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Measurements of *PVTx* Properties of Refrigerant Mixture HFC-32 + HFC-125 in the Gaseous Phase[1]

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The experimental 156 *PVTx* properties of an important binary refrigerant mixture, HFC-32 (difluoromethane) + HFC-125 (pentafluorethane), have been measured for three compositions, i.e., 50, 60, and 80 wt% HFC-32, by a constant-mass-method coupled with expansion procedure in an extensive range of temperatures T from 320 to 440 K, of pressures P from 1.8 to 5.3 MPa, and of densities ρ from 50 to 124 $kg \cdot m^{-3}$. The experimental uncertainties of the present measurements are estimated to be within ±7 mK in temperature, ±2 kPa in pressure, ±0.2% in density and ±0.02 wt% of HFC-32. The sample purities are 99.998 wt% for HFC-32 and 99.99 wt% for HFC-125. Seventy-eight second and third virial coefficients for temperatures from 320 to 440 K have been determined by the present measurements.

KEY WORDS: alternative refrigerant; binary refrigerant mixtures; HFC-32 + HFC-125 system; *PVTx* properties; thermodynamic properties; virial coefficients.

1. INTRODUCTION

One of the promising candidates for chlorodifluoromethane (HCFC-22) alternatives as a refrigerant in air-conditioning systems is a binary mixture of difluormethane (CH_2F_2, HFC-32) and pentafluoroethane (CH_3CHF_2, HFC-125). Because of its flammable characteristics, HFC-32 by itself is not considered a suitable working fluid for refrigeration systems. The mixture of HFC-32 with a nonflammable refrigerant, HFC-125, however, may overcome such a drawback in practical applications. HFC-32 and HFC-125 have no chlorine atoms, so the ozone depletion potential (ODP) is nil. The

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HFC-32 and HFC-125 blend is, therefore expected as a possible alternative of HCFC-22. It was also reported by Singh et al. [1] that this blend shows azeotropy at the composition of 60wt% HFC-32. Widiatmo et al. [2], on the other hand, reported that the azeotropic composition of this binary refrigerant is near 80wt% HFC-32, since its bubble-point pressure exceeds the vapor pressure of HFC-32. Such a difference in azeotropic composition may be due to the small difference between the bubble-point and dew-point pressures at the compositions 60–80wt% HFC-32.

Practical refrigerant drop-in tests in existing equipments and prediction of the thermodynamic properties for an HFC-32 and HFC-125 blend are being performed by many engineers and researchers. Reliable information about the thermodynamic properties of this blend is important for supporting further progress in the R&D of advanced air-conditioning equipment with refrigerant mixtures. This study provides a reliable experimental thermodynamic properties of this blend in the gaseous phase.

2. MEASUREMENTS

The apparatus and procedure have been reported by Takaishi et al. [3,4]. The constant-mass method coupled with isothermal expansion procedures was applied for measuring dew-point pressures and *PVTx* properties, i.e., *PVT* properties of binary refrigerant mixtures at different compositions. The apparatus shown in Fig. 1 consists of a sample cell (A), an expansion cell (B), a differential pressure detector (C), a platinium resistance thermometer (G) calibrated on ITS-90, a thermostated bath (H), temperature control/measuring devices, and pressure measuring instruments.

The inner volumes of the sample cell and expansion cell were carefully calibrated with pure water; they were 283.368 ± 0.027 and 55.583 ± 0.007 cm^3, respectively, at 273.15 K. The temperature in the silicone oil-filled thermostated bath was controlled within ±2 mK. After thermal equilibrium was reached, and the pressure remained unchanged for several hours, the temperature and the sample fluid were measured.

After a series of pressure measurements along an isochore was completed, we expanded part of the sample fluid into the expansion cell in the single gaseous phase to obtain another isochore, with composition unchanged. The valves between the sample cell and the expansion cell were closed when the temperature and the pressure became stable.

The experimental errors of the present measurements are estimated to be not greater than ±7 mK in temperature, ±2 kPa in pressure, ±0.2% in density, and ±0.02% in each composition. The sample purities are 99.998 wt% for HFC-32 and 99.99 wt% for HFC-125.

