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Volumetric Properties Under Pressure for 1,2-Dichlorofluoroethane (R141), 1-Fluoro-1,1,2-Trichloroethane (R131a), and 1,2-Dichloro-1,1-Difluoroethane (R132b)

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The effect of pressure on the volume of R141, R131, and R132b is reported as volume ratios (the volume under pressure relative to its value at atmospheric pressure) at six temperatures covering the range 278.15 to 338.13 K and pressures up to 380 MPa for R141 and R131a. For R132b the same temperature range has been used, but above its normal boiling point experimental arrangements have limited maximum pressures to below 300 MPa, with some loss of accuracy. Densities have been measured at atmospheric pressure for each liquid. The experimental data have been used to calculate isothermal compressibilities, thermal expansivities, and internal pressures; the change in isobaric heat capacity from its value at atmospheric pressure has also been estimated. The volume ratios for all three compounds can be represented by a version of the Tait equation based on previously reported data for 1,2-dichloroethane and 1,1,2-trichloroethane with the inclusion of allowances for the substitution in the former of chlorine or fluorine for the hydrogens on one of the carbons.

KEY WORDS: compressibility; density; heat capacity; refrigerants; R131a; R132b; R141; Tait equation; thermal expansivity.

1. INTRODUCTION

The compounds chosen for this study are substituted ethanes of commercial quality, which can be regarded as being derived from 1,2-dichloroethane. Each contains a CH_2Cl- group; the hydrogens of the other methyl group are partly or wholly substituted by Cl– and/or F–. This continues investigation

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of a proposal for the prediction of the effect of pressure, p, on the volumetric properties of a related series of compounds [1] which assumed that each of the characteristic groups of the compound made a specific contribution to the B parameter of the modified Tait equation for the volume ratio $k = V_p/V(0.1\ \text{MPa})$

$$1 - k = C \log[(B + p)/(B + 0.1)] \tag{1}$$

The specific contributions were determined by comparison of closely related compounds. The principal criterion for choosing them has been the ability to use a common value of C to represent their k within the required accuracy over the temperature range of the experimental data and to express the complementary B's by a (usually) linear function of the inverse of the reduced temperature $T_R = T/T_c$, where T_c is the critical temperature. The earlier work found that a C of 0.21 was suitable for a number of substituted methanes and ethanes [1].

2. EXPERIMENTS

The R141 (molecular weight, 0.116951 kg · mol^{-1}), R131a (molecular weight, 0.151394 kg · mol^{-1}), and R132b (molecular weight, 0.134940 kg · mol^{-1}) were from PCR Inc. (Gainesville, FL); the manufacturer states for each substance a purity in the range 97–99%. They were distilled before use in the experiments to provide a middle fraction with a boiling range within 72.9–73.0°C for R141, 86.9–87.0°C for R131a, and 45.0–45.1°C for R132b. No analysis was made to check the purity. The effects of impurities on the volumetric properties is minimized when the experimental method, such as that used here, determines the change in volume due to increase in pressure as volume ratios. The densities given in Table I were measured at atmospheric pressure (about 0.09 MPa) with an Anton Paar Model DMA 602 densimeter calibrated frequently with water and dry nitrogen [2]. The densimeter has a resolution of 0.001 kg · m^{-3} and the calibration reproducibility is typically ±0.002 kg · m^{-3} but for fluorocarbons the reproducibility is usually ±0.005 kg · m^{-3}. The calibration procedure for the DMA 602 has been studied extensively by Ashcroft et al. [3], who showed that extrapolation of the calibration constant to densities of 1580 kg · m^{-3} did not introduce errors greater than 0.05 kg · m^{-3} unless there was a large difference in viscosities. Because boiled samples were found to have higher densities than those that were not boiled, the densities in Table I have been adjusted to refer to the boiled condition where it was not practicable to repeat the measurements. Consequently the overall reproducibility of the densities is estimated as ±0.1 kg · m^{-3}. Temperatures

Table I. Density (in kg·m^{-3}) at Atmospheric Pressure for R141, R131a, and R132b

	T(K)					
	278.15	288.15	298.14	313.14	323.14	338.13
R141	1403.56	1386.41	1369.24	1343.20	1325.36	1298.22
R131a[a]	1517.89	1500.34	1482.59	1455.59	1437.34	1409.71
R132b[b]	1448.22	1427.66	1406.57	1374.37	[1352.38]	[1318.64]

[a] The experimental values at 288.15 and 298.14 K were increased by 0.32 kg·m^{-3}, respectively, so that at all temperatures the results given are those measured or estimated for the sample in the boiled condition.

