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Isochoric p–ρ–T and Heat Capacity C_v Measurements for Ternary Refrigerant Mixtures Containing Difluoromethane (R32), Pentafluoroethane (R125), and 1,1,1,2-Tetrafluoroethane (R134a) from 200 to 400 K at Pressures to 35 MPa

J. W. Magee[1]

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The p–ρ–T relationships and constant volume heat capacity C_v were measured for ternary refrigerant mixtures by isochoric methods with gravimetric determinations of the amount of substance. Temperatures ranged from 200 to 400 K for p–ρ–T and from 203 to 345 K for C_v, while for both data types pressures extended to 35 MPa. Measurements of p–ρ–T were carried out on compressed gas and liquid samples with the following mole fraction compositions: 0.3337 R32 + 0.3333 R125 + 0.3330 R134a and 0.3808 R32 + 0.1798 R125 + 0.4394 R134a. Measurements of C_v were carried out on liquid samples for the same two compositions. Published p–ρ–T data are in good agreement with this study. For the p–ρ–T apparatus, the uncertainty is 0.03 K for temperature and is 0.01 % for pressure at $p > 3$ MPa and 0.05 % at $p < 3$ MPa. The principal source of uncertainty is the cell volume ($\sim$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 calorimeter, the uncertainty of the temperature rise is 0.002 K and for the change-of-volume work it is 0.2 %; the latter is the principal source of uncertainty. When all components of experimental uncertainty are considered, the expanded relative uncertainty of the heat capacity measurements is estimated to be 0.7 %.

KEY WORDS: density; difluoromethane; heat capacity; p–ρ–T data; pentafluoroethane; R32; R125; R134a; ternary mixtures; 1,1,1,2-tetrafluoroethane.

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[1] Physical and Chemical Properties Division, Chemical Science and Technology Laboratory, National Institute of Standards and Technology, Boulder, Colorado 80303, U.S.A.

1. INTRODUCTION

Hydrofluorocarbon (HFC) blends are considered to be leading candidates to replace refrigerant 22 (R22), which will be phased out under the terms of the Montreal Protocol. Blends containing HFC substances R32, R125, and R134a are receiving a great deal of scrutiny for this purpose. Recently, Lemmon [1] analyzed the available data for ternary mixtures of R32, R125, and R134a and developed a Helmholtz energy model which represents the thermodynamic properties for such mixtures. Lemmon noted that published p–ρ–T data in the saturated and compressed liquid phases for these mixtures were scarce, especially at temperatures below 243 K. Lemmon also noted that no heat capacity data were published for these ternary mixtures. The chief goal of this work is to make benchmark measurements of densities and heat capacities for ternary mixtures, which would supplement earlier p–ρ–T data reported by this group on the pure components R32 and R125 [2] and R134a [3] and C_v data reported on R32 and R125 [4] and R134a [5], as well as p–ρ–T [6] and heat capacity [7] data reported for the binary mixtures of these components.

In this paper, new p–ρ–T measurements for ternary mixtures are reported for temperatures ranging from 200 K to a maximum temperature near 400 K and at pressures up to 35 MPa. In addition, new C_v measurements are reported for temperatures ranging from 203 to 345 K and at pressures extending to 35 MPa.

2. MEASUREMENTS

2.1. Apparatus and Procedures

The p–ρ–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 [8, 9]. In brief, 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 the experimental technique are available in recent publications [2, 3, 10].

The adiabatic constant-volume calorimeter used for these measurements has been described in detail by Goodwin [8] and Magee [11]. 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. The heat capacity is calculated with $C_\mathrm{v} = (Q - Q_0 - W_{pV})/n\,\Delta T$, 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 on this method are available in recently published work [4, 5].

2.2. Gas Mixture Preparation

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 (gc/ms). Each gas was added to the mixture sequentially while the cylinder rested on a load cell having a resolution 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. Based on repetitive weighings, the expanded uncertainty in the amount of each substance was estimated to be 5×10^{-6} kg. As the expanded uncertainty in the Class S weights is approximately 5×10^{-8} kg, the uncertainty is primarily dependent on the random scatter in the weighings.

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 [12]. Approximately 5 mol of each gas mixture was prepared for this study. Table I provides the mole fraction compositions and molar mass for each gas mixture.

The purities of the components used to make the mixtures are an important aspect of this study. The purity of the R32 sample was 0.9999 mass fraction. The largest impurities were R12, with a concentration of 19 parts per million by mass (ppm), and R23, with 18 ppm. Other impurities included 5 ppm of R22 and 1 ppm of R40. The purity of the R125 sample used in the ternary mixtures was 0.99997 mole fraction. An in-house analysis by gc/ms found no detectable impurities, other than a trace quantity of air. The sample of R134a had a purity of 0.999 mole fraction, with only a trace quantity of air impurity.

