PVTx Properties in the Gas Phase for Difluoromethane (HFC-32) + Pentafluoroethane (HFC-125)

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Gaseous *PVT* property measurements for difluoromethane (HFC-32) + pentafluoroethane (HFC-125) mixtures at 0.8191 (66.25 mass %), 0.5794 (37.38 mass %), and 0.4320 (24.79 mass %) mole fractions of HFC-32 are presented. Two hundred *PVTx* data points of this binary system were measured using Burnett isochoric methods in the range of temperature from (303.15 to 373.15) K, for pressures up to 3.246 MPa, and for densities up to 121 kg·m^{-3}. The experimental uncertainties are estimated to be within ±10 mK for temperature, ±0.3 kPa for pressure, ±0.10% for density, and 0.1 mol % for composition. The temperature dependence of the second and third virial coefficients, along with the cross second and third virial coefficients, was also determined.

Introduction

Because HCFC-22, as one of the most widely used working fluids in air-conditioning and heat pump systems, is scheduled to be phased out before 2030 by international agreement, hydrofluorocarbon (HFC) mixtures are expected to be promising interim and long-term alternatives. A near-azeotropic mixture of HFC-32 + HFC-125 is considered to meet the requirement to replace HCFC-22 for its zero ODP (ozone depletion potential) and similar refrigeration characteristics. Although many experimental studies have been reported for this mixture, reliable information about the thermodynamic properties of this blend is still required. New gaseous *PVTx* measurements along three isopleths of the HFC-32 + HFC-125 system with a Burnett apparatus are presented in this paper.

Samples

A sample of pure HFC-32 was purchased from the Zhejiang Fluoro-Chemical Technology Research Institute, which stated that the purity was more than 99.95 mass %. An HFC-125 sample was obtained from ICI Co. and was used without further purification. The manufacturer stated that the purity of the HFC-125 sample was better than 99.98 mass %. Before use, the samples' purities were checked by gas chromatographic analysis (Lunan SP-6800A) and were found to be more than 99.96% for both HFC-32 and HFC-125 on the basis of the area responses of a thermal conductivity detector.

Experimental Section

The Burnett isochoric coupling method was used for the present measurements. A diagram of the apparatus is shown in Figure 1. It is similar to that described in the publications of Fu et al.,[1] but the pressure measurement system and the vacuum and sample system were improved and the sample cells were reconstructed.

The thermostated bath temperature could be varied from (223 to 453) K. The temperature instability was less than ±2 mK in 1 h and less than ±5 mK in 8 h. Silicone oil was used as the bath fluid in this work. The temperature measurement system included a platinum resistance thermometer (Tinsley, 5187SA) with an uncertainty of ±2 mK, a precision thermometer bridge (Tinsley, 5840D) with an uncertainty of ±1 mK, a select switch (Tinsley, 5840CS/6T), and a personal computer. The overall temperature uncertainty for the bath instability and the temperature measurement system was less than ±10 mK. The temperatures were determined on the basis of the international temperature scale of 1990 (ITS-90).

The pressure measurement system, which could measure pressures up to 6 MPa, included a piston-type pressure gauge, a pressure transducer, and two digital manometers. A very sensitive diaphragm pressure transducer (Xi'an Instrument, 1151DP) separated the sample in the thermostated bath from nitrogen that transmitted the pressure outside the bath. The transducer uncertainty was 0.2%. An absolute pressure digital manometer (Yokogawa, MT210, 767367) was used to measure the atmospheric pressure. The uncertainty of the absolute pressure digital manometer was 0.015%, and the pressure range was (0.001 to 130) kPa. At pressures below 130 kPa, the nitrogen transmits the sample pressure directly to the absolute pressure digital manometer so that the pressure measurement system has a maximum uncertainty of ±100 Pa. In this work, pressures at (0.13 to 3.7) MPa were measured with a piston-type pressure gauge having an uncertainty of 0.005% in the pressure range of (0.04 to 6) MPa, with the atmospheric pressure measured by the digital manometer so that the overall pressure uncertainty was estimated to be less than ±300 Pa. For pressures below 3 MPa, a gauge pressure digital manometer (Yokogawa, MT210, 767366) was used to measure the pressure in parallel with the piston-type pressure gauge to avoid operator error. The uncertainty of the gauge pressure digital manometer was 0.015% for a pressure range of (−0.08 to 3) MPa gauge pressure. In this work, although the results measured by the gauge pressure digital manometer showed very good agreement with the

