Vapor Pressures, Gas-Phase *PVT* Properties, and Second Virial Coefficients for 1,1,1-Trifluoroethane

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The *PVT* properties of 1,1,1-trifluoroethane (R-143a) in the gas phase have been measured by a Burnett apparatus in the range of temperatures from 320 to 380 K and at pressures up to 6 MPa. The vapor pressures in the range of temperatures from 295 to 342 K have also been measured, and a vapor-pressure correlation has been developed. The critical pressure was determined to be (3.776 ± 0.005) MPa on the basis of the present measurements. The second virial coefficients have been determined along seven isotherms, and a truncated virial equation of state has also been developed to represent the temperature dependence of the second virial coefficients and the present Burnett *PVT* measurements. The experimental uncertainties of temperature, pressure, density, and second virial coefficient throughout the present study were estimated to be no more than ±8 mK, ±0.8 kPa, ±0.12%, and ±5%, respectively. The purity of the R-143a sample used was better than 99.95 mol %.

Introduction

1,1,1-Trifluoroethane (R-143a) has zero ozone depletion potential, but it is flammable. Therefore, it has recently been proposed to use this substance in refrigeration applications as a component of promising alternative refrigerant mixtures with other HFC refrigerants such as difluoromethane (R-32), pentafluoroethane (R-125), and/or 1,1,1,2-tetrafluoroethane (R-134a). Concerning its thermodynamic properties, vapor pressures and second virial coefficients were reported in the literature (Beckermann and Kohler, 1994; Fukushima, 1993; Russell et al., 1944; Widiatmo et al., 1994; Ye, 1993), but very few *PVT* results are available.

In this paper, we report vapor pressures and *PVT* properties for R-143a. The measurements have been performed by a Burnett apparatus whose operating performance and reliability were well established through our previous measurements for other alternative refrigerants including R-134a (Qian et al., 1992), R-32 (Qian et al., 1993), and R-125 (Ye et al., 1995). The second virial coefficients have been determined along seven isotherms, and a truncated virial equation of state and a vapor-pressure correlation have also been developed to represent the present measurements.

Experimental Section

The Burnett apparatus used in the present measurements is schematically shown in Figure 1. It consists of a cell system, a temperature control and measuring system, a pressure measuring system, and a vacuum discharge system. The cell system consists of two cells, a sample cell (A) and an expansion cell (B), and an expansion valve (V1). The two cells, which are thick-walled spherical vessels made of SUS-304 with about 500 and 250 cm^3 in their respective inner volumes, are connected by the expansion valve, a constant-volume valve that avoids any noxious volume change during valve operation. For the purpose of establishing a uniform temperature around the two cells and the diaphragm-type differential pressure detector (C), they are all coupled together and immersed in a thermostated oil bath (I) using silicone oil as a heat transfer medium.

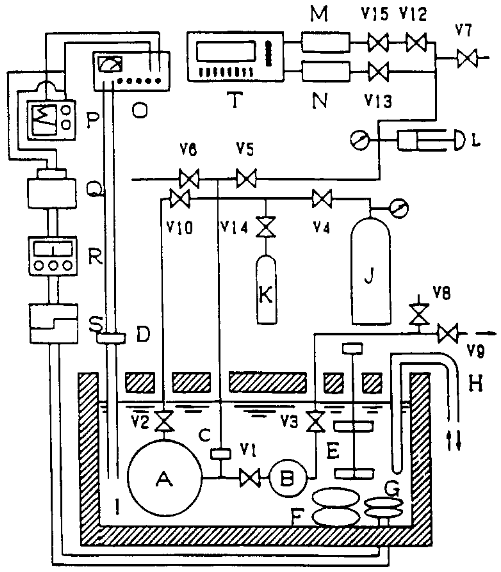

Figure 1. Burnett experimental apparatus: (A) sample cell; (B) expansion cell; (C) differential pressure detector; (D) platinum resistance thermometer; (E) stirrer; (F) main heater; (G) sub-heater; (H) cooler; (I) constant temperature bath; (J) N_2 bottle; (K) N_2 gas damper; (L) hand piston; (M, N) Digiquartz pressure transducer with temperature sensor; (O) thermometer bridge; (P) pen recorder; (Q) voltage/current converter; (R) PID controller; (S) dc power supply; (T) digital pressure gauge; (V1) constant volume valve; (V1−V15) valves.

