J. Chem. Eng. Data **1996,** *41,* 1401−1408

Gas Phase *PVT* Properties for the Difluoromethane + Pentafluoroethane (R-32 + 125) System

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We present new *PVT* measurements in the gas phase for difluoromethane (R-32) + pentafluoroethane (R-125) mixtures at 0.5001 (30.24 mass %) and 0.6977 (50.01 mass %) mole fractions of difluoromethane (R-32). The measurements were performed with a Burnett apparatus, and the expanded uncertainties of the measurements with a level of confidence of approximately 99% were estimated to be ±0.8 kPa for pressure, ±8 mK for temperature, ±0.15% for density, and ±0.1 mol % for composition. The *PVT* properties of pure R-32 and R-125, which were obtained from the reanalysis of earlier Burnett measurements for R-32 and R-125 at our laboratory, are also presented in this paper. A virial-type equation of state for the R-32 + 125 system has been developed on the basis of the present measurements and other experimental data; this equation reproduces the experimental data in the gas phase within ±0.3% in pressure.

Introduction

A near-azeotropic mixture of difluoromethane (R-32) and pentafluoroethane (R-125) is considered to be a very promising alternative to the refrigerant chlorodifluoromethane (R-22) for high-capacity air-conditioning and heat pump systems. Reliable information about the thermodynamic properties is required for the design of these equipment. In this paper, we present new *PVT* measurements in the gas phase and a virial-type equation of state developed for the binary R-32 + 125 system.

Experimental Section

The Burnett−isochoric coupling method was used for the present measurements. The Burnett apparatus has been used in the last several years to measure the *PVT* properties of pure alternative refrigerants such as difluoromethane (R-32) (Qian et al., 1993), pentafluoroethane (R-125) (Ye et al., 1995), 1,1,1-trifluoroethane (R-143a) (Zhang et al., 1995a), and 1,1,1,2,3,3-hexafluoropropane (R-236ea) (Zhang et al., 1996), and it was described in detail in those papers. The Burnett apparatus was applied for the first time to measure the thermodynamic properties of refrigerant mixtures at our laboratory. The Burnett apparatus used in the present measurements of mixtures is schematically shown in Figure 1. The mixture sample filling system, which consists of a variable-volume vessel (W), a pressure reducing and control valve (V17), and a high-pressure nitrogen gas bottle (K), was newly added to the present apparatus.

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. Since the valves (V2 and V3) and the constant-volume valve (V1) connected to the sample cell (A) and the expansion cell (B) were changed before starting the mixture measurements, the cell constant was recalibrated. Through two series of measurements at 380 K using gaseous helium whose thermodynamic properties are well established (*International Thermodynamic Tables of the Fluid State-Helium*, 1977), the cell constant, $N = (1.503\,00 \pm 0.000\,10)$, was determined.

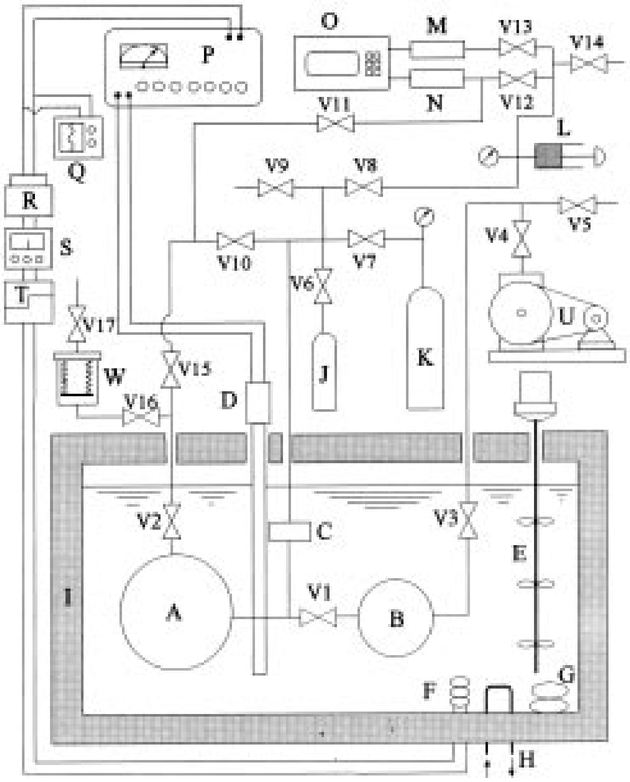

Figure 1. Burnett experimental apparatus: (A) sample cell; (B) expansion cell; (C) differential pressure detector; (D) platinum resistance thermometer; (E) stirrer; (F) subheater; (G) main heater; (H) cooler; (I) constant temperature bath; (J) N_2 gas damper; (K) N_2 bottle; (L) hand piston; (M, N) quartz pressure transducers with temperature sensor; (O) digital pressure gauge; (P) thermometer bridge; (Q) pen recorder; (R) voltage/current converter; (S) PID controller; (T) dc power supply; (U) vacuum pump; (V1) constant volume valve; (V17) pressure reducing and control valve; (V2−V16) valves; (W) variable-volume vessel.

The expanded uncertainty of the temperature measurements with a level of confidence of approximately 99% 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

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S0021-9568(96)00069-6 CCC: $12.00

temperature fluctuation of the thermostated bath. The temperature was then calculated on the basis of the International Temperature Scale of 1990 (ITS-90). The experimental uncertainty in the pressure measurements was estimated to be ±8 kPa, which consists of the reproducibility of the differential pressure measurements, ±0.6 kPa, and the accuracy of the pressure gauge, ±0.2 kPa. The uncertainty of the density values was estimated to be ±0.15%.

Crucial steps in the experimental procedures involve the preparation of the mixture samples and the filling of the sample cell while minimizing changes in the composition. Particularly, since the sample cell is difficult to disassemble and the cell constant may change due to dismantling and reassembling, we had to introduce the prepared mixture sample into the sample cell without dismantling the cell system. This was successfully performed by means of a variable-volume vessel.

For preparation of the mixture sample at a known composition, two additional cylindrical vessels were used, one for each of the components. The two vessels were filled with a known component mass of each of the components using a precision chemical balance (Chyo: Model C_2-3000) with an uncertainty of ±2 mg and total mass of 400 g. To mix the component fluids, the two vessels filled with the respective components were connected with the variable-volume vessel containing a metallic bellows made of Inconel 718. After the variable-volume vessel had been evacuated to around 2 mPa, the component fluids were transferred successively into the variable-volume vessel by cooling it with liquefied nitrogen. Since the total mass of the mixture was about 400 g, the composition uncertainty of the sample contained in the variable-volume vessel was estimated to be ±0.01%.