Table I. Mole Fraction Compositions of Ternary Mixtures Used in this Study

Designation	R32	R125	R134a	Molar mass ($g \cdot mol^{-1}$)
DOE17	0.3337	0.3333	0.3330	91.338
DOE18	0.3808	0.1798	0.4394	86.222

Table II. Expanded Uncertainties of the Measurements

p–ρ–T apparatus	
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)	0.0001
Density	0.05%
Adiabatic calorimeter	
Temperature	0.03 K
Pressure	0.05%
Density	0.15%
Electrical energy	0.02%
Change-of-volume work	0.2%
Moles	0.002%
Temperature rise	0.002 K
Heat capacity	0.7%

2.3. Assessment of Uncertainties

A detailed discussion of the uncertainties in the measured quantities is available in recent publications [2, 3, 10] for p–ρ–T and in Refs. 4 and 5 for C_v. The definition of the expanded uncertainty is taken to be two times the standard uncertainty, which corresponds to 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 listed in Table II.

3. RESULTS

3.1. p–ρ–T Results

The experimental compositions, temperatures (ITS-90), pressures, and densities for single-phase liquid and gaseous mixtures are presented in Table III. The number of digits presented represents the measurement precision; they were retained as an aid to equation fitting. To illustrate the range of measurements for each of the mixture, the isochoric data are plotted in Figs. 1 and 2.

Comparisons of the isochoric p–ρ–T measurements with other published data were facilitated by a Helmholtz energy formulation developed

Table III. Experimental *p*–*ρ*–*T* Data for Ternary Refrigerant Mixtures Containing R32, R125, and R134

T (K)	p (MPa)	ρ (mol · dm^{-3})
	0.3337 R32 + 0.3333 R125 + 0.3330 R134a	
200.000	3.3681	16.4366
200.999	4.8500	16.4338
202.000	6.3498	16.4312
202.998	7.8610	16.4289
203.999	9.3713	16.4268
204.999	10.8858	16.4247
205.999	12.3935	16.4226
208.001	15.4363	16.4188
210.000	18.4634	16.4151
212.001	21.4818	16.4115
214.001	24.4899	16.4080
215.999	27.4902	16.4046
218.000	30.4791	16.4013
220.000	33.4586	16.3979
220.000	3.4078	15.7942
220.999	4.6651	15.7917
221.999	5.9289	15.7894
222.999	7.2035	15.7873
223.999	8.4780	15.7853
225.000	9.7547	15.7834
226.000	11.0339	15.7816
227.999	13.5902	15.7780
230.000	16.1418	15.7746
232.000	18.6932	15.7713
233.999	21.2321	15.7680
236.002	23.7685	15.7648
238.000	26.2965	15.7617
240.000	28.8168	15.7586
241.999	31.3295	15.7555
244.001	33.8401	15.7525
240.001	3.3656	15.1165
240.999	4.4207	15.1142
242.000	5.4797	15.1121
243.000	6.5469	15.1102
244.000	7.6128	15.1084
246.000	9.7486	15.1049
248.000	11.8883	15.1016
250.002	14.0256	15.0984
252.000	16.1572	15.0953
253.999	18.2898	15.0923
256.000	20.4164	15.0893
258.001	22.5397	15.0864

Table III. *(Continued)*

T (K)	p (MPa)	ρ (mol·dm^{-3})
260.001	24.6555	15.0835
261.999	26.7677	15.0807
264.001	28.8784	15.0778
265.999	30.9784	15.0750
268.000	33.0744	15.0722
270.001	35.1653	15.0694
259.999	3.3196	14.3889
261.001	4.1919	14.3869
262.002	5.0697	14.3850
263.000	5.9491	14.3832
264.000	6.8308	14.3815
266.000	8.5940	14.3783
268.001	10.3602	14.3753
270.000	12.1285	14.3724
272.000	13.8929	14.3695
274.001	15.6559	14.3667
276.000	17.4190	14.3639
278.001	19.1806	14.3612
280.000	20.9347	14.3585
284.000	24.4395	14.3532
288.001	27.9347	14.3480
292.002	31.4112	14.3428
296.002	34.8795	14.3376
280.001	3.3556	13.5920
281.000	4.0643	13.5902
282.002	4.7794	13.5885
282.998	5.4909	13.5870
284.001	6.2092	13.5854
286.000	7.6399	13.5825
288.001	9.0735	13.5797
290.000	10.5041	13.5770
292.000	11.9412	13.5744
295.999	14.8103	13.5692
300.001	17.6765	13.5642
304.000	20.5336	13.5593
308.000	23.3911	13.5544
312.001	26.2396	13.5496
316.001	29.0759	13.5448
320.001	31.9103	13.5401
323.999	34.7338	13.5353
300.002	3.3778	12.6748
302.000	4.4946	12.6718
303.999	5.6163	12.6690
306.000	6.7410	12.6664
308.000	7.8692	12.6639

