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An Automated Volumometer: Thermodynamic Properties of 1,1-Dichloro-2,2,2-trifluoroethane (R123) for Temperatures of 278.15 to 338.15 K and Pressures of 0.1 to 380 MPa

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An automated bellows volumometer is described which is capable of obtaining *p-V-T* data in the form of volume ratios for pressures up to 380 MPa. Volume ratios for 1,1-dichloro-2,2,2-trifluoroethane (R123) have been measured for six temperatures in the range of 278.15 to 338.15 K in the liquid phase. The accuracy of the volume ratios is estimated to be ±0.05 to 0.1% for the experimental temperatures up to 298.15 K and better than ±0.15% for temperatures above the normal boiling point of R123 (300.15 K). They agree with the literature data (which do not extend beyond 4 MPa) within the experimental uncertainty of those results. Isothermal compressibilities, isobaric expansivities, internal pressures, and isobaric molar heat capacities have been evaluated from the volumetric data. The pressure dependence of isobaric molar heat capacities obtained from the data generally agree with the pressure dependence of experimentally measured literature values within the latter's accuracy of ±0.4%.

KEY WORDS: absolute saturated liquid densities; automated volumometer; compressibility; 1,1-dichloro-2,2,2-trifluoroethane; expansivities; heat capacities; *p-V-T* data; R123; specific heat.

1. INTRODUCTION

This work is part of an experimental program to determine the effect of high pressures on volumetric properties of some environmentally acceptable chlorofluorocarbons. In this paper we present *p-V-T* measurements and

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thermodynamic properties of 1,1-dichloro-2,2,2-trifluoroethane (R123) calculated from these data.

There are only three cited sources [1–3] of liquid p-V-T data for R123; these cover an extensive fluid range but only for pressures less than 4 MPa. Since the present work was commenced, there have been indications of some high-pressure p-V-T measurements in progress elsewhere [4]. The objective of the present study was to obtain volume ratios up to about 400 MPa in the liquid phase for the temperatures 278.15, 288.15, 298.15, 313.15, 323.15, and 338.15 K by using an existing bellows volumometer [5–8] which has a proven capability of making measurements of a high precision and accuracy [9, 10]. The present work in combination with representation of the data by the Tait equation of state is expected to facilitate the extrapolation of the experimental volumetric properties to temperatures outside the experimental range [11, 12]. In combination with liquid densities at either 0.1 MPa or values from the literature for liquid densities at the saturation pressure (when the experimental temperature was above the normal boiling point), the volume ratios provide the required p-V-T data in the liquid phase.

Significant alterations were made to the experimental apparatus to enable complete computer control of the measurements for pressures above 25 MPa using a pressure transducer to determine the pressure and a motor-driven screw injector to lower the pressure after each measurement. The reliability of the p-V-T data obtained under computer control has been tested by comparing results for R123 with corresponding measurements made with the volumometer under manual control.

The normal boiling point of R123 of 300.15 K [4] is lower than three of the temperatures of the present measurements. The usual experimental procedure and treatment of experimental data have been modified to enable the measurements to be made with the lowest pressure above, rather than at, 0.1 MPa. Details of those changed procedures are given below.

2. EXPERIMENTS

The 1,1-dichloro-2,2,2-trifluoroethane as supplied by Fluorochem Ltd., Derbyshire, was of unspecified purity. It was fractionally distilled to obtain the middle fraction at a constant boiling point of 299.95 K at 708.9 Torr. Densities of this sample were measured by a carefully calibrated Anton Paar Model 602 densimeter, with an accuracy of ±0.03% at 0.1 MPa, at 5° intervals for the temperature range 278.15 to 298.15 K obtaining the values 1513.21, 1500.47, 1488.11, 1475.61, and 1462.92 $\mathrm{kg \cdot m^{-3}}$.

Volume ratios, k $(= V_p/V_{\mathrm{ref}}$, where V_{ref} and V_p are the volumes of a fixed mass of R123 at a reference pressure, usually 0.1 MPa and pressure

p, respectively), were measured at each temperature employing a bellows volumometer. The experiments were always performed by starting at the lowest temperature and highest pressure. Temperatures were measured with a platinum resistance thermometer (Leeds & Northrup Model No. 8931) calibrated against a standard long-stem platinum resistance thermometer (IPTS-68) and were accurate to ±0.01 K and constant within ±0.005 K.

The volumometer with design features detailed elsewhere [5] has been upgraded to incorporate the computer-controlled lowering and measurement of the pressure. Lowering of the pressure is done largely with the use of a screw injector operated under computer control and illustrated schematically in Fig. 1. The screw injector consists of a piston-cylinder assembly with a cylinder working volume of 11 cm^3. The piston is driven horizontally by a screw thread coupled through a set of gears (ratio, 125:1) to a three-phase AC motor ($\frac{1}{4}$HP, 1440 rpm) whose operation and direction are computer-controlled using a STD interface. A pair of limit switches located at the two end positions on the outside of the cylinder prevents the piston being driven beyond preset limits. The status of the limit switches is monitored by the computer to check the operation and direction of the motor. The experiment is started at the maximum pressure with the piston fully in the cylinder. At the completion of the measurements at each pressure the motor is operated to partially remove the piston from the cylinder so as to lower the pressure by the desired amount.