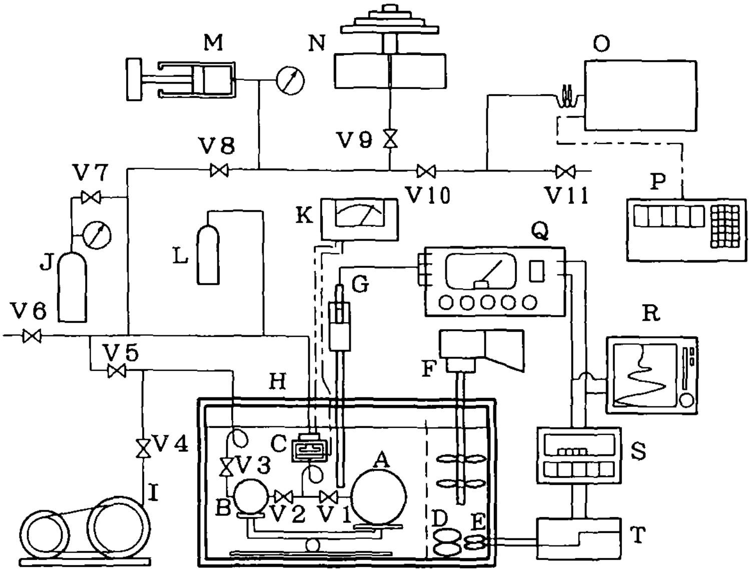

Fig. 1. Experimental apparatus. (A) sample cell; (B) expansion cell; (C) differential pressure detector; (D) main heater; (E) auxiliary heater; (F) stirrer; (G) platinum-resistance thermometer; (H) thermostated bath; (I) vacuum pump; (J) nitrogen cylinder; (K) electric resistance detector; (L) nitrogen-gas damper; (M) precise pressure-controller; (N) air-piston type dead-weight pressure gauge; (O) quartz pressure-transducer; (P) digital-quartz-pressure-transducer-computer; (Q) thermometer; (R) pen recorder; (S) PID controller; (T) DC power supply; (V_1)-(V_{11}) valves.

3. RESULTS

One hundred fifty-six density values were measured along 12 isochores at temperatures from 320 to 440 K, pressures from 1.8 to 5.3 MPa, and mass fractions of HFC-32 at 50.021 wt% (69.779 mol%), 60.004 wt% (77.584 mol%), and 79.988 wt% (90.216 mol%). These data are tabulated in Table I. Figure 2 shows the distribution of the *PVTx* data on a pressure-temperature plane, where the vapor pressure curves are calculated from the correlations of both pure components [5, 6].

The temperatures are given according to the temperature scale ITS-90.

Table I. *PVTx* Properties of the HFC-32 + HFC-125 System

ρ (kg · m^{-3})	T (K)	P (MPa)
(a) 50.021 wt% (69.779 mol%) HFC-32		
125.10	320.000	2.8260
125.04	330.000	3.0614
124.98	340.000	3.2825
124.92	350.000	3.4969
124.86	360.000	3.7049
124.80	370.000	3.9081
124.74	380.000	4.1088
124.68	390.000	4.3061
124.62	400.000	4.5001
124.56	410.000	4.6916
124.49	420.000	4.8803
124.43	430.000	5.0693
124.37	440.000	5.2559
99.39	320.000	2.4937
99.34	330.000	2.6626
99.30	340.000	2.8267
99.25	350.000	2.9893
99.20	360.000	3.1454
99.15	370.000	3.2985
99.11	380.000	3.4497
99.06	390.000	3.5981
99.01	400.000	3.7442
98.96	410.000	3.8884
98.91	420.000	4.0333
98.86	430.000	4.1751
98.81	440.000	4.3156
78.96	320.000	2.1459
78.92	330.000	2.2747
78.89	340.000	2.3974
78.85	350.000	2.5176
78.81	360.000	2.6355
78.78	370.000	2.7512
78.74	380.000	2.8656
78.70	390.000	2.9773
78.66	400.000	3.0884
78.62	410.000	3.1981
78.58	420.000	3.3074
78.54	430.000	3.4156
78.50	440.000	3.5230

Table I. *(Continued)*

ρ (kg·m^{-3})	T (K)	P (MPa)
62.73	320.000	1.8159
62.70	330.000	1.9106
62.67	340.000	2.0033
62.64	350.000	2.0945
62.61	360.000	2.1821
62.58	370.000	2.2723
62.55	380.000	2.3591
62.52	390.000	2.4446
62.49	400.000	2.5289
62.46	410.000	2.6133
62.43	420.000	2.6964
62.40	430.000	2.7791
62.37	440.000	2.8612
(b) 60.004 wt% (77.584 mol%) HFC-32		
112.84	320.000	2.8138
112.79	330.000	3.0381
112.73	340.000	3.2501
112.68	350.000	3.4552
112.63	360.000	3.6547
112.57	370.000	3.8517
112.52	380.000	4.0434
112.46	390.000	4.2327
112.41	400.000	4.4196
112.35	410.000	4.6022
112.29	420.000	4.7848
112.24	430.000	4.9648
112.18	440.000	5.1429
89.65	320.000	2.4713
89.61	330.000	2.6344
89.56	340.000	2.7919
89.52	350.000	2.9457
89.48	360.000	3.0955
89.44	370.000	3.2437
89.39	380.000	3.3877
89.35	390.000	3.5300
89.31	400.000	3.6706
89.26	410.000	3.8099
89.22	420.000	3.9476
89.17	430.000	4.0859
89.13	440.000	4.2200