Table III. *(Continued)*

T (K)	p (MPa)	ρ (mol · dm^{-3})
310.000	8.9974	12.6614
311.998	10.1254	12.6590
316.001	12.3880	12.6544
320.002	14.6499	12.6498
324.000	16.9146	12.6453
327.999	19.1785	12.6408
332.001	21.4400	12.6364
335.998	23.6947	12.6320
340.000	25.9505	12.6276
344.001	28.2022	12.6232
352.001	32.6878	12.6145
320.002	3.3717	11.5292
322.000	4.1922	11.5267
323.999	5.0165	11.5244
325.999	5.8442	11.5221
328.000	6.6752	11.5198
330.000	7.5086	11.5177
332.000	8.3432	11.5155
336.001	10.0183	11.5114
339.998	11.6989	11.5073
344.000	13.3818	11.5032
348.001	15.0703	11.4993
352.001	16.7604	11.4953
356.001	18.4536	11.4913
359.999	20.1456	11.4874
364.002	21.8353	11.4835
368.000	23.5262	11.4796
372.002	25.2168	11.4757
376.000	26.9052	11.4717
380.002	28.5933	11.4678
384.002	30.2794	11.4639
388.000	31.9604	11.4600
339.998	3.8576	9.9140
342.002	4.3817	9.9121
344.001	4.9097	9.9103
346.002	5.4425	9.9085
348.000	5.9777	9.9067
351.999	7.0592	9.9032
355.999	8.1499	9.8997
360.000	9.2505	9.8963
364.000	10.3565	9.8930
368.002	11.4684	9.8896
372.002	12.5849	9.8863
376.000	13.7055	9.8830
380.000	14.8294	9.8797

Table III. *(Continued)*

T (K)	p (MPa)	ρ (mol · dm^{-3})
384.000	15.9551	9.8764
388.001	17.0840	9.8730
392.000	18.2151	9.8697
395.999	19.3469	9.8664
400.000	20.4792	9.8631
360.001	7.0395	9.1054
364.002	7.9258	9.1024
368.001	8.8205	9.0993
372.000	9.7220	9.0963
376.001	10.6284	9.0933
380.000	11.5398	9.0902
383.999	12.4559	9.0872
387.999	13.3740	9.0842
392.001	14.2958	9.0812
395.999	15.2201	9.0782
400.001	16.1454	9.0752
359.999	5.4999	7.7480
364.001	6.1089	7.7456
367.999	6.7281	7.7431
372.000	7.3552	7.7407
376.001	7.9891	7.7382
380.001	8.6280	7.7357
384.001	9.2707	7.7332
388.002	9.9178	7.7307
392.001	10.5681	7.7282
396.001	11.2206	7.7256
400.000	11.8754	7.7231
359.999	4.8895	4.8485
364.001	5.2077	4.8472
367.999	5.5244	4.8457
371.999	5.8401	4.8442
376.001	6.1551	4.8428
379.999	6.4692	4.8413
384.000	6.7825	4.8398
388.002	7.0955	4.8384
392.000	7.4073	4.8369
396.000	7.7193	4.8354
399.999	8.0302	4.8339
359.999	3.2532	1.5787
363.999	3.3318	1.5815
368.001	3.4098	1.5810
372.000	3.4867	1.5805
375.999	3.5631	1.5800
380.001	3.6391	1.5795
384.000	3.7144	1.5790

Table III. *(Continued)*

T (K)	p (MPa)	ρ (mol · dm^{-3})
388.001	3.7891	1.5785
392.002	3.8633	1.5780
395.998	3.9370	1.5775
400.001	4.0103	1.5770
	0.3808 R32 + 0.1798 R125 + 0.4394 R134a	
199.999	3.2510	17.0895
201.000	4.7938	17.0868
202.000	6.3455	17.0844
202.999	7.9086	17.0821
204.000	9.4671	17.0799
205.999	12.5909	17.0757
208.000	15.7168	17.0718
210.000	18.8323	17.0680
211.999	21.9483	17.0643
213.999	25.0543	17.0606
215.998	28.1464	17.0571
217.999	31.2271	17.0536
219.999	34.3012	17.0501
221.001	3.2313	16.3982
221.998	4.5276	16.3958
223.000	5.8347	16.3936
224.001	7.1428	16.3915
225.999	9.7651	16.3876
228.000	12.3963	16.3838
230.000	15.0174	16.3803
232.001	17.6354	16.3768
234.000	20.2491	16.3734
235.999	22.8500	16.3701
238.000	25.4475	16.3668
240.000	28.0345	16.3636
242.000	30.6168	16.3604
244.000	33.1885	16.3572
240.000	3.1798	15.7406
241.001	4.2855	15.7384
242.001	5.3876	15.7363
242.999	6.5000	15.7344
244.001	7.6106	15.7325
246.000	9.8336	15.7290
248.000	12.0550	15.7256
250.000	14.2775	15.7224
252.001	16.4947	15.7192
254.001	18.7074	15.7160
256.000	20.9128	15.7129
258.000	23.1140	15.7099