While the sample cell of the Burnett apparatus was filled with the mixture sample, the sample was compressed and maintained at a liquid state. The mass introduced into the sample cell in a single charge was controlled to about 1 g when filling the sample cell. The final composition was confirmed by gas chromatographic analysis of the mixture sampled after the Burnett expansion process. Considering all the possible effects on the composition determination, the expanded uncertainty of the sample composition used in the present measurements was estimated to be ±0.1 mol % with a level of confidence of 99%.

According to the analysis performed by the chemical manufacturer, the purity of both the R-32 and R-125 samples used to blend the R-32 + 125 mixtures was 99.99 mol %.

Data-Processing

The observed information for a series of expansions with the Burnett apparatus is a pressure, P_j, with a corresponding expansion number, j, at a constant temperature, T. Then the successively-measured pressures for each series of isothermal expansions are reduced to compressibility factors and virial coefficients through data-processing. However, owing to the effects of the experimental uncertainties and/or possible adsorption, the plot of P_j/P_{j-1} vs P_j usually could not be extrapolated to the cell constant value at zero pressure. Deviations like that would have considerable effect on the determination of compressibility factors and virial coefficients.

During the analysis of the Burnett measurements for R-143a (Zhang et al., 1995a), we found that the compressibility factors determined by the conventional data analysis method depended on the weighting factor for each P_j/P_{j-1} value and the number of terms of the fitting polynomial. For this reason, the second and third virial coefficient values determined along an isotherm would vary up to 10%, if a different weighting factor and different number of terms of the fitting polynomial were adopted. To obtain more accurate compressibility factors and virial coefficients from the Burnett measurements, we developed a new data-processing procedure which is different from the conventional method in selecting weighting factors and number of terms of the fitting polynomial. This is principally done by selecting an appropriate weighting factor for each P_j/P_{j-1} value according to its uncertainty and the optimal number of terms of the fitting polynomial so that the fitted P_j/P_{j-1} function of P_j could be extrapolated to the cell constant value at zero pressure. This approach is rational in principle and much less arbitrary to analyze the raw data than the conventional method. Through analyzing the Burnett measurements for several hydrofluorocarbons (Zhang et al., 1995b), the results indicated that the developed data-processing procedure offers improvements in determining second virial coefficients, and this means that the accuracy of the compressibility factors, namely, the *PVT* values, particularly those at lower densities, have been improved. Other examples applied with this method include the analysis of the Burnett measurements for 1,1,1-trifluoroethane (R-143a) (Zhang et al., 1995a) and 1,1,1,2,3,3-hexafluoropropane (R-236ea) (Zhang et al., 1996). According to a recent report on thermodynamic properties of seven gaseous halogenated hydrocarbons from acoustic measurements by Gillis (1996), the agreement between the second virial coefficients derived from his acoustic measurements and those determined from our Burnett measurements for both R-143a and R-236ea is within ±1.0%.

It is needless to emphasize that reliable and consistent thermodynamic properties of pure components are essential to model the mixtures. For the purpose of providing more reliable *PVT* properties of pure R-32 and R-125, whose Burnett measurements were performed by Qian et al. (1993) and Ye et al. (1995), their raw data were reanalyzed using the present data-processing procedure. The maximum difference between the redetermined second virial coefficients and those determined using the conventional method (Qian et al., 1993; Ye et al., 1995) is about 3−5%, while the redetermined compressibility factors have changed slightly (maximum 0.13%).

We have applied the developed data-processing procedure to analyze the present Burnett measurements at 380 K for the R-32 + 125 mixtures.

Results

The data distributions of the measurements of the R-32 + 125 mixtures at 0.5001 (30.24 mass %) and 0.6977 (50.01 mass %) mole fractions of R-32 are shown in Figure 2. The Burnett expansion was only done at 380 K and the values at other temperatures were obtained by combining those measurements with the isochoric measurements. By this procedure, the *PVT* properties were able to be obtained over a wide range in the gaseous phase with a single filling. As shown in Figure 2, 61 and 63 *PVT* measurements were made at 0.5001 and 0.6977 mole fractions of R-32, respectively. The experimental values are given in Table 1.

The redetermined experimental *PVT* values for pure R-32 and R-125 are also plotted in Figure 2 and given in Table 1, which were obtained by analyzing the Burnett measurements for R-32 (99.98 mass %, Qian et al., 1993) and R-125 (99.998 mass %, Ye et al., 1995) using the data-processing procedure mentioned above. The data for the pure components along with the present measurements for the mixtures were used to develop a virial-type equation

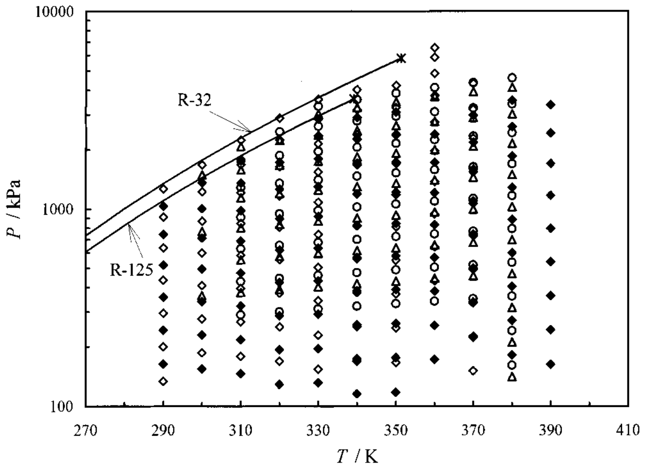

Figure 2. Distribution of the experimental *PVT* data for the R-32 + 125 system: (◇) R-32; ◆, R-125; (△) 0.5001 mole fraction of R-32; (○) 0.6977 mole fraction of R-32; (*) critical point of R-32 or R-125.

of state for the R-32 + 125 system described in the next section.