Table I. *(Continued)*

ρ (kg·m^{-3})	T (K)	P (MPa)
71.22	320.000	2.1150
71.19	330.000	2.2382
71.16	340.000	2.3572
71.12	350.000	2.4735
71.09	360.000	2.5855
71.06	370.000	2.6965
71.02	380.000	2.8055
70.99	390.000	2.9152
70.95	400.000	3.0215
70.92	410.000	3.1264
70.88	420.000	3.2350
70.85	430.000	3.3385
70.81	440.000	3.4412
56.58	320.000	1.7831
56.56	330.000	1.8753
56.53	340.000	1.9641
56.51	350.000	2.0521
56.48	360.000	2.1379
56.45	370.000	2.2246
56.42	380.000	2.3065
56.40	390.000	2.3908
56.37	400.000	2.4720
56.34	410.000	2.5516
56.31	420.000	2.6331
56.29	430.000	2.7130
56.26	440.000	2.7926
(c) 79.988 wt% (90.216 mol%) HFC-32		
101.08	320.000	2.8946
101.04	330.000	3.1183
100.99	340.000	3.3341
100.94	350.000	3.5436
100.89	360.000	3.7469
100.84	370.000	3.9471
100.79	380.000	4.1438
100.75	390.000	4.3368
100.70	400.000	4.5268
100.64	410.000	4.7145
100.59	420.000	4.9001
100.54	430.000	5.0842
100.49	440.000	5.2658

Table I. *(Continued)*

ρ ($kg \cdot m^{-3}$)	T (K)	P (MPa)
80.31	320.000	2.5374
80.27	330.000	2.7045
80.23	340.000	2.8651
80.20	350.000	3.0227
80.16	360.000	3.1739
80.12	370.000	3.3252
80.08	380.000	3.4740
80.04	390.000	3.6202
80.00	400.000	3.7638
79.96	410.000	3.9050
79.92	420.000	4.0458
79.88	430.000	4.1860
79.84	440.000	4.3242
63.80	320.000	2.1749
63.77	330.000	2.2993
63.74	340.000	2.4196
63.71	350.000	2.5364
63.68	360.000	2.6520
63.65	370.000	2.7662
63.62	380.000	2.8798
63.59	390.000	2.9906
63.56	400.000	3.0992
63.53	410.000	3.2067
63.50	420.000	3.3152
63.46	430.000	3.4227
63.43	440.000	3.5280
50.69	320.000	1.8334
50.67	330.000	1.9265
50.64	340.000	2.0176
50.62	350.000	2.1071
50.59	360.000	2.1955
50.57	370.000	2.2808
50.55	380.000	2.3681
50.52	390.000	2.4512
50.50	400.000	2.5356
50.47	410.000	2.6192
50.45	420.000	2.7016
50.42	430.000	2.7829
50.40	440.000	2.8640

