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Thermodynamic Properties of 2,2,2-Trifluoroethanol

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

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(p, V, T) data for 2,2,2-trifluoroethanol (TFE) have been obtained in the form of volume ratios for six temperatures in the range 278.15 to 338.15 K for pressures up to 280 MPa. Isothermal compressibilities, isobaric expansivities, and internal pressures have been evaluated from the volumetric data. The compressibilities and internal pressures indicate that the behavior of TFE is closer to that of methanol than of ethanol for most of the pressure range. The use of only the present volumetric results together with the requirement that the B coefficient of the Tait equation should become equal to the negative of the critical pressure at the critical temperature provides interpolations and extrapolations up to 413 K of comparable accuracy.

KEY WORDS: compressibility; high pressure; p-V-T data; Tait equation of state; 2,2,2-trifluoroethanol.

1. INTRODUCTION

The importance of 2,2,2-trifluoroethanol (TFE) as a working fluid for energy transformation purposes and its use in mixtures with tetraethyleneglycoldimethylether, as an alternative refrigerant to ammonia for absorption heat pumps, have been emphasized recently [1]. The lack of experimental thermophysical data for TFE [1], especially at high pressures, was the impetus for the present investigation, which provides accurate p-V-T data for TFE at temperatures from 278 to 338 K and pressures up to 280 MPa.

Recently we have endeavored to establish ways of using the Tait equation of state [2, 3] to extrapolate p-V-T measurements to a wider range of temperatures and pressures than the experimental measurements. The extrapolations are facilitated and their accuracy is improved when

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[1] Atomic and Molecular Physics Laboratories, Research School of Physical Sciences, The Australian National University, Canberra, A.C.T. 2601, Australia.

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accurate critical properties (p_c. T_c)are available to use the requirement that the B coefficient of the Tait equation of state should become equal to the negative of the critical pressure [4] at the critical temperature. The present results in combination with recently measured critical properties [1] have been fitted to the Tait equation of state and used to predict densities for comparison with literature data [1] for temperatures above 338 K and up to 413 K [1].

2. EXPERIMENTAL

The 2,2,2-trifluoroethanol (molecular weight, 0.10004 kg) was provided by Fluka, of stated purity minimum 99.5 mol%, and was used without further purification, except for storage over Type 4A molecular sieves for several weeks before use to remove water and other low molecular weight impurities.

Volume ratios, k ($= V_p/V_{0.1}$, where $V_{0.1}$ and V_p are the volumes of a fixed mass of TFE at 0.1 MPa and pressure p, respectively), were determined using a bellows volumometer described previously [5–7]. The measurements were made at 278.15, 288.15, 298.15, 313.15, 323.15, and 338.15 K for the pressure range from about 2.5 to 280 MPa. The overall accuracy of the measured volume ratios correspond to about ±0.02–0.04% for pressures above 50 MPa, increasing to ±0.1% at pressures approaching 0.1 MPa.

Densities of TFE were measured at 0.1 MPa with an Anton Paar Model DMA 602 densimeter at 278.15, 288.15, 313.15, 323.15, and 338.15 K with a maximum uncertainty of ±0.06%.

3. RESULTS AND DISCUSSION

3.1. Volumetric Data

The experimental values for the density at 0.1 MPa, $\rho_{0.1}$ (in $\mathrm{kg \cdot m^{-3}}$), together with literature data are given in Table I; the data over the temperature range 278 to 338 K can be represented by a third-degree polynomial,

$$\rho_{0.1} = 2531.269 - 8.5439T + 2.42742 \times 10^{-2} T^2 - 2.865 \times 10^{-5} T^3 \quad (1)$$

with a root mean square deviation (rmsd) of $\pm 0.09\ \mathrm{kg \cdot m^{-3}}$. The interpolated density at 298.15 K of $1382.38\ \mathrm{kg \cdot m^{-3}}$ is close to the experimental literature values of 1382.0 [8] and 1382.64 [9] $\mathrm{kg \cdot m^{-3}}$.