The temperature was controlled by means of a PID controller and was measured by a standard platinum resistance thermometer installed near the cells. The platinum resistance thermometer was calibrated at the National Research Laboratory of Metrology, Tsukuba, and the uncertainty of the temperature measurements was estimated to be ±8 mK, the sum of ±2 mK for the uncertainty of the thermometer, ±1 mK for the uncertainty of the thermometer bridge, and ±5 mK for the possible temperature fluctuation of the thermostated bath. The temperature was then calculated on the basis of the International Temperature Scale of 1990 (ITS-90).

The sample pressure was transmitted to an external pressure measuring system through the differential pres-

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0021-9568/95/1740-0887$09.00/0

Table 1. Vapor Pressures of R-143a

T/K	*P*/MPa	*T*/K	*P*/MPa
295.000	1.1635	330.000	2.6890
300.000	1.3270	335.000	2.9974
310.000	1.7019	340.000	3.3316
320.000	2.1518	340.000	3.3320
325.000	2.4091	342.000	3.4737
326.000	2.4637		

sure detector (C). By balancing the sample gas pressure with the nitrogen gas pressure in the pressure measuring system, the nitrogen gas pressure was directly measured by a Digiquartz pressure transducer gauge (M or N). One of them (M) was used for pressure measurements above 1.1 MPa, while the other (N) was used for pressures below 1.1 MPa. The experimental uncertainty in the pressure measurements was estimated to be no more than ±0.8 kPa, which consists of the reproducibility of the differential pressure measurements, ±0.5 kPa, and the accuracy of the pressure gauge, ±0.3 kPa, which includes the uncertainties of the correction for the hydrostatic pressure difference of nitrogen gas.

Accurate determination of the cell constant, which is the ratio of the two different volumes of cell A and cells A and B at zero pressure, is one of the essential factors in the Burnett method. By using gaseous helium whose thermodynamic properties are well established (*International Thermodynamic Tables of the Fluid State-Helium,* 1977), the cell constant, $N = 1.50368 \pm 0.00019$, was accurately determined by Qian et al. (1992).

The purity of the R-143a sample used in the present measurements was 99.95 mol % according to the analysis performed by the chemical manufacturer.

Results

Vapor Pressures. We measured the vapor pressures of R-143a by filling the sample cell to approximately the critical density. A total of 11 vapor-pressure values were obtained at temperatures from 295 to 342 K that correspond to the pressures from 1.16 to 3.47 MPa. The vapor pressure values are tabulated in Table 1.

PVT Properties. The Burnett expansion measurements were performed at temperatures from 320 to 380 K. A total of 84 compressibility factors for R-143a have been measured by 9 independent series of expansion. In addition, eight *PVT* property values have also been obtained along an isochore ($\varrho = 0.6534$ mol·L^{-1}) by a coupled isochoric-expansion procedure. Figure 2 summarizes the measured *PVT* points which cover the range of temperatures of 320–380 K, pressures of 0.11–6.0 MPa, and densities of 0.04–7.39 mol·L^{-1}. Note that two different symbols (○ and ●) represent two independent series of expansion which have been performed along two isotherms (350 and 370 K) for the purpose of examining the reproducibility of the present measurements.

The *PVT* data were analyzed with the cell constant mentioned above. The experimental pressures, *P*, temperatures, *T*, the compressibility factors, *Z*, and the calculated densities, ϱ, are given in Table 2.

Second Virial Coefficients. The second virial coefficients, *B*, have been determined from the *PVT* data along different isotherms in the low-density region by calculating $(Z - 1)/\varrho$ as a function of density, ϱ. In consideration of the experimental uncertainties, the following expression with three coefficients was used to fit the measured compressibility-factor data:

$$(Z - 1)/\varrho = B + C\varrho + D\varrho^2 \qquad (1)$$

As a typical example, the dependence of $(Z - 1)/\varrho$ on ϱ along the 370 K isotherm is shown in Figure 3. The experimental uncertainties, ±0.8 kPa for pressure and ±8 mK for temperature measurements, have been added as an error bar to each data point in Figure 3. The intercept with the ordinate gives the second virial coefficient, *B*. Using the same procedure, a total of seven second virial coefficient values have been determined, and they are tabulated in Table 3. The uncertainty of the second virial coefficients determined by the present study was estimated to be no more than ±5% on the basis of the compressibility-factor uncertainty and the data scatter.