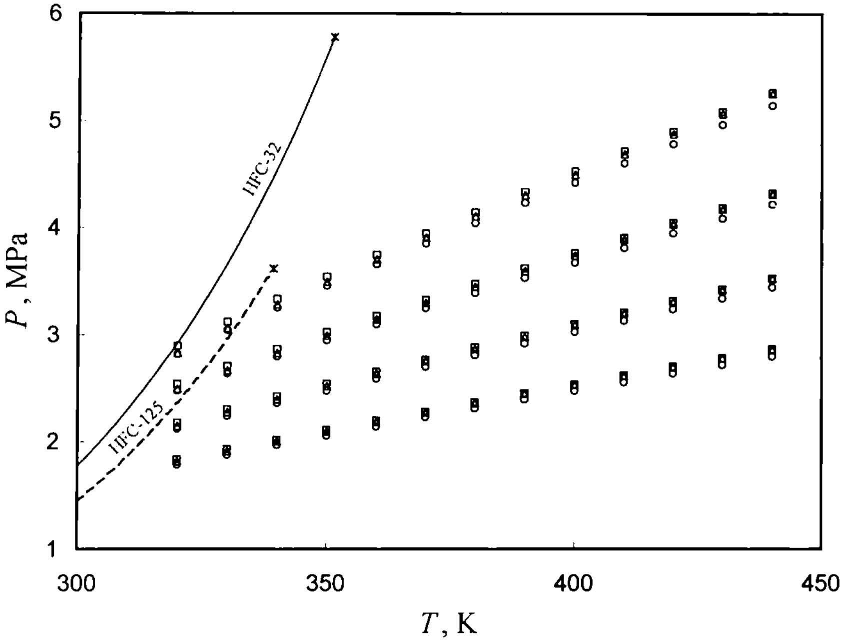

Fig. 2. Distribution of the $PVTx$ measurements on a pressure–temperature plane: (△) 50 wt% HFC-32; (○) 60 wt% HFC-32; (□) 80 wt% HFC-32. (——) Sato et al. (HFC-32) [5]; (- -) Sagawa et al. (HFC-125) [6].

4. DISCUSSION

The compressibility factors, Z, of the present binary refrigerant mixtures, with compositions of 50, 60, and 80 wt%HFC-32, were derived in the superheated vapor region from the measurements by using the relations

$$Z = \frac{P}{\rho RT} \tag{1}$$

and

$$R = \frac{R_0}{x_1 m_1 + x_2 m_2} \tag{2}$$

where P, ρ, and T denote pressure, density, and temperature, respectively. R_0 is the universal gas constant being $R_0 = 8.31451\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$ and x_1, x_2 and m_1, m_2 are mole fraction and respective molar mass of each component, respectively.

Table II. Second and Third Virial Coefficients

T (K)	B ($\mathrm{cm^3 \cdot mol^{-1}}$)	C ($\mathrm{dm^6 \cdot mol^{-2}}$)
(a) 50 wt% HFC-32		
320.00	−264.2	0.02456
330.00	−244.1	0.02304
340.00	−225.9	0.02139
350.00	−209.4	0.01986
360.00	−195.6	0.01909
370.00	−180.6	0.01678
380.00	−168.5	0.01573
390.00	−157.8	0.01502
400.00	−147.9	0.01436
410.00	−138.4	0.01348
420.00	−129.8	0.01287
430.00	−122.0	0.01244
440.00	−114.7	0.01199
(b) 60 wt% HFC-32		
320.00	−262.8	0.02572
330.00	−242.2	0.02392
340.00	−224.3	0.02236
350.00	−207.7	0.02047
360.00	−193.5	0.01926
370.00	−179.4	0.01740
380.00	−168.7	0.01711
390.00	−156.5	0.01529
400.00	−147.2	0.01489
410.00	−139.0	0.01472
420.00	−129.3	0.01329
430.00	−121.5	0.01283
440.00	−114.2	0.01218
(c) 80 wt% HFC-32		
320.00	−254.3	0.02363
330.00	−235.0	0.02202
340.00	−217.9	0.02056
350.00	−202.7	0.01932
360.00	−188.4	0.01766
370.00	−176.6	0.01717
380.00	−163.8	0.01538
390.00	−154.3	0.01513
400.00	−144.5	0.01413
410.00	−135.4	0.01324
420.00	−127.0	0.01260
430.00	−119.6	0.01203
440.00	−112.6	0.01153

The *PVTx* properties measured were represented within the estimated experimental uncertainty by the following truncated virial expression:

$$\frac{Z-1}{\rho}=B+C\rho \tag{3}$$

If we plot the values $(Z\text{-}1)/\rho$ vs density ρ along each isotherm, we can draw a simple straight line. The intersection with the ordinate corresponds to the second virial coeffient B, while the slope of each isotherm represents the third virial coefficient C. The second and third virial coefficient values thus determined from the present measurements are listed in Table II.

Figures 3 and 4 show the temperature dependence of B and C values thus determined for the binary mixtures with different compositions. It should be noted that the present B and C values are the first set of data ever reported for this important binary refrigerant for a wide range of temperatures of practical importance. Concerning HFC-32, the B and C values reported by the present authors [5, 7] and by Qian et al. [8] are included