[b] The value at 288.15 K has been increased by 0.32 kg·m^{-3} (see footnote *a*). Measurements were also made at 283.15 and 293.15 K: 1437.86 and 1417.17 kg·m^{-3}. Values above 313.14 K are from a quadratic fit (rmsd 0.04) of the six measured data.

were measured with thermometers calibrated to IPTS-48 and adjusted to ITS-90; they have an accuracy of ±0.01 K and were constant during experiments to ±0.005 K. Volume ratios were determined using a bellows volumometer described in detail elsewhere [4]. Because R132b has a normal boiling point below two of the experimental temperatures a modified procedure, described in Ref. 4, has to be used for those measurements. The reliability of the procedure is checked by using it to repeat the volumometer measurements made with the normal procedure at the experimental temperature immediately below the normal boiling point. The pressure measurement system for R141 was that of Ref. 4; but for R131a and R132b, Heise–Bourdon gauges (0–25 and 0–400 MPa) calibrated using dead weight gauges with an accuracy of ±0.05% were used.

3. RESULTS AND DISCUSSION

3.1. Volumetric Data

The experimental pressures and volume ratios are given in Tables II–IV. The volume ratios for R141 and R131a at all temperatures are expected to have an accuracy of ±0.03–0.05% for pressures of 50 MPa and above, increasing to ±0.1% as the pressure approaches 0.1 MPa. For R132b a similar accuracy is expected for the measurements up to 313.14 K, but the second set at that temperature in Table IV, and the measurements at higher temperatures, have an estimated accuracy of ±0.1% up to

Table II. Volume Ratios for 1,2-Dichlorofluoroethane (R141)

p (MPa)	k	p (MPa)	k	p (MPa)	k	p (MPa)	k
$T = 278.15$ K							
2.547	0.9979	23.96	0.9822	69.23	0.9561	120.63	0.9333
4.996	0.9960	29.52	0.9785	80.10	0.9508	140.36	0.9259
10.013	0.9921	40.04	0.9720	90.16	0.9462	157.97	0.9197
15.287	0.9882	50.09	0.9662	100.61	0.9416	172.32	0.9149
20.155	0.9848	60.07	0.9608				
$T = 288.15$ K							
2.547	0.9978	29.68	0.9770	89.65	0.9433	200.07	0.9016
4.996	0.9957	39.69	0.9704	100.37	0.9383	220.87	0.8954
10.473	0.9911	49.77	0.9643	120.14	0.9299	240.57	0.8899
15.364	0.9873	59.80	0.9585	140.53	0.9218	260.12	0.8847
20.058	0.9838	69.74	0.9532	159.67	0.9149	279.81	0.8797
24.064	0.9809	78.88	0.9485	179.38	0.9082		
$T = 298.14$ K							
2.547	0.9976	28.04	0.9766	139.40	0.9182	249.13	0.8825
4.996	0.9953	38.42	0.9693	158.98	0.9108	274.64	0.8758
10.218	0.9907	58.74	0.9565	179.59	0.9036	299.10	0.8697
15.055	0.9866	78.37	0.9457	199.38	0.8971	325.04	0.8637
19.729	0.9829	99.16	0.9354	225.12	0.8893	352.01	0.8578
24.000	0.9796	118.90	0.9266				
$T = 313.14$ K							
2.547	0.9972	27.09	0.9745	138.17	0.9115	273.95	0.8670
4.996	0.9946	38.40	0.9658	159.37	0.9031	300.08	0.8603
9.568	0.9901	59.02	0.9518	179.31	0.8958	325.22	0.8542
14.570	0.9853	78.60	0.9402	198.69	0.8892	350.34	0.8485
19.677	0.9807	98.69	0.9296	224.65	0.8810	371.71	0.8439
23.735	0.9773	118.51	0.9201	249.05	0.8738		
$T = 323.14$ K							
2.547	0.9971	28.80	0.9711	138.98	0.9061	273.94	0.8607
4.996	0.9943	40.79	0.9614	158.97	0.8979	299.61	0.8540
10.659	0.9882	58.53	0.9487	178.68	0.8905	323.27	0.8483
15.173	0.9837	78.40	0.9363	198.62	0.8835	351.92	0.8420
19.524	0.9795	98.64	0.9251	224.29	0.8752	372.79	0.8374
24.045	0.9753	118.74	0.9152	249.50	0.8676		
$T = 338.13$ K							
2.550	0.9966	28.55	0.9678	138.26	0.8988	274.31	0.8514
5.001	0.9935	40.96	0.9569	159.02	0.8898	299.58	0.8445
9.502	0.9879	58.79	0.9433	179.07	0.8819	325.15	0.8381
14.539	0.9822	79.33	0.9297	199.44	0.8746	350.66	0.8322
19.502	0.9768	99.07	0.9183	224.55	0.8662	382.29	0.8252
24.200	0.9720	119.34	0.9077	249.25	0.8586		

