1124	10.8849
230.000	15.5019	17.9523	258.000	11.7969	16.2267	289.999	10.7441	13.8597	360.001	20.4114	10.8750
232.000	17.2967	17.9473	260.001	13.0643	16.2210	292.001	11.5401	13.8549	370.000	22.7089	10.8655
233.999	19.0960	17.9427	261.999	14.3362	16.2161	296.001	13.1391	13.8468	380.002	25.0035	10.8561
235.998	20.8941	17.9385	264.000	15.6143	16.2118	300.001	14.7456	13.8399	389.999	27.2954	10.8468
238.001	22.6916	17.9344	266.000	16.8929	16.2078	303.998	16.3545	13.8336	400.001	29.5787	10.8374
240.002	24.4846	17.9306	268.000	18.1699	16.2041	308.000	17.9668	13.8279	310.001	6.7994	7.0459
241.998	26.2719	17.9269	272.001	20.7312	16.1970	312.000	19.5783	13.8224	312.002	7.0136	7.0441
243.999	28.0587	17.9232	276.002	23.2840	16.1905	316.000	21.1934	13.8172	314.002	7.2280	7.0423
246.000	29.8397	17.9197	280.000	25.8296	16.1842	319.999	22.8030	13.8120	316.001	7.4427	7.0404
248.000	31.6150	17.9162	284.000	28.3713	16.1781	323.998	24.4123	13.8070	320.000	7.8708	7.0366
250.000	33.3889	17.9128	288.001	30.9009	16.1722	328.001	26.0201	13.8021	330.001	8.9380	7.0288
252.002	35.1485	17.9094	291.999	33.4143	16.1664	332.001	27.6236	13.7973	340.000	10.0036	7.0183
230.002	6.8241	17.4587	259.998	6.6976	15.5618	336.002	29.2289	13.7925	349.998	11.0670	7.0089
231.001	7.6085	17.4539	262.002	7.7971	15.5547	340.000	30.8267	13.7877	359.999	12.1276	7.0007
232.000	8.3737	17.4485	264.000	8.8812	15.5465	344.000	32.4249	13.7829	370.000	13.1857	6.9932
233.002	9.1434	17.4430	266.002	9.9679	15.5384	348.000	34.0187	13.7782	380.001	14.2405	6.9862
234.000	9.9066	17.4375	268.000	11.0624	15.5316	289.999	6.7091	12.6834	389.999	15.2926	6.9795
235.999	11.4702	17.4286	270.001	12.1651	15.5258	292.000	7.3304	12.6791	400.002	16.3414	6.9730
237.998	13.0579	17.4216	272.000	13.2730	15.5208	294.000	7.9517	12.6742	320.000	6.2278	4.0468
240.001	14.6678	17.4159	276.000	15.5006	15.5125	295.999	8.5727	12.6692	329.999	6.7454	4.0422
241.999	16.2822	17.4110	280.002	17.7319	15.5052	298.000	9.1944	12.6639	340.001	7.2551	4.0373
244.001	17.9028	17.4065	284.002	19.9637	15.5017	300.000	9.8188	12.6589	349.998	7.7577	4.0323
245.999	19.5200	17.4023	287.999	22.1943	15.4925	303.999	11.0740	12.6500	359.998	8.2542	4.0270
248.001	21.1333	17.3984	292.000	24.4194	15.4866	308.000	12.3343	12.6426	369.999	8.7451	4.0216
249.999	22.7445	17.3946	295.998	26.6395	15.4808	312.001	13.6026	12.6362	380.000	9.2310	4.0161

Table 3. (Continued)