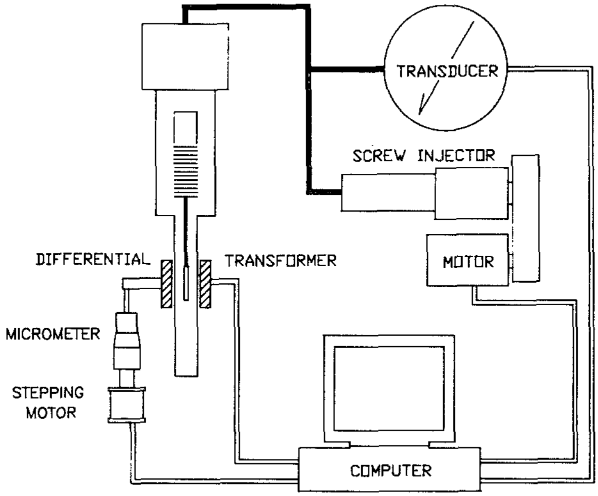

Fig. 1. Schematic diagram of an automated bellows volumometer for the pressure range of 0.1 to 400 MPa.

Pressures are measured with a commercial pressure transducer (Wika Model 891.01.2002, Alexander Wiegand GmbH and Co., Main, Germany) of range 0 to 400 MPa with an output of 4–20 mA DC. (The transducer output is converted to a voltage and coupled to an analog-to-digital converter for computer control.) Simultaneous measurements made with both the pressure transducer and a Heise gauge showed that the pressure transducer drifted linearly with time. The digital output of the transducer was calibrated in steps of 9.8 MPa ($100\ \text{kg} \cdot \text{cm}^{-2}$) with a deadweight gauge for the whole pressure range; the slope of the curve of transducer output versus pressure remained constant. The average difference in the digital output of the transducer for a constant step in pressure was within ±0.05 MPa for the transducer and was used to obtain the derivative $d(pt_{\text{cal}})/dp$ used in Eq. (1). The output of the transducer was converted to pressures by reference to the maximum experimental pressure, p_{ref},

$$p = p_{\text{ref}} - [d(pt_{\text{cal}})/dp](ptr_{\text{ref}} - ptr_{\text{p}}) \tag{1}$$

where ptr_{ref} and ptr_{p} are transducer outputs corresponding to pressures p_{ref} and p. Pressures could also be measured relative to atmospheric pressure with two calibrated Heise–Bourdon analogue gauges (covering the ranges 30 to 400 and 0 to 25 MPa). The pressure transducer was used to read pressures for the range 390 to 30 MPa; the analogue gauges were used to read pressures from 25 to 10 MPa and a deadweight gauge was used for the pressures 5 and 2.5 MPa. When the experimental pressure had been lowered to near 25 MPa the pressure read by the Heise gauge was used to adjust the time dependence of all the pressures measured with the pressure transducer to correspond to p_{ref} at zero elapsed time. Generally the correction was of the order of 0.002 to 0.003 $\text{MPa} \cdot \text{min}^{-1}$.

Because the normal boiling point of R123 is lower than three of the temperatures of the present measurements, the usual experimental procedure [10] and treatment of the experimental data were modified to enable the final measurements at each temperature to be made at pressures close to but above 0.1 MPa. Easteal and Woolf [14] described changes in the usual experimental procedure for measurements of volumetric properties of *n*-pentane at temperatures above its normal boiling point (309.3 K). A somewhat different procedure has been used in the present case. The modified procedure involved decreasing the extended length of the bellows at 0.1 MPa at a temperature (298.15 K) close to but below the normal boiling point of R123. The decrease in length was achieved with an external spacer which was estimated to provide a bellows volume sufficient to contain the liquid volume at just above the saturated vapor pressure at the highest temperature (338.15 K) of the measurements. After having brought the volumometer to temperature equilibrium at 298.15 K, it was closed and the spacer removed. The measurements made previously at 298.15 K when the extended length of the bellows was at its normal maximum at atmospheric pressure were then repeated using the same experimental procedure for pressures decreasing from about 380 to 2.5 MPa. However, for the subsequent measurements at temperatures 313.15, 323.15, and 338.15 K, the volumometer was raised to each of these temperatures in turn while maintaining the closed volumometer cell in its pressure vessel at a pressure above the normal vapor pressure. The measurements at each of these temperatures were made in the same manner except that the minimum pressure of measurement was always above the normal vapor pressure of R123 at that temperature.

This modification in experimental procedure requires corrections to be applied to the calibration factors of the volumometer to enable calculation of volume ratios. The basic equation [9] for the bellows volumometer is

$$V_{\mathrm{p}}/V_{0.1} = 1 - (A/V_{0.1})\,\Delta l \qquad (2)$$

where

$$\Delta l = (l_{0.1} - l_{\mathrm{p}}) \qquad (3)$$

and $V_{0.1}$ and V_{p} are the volumes of the volumometer cell at 0.1 MPa and pressure p, respectively; Δl is the change in length of the bellows resulting from the pressure change $p-0.1$; and A is the effective cross-sectional area of the volumometer cell. $A/V_{0.1}$ is a characteristic parameter for the volumometer cell; it depends on Δl [14] and is determined by calibration [10] with water at each temperature of the measurements. The $A/V_{0.1}$ evaluated for the present volumometer cell has been found to be independent of temperature.