The experimental pressures and volume ratios are given in Table II. The interpolated volume ratios from this work compare, well within the

Table I. Densities of TFE at 0.1 MPa

T (K)	ρ (kg·m^{-3}) This work	ρ (kg·m^{-3}) Literature
278.15	1416.24	
288.15	1399.43	
313.15	1356.22	1356.70 [21]
323.15	1338.45	1338.50 [21] 1337.28 [9]
338.15	1309.97	

experimental uncertainty of ±0.06%, with the volume ratios of [9, 10] up to their maximum experimental pressures of 40 MPa.

The secant bulk modulus (SBM), K [$=p/(1-k)$, where k is the experimentally determined volume ratio], was represented by cubic equations of the form

$$K=\sum_{i=0}^{3} A_i p^i \qquad (2)$$

The coefficients of Eq. (2) are listed in Table III; the maximum rmsd between the calculated and the experimental volume ratios at any temperature is 0.013%.

The measured volume ratios were also fitted to the modified Tait equation [11], expressed here as

$$1-k=C\log[(B+p)/(B+p_0)] \qquad (3)$$

where p_0 is the reference pressure, usually 0.1 MPa, and the constants B and C are adjustable parameters. The coefficients B and C of Eq. (3) are given in Table IV; the maximum rmsd between the calculated and the experimental volume ratios was 0.04% for the measurements at 338.15 K. The maximum deviation for a set of volume ratios at any temperature was generally at the highest pressure of the measurement and the largest deviation between the calculated and the experimental measurement was 0.032% for 274 MPa at 338.15 K.

3.2. The Tait Equation of State

Equation (3) has been widely used for interpolation of the densities (or volumes) of liquids at intermediate temperatures [12–14] for individual

Table II. Experimental Values of Pressures and Volume Ratios for 2,2,2-Trifluoroethanol from 278.15 to 338.15 K

p (MPa)	$V_p/V_{0.1}$	p (MPa)	$V_p/V_{0.1}$	p (MPa)	$V_p/V_{0.1}$	p (MPa)	$V_p/V_{0.1}$
T (K) = 278.15							
2.547	0.9973	29.77	0.9723	88.95	0.9343	200.27	0.8887
4.837	0.9949	39.89	0.9646	100.73	0.9283	220.08	0.8825
10.135	0.9896	50.45	0.9571	120.04	0.9192	239.79	0.8766
15.256	0.9848	59.79	0.9511	139.42	0.9109	259.74	0.8710
19.363	0.9811	68.77	0.9456	158.98	0.9032	281.62	0.8654
25.49	0.9758	79.49	0.9394	180.36	0.8954		
T (K) = 288.15							
2.622	0.9970	29.97	0.9703	88.85	0.9308	198.47	0.8844
5.069	0.9943	39.64	0.9625	100.32	0.9248	219.41	0.8776
9.983	0.9891	49.54	0.9551	119.40	0.9156	239.58	0.8716
15.390	0.9836	59.23	0.9485	139.67	0.9066	259.49	0.8659
19.855	0.9793	69.17	0.9422	159.18	0.8987	281.62	0.8600
24.397	0.9752	79.34	0.9362	180.17	0.8908		
T (K) = 298.15							
2.651	0.9968	29.82	0.9687	89.20	0.9272	199.54	0.8798
5.167	0.9938	39.84	0.9602	100.93	0.9209	219.91	0.8731
9.980	0.9884	49.59	0.9526	119.45	0.9117	239.69	0.8671
15.250	0.9828	59.44	0.9456	139.47	0.9027	258.92	0.8615
19.863	0.9781	68.92	0.9393	159.23	0.8945	281.57	0.8553
24.603	0.9735	79.34	0.9329	179.83	0.8867		
T (K) = 313.15							
2.547	0.9966	30.02	0.9654	89.05	0.9213	196.26	0.8733
4.972	0.9934	39.69	0.9564	99.80	0.9153	219.25	0.8656
10.218	0.9869	49.44	0.9483	119.55	0.9050	237.83	0.8597
15.179	0.9810	59.38	0.9407	137.09	0.8968	259.28	0.8534
20.162	0.9755	69.42	0.9337	159.18	0.8873	281.70	0.8472
25.97	0.9694	79.18	0.9273	179.00	0.8796		
T (K) = 323.15							
2.646	0.9962	29.97	0.9631	89.35	0.9167	198.95	0.8660
5.014	0.9929	39.62	0.9537	100.11	0.9103	219.30	0.8590
10.034	0.9862	49.28	0.9452	119.94	0.8996	239.90	0.8523
15.306	0.9795	59.44	0.9370	139.72	0.8901	259.03	0.8465
20.132	0.9738	69.12	0.9299	159.79	0.8812	281.30	0.8401
25.29	0.9680	79.28	0.9230	179.83	0.8731		
T (K) = 338.15							
2.792	0.9954	29.77	0.9593	89.30	0.9104	199.34	0.8583
5.180	0.9916	39.89	0.9488	100.27	0.9037	219.52	0.8513
10.277	0.9840	49.69	0.9397	119.99	0.8927	239.53	0.8448
15.278	0.9770	59.13	0.9318	139.37	0.8830	258.92	0.8388
19.769	0.9712	69.32	0.9240	159.69	0.8738	281.13	0.8326
25.32	0.9644	79.59	0.9167	179.83	0.8656		