T/K	*p*/MPa	*ρ*/(mol·dm^{-3})	*T*/K	*p*/MPa	*ρ*/(mol·dm^{-3})	*T*/K	*p*/MPa	*ρ*/(mol·dm^{-3})	*T*/K	*p*/MPa	*ρ*/(mol·dm^{-3})
					$x = 0.251\ 68$						
252.002	24.3574	17.3910	300.000	28.8549	15.4752	316.001	14.8762	12.6304	390.002	9.7130	4.0107
254.002	25.9727	17.3875	303.999	31.0627	15.4696	320.000	16.1493	12.6250	399.999	10.1919	4.0056
256.000	27.5731	17.3841	308.001	33.2624	15.4642	324.002	17.4279	12.6199	320.000	4.6247	2.4252
258.000	29.1746	17.3807	312.000	35.4560	15.4588	328.002	18.7056	12.6151	329.999	4.8951	2.4229
260.000	30.7723	17.3774	270.002	6.8171	14.8041	332.000	19.9685	12.6110	340.000	5.1621	2.4206
262.000	32.3642	17.3741	272.000	7.7646	14.7977	336.001	21.2459	12.6063	349.999	5.4258	2.4182
263.999	33.9557	17.3709	274.000	8.7078	14.7905	339.999	22.5238	12.6018	359.999	5.6867	2.4158
240.000	6.8180	16.8826	276.000	9.6475	14.7833	344.000	23.8010	12.5973	370.000	5.9451	2.4133
240.998	7.5221	16.8783	278.000	10.5908	14.7767	347.999	25.0786	12.5929	380.002	6.2010	2.4108
242.001	8.2183	16.8734	280.000	11.5397	14.7711	352.001	26.3547	12.5885	390.001	6.4546	2.4082
243.999	9.6007	16.8634	281.999	12.4974	14.7663	356.001	27.6290	12.5842	400.000	6.7064	2.4055
246.001	11.0013	16.8546	284.000	13.4535	14.7620	360.002	28.9014	12.5798	319.999	2.7626	1.2307
248.000	12.4169	16.8476	288.000	15.3769	14.7553	364.001	30.1726	12.5755	330.001	2.8824	1.2296
250.002	13.8504	16.8419	292.000	17.3019	14.7478	368.000	31.4415	12.5712	340.001	3.0009	1.2286
251.999	15.2922	16.8370	295.999	19.2290	14.7417	372.001	32.7067	12.5669	350.002	3.1186	1.2276
254.001	16.7348	16.8327	300.002	21.1537	14.7358	376.001	33.9700	12.5626	360.000	3.2354	1.2266
256.002	18.1797	16.8286	304.000	23.0783	14.7302	380.001	35.2313	12.5583	370.001	3.3515	1.2255
258.000	19.6250	16.8247	308.000	24.9954	14.7248	300.000	6.8226	10.9553	379.998	3.4669	1.2244
259.998	21.0690	16.8211	312.000	26.9115	14.7195	302.001	7.2588	10.9520	389.999	3.5817	1.2233
264.000	23.9505	16.8141	316.000	28.8224	14.7142	304.002	7.6977	10.9484	400.001	3.6960	1.2222
268.001	26.8248	16.8074	320.000	30.7312	14.7091	306.000	8.1394	10.9447			
					$x = 0.739\ 79$						
220.000	6.8478	22.2807	254.002	10.0104	19.9070	288.000	10.5410	16.5845	339.999	13.7363	9.6722
220.999	7.9943	22.2749	256.000	11.5747	19.8957	290.001	11.4630	16.5773	350.000	15.3357	9.6607
222.000	9.1234	22.2684	258.001	13.1431	19.8853	292.001	12.3868	16.5702	360.002	16.9328	9.6503
223.000	10.2405	22.2613	259.999	14.7246	19.8767	296.000	14.2425	16.5581	370.000	18.5262	9.6407
224.001	11.3374	22.2535	264.000	17.9268	19.8633	300.001	16.1101	16.5482	380.000	20.1152	9.6315
225.999	13.5525	22.2396	267.999	21.1471	19.8525	304.001	17.9857	16.5397	390.002	21.6978	9.6226
228.000	15.8297	22.2290	272.001	24.3653	19.8431	308.000	19.8676	16.5320	400.000	23.2737	9.6139
230.000	18.1390	22.2206	276.000	27.5842	19.8344	312.001	21.7490	16.5249	310.001	7.8826	6.5376
232.001	20.4460	22.2135	280.002	30.7928	19.8261	316.001	23.6310	16.5181	312.000	8.0725	6.5362
234.000	22.7791	22.2072	284.000	33.9929	19.8181	320.000	25.5097	16.5116	313.999	8.2615	6.5346
236.001	25.0982	22.2014	260.002	6.7645	18.9678	324.001	27.3926	16.5053	316.000	8.4503	6.5331
238.002	27.4302	22.1959	261.000	7.4520	18.9641	327.999	29.2712	16.4991	318.000	8.6377	6.5315
240.000	29.7630	22.1908	262.000	8.1403	18.9603	332.000	31.1463	16.4930	320.000	8.8248	6.5300