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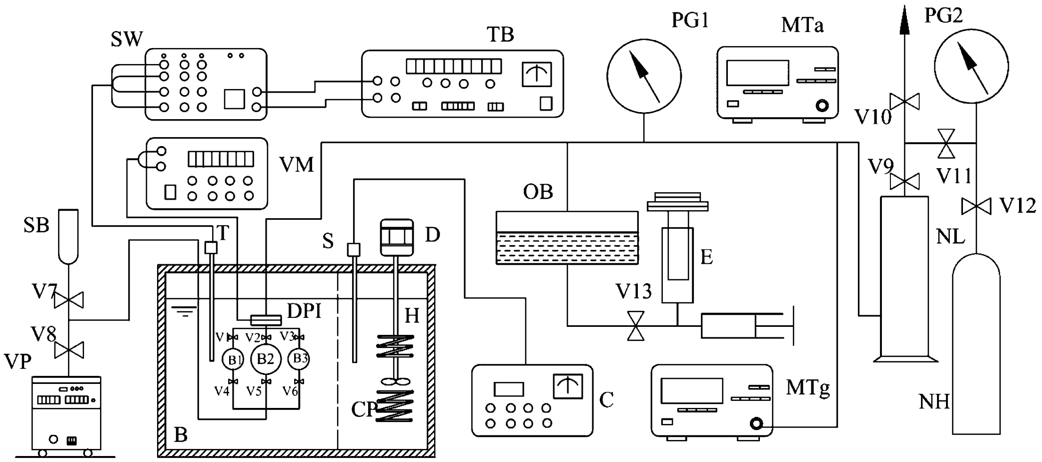

Figure 1. Burnett experimental apparatus: B, thermostated bath; B1, expansion cell (200 mL); B2, sample cell (500 mL); B3, sample cell (1000 mL); C, temperature controller; CP, cooler; D, stirrer; DPI, differential pressure detector; E, oil piston-type pressure gauge; H, heater; NH, N_2 bottle; NL, pressure damper; OB, oil−gas separator; PG1, PG2, pressure gauges; T, platinum resistance thermometer; S, temperature sensor; SB, sample bottle; SW, selector switch; TB, thermometer bridge; V1−V13, valves; VM, digital multimeter; VP, vacuum pump; MTa, absolute pressure digital manometer; MTg, gauge pressure digital manometer.

data measured by the piston-type pressure gauge, only the piston-type pressure gauge results were published because of the smaller uncertainty.

The highest vacuum provided by the turbomolecular pump (KYKY FD110) was about 1×10^{-6} Pa.

Before the experiment, the platinum resistance thermometer, the thermometer bridge with the select switch, the digital manometers, and the piston-type pressure gauge were calibrated by NIM (National Institute of Metrology, China). Before and after use, the sensitive diaphragm pressure transducer was tested using the digital manometers.

The Burnett apparatus included three sample cells made of 1Cr18Ni9Ti stainless steel. The sample cell, B2, and the expansion cell, B1, were used (B3 unused) in this work with volumes of approximately (500 and 200) mL, respectively. Before the experiment, the sample cells were rinsed with acetone to remove any residue from previous experiments.

The cell constant, N_0, defined as the ratio of the volume of cell B2 to the sum of the volumes of cells B1 and B2 at zero pressure, was determined by means of gaseous helium measurements. Giving careful consideration that N used in the data processing is not dependent on temperature but a weak function of pressure

$$N(p_{i-1}, p_i) = N_0 \frac{1 + mp_i}{1 + mp_{i-1}} \tag{1}$$

where the coefficient m is considered to be a constant equal to 4.0135×10^{-11} Pa^{-1} in this work, corresponding corrections were made in the data processing. Through two series of expansion for helium at 318.15 K and 373.15 K, the cell constant $N_0 = 1.37445 \pm 0.00001$ was obtained.

The mass of each component introduced into cell B2 was determined with an accurate electronic balance (Mettler Toledo PR1203) with a resolution of ±0.001 g. Three HFC-32 (1) + HFC-125 (2) binary mixtures were prepared at mole fractions x_1 of 0.8191, 0.5794, and 0.4320. The binary mixture in cell B2 was prepared by placing the required mass of HFC-32 and HFC-125 in separate gas cylinders. Before use, the working fluids in two gas cylinders were frozen with liquefied nitrogen, and the vapor space was evacuated by the vacuum pump to remove possible air impurities. Then the two cylinders were precisely weighed on an accurate electronic balance. The two Burnett cells and connections were then evacuated by the vacuum pump to remove impurities. The vacuum in the system was better than 5×10^{-5} Pa and was maintained for at least 5 h. Taking into account that the vapor pressure of HFC-125 is a little lower than that of HFC-32 at the same temperature, a target amount of HFC-125 was first introduced into cell B2 from the gas cylinder, and then the valve was closed and the cylinder was cooled by liquefied nitrogen to force the vapor in the pipeline back into the gas cylinder. After cell B2 was cooled by liquefied nitrogen, the required mass of HFC-32 was added to cell B2 from the other gas cylinder using the same procedure as that for HFC-125. The mass differences between the gas cylinders before and after the charging process were taken as the mass of each refrigerant in the sample cell and were used to calculate the nominal mass fractions in the sample cell. Because the sample mass to fill the sample cell was about 50 g, the uncertainty of the mixture's composition was estimated to be lower than ±0.1 mole fraction %.