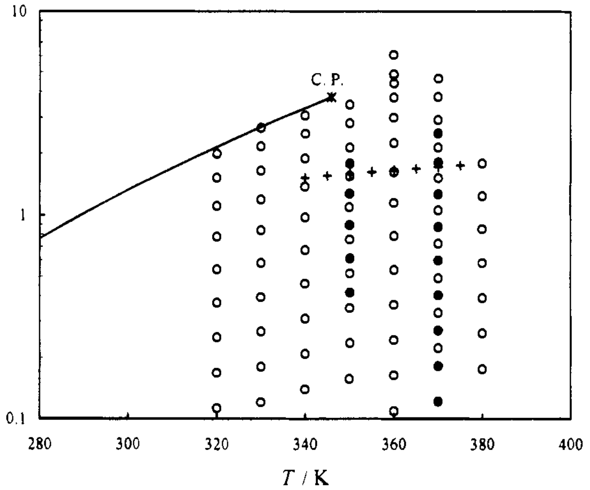

Figure 2. Distribution of the experimental *PVT* data for R-143a; ○, series 1 for 350 and 370 K isotherms; ●, series 2 for 350 and 370 K isotherms; +, isochore ($\varrho = 0.6534$ mol·L^{-1}); *, critical point.

It should be noted that, in Figure 3, the two independent series of measurements along the 370 K isotherm show a very consistent behavior. Since a similar consistent behavior by two independent series of measurements has also been observed along the 350 K isotherm, the reproducibility of the present measurements has been confirmed.

Discussion

Vapor Pressures. The 11 experimental vapor-pressure data given in Table 1 were correlated with the following functional form:

$$\ln(P/P_c) = [-7.33064(1 - T_r) + 1.53338(1 - T_r)^{1.5} - 3.16056(1 - T_r)^3]/T_r \qquad (2)$$

where *P* and P_c denote the vapor pressure and the critical pressure, T_r denotes the dimensionless temperature defined by $T_r = T/T_c$, and *T* and T_c denote the temperature and the critical temperature. The value used for T_c is (345.97 ± 0.03) K which was determined by Fukushima (1993).

The input data for developing the vapor-pressure correlation, eq 2, include the present measurements for temperature 295–342 K, and nine data for 174–226 K reported by Russell at el. (1944). The critical pressure, P_c, in eq 2 has been determined to be (3.776 ± 0.005) MPa in fitting the input data so as to be consistent with the critical temperature mentioned above. Equation 2 is effective for the range of temperatures from 174 K to the critical temperature.

All of the vapor-pressure data measured by this work, Russell at al. (1994), Fukushima (1993), Widiatmo at al. (1994), and Ye (1993), were compared with eq 2 in Figure 4. The absolute deviation of the vapor pressures measured by the present study from eq 2 is less than ±1.0 kPa, which is slightly greater than the accuracy of the pressure measurements (±0.8 kPa). If the uncertainty of the present temperature measurements (±8 mK) is also taken into account, however, then the agreement should be

