International Journal of Thermophysics, Vol. 18, No. 1, 1997

Volumetric Properties Under Pressure for 1-Fluoro-1,2,2-Trichloroethane (R131) and 1,1-Difluoro-1,2,2-Trichloroethane (R122)

R. Malhotra[1] **and L. A. Woolf**[1, 2]

Received April 1, 1996

The effect of pressure on the volume of R131 and R122 is reported for six temperatures covering the range 278.15 to 338.13 K and pressures up to 380 MPa. Densities at the same temperatures 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 modified Tait equation has been used to show that the volume ratios for both compounds can be combined with those for R123 (2,2-dichloro-1,1,1-trifluoroethane) and represented by a common equation.

KEY WORDS: compressibility; density; expansivity; heat capacity; R122; R131; volume ratios.

1. INTRODUCTION

This is a continuation of work commenced in earlier papers which used experimental data to investigate a proposal for the prediction of the effect of pressure, p, on the volumetric properties of a related series of compounds [1]. This was done by assuming that each of the characteristic groups making up each compound made a specific contribution to the B parameter of the modified Tait equation for the volume ratio $k = V_p/V$ (0.1 MPa)

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

---

[1] Research School of Physical Sciences and Engineering, Australian National University, Canberra, ACT 0200, Australia.

[2] To whom correspondence should be addressed.

0195-928X/97/0100-0037$12.50/0

The specific contributions were determined by comparison of related compounds. The principal criterion for choosing related compounds has been the ability to select 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 function 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] and ethanols [2].

R122 differs from R131 only by the replacement of a hydrogen atom by an additional fluorine atom on the ethane carbon, which already has a substituted chlorine and fluorine atom. These two compounds are, in a sense, precursors of 2,2-dichloro-1,1,1-trifluoroethane (R123), which we have studied [3]. All three compounds have a $-CHCl_2$ group. The third fluorine in R123 can be regarded as the replacement for a chlorine in R122; this is a substitution for which we have not previously estimated the contribution to the overall B value. [The comparison of R123 and its isomer 1,2-dichlorotrifluoroethane (R123a) indicated that the lesser symmetry of the latter (the presence of both a chlorine and at least one fluorine atom on each carbon) may have a particular effect on the B's [4]]. A search of *Chemical* Abstracts for the period 1962–1995 did not reveal any data for the volumetric properties of either R131 or R122.

2. EXPERIMENTS

Both chemicals were of commercial quality. The R131 (molecular weight, 1513.94 $kg \cdot mol^{-1}$; Inc., Gainesville, FL) had a stated purity of 97–99% and that of the R122 (molecular weight, 1693.85 $kg \cdot mol^{-1}$; Fluorochem Ltd., Derbyshire, UK) was 97%. Both substances were distilled before use in the experiments. The R131 that was collected had a boiling range between 100.5 and 100.7°C (716 Torr), indicating a purity of about 99%, and that for R122 was 70.8–72.1°C (710 Torr), which corresponds with the purity stated by its manufacturer. 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 [5]; they have been adjusted to refer to 0.1 MPa. Calibration accuracy was ensured after a temperature change by waiting several days to stabilize the rate of drift. Although the densities of R122 and R131 are outside the range of the calibrating fluids, careful work by Ashcroft et al. [6] with a DMA 602 using a liquid of similar density, tetrachloromethane, has shown that the calibration procedure was reliable to 0.05 $kg \cdot m^{-3}$ or better. Boiled samples were found during the lengthy period of this work to have higher densities than those that were not

Table I. Density (in $\mathrm{kg \cdot m^{-3}}$) at 0.1-MPa Pressure for R122 and R131

	T(K)					
	278.15	288.15	298.14	313.14	323.14	338.13
R122[a]	1585.63	1566.11	1545.83	1515.03	1494.19	1462.27
R131[b]	1564.62	1547.33	1529.83	1503.28	1485.56	1458.34

[a] The values at 288.15, 298.14, and 338.13 K were adjusted to the boiled condition by adding 0.464 $\mathrm{kg \cdot m^{-3}}$ determined from the measurements at 278.15 and 313.14 K for boiled and unboiled samples.

