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Isochoric $p-\rho-T$ and Heat Capacity C_v Measurements on $\{xC_3H_8 + (1 - x)i\text{-}C_4H_{10}, x \approx 0.7, 0.3\}$ from 200 to 400 K at Pressures to 35 MPa

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The $p-\rho-T$ relationships and constant volume heat capacity C_v were measured for binary hydrocarbon mixtures containing propane (C_3H_8) and isobutane ($i\text{-}C_4H_{10}$). Temperatures ranged from 200 K to 400 K for $p-\rho-T$ and from 203 K to 342 K for C_v with pressures up to 35 MPa for both measurements. Measurements of $p-\rho-T$ and C_v were conducted on liquid samples with the mole fraction compositions $\{xC_3H_8 + (1 - x)i\text{-}C_4H_{10}\}$ for $x = 0.7006$ and $x = 0.2979$. Determinations of saturated-liquid densities were made by extrapolating each isochore to the saturated-liquid pressure and determining the temperature and density at the intersection. Published $p-\rho-T$ data are in good agreement with this study. For the $p-\rho-T$ apparatus, 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) with a standard uncertainty of 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%. For the C_v apparatus, the uncertainty is 0.002 K for the temperature rise and 0.2% for the change-of-volume work, which is the principal source of uncertainty. The expanded relative uncertainty of the heat capacity measurements is estimated to be 0.7%.

Introduction

Hydrocarbon mixtures are considered to be leading candidates to replace chlorofluorocarbon refrigerants, which will be phased out under the terms of the Montreal Protocol. Mixtures containing propane and isobutane are receiving a great deal of scrutiny for this purpose. Recently, McLinden et al. (1997) analyzed the available data for 14 mixtures, including 6 mixtures of various hydrocarbons, and made recommendations for models which represent the thermodynamic properties for such mixtures. They noted that published $p-\rho-T$ data in the saturated- and compressed-liquid phases for propane + isobutane mixtures were scarce, with a total of 31 data points covering a very limited range. McLinden et al. (1997) also noted that no liquid heat capacity data were published for these binary mixtures. The chief goal of this work is to make benchmark measurements of densities and heat capacities for binary mixtures, which supplement earlier $p-\rho-T$ data reported by this group on both pure propane and isobutane (Haynes and Hiza, 1977; Haynes, 1983a,b) and C_v data reported on pure propane (Goodwin, 1978).

In this paper, new $p-\rho-T$ measurements for binary mixtures are reported for temperatures ranging from 200 K to a maximum temperature of 400 K and at pressures up to 35 MPa. Saturated-liquid densities for these binary mixtures are also reported. In addition, new C_v measurements are reported for temperatures ranging from 203 to 342 K and at pressures to 33 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 apparatus are available in previous publications (Goodwin, 1961; Magee and Ely, 1988). 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 (Magee, 1996a,b; Magee et al., 1997).

The adiabatic constant-volume calorimeter used for these measurements has been described in detail by Goodwin (1961) and Magee (1991). For the heat-capacity measurement, a precisely determined electrical energy (Q) is applied and the resulting temperature rise ($\Delta T = T_2 - T_1$) is measured. We obtain the heat capacity from $C_v = (Q - Q_0 - W_{pV})/n\Delta T$, where Q_0 is the energy required to heat the empty calorimeter, W_{pV} is the change-of-volume work that results from the slight dilation of the bomb, and n is the number of moles enclosed in the bomb. Further details of this method are available in recently published work (Magee, 1992; Lüddecke and Magee, 1996).

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 5×10^{-6}

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Table 1. Mole Fraction Compositions and Molar Masses of $\{xC_3H_8 + (1 - x)i\text{-}C_4H_{10}\}$ Used in This Study

designation	x	molar mass/g·mol^{-1}
DOE15	0.7006	48.296
DOE16	0.2979	53.945

kg. As the expanded uncertainty in the Class S weights is approximately 5×10^{-8} kg, 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 nominal composition. The final pressure of each gas was close to 90% of the estimated dew point pressure for each mixture. This dew point was calculated with an extended corresponding states model (Huber, 1997). Approximately 5 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 propane sample was 0.9997 mole fraction. According to an analysis by the supplier, the largest impurities were ethane with a concentration of 150 parts per million by mole (ppm), isobutane with 100 ppm, and propylene with 50 ppm. Our own electrochemical oxygen analysis revealed 3 ppm of oxygen. The purity of the isobutane sample used in the mixtures was 0.9999 mole fraction. From the supplier's analysis, the largest impurities were ethane with a concentration of 10 ppm, butane with 10 ppm, and 1-butene with 10 ppm. An in-house electrochemical oxygen analysis measured 3 ppm of oxygen. Calculations, based on these analyses, of the average molar mass of the samples were made. Because the calculated average molar masses for both the propane and isobutane 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 both the densimetric and calorimetric data from massic to molar units.