Table III. Coefficients of Eq. (2) for SBM

T (K)	A_0 (MPa)	A_1	$-A_2$ (GPa^{-1})	A_3 (GPa^{-2})	rmsd (%)	maxd[a] (%)
278.15	922.11	5.3448	6.2627	7.224	0.003	0.006
288.15	859.73	5.2370	5.8220	6.206	0.006	−0.011
298.15	810.86	4.9699	4.0681	2.557	0.008	−0.016
313.15	728.82	4.7918	3.3201	1.187	0.012	−0.020
323.15	678.82	4.6517	3.1631	0.924	0.013	−0.025
338.15	591.47	4.9615	5.4953	5.688	0.010	−0.019

[a] Maximum deviation between the calculated and the experimental volume ratios in a set.

substances; it has also been employed to correlate p-V-T data for a series of alkanes and their mixtures [15], aromatics [16], and other compressed liquids and their binary mixtures [17]. The significance of the use of the Tait equation of state has been reviewed recently [16].

The B values obtained from the present measurements can be represented by a fixed value of C ($=0.211$) chosen to give the best fit to the whole data set of $V_p/V_{0.1}$ values, with B expressed as a function of temperature,

$$B = 353.65 - 1.3429T + 1.3482 \times 10^{-3}T^2 \qquad [278.15 \leqslant T(\mathrm{K}) \leqslant 338.15] \tag{4}$$

Table IV. Optimized Tait Coefficients [Eq. (3)] and Comparison of Calculated $V_p/V_{0.1}$ from Eqs. (4), (5), and (7) with Measured $V_p/V_{0.1}$

T (K)	B (MPa)	C	rmsd[a] (%)	rmsd[b] (%)	rmsd[c] (%)	rmsd[d] (%)
278.15	85.20	0.2123	0.013	0.015	0.020	0.023
288.15	79.32	0.2126	0.017	0.028	0.030	0.028
298.15	73.28	0.2110	0.015	0.020	0.015	0.015
313.15	64.60	0.2094	0.013	0.021	0.020	0.021
323.15	61.22	0.2137	0.015	0.065	0.075	0.079
338.15	52.61	0.2087	0.016	0.025	0.048	0.042

[a] Using optimized coefficients B and C in Eq. (3).
[b] Using $C=0.211$ and B obtained from Eq. (4).
[c] Using $C=0.211$ and B obtained from Eq. (5).
[d] Using $C=0.211$ and B obtained from Eq. (7).

with a standard deviation of 0.35. The rmsd of the calculated $V_p/V_{0.1}$ [using B from Eq. (4) in Eq. (3)] from the measured $V_p/V_{0.1}$ are tabulated for each temperature in Table IV. The maximum deviation, of the calculated volume ratio from the experimental value, at any temperature was less than $\pm 0.07\%$ with the exception of a deviation of $\pm 0.16\%$ at 323.15 K.

