International Journal of Thermophysics, Vol. 21, No. 6, 2000

Isochoric p–ρ–T Measurements for 2,2-Dichloro-1,1,1-Trifluoroethane (R123) at Temperatures from 176 to 380 K and 1-Chloro-1,2,2,2-Tetrafluoroethane (R124) from 104 to 400 K at Pressures to 35 MPa

J. W. Magee[1]

Received July 15, 2000

The p–ρ–T relationships were measured for 2,2-dichloro-1,1,1-trifluoroethane (R123) and 1-chloro-1,2,2,2-tetrafluoroethane (R124) by an isochoric method with gravimetric determinations of the amount of substance. Temperatures ranged from 176 to 380 K for R123 and from 104 to 400 K for R124, while pressures extended up to 35 MPa. Measurements were conducted on compressed liquid samples. Most published p–ρ–T data are in good agreement with this study. The uncertainty is 0.03 K for temperature and 0.01 % for pressure at $p > 3$ MPa and 0.05 % at $p < 3$ MPa. The principal source of uncertainty 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 2-SD estimate) of the density measurements is estimated to be 0.05 %.

KEY WORDS: 1-chloro-1,2,2,2-tetrafluoroethane; density; 2,2-dichloro-1,1,1-trifluoroethane; p–ρ–T data; R123; R124; saturated liquid.

1. INTRODUCTION

Both 2,2-dichloro-1,1,1-trifluoroethane (R123) and 1-chloro-1,2,2,2-tetrafluoroethane (R124) are hydrochorofluorocarbons which have been investigated in recent years in the search for less harmful refrigerants. Younglove and McLinden [1] have analyzed the available thermodynamic data for R123 and described an equation of state formulation for this substance.

[1] Physical and Chemical Properties Division, Chemical Science and Technology Laboratory, National Institute of Standards and Technology, Boulder, Colorado 80305, U.S.A. E-mail: joe.magee@nist.gov.

0195-928X/00/1100-1291$18.00/0

Similarly, de Vries et al. [2] have studied R124 and developed a fundamental equation of state for the reduced Helmholtz energy. The authors of Refs. 1 and 2 noted that, prior to this work, published p–ρ–T data in the saturated and compressed liquid phases for these substances were scarce, especially at temperatures below 280 K for R123 and below 243 K for R124. Accurate measurements were needed at subambient temperatures which would supplement the published p–ρ–T data.

In this paper, new p–ρ–T measurements for pure R123 and R124 are reported for temperatures ranging from as low as 100 K to a maximum temperature near 400 K and at pressures up to 35 MPa. Comparisons with published densities and an equation of state model are also reported.

2. MEASUREMENTS

2.1. p–ρ–T Apparatus and Procedures

The 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 [3, 4]. 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 [3–5].

2.2. Sample Purity

The purities of the components used to make the mixtures are an important aspect of this study. The manufacturers stated purity of the R123 sample was 0.9999 mass fraction. The sample was poured from a metal screw-top container into a clean, dry Type-304 stainless-steel vessel, which was filled to 25% of its volume with pretreated and dried molecular seive pellets. A freeze–pump–thaw cycle was repeated five times to degas the sample. The liquid sample was dried over the seive pellets for 2 weeks before its use in this study. The manufacturer's analysis of the R124 in our supply cylinder gave a purity of 0.999985 mass fraction. Samples of R124 were charged directly into our apparatus without further purification.

2.3. Assessment of Uncertainties

A detailed discussion of the uncertainties in the measured quantities is available in a recent publication [5]. We use a definition for the expanded uncertainty which is two times the standard uncertainty (a coverage factor $k = 2$ and, thus, a 2-SD estimate). The expanded uncertainties of the

Table I. Expanded Uncertainties of Temperature, Pressure, Mass, Volume, and Density

Temperature	0.03 K
Pressure	
<3 MPa	0.05%
>3 MPa	0.01%
Mass	0.002 g
Volume	0.003 cm^3
Density	0.05%

original measurements and the resulting combined uncertainties are listed in Table I.