Table III. Volume Ratios for 1-Fluoro-1,1,2-Trichloroethane (R131a)

p (MPa)	k	p (MPa)	k	p (MPa)	k	p (MPa)	k
$T = 278.15$ K							
1.987	0.9983	31.02	0.9768	151.26	0.9203	302.69	0.8775
4.496	0.9962	40.04	0.9711	175.27	0.9121	326.59	0.8722
10.175	0.9917	60.07	0.9596	201.37	0.9040	342.91	0.8688
15.470	0.9876	81.04	0.9491	225.44	0.8970	372.76	0.8628
21.175	0.9835	101.65	0.9397	250.72	0.8902	389.83	0.8594
25.000	0.9808	126.01	0.9297	277.50	0.8835		
$T = 288.15$ K							
2.399	0.9978	39.07	0.9696	175.80	0.9074	301.38	0.8725
4.617	0.9958	59.39	0.9573	201.00	0.8993	325.40	0.8670
10.353	0.9908	80.06	0.9463	226.82	0.8917	343.26	0.8632
19.760	0.9832	100.53	0.9365	251.88	0.8849	372.93	0.8571
24.096	0.9800	125.24	0.9259	277.68	0.8783	388.63	0.8539
29.124	0.9764	150.80	0.9161				
$T = 298.14$ K							
2.452	0.9975	27.94	0.9755	125.18	0.9216	252.41	0.8792
9.899	0.9905	39.35	0.9673	150.58	0.9114	275.94	0.8730
15.025	0.9860	58.88	0.9548	175.09	0.9026	296.60	0.8679
20.725	0.9812	76.88	0.9446	200.54	0.8943	322.68	0.8617
23.521	0.9790	100.09	0.9329	226.02	0.8866		
$T = 313.14$ K							
2.820	0.9968	27.75	0.9728	149.55	0.9048	301.80	0.8581
5.098	0.9943	40.13	0.9632	175.07	0.8951	326.40	0.8521
10.022	0.9891	58.50	0.9506	200.60	0.8865	344.22	0.8480
14.473	0.9847	79.27	0.9381	227.05	0.8784	374.03	0.8417
19.423	0.9801	99.52	0.9273	251.41	0.8714	390.52	0.8382
24.191	0.9758	125.07	0.9151	275.50	0.8649		
$T = 323.14$ K							
2.550	0.9969	27.36	0.9712	149.04	0.9003	301.38	0.8523
4.974	0.9940	38.08	0.9621	175.74	0.8900	324.63	0.8466
10.073	0.9883	59.08	0.9468	200.03	0.8815	343.72	0.8422
14.809	0.9833	78.46	0.9346	226.99	0.8729	374.40	0.8355
19.723	0.9783	99.51	0.9231	250.30	0.8660	388.23	0.8326
23.694	0.9746	124.05	0.9111	276.14	0.8589		
$T = 338.13$ K							
4.814	0.9936	58.48	0.9422	174.80	0.8821	301.25	0.8430
9.939	0.9872	79.06	0.9284	200.87	0.8727	325.38	0.8369
14.810	0.9815	99.01	0.9168	226.27	0.8644	344.84	0.8323
23.486	0.9722	124.50	0.9036	251.96	0.8566	374.01	0.8259
27.060	0.9686	150.05	0.8920	276.36	0.8497	392.64	0.8219
38.980	0.9576						

Table IV. Volume Ratios for 1,2-Dichloro-1,1-Difluoroethane (R132b)