242.001	32.0828	22.1857	263.001	8.8247	18.9560	335.999	33.0248	16.4870	329.999	9.7503	6.5239
244.000	34.3964	22.1808	264.001	9.5094	18.9514	339.999	34.8935	16.4810	340.002	10.6636	6.5150
230.002	6.8035	21.5534	266.001	10.8636	18.9417	290.000	6.8578	14.5272	350.001	11.5659	6.5059
231.000	7.8268	21.5482	268.000	12.2172	18.9319	291.999	7.5061	14.5231	359.998	12.4590	6.4971
232.001	8.8452	21.5424	269.998	13.5755	18.9232	293.999	8.1588	14.5187	370.001	13.3440	6.4889
233.000	9.8516	21.5360	271.999	14.9423	18.9158	295.999	8.8152	14.5141	380.001	14.2227	6.4813
234.000	10.8457	21.5291	276.001	17.7030	18.9039	298.001	9.4736	14.5091	390.001	15.0959	6.4741
236.001	12.8374	21.5157	279.999	20.4708	18.8940	300.001	10.1359	14.5039	399.999	15.9631	6.4673
237.999	14.8531	21.5050	284.000	23.2418	18.8852	302.002	10.7975	14.4984	320.000	7.5108	4.6615
240.001	16.9072	21.4966	288.000	26.0096	18.8771	304.002	11.4610	14.4929	330.001	8.1077	4.6567
241.999	18.9724	21.4895	291.999	28.7751	18.8693	307.999	12.7952	14.4825	340.000	8.6943	4.6514
243.999	21.0538	21.4833	296.001	31.5331	18.8618	311.998	14.1381	14.4733	349.999	9.2721	4.6459
246.001	23.1327	21.4775	299.999	34.2855	18.8545	315.999	15.4870	14.4652	360.001	9.8424	4.6401
248.000	25.2130	21.4721	270.001	6.8381	17.9862	320.001	16.8393	14.4581	370.002	10.4058	4.6341
250.000	27.2905	21.4670	271.001	7.4159	17.9830	324.000	18.1956	14.4515	379.999	10.9627	4.6280
252.000	29.3625	21.4621	272.000	7.9943	17.9796	328.000	19.5573	14.4453	389.999	11.5137	4.6219
254.001	31.4331	21.4574	273.000	8.5699	17.9760	332.000	20.9196	14.4394	400.000	12.0611	4.6158
256.000	33.4954	21.4528	274.001	9.1460	17.9722	335.999	22.2804	14.4337	319.999	5.5705	2.8649
239.999	6.8431	20.7764	276.000	10.2936	17.9640	340.001	23.6318	14.4289	330.000	5.8912	2.8622
241.001	7.7549	20.7717	277.998	11.4391	17.9553	344.000	24.9944	14.4236	340.001	6.2075	2.8595
242.000	8.6607	20.7665	280.000	12.5851	17.9470	348.001	26.3568	14.4183	350.000	6.5197	2.8567
243.001	9.5640	20.7610	283.999	14.8879	17.9332	352.001	27.7182	14.4130	360.000	6.8283	2.8539
244.000	10.4517	20.7547	288.001	17.2112	17.9225	355.998	29.0788	14.4078	370.001	7.1338	2.8510
246.002	12.2236	20.7423	292.002	19.5410	17.9134	360.002	30.4385	14.4027	380.000	7.4362	2.8480
247.999	14.0141	20.7316	296.000	21.8763	17.9052	364.002	31.7949	14.3976	389.999	7.7361	2.8450
250.000	15.8261	20.7232	300.000	24.2082	17.8975	371.999	34.5029	14.3874	399.999	8.0334	2.8419
252.000	17.6552	20.7160	304.001	26.5450	17.8902	300.001	7.3574	9.7247	320.001	3.0636	1.3327
254.000	19.4942	20.7098	308.000	28.8747	17.8832	302.000	7.6712	9.7224	330.000	3.1920	1.3316
256.001	21.3312	20.7041	312.000	31.1986	17.8763	304.000	7.9871	9.7200	339.998	3.3192	1.3305
260.002	25.0147	20.6939	316.000	33.5200	17.8696	306.000	8.3047	9.7176	350.000	3.4453	1.3294
264.001	28.6910	20.6847	280.002	6.8517	16.6094	308.001	8.6224	9.7151	360.000	3.5708	1.3283
268.000	32.3546	20.6759	281.000	7.3110	16.6068	310.000	8.9409	9.7125	370.001	3.6953	1.3272
250.001	6.8347	19.9260	282.001	7.7738	16.6040	312.001	9.2598	9.7099	380.000	3.8191	1.3260
251.000	7.6352	19.9218	283.000	8.2342	16.6011	316.002	9.8996	9.7043	390.001	3.9421	1.3249
252.001	8.4295	19.9172	284.000	8.6964	16.5980	320.000	10.5340	9.7003	400.000	4.0645	1.3237
253.000	9.2245	19.9124	286.002	9.6172	16.5916	330.002	12.1353	9.6855			