Results

Assessment of Uncertainties. A detailed discussion of the uncertainties in measured quantities is available in recent publications (Magee et al., 1997; Magee, 1996a,b) for $p-\rho-T$ and for C_v (Magee, 1991, 1992; Lüddecke and Magee, 1996). The effect of sample impurites on the uncertainty in mixture compostion was calculated from a mole balance based on the impurities discussed in the previous section. We use a definition for the expanded uncertainty which is two times 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.

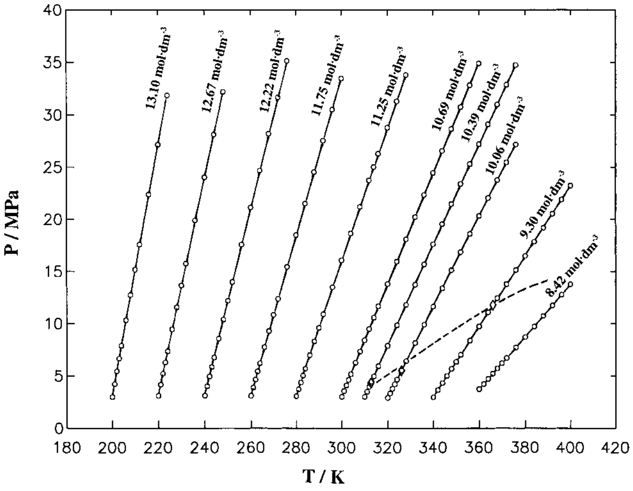

Figure 1. Range of $p-\rho-T$ measurements (○) for $\{xC_3H_8 + (1 - x)i\text{-}C_4H_{10}\}$, $x = 0.7006$ (DOE15) and inflection points (◊) defined by $(\partial^2 p/\partial T^2)_\rho = 0$.

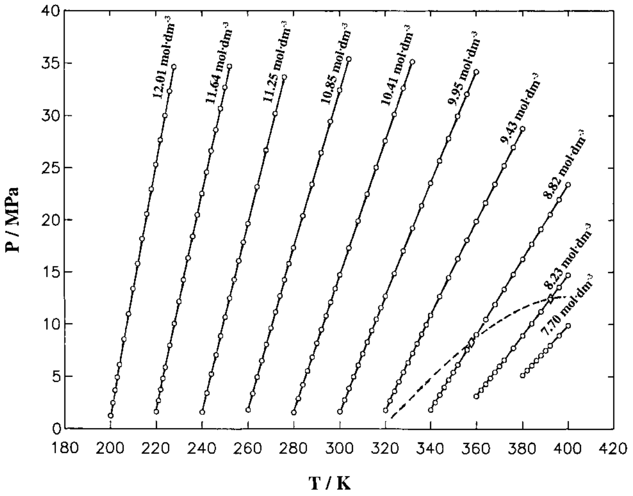

Figure 2. Range of $p-\rho-T$ measurements (○) for $\{xC_3H_8 + (1 - x)i\text{-}C_4H_{10}\}$, $x = 0.2979$ (DOE16) and inflection points (◊) defined by $(\partial^2 p/\partial T^2)_\rho = 0$.

p−ρ−T Measurements. The experimental compositions, temperatures, pressures, and densities for single-phase liquid 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 and 2.

Comparisons of the isochoric $p-\rho-T$ measurements with published data for $\{xC_3H_8 + (1 - x)i\text{-}C_4H_{10}\}$ have been

Table 2. Expanded Uncertainties of the Measurements

parameter	uncertainty	parameter	uncertainty
	p-ρ-T Apparatus		
temperature	0.03 K	mass	0.002 g
pressure		volume	0.003 cm^3
$p < 3$ MPa	0.05%	composition, mole fraction	0.0002
$p > 3$ MPa	0.01%	density	0.05%
	Adiabatic Calorimeter		
temperature	0.03 K	change-of-volume work	0.2%
pressure	0.05%	moles	0.002%
density	0.15%	temperature rise	0.002 K
electrical energy	0.02%	heat capacity	0.7%