Table III. *(Continued)*

T (K)	p (MPa)	ρ ($\mathrm{mol \cdot dm^{-3}}$)
260.000	25.3117	15.7069
264.000	29.6923	15.7010
268.000	34.0497	15.6951
260.002	2.9720	14.9966
260.999	3.8832	14.9947
262.000	4.8015	14.9928
263.001	5.7202	14.9910
263.999	6.6396	14.9893
266.002	8.4795	14.9861
268.000	10.3213	14.9829
269.999	12.1662	14.9799
272.000	14.0077	14.9769
273.999	15.8493	14.9740
276.001	17.6826	14.9711
278.000	19.6458	14.9682
280.001	21.3478	14.9655
283.999	24.9968	14.9600
287.999	28.6332	14.9545
292.001	32.2518	14.9491
280.000	3.1303	14.1950
281.000	3.8773	14.1933
282.001	4.6273	14.1917
282.999	5.3769	14.1901
284.000	6.1336	14.1885
285.999	7.6384	14.1855
288.001	9.1465	14.1827
289.998	10.6558	14.1799
292.000	12.1577	14.1772
295.999	15.1714	14.1718
300.002	18.1816	14.1666
304.001	21.1810	14.1615
311.998	27.1654	14.1514
319.999	33.1146	14.1414
300.000	3.1476	13.2764
301.001	3.7412	13.2749
302.002	4.3359	13.2734
303.001	4.9335	13.2720
304.001	5.5286	13.2706
305.999	6.7240	13.2680
307.999	7.9198	13.2654
310.000	9.1178	13.2628
312.000	10.3146	13.2604
316.000	12.7140	13.2555
320.002	15.1141	13.2507

Table III. *(Continued)*

T (K)	p (MPa)	ρ (mol · dm^{-3})
323.999	17.5096	13.2460
332.002	22.3009	13.2367
340.000	27.0712	13.2274
348.000	31.8227	13.2183
352.000	34.1907	13.2137
319.999	3.2105	12.1585
321.999	4.1011	12.1560
324.002	4.9956	12.1535
326.002	5.8922	12.1512
328.000	6.7923	12.1489
330.000	7.6939	12.1467
332.002	8.5975	12.1445
336.001	10.4082	12.1401
340.000	12.2242	12.1358
344.000	14.0425	12.1316
348.001	15.8648	12.1273
352.001	17.6881	12.1232
356.000	19.5117	12.1190
360.001	21.3358	12.1149
364.002	23.1606	12.1107
368.000	24.9811	12.1066
372.000	26.8003	12.1024
376.002	28.6179	12.0983
380.001	30.4318	12.0941
383.999	32.2431	12.0899
340.001	3.8080	10.6888
342.000	4.4117	10.6868
344.002	5.0201	10.6849
346.001	5.6308	10.6829
347.999	6.2454	10.6811
350.001	6.8629	10.6792
352.000	7.4832	10.6773
356.002	8.7306	10.6736
360.001	9.9843	10.6700
364.000	11.2456	10.6664
368.002	12.5121	10.6627
372.000	13.7824	10.6592
376.001	15.0560	10.6556
380.001	16.3325	10.6520
383.999	17.6121	10.6484
387.999	18.8933	10.6448
392.001	20.1763	10.6412
396.000	21.4594	10.6376
399.999	22.7421	10.6340

