J. Chem. Eng. Data **1995,** *40,* 148−152

Gas-Phase *PVT* Properties and Vapor Pressures of Pentafluoroethane (HFC-125) Determined According to the Burnett Method

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The gaseous compressibility factors of pentafluoroethane (HFC-125) have been measured by a Burnett apparatus in the range of temperatures from 290 to 390 K and pressures up to 3.6 MPa. The vapor pressures in the range of temperatures from 290 K to the critical temperature have also been measured, and a vapor-pressure correlation has been developed. The critical pressure was determined to be 3.6199 ± 0.0018 MPa on the basis of the present measurements. The second virial coefficients have been determined along 11 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 measurements. The experimental uncertainties of temperature, pressure, and density measurements throughout the present study were estimated to be better than ±10 mK, ±0.8 kPa, and ±0.12%, respectively. The purity of the HFC-125 sample used was better than 99.998 mass %.

1. Introduction

Pentafluoroethane (HFC-125, CF_3CHF_2) is considered as an important alternative refrigerant to be used as a constituent in some binary and/or ternary refrigerant mixtures that are promising replacements for HCFC-22. The thermodynamic properties of this refrigerant, therefore, are essential for any application involving binary and/or ternary systems that include HFC-125.

Although several earlier measurements (*1*−*9*) have been reported for both the vapor-pressure and *PVT* properties, some of them are limited not only in some specified range of temperatures and pressures but also in their reported accuracy. In the present study, we have measured the vapor pressures and the compressibility factors of gaseous HFC-125 in the range of temperatures from 290 to 390 K and pressures up to 3.6 MPa by using a Burnett apparatus. We report 12 vapor-pressure data and 93 *PVT* values along 11 isotherms with 11 second virial coefficients. The purity of the HFC-125 sample used was better than 99.998 mass %.

2. Experimental Section

The Burnett apparatus is schematically shown in Figure 1. It consists of a cell system, temperature control and measuring devices, a pressure measuring system, and a vacuum discharge system.

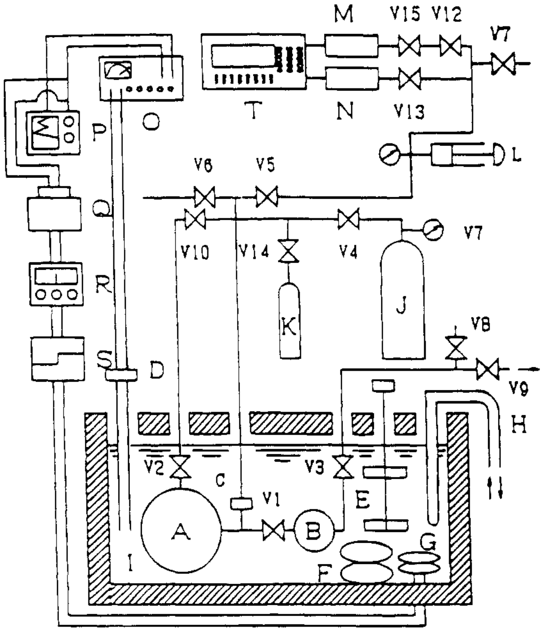

Figure 1. Burnett experimental apparatus: A, sample cell; B, expansion cell; C, differential pressure detector; D, platinum resistance thermometer; E, stirrer; F, main heater; G, subheater; H, cooler; I, constant temperature bath; J, N_2 bottle; K, N_2 gas damper; L, hand piston; M, digiquartz pressure transducer with temperature sensor (0−200 psi); N, digiquartz pressure transducer with temperature sensor (0−1000 psi); O, thermometer bridge; P, pen recorder; Q, voltage/current converter; R, PID controller; S, DC power supply; V1, constant volume valve; V2−V14, valves; V15, adjustable relief valve.