Table 3. Experimental Densities (ρ) for {x C_3H_8 + (1-x) *i*-C_4H_{10}} 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}
$x = 0.7006$								
199.999	2.9999	13.0959	280.999	3.7292	11.2467	364.001	29.1039	10.3443
201.000	4.2262	13.0942	282.000	4.3794	11.2455	368.000	30.9941	10.3408
202.000	5.4438	13.0927	283.001	5.0372	11.2444	372.000	32.8784	10.3373
203.000	6.6652	13.0912	284.000	5.6887	11.2433	376.001	34.7558	10.3338
203.999	7.8946	13.0898	286.001	6.9950	11.2412	320.001	2.9209	10.0607
205.999	10.3314	13.0870	288.001	8.2998	11.2391	320.998	3.3555	10.0598
208.000	12.7444	13.0844	290.000	9.6011	11.2371	322.002	3.7951	10.0589
210.000	15.1706	13.0818	292.000	10.9029	11.2351	323.001	4.2295	10.0579
212.001	17.5805	13.0792	296.001	13.4938	11.2311	324.001	4.6677	10.0570
216.000	22.3814	13.0743	300.002	16.0766	11.2272	326.001	5.5396	10.0552
220.000	27.1450	13.0695	304.002	18.6436	11.2233	328.001	6.4131	10.0534
223.999	31.8632	13.0647	308.001	21.2048	11.2195	332.001	8.1619	10.0499
220.000	3.1102	12.6703	311.999	23.7518	11.2157	335.999	9.9062	10.0464
221.002	4.1707	12.6688	314.000	25.0204	11.2137	340.001	11.6496	10.0429
222.000	5.2256	12.6674	316.001	26.2864	11.2119	344.002	13.3896	10.0395
223.000	6.2958	12.6660	320.000	28.7917	11.2082	348.000	15.1263	10.0361
224.001	7.3514	12.6647	323.999	31.3003	11.2044	352.002	16.8626	10.0327
226.000	9.4558	12.6621	328.000	33.7994	11.2007	356.000	18.5924	10.0294
227.998	11.5703	12.6596	300.002	3.0186	10.6932	360.001	20.3208	10.0260
229.999	13.6619	12.6571	300.999	3.5603	10.6922	364.000	22.0428	10.0226
231.999	15.7552	12.6548	302.001	4.0997	10.6912	368.000	23.7596	10.0193
235.999	19.9099	12.6501	303.002	4.6427	10.6901	372.001	25.4741	10.0159
239.999	24.0375	12.6455	304.000	5.1836	10.6891	376.001	27.1819	10.0125
243.999	28.1350	12.6410	306.000	6.2677	10.6871	339.998	2.9827	9.3045
247.999	32.1984	12.6365	308.001	7.3497	10.6852	342.001	3.6535	9.3028
239.998	3.1234	12.2243	310.002	8.4330	10.6833	344.000	4.3256	9.3011
241.000	4.0288	12.2230	312.000	9.5129	10.6814	346.001	4.9982	9.2995
242.001	4.9508	12.2217	314.000	10.5893	10.6795	348.000	5.6722	9.2979
243.002	5.8580	12.2204	315.999	11.6707	10.6776	350.001	6.3461	9.2962
244.001	6.7636	12.2191	320.001	13.8068	10.6742	352.001	7.0215	9.2946
246.000	8.5803	12.2167	324.000	15.9513	10.6705	356.001	8.3734	9.2914
247.998	10.3922	12.2143	328.000	18.0884	10.6669	359.999	9.7265	9.2883
250.000	12.1928	12.2120	332.001	20.2182	10.6633	364.001	11.0805	9.2852
252.001	13.9962	12.2097	335.998	22.3402	10.6597	368.001	12.4353	9.2821
256.001	17.5831	12.2053	340.001	24.4545	10.6561	372.001	13.7896	9.2790
260.002	21.1422	12.2010	344.000	26.5588	10.6525	376.000	15.1428	9.2759
264.000	24.6833	12.1967	348.000	28.6561	10.6489	380.002	16.4958	9.2727
268.000	28.1968	12.1924	352.001	30.7451	10.6453	384.001	17.8467	9.2696
272.000	31.6847	12.1882	356.001	32.8255	10.6417	388.002	19.1966	9.2665
276.000	35.1467	12.1840	360.000	34.8938	10.6381	392.000	20.5443	9.2634
260.000	3.0970	11.7522	310.000	3.0192	10.3924	396.001	21.8905	9.2603
261.002	3.8796	11.7510	310.999	3.5103	10.3914	400.002	23.2338	9.2571
262.000	4.6554	11.7498	312.000	3.9959	10.3904	360.001	3.7363	8.4215
263.002	5.4326	11.7485	313.000	4.4897	10.3894	361.999	4.2270	8.4201
264.001	6.2046	11.7474	314.002	4.9779	10.3884	364.002	4.7201	8.4187
266.000	7.7515	11.7451	316.002	5.9413	10.3867	366.002	5.2146	8.4173
268.001	9.2992	11.7429	320.000	7.8978	10.3830	368.001	5.7112	8.4159
270.001	10.8422	11.7407	324.001	9.8507	10.3794	370.001	6.2091	8.4145
272.000	12.3794	11.7386	328.000	11.7992	10.3758	372.001	6.7082	8.4130
276.002	15.4396	11.7343	331.998	13.7430	10.3723	376.001	7.7089	8.4102
280.002	18.4887	11.7302	336.000	15.6820	10.3687	379.998	8.7133	8.4074
283.999	21.5225	11.7261	340.000	17.6168	10.3652	383.999	9.7212	8.4046
288.000	24.5372	11.7221	344.000	19.5450	10.3617	388.001	10.7317	8.4018
292.001	27.5351	11.7181	348.002	21.4692	10.3582	392.000	11.7436	8.3991
296.000	30.5163	11.7141	352.001	23.3870	10.3547	395.998	12.7575	8.3963
299.999	33.4711	11.7101	356.000	25.2999	10.3513	400.001	13.7721	8.3935
279.999	3.0681	11.2478	360.001	27.2044	10.3478			
$x = 0.2979$								
199.999	1.2353	12.0133	272.000	11.1908	10.8393	332.001	7.2465	9.4201
200.998	2.4572	12.0119	273.998	12.7344	10.8374	334.001	8.1561	9.4184
201.999	3.6773	12.0106	276.000	14.2797	10.8355	336.002	9.0635	9.4168
203.001	4.9052	12.0092	278.001	15.8179	10.8336	338.001	9.9711	9.4152
203.998	6.1217	12.0080	279.999	17.3496	10.8317	340.000	10.8752	9.4137
205.999	8.5598	12.0055	284.002	20.4066	10.8280	344.001	12.6882	9.4105
208.000	10.9865	12.0031	287.998	23.4439	10.8243	348.000	14.4948	9.4073
209.999	13.4038	12.0008	291.999	26.4588	10.8207	352.001	16.2973	9.4041
212.000	15.8048	11.9985	296.001	29.4620	10.8170	356.000	18.0951	9.4010
213.999	18.2001	11.9962	300.001	32.4393	10.8133	360.001	19.8885	9.3978
216.000	20.5852	11.9940	304.001	35.4006	10.8097	364.000	21.6758	9.3947
217.999	22.9595	11.9918	280.002	1.5647	10.4109	368.002	23.4572	9.3915
220.001	25.3205	11.9896	282.000	2.8919	10.4089	371.999	25.2329	9.3884
221.999	27.6706	11.9875	284.001	4.2174	10.4069	376.001	27.0024	9.3852
224.001	30.0121	11.9853	286.000	5.5410	10.4050	380.001	28.7673	9.3820
226.000	32.3416	11.9832	288.000	6.8614	10.4031	340.000	1.8250	8.8221