Table III. *(Continued)*

T (K)	p (MPa)	ρ (mol · dm^{-3})
360.002	7.3575	9.9447
364.000	8.3936	9.9413
368.001	9.4376	9.9380
371.999	10.4876	9.9346
376.002	11.5450	9.9313
379.999	12.6060	9.9280
384.002	13.6722	9.9247
388.002	14.7403	9.9214
392.002	15.8118	9.9181
395.999	16.8845	9.9148
400.000	17.9593	9.9115
360.000	5.4493	8.8140
364.002	6.2055	8.8111
368.002	6.9740	8.8082
372.001	7.7525	8.8054
376.001	8.5383	8.8025
380.002	9.3315	8.7996
384.000	10.1298	8.7967
388.000	10.9331	8.7939
392.000	11.7404	8.7910
396.001	12.5512	8.7881
400.001	13.3645	8.7852
360.000	4.7135	6.0295
363.998	5.1059	6.0277
368.000	5.5055	6.0259
371.999	5.9089	6.0241
376.001	6.3152	6.0222
379.999	6.7237	6.0204
384.000	7.1345	6.0185
388.001	7.5462	6.0166
392.000	7.9589	6.0148
396.000	8.3722	6.0129
399.999	8.7866	6.0111
360.000	3.3290	1.6692
363.999	3.4140	1.6688
368.000	3.4981	1.6684
372.002	3.5813	1.6712
376.000	3.6637	1.6707
380.000	3.7455	1.6702
384.001	3.8265	1.6697
388.001	3.9068	1.6692
392.000	3.9866	1.6687
396.001	4.0658	1.6682
400.002	4.1445	1.6677

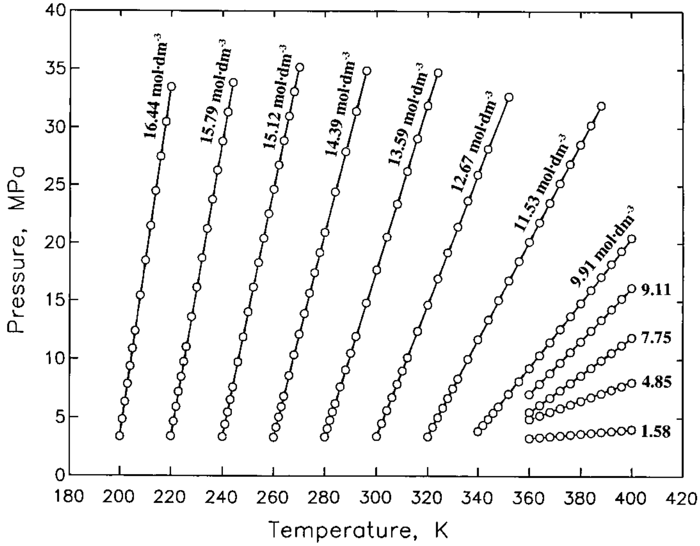

Fig. 1. Range of p–ρ–T measurements for 0.3337 R32 + 0.3333 R125 + 0.3330 R134a (designated DOE17).

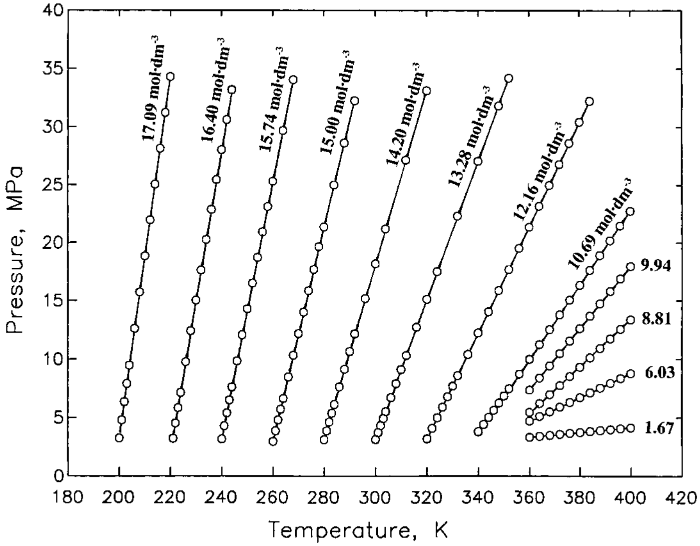

Fig. 2. Range of p–ρ–T measurements for 0.3808 R32 + 0.1798 R125 + 0.4394 R134a (designated DOE18).

by Lemmon and Jacobsen [13]. The data reported in this study were not used to develop this model. Figure 3 depicts the deviations between experimental densities and calculated densities from the Helmholtz energy model. The experimental densities include selected published data and the results of this study. For liquid phase states, this study agrees with Widiatmo et al. [14] within ±0.15% and with Kleemis [15] within ±0.05%. The R32 mole fraction compostions of Widiatmo (0.38 to 0.46) and Kleemis (0.34) overlapped those of this study (0.33 to 0.38). Likewise, most of the published results agree very well with the model. Most of the results in the supercritical gas phase agree within ±0.2%, including those of Oguchi et al. [16], with an R32 mole fraction range of 0.38 to 0.47, with the possible exception of certain data which were measured in the vicinity of the critical point. At pressures and temperatures in a broad region surrounding a critical point, predictions from the Helmholtz energy model differed by as much as ±1% from the measurements. Perhaps this result is not surprising because the formulation's underlying equations do not reproduce the observed flatness of pressure–density isotherms in the critical region and thus the relative deviations of calculated densities become large.