Virial-Type Equation of State

In order to facilitate calculation of the thermodynamic properties, we have developed a virial-type equation of state for the R-32 + 125 system. This was done by fitting the data given in Table 1, together with experimental data reported by Sato et al. (1996) as well as those by Kiyoura et al. (1996), with the following functional form:

$$\begin{aligned} Z &= P/(\rho RT) \\ &= 1 + B\rho + C\rho^2 + D\rho^3 \end{aligned} \tag{1}$$

and

$$B = b_1 + b_2 T_r^{-1} + b_3 \exp(T_r^{-1}) \tag{2}$$

$$C = c_1 + c_2 T_r^{-3} + c_3 T_r^{-6} \tag{3}$$

$$D = d_1 T_r^{-3} \tag{4}$$

where Z, P, T, and ρ denote the compressibility factor, pressure, temperature and molar density, respectively; B, C, and D are the second, third, and fourth virial coefficients, respectively; R is the universal gas constant; and T_r is T/T_c, the reduced temperature. For the pseudocritical temperature T_c of the R-32 + 125 system, since it is just a parameter in the present equation, the simple expression given below was used:

$$T_c = \sum_{i=1}^{2} x_i T_{c,i} \tag{5}$$

where x_i denotes the mole fraction of component i in the mixture, $T_{c,i}$ denotes the critical temperature of component i, and the subscript $i = 1$ is for the pure R-32; $i = 2$ for the pure R-125 (Kuwabara et al., 1995). The coefficients in eqs 2−4 are calculated using the following mixing rules:

$$b_1 = \sum_{i=1}^{2} x_i b_{1,i} \tag{6}$$

$$b_n = \sum_{i=1}^{2}\sum_{j=1}^{2} x_i x_j b_{n,ij} \qquad \text{for } n = 2, 3 \tag{7}$$

$$c_1 = \sum_{i=1}^{2} x_i c_{1,i} \tag{8}$$

$$c_n = \sum_{i=1}^{2}\sum_{j=1}^{2}\sum_{k=1}^{2} x_i x_j x_k c_{n,ijk} \qquad \text{for } n = 2, 3 \tag{9}$$

$$d_1 = \sum_{i=1}^{2} x_i d_{1,i} \tag{10}$$

where

$$b_{n,i} = b_{n,ii} \qquad \text{for } n = 2, 3$$

$$c_{n,i} = c_{n,ii} = c_{n,iii} \qquad \text{for } n = 2, 3$$

and $b_{n,i}$ (n = 1−3), $c_{n,i}$ (n = 1−3), and $d_{n,i}$ (n = 1) are the numerical constants in the virial equation for the pure component i, and the other numerical constants in eqs 7 and 9 were obtained by fitting the experimental *PVT* data for the mixtures with eqs 1−10. The numerical constants in eqs 5 through 10 are listed in Table 2. The total data points applied to develop the present equation were around 550.

Discussion

The deviations from eq 1 of the present measurements at 0.5001 (30.24 mass %) and 0.6977 (50.01 mass %) mole fractions of R-32 given in Table 1 are illustrated in Figure 3. The deviations of the experimental values by Sato et al. (1996) and of those by Kiyoura et al. (1996) from eq 1 are also plotted in Figure 3 which were measured using a constant-volume apparatus at 0.3671 (20.09 mass %), 0.6058 (39.98 mass %), 0.6978 (50.02 mass %), 0.7758 (60.00 mass %), and 0.9022 (79.99 mass %) mole fractions of R-32, respectively. The data by Sato et al. (1996) for input are in the range of temperatures from 320 K to 440 K and at pressures to 5.3 MPa, while those of Kiyoura et al. (1996) are in the range of temperatures from 330 K to 440 K and at pressures to 5.2 MPa. It is apparent from Figure 3 that eq 1 represents the experimental values measured by the two different methods within ±0.3% in pressure. As a direct comparison of the present measurements with those measured using a constant-volume method by Sato et al. (1996), the deviations of the two independent measurements in the same density range and at nearly the same composition (0.6977 and 0.6978 mole fractions of R-32) from eq 1 are shown in Figure 4. They are in agreement within ±0.2%. It can be concluded that no significant discord exists between the two different measurements in terms of the stated uncertainties.

In Figure 5, the reanalyzed data for R-32 are compared with eq 1 and other experimental data (not used as input data) in the range where eq 1 is effective. The deviations of the values by the present study from eq 1 lie between −0.1% and +0.15%; those measured using a Burnett−isochoric apparatus by Defibaugh et al. (1994) between −0.3% and +0.2%; those measured using a constant-volume apparatus by Sato et al. (1994) between −0.1% and +0.3%. Note that the Burnett measurements at 373.124 K by Defibaugh et al. are in good agreement with the present data within ±0.1%. In Figure 6, the reanalyzed data for R-125 as well as other experimental data (not used as input data) from the literature are also compared with

Table 1. Experimental *PVT* Properties of Difluoromethane (1) + Pentafluoroethane (2)