p (MPa)	k	p (MPa)	k	p (MPa)	k	p (MPa)	k
$T = 278.15$ K							
2.618	0.9969	28.04	0.9722	176.52	0.8928	302.10	0.8553
4.798	0.9944	61.80	0.9482	201.10	0.8843	326.27	0.8494
9.750	0.9891	83.41	0.9355	226.28	0.8764	343.31	0.8455
14.549	0.9842	101.94	0.9255	252.52	0.8687	374.10	0.8390
19.223	0.9798	126.91	0.9133	276.34	0.8620	386.63	0.8361
23.769	0.9758	151.48	0.9026				
$T = 288.15$ K							
2.380	0.9969	27.06	0.9703	151.33	0.8965	301.53	0.8480
4.900	0.9937	40.00	0.9595	177.75	0.8859	325.01	0.8421
9.800	0.9878	61.27	0.9443	201.56	0.8774	343.57	0.8379
14.600	0.9825	80.91	0.9321	226.81	0.8693	373.74	0.8314
19.634	0.9774	101.63	0.9205	252.15	0.8617	388.57	0.8280
22.935	0.9741	126.54	0.9078	276.21	0.8548		
$T = 298.14$ K							
2.546	0.9963	27.40	0.9666	151.48	0.8898	300.05	0.8406
5.321	0.9924	40.43	0.9547	176.17	0.8796	325.59	0.8341
10.454	0.9856	58.48	0.9407	200.52	0.8705	345.16	0.8295
14.649	0.9805	80.36	0.9263	220.72	0.8637	366.95	0.8246
19.811	0.9746	100.88	0.9145	248.71	0.8549	386.46	0.8204
23.445	0.9707	126.64	0.9012	276.05	0.8470		
$T = 313.14$ K							
2.380	0.9961	27.36	0.9629	151.35	0.8800	300.70	0.8291
4.572	0.9927	40.77	0.9492	177.16	0.8690	325.47	0.8228
10.251	0.9843	59.52	0.9332	201.40	0.8597	343.54	0.8184
14.975	0.9779	79.91	0.9187	227.21	0.8508	372.98	0.8118
19.574	0.9720	101.22	0.9056	250.36	0.8434	391.58	0.8077
22.710	0.9683	126.25	0.8920	274.82	0.8362		
$T = 313.14$ K[a]							
2.691	0.9956	28.93	0.9607	89.01	0.9113	201.02	0.8576
5.099	0.9918	39.25	0.9500	101.00	0.9039	219.33	0.8510
10.262	0.9841	49.04	0.9409	120.69	0.8930	235.50	0.8455
15.084	0.9774	58.62	0.9329	140.56	0.8830	256.79	0.8387
19.850	0.9713	68.58	0.9252	161.27	0.8736	279.44	0.8319
23.372	0.9670	79.59	0.9174	181.14	0.8653		

[a] The values at this and higher temperatures were obtained with the bellows having a volume at 0.1 MPa different from its value at the lower temperatures.

Table IV. *(Continued)*

p (MPa)	k	p (MPa)	k	p (MPa)	k	p (MPa)	k
$T = 323.14$ K							
2.947	0.9947	28.39	0.9578	88.27	0.9054	200.28	0.8503
5.559	0.9902	38.15	0.9469	99.20	0.8984	220.46	0.8428
10.623	0.9820	48.41	0.9367	119.26	0.8868	238.11	0.8367
15.312	0.9749	58.15	0.9280	140.80	0.8758	260.10	0.8297
20.255	0.9681	68.89	0.9193	161.04	0.8665	278.26	0.8242
23.040	0.9644	78.86	0.9119	181.49	0.8577		
$T = 338.13$ K							
2.633	0.9947	47.61	0.9292	99.57	0.8876	200.35	0.8377
5.243	0.9896	57.50	0.9194	119.87	0.8757	220.64	0.8302
9.840	0.9811	68.43	0.9099	140.90	0.8645	239.19	0.8240
13.908	0.9740	78.63	0.9019	160.39	0.8550	259.22	0.8177
18.881	0.9660	89.55	0.8942	180.49	0.8459	282.17	0.8103
23.935	0.9584						

100 MPa, increasing to ±0.35 at the highest pressure. The most accurate representation of the k is by the secant bulk modulus equation (SBM),

$$K = p/(1-k) = a_0 + a_1 p + a_2 p^2 + a_3 p^3 \tag{2}$$

for which the coefficients and accuracy of the fit are given in Table V. The k were also fitted to Eq. (1), which enables extrapolation to higher pressures with greater reliability than Eq. (2). (Interpolation and extrapolation of the k for each compound can also be done by using the mean value of the C's and fitting the redetermined B's to a quadratic in T.)

Comparison of such compounds can be made by choosing a value of C, independent of temperature, for each compound in Eq. (1), redetermining the corresponding B's, and representing their temperature dependence by using the inverse of the reduced temperature. The B's for $C = 0.21$ are given in Table V. There is a loss of accuracy in the reproduction of the experimental k's as a consequence of the use of the fixed C as can be seen from columns 9 and 11 in Table V. The Comparison of those B values at each reduced temperature is made in Fig. 1, which also includes data for 1,2-dichloroethane [5]; the T_c for 1,2-dichloroethane was from Ref. 6, while the Joback group contribution method [7] was used to estimate a T_c of 541.5 K for R141, 546.7 K for R131a, and 498.6 K for R132b.