Modification of the experimental procedure to account for the partial decrease in the extended length of the bellows requires that Eq. (2) is modified [14] to include volume and area corrections:

$$(A/V_{0.1})'_T = (A/V_{0.1})_T\, \Phi_{V,T} \Phi_{A,T} \qquad (4)$$

where the prime signifies that the volumometer cell is not fully extended at 0.1 MPa. For the present volumometer cell the bellows calibration factor $A/V_{0.1}$ in normal operation without the use of any spacer was obtained with water and *n*-heptane as calibration fluids and was found to be dependent only on pressure and independent of temperature [7]. Consequently, the area correction factor $\Phi_{A,T}$ for this volumometer was considered to be unity. The volume correction factor $\Phi_{V,T}$ allows for the volume expansion of the fluid contained in the cell at temperatures above the reference temperature T_{ref} at which the extended length of the bellows was decreased. It is evaluated from

$$\Phi_{V,T} = V_{0.1,T,ns}/V_{0.1,T,ws} \tag{5}$$

where $V_{0.1,T,ns}$ is the volume of the fully extended bellows at 0.1 MPa and temperature T, and $V_{0.1,T,ws}$ is the calculated volume at T of the mass of fluid contained at 0.1 MPa and T_{ref} with the spacer in place. $V_{0.1,T,ns}$ was determined at the temperatures 298.15, 313.15, 323.15, and 338.15 K with water and is represented by

$$V_{0.1,T,ns} = 51.422 + 0.0031T \tag{6}$$

where $V_{0.1,T,ns}$ is in cm^3 and T is in K.

Values of $V_{0.1,T,ws}$ for use in Eq. (5) were obtained from an estimate of the density of the fluid at temperature T and the mass of the fluid in the volumometer cell. For this purpose, the atmospheric pressure density $\rho_{0.1}$ for R123 obtained for the temperatures (273.15 to 298.15 K) was represented with a standard deviation of $0.11\ \mathrm{kg \cdot m^{-3}}$ by a linear fit,

$$\rho_{0.1} = 2210.975 - 2.5088T \tag{7}$$

where $\rho_{0.1}$ is in $\mathrm{kg \cdot m^{-3}}$ and T is in K. The volume of the volumometer cell at atmospheric pressure with the length of the bellows compressed at T_{ref} (298.15 K) was 44.511 cm^3; this was obtained with water as the calibration fluid.

Easteal and Woolf [14], in their modification of the procedure to obtain $\Phi_{V,T}$, when the bellows was compressed at T_{ref}, allowed for the volume expansion of the fluid contained in the cell at T_{ref} as a result of temperature increase and the counteracting increase in volume of the cell material, stainless steel, using for $V_{0.1,T,ws}$

$$V_{0.1,T,ws} = V'_{0.1}[1 + \alpha_1(T - T_{\mathrm{ref}}) - \alpha_{\mathrm{ss}}(T - T_{\mathrm{ref}})] \tag{8}$$

where $V'_{0.1}$ is the volume of the bellows with spacer in place at T_{ref}, α_1 and α_{ss} are isobaric expansivities at 0.1 MPa of the fluid and the stainless steel, and α_{ss} can be determined from the volume of the bellows at different temperatures. It was found that the term α_{ss} which can be obtained from Eq. (6) was of the order of $10^{-4}\ \mathrm{K}^{-1}$ and insignificant compared to α_1.

The values of $\Phi_{V,T}$ at 298.15, 313.15, 323.15, and 338.15 K of 1.0777, 1.0509, 1.0332, and 1.0062, respectively, were calculated with Eqs. (5)–(8). The overall accuracy of the measured volume ratios under normal conditions with the bellows fully extended for temperatures (278.15 to 298.15 K) is estimated to be ±0.02–0.04% for pressures above 50 MPa, varying to ±0.1% at pressures approaching 0.1 MPa. With the use of the volume correction factor $\Phi_{V,T}$ for $A/V_{0.1}$ in Eq. (4), the accuracy of measured volume ratios for temperatures (313.15 to 338.15 K) is estimated to be ±0.1% for pressures above 50 MPa, varying to ±0.15–0.20% at pressures approaching 0.1 MPa.

3. RESULTS AND DISCUSSION

3.1. Volumetric Data

The interpolated values of the densities of R123 at 0.1 MPa ($\rho_{0.1}$) for temperatures ($273.15 \leqslant T \leqslant 298.15$ K) from Eq. (7) agree within ±(0.02–0.06)% with the experimental values of Schmidt reported in Ref. 3; ±(0.08–0.10)% [15]; ±(0.14–0.17)% [1]. Yokoyama and Takahashi [15] observed that the atmospheric pressure densities of Maezawa et al. [1] were about 0.1 to 0.2% lower than their results.

The experimental pressures p are given in Table I with the volume ratios k [$= V_p/V_{0.1}$; $V_{0.1}$ for temperatures above the normal boiling point are based on extrapolation of $\rho_{0.1}$ employing Eq. (7)]. The data with the exception of those at 313.15 and 338.15 K were obtained with the computer-controlled experiment as explained in the previous section (for pressures $30 \leqslant p \leqslant 390$ MPa, computer read and lowered; $10 \leqslant p \leqslant 25$ MPa, read with calibrated Heise gauge; and 5 and 2.5 MPa, deadweight gauge). All the values of k reported as Set II in Table I at (298.15, 313.15, 323.15, and 338.15 K) were obtained with the bellows initially compressed by the spacer at temperature 298.15 K and obtaining the value of $(A/V_{0.1})'_T$ using Eqs. (4)–(8) for each corresponding temperature. The deviations in k of the two sets of measurements (one with the bellows initially compressed, the other with it fully extended) at 298.15 K are within ±0.05%. Some k values not reported here (measurements made with all pressures read using a Heise gauge) were also obtained for the temperatures 278.15, 288.15, 298.15, and 323.15 K. The comparison of those values of k with the corresponding values tabulated in Table I is shown in Fig. 2. The differences between the two sets of data are within the experimental uncertainty of the experiment.