The usefulness of the Tait equation to extrapolate well outside the experimental range of temperatures was demonstrated for 2,2,4-trimethylpentane [3]. The basis for this extrapolation was to combine the B data for a fixed value of C with the theoretical requirement that $B = -p_c$ at the critical temperature T_c and representing B as a function of $(T - T_c)$. Applying this procedure to TFE using $p_c = 4.86$ MPa [1] at $T_c = 499.3$ K [1] gives a fit to B,

$$B = -4.8462 - 0.2501\,(T - T_c) + 6.8887 \times 10^{-4}\,(T - T_c)^2$$

$$[278 \leqslant T(\mathrm{K}) \leqslant 338] \tag{5}$$

with a standard deviation of 0.40. The B values obtained by using Eq. (5) produce only trivial changes in the differences between the correlated and the experimental volume ratios (Table IV).

The general expression for the principle of corresponding states [17] is of the form

$$p/p_c = u(T/T_c,\ V/V_c) \tag{6}$$

where u is a universal, but complicated, function. Analogously, we find that the reduced value of B (i.e., B/P_c) for TFE is a simple function of the reduced temperature, T_r $(= T/T_c)$,

$$B/P_c = -1 + 25.939\,(1 - T_r) + 34.721\,(1 - T_r)^2 \tag{7}$$

which incorporates the theoretical requirement that B equals $-p_c$ at the critical temperature $(T_r = 1)$ [4]. The fitted B values have a standard deviation of 0.43 and produce only trivial changes in the differences between the correlated and the experimental volume ratios as compared to the other two sets (Table IV).

The Tait equation of state [Eq. (3)] was used with Eq. (7) and saturation pressures [1] as the reference pressure (p_0) to obtain volume ratios up to 413.16 K (75 K above the highest temperature of our measurements) to compare with literature data [1] for the pressure range 0.5–16 MPa, the maximum pressure of those measurements. The agreement is within the estimated experimental uncertainty of $\pm 0.3\%$.

Thomson et al. [17] generalized the Tait equation to enable the calculations of densities of compressed liquids and their mixtures and represented B as a function of reduced temperature in the form

$$B/P_c = -1 + \sum_{i=1}^{4} B_i(1 - T_r)^{i(1/3)} \tag{8}$$

similar to the expression developed for ρ/ρ_c as a function of T/T_c [18] for generally monatomic, diatomic molecules and methane. The advantage of Eq. (7) is that it uses only three coefficients instead of the five in Eq. (8).

3.3. Compressibilities and Expansivities

Isothermal compressibilities, κ_T, given in Table V, were calculated from the coefficients given in Table III for Eq. (2) by using the relationship [19]

$$\kappa_T = -[1/(p - K)][1 - (p/K)(\partial K/\partial p)_T] \tag{9}$$

The compressibilities, which have a probable uncertainty of ±1–2%, are given in Table V, where they are compared with those for methanol [4] and ethanol [20]. The compressibilities for TFE at 0.1 MPa are larger

Table V. Isobaric Compressibilities (κ_T, in MPa^{-1}) and Isobaric Expansivities (α, in K^{-1})