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}
				$x = 0.2979$				
227.999	34.6609	11.9811	290.000	8.1809	10.4013	342.001	2.5441	8.8205
220.001	1.6335	11.6434	292.000	9.4982	10.3994	344.000	3.2640	8.8190
221.001	2.6910	11.6421	294.000	10.8132	10.3976	346.000	3.9849	8.8175
222.000	3.7543	11.6408	296.000	12.1222	10.3958	348.000	4.7070	8.8159
223.000	4.8123	11.6396	298.001	13.4273	10.3940	350.000	5.4285	8.8144
223.999	5.8725	11.6384	299.999	14.7306	10.3922	351.998	6.1504	8.8129
226.000	7.9796	11.6361	304.000	17.3296	10.3887	356.001	7.5958	8.8100
227.999	10.0814	11.6339	307.999	19.9151	10.3851	360.000	9.0402	8.8070
230.000	12.1841	11.6317	312.002	22.4912	10.3816	364.002	10.4853	8.8040
232.000	14.2744	11.6295	316.000	25.0521	10.3781	368.002	11.9291	8.8011
234.001	16.3574	11.6274	320.001	27.5976	10.3746	371.999	13.3714	8.7981
236.000	18.4313	11.6252	324.002	30.1343	10.3711	376.001	14.8130	8.7952
238.000	20.4981	11.6232	328.001	32.6532	10.3677	379.998	16.2532	8.7923
239.999	22.5488	11.6211	332.002	35.1593	10.3642	384.002	17.6912	8.7893
242.001	24.6003	11.6190	300.002	1.6482	9.9455	388.000	19.1253	8.7864
244.000	26.6430	11.6170	302.000	2.7594	9.9436	392.000	20.5572	8.7834
246.002	28.6729	11.6150	304.001	3.8713	9.9418	396.000	21.9857	8.7805
248.001	30.6987	11.6129	306.002	4.9768	9.9400	399.999	23.4118	8.7775
250.001	32.7161	11.6109	308.000	6.0848	9.9383	360.002	3.1451	8.2327
252.000	34.7222	11.6089	310.000	7.1925	9.9365	362.000	3.7178	8.2313
240.000	1.6017	11.2531	312.000	8.2943	9.9348	363.998	4.2918	8.2300
242.002	3.4313	11.2508	314.002	9.3988	9.9330	366.000	4.8667	8.2286
244.000	5.2543	11.2485	315.998	10.4994	9.9313	368.000	5.4424	8.2272
246.000	7.0750	11.2463	318.001	11.5998	9.9296	370.000	6.0187	8.2258
248.001	8.8927	11.2442	320.001	12.6995	9.9279	371.998	6.5970	8.2244
249.999	10.7016	11.2421	324.001	14.8735	9.9248	376.000	7.7540	8.2217
252.002	12.5100	11.2401	328.000	17.0558	9.9214	380.001	8.9139	8.2190
254.000	14.3060	11.2380	332.000	19.2297	9.9181	384.000	10.0743	8.2163
255.999	16.0979	11.2360	336.000	21.3944	9.9147	388.001	11.2355	8.2135
258.001	17.8777	11.2340	340.000	23.5507	9.9114	391.999	12.3976	8.2108
260.000	19.6596	11.2321	344.001	25.6997	9.9081	396.001	13.5601	8.2081
264.001	23.2032	11.2282	348.000	27.8373	9.9048	400.001	14.7220	8.2053
268.001	26.7186	11.2243	352.000	29.9651	9.9014	380.001	5.1338	7.7000
272.000	30.2115	11.2204	356.000	32.0838	9.8981	382.001	5.6039	7.6987
276.000	33.6788	11.2166	360.001	34.1922	9.8948	384.000	6.0764	7.6974
260.001	1.8248	10.8516	320.000	1.7801	9.4301	386.000	6.5485	7.6962
262.001	3.3959	10.8494	322.000	2.6927	9.4283	388.000	7.0235	7.6949
264.001	4.9635	10.8473	324.001	3.6041	9.4267	390.001	7.4979	7.6936
266.001	6.5253	10.8453	326.000	4.5154	9.4250	392.002	7.9733	7.6924
268.001	8.0857	10.8432	328.000	5.4272	9.4233	396.001	8.9260	7.6898
270.001	9.6408	10.8413	330.001	6.3374	9.4217	400.001	9.8822	7.6873