Table 2. *PVT* Properties of R-143a

T/K	P/MPa	ϱ/(mol·L^{-1})	Z
320.000	1.9870	1.1229	0.6651
320.000	1.5220	0.7468	0.7660
320.000	1.1088	0.4966	0.8391
320.000	0.7825	0.3303	0.8904
320.000	0.5412	0.2197	0.9260
320.000	0.3694	0.1461	0.9504
320.000	0.2499	0.09714	0.9669
320.000	0.1681	0.06461	0.9779
320.000	0.1126	0.04297	0.9854
330.000	2.6581	1.7459	0.5549
330.000	2.1679	1.1611	0.6805
330.000	1.6443	0.7722	0.7761
330.000	1.1918	0.5135	0.8458
330.000	0.8384	0.3415	0.8948
330.000	0.5789	0.2271	0.9289
330.000	0.3947	0.1510	0.9524
330.000	0.2669	0.1005	0.9684
330.000	0.1797	0.06680	0.9803
330.000	0.1203	0.04443	0.9866
340.000	3.0580	1.9721	0.5485
340.000	2.4961	1.3115	0.6732
340.000	1.8959	0.8722	0.7689
340.000	1.3774	0.5801	0.8399
340.000	0.9713	0.3858	0.8906
340.000	0.6717	0.2566	0.9261
340.000	0.4584	0.1706	0.9505
340.000	0.3102	0.1135	0.9669
340.000	0.2086	0.07546	0.9781
340.000	0.1399	0.05019	0.9859
350.000	3.4563	2.1535	0.5515
350.000	2.8039	1.4322	0.6728
350.000	2.1307	0.9525	0.7687
350.000	1.7862	0.7570	0.8109
350.000	1.5482	0.6334	0.8399
350.000	1.2747	0.5034	0.8701
350.000	1.0924	0.4213	0.8911
350.000	0.8886	0.3348	0.9120
350.000	0.7557	0.2802	0.9270
350.000	0.6097	0.2227	0.9410
350.000	0.5159	0.1863	0.9515
350.000	0.4139	0.1481	0.9606
350.000	0.3490	0.1239	0.9679
350.000	0.2347	0.08240	0.9789
350.000	0.1573	0.05481	0.9862
360.000	6.0653	7.3950	0.2740
360.000	4.8714	4.9181	0.3309
360.000	4.4060	3.2708	0.4500
360.000	3.7640	2.1752	0.5781
360.000	2.9946	1.4466	0.6916
360.000	2.2507	0.9621	0.7816
360.000	1.6251	0.6398	0.8485
360.000	1.1418	0.4255	0.8965
360.000	0.7877	0.2830	0.9300
360.000	0.5368	0.1882	0.9529
360.000	0.3628	0.1252	0.9685
360.000	0.2439	0.08323	0.9789
360.000	0.1634	0.05535	0.9860
360.000	0.1092	0.03682	0.9907
370.000	4.6434	2.8889	0.5225
370.000	3.7817	1.9212	0.6398
370.000	2.9068	1.2777	0.7395
370.000	2.5042	1.0428	0.7806
370.000	2.1354	0.8498	0.8168
370.000	1.8075	0.6935	0.8472
370.000	1.5189	0.5651	0.8736
370.000	1.2702	0.4612	0.8952
370.000	1.0567	0.3758	0.9140
370.000	0.8765	0.3067	0.9289
370.000	0.7243	0.2499	0.9419
370.000	0.5975	0.2040	0.9521
370.000	0.4915	0.1662	0.9611
370.000	0.4039	0.1357	0.9678
370.000	0.3313	0.1105	0.9741
370.000	0.2716	0.09022	0.9785
370.000	0.2223	0.07351	0.9828
370.000	0.1819	0.06000	0.9856
370.000	0.1216	0.03990	0.9904
380.000	1.7847	0.6534	0.8645
380.000	1.2455	0.4345	0.9072
380.000	0.8553	0.2890	0.9368
380.000	0.5814	0.1922	0.9576
380.000	0.3923	0.1278	0.9716
380.000	0.2635	0.08499	0.9812
380.000	0.1764	0.05653	0.9878
340.000	1.5196	0.6534	0.8227
345.000	1.5538	0.6534	0.8290
350.000	1.5875	0.6534	0.8349
355.000	1.6212	0.6534	0.8406
360.000	1.6540	0.6534	0.8457
365.000	1.6869	0.6534	0.8507
370.000	1.7197	0.6534	0.8556
375.000	1.7523	0.6534	0.8602