The cell system consists of two cells, a sample cell (A) and an expansion cell (B), and an expansion valve (V1). The two cells are thick-walled spherical vessels made of SUS-304, of about 500 and 250 cm^3 in their respective inner volumes. The expansion valve (V1) is a constant-volume valve by which we can avoid any noxious volume change during valve operation. To establish 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 bath (I) using silicone oil as a heat transfer medium. The temperature was controlled by means of a PID controller and was measured using 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 temperature was then calculated on the basis of the International Temperature Scale of 1990 (ITS-90). The uncertainty of the temperature measurements was estimated to be better than ±10 mK.

The sample pressure was transmitted to an external pressure measuring system through the differential pressure detector (C) by balancing the sample gas pressure with

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0021-9568/95/1740-0148$09.00/0

Table 1. Vapor Pressure P_s of HFC-125

T/K	P_s/MPa	T/K	P_s/MPa
290.00	1.1069	330.00	2.9603
300.00	1.4466	335.00	3.3040
310.00	1.8614	336.00	3.3774
315.00	2.1004	337.00	3.4516
320.00	2.3608	338.00	3.5282
325.00	2.6467	339.00	3.6065

the nitrogen gas pressure in the pressure measuring system. Then 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) for pressures below 1.1 MPa. The experimental uncertainty in the pressure measurements, ±0.8 kPa, consists of that of the differential pressure measurements by the detector, ±0.5 kPa, and that of ±0.3 kPa that includes the uncertainties due to 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. The cell constant, $N = 1.50368 \pm 0.00019$, was determined on the basis of the measurements of gaseous helium whose thermodynamic properties are well established *(10)*. The purity of helium used by Qian et al. *(11)* was higher than 99.9999 mol %.

3. Measured Vapor Pressures and Discussion

By filling the liquid sample into half a volume of the sample cell to get the critical density, we measured vapor pressures of HFC-125. The vapor-pressure values are given in Table 1. A total of 12 vapor-pressure values have been obtained from 290 to 339 K that correspond to pressures from 1.1 to 3.6 MPa. The temperature was controlled to be within ±10 mK at the prescribed temperature with the nominal value by the PID controller.

On the basis of the present vapor-pressure measurements, we have developed a vapor-pressure correlation with the functional form

$$\ln(P_s/P_c) = [-7.5551755(1-\tau) + 1.9454869(1-\tau)^{1.5} - 3.2021138(1-\tau)^{2.5}]/\tau \quad (1)$$

where P_s denotes vapor pressure, P_c denotes the critical pressure, and τ denotes the dimensionless temperature defined by $\tau = T/T_c$.

For the purpose of developing eq 1, we have used a total of 33 data points that consist of 12 data from the present study for temperatures above 290 K and 21 data points from Wilson et al. *(1)* below 288 K but excluding 4 data points reported by them. Those four data are shown by solid pentagonal symbols in Figure 2. These are explicitly greater than other data reported by Wilson et al. for temperatures below 288 K. The least-squares fitting procedure was applied by taking into account the statistical analysis developed by Kubota et al. *(12)*.

The critical pressure, P_c, in eq 1 has been determined to be 3.6199 ± 0.0018 MPa so as to correspond to the critical temperature, $T_c = 339.165 \pm 0.010$ K, which was directly observed by Kuwabara et al. *(13)*. Note that eq 1 is effective for the range of temperatures from 195 K to the critical temperature.

The absolute deviation of all the measured values including the present study and those by Sagawa et al. *(2)*, Murano et al. *(3)*, Wilson et al. *(1)*, Fukushima and Watanabe *(4)*, Monluc et al. *(5)*, Baroncini et al. *(6)*, and Widiatmo et al. *(7)* from eq 1 is shown in Figure 2. The present measurements show a maximum deviation by about 1.2 kPa at 300 K from eq 1, while the data of Wilson et al. *(1)* show maximum deviations of +14 kPa at 335 K and that about −36 kPa at 339.04 K that is omitted from Figure 2. The data reported by Baroncini et al. *(6)* show a maximum deviation of −3.4 kPa at 333.2 K, and the data reported by Sagawa et al. *(2)* show a maximum deviation of 1.5 kPa from eq 1. The data of Widiatmo et al. *(7)* show a maximum deviation of −4.5 kPa from eq 1. As shown in Figure 2, the present vapor-pressure measurements agree very well with another set of data obtained with an isochoric apparatus by Sagawa et al. *(2)* which were reproduced by eq 1 within ±1.5 kPa.