apparatus are available in previous publications.[11,12] An isochoric technique was employed to measure the single-phase densities in this study. In this method, a sample of fixed mass is confined in a container of nearly fixed volume. Details of this method are available in recent publications.[13−15]

Materials. The gas mixtures were prepared gravimetrically in thoroughly cleaned and dried aluminum cylinders, each with a free volume of about 16 dm^3 and a tare mass of about 14.5 kg. All gases were of high purity and were analyzed before use by gas chromatography/mass spectrometry. Each gas was added to the mixture sequentially while the cylinder rested on a load cell having a resolution in the mass of 10^{-4} kg, followed by a precise weighing with an equal-arm balance with a capacity of 25 kg. The amount of each component added to a cylinder was determined by difference weighings using a Class S weight set and the equal-arm balance. An evacuated identical cylinder was used as a ballast on the opposite pan. On the basis of repetitive weighings, the expanded uncertainty in the amount of each substance was estimated to be 5 mg. As the expanded uncertainty in the Class S weights is approximately 0.05 mg, the uncertainty primarily depends on the random scatter in the weighings. Nonetheless, the relative uncertainty of a mole fraction composition is likely to be considerably higher due to the presence of impurities in the component gases.

A cylinder of gas was prepared for each mixture with the target CO_2 compositions of $x = 0.251\,66$, 0.492 45, and 0.739 78, which are the compositions from the previous study begun in 1985. The final pressure of each gas mixture was close to 90% of the estimated dew-point pressure for each mixture. This dew point was calculated with an extended corresponding states model.[16] Approximately 40 mol of each gas mixture was prepared for this study. Table 1 provides the mole fraction compositions and molar mass for each gas mixture, where each value is quoted to within the precision of the measurements.

The purities of the components used to make the mixtures are an important aspect of this study. The purity of the carbon dioxide sample was 0.999 987 mole fraction. According to an analysis by the supplier, the largest impurity was water at 7.5 parts per million by mole (ppm). Nitrogen, oxygen, helium, and hydrogen were below the 1 ppm detection limit; methane and carbon monoxide were below the 0.1 ppm detection limit. The purity of the ethane sample used in the mixtures was 0.999 985 mole fraction. From the supplier's analysis, the largest impurities were ethylene with a concentration of 6 ppm and carbon monoxide/carbon dioxide with 2 ppm. The measured concentrations of nitrogen, oxygen, methane, and water were less than 2 ppm for each substance. No hydrogen was detected. On the basis of these analyses, the average molar masses of the samples were calculated. Because the calculated average molar masses for both the ethane and carbon dioxide samples differ from the well-established molar mass of each pure species by less than 5 ppm, the net effect of impurities on the mixture molar masses in Table 1 is negligible. The mixture molar masses in Table 1 were used to convert the density measurements from mass to molar units.