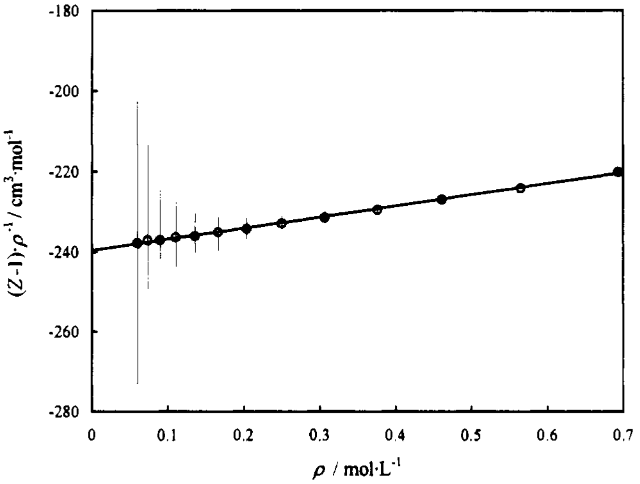

Figure 3. Dependence of $(Z - 1)/\varrho$ on ϱ along the 370 K isotherm: ○, series 1; ●, series 2.

considered acceptable. The deviations of the reported data (Fukushima, 1993; Russell et al., 1944; Widiatmo et al., 1994; Ye, 1993) from the equation are random, and are approximately within the claimed uncertainty of each measurement.

Table 3. Second Virial Coefficients of R-143a

T/K	B/(cm^3·mol^{-1})	T/K	B/(cm^3·mol^{-1})
320.000	−345.5	360.000	−257.0
330.000	−320.4	370.000	−239.5
340.000	−295.7	380.000	−224.1
350.000	−274.1		

Second Virial Coefficients. The temperature dependence of the second virial coefficients given in Table 3 is represented by

$$B = 4.33476 \times 10^{-1} + 6.09455 \times 10^{-1} T_r^{-1} - 4.87858 \times 10^{-1} \exp(T_r^{-1}) \quad (3)$$

where B is given in liters per mole. In Figure 5, the B values by Beckermann and Kohler (1994) obtained from acoustic measurements are compared with eq 3 and the present data. Although the values by Beckermann and Kohler are systematically higher than the present results, the two different measurements show agreement within 2%. Equation 3 represents the second virial coefficient data given in Table 3 within ±0.33%.

Virial Equation of State. In order to facilitate calculation of the thermodynamic properties, we have developed a truncated virial equation of state. This was done by

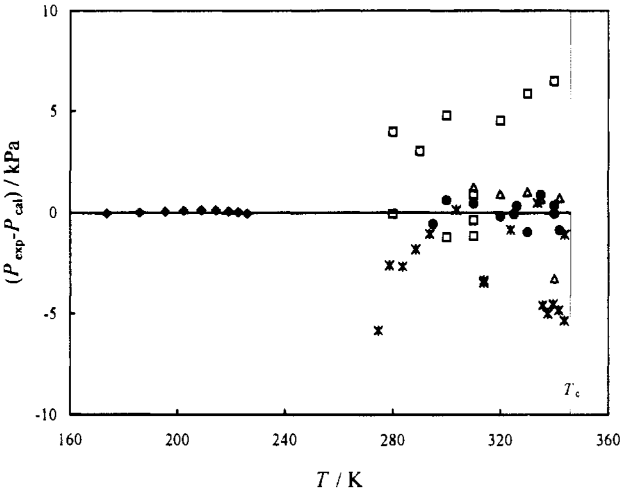

Figure 4. Vapor-pressure deviations from eq 2: ◆, Russell et al. 1944; △, Ye 1993; □, Widiatmo et al. 1994; *, Fukushima 1993; ●, this work; —, eq 2.

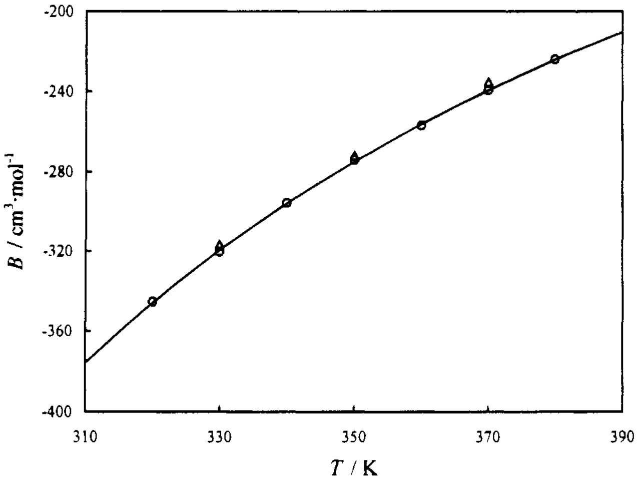

Figure 5. Temperature dependence of the second virial coefficient: △, Beckermann and Kohler (1994); ○, this work; —, eq 3.