[b] As in footnote a, except that the adjustment was 0.155 $\mathrm{kg \cdot m^{-3}}$.

boiled. Because it was not feasible to repeat the measurements at some temperatures, the densities in the table have been adjusted where necessary to refer to the boiled condition. The reproducibility of the densities is estimated as $\pm 0.1\ \mathrm{kg \cdot m^{-3}}$. Temperatures were measured with thermometers calibrated to IPTS-68 and adjusted to ITS-90; they have an overall accuracy, including the calibration, 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 [3]; the pressure measurement system for R122 was that of Ref. 3, but for R123 calibrated Heise–Bourdon gauges (0–25 and 0–400 MPa) were used except for the lowest pressure (2.5 MPa), where a deadweight gauge was used for all temperatures other than 288.15 K. The pressures have an estimated accuracy of ±0.06% for those generated with the dead weight gauge and ±0.1% for those read from the analogue gauges.

3. RESULTS AND DISCUSSION

3.1. Volumetric Data

The experimental pressures and volume ratios are given in Tables II and III. The volume ratios 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. 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 are given in Table IV. The k were also fitted to Eq. (1), which enables extrapolation to higher pressures with greater reliability than Eq. (2). The coefficients determined for Eq. (1) are given in

Table II. Volume Ratios for 1,1,2-Trichloro-2-Fluoroethane (R131)

p (MPa)	k	p (MPa)	k	p (MPa)	k	p (MPa)	k
$T = 278.15$ K							
2.547	0.9981	27.45	0.9817	150.26	0.9284	301.17	0.8882
5.124	0.9963	39.43	0.9749	175.59	0.9203	324.58	0.8832
9.899	0.9929	59.45	0.9646	200.91	0.9129	341.51	0.8797
15.815	0.9890	79.22	0.9555	227.24	0.9058	374.40	0.8733
20.590	0.9859	101.01	0.9463	250.99	0.8998	390.05	0.8705
22.625	0.9846	125.01	0.9372	276.57	0.8938		
$T = 288.15$ K							
2.560	0.9980	27.80	0.9802	150.57	0.9245	300.50	0.8835
5.123	0.9960	39.09	0.9734	176.41	0.9161	325.41	0.8780
9.848	0.9924	59.49	0.9623	200.15	0.9090	350.80	0.8727
14.849	0.9888	80.00	0.9523	225.59	0.9019	374.33	0.8681
19.974	0.9853	100.07	0.9436	251.29	0.8952	389.52	0.8653
22.534	0.9836	127.00	0.9329	276.11	0.8892		
$T = 298.14$ K							
2.547	0.9978	26.42	0.9799	150.54	0.9207	301.24	0.8785
5.346	0.9955	39.69	0.9714	176.39	0.9120	325.47	0.8730
10.276	0.9916	58.84	0.9605	200.00	0.9047	342.31	0.8694
15.049	0.9880	79.33	0.9500	225.37	0.8975	373.29	0.8632
19.223	0.9850	100.41	0.9403	251.21	0.8906	389.36	0.8601
21.799	0.9831	124.31	0.9305	277.04	0.8842		
$T = 313.14$ K							
2.547	0.9976	27.15	0.9772	150.69	0.9144	299.43	0.8711
3.949	0.9963	37.57	0.9698	175.75	0.9056	325.27	0.8652
9.608	0.9912	59.46	0.9561	199.81	0.8979	342.66	0.8613
14.182	0.9873	79.09	0.9455	227.19	0.8898	373.11	0.8550
18.931	0.9835	99.63	0.9355	252.23	0.8830	391.08	0.8515
22.915	0.9803	125.41	0.9243	276.81	0.8767		
$T = 323.14$ K							
2.547	0.9974	23.87	0.9782	150.72	0.9102	300.69	0.8654
4.395	0.9956	30.92	0.9727	175.04	0.9014	325.42	0.8596
9.746	0.9904	57.68	0.9547	200.31	0.8930	351.26	0.8539
14.444	0.9862	79.24	0.9424	225.57	0.8854	372.53	0.8495
19.231	0.9820	100.12	0.9318	252.17	0.8779	389.25	0.8461
22.707	0.9792	125.11	0.9206	276.21	0.8715		
$T = 338.13$ K							
2.547	0.9971	27.50	0.9728	150.71	0.9032	301.15	0.8569
4.722	0.9947	38.29	0.9641	177.96	0.8930	325.21	0.8511
9.873	0.9893	54.61	0.9523	199.77	0.8855	343.33	0.8469
14.724	0.9844	78.86	0.9373	226.27	0.8772	375.15	0.8401
19.448	0.9800	100.30	0.9258	251.10	0.8701	392.66	0.8365
23.371	0.9764	125.35	0.9139	275.57	0.8634		