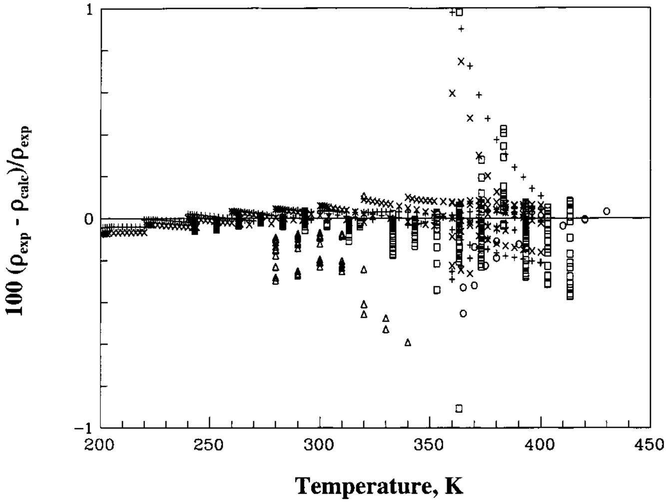

Fig. 3. Percentage deviations of the experimental densities for 0.3337 R32 + 0.3333 R125 + 0.3330 R134a (DOE17) (+) and 0.3808 R32 + 0.1798 R125 + 0.4394 R134a (DOE18) (×) obtained in this work, by Widiatmo et al. [14] (△), by Kleemis [15] (□), and by Oguchi et al. [16] (○) from the values calculated with the Helmholtz energy model of Lemmon and Jacobsen [13].

Table IV. Isochoric Heat Capacity C_v Data for Ternary Refrigerant Mixtures Containing R32, R125, and R134a

T (K)	ρ $(\mathrm{mol \cdot dm^{-3}})$	$p_{\mathrm{avg}}{}^{a}$ (MPa)	C_v $(\mathrm{J \cdot mol^{-1} \cdot K^{-1}})$
0.3337 R32 + 0.3333 R125 + 0.3330 R134a			
203.5579	16.402	6.179	73.26
207.4602	16.386	11.710	73.79
211.3435	16.370	17.153	74.30
215.2044	16.354	22.489	74.68
219.0384	16.339	27.707	75.06
222.5060	15.791	5.714	74.49
226.4209	15.777	10.500	74.72
230.3147	15.763	15.219	74.96
234.1817	15.749	19.859	75.31
238.0333	15.735	24.428	75.64
241.8793	15.722	28.936	76.47
242.4650	15.111	5.221	75.55
246.3986	15.098	9.285	75.93
250.3202	15.086	13.309	76.48
254.2242	15.075	17.283	76.81
258.1094	15.063	21.205	76.99
261.9683	15.051	25.066	77.78
265.8188	15.039	28.880	78.01
269.6440	15.028	32.628	78.57
262.1888	14.395	4.913	77.49
266.1578	14.385	8.342	77.80
270.1111	14.374	11.741	78.34
274.0505	14.364	15.109	78.67
277.9761	14.354	18.444	78.95
281.8821	14.344	21.741	79.36
285.7725	14.334	25.001	80.17
289.6535	14.324	28.229	80.49
293.5178	14.314	31.420	80.73
282.6915	13.574	4.603	79.49
286.7219	13.565	7.430	79.80
290.7313	13.556	10.236	80.10
294.7332	13.548	13.028	80.41
298.7286	13.539	15.806	80.59
302.7043	13.530	18.557	81.32
306.6865	13.522	21.299	81.57
310.6486	13.513	24.014	81.68
314.6019	13.505	26.709	82.25
318.5472	13.496	29.383	83.30
322.4869	13.488	32.041	83.81
303.0394	12.638	4.387	81.74
307.1825	12.631	6.668	82.21
311.3348	12.623	8.956	82.41
315.4784	12.616	11.239	82.80