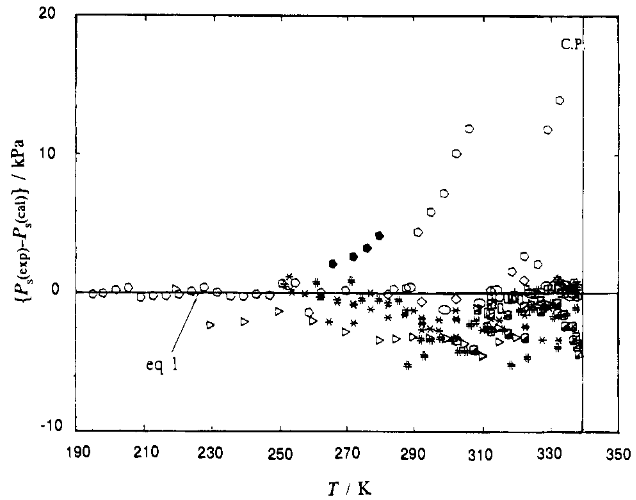

Figure 2. Vapor-pressure deviation from eq 1: ○, this work; ◇, Murano et al.; ∗, Baroncini et al.; open triangle pointing right, Widiatmo et al.; □, Sagawa et al.; ⬠, ⬟, Wilson et al.; ◪, Monluc et al.; #, Fukushima and Watanabe.

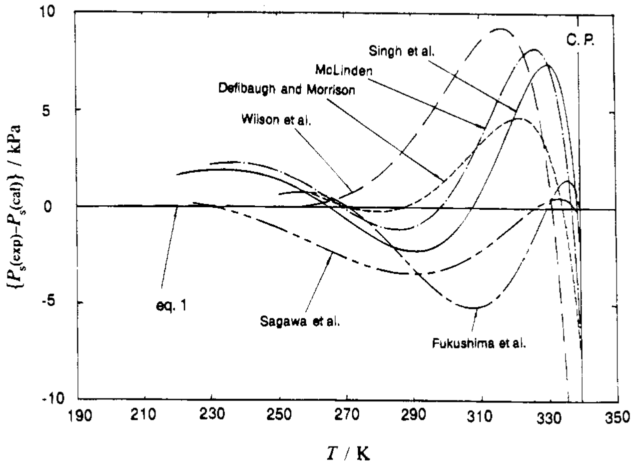

Figure 3. Comparison with several vapor-pressure correlations from eq 1.

Besides these measurements mentioned above, several vapor-pressure correlations have been proposed for HFC-125 by Sagawa et al. *(2)*, Defibaugh and Morrison *(8)*, Wilson et al. *(1)*, Singh et al. *(9)*, Fukushima and Watanabe *(4)*, and McLinden *(14)*. A comparison of these reported vapor-pressure correlations with eq 1 is shown in Figure 3. It should be noted that the correlations by Wilson et al. *(1)*, Singh et al. *(9)*, and McLinden *(14)* showed significant difference at higher temperatures, because they have been developed earlier at the stage when an insufficient number of measurements were available.

4. Experimental *PVT* Results and Discussion

4.1. PVT Properties. A total of 93 compressibility factors for HFC-125 shown in Figure 4 have been measured

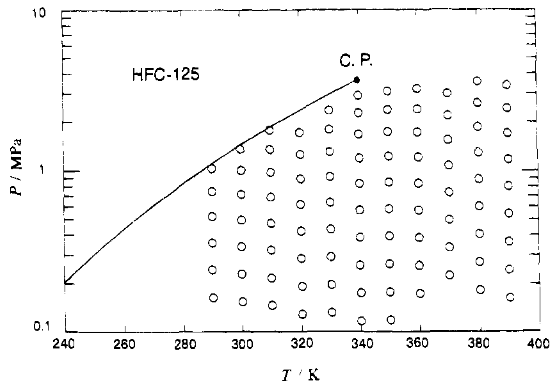

Figure 4. Distribution of measured *PVT* data for HFC-125.