T/K	P/kPa	ρ/mol·dm^{-3}	Z	$x_1{}^a$
380.000	4131.0	1.7593	0.7432	0.5001
380.000	3030.1	1.1706	0.8193	0.5001
380.000	2153.3	0.7788	0.8751	0.5001
380.000	1497.7	0.5182	0.9148	0.5001
380.000	1026.6	0.3448	0.9424	0.5001
380.000	696.7	0.2294	0.9613	0.5001
380.000	469.7	0.1526	0.9740	0.5001
380.000	315.3	0.1015	0.9826	0.5001
380.000	211.0	0.0676	0.9884	0.5001
380.000	140.9	0.0450	0.9923	0.5001
380.000	94.0	0.0299	0.9949	0.5001
370.000	3918.9	1.7602	0.7237	0.5001
370.000	2903.4	1.1711	0.8059	0.5001
370.000	2076.4	0.7792	0.8662	0.5001
370.000	1449.6	0.5184	0.9089	0.5001
370.000	996.3	0.3449	0.9388	0.5001
370.000	676.6	0.2295	0.9582	0.5001
370.000	457.0	0.1527	0.9728	0.5001
360.000	3705.3	1.7610	0.7029	0.5001
360.000	2774.1	1.1717	0.7910	0.5001
360.000	1997.3	0.7796	0.8559	0.5001
360.000	1400.2	0.5187	0.9018	0.5001
360.000	964.3	0.3451	0.9335	0.5001
360.000	656.1	0.2296	0.9546	0.5001
360.000	443.8	0.1528	0.9705	0.5001
350.000	3485.3	1.7619	0.6798	0.5001
350.000	2640.8	1.1723	0.7741	0.5001
350.000	1917.0	0.7800	0.8446	0.5001
350.000	1349.5	0.5190	0.8936	0.5001
350.000	932.5	0.3453	0.9281	0.5001
350.000	635.7	0.2297	0.9509	0.5001
350.000	430.6	0.1528	0.9680	0.5001
340.000	3258.5	1.7627	0.6539	0.5001
340.000	2506.9	1.1728	0.7561	0.5001
340.000	1835.4	0.7803	0.8320	0.5001
340.000	1299.9	0.5192	0.8856	0.5001
340.000	900.2	0.3454	0.9218	0.5001
340.000	615.6	0.2298	0.9475	0.5001
340.000	417.2	0.1529	0.9651	0.5001
330.000	3025.8	1.7636	0.6253	0.5001
330.000	2369.8	1.1734	0.7361	0.5001
330.000	1752.5	0.7807	0.8181	0.5001
330.000	1248.7	0.5194	0.8761	0.5001
330.000	868.9	0.3456	0.9163	0.5001
330.000	595.3	0.2299	0.9435	0.5001
330.000	403.8	0.1530	0.9619	0.5001
320.000	2227.2	1.1740	0.7131	0.5001
320.000	1667.5	0.7811	0.8024	0.5001
320.000	1196.8	0.5197	0.8655	0.5001
320.000	835.9	0.3458	0.9086	0.5001
320.000	574.7	0.2301	0.9389	0.5001
320.000	390.6	0.1531	0.9590	0.5001
310.000	2079.9	1.1745	0.6871	0.5001
310.000	1580.4	0.7815	0.7846	0.5001
310.000	1142.3	0.5199	0.8524	0.5001
310.000	803.2	0.3459	0.9008	0.5001
310.000	553.7	0.2302	0.9333	0.5001
310.000	377.0	0.1531	0.9552	0.5001
300.000	1490.2	0.7818	0.7642	0.5001
300.000	769.5	0.3461	0.8913	0.5001
300.000	363.5	0.1532	0.9511	0.5001
380.000	4600.4	2.0134	0.7232	0.6977
380.000	3401.8	1.3396	0.8037	0.6977
380.000	2429.0	0.8913	0.8625	0.6977
380.000	1697.0	0.5930	0.9057	0.6977
380.000	1167.0	0.3946	0.9361	0.6977
380.000	793.8	0.2625	0.9570	0.6977
380.000	536.0	0.1747	0.9712	0.6977
380.000	360.1	0.1162	0.9808	0.6977
380.000	241.2	0.0773	0.9872	0.6977
380.000	161.2	0.0514	0.9915	0.6977
370.000	4355.8	2.0144	0.7029	0.6977
370.000	3253.0	1.3403	0.7889	0.6977
370.000	2338.8	0.8918	0.8525	0.6977
370.000	1638.2	0.5933	0.8975	0.6977
370.000	1131.1	0.3948	0.9314	0.6977
370.000	770.3	0.2627	0.9533	0.6977
370.000	520.6	0.1748	0.9684	0.6977
370.000	350.0	0.1163	0.9786	0.6977
360.000	4108.3	2.0154	0.6810	0.6977
360.000	3102.7	1.3410	0.7730	0.6977
360.000	2246.9	0.8922	0.8413	0.6977
360.000	1581.3	0.5936	0.8900	0.6977
360.000	1094.8	0.3950	0.9260	0.6977
360.000	747.1	0.2628	0.9499	0.6977
360.000	505.6	0.1748	0.9661	0.6977
360.000	340.4	0.1163	0.9775	0.6977
350.000	3851.5	2.0164	0.6564	0.6977
350.000	2949.5	1.3416	0.7555	0.6977
350.000	2154.9	0.8926	0.8296	0.6977
350.000	1526.4	0.5939	0.8831	0.6977
350.000	1058.7	0.3952	0.9207	0.6977
350.000	723.9	0.2629	0.9461	0.6977
350.000	490.5	0.1749	0.9636	0.6977
350.000	330.5	0.1164	0.9759	0.6977
340.000	3584.2	2.0174	0.6285	0.6977
340.000	2792.7	1.3423	0.7360	0.6977
340.000	2060.2	0.8931	0.8160	0.6977
340.000	1468.1	0.5942	0.8740	0.6977
340.000	1021.8	0.3954	0.9143	0.6977
340.000	699.5	0.2630	0.9407	0.6977
340.000	475.3	0.1750	0.9606	0.6977
340.000	320.6	0.1164	0.9739	0.6977
330.000	3311.8	2.0183	0.5980	0.6977
330.000	2631.8	1.3429	0.7143	0.6977
330.000	1963.1	0.8935	0.8008	0.6977
330.000	1408.7	0.5945	0.8636	0.6977
330.000	984.5	0.3955	0.9072	0.6977
330.000	676.6	0.2632	0.9371	0.6977
330.000	460.0	0.1751	0.9574	0.6977
330.000	310.7	0.1165	0.9720	0.6977
320.000	2463.7	1.3435	0.6892	0.6977
320.000	1864.9	0.8939	0.7841	0.6977
320.000	1348.2	0.5948	0.8519	0.6977
320.000	946.7	0.3957	0.8991	0.6977
320.000	652.7	0.2633	0.9317	0.6977
320.000	444.5	0.1752	0.9538	0.6977
320.000	300.6	0.1166	0.9693	0.6977
310.000	1763.8	0.8943	0.7652	0.6977
310.000	1286.6	0.5950	0.8389	0.6977
310.000	906.5	0.3959	0.8884	0.6977
310.000	628.5	0.2634	0.9257	0.6977
310.000	429.0	0.1753	0.9497	0.6977
310.000	290.7	0.1166	0.9672	0.6977
290.000	1263.9	0.6555	0.7997	1.0000
290.000	909.6	0.4359	0.8654	1.0000
290.000	634.4	0.2899	0.9076	1.0000
290.000	436.0	0.1928	0.9379	1.0000
290.000	296.4	0.1282	0.9586	1.0000
290.000	199.9	0.0853	0.9723	1.0000
290.000	134.2	0.0567	0.9815	1.0000
300.000	1675.7	0.8837	0.7602	1.0000
300.000	1225.3	0.5877	0.8358	1.0000
300.000	866.5	0.3909	0.8888	1.0000
300.000	599.8	0.2599	0.9251	1.0000
300.000	409.6	0.1729	0.9500	1.0000
300.000	277.1	0.1150	0.9663	1.0000
300.000	186.5	0.0765	0.9778	1.0000
310.000	2235.9	1.2323	0.7039	1.0000
310.000	1679.2	0.8195	0.7949	1.0000
310.000	1207.8	0.5450	0.8598	1.0000
310.000	845.4	0.3625	0.9049	1.0000
310.000	581.6	0.2411	0.9361	1.0000
310.000	395.5	0.1603	0.9572	1.0000
310.000	267.0	0.1066	0.9717	1.0000
310.000	179.3	0.0709	0.9810	1.0000
320.000	2887.3	1.6878	0.6430	1.0000
320.000	2236.9	1.1225	0.7490	1.0000
320.000	1642.0	0.7465	0.8267	1.0000