Results

Assessment of Uncertainties. A detailed discussion of the uncertainties in measured quantities is available in recent publications.[13−15] The effect of sample impurities on the uncertainty in mixture compostion was calculated from a molar balance based on the impurities discussed in the previous section. We use a definition for the expanded uncertainty which is twice the standard uncertainty (a coverage factor $k = 2$ and thus a two-standard-deviation estimate). The expanded uncertainties of the original measurements and the resulting combined uncertainties are shown in Table 2.

p−ρ−T Measurements. The experimental compositions, temperatures, pressures, and densities for single-phase fluid mixtures are presented in Table 3. In this table, the values are quoted within the reproducibility of the measurements to better accommodate regression analysis of these data. To illustrate the range of measurements for each of the mixtures, the data points are plotted in Figures 1−3.

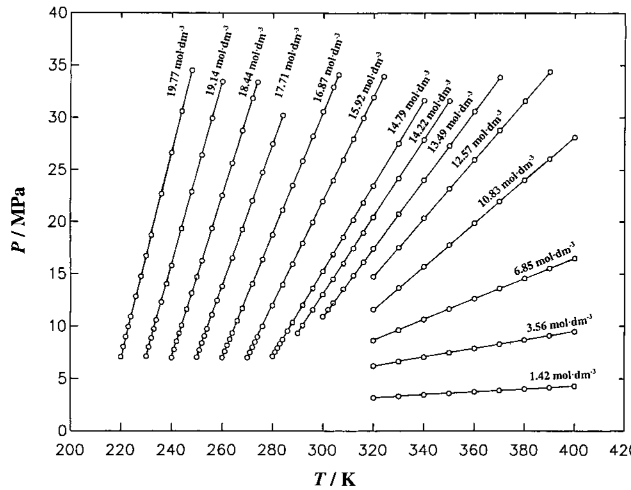

Figure 1. Range of $p-\rho-T$ measurements for $\{(x)CO_2 + (1 - x)C_2H_6\}$, $x = 0.492\,33$.

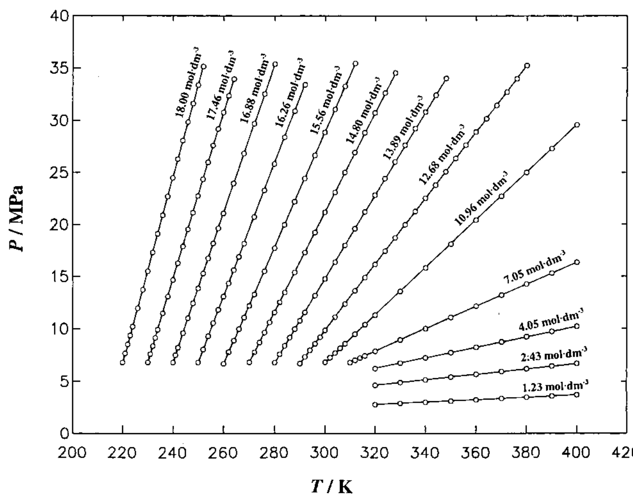

Figure 2. Range of $p-\rho-T$ measurements for $\{(x)CO_2 + (1 - x)C_2H_6\}$, $x = 0.251\,68$.