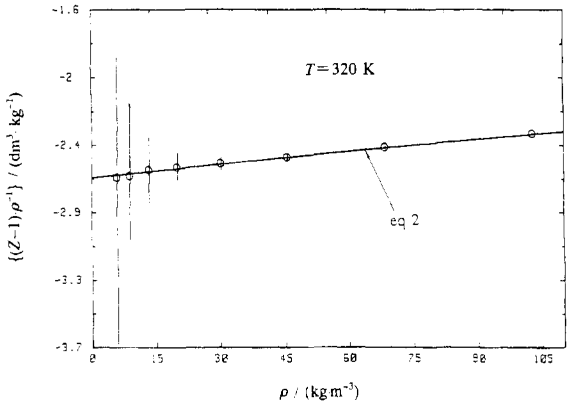

Figure 5. Relationship of $(Z - 1)/\varrho$ vs ϱ for HFC-125.

at temperatures from 290 to 390 K and at pressures from 0.1 to 3.6 MPa. From the present measurements of compressibility factors, the density values or *PVT* properties of HFC-125 have been calculated, and they are given in Table 2.

A following truncated virial expansion expression is applied to represent the present measurements along each isotherm:

$$(Z - 1)/\varrho = B + C\varrho + D\varrho^2 \quad \text{(at constant temperature)} \tag{2}$$

where Z is the compressibility factor and ϱ is the density. When the experimental data can be expressed by the virial equation, eq 2, having second, $B\varrho$, third, $C\varrho^2$, and fourth, $D\varrho^3$, virial terms, a typical example of density dependence of the values $(Z - 1)/\varrho$ along a 320 K isotherm is represented by a curve as shown in Figure 5. The uncertainty of the pressure measurements, ±0.8 kPa, has been added as error bars to each data point in Figure 5. It should be noted that, in Figure 5, the intercept with the ordinate gives the second virial coefficient, B, and the slope of the fitted curve provides the coefficient of the third term, C. The fourth term is then determined as the curvature of the fitted curve. The values B and C thus determined from eq 2 are summarized in Table 3 for respective isotherms. The coefficient of the third term, C, could be regarded as the third virial coefficient with roughly more than 50% uncertainty.

4.2. Second Virial Coefficient. The temperature dependence of the second virial coefficients is represented for HFC-125 by