Table 1 (Continued)

T/K	P/kPa	ρ/mol·dm^{-3}	Z	x_1[a]	T/K	P/kPa	ρ/mol·dm^{-3}	Z	x_1[a]
320.000	1164.7	0.4965	0.8817	1.0000	310.000	217.4	0.0869	0.9707	0.0000
320.000	808.3	0.3302	0.9202	1.0000	310.000	146.0	0.0578	0.9803	0.0000
320.000	553.0	0.2196	0.9466	1.0000	320.000	1723.6	0.8563	0.7565	0.0000
320.000	374.7	0.1460	0.9644	1.0000	320.000	1261.2	0.5695	0.8323	0.0000
320.000	252.3	0.0971	0.9765	1.0000	320.000	892.7	0.3787	0.8859	0.0000
320.000	169.1	0.0646	0.9841	1.0000	320.000	618.7	0.2519	0.9232	0.0000
330.000	3590.3	2.2318	0.5863	1.0000	320.000	422.8	0.1675	0.9487	0.0000
330.000	2867.1	1.4842	0.7040	1.0000	320.000	286.2	0.1114	0.9656	0.0000
330.000	2148.3	0.9871	0.7932	1.0000	320.000	192.6	0.0741	0.9771	0.0000
330.000	1545.2	0.6565	0.8579	1.0000	320.000	129.1	0.0493	0.9849	0.0000
330.000	1082.1	0.4366	0.9034	1.0000	330.000	2859.9	1.9102	0.5457	0.0000
330.000	744.7	0.2903	0.9348	1.0000	330.000	2356.4	1.2704	0.6760	0.0000
330.000	506.8	0.1931	0.9566	1.0000	330.000	1796.0	0.8449	0.7748	0.0000
330.000	342.2	0.1284	0.9713	1.0000	330.000	1303.6	0.5619	0.8456	0.0000
330.000	229.8	0.0854	0.9807	1.0000	330.000	917.5	0.3737	0.8949	0.0000
330.000	153.9	0.0568	0.9875	1.0000	330.000	633.3	0.2485	0.9288	0.0000
340.000	4022.2	2.3833	0.5970	1.0000	330.000	431.8	0.1653	0.9522	0.0000
340.000	3185.0	1.5850	0.7108	1.0000	330.000	291.9	0.1099	0.9680	0.0000
340.000	2377.6	1.0541	0.7979	1.0000	330.000	196.3	0.0731	0.9788	0.0000
340.000	1706.5	0.7010	0.8611	1.0000	330.000	131.5	0.0486	0.9860	0.0000
340.000	1194.0	0.4662	0.9059	1.0000	340.000	2908.3	1.6317	0.6305	0.0000
340.000	821.3	0.3100	0.9370	1.0000	340.000	2267.8	1.0852	0.7392	0.0000
340.000	558.1	0.2062	0.9575	1.0000	340.000	1672.8	0.7217	0.8199	0.0000
340.000	376.6	0.1371	0.9715	1.0000	340.000	1190.2	0.4800	0.8772	0.0000
340.000	252.9	0.0912	0.9811	1.0000	340.000	827.2	0.3192	0.9167	0.0000
340.000	169.3	0.0606	0.9875	1.0000	340.000	566.5	0.2123	0.9440	0.0000
350.000	4220.2	2.2716	0.6384	1.0000	340.000	384.2	0.1412	0.9627	0.0000
350.000	3258.8	1.5108	0.7412	1.0000	340.000	258.8	0.0939	0.9751	0.0000
350.000	2395.4	1.0047	0.8193	1.0000	340.000	173.6	0.0624	0.9835	0.0000
350.000	1702.9	0.6682	0.8758	1.0000	340.000	116.1	0.0415	0.9890	0.0000
350.000	1184.0	0.4444	0.9156	1.0000	350.000	3096.6	1.6071	0.6621	0.0000
350.000	811.2	0.2955	0.9432	1.0000	350.000	2369.3	1.0688	0.7618	0.0000
350.000	550.2	0.1965	0.9620	1.0000	350.000	1728.7	0.7108	0.8357	0.0000
350.000	370.7	0.1307	0.9746	1.0000	350.000	1221.9	0.4727	0.8882	0.0000
350.000	248.7	0.0869	0.9832	1.0000	350.000	845.9	0.3144	0.9246	0.0000
350.000	166.3	0.0578	0.9887	1.0000	350.000	577.6	0.2091	0.9494	0.0000
360.000	6537.2	5.8211	0.3752	1.0000	350.000	391.0	0.1390	0.9663	0.0000
360.000	5858.1	3.8713	0.5055	1.0000	350.000	263.0	0.0925	0.9774	0.0000
360.000	4849.5	2.5747	0.6293	1.0000	350.000	176.3	0.0615	0.9851	0.0000
360.000	3757.5	1.7123	0.7331	1.0000	350.000	117.8	0.0409	0.9899	0.0000
360.000	2770.9	1.1388	0.8129	1.0000	360.000	2393.0	1.0133	0.7890	0.0000
360.000	1975.5	0.7573	0.8715	1.0000	360.000	1724.1	0.6739	0.8548	0.0000
360.000	1376.0	0.5037	0.9127	1.0000	360.000	1208.9	0.4482	0.9012	0.0000
360.000	943.6	0.3350	0.9411	1.0000	360.000	832.7	0.2980	0.9334	0.0000
360.000	640.5	0.2228	0.9606	1.0000	360.000	566.8	0.1982	0.9553	0.0000
360.000	431.7	0.1481	0.9736	1.0000	360.000	382.8	0.1318	0.9702	0.0000
370.000	4319.3	1.9437	0.7224	1.0000	360.000	257.2	0.0877	0.9802	0.0000
370.000	3196.3	1.2927	0.8038	1.0000	360.000	172.2	0.0583	0.9868	0.0000
370.000	2285.1	0.8597	0.8640	1.0000	370.000	2991.0	1.2818	0.7585	0.0000
370.000	1595.5	0.5717	0.9071	1.0000	370.000	2180.8	0.8525	0.8316	0.0000
370.000	1096.4	0.3802	0.9373	1.0000	370.000	1542.5	0.5669	0.8844	0.0000
370.000	745.2	0.2529	0.9580	1.0000	370.000	1069.0	0.3770	0.9216	0.0000
370.000	502.8	0.1682	0.9719	1.0000	370.000	730.8	0.2507	0.9474	0.0000
370.000	337.6	0.1118	0.9813	1.0000	370.000	494.9	0.1668	0.9647	0.0000
370.000	225.9	0.0744	0.9874	1.0000	370.000	333.2	0.1109	0.9767	0.0000
370.000	150.9	0.0495	0.9918	1.0000	370.000	223.3	0.0738	0.9842	0.0000
290.000	1031.2	0.5364	0.7972	0.0000	380.000	3553.1	1.5179	0.7409	0.0000
290.000	743.2	0.3568	0.8640	0.0000	380.000	2607.3	1.0095	0.8175	0.0000
290.000	519.8	0.2373	0.9086	0.0000	380.000	1854.1	0.6714	0.8741	0.0000
290.000	357.1	0.1578	0.9386	0.0000	380.000	1289.7	0.4465	0.9142	0.0000
290.000	242.6	0.1049	0.9589	0.0000	380.000	883.8	0.2969	0.9420	0.0000
290.000	163.6	0.0698	0.9722	0.0000	380.000	599.6	0.1975	0.9610	0.0000
300.000	1363.6	0.7322	0.7466	0.0000	380.000	404.1	0.1313	0.9739	0.0000
300.000	1005.3	0.4870	0.8277	0.0000	380.000	271.1	0.0873	0.9824	0.0000
300.000	713.5	0.3238	0.8833	0.0000	380.000	181.4	0.0581	0.9885	0.0000
300.000	494.8	0.2154	0.9211	0.0000	390.000	3365.4	1.3210	0.7857	0.0000
300.000	338.4	0.1432	0.9472	0.0000	390.000	2421.7	0.8785	0.8501	0.0000
300.000	229.3	0.0952	0.9651	0.0000	390.000	1699.5	0.5843	0.8970	0.0000
300.000	154.4	0.0633	0.9772	0.0000	390.000	1172.0	0.3886	0.9302	0.0000
310.000	1785.0	1.0043	0.6895	0.0000	390.000	798.5	0.2584	0.9529	0.0000
310.000	1355.7	0.6679	0.7875	0.0000	390.000	539.7	0.1719	0.9685	0.0000
310.000	979.8	0.4442	0.8558	0.0000	390.000	362.8	0.1143	0.9790	0.0000
310.000	687.3	0.2954	0.9027	0.0000	390.000	243.0	0.0760	0.9860	0.0000
310.000	473.3	0.1965	0.9347	0.0000	390.000	162.4	0.0505	0.9908	0.0000
310.000	322.0	0.1307	0.9562	0.0000					