Table III. Volume Ratios for 1,1-Difluoro-1,2,2-Trichloroethane (R122)

p (MPa)	k	p (MPa)	k	p (MPa)	k	p (MPa)	k
$T = 278.15$ K							
2.547	0.9973	41.52	0.9641	175.72	0.8989	301.92	0.8628
4.996	0.9948	61.28	0.9510	201.68	0.8903	326.83	0.8570
10.055	0.9898	80.97	0.9399	226.51	0.8828	351.50	0.8517
15.149	0.9851	102.00	0.9291	250.64	0.8759	375.45	0.8468
20.025	0.9808	125.95	0.9182	275.55	0.8693	390.07	0.8438
24.060	0.9774	150.80	0.9081				
$T = 288.15$ K							
2.547	0.9971	40.50	0.9624	175.52	0.8942	301.04	0.8575
4.996	0.9944	80.87	0.9363	197.23	0.8868	326.20	0.8516
10.300	0.9888	100.79	0.9258	224.71	0.8781	356.85	0.8448
17.203	0.9820	126.75	0.9136	249.55	0.8710	373.15	0.8414
19.910	0.9795	148.24	0.9045	275.01	0.8641	389.07	0.8382
24.154	0.9757						
$T = 298.14$ K							
2.547	0.9969	30.07	0.9685	149.94	0.8983	301.13	0.8508
4.996	0.9937	42.03	0.9585	175.32	0.8884	326.73	0.8446
10.245	0.9880	59.97	0.9452	201.58	0.8793	349.15	0.8396
15.238	0.9826	79.17	0.9331	224.81	0.8719	368.86	0.8354
20.082	0.9778	100.58	0.9212	249.45	0.8646	394.54	0.8301
24.145	0.9739	125.25	0.9091	275.62	0.8574		
$T = 313.14$ K							
2.547	0.9964	43.82	0.9522	174.72	0.8801	301.53	0.8411
4.996	0.9930	61.18	0.9386	201.68	0.8703	326.40	0.8349
10.068	0.9865	80.62	0.9258	226.11	0.8623	352.40	0.8290
15.162	0.9804	100.79	0.9140	250.39	0.8550	374.85	0.8242
20.236	0.9747	126.05	0.9010	275.87	0.8478	393.65	0.8202
24.033	0.9707	149.95	0.8901				
$T = 323.14$ K							
2.547	0.9960	61.28	0.9341	175.78	0.8731	302.46	0.8334
4.996	0.9924	80.42	0.9209	201.27	0.8637	326.98	0.8273
10.396	0.9848	100.79	0.9086	223.31	0.8563	352.45	0.8214
15.307	0.9784	125.55	0.8954	250.14	0.8480	374.05	0.8168
24.284	0.9678	152.54	0.8827	277.08	0.8403	391.76	0.8129
39.943	0.9520						
$T = 338.13$ K							
2.547	0.9955	30.25	0.9567	150.56	0.8735	299.41	0.8228
4.996	0.9914	39.58	0.9467	174.36	0.8632	324.47	0.8163
10.169	0.9832	60.17	0.9277	198.08	0.8541	349.10	0.8103
15.542	0.9753	80.27	0.9128	224.10	0.8450	374.40	0.8049
20.187	0.9690	100.65	0.8997	250.61	0.8367	395.24	0.8010
23.984	0.9642	124.13	0.8865	273.66	0.8300		