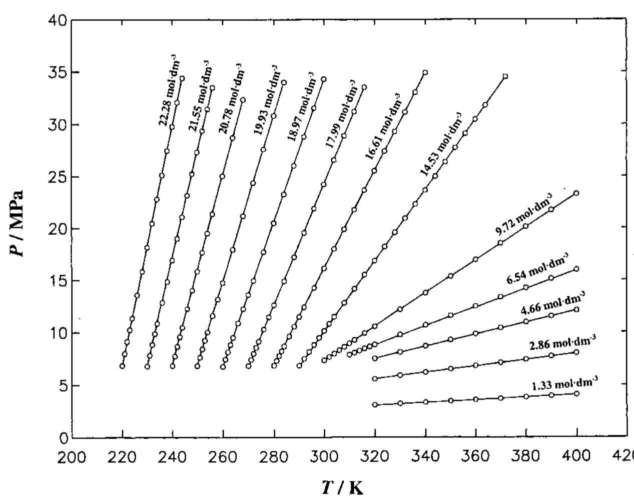

Figure 3. Range of $p-\rho-T$ measurements for $\{(x)CO_2 + (1 - x)C_2H_6\}$, $x = 0.739\,79$.

Comparisons of the isochoric $p-\rho-T$ measurements with published data for $\{(x)CO_2 + (1 - x)C_2H_6\}$ have been

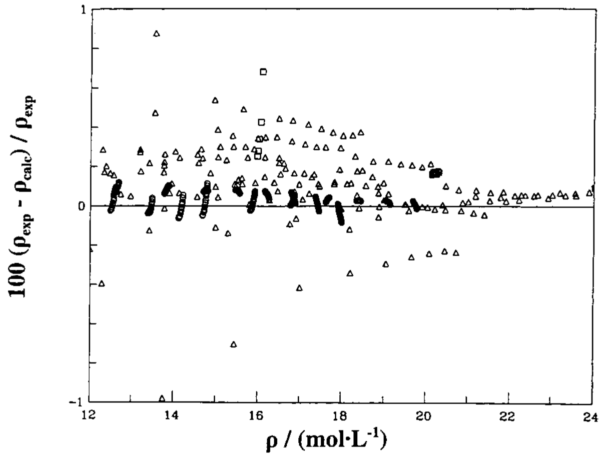

Figure 4. Percentage deviations of experimental liquid densities for $\{(x)CO_2 + (1 - x)C_2H_6\}$ (○, this work; △, Lau et al.;[5,18] □, Sherman et al.[19]) from the values calculated with the Helmholtz energy model of Lemmon and Jacobsen.[17]

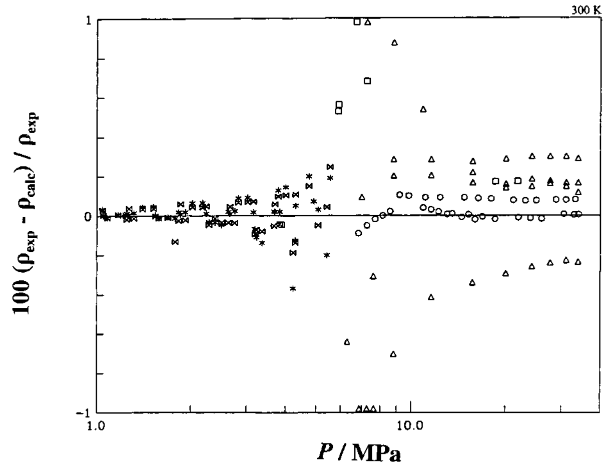

Figure 5. Percentage deviations of experimental supercritical fluid densities at $T = 300$ K for $\{(x)CO_2 + (1 - x)C_2H_6\}$ (○, this work; △, Lau et al.;[5,18] □, Sherman et al.;[19] ⋈, Brugge et al.;[21] ∗, Lemming[22]) from the values calculated with the Helmholtz energy model of Lemmon and Jacobsen.[17]