3. RESULTS

3.1. p–ρ–T Measurements

The experimental compositions, temperatures (ITS-90), pressures, and densities for single-phase liquid and gaseous mixtures are presented in Tables II and III. The number of digits presented in Tables II and III represents the measurement precision; they were retained to avoid round-off errors when modeling equations are fitted to them. For R123, a total of 104 p–ρ–T state conditions has been reported. For R124, the total is 149 points. 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 for R123 were made with a 32-term modified Benedict–Webb–Rubin equation-of-state formulation developed by Younglove and McLinden [1]. This formulation has been selected as an international standard by a group working under the auspices of the International Energy Agency. The measurements of this study were used to develop the formulation along with selected data sets from other laboratories. Figure 8 in Ref. 1 graphically depicts the deviations of the calculated density from the experimental density for these selected data and the results of this study. All of the liquid-phase data of this work agree with the model within $\pm 0.05\%$. With the exception of one data set [6], this figure shows that agreement with published data is within $\pm 0.1\%$.

Comparisons of the isochoric p–ρ–T measurements for R124 were made with a fundamental equation-of-state formulation developed by de Vries et al. [2]. This formulation is expressed in terms of the Helmholtz energy and contains 20 adjustable coefficients. The p–ρ–T measurements in

Table II. Experimental p–ρ–T Data for Liquid R123

T (K)	p (MPa)	ρ (mol · dm^{-3})
176.002	3.9324	11.4544
178.000	7.8440	11.4520
180.000	11.7393	11.4495
182.000	15.6036	11.4471
184.000	19.4365	11.4448
186.000	23.2508	11.4424
188.001	27.0433	11.4401
190.000	30.7990	11.4378
191.999	34.5455	11.4355
189.999	1.7694	11.2364
191.999	5.2974	11.2340
194.000	8.7954	11.2317
195.999	12.2831	11.2295
198.001	15.7501	11.2272
199.999	19.1966	11.2250
202.000	22.6245	11.2228
204.000	26.0342	11.2206
206.000	29.4151	11.2184
207.999	32.7748	11.2162
206.000	2.1241	11.0062
208.002	5.2733	11.0040
210.001	8.4118	11.0019
212.001	11.5355	10.9997
214.000	14.6379	10.9976
216.000	17.7228	10.9954
218.000	20.7961	10.9933
220.000	23.8508	10.9912
222.000	26.8919	10.9892
224.001	29.9176	10.9871
226.000	32.9290	10.9850
226.002	1.8104	10.7103
228.001	4.5494	10.7083
230.000	7.2733	10.7062
231.999	9.9884	10.7042
234.000	12.6913	10.7022
236.001	15.3802	10.7002
238.000	18.0561	10.6982
240.001	20.7273	10.6962
241.998	23.3777	10.6942
244.001	26.0227	10.6923
245.999	28.6503	10.6903
248.002	31.2719	10.6883
250.001	33.8768	10.6864
249.001	0.8409	10.3564
250.002	2.0013	10.3554
252.000	4.3214	10.3535
254.000	6.6312	10.3516
255.999	8.9309	10.3497
258.000	11.2254	10.3478
259.999	13.5089	10.3459
262.001	15.7855	10.3440
263.999	18.0494	10.3422