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

	a_0 (MPa)	a_1	$-a_2$ (GPa)$^{-1}$	a_3 (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					
R131	1338.61	6.0321	7.4604	7.725	0.013	127.80	0.2129	0.024	123.88	0.053
R122	931.61	5.5694	6.6116	6.794	0.015	87.31	0.2115	0.021	85.55	0.049
					$T = 288.15$ K					
R131	1244.42	5.8820	6.8272	6.664	0.010	118.49	0.2127	0.028	114.95	0.056
R122	862.04	5.4615	6.2077	6.116	0.013	80.39	0.2109	0.024	79.10	0.057
					$T = 298.14$ K					
R131	1169.83	5.6620	6.2088	5.981	0.011	110.73	0.2133	0.023	107.20	0.042
R122	791.6	5.3955	6.3918	6.539	0.022	73.57	0.2112	0.021	72.32	0.045
					$T = 313.14$ K					
R131	1040.46	5.5777	5.9949	5.530	0.009	97.93	0.2122	0.029	95.44	0.054
R122	693.73	5.2787	6.1494	6.141	0.020	63.94	0.2101	0.026	63.39	0.056
					$T = 323.14$ K					
R131	964.99	5.6051	6.5868	6.505	0.014	91.85	0.2136	0.031	88.50	0.055
R122	630.57	5.2098	6.1653	6.191	0.022	58.15	0.2104	0.029	57.55	0.057
					$T = 338.13$ K					
R131	869.46	5.2912	5.4730	4.967	0.012	81.35	0.2132	0.026	78.84	0.041
R122	554.08	4.9333	5.4209	5.315	0.018	49.65	0.2094	0.022	49.74	0.038

[a] The values in the last two columns refer to a constant C of 0.2100 in Eq. (1).

Table IV. 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,

$$\text{R131}, \quad C = 0.213; \quad B = 561.56 - 2.2247T + 0.002373T^2 \tag{3}$$

$$\text{R122}, \quad C = 0.210; \quad B = 397.223 - 1.5486T + 0.00154T^2 \tag{4}$$

with a standard deviation in B of 0.19 MPa for R131 and 0.17 MPa for R122. These equations represent the k within their estimated experimental accuracy.

Comparison of the two compounds can be made by choosing a common value of C to obtain the second set of B's given in Table IV and representing their temperature dependence by using the reduced temperature, T_r ($= T/T_c$), with a T_c of 577 K for R131 and 529 K for R122 estimated from the Joback group contribution method [7]. The comparison is made in