After the sample cell was filled, the thermostated bath temperature was controlled at the experimental temperature. After thermal equilibrium was established between the sample and the heat-transfer fluid in the bath and the pressure remained constant, the temperature and the pressure of the sample were measured. When a series of pressure measurements at an interval of 10 K along an isochore was completed, each Burnett expansion was measured at 373.15 K. First, the expansion cell was evacuated, the valve was closed, and the corresponding valves were opened gradually to expand part of the sample fluid into the expansion cell in the single phase. The valves were kept open for at least 30 min to ensure uniform density and to promote the homogeneity of the sample. The valves were then closed when the temperature and the pressure became stable. After the expansion at 373.15 K, the apparatus was cooled along the isochors. By using these procedures, the *PVTx* measurements and the isothermal expansion procedures were repeated for several isochors. To verify the mixture's composition, after each expansion the sample's composition in the expansion cell was checked using the gas chromatograph. The detector response was carefully calibrated using gravimetrically prepared mixtures, and the reproducibility of the gas chromatograph for each sample was within ±0.1%.

Table 1. Experimental *PVTx* Properties of the HFC-32 + HFC-125 System

T/K	*P*/kPa	ρ/kg·m^{-3}	Z	x_1	*T*/K	*P*/kPa	ρ/kg·m^{-3}	Z	x_1	*T*/K	*P*/kPa	ρ/kg·m^{-3}	Z	x_1
373.15	2921.91	73.386	0.82547	0.8191	373.15	939.88	20.565	0.94751	0.8191	373.15	273.76	5.763	0.98491	0.8191
373.15	2239.47	53.394	0.86955	0.8191	373.15	693.94	14.963	0.96152	0.8191	373.15	200.00	4.193	0.98897	0.8191
373.15	1692.40	38.849	0.90318	0.8191	373.15	510.29	10.886	0.97181	0.8191	373.15	145.96	3.051	0.99202	0.8191
373.15	1265.95	28.265	0.92855	0.8191	373.15	374.18	7.921	0.97944	0.8191	373.15	106.43	2.219	0.99415	0.8191
363.15	2800.14	73.423	0.81244	0.8191	363.15	1225.48	28.280	0.92316	0.8191	363.15	495.73	10.892	0.96959	0.8191
363.15	2155.96	53.421	0.85975	0.8191	363.15	911.28	20.575	0.94351	0.8191	363.15	363.71	7.924	0.97776	0.8191
363.15	1634.56	38.868	0.89588	0.8191	363.15	673.57	14.970	0.95853	0.8191					
353.15	2676.40	73.460	0.79813	0.8191	353.15	1184.59	28.294	0.91717	0.8191	353.15	481.12	10.897	0.96719	0.8191
353.15	2071.30	53.448	0.84895	0.8191	353.15	882.48	20.586	0.93909	0.8191	353.15	353.22	7.928	0.97597	0.8191
353.15	1576.05	38.888	0.88783	0.8191	353.15	653.13	14.978	0.95528	0.8191					
343.15	2550.28	73.497	0.78229	0.8191	343.15	1143.35	28.308	0.91058	0.8191	343.15	466.44	10.903	0.96452	0.8191
343.15	1985.42	53.475	0.83705	0.8191	343.15	853.45	20.596	0.93420	0.8191	343.15	342.71	7.932	0.97401	0.8191
343.15	1516.82	38.907	0.87892	0.8191	343.15	632.57	14.985	0.95169	0.8191					
333.15	2421.33	73.534	0.76464	0.8191	333.15	1101.62	28.322	0.90323	0.8191	333.15	451.69	10.908	0.96157	0.8191
333.15	1897.94	53.502	0.82377	0.8191	333.15	824.17	20.606	0.92877	0.8191	333.15	332.14	7.936	0.97183	0.8191
333.15	1456.78	38.926	0.86904	0.8191	333.15	611.86	14.992	0.94769	0.8191					
323.15	2288.87	73.571	0.74481	0.8191	323.15	1059.36	28.336	0.89501	0.8191	323.15	436.86	10.913	0.95831	0.8191
323.15	1808.61	53.528	0.80888	0.8191	323.15	794.60	20.617	0.92270	0.8191	323.15	321.52	7.940	0.96939	0.8191
323.15	1395.73	38.946	0.85796	0.8191	323.15	590.99	15.000	0.94324	0.8191					
313.15	2152.05	73.608	0.72228	0.8191	313.15	1016.48	28.350	0.88577	0.8191	313.15	421.93	10.919	0.95465	0.8191
313.15	1717.10	53.555	0.79208	0.8191	313.15	764.64	20.627	0.91581	0.8191	313.15	310.85	7.944	0.96667	0.8191
313.15	1333.47	38.965	0.84544	0.8191	313.15	569.94	15.007	0.93821	0.8191					
303.15	1622.78	53.582	0.77288	0.8191	303.15	734.36	20.637	0.90810	0.8191	303.15	406.86	10.924	0.95043	0.8191
303.15	1269.80	38.985	0.83121	0.8191	303.15	548.65	15.015	0.93249	0.8191	303.15	300.13	7.948	0.96363	0.8191
303.15	972.79	28.364	0.87522	0.8191										
373.15	3236.45	106.009	0.79338	0.5794	373.15	793.41	21.614	0.95393	0.5794	373.15	229.98	6.057	0.98677	0.5794