Table IV. *(Continued)*

T (K)	ρ ($\mathrm{mol \cdot dm^{-3}}$)	$p_{\mathrm{avg}}{}^{a}$ (MPa)	C_v ($\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$)
319.6208	12.609	13.519	83.04
323.7603	12.601	15.794	83.09
327.9024	12.594	18.064	83.63
332.0372	12.587	20.325	84.22
336.1895	12.580	22.589	84.24
340.3303	12.572	24.838	84.41
312.8612	12.107	4.232	83.15
317.0938	12.100	6.259	83.13
321.3435	12.094	8.299	83.58
325.5865	12.087	10.339	84.03
329.8511	12.080	12.391	84.39
317.0935	12.100	6.259	83.27
321.3440	12.094	8.299	83.63
329.8726	12.080	12.401	84.32
338.4221	12.067	16.513	84.76
342.7110	12.060	18.572	84.99
327.0315	11.486	5.854	84.47
331.3887	11.480	7.633	84.82
335.7665	11.475	9.428	85.53
340.1579	11.469	11.233	85.65
344.5627	11.463	13.047	85.99
	0.3808 R32 + 0.1798 R125 + 0.4394 R134a		
202.7378	17.086	6.179	70.99
206.6297	17.069	11.912	71.27
210.5135	17.052	17.564	71.56
214.3544	17.035	23.066	71.95
218.1525	17.019	28.409	72.27
222.9018	16.422	5.766	71.70
226.7929	16.408	10.662	71.99
230.6659	16.393	15.490	72.54
234.5255	16.378	20.251	72.91
238.3618	16.364	24.929	73.14
242.1805	16.350	29.525	73.10
242.5749	15.740	5.257	72.95
246.4949	15.727	9.452	73.40
250.3982	15.714	13.601	73.71
254.2829	15.701	17.696	73.66
258.1419	15.689	21.727	73.94
261.9853	15.676	25.702	74.74
265.8203	15.664	29.628	75.23
262.7931	14.995	4.926	74.41
266.7505	14.983	8.473	74.64
270.6901	14.972	11.985	75.23
274.6288	14.961	15.474	75.45
278.5403	14.950	18.916	75.79

Table IV. *(Continued)*

T (K)	ρ (mol · dm^{-3})	p_{avg}[a] (MPa)	C_v (J · mol^{-1} · K^{-1})
282.4471	14.940	22.329	76.37
286.3370	14.929	25.702	76.91
290.2154	14.918	29.039	77.28
294.0789	14.908	32.338	77.64
282.6988	14.191	4.636	76.36
286.7112	14.182	7.597	76.88
290.7191	14.172	10.545	77.14
294.7176	14.163	13.475	77.23
298.7109	14.154	16.388	77.44
302.6904	14.144	19.277	77.77
306.6585	14.135	22.143	78.39
310.6200	14.126	24.989	78.98
314.5705	14.117	27.810	79.17
318.5150	14.107	30.611	79.52
322.4557	14.098	33.394	80.28
302.4583	13.283	4.364	78.51
306.5733	13.275	6.792	78.81
310.6894	13.268	9.220	79.08
318.8997	13.252	14.054	79.51
323.0102	13.244	16.466	80.41
327.1064	13.236	18.862	80.61
335.3080	13.220	23.635	80.98
339.4116	13.212	26.010	81.44
311.0487	13.267	9.432	79.17
315.2173	13.259	11.888	79.45
319.3810	13.251	14.337	79.67
335.9866	13.219	24.029	80.94
340.1343	13.211	26.427	81.53
321.0987	12.739	8.675	80.18
325.3415	12.732	10.871	80.45
333.8390	12.718	15.267	81.03
338.0926	12.710	17.463	81.39
342.3507	12.703	19.657	81.81
316.9720	12.746	6.540	79.70
321.2117	12.739	8.734	80.22
329.7082	12.725	13.131	80.68
333.9658	12.717	15.333	81.04
338.2278	12.710	17.533	81.31
323.8234	12.093	4.264	81.08
328.1646	12.086	6.159	81.37
332.5328	12.080	8.074	81.49
323.7565	12.093	4.235	81.20
336.8795	12.073	9.985	81.62
341.2719	12.067	11.920	81.87

[a] Subscript avg denotes a condition evaluated at the average of the initial and final temperatures.

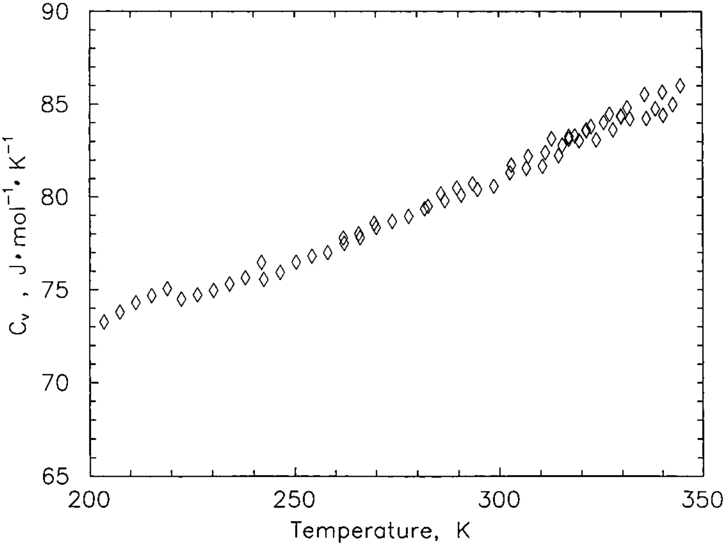

Fig. 4. Range of C_v–T measurements for 0.3337 R32 + 0.3333 R125 + 0.3330 R134a (DOE17).