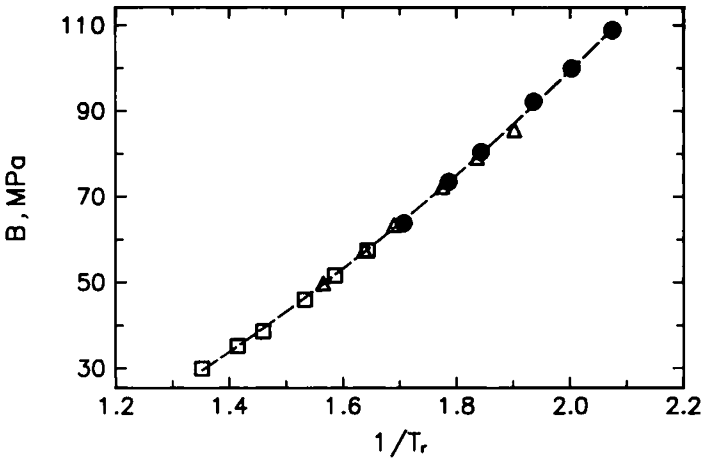

Fig. 1. Variation of the optimized B values ($C=0.21$) in Eq. (1) with the reciprocal of the reduced temperature for (●) R131, (△) R122, and (□) R123. The values shown for R131 are 15 MPa less than the actual ones. The dashed curve represents Eq. (5).

Fig. 1, which also includes data for R123 [3]. The data in Ref. 3 did not include numerical values of B for a C of 0.21; for the temperatures of Table IV those values are 57.41, 51.57, 46.00, 38.57, 35.14, and 29.90 MPa. The differences between the curves for R131 ($CHCl_2$–CHClF) and R122 ($CHCl_2$–$CClF_2$) were previously interpreted as suggesting that the additional fluorine (replacing a hydrogen) decreases the overall B by 14 MPa [1]. However, the replacement of a chlorine by fluorine to go from R122 to A123 ($CHCl_2$–CF_3) has only a marginal effect on the B's. It is clear that the latter two curves could be combined to provide predictions of k for either compound in the range $0.48 \leqslant T_r \leqslant 0.74$. The values for R131 also can be included by reducing its B's by 15 MPa; the combined data for the three chlorofluorocarbons are then represented with a standard deviation of 0.63 MPa by

$$B = -31.458 + 2.8135/T_r + 31.305/T_r^2 \tag{5}$$

3.2. Compressibilities and Expansivities

The isothermal compressibilities, κ_T are given in Tables V and VI. They were calculated from the appropriate SBM coefficients in Table IV by expressing κ_T as

$$\kappa_T = -\{1/(p-K)\}\{1-(p/K)(\partial K/\partial p)_T\} \tag{6}$$

Table V. 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}) for R131

	p (MPa)									
Property	0.1	10	20	50	100	150	200	250	300	350
					$T = 278.15$ K					
$10^4\kappa_T$	7.47	6.90	6.41	5.31	4.20	3.55	3.11	2.78	2.49	2.20
$10^3\alpha$	1.10	1.05	1.01	0.91	0.79	0.71	0.66	0.61	0.58	0.54
ΔC_p	0.0	−1.0	−1.7	−3.4	−5.1	−6.3	−7.1	−7.7	−8.2	−8.6
					$T = 288.15$ K					
$10^4\kappa_T$	8.03	7.40	6.85	5.62	4.39	3.67	3.20	2.85	2.56	2.28
$10^3\alpha$	1.12	1.07	1.02	0.91	0.79	0.72	0.66	0.61	0.58	0.54
ΔC_p	0.0	−1.1	−1.8	−3.6	−5.5	−6.7	−7.5	−8.1	−8.6	−9.0
					$T = 298.14$ K					
$10^4\kappa_T$	8.54	7.85	7.26	5.93	4.60	3.82	3.31	2.93	2.62	2.33
$10^3\alpha$	1.15	1.09	1.04	0.92	0.80	0.72	0.66	0.61	0.58	0.54
ΔC_p	0.0	−1.1	−2.0	−3.8	−5.8	−7.1	−7.9	−8.6	−9.0	−9.5
					$T = 313.14$ K					
$10^4\kappa_T$	9.60	8.75	8.03	6.43	4.89	4.01	3.45	3.05	2.73	2.43
$10^3\alpha$	1.18	1.12	1.07	0.94	0.81	0.72	0.66	0.61	0.58	0.54
ΔC_p	0.0	−1.2	−2.1	−4.1	−6.3	−7.6	−8.6	−9.2	−9.8	−10.2
					$T = 323.14$ K					
$10^4\kappa_T$	10.35	9.37	8.54	6.75	5.08	4.16	3.58	3.16	2.81	2.47
$10^3\alpha$	1.21	1.14	1.08	0.95	0.81	0.72	0.66	0.61	0.58	0.54
ΔC_p	0.0	−1.3	−2.3	−4.4	−6.7	−8.0	−9.0	−9.7	−10.2	−10.7
					$T = 338.13$ K					
$10^4\kappa_T$	11.49	10.35	9.40	7.35	5.43	4.38	3.73	3.27	2.90	2.57
$10^3\alpha$	1.25	1.17	1.11	0.96	0.82	0.73	0.66	0.62	0.58	0.55
ΔC_p	0.0	−1.4	−2.5	−4.7	−7.2	−8.7	−9.7	−10.4	−11.0	−11.5