Table II. *(Continued)*

T (K)	p (MPa)	ρ (mol · dm^{-3})
266.000	20.3111	10.3403
268.001	22.5604	10.3385
270.000	24.7981	10.3366
272.000	27.0352	10.3348
274.000	29.2599	10.3329
276.001	31.4758	10.3311
278.000	33.6812	10.3293
269.999	2.6886	10.0590
272.000	4.6983	10.0572
274.001	6.7046	10.0554
275.998	8.7124	10.0536
278.002	10.7018	10.0518
280.002	12.6960	10.0501
282.001	14.6870	10.0483
284.001	16.6716	10.0465
286.002	18.6491	10.0447
288.001	20.6123	10.0430
290.002	22.5807	10.0412
291.998	24.5384	10.0394
293.999	26.4898	10.0376
296.000	28.4346	10.0359
298.001	30.3690	10.0341
300.000	32.3008	10.0324
302.001	34.2147	10.0306
298.001	3.1667	9.6272
300.001	4.8225	9.6255
302.000	6.4752	9.6238
303.999	8.1252	9.6222
306.001	9.7712	9.6205
307.998	11.4065	9.6189
310.001	13.0503	9.6172
312.001	14.6840	9.6155
313.999	16.3105	9.6138
316.001	17.9326	9.6122
320.000	21.1726	9.6088
324.000	24.3920	9.6055
328.001	27.5896	9.6022
332.001	30.7721	9.5988
336.001	33.9329	9.5955
332.002	2.5886	9.0403
336.000	5.1321	9.0372
340.002	7.6545	9.0343
344.001	10.1909	9.0310
348.000	12.6999	9.0280
352.000	15.2108	9.0250
356.002	17.7039	9.0220
360.000	20.1917	9.0189
364.000	22.6813	9.0158
368.000	25.1468	9.0127
372.001	27.6018	9.0096
376.000	30.0495	9.0064
379.999	32.4875	9.0033

Table III. Experimental p–ρ–T Data for Liquid R124

T (K)	p (MPa)	ρ (mol · dm^{-3})
103.999	6.2268	13.9186
105.999	12.7788	13.9142
107.999	19.2875	13.9101
109.999	25.7604	13.9062
111.998	32.1549	13.9024
113.999	3.2584	13.7093
116.000	9.2410	13.7050
117.998	15.1679	13.7010
119.999	21.0632	13.6973
121.999	26.9213	13.6937
123.998	32.7205	13.6902
124.000	3.1570	13.5172
126.000	8.6087	13.5132
127.999	14.0560	13.5094
129.999	19.4713	13.5059
131.999	24.8440	13.5025
134.000	30.1746	13.4992
136.000	35.4728	13.4959
135.999	2.4742	13.2858
138.000	7.3913	13.2820
139.999	12.2966	13.2784
142.000	17.1916	13.2751
143.999	22.0515	13.2718
146.000	26.8645	13.2687
147.999	31.6410	13.2657
148.000	2.4580	13.0604
149.999	6.9158	13.0568
151.999	11.3732	13.0535
154.000	15.8069	13.0504
155.998	20.2208	13.0473
157.999	24.6066	13.0443
159.999	28.9692	13.0414
161.999	33.3026	13.0385
162.000	1.8922	12.7934
164.000	5.8757	12.7901
166.000	9.8563	12.7870
167.999	13.8155	12.7840
169.999	17.7584	12.7811
172.000	21.6837	12.7783
174.001	25.5882	12.7755
175.999	29.4638	12.7728
177.999	33.3198	12.7701
177.999	2.9319	12.5017
180.000	6.4591	12.4986
182.000	9.9737	12.4958
184.000	13.4823	12.4930
185.999	16.9688	12.4903
188.001	20.4409	12.4877
190.001	23.9030	12.4851
191.999	27.3413	12.4825

Table III. *(Continued)*

T (K)	p (MPa)	ρ (mol · dm^{-3})
193.999	30.7593	12.4800
195.999	34.1574	12.4775
194.000	1.9315	12.1891
196.000	5.0333	12.1862
197.999	8.1228	12.1835
200.000	11.2094	12.1809
202.000	14.2864	12.1783
204.001	17.3480	12.1758
206.000	20.3974	12.1734
208.000	23.4291	12.1710
210.001	26.4524	12.1686
212.002	29.4032	12.1662
214.000	32.3968	12.1639
216.000	35.3752	12.1616
209.999	2.6133	11.8909
212.000	5.3600	11.8882
214.000	8.1038	11.8857
216.000	10.8358	11.8832
218.001	13.5546	11.8808
219.999	16.2685	11.8785
222.000	18.9676	11.8762
224.000	21.6631	11.8739
226.000	24.3446	11.8716
228.000	27.0182	11.8694
230.002	29.6810	11.8671
232.000	32.3235	11.8649
233.998	34.9617	11.8627
228.000	2.6873	11.5402
229.999	5.0685	11.5377
232.000	7.4418	11.5354
234.001	9.8187	11.5331
235.999	12.1780	11.5308
238.000	14.5381	11.5286
240.001	16.8926	11.5264
241.999	19.2360	11.5242
244.000	21.5739	11.5221
245.999	23.8994	11.5200
248.001	26.2195	11.5179
250.001	28.5322	11.5158
252.000	30.8304	11.5137
254.000	33.1236	11.5116
256.001	35.4092	11.5095
250.000	2.5919	11.0932
251.999	4.5844	11.0910
253.999	6.5760	11.0888
256.001	8.5638	11.0866
258.000	10.5412	11.0846
260.000	12.5228	11.0825
262.000	14.4964	11.0804
263.999	16.4607	11.0784