$$B(\tau) = (b_1 + b_2\tau^{-1} + b_3\tau^{-6})/\varrho_c \tag{3}$$

Table 2. *PVT* Properties of HFC-125

T/K	P/MPa	ϱ/ kg·m^{-3}	Z	T/K	P/MPa	ϱ/ kg·m^{-3}	Z
290.00	1.0312	64.47	0.7962	350.00	3.0966	193.1	0.6614
290.00	0.7432	42.87	0.8629	350.00	2.3693	128.4	0.7610
290.00	0.5198	28.51	0.9074	350.00	1.7287	85.40	0.8348
290.00	0.3571	18.96	0.9374	350.00	1.2219	56.80	0.8873
290.00	0.2426	12.61	0.9577	350.00	0.8458	37.77	0.9235
290.00	0.1636	8.387	0.9709	350.00	0.5776	25.12	0.9483
				350.00	0.3910	16.71	0.9652
300.00	1.3636	87.96	0.7459	350.00	0.2632	11.11	0.9770
300.00	1.0053	58.50	0.8269	350.00	0.1765	7.389	0.9854
300.00	0.7135	38.91	0.8824	350.00	0.1180	4.914	0.9900
300.00	0.4948	25.87	0.9202				
300.00	0.3384	17.21	0.9464	360.00	2.3929	121.7	0.7886
300.00	0.2293	11.44	0.9640	360.00	1.7240	80.92	0.8543
300.00	0.1545	7.610	0.9767	360.00	1.2090	53.82	0.9008
				360.00	0.8326	35.79	0.9328
310.00	1.7850	120.7	0.6887	360.00	0.5669	23.80	0.9550
310.00	1.3557	80.26	0.7866	360.00	0.3829	15.83	0.9699
310.00	0.9798	53.38	0.8548	360.00	0.2571	10.53	0.9795
310.00	0.6873	35.50	0.9016	360.00	0.1722	7.001	0.9863
310.00	0.4733	23.61	0.9335				
310.00	0.3220	15.70	0.9552	370.00	2.9910	153.9	0.7585
310.00	0.2174	10.44	0.9694	370.00	2.1808	102.4	0.8315
310.00	0.1461	6.944	0.9798	370.00	1.5425	68.05	0.8843
				370.00	1.0690	45.26	0.9215
320.00	1.7235	102.8	0.7560	370.00	0.7307	30.10	0.9472
320.00	1.2612	68.40	0.8318	370.00	0.4952	20.02	0.9652
320.00	0.8927	45.49	0.8853	370.00	0.3333	13.31	0.9769
320.00	0.6186	30.25	0.9225	370.00	0.2236	8.853	0.9854
320.00	0.4228	20.12	0.9480				
320.00	0.2863	13.38	0.9652	380.00	3.5531	182.3	0.7404
320.00	0.1926	8.897	0.9764	380.00	2.6073	121.2	0.8170
320.00	0.1291	5.917	0.9842	380.00	1.8541	80.63	0.8735
				380.00	1.2897	53.62	0.9137
330.00	2.8599	229.3	0.5456	380.00	0.8837	35.66	0.9414
330.00	2.3564	152.5	0.6760	380.00	0.5998	23.72	0.9607
330.00	1.7960	101.4	0.7746	380.00	0.4042	15.77	0.9736
330.00	1.3036	67.45	0.8454	380.00	0.2712	10.49	0.9823
330.00	0.9175	44.85	0.8947	380.00	0.1815	6.975	0.9885
330.00	0.6333	29.83	0.9287				
330.00	0.4316	19.84	0.9517	390.00	3.3654	158.6	0.7853
330.00	0.2918	13.19	0.9676	390.00	2.4217	105.5	0.8497
330.00	0.1962	8.774	0.9784	390.00	1.6995	70.16	0.8967
330.00	0.1315	5.835	0.9855	390.00	1.1720	46.66	0.9298
				390.00	0.7984	31.03	0.9524
340.00	2.9083	195.9	0.6300	390.00	0.5398	20.64	0.9682
340.00	2.2678	130.3	0.7387	390.00	0.3630	13.72	0.9791
340.00	1.6728	86.69	0.8193	390.00	0.2432	9.126	0.9865
340.00	1.1902	57.65	0.8765	390.00	0.1625	6.069	0.9912
340.00	0.8272	38.34	0.9160				
340.00	0.5665	25.50	0.9433				
340.00	0.3841	16.96	0.9618				
340.00	0.2587	11.28	0.9742				
340.00	0.1737	7.500	0.9832				
340.00	0.1161	4.988	0.9886				

Table 3. Second Virial Coefficient, *B*, and *C* of Equation 2 Determined along Isotherm for HFC-125

T/K	B/(dm^3·kg^{-1})	C/(dm^6·kg^{-2})
290.00	−3.4072	6.96
300.00	−3.1418	3.48
310.00	−2.8728	3.13
320.00	−2.6441	2.82
330.00	−2.4365	2.18
340.00	−2.2530	1.99
350.00	−2.0953	1.95
360.00	−1.9401	1.87
370.00	−1.8032	1.54
380.00	−1.6723	1.27
390.00	−1.5612	1.23

In eq 3, $\tau = T/T_c$ with T_c as the critical temperature *(13)*. The critical temperature T_c = 339.165 ± 0.010 K and critical density ϱ_c = 568 ± 1 kg·m^{-3} measured by Kuwabara et al. *(13)* were adopted. The numerical constants in eq 3 are b_1 = 1.4142, b_2 = −2.5707, and b_3 = −0.13465.