with the differentiation made analytically. They have an estimated uncertainty of ±1–2% and do not show any obvious singularities. The similarities of the volumetric data for R122 and R123 were noted in Fig. 1. Their κ_T can be compared most readily at a reduced temperature of about 0.6, corresponding to 278.15 K (R123) and 323.14 K (R122), with the use of the data from Table VI and Table III of Ref. 3; they differ by less than the combined estimated errors. Tables V and VI also record isobaric

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}) for R122

Property	p (MPa)									
	0.1	10	20	50	100	150	200	250	300	350
					$T = 278.15$ K					
$10^4\kappa_T$	10.72	9.67	8.80	6.92	5.18	4.23	3.62	3.18	2.80	2.44
$10^3\alpha$	1.23	1.16	1.09	0.96	0.83	0.74	0.68	0.63	0.59	0.55
ΔC_p	0.0	−1.5	−2.5	−4.2	−5.0	−4.4	−3.2	−1.9	−0.6	0.5
					$T = 288.15$ K					
$10^4\kappa_T$	11.59	10.39	9.40	7.31	5.39	4.35	3.71	3.25	2.86	2.51
$10^3\alpha$	1.27	1.19	1.11	0.96	0.82	0.73	0.66	0.61	0.57	0.54
ΔC_p	0.0	−1.6	−2.7	−4.5	−5.3	−4.6	−3.4	−2.0	−0.6	0.6
					$T = 298.14$ K					
$10^4\kappa_T$	12.62	11.23	10.09	7.73	5.63	4.53	3.85	3.36	2.94	2.55
$10^3\alpha$	1.31	1.21	1.13	0.97	0.81	0.72	0.65	0.60	0.56	0.53
ΔC_p	0.0	−1.7	−2.9	−4.8	−5.6	−4.9	−3.6	−2.1	−0.7	0.7
					$T = 313.14$ K					
$10^4\kappa_T$	14.40	12.65	11.24	8.40	5.97	4.75	4.01	3.48	3.05	2.64
$10^3\alpha$	1.37	1.26	1.16	0.97	0.80	0.70	0.63	0.58	0.54	0.51
ΔC_p	0.0	−1.9	−3.1	−5.2	−6.1	−5.3	−3.9	−2.3	−0.7	0.7
					$T = 323.14$ K					
$10^4\kappa_T$	15.84	13.77	12.13	8.90	6.23	4.91	4.13	3.59	3.13	2.70
$10^3\alpha$	1.41	1.28	1.18	0.98	0.79	0.68	0.62	0.56	0.53	0.50
ΔC_p	0.0	−2.0	−3.3	−5.5	−6.4	−5.6	−4.0	−2.4	−0.7	0.8
					$T = 338.13$ K					
$10^4\kappa_T$	18.02	15.52	13.56	9.74	6.66	5.17	4.30	3.70	3.21	2.77
$10^3\alpha$	1.47	1.33	1.21	0.98	0.78	0.67	0.59	0.54	0.51	0.48
ΔC_p	0.0	−2.2	−3.6	−6.2	−7.0	−6.0	−4.4	−2.6	−0.8	0.8

expansivities, α, which were calculated by fitting the isobaric molar volume, V_m, to a quadratic in the temperature, T, and analytically differentiating.