facilitated with a new preliminary Helmholtz energy formulation developed by Lemmon and Jacobsen[17] for mixtures containing CO_2. This model, which is similar to the earlier model given in ref 2, uses reference equations of state to anchor the pure component states. For mixtures, it uses a new Helmholtz energy mixture model consisting of a generalized excess function with five coefficients and three binary parameters for the $CO_2 + C_2H_6$ mixture. The generalized function is applicable to all binary mixtures containing CO_2. The mixture model was fitted to this work and to published density data for carbon dioxide + ethane mixtures. Lemmon and Jacobsen have pointed out that, aside from mixtures containing hydrogen or helium, mixtures of carbon dioxide with hydrocarbons are among the most difficult systems to model among the major components in natural gas systems, and work is in progress to improve the models with new correlating equations. Comparisons with this model, depicted in Figures 4−6, show that the model represents the present data within ±0.15%, except in the critical region. There is fair agreement (with most deviations less than ±0.4%) with the liquid densities from Lau et al.[5,18] (same compositions as this work) and Sherman et al.[19] ($x = 0.99$) shown in Figure 4. Figure 4 also shows that there is considerable scatter (±1%) in the liquid-phase data of Lau et al., while the scatter for our work is ±0.15%. Some of the scatter is linked to the model calculations, but most is due to artifacts of the experimental measurements. Figure 5 shows deviations for supercritical fluid densities on a near-critical isotherm at $T = 300$ K, and Figure 6 shows deviations at a slightly higher temperature, $T = 320$ K. At pressures less than 3 MPa, agreement for supercritical fluid densities is very good, with most deviations less than ±0.15% for nearly all density results including those of this work, GERG TM4[20] ($x = 0.28-0.77$), Brugge et al.[21] ($x = 0.10-0.90$), and Lemming[22] ($x = 0.10-0.90$). Deviations of the supercritical density measurements from ref 4 (same compositions as those in this work) are not shown in Figure 5 because they were typically larger than the full-scale range (±1%) of the graph. At pressures greater than 10 MPa, the present results are within ±0.1%; however, significant scatter (±0.4%), distributed about the zero lines in Figures 5 and 6, can be seen for the results of Lau et al.

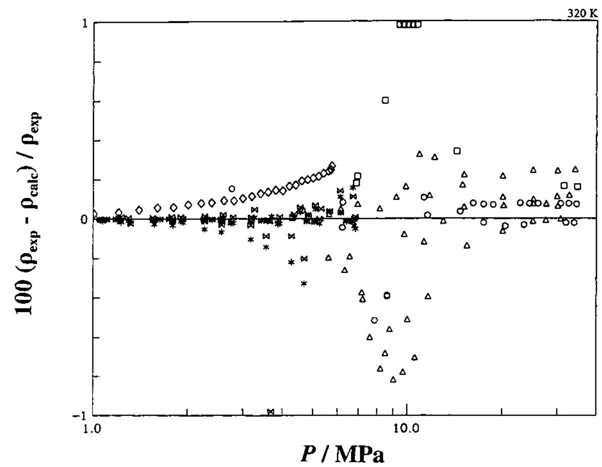

Figure 6. Percentage deviations of experimental supercritical fluid densities at $T = 320$ K for $\{(x)CO_2 + (1 - x)C_2H_6\}$ (○, this work; △, Lau et al.;[5,18] □, Sherman et al.;[19] ◇, GERG Technical Monograph 4;[20] ⋈, Brugge et al.;[21] ∗, Lemming[22]) from the values calculated with the Helmholtz energy model of Lemmon and Jacobsen.[17]

Conclusions

For three binary mixtures of carbon dioxide and ethane, 585 $p-\rho-T$ state conditions were reported. The uncertainty of pressure is 0.01−0.05%, that of density is 0.05%, and that of temperature is 0.03 K. For single-phase liquid densities of the mixtures, agreement with most of the published data is within ±0.4%. This falls within a band whose width is about three times the combined uncertainty of the results.

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Literature Cited

(1) Lemmon, E. W. A Generalized Model for the Prediction of the Thermodynamic Properties of Mixtures Including Vapor-Liquid Equilibrium. Ph.D. Dissertation, University of Idaho, 1996.
(2) Lemmon, E. W.; Jacobsen, R. T. A Generalized Model for the Thermodynamic Properties of Mixtures. *Int. J. Thermophys.* **1999**, *20*, 825−835.

(3) Magee, J. W. Molar Heat Capacity at Constant Volume for {$x$$CO_2$ + (1-x)C_2H_6} from 220 to 340 K at Pressures to 35 MPa. *J. Chem. Eng. Data* **1995**, *40*, 438−442.