373.15	2507.25	77.131	0.84475	0.5794	373.15	584.76	15.726	0.96631	0.5794	373.15	167.94	4.407	0.99036	0.5794
373.15	1910.03	56.119	0.88448	0.5794	373.15	429.43	11.442	0.97535	0.5794	373.15	122.50	3.206	0.99288	0.5794
373.15	1437.06	40.831	0.91463	0.5794	373.15	314.55	8.325	0.98193	0.5794	373.15	89.29	2.333	0.99477	0.5794
373.15	1071.31	29.707	0.93714	0.5794										
363.15	3089.12	106.062	0.77773	0.5794	363.15	1389.19	40.851	0.90805	0.5794	363.15	567.79	15.734	0.96363	0.5794
363.15	2407.14	77.169	0.83294	0.5794	363.15	1037.71	29.722	0.93229	0.5794	363.15	417.23	11.447	0.97325	0.5794
363.15	1841.21	56.147	0.87565	0.5794	363.15	769.59	21.625	0.95029	0.5794					
353.15	2939.27	106.116	0.76057	0.5794	353.15	1340.89	40.872	0.90085	0.5794	353.15	550.74	15.742	0.96069	0.5794
353.15	2305.51	77.208	0.81995	0.5794	353.15	1003.89	29.737	0.92698	0.5794	353.15	405.05	11.453	0.97111	0.5794
353.15	1771.60	56.175	0.86597	0.5794	353.15	745.66	21.636	0.94635	0.5794					
343.15	2786.02	106.169	0.74155	0.5794	343.15	1292.07	40.892	0.89290	0.5794	343.15	533.63	15.749	0.95749	0.5794
343.15	2202.15	77.247	0.80561	0.5794	343.15	969.77	29.752	0.92111	0.5794	343.15	392.84	11.459	0.96880	0.5794
343.15	1700.98	56.203	0.85525	0.5794	343.15	721.61	21.647	0.94203	0.5794					
333.15	2628.88	106.223	0.72037	0.5794	333.15	1242.63	40.912	0.88407	0.5794	333.15	516.42	15.757	0.95395	0.5794
333.15	2096.64	77.285	0.78964	0.5794	333.15	935.29	29.767	0.91457	0.5794	333.15	380.55	11.464	0.96619	0.5794
333.15	1629.14	56.231	0.84330	0.5794	333.15	697.33	21.657	0.93720	0.5794					
323.15	2466.76	106.276	0.69651	0.5794	323.15	1192.48	40.933	0.87421	0.5794	323.15	499.11	15.765	0.95002	0.5794
323.15	1988.62	77.324	0.77174	0.5794	323.15	900.44	29.782	0.90728	0.5794	323.15	368.22	11.470	0.96332	0.5794
323.15	1556.12	56.259	0.83001	0.5794	323.15	672.89	21.668	0.93188	0.5794					
313.15	2299.01	106.330	0.66953	0.5794	313.15	1141.43	40.953	0.86308	0.5794	313.15	481.65	15.773	0.94560	0.5794
313.15	1877.46	77.363	0.75149	0.5794	313.15	865.14	29.796	0.89911	0.5794	313.15	355.83	11.476	0.96016	0.5794
313.15	1481.34	56.288	0.81495	0.5794	313.15	648.19	21.679	0.92587	0.5794					
303.15	1089.31	40.974	0.85041	0.5794	303.15	623.14	21.690	0.91899	0.5794	303.15	343.31	11.482	0.95645	0.5794
303.15	829.27	29.811	0.88981	0.5794	303.15	464.03	15.781	0.94058	0.5794					
373.15	3246.55	121.073	0.78347	0.4320	373.15	803.84	24.686	0.95142	0.4320	373.15	233.46	6.917	0.98611	0.4320
373.15	2523.43	88.091	0.83697	0.4320	373.15	592.79	17.961	0.96434	0.4320	373.15	170.53	5.033	0.99001	0.4320
373.15	1927.02	64.093	0.87846	0.4320	373.15	435.61	13.068	0.97399	0.4320	373.15	124.41	3.662	0.99269	0.4320
373.15	1452.47	46.633	0.91005	0.4320	373.15	319.20	9.507	0.98094	0.4320	373.15	90.68	2.664	0.99452	0.4320
373.15	1084.26	33.929	0.93371	0.4320										
363.15	3094.73	121.134	0.76701	0.4320	363.15	1403.51	46.656	0.90313	0.4320	363.15	575.46	17.969	0.96145	0.4320
363.15	2420.58	88.135	0.82455	0.4320	363.15	1049.93	33.934	0.92891	0.4320	363.15	423.19	13.074	0.97178	0.4320
363.15	1856.43	64.125	0.86915	0.4320	363.15	779.52	24.698	0.94757	0.4320					
353.15	2939.87	121.195	0.74889	0.4320	353.15	1354.11	46.679	0.89557	0.4320	353.15	558.16	17.978	0.95848	0.4320
353.15	2316.10	88.179	0.81089	0.4320	353.15	1015.38	33.951	0.92332	0.4320	353.15	410.80	13.081	0.96956	0.4320
353.15	1785.05	64.157	0.85896	0.4320	353.15	755.14	24.710	0.94345	0.4320					
343.15	2781.68	121.256	0.72887	0.4320	343.15	1304.18	46.703	0.88724	0.4320	343.15	540.74	17.987	0.95514	0.4320
343.15	2209.74	88.223	0.79580	0.4320	343.15	980.58	33.968	0.91720	0.4320	343.15	398.37	13.087	0.96713	0.4320
343.15	1712.69	64.189	0.84774	0.4320	343.15	730.59	24.723	0.93891	0.4320					
333.15	2619.38	121.317	0.70659	0.4320	333.15	1253.62	46.726	0.87801	0.4320	333.15	523.22	17.996	0.95146	0.4320
333.15	2101.20	88.268	0.77904	0.4320	333.15	945.40	33.985	0.91038	0.4320	333.15	385.86	13.094	0.96442	0.4320
333.15	1639.12	64.222	0.83526	0.4320	333.15	705.87	24.735	0.93391	0.4320					