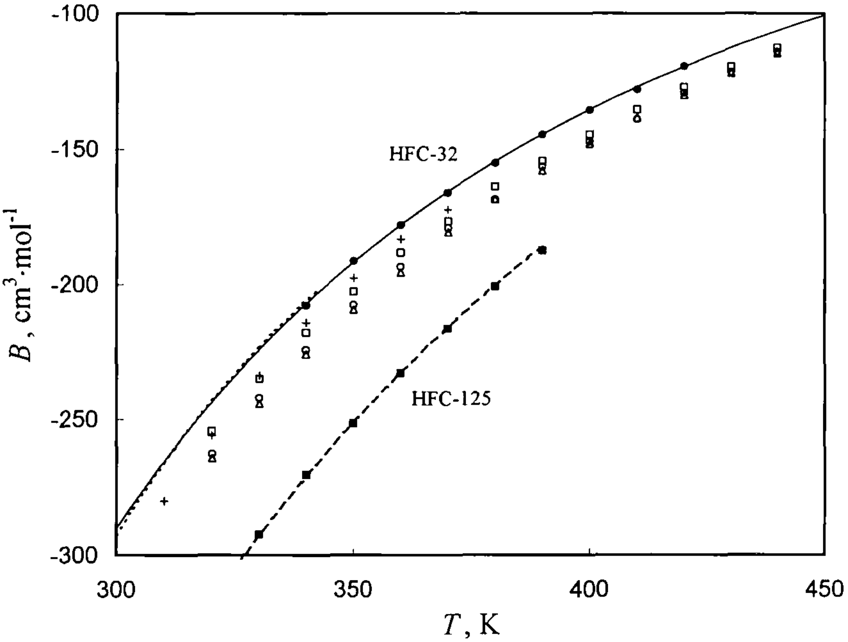

Fig. 3. Temperature dependence of the determined second virial coefficients for binary HFC-32 + HFC-125: (△) 50 wt% HFC-32; (○) 60 wt% HFC-32; (□) 80 wt% HFC-32. (●) Sato et al. (HFC-32) [5, 7]; (+) Qian et al. (HFC-32) [8]; (■) Ye et al. (HFC-125) [9]; (——) Sato et al. (HFC-32) [7]; (----) Hozumi et al. (HFC-32) [10]; (--) Ye et al. (HFC-125) [9].

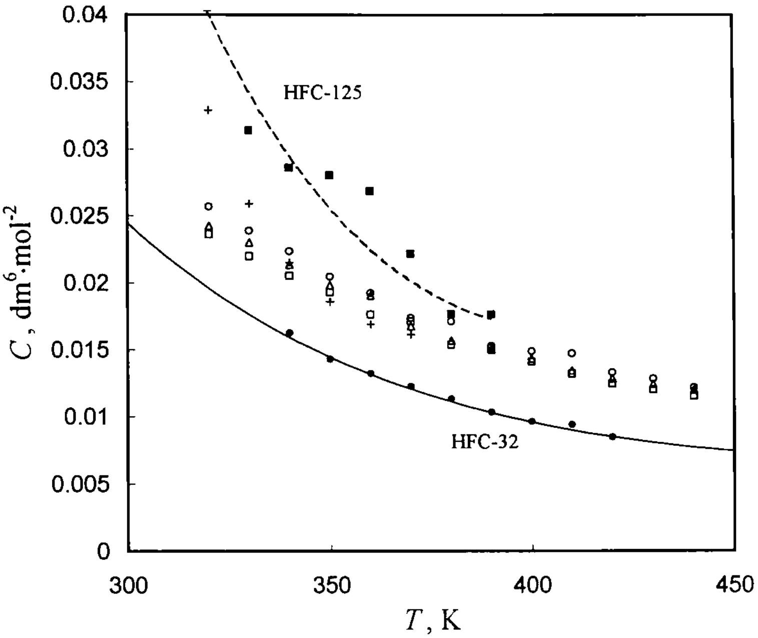

Fig. 4. Temperature dependence of the determined third virial coefficients for the binary HFC-32 + HFC-125: (△) 50 wt% HFC-32; (○) 60 wt% HFC-32; (□) 80 wt% HFC-32. (●) Sato et al. (HFC-32) [5, 7]; (+) Qian et al. (HFC-32) [8]; (■) Ye et al. (HFC-125) [9]; (——) Sato et al. (HFC-32) [7]; (--) Ye et al. (HFC-125) [9].

in Figs. 3 and 4; similar comparisons with the values for HFC-125 by Ye et al. [9] are also included. As shown in Fig. 3, the present second virial coefficients *B* agree well with the available data except for the values by Qian et al. [8] for pure HFC-32 which have some systematic difference from the present values. Concerning the third virial coefficient *C*, however, a significant disagreement with the reported values by Qian et al. [8] was found for both pure components. This disagreement is probably the reason why Qian et al. [8], in calculating their *C* values, required a virial equation truncated at the fourth virial coefficient, while we have applied here a simpler representation given in Eq. (3) in the present analysis.

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