Table V. Coefficients of the SBM Equation, Eq. (2), and Tait Equation, Eq. (1)[a]

System	a_0 (MPa)	a_1	$-a_2$ $(\mathrm{GPa})^{-1}$	a_3 $(\mathrm{GPa})^{-2}$	10^2 $\langle \Delta k/k \rangle$	B (MPa)	C	10^2 $\langle \Delta k/k \rangle$	B (MPa)	10^2 $\langle \Delta k/k \rangle$
$T = 278.15$ K										
R141	1208.34	5.9745	10.5863	19.972	0.001	110.25	0.2081	0.010	110.78	0.032
R131a	1161.06	5.7888	7.0478	7.264	0.011	111.64	0.2152	0.026	106.53	0.048
R132b	837.26	6.0737	10.1320	12.073	0.050	85.66	0.2208	0.050	77.75	0.101
$T = 288.15$ K										
R141	1122.06	5.8149	8.7541	12.105	0.007	106.93	0.2152	0.016	102.64	0.030
R131a	1068.69	5.7264	6.8183	6.819	0.012	102.12	0.2138	0.029	98.33	0.052
R132b	751.46	6.0508	10.2840	12.259	0.053	76.34	0.2189	0.060	70.14	0.119
$T = 298.14$ K										
R141	1041.95	5.5952	7.0273	7.729	0.010	100.65	0.2175	0.024	94.76	0.047
R131a	986.02	5.7274	7.7251	9.144	0.014	92.50	0.2117	0.024	90.67	0.045
R132b	668.77	5.8232	9.0626	10.258	0.035	65.66	0.2139	0.071	62.65	0.157
$T = 313.14$ K										
R141	909.88	5.6630	7.7805	8.690	0.020	89.37	0.2187	0.031	83.08	0.065
R131a	865.37	5.6968	7.3787	7.622	0.028	83.01	0.2134	0.039	79.95	0.067
R132b	601.84	5.2032	6.5543	6.756	0.022	56.83	0.2141	0.046	54.50	0.102
R132b[b]	592.26	5.1823	7.1999	8.443	0.004	55.85	0.2154	0.076	53.33	0.061
$T = 323.14$ K										
R141	850.19	5.2618	6.0339	6.214	0.007	81.08	0.2173	0.023	76.43	0.059
R131a	805.88	5.4427	6.2960	6.003	0.013	76.09	0.2126	0.041	73.84	0.062
R132b	536.21	5.0079	6.4073	6.915	0.004	49.63	0.2139	0.038	47.98	0.065
$T = 338.13$ K										
R141	738.83	5.3645	6.8669	7.245	0.021	71.44	0.2174	0.037	66.95	0.071
R131a	725.39	5.1610	5.5303	5.087	0.015	67.96	0.2139	0.032	65.56	0.048
R132b	476.60	4.3416	2.6261	−0.312	0.040	41.58	0.2124	0.047	40.95	0.059

[a] The values in the last two columns refer to a constant C of 0.21 in Eq. (1).

[b] The values for this entry and at higher temperatures for this compound were made with the bellows having a volume at 0.1 MPa different from its value at the lower temperatures.

The method proposed in Ref. 1 for prediction of k's even when limited to a maximum pressure of 200 MPa has errors of 1.0 to 2.1% over the experimental temperature range for R131a and 1.5 to 2.6% for R141; for R132b the differences, as expected, are worse, with the errors ranging from 2.1 to 5.7%. These relatively large errors are due principally to an overestimation of the contribution to the overall B of Eq. (1) by the F– and

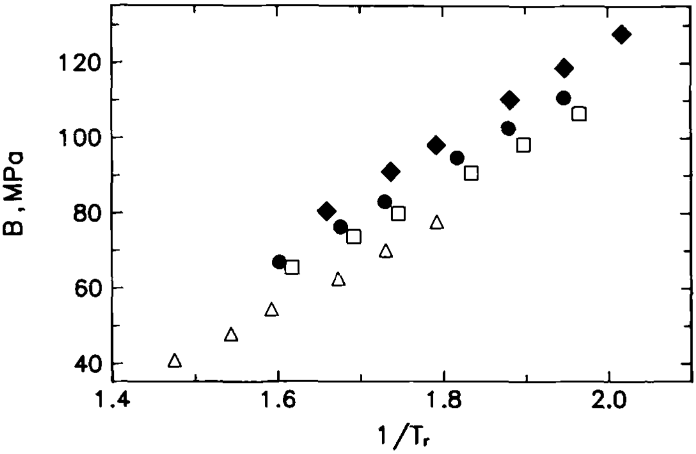

Fig. 1. Variation of the optimized B value ($C = 0.21$) in Eq. (1) with the reciprocal of the reduced temperature for (◆) 1,2-dichloroethane, (●) R141, (□) R131a, and (△) R132b.