Table III. *(Continued)*

T (K)	p (MPa)	ρ (mol · dm^{-3})
266.000	18.4222	11.0764
268.000	20.3793	11.0744
270.000	22.3259	11.0724
271.998	24.2729	11.0705
274.001	26.2116	11.0685
276.000	28.1464	11.0666
278.000	30.0761	11.0646
279.998	31.9972	11.0627
282.000	33.9127	11.0607
276.000	1.2151	10.4985
279.999	4.3650	10.4944
283.999	7.5075	10.4905
288.000	10.6371	10.4867
292.001	13.7622	10.4830
296.001	16.8728	10.4793
299.998	19.9708	10.4757
304.000	23.0583	10.4720
308.000	26.1313	10.4684
311.999	29.1859	10.4648
316.000	32.2262	10.4612
320.001	35.2525	10.4576
315.998	2.6691	9.5662
320.000	4.8512	9.5628
323.998	7.0293	9.5595
328.000	9.2092	9.5562
331.998	11.3872	9.5529
336.000	13.5620	9.5497
339.998	15.7314	9.5464
343.999	17.8983	9.5432
348.001	20.0604	9.5400
352.000	22.2125	9.5368
355.998	24.3571	9.5338
360.001	26.5022	9.5306
364.002	28.6410	9.5273
368.000	30.7712	9.5241
372.001	32.8936	9.5209
375.998	35.0045	9.5176
356.001	2.7162	8.2846
360.000	4.0229	8.2818
364.000	5.3353	8.2790
368.000	6.6542	8.2763
372.001	7.9773	8.2735
376.001	9.3032	8.2708
380.000	10.6331	8.2680
384.000	11.9637	8.2653
387.998	13.2964	8.2625
392.001	14.6308	8.2598
396.001	15.9643	8.2570
400.000	17.2975	8.2542

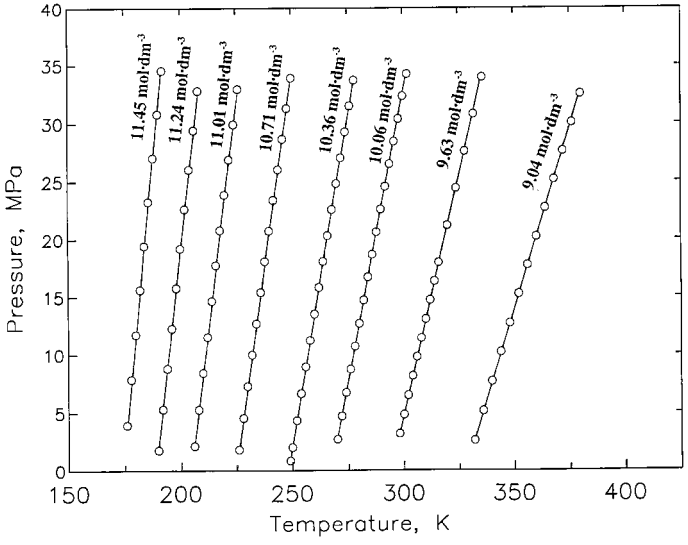

Fig. 1. Range of *p*-ρ-*T* measurements for liquid R123.