$$\alpha = (1/V_m)(\partial V_m/\partial T)_p \tag{7}$$

V_m was estimated from the densities in Table I and the k from the SBM coefficients in Table IV. The estimated error in α is ±2–3% but may be

Table VII. Internal Pressure, π (MPa), of (R131) and R122

V_m	π (MPa) at T (K)					
($\mathrm{cm^3 \cdot mol^{-1}}$)	278.15	288.15	298.14	313.14	323.14	338.13
			R131			
88.0	383	382	381	380	379	377
89.5	397	396	394	393	392	390
91.0	407	405	403	402	400	397
92.5	413	411	409	406	404	400
94.0	417	414	412	408	405	400
95.5	419	416	412	407	404	398
96.5	420	416	412	406	402	395
			R122			
97.0	330	319	310	292	281	263
98.5	334	325	316	300	290	274
100.0	336	327	319	305	296	282
101.5	336	329	321	308	300	287
103.0	335	328	321	310	302	290
104.5	334	327	321	310	302	291
106.5	331	325	318	308	301	290

larger at the extremes of the temperature range. The change in the molar heat capacity, C_p, from its value at 0.1 MPa is given by

$$\Delta C_p = C_p - C(0.1\ \mathrm{MPa}) = -\int_{0.1}^{p} (TM/\rho)\{(\partial\alpha/\partial T)_p + \alpha^2\}\, d_p \qquad (8)$$

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 V and VI are estimated to have an error of ±5–6%. Those for R122 go through a minimum and then increase with pressure at each temperature, in contrast to the continual decrease for R131 and R123. Lebedev and Kulagina [8] determined C(0.1 MPa) for what they described as R122; the compound they studied was, however, the isomer 1,2-difluoro-1,2,2-trichloroethane.

3.3. Internal Pressures

The internal pressure, π, given in Table VII was obtained by use of the relation

$$\pi = T(\partial p/\partial T)_V - p \qquad (9)$$

with the derivatives determined analytically from a quadratic fit [3]. The estimated error is ±2 MPa but it may be 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 each compound do not intersect; the variation of the isotherms with V_m shows a small maximum.

4. CONCLUSION

The replacement of a hydrogen atom by a fluorine in going from R131 to R122 has a strong effect on the volumetric properties at the same reduced temperature. However, the replacement of a chlorine atom by a fluorine in going from R122 to R123 has little effect. The ability to combine the Tait equation B coefficients for R131, R124 and R123 to cover a wide range of reduced temperatures indicates that this approach may be useful for similar correlations of data for other closely related compounds. A related aggregation of those coefficients has been done for a number of fluorinated ethers [9].

REFERENCES

1. See, e.g., R. Malhotra and L. A. Woolf, *High Temp. High Press.* **25**:179 (1993).
2. R. Malhotra and L. A. Woolf, *Int. J. Thermophys.* **16**:901 (1995).
3. R. Malhotra and L. A. Woolf, *Int. J. Thermophys.* **14**:1021 (1993).
4. R. Malhotra and L. A. Woolf, *J. Chem. Eng. Data* **41**:254 (1996).
5. R. Malhotra and L. A. Woolf, *Fluid Phase Equil.* **94**:227 (1994).
6. S. J. Ashcroft, D. R. Booker, and J. C. R. Turner, *J. Chem. Soc. Faraday Trans.* **86**:145 (1990).
7. R. C. Reid, J. M. Prausnitz, and B. E. Poling, *The Properties of Gases and Liquids*, 4th ed. (McGraw-Hill, New York, 1987).
8. B. V. Lebedev and T. G. Kulagina, *J. Chem. Thermodyn.* **24**:751 (1992).
9. R. Malhotra, W. A. Van Hook, and L. A. Woolf, *Int. J. Thermophys.* **16**:111 (1995).