Cl- when these replace H-in 1,2-dichloroethane. The data used in Fig. 1 can be represented by linear equations:

$$B(\text{1.2-DCE}) = -137.912 + 131.802/T_r \tag{3}$$

$$B(\text{R141}) = -137.566 + 127.718/T_r \tag{4}$$

$$B(\text{R131a}) = -125.867 + 118.136/T_r \tag{5}$$

$$B(\text{R132b}) = -130.105 + 115.715/T_r \tag{6}$$

The root mean square deviations (rmsd) in B for these equations are, respectively, 0.16, 0.27, 0.44, and 0.57. An analysis of the B's from Eqs. (3)–(6) for $1/T_r = 1.7$ together with the corresponding value for 1,1,2-trichloroethane [8] in terms of the differences in molecular composition produces the following equation:

$$B = -137.912 + 131.802/T_r - 4(N_{\text{Cl}} - 2) - 6.4N_{\text{F}} \tag{7}$$

where N_{Cl} and N_{F} are the number of chlorine and fluorine atoms present in each derivative of 1,2-dichloroethane. Equation (7) reproduces the experimental k for R141 with an rmsd of 0.02 (278.15 K) to 0.07% (338.15 K); for R131a the corresponding results are 0.05 to 0.42%, and for R132b, 0.6 to 0.5%. The better results for R141 are largely a consequence of the similarity of the slopes of Eqs. (3) and (4). The rmsd for R131a and

Table VI. Isothermal Compressibilities (κ_T; in MPa^{-1}), Isobaric Expansivities (α; in K^{-1}), and Change in Molar Heat Capacity (ΔC_p; in J · mol^{-1} · K^{-1}) of 1,2-Dichlorofluoroethane (R141)[a]

	p (MPa)									
Property	0.1	10	20	40	60	80	100	150	200	250
$T = 278.15$ K										
$10^4\kappa_T$	8.27	7.59	7.02	6.14	5.48	4.98	4.57	3.80		
$10^3\alpha$	1.18	1.13	1.08	1.00	0.93	0.88	0.84	0.76		
ΔC_p	0.0	−1.3	−2.2	−3.7	−4.8	−5.7	−6.6	−8.2		
$T = 288.15$ K										
$10^4\kappa_T$	8.90	8.14	7.50	6.50	5.76	5.20	4.76	3.99	3.44	2.96
$10^3\alpha$	1.22	1.16	1.11	1.02	0.95	0.89	0.85	0.76	0.67	0.61
ΔC_p	0.0	−1.5	−2.7	−4.5	−6.1	−7.6	−8.9	−11.7	−14.1	−16.4
$T = 298.14$ K										
$10^4\kappa_T$	9.59	8.74	8.02	6.90	6.07	5.44	4.95	4.10	3.55	3.12
$10^3\alpha$	1.25	1.19	1.13	1.04	0.96	0.91	0.86	0.77	0.69	0.63
ΔC_p	0.0	−1.6	−2.8	−4.8	−6.6	−8.1	−9.4	−12.4	−14.9	−17.4
$T = 313.14$ K										
$10^4\kappa_T$	10.98	9.87	8.95	7.55	6.56	5.83	5.28	4.35	3.75	3.30
$10^3\alpha$	1.33	1.24	1.17	1.07	0.99	0.92	0.87	0.78	0.71	0.66
ΔC_p	0.0	−1.8	−3.1	−5.3	−7.2	−8.8	−10.3	−13.5	−16.2	−18.9
$T = 323.14$ K										
$10^4\kappa_T$	11.75	10.57	9.59	8.08	6.99	6.18	5.56	4.50	3.84	3.35
$10^3\alpha$	1.37	1.28	1.20	1.08	1.00	0.94	0.88	0.79	0.73	0.67
ΔC_p	0.0	−1.9	−3.3	−5.6	−7.6	−9.4	−10.9	−14.3	−17.2	−19.9
$T = 338.13$ K										
$10^4\kappa_T$	13.52	11.95	10.68	8.80	7.50	6.56	5.86	4.73	4.04	3.53
$10^3\alpha$	1.43	1.33	1.24	1.11	1.02	0.95	0.90	0.80	0.75	0.70
ΔC_p	0.0	−2.1	−3.6	−6.1	−8.4	−10.2	−11.9	−15.5	−18.6	−21.6

[a] The α at pressures up to 150 MPa utilized the volume ratios for all temperatures. Those above 150 MPa are based on data at 288.15 K and the higher temperatures; these α will have a greater uncertainty than at the lower pressures, particularly at 288.15 K.