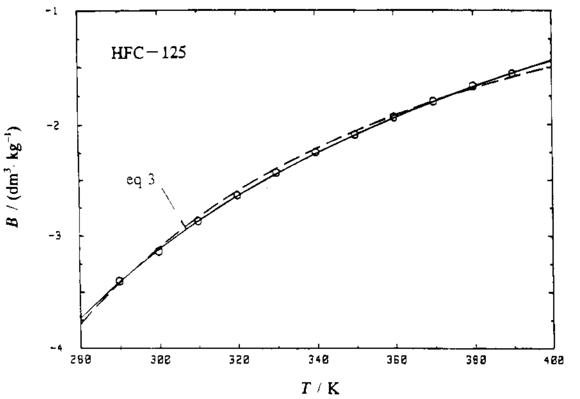

Figure 6. Temperature dependence of the second virial coefficient: —, ○ this work; – –, Hozumi et al.

The temperature dependence of the present second virial coefficients is shown in Figure 6, where the present truncated virial expression, eq 3, and a similar correlation by Hozumi et al. (*15*) are also included. Equation 3 represents the second virial coefficients given in Table 3 within ±0.8%. The correlation developed by Hozumi et al. (*15*) on the basis of our recent speed of sound measurements of HFC-125 also agrees well with the present results within the maximum deviation of 1.8%.

4.3. Virial Equation of State. From the present 93 *PVT* data points in the gaseous phase, a truncated virial equation of state has been developed for HFC-125 with the fixed second virial coefficient expressed by eq 3. The virial-expansion type equation of state thus developed is

$$Z = 1 + B(\tau)\varrho + C(\tau)\varrho^2 + D(\tau)\varrho^3 \qquad (4)$$

where $Z = P/(\varrho RT)$, $R = R_0/M$ with molar mass $M = 120.02$ g·mol^{-1} and gas constant $R_0 = 8.314471$ J·mol^{-1}·K^{-1} (*16*), density (ϱ) is in kg·m^{-3}, and temperature (T) is in K. Equation 4 is effective in the entire region of the present measurements covering temperatures up to 390 K, pressures up to 3.6 MPa, and densities up to 280 kg·m^{-3}, respectively. The function $C(\tau)$ in eq 4 is given by

$$C(\tau) = (c_1\tau^9 + c_2\tau^{-6} + c_3\tau^{-16})/\varrho_c^{\,2} \qquad (5)$$

and the function $D(\tau)$ is

$$D(\tau) = (d_1\tau^{-8} + d_2\tau^{-15})/\varrho_c^{\,3} \qquad (6)$$

where $\tau = T/T_c$, $c_1 = 0.02977$, $c_2 = 0.6605$, $c_3 = -0.02197$, $d_1 = 0.397$, and $d_2 = -0.531$, respectively.

The coefficients of the third term in eq 4, C, given in Table 3, are compared with eq 5 in Figure 7, which clearly shows that eq 5 represents the present results satisfactorily except at a single point at the lowest temperature of 290 K.

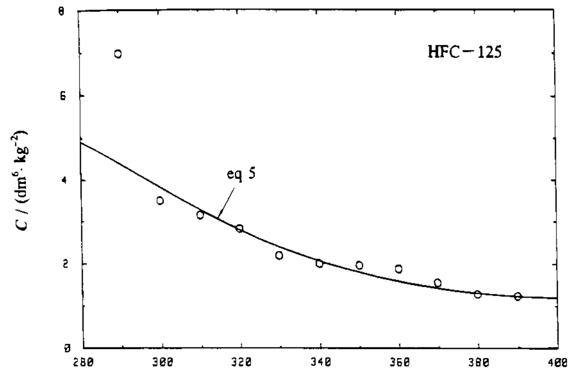

Figure 7. Temperature dependence of C in eqs 2 and 5: ○, this work (eq 2); —, this work (eq 5).