[a] The values for pure difluoromethane ($x_1 = 1$) and the values for pure pentafluoroethane ($x_1 = 0$) were obtained from the reanalysis of the Burnett measurements by Qian et al. (1993) and by Ye et al. (1995), respectively.

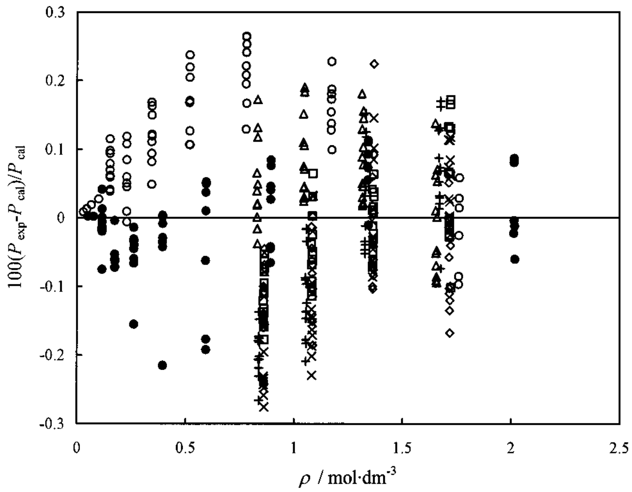

Figure 3. Deviations of experimental *PVTx* data from eq 1: (○) 0.5001 mole fraction of R-32 (this work); (●) 0.6977 mole fraction of R-32 (this work); (△) 0.3671 mole fraction of R-32 (Kiyoura et al., 1996); (◇) 0.6058 mole fraction of R-32 (Kiyoura et al., 1996); (□) 0.6978 mole fraction of R-32 (Sato et al., 1996); (+) 0.7758 mole fraction of R-32 (Sato et al., 1996); (×) 0.9022 mole fraction of R-32 (Sato et al., 1996).

Table 2. Numerical Constants in Eqs 5−10

T_{c1}/K	351.26
T_{c2}/K	339.17
$b_{1,1}$/dm^3·mol^{-1}	0.326 736 0
$b_{1,2}$/dm^3·mol^{-1}	0.419 992 0
$b_{2,1}$/dm^3·mol^{-1}	0.335 168 8
$b_{2,2}$/dm^3·mol^{-1}	0.363 130 2
$b_{2,12}$, $b_{2,21}$/dm^3·mol^{-1}	0.368 638 9
$b_{3,1}$/dm^3·mol^{-1}	−0.315 419 0
$b_{3,2}$/dm^3·mol^{-1}	−0.388 010 0
$b_{3,12}$, $b_{3,21}$/dm^3·mol^{-1}	−0.353 673 8
$c_{1,1}$/dm^6·mol^{-2}	$-0.185\ 398\ 2 \times 10^{-2}$
$c_{1,2}$/dm^6·mol^{-2}	$0.917\ 291\ 2 \times 10^{-2}$
$c_{2,1}$/dm^6·mol^{-2}	$0.199\ 285\ 9 \times 10^{-1}$
$c_{2,2}$/dm^6·mol^{-2}	$0.180\ 074\ 9 \times 10^{-1}$
$c_{2,112}$, $c_{2,121}$, $c_{2,211}$/dm^6·mol^{-2}	$0.153\ 646\ 7 \times 10^{-1}$
$c_{2,221}$, $c_{2,212}$, $c_{2,122}$/dm^6·mol^{-2}	$0.219\ 178\ 5 \times 10^{-1}$
$c_{3,1}$/dm^6·mol^{-2}	$0.153\ 954\ 5 \times 10^{-3}$
$c_{3,2}$/dm^6·mol^{-2}	$0.710\ 818\ 4 \times 10^{-3}$
$c_{3,112}$, $c_{3,121}$, $c_{3,211}$/dm^6·mol^{-2}	$0.284\ 329\ 9 \times 10^{-2}$
$c_{3,221}$, $c_{3,212}$, $c_{3,212}$/dm^6·mol^{-2}	$-0.239\ 653\ 6 \times 10^{-2}$
$d_{1,1}$/dm^9·mol^{-3}	$-0.699\ 270\ 8 \times 10^{-3}$
$d_{1,2}$/dm^9·mol^{-3}	$-0.652\ 549\ 7 \times 10^{-3}$

eq 1. Equation 1 represents the data by the present study within ±0.2%, except four points (off scale) with maximum deviation of 0.5%, and those measured using the Burnett−isochoric apparatus by Boyes and Weber (1995) within ±0.15%. The Burnett measurements at 363.153 K by Boyes and Weber are in agreement with the present data within ±0.1%. In addition, the reported data for R-125 obtained using a constant-volume method by Oguchi et al. (1996) have also been compared with eq 1. Since the deviations between the data by Oguchi et al. and eq 1 are relatively large, they are not plotted in Figure 6. The data by Oguchi et al. show systematically negative deviations from eq 1 in the density range where eq 1 is effective, and the maximum and the standard deviations are −0.76% and +0.41%, respectively. As reported by Oguchi et al., the same data also showed systematically negative bias from a BWRS equation of state developed by Wilson et al. (1992) with maximum deviation of about −2.0%.