facilitated with a Helmholtz energy formulation developed by Lemmon and Jacobsen (1999). This model uses reference equations of state to anchor the pure component states and, in between, it uses a simple Helmholtz energy mixture model with two fitted parameters. The two parameter mixture model was fitted to the density data from this study along with selected data sets from other laboratories. Comparisons with this model, depicted in Figure 3, show both that the model represents the present data within ±0.1% and that there is good agreement (deviations less than ±0.3%) with most of the published data (Kahre, 1973; Thompson and Miller, 1980).

Densities of the Saturated Liquid. The saturated-liquid densities derived in this study were obtained by extrapolating the isochoric data to their intersection with the saturated-liquid (bubble point) pressures calculated with the model of Lemmon and Jacobson (1999). The uncertainty of the extrapolation depends primarily on the difference in the slopes of the experimental isochore and the bubble point curve. At the high densities of this work, the uncertainty of the temperature intersection is approximately 0.01 K. This leads to a relative uncertainty of 0.1% in the density of the saturated liquid, including the experimental uncertainty of a single-phase density measurement. The estimated uncertainty has been confirmed by intercomparison with published data for pure substances (Magee, 1996a,b). The results of the saturated-liquid density extrapolations are presented in Table 4. Comparisons were not possible with the prior study of Hiza et al. (1977), who reported saturated liquid densities at temperatures from 105 to 130 K. No other saturated-liquid densities were located for this comparison.

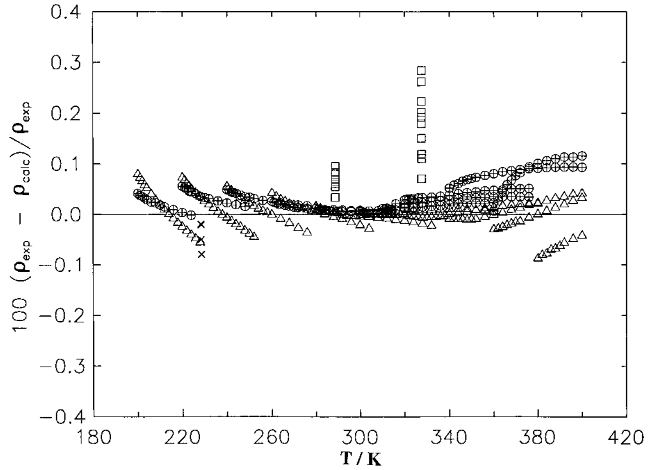

Figure 3. Percentage deviations of experimental liquid densities for $\{xC_3H_8 + (1 - x)i\text{-}C_4H_{10}\}$ obtained in this work, [$x = 0.7006$ (⊕) and $x = 0.2979$ (△)], by Kahre (1973) (□) and by Thompson and Miller (1980) (×) from the values calculated with the Helmholtz energy model of Lemmon and Jacobsen (1999).