T(K)	Property	0.1	20	50	100	150	200	250	275
278.15	$10^4\,\kappa_T$	10.83	8.95	7.09	5.32	4.33	3.68	3.18	2.95
	$10^4\,\kappa_T{}^a$	9.99	8.36	6.73	5.15	4.23	3.63	3.15	
	$10^4\,\kappa_T{}^b$	10.71	9.22	7.38	5.49	4.41	3.75		
	$10^3\,\alpha$	1.15	1.04	0.90	0.76	0.69	0.65	0.60	0.56
288.15	$10^4\,\kappa_T$	11.62	9.51	7.45	5.52	4.46	3.78	3.28	3.06
	$10^3\,\alpha$	1.20	1.07	0.93	0.79	0.71	0.67	0.62	0.59
298.15	$10^4\,\kappa$	12.32	10.06	7.82	5.70	4.54	3.84	3.37	3.19
	$10^3\,\alpha$	1.25	1.10	0.96	0.81	0.74	0.69	0.64	0.62
313.15	$10^4\,\kappa_T$	13.70	11.04	8.43	6.00	4.71	3.95	3.48	3.31
	$10^3\,\alpha$	1.32	1.15	0.99	0.85	0.77	0.72	0.68	0.66
323.15	$10^4\,\kappa_T$	14.71	11.76	8.90	6.28	4.91	4.11	3.63	3.46
	$10^4\,\kappa_T{}^a$	13.38	10.64	8.14	5.96	4.81	4.07	3.49	
	$10^4\,\kappa_T{}^b$	14.17	11.78	8.99	6.40	5.05	4.28		
	$10^3\,\alpha$	1.37	1.18	1.02	0.88	0.80	0.74	0.70	0.69
338.15	$10^4\,\kappa_T$	16.88	12.89	9.41	6.52	5.08	4.23	3.62	3.36
	$10^3\,\alpha$	1.44	1.23	1.06	0.92	0.83	0.77	0.73	0.73

[a] Calculated compressibilities for ethanol using densities [20].

[b] Compressibilities reported for methanol [19].

than those of methanol and the difference increases with temperature. With increasing pressure the compressibility of TFE becomes less than that of methanol and, above 100 MPa, approaches that of ethanol. The compressibilities were also calculated with a fixed value of $C = 0.211$ and B from Eqs. (4), (5), and (7) using the relationship [19]

$$\kappa_T = \frac{1}{2.3026\,k}\frac{C}{(B+p)} \tag{10}$$

The calculated compressibilities agreed with the tabled compressibilities (Table V) within ±2% up to 200 MPa; with the exception of the compressibilities at 323.15 K, the maximum deviation, of the compressibilities using Eq. (10) from the compressibilities (Table V) above 200 MPa, was ±2–4%.

Isobaric expansivities, α, were calculated fitting V_m at a constant pressure, p, to a quadratic in T and using

$$\alpha = (1/V_m)(\partial V_m/\partial T)_p \tag{11}$$

The molar volumes, V_m, were calculated as a function of temperature at seven pressures (20, 50, 100, 150, 200, 250, and 275 MPa) from the densities at 0.1 MPa given by Eq. (1), and volume ratios from the SBM given by Eq. (2) using the coefficients in Table III. The expansivities are listed in Table V; they have a probable uncertainty of ±2–3%.

3.4. Internal Pressure

The internal pressure p_{int} is related to the thermal pressure coefficients $(\partial p/\partial T)_v$ by

$$p_{int} = T(\partial p/\partial T)_v - p \tag{12}$$

Table VI. Internal Pressure (p_{int}, in MPa)

V_m	T(K)					
($cm^3 \cdot mol^{-1}$)	278.15	288.15	298.15	313.15	323.15	338.15
64.0	278.6	303.7	328.6	370.1	403.2	443.5
65.0	284.8	306.2	327.6	363.1	390.8	425.7
66.0	288.8	306.8	325.2	355.4	378.5	408.4
67.0	291.0	306.2	321.7	347.3	366.4	391.9
68.0	291.9	304.5	317.6	339.0	354.7	376.2
69.0	291.9	302.2	313.1	330.7	343.6	361.4
70.0	291.1	299.4	308.3	322.7	333.0	347.6

Thermal pressure coefficients $(\partial p/\partial T)_v$ for selected values of V_m were calculated as described in Ref. 2. The values of p_{int} are listed in Table VI; they are estimated to have a probable uncertainty of the order of ±4–5%. The volume dependence of the internal pressure for TFE, at constant temperature, is shown in Fig. 1 for comparison with internal pressures calculated for ethanol from literature data [20] (Fig. 2). The variation of p_{int} with increasing pressure for TFE does not resemble that of ethanol but is similar for most of the range to methanol [19], although it does not show the turning point at the three lower temperatures at high pressures. This may indicate the differences in hydrogen-bonding capabilities of the two alcohols.