To discuss the behaviors of the second virial coefficients described by the present equation and of those determined from experimental measurements, the temperature dependence of the second virial coefficients for the R-32 + 125 system is illustrated in Figures 7 and 8.

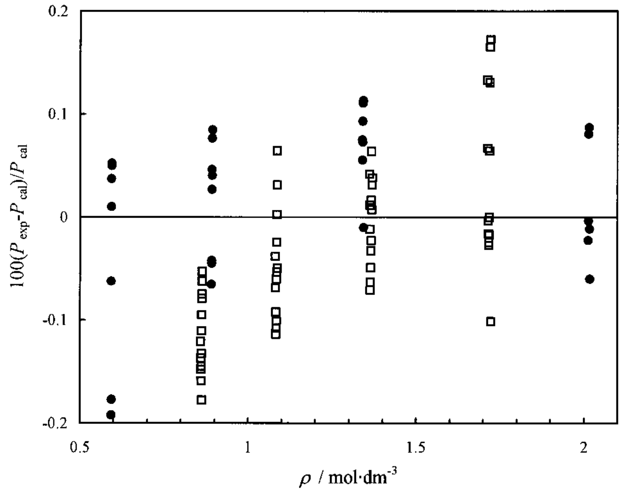

Figure 4. Comparison of the present measurements at 0.6977 mole fraction of R-32 with those by Sato et al. (1996): (●) 0.6977 mole fraction of R-32 (this work); (□) 0.6978 mole fraction of R-32 (Sato et al., 1996).

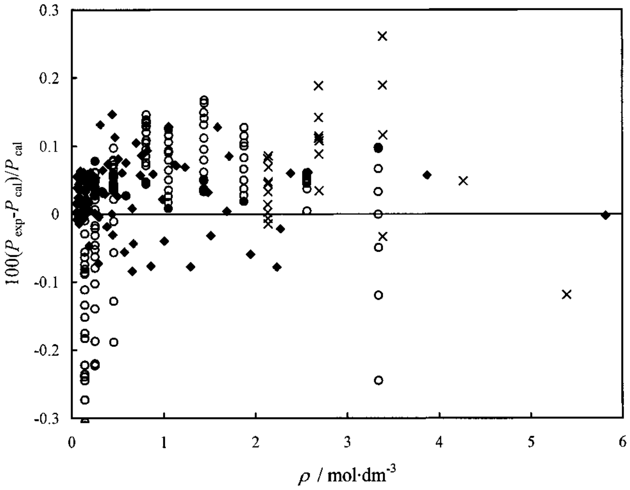

Figure 5. Deviations of experimental *PVT* data for R-32 from eq 1: (◆) this work (○) Defibaugh et al. (1994); (●) Burnett measurements (Defibaugh et al. 1994); (×) Sato et al. (1994).

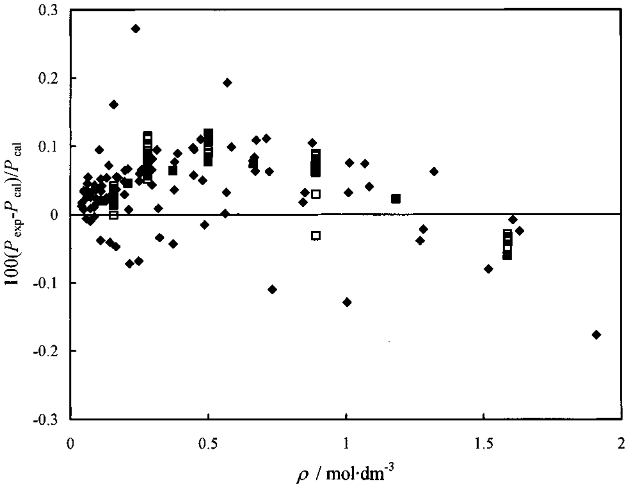

Figure 6. Deviations of experimental *PVT* data for R-125 from eq 1: (◆) this work; (□) Boyes and Weber (1995); (■) Burnett measurements (Boyes and Weber, 1995).

As shown in Figure 7, the redetermined values of R-32 by Zhang et al. (1995b) are well represented by eq 2; the single value derived from Burnett measurements and the correlation (dashed line) by Defibaugh et al. (1994) are also

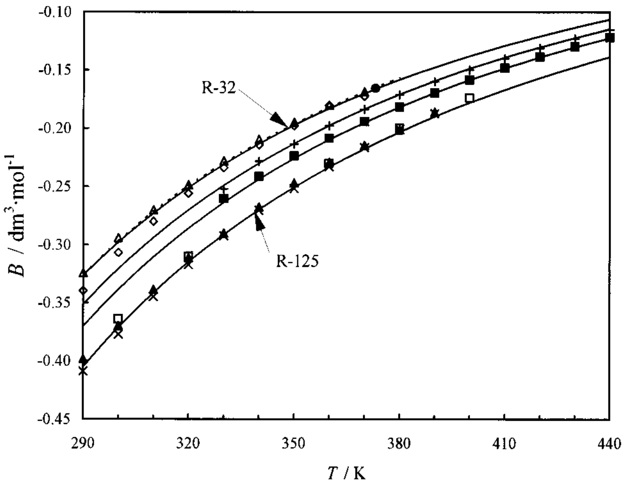

Figure 7. Temperature dependence of second virial coefficients for the R-32 + 125 system: (△) R-32 (Zhang et al., 1995b); (◇) R-32 (Qian et al., 1993); (●) R-32 (Defibaugh et al., 1994); (- - -) correlation for R-32 (Defibaugh et al., 1994); (▲) R-125 (Zhang et al., 1995b); (□) R-125 (Gillis, 1996); (×) R-125 (Ye et al., 1995); (■) 0.3671 mole fraction of R-32 (Kiyoura et al., 1996); (+) 0.6058 mole fraction of R-32 (Kiyoura et al., 1996); (—) present equation.