The secant bulk modulus (SBM), K [$=p/(1-k)$], was represented by cubic equations

$$K = \sum_{i=0}^{3} A_i p^i \tag{9}$$

Table I. Experimental Pressures and Volume Ratios for R123 at Temperatures from 278.15 to 338.15 K

p (MPa)	k	p (MPa)	k	p (MPa)	k	p (MPa)	k
$T = 278.15$ K							
2.550	0.9960	29.57	0.9620	150.55	0.8832	299.78	0.8339
5.001	0.9923	40.59	0.9512	175.39	0.8730	323.09	0.8281
9.700	0.9857	60.86	0.9341	197.92	0.8646	349.29	0.8223
14.691	0.9791	80.39	0.9206	222.07	0.8564	370.19	0.8179
19.500	0.9732	100.76	0.9081	249.70	0.8479	387.88	0.8140
24.073	0.9680	125.62	0.8949	274.87	0.8406		
$T = 288.15$ K							
2.550	0.9956	29.69	0.9585	150.67	0.8757	300.46	0.8254
5.001	0.9916	40.70	0.9470	175.58	0.8652	325.25	0.8191
10.412	0.9833	60.64	0.9290	198.38	0.8566	349.77	0.8135
15.120	0.9766	79.73	0.9150	225.62	0.8474	372.27	0.8087
19.860	0.9703	99.95	0.9021	250.59	0.8396	384.43	0.8060
23.540	0.9657	125.28	0.8880	275.55	0.8323		
$T = 298.15$ K							
2.550	0.9951	29.77	0.9544	151.09	0.8679	300.29	0.8165
5.001	0.9906	40.36	0.9424	177.52	0.8564	324.97	0.8102
10.050	0.9820	61.21	0.9227	200.60	0.8475	349.27	0.8045
15.240	0.9739	80.07	0.9084	225.45	0.8389	372.69	0.7994
20.030	0.9670	100.21	0.8951	250.32	0.8309	390.03	0.7955
24.030	0.9616	125.37	0.8807	275.68	0.8234		
(Set II—bellows compressed)							
$T = 298.15$ K							
2.550	0.9951	40.35	0.9424	174.23	0.8576	300.06	0.8164
5.001	0.9906	61.80	0.9221	199.66	0.8477	325.00	0.8100
10.120	0.9819	79.80	0.9084	224.50	0.8390	350.29	0.8040
19.280	0.9680	100.04	0.8951	250.18	0.8308	375.85	0.7983
24.130	0.9615	125.31	0.8806	274.82	0.8235	385.70	0.7961
29.628	0.9545	150.68	0.8680				
$T = 313.15$ K							
5.001	0.9892	40.18	0.9348	174.81	0.8442	298.82	0.8023
10.246	0.9789	79.92	0.8978	198.93	0.8344	325.22	0.7953
14.725	0.9709	98.47	0.8848	225.35	0.8249	349.45	0.7894
19.454	0.9630	124.78	0.8688	250.46	0.8166	373.06	0.7840
24.505	0.9553	150.11	0.8555	274.99	0.8092	386.32	0.7810
29.37	0.9484						
$T = 323.15$ K							
5.001	0.9885	59.79	0.9089	174.74	0.8365	299.46	0.7942
9.905	0.9782	80.12	0.8914	198.92	0.8266	324.62	0.7874
14.847	0.9688	99.28	0.8774	225.03	0.8171	349.77	0.7813
19.047	0.9613	124.83	0.8614	250.26	0.8088	372.59	0.7761
23.209	0.9545	150.01	0.8480	274.97	0.8012	389.05	0.7723
39.532	0.9314						
$T = 338.15$ K							
19.534	0.9562	79.43	0.8817	195.64	0.8150	324.82	0.7735
23.581	0.9489	99.69	0.8661	224.40	0.8041	350.34	0.7672
29.019	0.9398	124.68	0.8499	250.51	0.7953	373.75	0.7618
39.729	0.9240	150.01	0.8359	275.48	0.7874	392.29	0.7575
59.136	0.9005	174.86	0.8239				

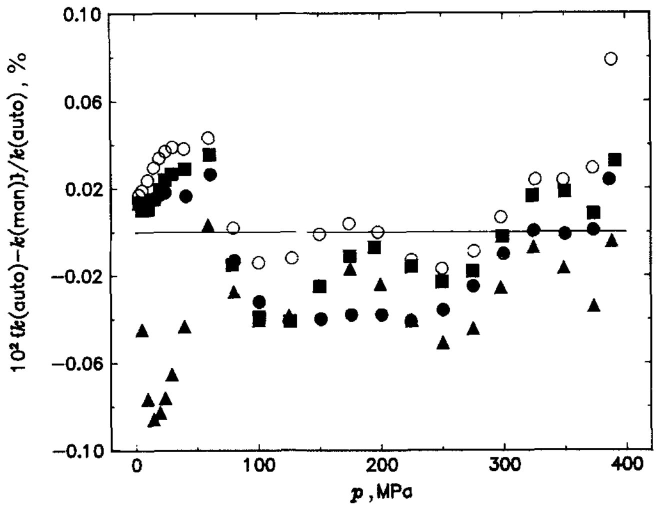

Fig. 2. Comparison of volume ratios measured for R123 under computer (auto) and manual control of the experiment: ●, 278.15 K; ○, 288.15 K; ■, 298.15 K; ▲, 323.15 K.