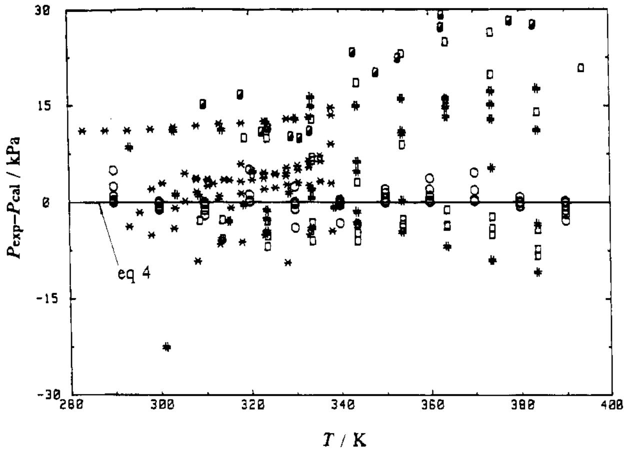

Figure 8. Absolute pressure deviation of *PVT* measurements from eq 4: ○, this work; □, Sagawa et al.; *, Baroncini et al.; #, Fukushima and Watanabe; ◪, Monluc et al.

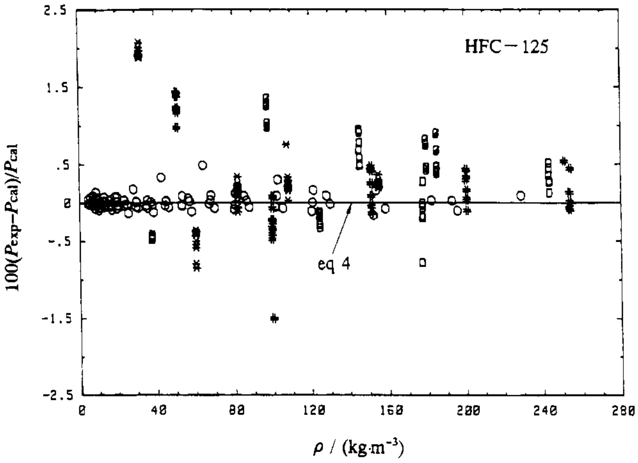

Figure 9. Percent pressure deviations of *PVT* measurements from eq 4: ○, this work; □, Sagawa et al.; *, Baroncini et al.; #, Fukushima and Watanabe; ◪, Monluc et al.

The absolute pressure deviation of *PVT* property measurements including the present results is shown for different temperatures in Figure 8, where the reference standard is eq 4. All of the present data agree with eq 4 within ±5 kPa, and they also agree well with our recent *PVT* measurements using the isochoric apparatus (*2*). In Figure 9, on the other hand, the percentage deviation in pressure of the same sets of data from eq 4 is plotted against density. The agreement between the present Burnett measurements and the isochoric results by Sagawa et al. (*2*) with eq 4 is excellent, while the reported *PVT* property data of Monluc et al. (*5*) and of Fukushima and Watanake (*4*) deviate from eq 4 with the maximum deviation of about 1.5% and those by Baroncini et al. (*6*) show some larger scatter.

5. Conclusions

We have measured 12 vapor pressures at temperatures from 290 to 339 K and 93 compressibility factors at temperatures from 290 to 390 K and at pressures up to 3.6 MPa for HFC-125 using the Burnett apparatus. On the basis of these vapor-pressure measurements, the critical pressure has been determined as P_c = 3.6199 ± 0.0018 MPa and a vapor-pressure correlation has been developed. The present vapor-pressure data are represented by the developed vapor-pressure correlation within ±0.08%.

Throughout the present analysis of Burnett measurements, the second virial coefficients of HFC-125 have been determined over the measured range of temperatures. The truncated virial equation of state which is effective for the gaseous HFC-125 has also been developed, and a comparison of available *PVT* property data has been performed on the basis of the simplified equation of state developed.

Acknowledgment

We acknowledge Atsuo Nishimura, Showa Denko Co., Ltd., Zhen-Yi Qian, a former Ph.D. student, and Chen-Bin Dong, a graduate student, for their valuable assistance. We are indebted to the National Research Laboratory of Metrology, Tsukuba, for the calibration of the platinum resistance thermometer. We are also indebted to Asahi Glass Co., Ltd., Tokyo, for furnishing the sample.

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Received for review April 18, 1994. Accepted August 17, 1994.[⊗] This work was financially supported in part by Grant-in-Aid for Scientific Research 04402025 from the Ministry of Education, Science and Culture, Japan.

JE940070J

[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1994.