Inflection Points. Magee and Kobayashi (1982) have discussed methods for determining the locus of isochoric

Table 4. Saturated Liquid Densities (ρ_{sat}) for {xC_3H_8 + (1 − x)i-C_4H_{10}} As a Function of Temperature (*T*, ITS-90)

T/K	ρ_{sat}/mol·dm^{-3}	T/K	ρ_{sat}/mol·dm^{-3}
	x = 0.7006		
197.57	13.100	295.74	10.698
217.12	12.675	305.68	10.397
236.70	12.229	315.98	10.065
256.30	11.757	336.50	9.308
275.94	11.253	355.35	8.424
	x = 0.2979		
199.00	12.015	297.96	9.947
218.49	11.645	317.96	9.432
238.32	11.255	338.65	8.823
257.87	10.854	355.57	8.236
278.08	10.413	368.17	7.708

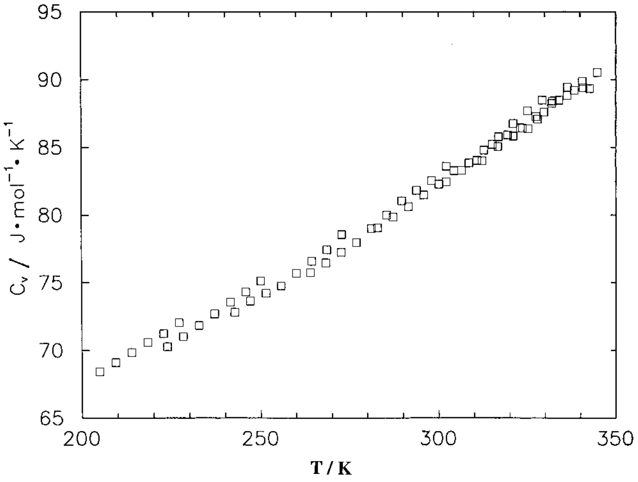

Figure 4. Isochoric heat capacity measurements (□) for {xC_3H_8 + (1 − x)i-C_4H_{10}}, x = 0.7006 (DOE15).

inflection points from compressed-gas and liquid $p-\rho-T$ measurements. Because each $p-\rho-T$ inflection point is defined by $(\partial^2 p/\partial T^2)_\rho = 0 = -\rho^2\ T^{-1}(\partial C_v/\partial\rho)_T$, it is the state condition where the isochoric heat capacity has an extremum. The locus of such inflection points maps the state conditions where a small density change, occurring at a constant temperature, results in no change in C_v. At the locus of inflection points, the value of $(\partial C_v/\partial\rho)_T$ passes through zero with a reversal of the sign of this derivative. An inflection point is a fundamental molecular property which is associated with the close-packed interactions of molecules in a condensed phase. The inflection points and the loci connecting them (dashed lines) are plotted in Figures 1 and 2. The shape of the loci of inflection points for these mixtures has the same general appearance as those reported previously for methane, ethane, and propane (Magee and Kobayashi, 1982).

Heat Capacities at Constant Volume. The experimental compositions, temperatures, pressures, densities, and heat capacities at constant volume C_v are presented in Table 5, where the values are quoted within their reproducibilities. For each binary mixture composition, these measurements were carried out at eight liquid-phase filling densities. To illustrate the range of measurements for each mixture, the heat capacity data are plotted in Figures 4 and 5, which clearly show a weak dependence of the slope $(\partial C_v/\partial T)_\rho$ on the density. The same behavior has been experimentally observed for liquid densities larger than 1.5 times the critical density.

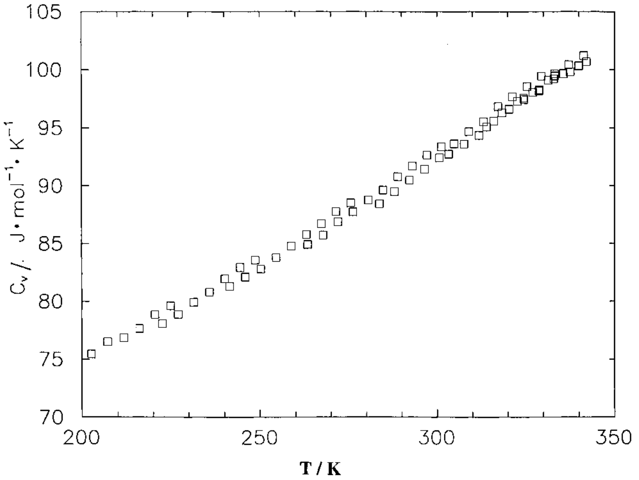

Figure 5. Isochoric heat capacity measurements (□) for {xC_3H_8 + (1 − x)i-C_4H_{10}}, x = 0.2979 (DOE16).