The A_i in Eq. (9) are listed in Table II with the coefficients B and C of the modified Tait equation [16] expressed here as

$$1 - k = C \log[(B + p)/(B + p_0)] \tag{10}$$

where p_0 is the reference pressure, usually 0.1 MPa, and the constants B and C are adjustable parameters. Table II also lists the root mean square deviation (rmsd) in volume ratios calculated using the coefficients of Eq. (9). The maximum deviation in representing a set of volume ratios at

Table II. Coefficients of Eq. (9) for SBM and of Eq. (10) for the Tait Equation for R-123

T (K)	A_1 (MPa)	A_2	$-A_3$ (GPa^{-1})	A_4 (GPa^{-2})	$10^2\langle \Delta k/k \rangle$	B (MPa)	C
278.15	632.03	5.1253	5.8199	5.910	0.015	56.79	0.2081
288.15	573.46	4.9336	5.2242	5.035	0.015	50.94	0.2082
298.15	512.28	4.8831	5.3556	5.188	0.019	45.53	0.2085
298.15	513.20	4.8473	5.1863	4.928	0.017	45.61	0.2089
313.15	438.50	4.6346	4.8682	4.564	0.021	38.85	0.2108
323.15	412.42	4.3180	3.6979	3.006	0.017	35.32	0.2111
338.15	366.72	4.0821	3.2894	2.599	0.019	31.09	0.2152

any temperature was generally at the highest pressure of the measurements, with the worst being 0.052% at 389.4 MPa and 313.15 K. The rmsd for volume ratios calculated using constants B and C of Eq. (10) at all temperatures are larger (although within the experimental uncertainty of the experiment) than those obtained with the coefficients of Eq. (9); the maximum rmsd was 0.053% for the temperature 338.15 K.

The density ρ_p at pressure p can be calculated by Eq. (11),

$$\rho_p = \rho_{0.1}/k = \rho_{0.1}/(1 - p/K) \qquad (11)$$

and Eq. (7) with k from Eq. (9) or Eq. (10). The liquid density ρ_{sat} along the saturated vapor-pressure line for experimental temperatures (313.15 to 338.15 K) above the normal boiling point may be estimated from the saturated vapor pressure at those temperatures and the density $\rho_{0.1}$ extrapolated from Eq. (7). The saturated vapor pressures of R123 used for the temperatures 313.15, 323.15, and 338.15 K were 0.155, 0.213, and 0.329 MPa [2], in agreement with those of Morrison and Ward [3] for the temperatures 313.15 and 323.15 K (at 338.15 K the saturated vapor pressure has also been reported as 0.332 [3] and 0.330 MPa [17]); the liquid densities calculated at those saturated vapor pressures are 1425.60 $\text{kg} \cdot \text{m}^{-3}$ at 313.15 K, 1400.66 $\text{kg} \cdot \text{m}^{-3}$ at 323.15 K, and 1363.57 $\text{kg} \cdot \text{m}^{-3}$ at 338.15 K. The agreement with values interpolated from fitting a cubic equation in temperature to the experimental values of Ref. 15 up to 350 K is within 0.3% (for $T = 313.15$ and 323.15 K) and 0.6% ($T = 338.15$ K). A cubic equation, however, is not as good a representation of the experimental data of Morrison and Ward [3] up to 343 K as is the equation: $\rho_{0.1} = 0.3518 + 1.5784(1 - T_r)^{1/3}$ where $T_r = T/T_c$ and the critical temperature $T_c = 456.94$ K [3]. Densities interpolated from this equation agree within 0.3% (the experimental error of the data [3]) with those estimated from the present work for temperatures 313.15, 323.15, and 338.15 K. (The latter equation does not represent the data of Ref. 15 as accurately as does the cubic fit.) This method of estimation of saturated liquid densities at temperatures 30–40 K above the normal boiling point is suitable if direct experimental values are not available.

The Tait equation [Eq. (10)] also allows the calculation of ρ_p using a reference density at a pressure above 0.1 MPa. For temperatures above the normal boiling point, where accurate experimental values of the saturated liquid density and vapor pressure are available, the data sets $V_p/V_{0.1}$ in Table I can be adjusted to volume ratios V_p/V_{sat} (where V_{sat} is the volume of the fluid at the saturated vapor pressure) using

$$k_{\text{sat}} = V_p/V_{\text{sat}} = (V_p/V_{0.1})/(V_{\text{sat}}/V_{0.1}) \qquad (12)$$

The absolute density ρ_p at pressure p then corresponds to $\rho_{\text{sat}}/k_{\text{sat}}$. The values of $V_{\text{sat}}/V_{0.1}$ at temperatures of 313.15, 323.15, and 338.15 K are 0.9999, 0.9997, and 0.9993, respectively.

To enable interpolation of volume ratios in the temperature range in Table I to compare with literature values, the parameter C in Eq. (10) was assigned a temperature-independent common value (=0.2100) chosen to give the best fit for all the experimental temperatures. The corresponding B's were fitted to a second-order equation in T:

$$B = 459.453 - 2.2566T + 0.00292T^2 \qquad (278.15 \leqslant T \leqslant 338.15) \qquad (13)$$

where B is in MPa and T is in K. This equation reproduces the present experimental volume ratios within the estimated accuracy and covers the p-V-T surface for the temperature and pressure range of the measurements.