Table VII. Isothermal Compressibilities (κ_T; in MPa^{-1}), Isobaric Expansivities (α; in K^{-1}), and Change in Molar Heat Capacity (ΔC_p; in J · mol^{-1} · K^{-1}) of 1-Fluoro-1,1,2-Trichloroethane (R131a)

	p (MPa)									
Property	0.1	10	20	50	100	150	200	250	300	320
					$T = 278.15$ K					
$10^4\kappa_T$	8.60	7.89	7.28	5.93	4.60	3.84	3.34	2.97	2.64	2.52
$10^3\alpha$	1.15	1.08	1.02	0.90	0.78	0.69	0.63	0.58	0.54	0.53
ΔC_p	0.0	−1.1	−2.0	−4.3	−6.7	−8.2	−9.6	−10.9	−12.3	−12.7
					$T = 288.15$ K					
$10^4\kappa_T$	9.35	8.52	7.82	6.28	4.80	3.97	3.44	3.04	2.71	2.58
$10^3\alpha$	1.18	1.11	1.04	0.91	0.78	0.70	0.63	0.58	0.55	0.53
ΔC_p	0.0	−1.2	−2.1	−4.6	−7.1	−8.7	−10.1	−11.6	−13.0	−13.4
					$T = 298.14$ K					
$10^4\kappa_T$	10.13	9.17	8.36	6.64	5.04	4.16	3.57	3.11	2.69	2.52
$10^3\alpha$	1.20	1.13	1.07	0.93	0.79	0.70	0.64	0.59	0.55	0.54
ΔC_p	0.0	−1.3	−2.3	−4.9	−7.5	−9.2	−10.7	−12.2	−13.7	−14.1
					$T = 313.14$ K					
$10^4\kappa_T$	11.54	10.31	9.30	7.19	5.32	4.34	3.73	3.29	2.91	2.76
$10^3\alpha$	1.24	1.16	1.10	0.95	0.80	0.71	0.65	0.60	0.56	0.54
ΔC_p	0.0	−1.4	−2.5	−5.3	−8.1	−10.0	−11.5	−13.2	−14.8	−15.3
					$T = 323.14$ K					
$10^4\kappa_T$	12.39	11.04	9.93	7.62	5.55	4.47	3.82	3.35	2.97	2.83
$10^3\alpha$	1.27	1.19	1.12	0.96	0.81	0.71	0.65	0.61	0.56	0.55
ΔC_p	0.0	−1.5	−2.6	−5.6	−8.6	−10.5	−12.2	−13.9	−15.5	−16.0
					$T = 338.13$ K					
$10^4\kappa_T$	13.77	12.20	10.92	8.26	5.93	4.71	3.98	3.48	3.07	2.92
$10^3\alpha$	1.31	1.22	1.15	0.98	0.81	0.72	0.66	0.62	0.57	0.55
ΔC_p	0.0	−1.6	−2.9	−6.1	−9.3	−11.4	−13.1	−15.0	−16.7	−17.3

R132b could be decreased, if required, by establishing a set of Eq. (7) to cover the range of $1/T$, shown in Fig. 1.

3.2. Compressibilities and Expansivities

The isothermal compressibilities, κ_T, in Tables VI–VIII were calculated from the SBM coefficients in Table V using

$$\kappa_T = -\{1/(p-K)\}\{1-(p/K)(\partial K/\partial p)_T\} \tag{8}$$

Table VIII. Isothermal Compressibilities (κ_T; in MPa^{-1}), Isobaric Expansivities (α; in K^{-1}), and Change in Molar Heat Capacity (ΔC_p; in $J \cdot mol^{-1} \cdot K^{-1}$) of 1,2-Dichloro-1,1-Difluoroethane (R132b)