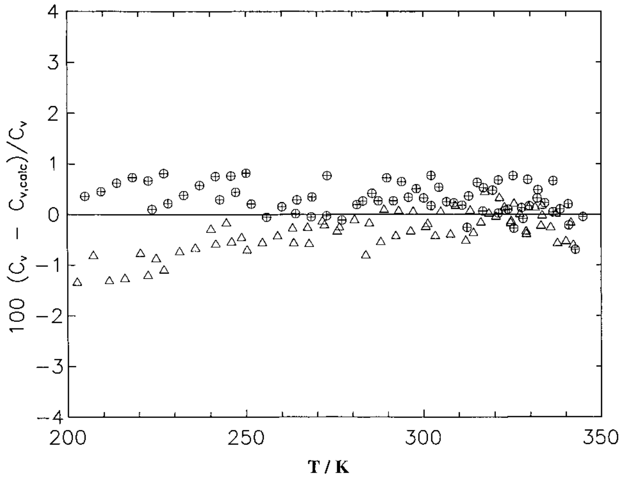

Figure 6. Percentage deviations of experimental liquid heat capacities for {xC_3H_8 + (1 − x)i-C_4H_{10}}, x = 0.7006 (⊕) and x = 0.2979 (△) obtained in this work from the values calculated with the Helmholtz energy model of Lemmon and Jacobsen (1999).

Comparisons of the C_v measurements were made with values calculated from the Helmholtz energy formulation developed by Lemmon and Jacobsen (1999). Because no heat capacities were used to fit the mixture model, C_v calculations are predicted values to which Lemmon and Jacobsen have assigned a 0.5 to 1% uncertainty. Since the measured pressure is more accurate than the density given in Table 5, the heat capacities were calculated at pressure−temperature state conditions. Heat capacities for these mixtures are scarce. The only published heat capacities located were the gaseous mixture heat capacities at constant pressure of Bier et al. (1973) at temperatures from 293 to 353 K and at pressures up to 1.4 MPa. Comparisons of these data are not possible, since they do not overlap the state conditions of this study. Nonetheless, Figure 6 illustrates that the model's calculations are within 1.3% of the measurements presented here, which is less than the combined uncertainties of the calculations and the measurements.

Conclusions

For two binary mixtures of propane and isobutane, 341 $p-\rho-T$ state conditions and 20 saturated liquid densities have been reported. For $p-\rho-T$, the uncertainty of pressure is 0.01 to 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 published data is within ±0.3%. This falls within the combined uncertainty of the results and shows good agreement with other data. For the

Table 5. Measurements of Heat Capacity (C_v) for Liquid $\{xC_3H_8 + (1 - x)i\text{-}C_4H_{10}\}$ As a Function of Temperature (T, ITS-90), Density (ρ), and Pressure (p) Where Subscript a Denotes a Condition Evaluated at the Average of the Initial and Final Temperatures