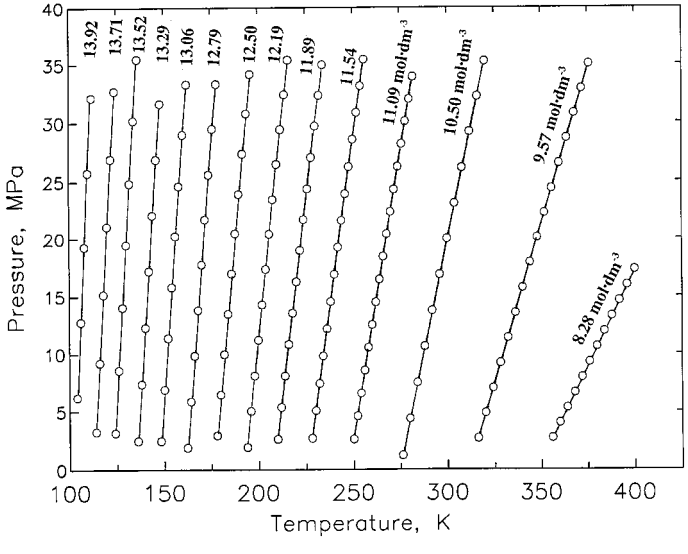

Fig. 2. Range of *p*-ρ-*T* measurements for liquid R124.

Table IV. Saturated Liquid Densities for R123

T (K)	ρ_σ (mol·dm^{-3})
174.01	11.4574
189.00	11.2371
204.66	11.0072
224.69	10.7113
248.29	10.3570
267.37	10.0610
294.30	9.6303
328.35	9.0430

Table III were not used to develop the formulation since the authors used a total of 1268 measurements from their laboratory. Figure 2 in Ref. 2 graphically depicts the deviations of the experimental density from the calculated density the measurements of de Vries et al. and the results of this study. The observed agreement of this work with the data of de Vries et al. is within $\pm 0.05\%$. Other published data agree with the formulation within $\pm 0.2\%$.

3.2. Saturated Liquid Densities

Saturated liquid densities were calculated from the measurements by determining the intersection of an equation fitted to p–T data, another

Table V. Saturated Liquid Densities for R124

T (K)	ρ_σ (mol·dm^{-3})
102.12	13.9234
112.92	13.7118
122.86	13.5197
135.10	13.2873
146.91	13.0624
161.06	12.7951
176.35	12.5046
192.78	12.1907
208.11	11.8936
225.78	11.5430
247.48	11.0962
274.70	10.4993
312.22	9.5692
352.48	8.2870

equation fitted to ρ–T data, and the vapor pressure equation. The results are given in Table IV for R123 and Table V for R124. After incorporating the additional uncertainty due to data correlation, the estimated uncertainty of these density values is 0.07%. Figure 6 in Ref. 1 shows that the agreement between the results in Table IV for R123 are within 0.1% of other reliable measurements.

ACKNOWLEDGMENTS

A special thanks is due to John Howley for able assistance with these measurements. I am grateful to Ben Younglove and Mark McLinden for generous technical assistance with the calculations and many helpful discussions during this study. I have profited from many discussions with Gerald Straty and Marcia Huber.

REFERENCES

1. B. A. Younglove and M. O. McLinden, *J. Phys. Chem. Ref. Data* **23**:731 (1994).
2. B. de Vries, R. Tillner-Roth, and H. D. Baehr, *Proc. 19th Int. Congr. Refrig., Vol. IVa* (1995).
3. R. D. Goodwin, *J. Res. Natl. Bur. Stand. (US)* **65C**:231 (1961).
4. J. W. Magee and J. F. Ely, *Int. J. Thermophys.* **9**:547 (1988).
5. J. W. Magee, W. M. Haynes, and M. J. Hiza, *J. Chem. Thermodyn.* **29**:1439 (1998).
6. Y. Maezawa, H. Sato, and K. Watanabe, *J. Chem. Eng. Data* **35**:225 (1990).