(4) 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.

(5) Lau, W.-W. R.; Hwang, C.-A.; Holste, J. C.; Hall, K. R.; Gammon, B. E.; Marsh, K. N. Densities of Carbon Dioxide + Ethane Mixtures from 240 to 450 K at Pressures up to 35 MPa. *J. Chem. Eng. Data* **1997**, *42*, 900−902.

(6) Goodwin, A. R. H.; Moldover, M. R. Phase Border and Density Determinations in the Critical Region of (Carbon Dioxide + Ethane) Determined from Dielectric Permittivity Measurements. *J. Chem. Thermodyn.* **1997**, *29*, 1481−1494.

(7) Diller, D. E.; Magee, J. W. *Thermophysical Properties of Mixtures of Natural Gas Components: A Bibliography of Experimental Data, NISTIR 5100*; National Institute of Standards and Technology: Gaithersburg, MD, 2000.

(8) Haynes, W. M. Orthobaric Liquid Densities and Dielectric Constants of Carbon Dioxide. *Adv. Cryog. Eng.* **1986**, *31*, 1199−1204.

(9) Ely, J. F.; Haynes, W. M.; Bain, B. C. Isochoric (p, V_m, T) Measurements on CO_2 and on (0.982 CO_2 + 0.018 N_2) from 250 to 330 K at Pressures to 35 MPa. *J. Chem. Thermodyn.* **1989**, *21*, 879−894.

(10) Straty, G. C.; Tsumura, R. PVT and Vapor Pressure Measurements on Ethane. *J. Res. Natl. Bur. Stand. (U.S.)* **1976**, *80A*, 35−39.

(11) Goodwin, R. D. Apparatus for Determination of Pressure−Density−Temperature Relations and Specific Heats of Hydrogen to 350 Atmospheres at Temperatures above 14 K. *J. Res. Natl. Bur. Stand. (U.S.)* **1961**, *65C*, 231−243.

(12) Magee, J. W.; Ely, J. F. Isochoric (*p*, *v*, *T*) Measurements on CO_2 and (0.98 CO_2 + 0.02 CH_4) from 225 to 400 K and Pressures to 35 MPa. *Int. J. Thermophys.* **1988**, *9*, 547−557.

(13) Magee, J. W. Isochoric *p*-*ρ*-*T* Measurements on Difluoromethane (R32) from 142 to 396 K and Pentafluoroethane (R125) from 178 to 398 K at Pressures to 35 MPa. *Int. J. Thermophys.* **1996**, *17*, 803−822.

(14) Magee, J. W. Isochoric (p, ρ, T) Measurements for Compressed 1,1,1,2-Tetrafluoroethane (R134a). *Proceedings of the Symposium Honoring Riki Kobayashi's Ongoing Career*; Sloan, E. D., Ely, J. F., Eds.; Colorado School of Mines: Golden, Colorado, 1996; pp 23−40.

(15) Magee, J. W.; Haynes, W. M.; Hiza, M. J. Isochoric (*p*, *ρ*, *T*) Measurements for Five Natural Gas Mixtures from *T*=225 to 350 K at Pressures to 35 MPa. *J. Chem. Thermodyn.* **1997**, *29*, 1439−1454.

(16) Huber, M. L. National Institute of Standards and Technology, Boulder, CO, personal communication, 1997.

(17) Lemmon, E. W.; Jacobsen, R. T National Institute of Standards and Technology, Boulder, CO, personal communication, 2000.

(18) 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.

(19) Sherman, G. J.; Magee, J. W.; Ely, J. F. PVT Relationships in a Carbon Dioxide-Rich Mixture with Ethane. *Int. J. Thermophys.* **1989**, *10*, 47−59.

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

(21) 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.

(22) Lemming, W. *Experimentelle Bestimmung Akustischer und Thermischer Virialkoeffizienten von Arbeits-stoffen der Energietechnik*; Fortschritt-Berichte VDI, *19* (32), 1989.

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