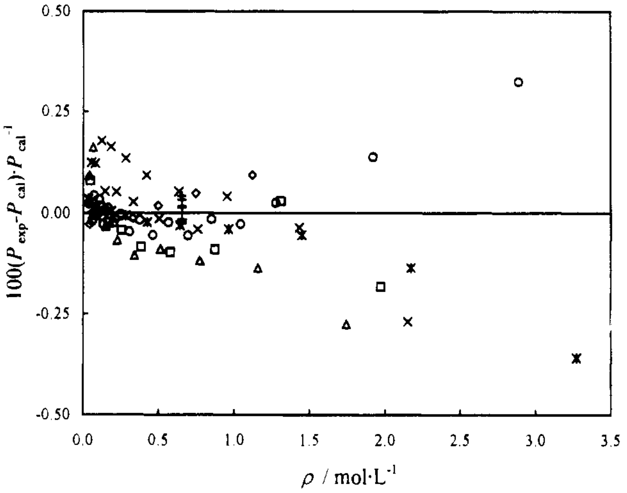

Figure 6. Pressure deviations of the experimental *PVT* data from eq 4: ◇, 320 K; △, 330 K; □, 340 K; ×, 350 K; *, 360 K; ○, 370 K; +, isochore (ϱ = 0.6534 mol·L^{-1}); —, eq 4.

fitting the data given in Table 2 with the following function:

$$Z = 1 + B\varrho + C\varrho^2 + D\varrho^3 \tag{4}$$

where

$$Z = P/(\varrho RT)$$

$$C = c_1 T_r^{-1} + c_2 T_r^{-3} + c_3 T_r^{-5}$$

$$D = d_1 T_r^{-2} + d_2 T_r^{-5.5}$$

B is expressed by eq 3, T is in kelvin, ϱ in moles per liter, P in kilopascals, R is the universal gas constant (8.314 510 7 J·mol^{-1}·K^{-1}), $c_1 = -2.78455 \times 10^{-2}$, $c_2 = 9.30967 \times 10^{-2}$, $c_3 = -2.88435 \times 10^{-2}$, $d_1 = -0.474641 \times 10^{-3}$, and $d_2 = -1.40684 \times 10^{-3}$. This equation is effective for the range of temperatures from 320 to 380 K, for pressures up to 4.6 MPa, and for densities up to 3.5 mol·L^{-1}.

The pressure deviations of the present data from eq 4 are shown in Figure 6. Excluding several points in the higher density region, eq 4 represents the data given in Table 2 within ±0.2%. It should be noted that, as shown in Figure 6, the isochoric data (symbol +) do not show any significant difference from those measured along isotherms. It has also been confirmed, therefore, that the present measurements are self-consistent.

Conclusions

We have measured 11 vapor pressures for temperatures from 295 to 342 K and 92 *PVT* data for temperatures from 320 to 380 K at pressures up to 6.0 MPa for R-143a. On the basis of these vapor-pressure measurements, a vapor-pressure correlation has been developed and the critical pressure has been determined as $P_c = (3.776 \pm 0.005)$ MPa. Throughout the present analysis of the Burnett measurements, the second virial coefficients of R-143a have been determined over the measured range of temperatures, and a truncated virial equation of state which is effective for gaseous R-143a has also been developed.

Acknowledgment

We acknowledge Daikin Industries, Osaka, for kindly furnishing the sample of R-143a. We also thank M. Miyamoto, an undergraduate student at Keio University, for his valuable assistance in this work.

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Received for review December 7, 1994. Accepted February 28, 1995.[⊗] The Ministry of Education, Science and Culture, Japan, has partially supported this study as Grant-in-Aid No. 04402025.

JE9402684

[⊗] Abstract published in *Advance ACS Abstracts,* May 1, 1995.