A recent statistical-mechanical analysis [19] shows that the range of application of the Tait form of correlation may not be expected to be suitable for correlation and prediction of p-V-T properties for a large range of densities because of the increasing nonlinearity of the secant bulk modulus. Therefore, for the present analysis of volumetric data for R123, where extrapolation of the volume ratios is to be made at low pressures which are outside the temperature range of the measurements, the analysis of the experimental data has been restricted to a maximum pressure of 150 MPa (i.e., in the density region where the SBM is also linear [19]). For a fixed value of C (=0.2100) the temperature dependence of B has been represented as inversely proportional to T_{r},

$$B = -95.087 + 92.224/T_{\text{r}} \qquad (B \neq -P_{\text{c}} \text{ at } T_{\text{r}} = 1) \qquad (278.15 \leqslant T \leqslant 338.15) \qquad (14)$$

where the critical temperature T_{c} is 456.82 K on the IPTS-68 scale for R123 [20].

Experimental volumetric data measurements made employing a magnetic densimeter by Maezawa et al. [1] cover the temperature range 280 to 340 K for the pressure range 0.1 to 2 MPa with a maximum uncertainty in volume of ±0.2%, while those obtained with a vibrating-tube densimeter by Morrison and Ward [3] for the temperature range 280 to 363.5 K have a pressure maximum up to 4 MPa with a stated maximum uncertainty in compressed volume of ±0.05%. Although our volume ratio measurements for any temperature include only two data points below 10 MPa (at 5 and 2.5 MPa) and our volume ratios are less accurate in that low-pressure region, the volume ratios interpolated in the experimental temperature range 278 to 338 K from Eq. (14) agree within ±0.1% with

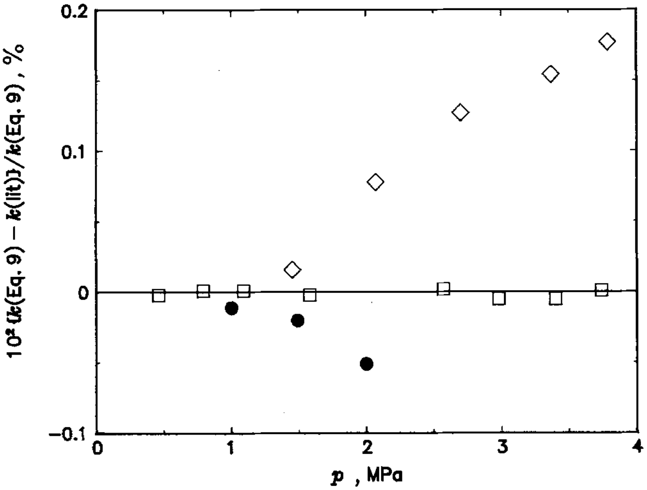

Fig. 3. Comparison of the literature experimental volume ratios for R123 with those obtained from the Tait equation with $C = 0.21$ and B from Eq. (19): □, 285 K [3]; ◇, 352 K [3]; ●, 280 K [1].

those of Refs. 1 and 3. Our extrapolated volume ratios disagree with Ref. 3 by 0.2% at 352 K, as shown in Fig. 3. The comparison of the extrapolated volume ratios with those of Morrison and Ward [3] is within ±0.2% for temperatures of 343 and 353 K and ±0.3% at 363.5 K.

3.2. Compressibilities and Expansivities

Isothermal compressibilities, κ_T, are related to k $(=1-p/K)$ calculated from the SBM coefficients given in Table II for Eq. (9) by using the relationship

$$\kappa_T = -(1/k)(\partial k/\partial p)_T \tag{15}$$

Isobaric expansivities, α, are calculated by fitting molar volumes V_m [obtained from ρ_p given by Eqs. (7) and (11) with a molecular mass of 152.93 $g \cdot mol^{-1}$] at a constant pressure, p, to a quadratic in T and use of the expression

$$\alpha = (1/V_m)(\partial V_m/\partial T)_p \tag{16}$$

The compressibilities and expansivities with estimated uncertainties of ±1–2 and ±2–3%, respectively, are tabulated in Table III. An indication of the accuracy of the p-V-T data for temperatures above the boiling point was obtained by comparing the two sets of isothermal compressibilities at 298.15 K calculated from volume ratios measured with the bellows initially fully extended and later (Set II) partially compressed at 0.1 MPa. The compressibilities calculated from both sets agree well within the expected uncertainty of ±2%, the maximum difference being 0.8% at the maximum pressure of 375 MPa. κ_T for R123 at other temperatures and pressures can also be calculated by the relation

$$\kappa_T = C/[k(B+p)\ln 10] \tag{17}$$

where $C=0.2100$, k is calculated by use of Eq. (10), and B from Eq. (14).

Table III. Isothermal Compressibilities and Isobaric Expansivities for R123

	p (MPa)									
Property	0.1	20	50	100	150	200	250	300	350	375
$T=278.15$ K										
$10^4\kappa_T$ (MPa^{-1})	15.80	12.16	8.95	6.26	4.92	4.12	3.55	3.08	2.64	2.42
$10^3\alpha$ (K^{-1})	1.66	1.35	1.10	0.88	0.77	0.69	0.64	0.58	0.53	0.51
$T=288.15$ K										
$10^4\kappa_T$ (MPa^{-1})	17.41	13.21	9.56	6.57	5.10	4.23	3.64	3.16	2.73	2.52
$10^3\alpha$ (K^{-1})	1.69	1.39	1.13	0.90	0.79	0.71	0.65	0.60	0.55	0.52
$T=298.15$ K										
$10^4\kappa_T$ (MPa^{-1})	19.49	14.39	10.16	6.84	5.28	4.38	3.77	3.27	2.81	2.59
$10^3\alpha$ (K^{-1})	1.72	1.42	1.15	0.93	0.80	0.73	0.67	0.62	0.57	0.55
$T=298.15$ K (Set II—bellows compressed)										
$10^4\kappa_T$ (MPa^{-1})	19.45	14.41	10.19	6.86	5.28	4.38	3.77	3.28	2.83	2.61
$T=313.15$ K										
$10^4\kappa_T$ (MPa^{-1})	22.76	16.34	11.21	7.35	5.59	4.61	3.95	3.43	2.96	2.73
$10^3\alpha$ (K^{-1})	1.76	1.47	1.20	0.96	0.83	0.75	0.70	0.66	0.61	0.59
$T=323.15$ K										
$10^4\kappa_T$ (MPa^{-1})	24.20	17.43	11.97	7.70	5.75	4.65	3.97	3.46	3.04	2.85
$10^3\alpha$ (K^{-1})	1.79	1.48	1.20	0.96	0.82	0.75	0.70	0.66	0.62	0.60
$T=338.15$ K										
$10^4\kappa_T$ (MPa^{-1})	27.22	19.27	12.96	8.22	6.06	4.88	4.13	3.59	3.15	2.95
$10^3\alpha$ (K^{-1})	1.83	1.53	1.24	0.98	0.84	0.76	0.72	0.68	0.65	0.63