Table 1 (Continued)

T/K	P/kPa	ρ/kg·m^{-3}	Z	x_1	T/K	P/kPa	ρ/kg·m^{-3}	Z	x_1	T/K	P/kPa	ρ/kg·m^{-3}	Z	x_1
323.15	2451.66	121.378	0.68147	0.4320	323.15	1202.30	46.749	0.86769	0.4320	323.15	505.56	18.005	0.94733	0.4320
323.15	1990.02	88.312	0.76027	0.4320	323.15	909.80	34.002	0.90277	0.4320	323.15	373.29	13.100	0.96138	0.4320
323.15	1564.16	64.254	0.82131	0.4320	323.15	680.93	24.747	0.92833	0.4320					
313.15	1875.22	88.356	0.73891	0.4320	313.15	873.79	34.019	0.89427	0.4320	313.15	487.81	18.014	0.94278	0.4320
313.15	1487.42	64.286	0.80555	0.4320	313.15	655.74	24.760	0.92207	0.4320	313.15	360.67	13.107	0.95807	0.4320
313.15	1150.09	46.773	0.85608	0.4320										
303.15	1755.92	88.401	0.71437	0.4320	303.15	837.15	34.048	0.88428	0.4320	303.15	469.87	18.023	0.93760	0.4320
303.15	1408.59	64.318	0.78763	0.4320	303.15	630.24	24.772	0.91499	0.4320	303.15	347.95	13.113	0.95429	0.4320
303.15	1096.82	46.796	0.84295	0.4320										