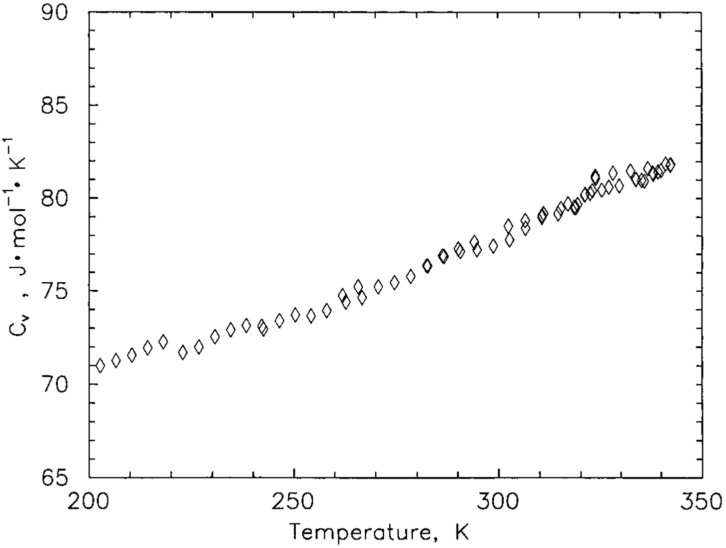

Fig. 5. Range of C_v–T measurements for 0.3808 R32 + 0.1798 R125 + 0.4394 R134a (DOE18).

3.2. Heat Capacities at Constant Volume

The experimental compositions, temperatures (ITS-90), pressures, densities, and heat capacities at constant volume C_v are presented in Table IV. As before, the number of digits presented represents the measurement precision. For each ternary mixture, these measurements were carried out at eight liquid-phase filling densities. To illustrate the range of measurements for each of the mixtures, the heat capacity data are plotted in Figs. 4 and 5.

Comparisons of the C_v measurements were made with calculated values from a Helmholtz energy model developed by Lemmon and Jacobsen [13], who estimate the uncertainty of calculated C_v to be 0.5 to 1.0%. Although no published data were available for comparisons, Fig. 6 shows that the model predictions are within ±2% of the measurements. Most of the calculations are within ±1.5%. Though slightly larger than the experimental uncertainty of C_v, the observed agreement of the predicted values is reasonable. Despite the added complexity of the calculations for ternary mixtures over those for binary mixtures, the predictions are just as close to experimental values as observed previously for binary mixtures containing R32, R125, and R134a [7].

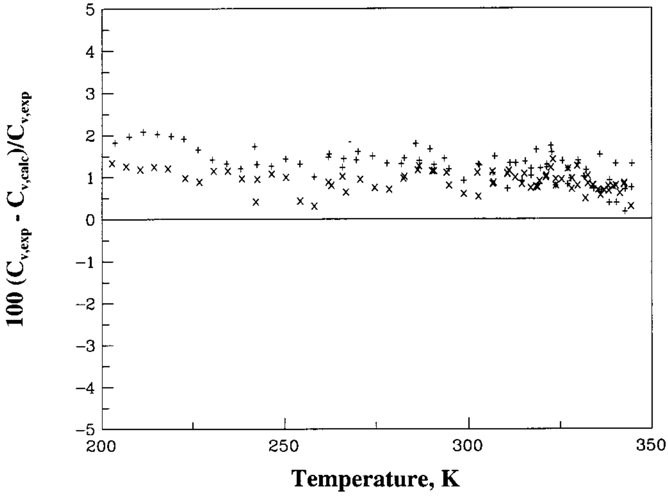

Fig. 6. Percentage deviations of the experimental liquid heat capacities for 0.3337 R32 + 0.3333 R125 + 0.3330 R134a (DOE17) (+) and 0.3808 R32 + 0.1798 R125 + 0.4394 R134a (DOE18) (×) obtained in this work from the values calculated with the Helmholtz energy model of Lemmon and Jacobsen [13].

4. CONCLUSIONS

For two ternary mixtures of R32 + R125 + R134a, 352 p–ρ–T state conditions have been reported. For p–ρ–T, the uncertainty of pressure is 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 $\pm 0.2\%$, which falls within the combined uncertainty of the results. For the same two ternary mixtures, 132 C_v measurements have been made. 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 emperature rise is 0.002 K, and that of heat capacity is 0.7%. No published heat capacities were available for comparison.

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