T_a/K	ρ_a/mol·dm^{-3}	p_a/MPa	C_v/J·mol^{-1}·K^{-1}	T_a/K	ρ_a/mol·dm^{-3}	p_a/MPa	C_v/J·mol^{-1}·K^{-1}
$x = 0.7006$							
204.9034	13.059	5.861	68.44	295.8552	11.209	12.190	81.50
209.4344	13.046	11.005	69.10	300.1101	11.202	14.836	82.30
213.9154	13.034	16.008	69.85	304.3369	11.195	17.445	83.30
218.3516	13.022	20.879	70.59	308.5489	11.188	20.026	83.87
222.7393	13.011	25.616	71.23	312.7273	11.181	22.567	84.82
227.0814	12.999	30.225	72.04	316.8908	11.174	25.080	85.80
223.8105	12.642	4.944	70.27	321.0327	11.167	27.561	86.78
228.2812	12.631	9.399	71.02	325.1628	11.161	30.017	87.71
232.7068	12.621	13.756	71.83	329.2747	11.154	32.444	88.50
237.0922	12.610	18.019	72.69	302.1745	10.700	3.957	82.46
241.4378	12.600	22.187	73.56	306.5195	10.693	6.273	83.31
245.7438	12.589	26.262	74.32	310.8472	10.687	8.570	84.05
250.0101	12.579	30.243	75.13	315.1442	10.681	10.840	85.24
242.6578	12.217	4.522	72.81	319.4336	10.675	13.095	85.93
247.0741	12.207	8.368	73.64	323.6958	10.669	15.324	86.43
251.4626	12.197	12.151	74.21	327.9416	10.662	17.532	87.10
255.7968	12.188	15.847	74.77	332.1731	10.656	19.720	88.44
260.1021	12.179	19.477	75.70	336.3979	10.650	21.892	89.45
264.3713	12.170	23.037	76.59	340.6194	10.644	24.049	89.89
268.6031	12.161	26.526	77.43	344.8187	10.638	26.182	90.52
272.8021	12.152	29.947	78.57	312.2818	10.410	4.115	84.02
263.9818	11.715	4.359	75.75	316.6650	10.404	6.237	85.08
268.3500	11.707	7.598	76.46	321.0457	10.398	8.351	85.85
272.6843	11.698	10.785	77.25	325.4020	10.393	10.447	86.40
276.9860	11.690	13.922	77.97	329.7277	10.387	12.519	87.61
281.2545	11.682	17.008	79.01	334.0373	10.381	14.576	88.49
285.4920	11.674	20.043	80.00	338.3463	10.376	16.622	89.22
289.7019	11.666	23.031	81.07	342.6477	10.370	18.655	89.35
293.8869	11.658	25.973	81.84	323.0900	10.051	3.905	86.46
298.0419	11.651	28.866	82.56	327.5294	10.046	5.811	87.29
302.1715	11.643	31.715	83.62	331.9598	10.041	7.710	88.26
282.9436	11.230	4.053	79.07	336.3861	10.035	9.604	88.83
287.2788	11.223	6.802	79.85	340.7984	10.030	11.487	89.42
291.5808	11.216	9.514	80.64				
$x = 0.2979$							
202.6842	12.028	4.459	75.45	292.2544	10.396	8.894	90.47
207.2213	12.016	9.652	76.50	296.4778	10.389	11.570	91.44
211.7246	12.005	14.733	76.84	300.6841	10.382	14.215	92.42
216.1577	11.994	19.660	77.64	304.8561	10.376	16.819	93.62
220.5644	11.983	24.477	78.83	309.0179	10.370	19.397	94.67
224.9187	11.973	29.153	79.59	313.1487	10.363	21.936	95.52
222.6426	11.653	4.104	78.05	317.2606	10.357	24.443	96.83
227.0974	11.643	8.578	78.86	321.3536	10.351	26.918	97.68
231.5057	11.634	12.947	79.92	325.4346	10.345	29.367	98.54
235.8789	11.624	17.224	80.79	329.5030	10.338	31.789	99.44
240.2068	11.614	21.400	81.94	303.3264	9.954	3.282	92.73
244.4966	11.605	25.484	82.92	307.6208	9.948	5.618	93.60
248.7465	11.595	29.473	83.57	311.8931	9.943	7.931	94.35
241.5681	11.292	4.125	81.28	316.1453	9.937	10.221	95.58
245.9588	11.283	8.000	82.10	320.3828	9.931	12.491	96.60
250.3110	11.274	11.800	82.79	324.6085	9.926	14.741	97.44
254.6183	11.266	15.519	83.76	328.8115	9.920	16.966	98.17
258.8959	11.257	19.170	84.75	333.0119	9.914	19.175	99.23
263.1350	11.249	22.746	85.78	337.2013	9.909	21.365	100.43
267.3411	11.241	26.251	86.71	341.4028	9.903	23.546	101.22
271.5138	11.232	29.685	87.75	314.0493	9.701	3.522	95.07
275.6517	11.224	33.048	88.51	318.4000	9.696	5.675	96.29
263.4724	10.848	3.792	84.91	322.7396	9.690	7.814	97.29
267.7984	10.841	7.048	85.72	327.0667	9.685	9.938	98.06
272.0825	10.833	10.246	86.89	331.3847	9.680	12.050	99.11
276.3386	10.826	13.395	87.73	335.7002	9.674	14.151	99.66
280.5656	10.818	16.492	88.76	339.9960	9.669	16.231	100.33
284.7576	10.811	19.535	89.62	328.8657	9.423	5.455	98.26
288.9212	10.804	22.527	90.79	333.2516	9.418	7.413	99.64
293.0559	10.796	25.470	91.71	337.6329	9.413	9.362	99.80
297.1697	10.789	28.370	92.65	324.5003	9.428	3.502	97.58
301.2506	10.782	31.219	93.38	328.9191	9.423	5.479	98.22
283.7179	10.409	3.428	88.43	333.3052	9.418	7.437	99.46
287.9944	10.402	6.176	89.50	342.0994	9.408	11.341	100.70

same two binary mixtures, 135 C_v measurements have been reported. For C_v, the uncertainty of pressure is 0.05%, that of density is 0.15%, that of temperature is 0.03 K, that of temperature rise is 0.002 K, and that of heat capacity is 0.7%. No published heat capacities which overlapped the measured state conditions were available for comparison.

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