Results and Discussion

The Burnett expansion was done only at 373.15 K, and the density values at other temperatures were obtained by combining the Burnett measurements with the isochoric measurements. Corrections were made for cell distortions with pressure and, more importantly, temperature (for isochors) and a host of other standard corrections given by Gupta.[2] Because significant physical adsorption was not observed, additional corrections were not needed. As a result, a total of 200 *PVTx* data points for the binary HFC-32 (1) + HFC-125 (2) mixture in the gaseous phase were obtained over the range of temperatures (303.15 to 373.15) K, at pressures up to 3.3 MPa, and at three different compositions of $x_1 = 0.8191$ ($w_1 = 0.6625$), $x_1 = 0.5794$ ($w_1 = 0.3738$), and $x_1 = 0.4320$ ($w_1 = 0.2479$), and the results are listed in Table 1. The data distributions are shown on a pressure−temperature plane in Figure 2, where the vapor pressure curves were calculated from the equation of state for both pure components.[3]

The deviations of the experimental *PVTx* data and other literature data from an equation of state for the mixtures[3] are shown in Figure 3. The present work can be well represented by the equation of state over the entire range within ±0.13% in pressure, and the comparative results are shown in Table 2. Although a slight positive systematic offset of about 0.06% was observed, the deviations (rms, aad) of our data are the smallest, and the data of Weber and Defibaugh[6] show similar positive deviations. Note that the distribution of the experimental data points of Zhang et al.,[4] Sato et al.,[5] and Kiyoura et al.[7] is relatively symmetrical but that relative large deviations are observed.

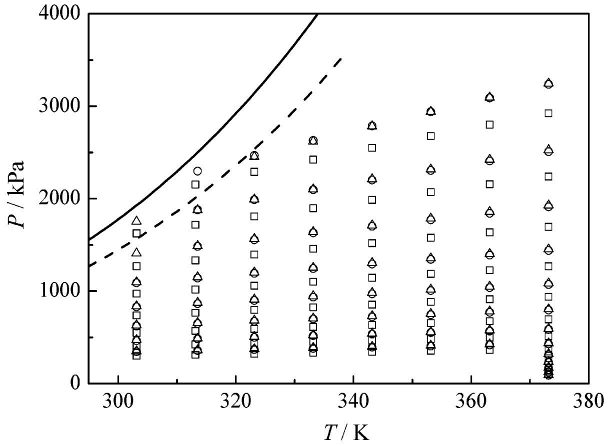

Figure 2. Experimental data distribution of the HFC-32 (1) + HFC-125 (2) system: □, $x_1 = 0.8191$; ○, $x_1 = 0.5794$; Δ, $x_1 = 0.4320$; —, vapor pressures of HFC-32[3]; - - -, vapor pressures of HFC-125[3].

The experimental values of the second virial coefficient, B_m, and the third virial coefficient, C_m, were determined by fitting eq 2 to the respective isothermal data.

$$\frac{z-1}{\rho} = B_m + C_m\rho \tag{2}$$

where Z and ρ denote the compressibility factor and molar density, respectively. The results are listed in Table 3. Figures 4 and 5 show the temperature dependence of B_m and C_m values thus determined for the binary mixtures with different compositions. For the second virial coef-

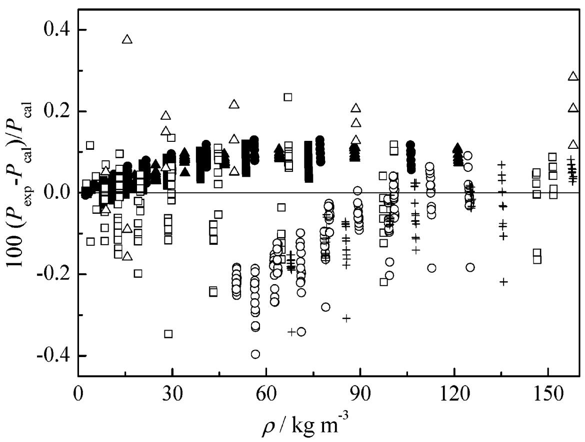

Figure 3. Deviations of experimental *PVTx* data of HFC-32 (1) + HFC-125 (2) from an equation of state for the mixture[3]: ■, $x_1 = 0.8191$; ●, $x_1 = 0.5794$; ▲, $x_1 = 0.4320$; □, Zhang et al.;[4] ○, Sato et al.;[5] Δ, Weber and Defibaugh;[6] +, Kiyoura et al.[7]

Table 2. Pressure Deviations of Experimental Data from the Equation of State in Reference 3 for the HFC-32 + HFC-125 System

first author	$\delta_{a,rms}^a$ kPa	$\delta_{a,aad}^a$ kPa	$\delta_{r,rms}^a$ %	$\delta_{r,aad}^a$ %
present work	1.255	0.869	0.067	0.056
Weber[6]	4.006	2.847	0.182	0.154
Kiyoura[7]	2.992	2.494	0.110	0.087
Sato[5]	3.863	3.326	0.152	0.123
Zhang[4]	1.650	1.125	0.096	0.076