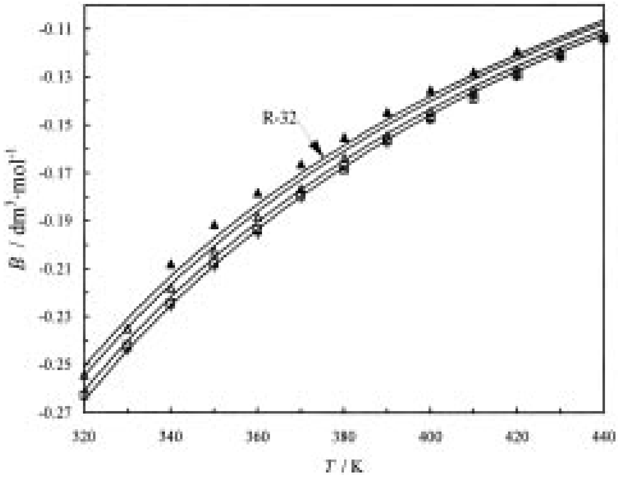

Figure 8. Comparison of second virial coefficients by Sato et al. with the present equation: (+) 0.6978 mole fraction of R-32 (Sato et al., 1996); (□) 0.7758 mole fraction of R-32 (Sato et al., 1996); (△) 0.9022 mole fraction of R-32 (Sato et al., 1996); (▲) R-32 (Sato et al., 1994); (—) present equation.

in good agreement with the reanalyzed data. The data by Qian et al. (1993), which were derived from the same Burnett measurements as those used by Zhang et al. (1995b), show increasing deviations, from both eq 2 and the correlation by Defibaugh et al. (1994), with decreasing temperature, and reach the maximum deviation of 5% at 290 K. Concerning R-125, as shown in Figure 7, behavior similar to R-32 is observed: the difference between the reanalyzed values by Zhang et al. (1995b) and those by Ye et al. (1995) reaches the maximum (3%) at 290 K, although the same Burnett data were used; the reanalyzed values are found closer to those derived from acoustic measurements by Gillis (1996). It should be noted that the maximum difference for both R-32 and R-125 between the reanalyzed values and those by the conventional data-processing method appears at the lowest temperature. This is due to the well-known fact that lower-temperature Burnett measurements are relatively easily influenced by uncertainty of the pressure measurements and/or sample adsorption. Although we could not conclude that the present data-processing procedure has completely overcome the shortcomings of the conventional method for Burnett data analysis, it was confirmed that the present procedure offers more reliable compressibility factors and second virial coefficients.

From Figure 7, it can also be seen that the second virial coefficients at 0.3671 and 0.6058 mole fractions of R-32 derived by Kiyoura et al. (1996) from their *PVT* measurements are in good agreement (within ±1.1%) with the present equation of state. The second virial coefficient at 0.6978, 0.7758, and 0.9022 mole fractions of R-32 derived by Sato et al. (1996) from their *PVT* measurements are plotted in Figure 8. The data at 0.6978 mole fraction of R-32 are well represented by the present equation, although they show a negative maximum deviation of −2.1% at 440 K. The data at 0.7758 and 0.9022 mole fractions of R-32 deviate from the present equation by −3.4% to +0.7% and by −4.3% to +0.2%, respectively. In consideration of the uncertainties of *PVT* measurements reported by Sato et al. (1996), however, these deviations are not inconsistent with the realistic uncertainty of the second virial coefficients. On the other hand, as observed in Figure 8, with increasing temperatures the three series of second virial coefficients at different compositions show a tendency to overlap each other and seem somewhat out of position at higher temperatures as compared with those for pure R-32 reported by the same authors (Sato et al., 1994). A possible reason we presume is virial coefficients derived from *PVT* measurements along isotherms are very sensitive to the measured pressure and density values; as shown in Figure 3, the data at densities below 1.2 mol·dm^{-3} reported by Sato et al. (1996) show systematic negative bias from the present equation and at the lowest densities the deviations reach −0.3% for the measurements at 0.7758 and 0.9022 mole fractions of R-32 and −0.2% for those at 0.6978 mole fraction, respectively. These facts would make an impact on the determination of second coefficient values by plotting values $(Z - 1)/\rho$ vs density ρ along isotherms (the intersection with the ordinate corresponds to the second virial coefficient), because at a given temperature and density the value $(Z - 1)/\rho$ depends on the compressibility factor, i.e., the measured pressure. In these measurements for three isopleths performed by Sato et al. (1996), only four points are available along each isotherm. Therefore, if pressures at the lowest-density point and next-to-lowest density point were lower than the true values the determined second virial coefficient would become much smaller, although the deviations (−0.3% to −0.2%) discussed above do not exceed the estimated uncertainty.

Since the uncertainties of third and fourth virial coefficients derived from *PVT* measurements would be much larger than those of the second virial coefficients, discussion on them is omitted in this paper.

In consideration of the range of the input data, the present equation is effective for the entire composition range including pure components and for temperatures from 290 K to 440 K and pressures up to 5.3 MPa.

Conclusions

The *PVTx* properties in the gas phase for the binary mixture of difluoromethane (R-32) and pentafluoroethane (R-125), a very promising alternative to the refrigerant R-22, have been measured using the Burnett apparatus. Sixty-one and sixty-three *PVT* properties have been obtained at 0.5001 (30.24 mass %) and 0.6977 (50.01 mass %) mole fraction of R-32, respectively. The earlier Burnett measurements of pure R-32 and R-125 were also reanalyzed using a new data-processing procedure. The redetermined second virial coefficients changed from those determined using the conventional method by a maximum of 3−5%, while the redetermined compressibility factors only changed slightly (maximum 0.13%). By using these experimental values and the isochoric *PVTx* data (Sato et al., 1996; Kiyoura et al., 1996), a virial-type equation of state for the R-32 + 125 system has been developed which could represent the experimental values within ±0.3% in pressure for the range of temperatures 290 K to 440 K and pressures up to 5.3 MPa.

Acknowledgment

We acknowledge Daikin Industries, Osaka, for kindly furnishing the samples of R-32 and R-125. We also thank A. Miyoshi, a former undergraduate student at Keio University, for his valuable assistance in measurements.

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Received for review February 19, 1996. Accepted July 18, 1996.[⊗]

JE960069F

[⊗] Abstract published in *Advance ACS Abstracts,* September 1, 1996.