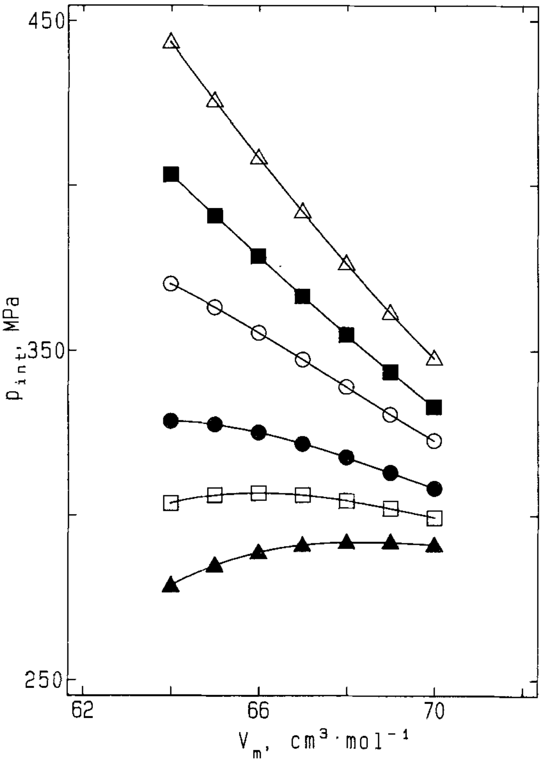

Fig. 1. Volume and temperature dependence of the internal pressure for TFE: ▲, 278 K; □, 288 K; ●, 298 K; ○, 313 K; ■, 323 K; △, 338 K.

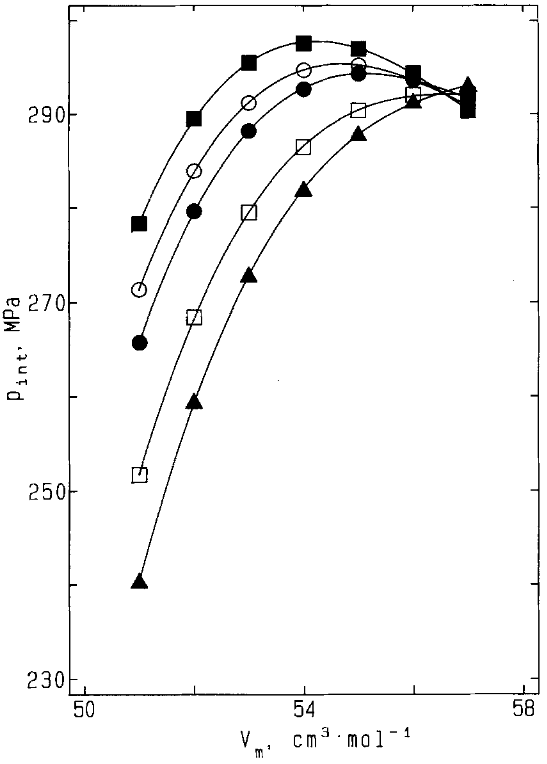

Fig. 2. Volume and temperature dependence of the internal pressure for ethanol (molecular weight = 0.046069 kg): ▲, 273 K; □, 293 K; ●, 313 K; ○, 323 K; ■, 333 K.

4. CONCLUSION

The use of the Tait equation of state to represent the $V_p/V_{0.1}$ data for TFE for the temperature range 278 to 338 K has been studied in detail. The measurements of this work in combination with the critical properties for TFE [1] provide an equation which enables accurate prediction of properties outside the temperature range of the measurements. The representation of B as a function of reduced temperature in the form of [Eq. (7)] has the advantage of being derived from the principle of corresponding states and its inclusion of the theoretical value of B at the critical pressure.

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