3.3. Internal Pressures

The internal pressure π is related to the thermal pressure coefficient $(\partial p/\partial T)_V$ by

$$\pi = T(\partial p/\partial T)_V - p \tag{18}$$

Values of π were obtained by first determining values of p corresponding to chosen V_m by interpolation of a cubic spline fit of 10 values of p to V_m at each temperature. Then the derivative for Eq. (18) was determined analytically from second-order fits in T of the p's. The volume dependence of the internal pressure for temperatures of 278.15, 298.15, 313.15, and 338.15 K is shown in Fig. 4. π increases with increases in temperature and shows an inversion in the volume dependence at a molar volume close to 90–92 $\mathrm{cm^3 \cdot mol^{-1}}$ for all temperatures with the exception of 278.15 K (Table IV).

3.4. Molar Heat Capacities

The pressure dependence of the isobaric molar heat capacity ΔC_p is related to molar volume V_m by

$$\Delta C_p = C_p(p) - C_p(0.1\ \mathrm{MPa}) = -T\int_0^p (\partial^2 V_m/\partial T^2)_p\, dp$$

$$= -\int_0^p (TM/\rho)[(\partial\alpha/\partial T)_p + \alpha^2]\, dp \tag{19}$$

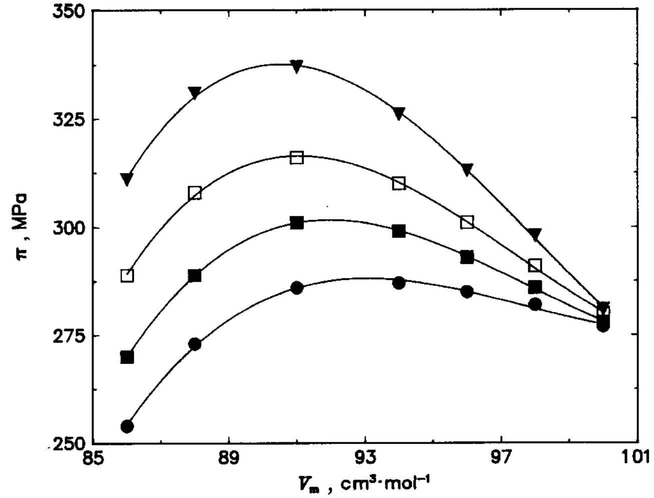

Fig. 4. Volume and temperature dependence of the internal pressure of R123: ●, 278.15 K; ■, 298.15 K; □, 313.15 K; ▼, 338.15 K.

Table IV. Internal Pressure of R123

	π (MPa) at T (K)					
V_m ($cm^3 \cdot mol^{-1}$)	278.15	288.15	298.15	313.15	323.15	338.15
86	255	261	270	289	295	311
88	273	280	289	308	315	331
91	286	292	301	316	323	337
94	287	293	299	310	316	326
96	285	289	293	301	306	313
98	282	284	286	291	294	298
100	277	278	278	280	281	281

where C_p (0.1 MPa) is the molar heat capacity at 0.1 MPa. Values of ΔC_p were obtained as detailed before [7]. The uncertainty in ΔC_p is estimated to be 3–4%, the maximum deviation being in the low-pressure range. To calculate the values of the isobaric molar heat capacities $C_p(p)$ tabulated in Table V, the values for C_p (0.1 MPa) for temperatures of 278.15, 288.15, 298.15, 313.15, 323.15 and 338.15 K were obtained from Eq. (2) of Nakagawa et al. [21]; the C_p (0.1 MPa) values were represented as a quadratic function of temperature,

$$C_p\,(0.1\ \mathrm{MPa}) = 155.609 - 0.1869T + 6.55 \times 10^{-4}T^2 \qquad (20)$$

with a standard deviation of 0.041, where C_p is in $J \cdot mol^{-1} \cdot K^{-1}$ and T in K. The pressure dependence of $C_p(p)$ for temperatures of 278.15, 298.15,

Table V. Isobaric Molar Heat Capacities C_p of R123

	C_p ($J \cdot mol^{-1} \cdot K^{-1}$) at T (K)					
p (MPa)	278.15	288.15	298.15	313.15	323.15	338.15
0.1	154.3	156.1	158.1	161.3	163.6	167.3
20	151.4	153.0	154.8	157.6	159.7	163.0
50	148.3	149.8	151.3	153.9	155.7	158.7
100	145.2	146.4	147.8	150.1	151.8	154.4
150	143.2	144.4	145.7	147.8	149.4	151.9
200	141.7	142.8	144.0	146.0	147.5	149.9
250	140.0	141.0	142.2	144.1	145.5	147.8
300	138.1	139.0	140.0	141.8	143.1	145.2
350	135.8	136.6	137.5	139.2	140.3	142.2
375	134.6	135.4	136.3	137.8	138.9	140.7

313.15, and 338.15 K is shown in Fig. 5. The values of C_p (0.1 MPa) for temperatures 310 to 340 K were only slightly different from those at the saturation vapor pressures; hence the volume-ratio data (Table I) for temperatures above the normal boiling point of R123 were not adjusted to the saturated vapor pressure for the calculation of expansivities and derivatives of expansivities as a function of pressure.