	p (MPa)							
Property	0.1	10	20	50	100	150	200	250
				$T = 278.15$ K				
$10^4\kappa_T$	11.93	10.54	9.42	7.21	5.37	4.47	3.90	3.44
$10^3\alpha$	1.40	1.29	1.20	1.02	0.83	0.71	0.62	0.57
ΔC_p	0.0	−1.9	−3.2	−5.9	−7.8	−8.6	−9.7	−11.0
				$T = 288.15$ K				
$10^4\kappa_T$	13.29	11.58	10.25	7.67	5.62	4.64	4.05	3.57
$10^3\alpha$	1.45	1.34	1.24	1.03	0.83	0.71	0.63	0.58
ΔC_p	0.0	−2.0	−3.4	−6.4	−8.3	−9.1	−10.3	−11.6
				$T = 298.14$ K				
$10^4\kappa_T$	14.93	12.88	11.29	8.26	5.89	4.78	4.13	3.62
$10^3\alpha$	1.51	1.38	1.27	1.05	0.83	0.71	0.63	0.58
ΔC_p	0.0	−2.1	−3.7	−6.8	−8.8	−9.7	−10.9	−12.3
				$T = 313.14$ K				
$10^4\kappa_T$	16.59	14.34	12.57	9.15	6.38	5.05	4.27	3.71
$10^3\alpha$	1.58	1.45	1.33	1.07	0.84	0.71	0.65	0.59
ΔC_p	0.0	−2.4	−4.1	−7.5	−9.6	−10.6	−11.9	−13.4
				$T = 313.14$ K				
$10^4\kappa_T$	16.86	14.55	12.75	9.29	6.53	5.19	4.38	3.76
$10^3\alpha$	1.58	1.45	1.33	1.07	0.84	0.71	0.65	0.59
ΔC_p	0.0	−2.4	−4.1	−7.5	−9.6	−10.6	−11.9	−13.4
				$T = 323.14$ K				
$10^4\kappa_T$	18.62	15.92	13.84	9.89	6.80	5.34	4.49	3.87
$10^3\alpha$	1.64	1.49	1.37	1.09	0.84	0.72	0.65	0.60
ΔC_p	0.0	−2.5	−4.3	−8.0	−10.2	−11.2	−12.6	−14.2
				$T = 338.13$ K				
$10^4\kappa_T$	20.95	18.00	15.66	11.04	7.26	5.49	4.57	4.09
$10^3\alpha$	1.71	1.56	1.42	1.11	0.84	0.72	0.67	0.61
ΔC_p	0.0	−2.8	−4.8	−8.8	−11.2	−12.2	−13.7	−15.4

Table IX. Internal Pressure, π (MPa), of R141, R131a, and R132b

V_m	π (MPa) at T (K)						
($cm^3 \cdot mol^{-1}$)	278.15	288.15	298.14	313.14	313.14	323.14	338.13
			R141				
79.8	409	409	409	410		411	410
80.3	411	410	409	410		410	409
80.8	412	411	410	410		410	408
81.3	412	411	410	409		409	407
81.8	411	410	409	408		408	405
82.3	410	409	408	407		406	404
83.3	407	406	405	404		404	402
			R131a				
90.0	320	321	323	328		329	333
91.5	334	336	338	342		344	348
93.0	345	346	348	352		354	357
94.5	354	355	356	358		359	360
96.0	361	361	361	361		361	360
97.5	367	365	364	362		360	357
99.5	373	369	366	361		357	351
			R132b				
84.0	278	278	279	278	284	284	284
85.5	293	292	293	290	294	293	292
87.0	305	303	302	298	302	299	296
88.5	316	312	310	303	306	302	296
90.0	324	319	315	306	308	303	294
91.5	331	325	319	307	309	302	290
93.0	337	329	321	308	309	300	285

with the differentiation made analytically. The κ_T for R132b show that it is a much more compressible liquid than R131a and R141, even at similar reduced temperatures. The tables also record isobaric expansivities, α, which were calculated by fitting the isobaric molar volume, V_m, to a quadratic in the temperature, T, and analytically differentiating.

$$\alpha = (1/V_m)(\partial V_m/\partial T)_p \tag{9}$$

V_m was estimated using the densities from Table I and the k from the SBM coefficients of Table V. The α have an estimated error of ±2–3%. The change in the molar heat capacity, C_p, from its value at 0.1 MPa is given by

$$\Delta C_p = C_p - C(0.1\ \mathrm{MPa}) = -\int_{0.1}^{P} (TM/\rho)\{(\partial\alpha/\partial T)_P + \alpha^2\}\, dP \qquad (10)$$

where M is the molar mass and ρ the density at p. The α were represented by a quadratic in T to enable analytic differentiation. The ΔC_p given in Tables VI–VIII are estimated to have an error of ±6–8%. They all change monotonically with increasing pressure or temperature; those for R141 show the largest change.

3.3. Internal Pressures

The internal pressure, π, given in Table IX was obtained using the relation

$$\pi = T(\partial p/\partial T)_v - p \qquad (11)$$

with the derivatives determined analytically from a quadratic fit [2]. The estimated error is ±2 MPa becoming larger at the extremes of the temperature range. The variation of π with molar volume, V_m, at constant T for either compound is not exceptional: the isotherms for R141 are virtually coincident within the estimated error; there is a similar behavior for those of R131 a above a molar volume of $94.5\ \mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$, while the isotherms for R132b diverge increasingly as the molar volume increases.

4. CONCLUSION

The effect of pressure and temperature on the volume of a fixed mass of any of the liquids R141, R131a, and R132b (and 1,2-dichloroethane) can be reproduced with good precision by Eq. (7), which uses the Tait equation for 1,2-dichloroethane in conjunction with additional contributions for the replacement of the hydrogen atoms on one of the carbons by fluorine and/or chlorine. Equation (7) would be expected to enable interpolations for temperatures within the experimental range of 278.15 to 338.13 K.

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