[a] $$\delta_{a,rms} = \sqrt{\sum_{i=1}^{n}(P_{i,exptl} - P_{i,calcd})^2/(n-1)};$$

$$\delta_{r,rms} = \sqrt{\sum_{i=1}^{n}\left(\frac{P_{i,exptl} - P_{i,calcd}}{P_{i,calcd}}\right)^2/(n-1)};$$

$$\delta_{a,aad} = \sum_{i=1}^{n}|P_{i,exptl} - P_{i,calcd}|/n;\ \delta_{r,aad} = \sum_{i=1}^{n}\left|\frac{P_{i,exptl} - P_{i,calcd}}{P_{i,calcd}}\right|/n$$

Table 3. Second and Third Virial Coefficients for the HFC-32 + HFC-125 System

T/K	B_m/cm^3·mol^{-1}	C_m/cm^6·mol^{-2}
	$x_1 = 0.8191$	
303.15	−294.0	25 580
313.15	−268.9	22 900
323.15	−247.6	21 410
333.15	−228.3	19 620
343.15	−211.1	18 000
353.15	−195.4	16 330
363.15	−181.2	14 800
373.15	−168.5	13 610
	$x_1 = 0.5794$	
303.15	−308.0	26 500
313.15	−281.7	23 600
323.15	−258.6	21 490
333.15	−238.6	19 990
343.15	−220.5	18 400
353.15	−204.3	17 000
363.15	−189.3	15 430
373.15	−175.8	14 160
	$x_1 = 0.4320$	
303.15	−317.8	26 000
313.15	−291.2	24 000
323.15	−268.0	22 480
333.15	−247.5	21 120
343.15	−228.9	19 600
353.15	−212.2	18 240
363.15	−196.8	16 800
373.15	−182.9	15 560

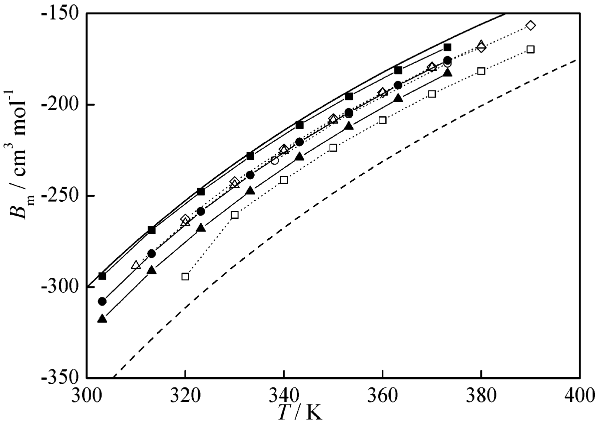

Figure 4. Temperature dependence of the experimental second virial coefficients for the HFC-32 (1) + HFC-125 (2) system, B_m: ■, $x_1 = 0.8191$; ●, $x_1 = 0.5794$; ▲, $x_1 = 0.4320$; □, $x_1 = 0.3670$;[7] ○, $x_1 = 0.5460$;[6] Δ, $x_1 = 0.7000$;[4] ◇, $x_1 = 0.7760$;[5] —, smoothing functions for HFC-32 by Dymond et al.;[8] - - -, smoothing functions for HFC-125 by Dymond et al.[8]

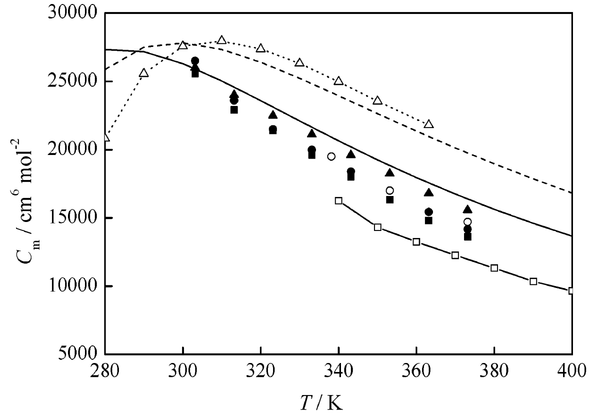

Figure 5. Temperature dependence of the experimental third virial coefficients for the HFC-32 (1) + HFC-125 (2) system, C_m: ■, $x_1 = 0.8191$; ●, $x_1 = 0.5794$; ▲, $x_1 = 0.4320$; ○, $x_1 = 0.5460$;[6] □, Sato et al.[10] (HFC-32); Δ, Boyes and Weber[11] (HFC-125); —, Yokozeki et al.[9] (HFC-32); - - -, Yokozeki et al.[9] (HFC-125).