Nakagawa et al. [21] were unable to find any source of measured C_p values for R123 with which to compare their data and estimated their accuracy as ±0.4%. This work enables a comparison of ΔC_p, because it uses their atmospheric pressure values of C_p (0.1 MPa); the pressure dependence of the isobaric molar heat capacities, however, is obtained from the volumetric data measurements using Eq. (19). The comparison of interpolated values of $C_p(p)$ in the temperature range 278.15 to 338.15 K with those of Nakagawa et al. [21] is within ±0.5% with the exception of 300 K, where the comparison is within ±0.7–0.8%.

3.5. Comparison of Volumetric Data with Correlations

The existing recommended method [22] for estimating liquid densities under pressure is the COSTALD (COrresponding STates And Liquid Density) correlation, which applies the Tait equation [23] to nonpolar, polar, and quantum fluids and is represented as a generalized equation. This

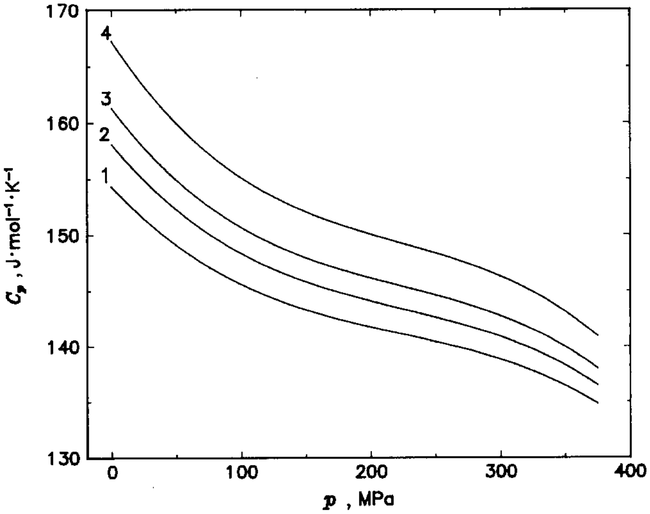

Fig. 5. Pressure and temperature dependence of isobaric molar heat capacity for R123: (1) 278.15 K; (2) 298.15 K; (3) 313.15 K; (4) 338.15 K.

correlation in conjunction with one for the saturated liquid density [24] has its application limited to a maximum pressure of 69 MPa, for which the correlation has been developed. It relates C of the Tait equation to an acentric factor ω_{SRK} and, with the use of selected data sets, representing a wide variety of compounds, develops an expression which relates reduced values of B $(=B/P_{\mathrm{c}})$ to the reduced temperature T_{r},

$$B/P_{\mathrm{c}}=-1+a(1-T_{\mathrm{r}})^{1/3}+b(1-T_{\mathrm{r}})^{2/3}+d(1-T_{\mathrm{r}})+e(1-T_{\mathrm{r}})^{4/3} \quad (21)$$

$$e=\exp(f+g\omega_{\mathrm{SRK}}+h\omega_{\mathrm{SRK}}^{2}) \quad (22)$$

$$C=j+k\omega_{\mathrm{SRK}} \quad (23)$$

The values of the coefficients for Eqs. (21)–(23) are given in Ref. 23; ω_{SRK} for R123 is 0.2850 and P_{c} is 3.676 MPa [15]. The estimated accuracy of absolute liquid densities for polar compounds under pressure predicted with the COSTALD method is 2.57% [23]. Yokoyama and Takahashi [15] reported an average absolute deviation of 0.096% using the Hankinson and Thomson method [24] to estimate the saturated liquid densities for R123. The comparison of experimental values of volume ratios for R123 with those from COSTALD for pressures up to 60 MPa and in the temperature range of our measurements is 0.6–0.7%, the maximum deviation close to 1% is generally at the highest pressure. Therefore the estimated average deviation for calculation of absolute liquid densities of R123 under pressure from the COSTALD method is better than 1%.

Another existing prediction method was developed by Kumagai [25]; the method is based on using a van der Waals-type model for the specific volumes of compressed liquids of halogenated hydrocarbons to obtain the Tait parameters. A comparison of densities estimated [26] for R123 from that method with those extrapolated and interpolated from the present work using Eqs. (10) and (14) with $C=0.21$ indicates that, overall, the COSTALD method of estimation of liquid densities is somewhat better.

4. CONCLUSION

This work for R123 demonstrates that saturated liquid densities above the normal boiling point can be obtained by extrapolation of volume-ratio measurements made in the liquid phase only. The accuracy is comparable with direct measurements of the saturated liquid densities. The experimental data over the complete range of temperatures can be represented by the Tait equation with the use of a fixed value of C and temperature-dependent values of B. These equations can also be used to obtain volume ratios at interpolated and extrapolated temperatures. The volumetric data reported in Table I are of sufficient accuracy to calculate the pressure dependence of heat capacities which is consistent with the pressure dependence measured experimentally.

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