ficient, the smoothing functions of the Dymond et al. compilation[8] for pure HFC-32 and HFC-125 are also plotted in Figure 4. The results clearly follow a common temperature trend with data from the literature, and reasonable results were found between different compositions from various sources. In Figure 5, our experimental data are in a certain agreement with those reported by Weber and Defibaugh[6] because the uncertainty of the third virial coefficient is very large. To our knowledge, the data points of C_m should be located between the two data lines of pure compounds in that temperature range, but the present data and Weber's data are both below the two lines; the smoothing curves were obtained from the Stockmayer potential calculation.[9] We do not have an explanation for this disagreement because of the large uncertainties in the third virial coefficients of both pure components and mixtures.

The values of B_m and C_m, along with the values of the virial coefficients for the pure compounds, were used to derive the cross virial coefficients. The cross second virial coefficients were calculated from the expression

$$B_{12} = \frac{B_m - {x_1}^2 B_{11} - {x_2}^2 B_{22}}{2 x_1 x_2} \tag{3}$$

where x_i denotes the mole fraction of component i in the mixture and $x_2 = 1 - x_1$. The B_{12} values for each temperature were averaged. Likewise, the determination of C_{112} and C_{122} for the binary mixture can be achieved as average values by combining data for each temperature. The equation

$$C_m = (x_1)^3 C_{111} + (x_2)^3 C_{222} + 3(x_1)^2 x_2 C_{112} + 3 x_1 (x_2)^2 C_{122} \tag{4}$$

was used to obtain two values of C_{112} and C_{122}. The results are shown in Table 4. The estimated standard uncertainties

Table 4. Cross Second and Third Virial Coefficients for the HFC-32 (1) + HFC-125 (2) System

T/K	B_{11}[a] cm^3·mol^{-1}	B_{12} cm^3·mol^{-1}	B_{22}[a] cm^3·mol^{-1}	C_{111}[b] cm^6·mol^{-2}	C_{112} cm^6·mol^{-2}	C_{122} cm^6·mol^{-2}	C_{222}[b] cm^6·mol^{-2}
303.15	−292.0	−298.6	−356.0	25 923	26 076	26 264	27 726
313.15	−267.7	−271.6	−328.5	24 580	20 398	25 972	27 074
323.15	−246.0	−249.6	−303.8	23 112	18 116	24 057	26 047
333.15	−226.4	−230.4	−281.5	21 628	15 726	23 585	24 828
343.15	−208.7	−213.4	−261.3	20 188	13 783	22 297	23 533
353.15	−192.6	−198.2	−242.8	18 824	11 632	21 716	22 230
363.15	−177.9	−184.1	−226.0	17 551	9570	20 599	20 960
373.15	−164.5	−171.9	−210.5	16 373	8320	19 282	19 745

[a] The second virial coefficients of pure HFC-32 and HFC-125 were obtained from the smoothing functions by Dymond et al.[8] [b] The third virial coefficients of pure compounds are calculated from the Stockmayer potential.[9]

are ±1 $\text{cm}^3\cdot\text{mol}^{-1}$ for B_m, ±3 $\text{cm}^3\cdot\text{mol}^{-1}$ for B_{12}, ±500 $\text{cm}^6\cdot\text{mol}^{-2}$ for C_m, and ±4000 $\text{cm}^6\cdot\text{mol}^{-2}$ for C_{112} and C_{122}. To our knowledge, there is only one published paper[6] that can offer the cross second virial coefficients for the HFC-32 + HFC-125 mixture. Surprisingly, the only three data points of the cross second virial coefficients reported by Weber and Defibaugh[6] are very similar to our data. The differences are merely 0.8 $\text{cm}^3\cdot\text{mol}^{-1}$ at 353.15 K and 0.7 $\text{cm}^3\cdot\text{mol}^{-1}$ at 373.15 K; the value at 338.15 K could not be compared because there were no data available in the present work at that temperature. The cross third virial coefficients are not compared in this paper because there are no other available data for C_{112} and C_{122} for the HFC-32 + HFC-125 mixture.

Conclusions

A total of 200 *PVTx* properties for the binary HFC-32 + HFC-125 mixture in the gaseous phase were obtained using the Burnett apparatus along three isopleths ($x_1 = 0.8191$, $x_1 = 0.5794$, and $x_1 = 0.4320$), and our experimental results are in excellent agreement with the calculations from an equation of state for the mixture.[3] The second and third virial coefficients for the mixtures, along with the cross virial coefficients, were derived, and good consistency was found between the present virial coefficients and those reported in the literature.

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