Gaseous *PVT* Behavior of 1,1,1,2,3,3,3-Heptafluoropropane

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The gaseous *PVT* properties of 1,1,1,2,3,3,3-heptafluoropropane (HFC-227ea) were measured at temperatures from 318.15 K to 348.15 K using the Burnett−isochoric coupled method and at 330.15 K and 380.15 K using the Burnett expansion method, respectively. The maximum uncertainties of the measurements were estimated to be within ±1.5 kPa for pressure and within ±5 mK for temperature. A Virial equation for HFC-227ea was developed. The purity of the HFC-227ea sample used in the present measurements was 99.9 mol %.

Introduction

1,1,1,2,3,3,3-Heptafluoropropane (HFC-227ea), which is chlorine-free, could be considered as a possible alternative refrigerant. It is intended as a potential alternative for CFC12 and CFC114 for units with high condensing temperatures, and blends containing HFC-227ea are potential alternatives to HCFC22 and R502. It can be used in fire suppression, sterilization, and propellant applications.

There are limited data of gaseous pressure−volume−temperature (*PVT*) properties of HFC-227ea published in the literature. Pátek et al.[1] measured the gaseous *PVT* properties with a Burnett apparatus at 393 K and 423 K; Shi et al.[2] measured 141 *PVT* data in the gaseous phase with Burnett−isochoric methods. In this paper, a total of 97 gaseous *PVT* data for HFC-227ea were measured using the Burnett−isochoric coupled method at temperatures from 318.15 K to 348.1 5 K and the Burnett method at 330.15 K and 380.15 K.

Experimental Section

Reagent. The sample of HFC-227ea was obtained from Zhejiang Chemical Industry Research Institute, with a stated purity of 99.9 mol %. It was used without further purification.

Apparatus. A schematic diagram of the apparatus used in this work is given in Figure 1. It includes a cell system, a thermostatic bath, a temperature-measurement and control system, a pressure-measurement system, and a vacuum system. This apparatus is the same as the one described previously except for the cell system,[3] and it will be introduced briefly here and any modification will be noted.

The thermostatic bath has two glass windows with inner dimensions (350 × 350 × 500) mm^3. The temperature can be varied from (233 to 453) K. Its uncertainty is ±2 mK. The temperature measurements are made with a 4-lead 25-Ω platinum resistance thermometer with an uncertainty of ±2 mK (ITS-90), which was calibrated by the water's triple point temperature before the experiment, and a HP34970A data acquisition/switch unit with an uncertainty of less than ±1 mK. The overall temperature uncertainty is about ±5 mK. The temperature of the thermostatic bath is controlled by a personal computer, which controls the electric power of the heaters on the basis of an incremental digital PID algorithm.

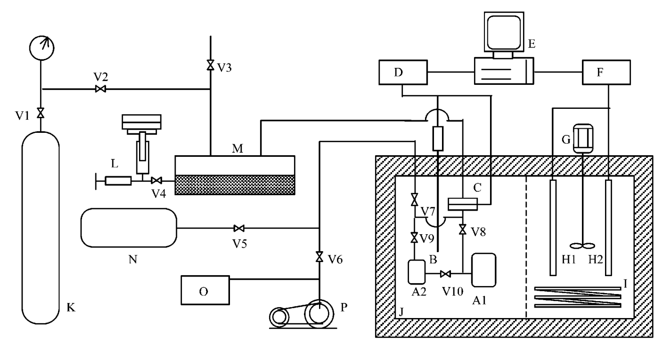

Figure 1. Experimental apparatus: (A1) sample cell; (A2) expansion cell; (B) platinum resistance thermometer; (C) differential pressure detector; (D) HP34970A data acquisition/switch unit; (E) personal computer; (F) silicon-controlled switch; (G) stirrer; (H1, H2) heaters; (I) cooler; (J) thermostatic bath; (K) nitrogen gas; (L) oil-piston type dead-weight pressure gauge; (M) oil−gas separator; (N) sample bottle; (O) vacuum gauge; (P) vacuum pump; (V1 to V10) valves.

Table 1. Experimental Results of Nitrogen Using *N* = 1.3885

T/K	*P*/kPa	ρ/kg·m^{-3}	ρ_{cal}/kg·m^{-3}	$100(\rho - \rho_{cal})/\rho$
318.15	1909.12	20.222	20.229	−0.032
318.15	1374.81	14.564	14.569	−0.034
318.15	990.03	10.488	10.492	−0.046
318.15	713.39	7.557	7.557	0.002
318.15	514.07	5.445	5.442	0.052
318.15	370.26	3.922	3.920	0.055
318.15	266.46	2.822	2.823	−0.023
318.15	191.91	2.032	2.033	−0.027
318.15	138.22	1.464	1.464	−0.024

The pressure-measurement system includes an oil-piston type dead-weight pressure gauge (Xi′an Instrument, China; YS-60), a differential pressure detector (Xi′an Instrument, China; 1151DP), and a mercury atmosphere gauge (Ningbo Instrument, China; DYM-1). The accuracy of the oil-piston type dead-weight pressure gauge is 0.02% in the range from (0.1 to 6.0) MPa, and its maximum uncertainty is 1.2 kPa. The accuracy of the differential pressure detector is 0.2% in the range from (0 to 50) kPa, its maximum uncertainty is 0.1 kPa, and that of the mercury atmosphere gauge is ±50 Pa. The overall maximum experimental uncertainty

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10.1021/je025582+ CCC: $25.00
Published on Web 02/20/2003

Table 2. Experimental Results of HFC-227ea

T/K	P/kPa	ρ/kg·m^{-3}	ρ_{cal}/kg·m^{-3}	$100[(\rho - \rho_{cal})/\rho]$	T/K	P/kPa	ρ/kg·m^{-3}	ρ_{cal}/kg·m^{-3}	$100[(\rho - \rho_{cal})/\rho]$
345.15	1358.0	110.79	110.76	0.027	318.15	312.0	21.61	21.57	0.201
342.15	1333.9	110.80	110.74	0.056	345.15	250.2	15.46	15.46	0.034
339.15	1310.5	110.84	110.85	−0.009	342.15	248.2	15.46	15.48	−0.117
345.15	1074.6	79.79	79.72	0.093	339.15	245.7	15.47	15.48	−0.065
342.15	1059.6	79.80	79.79	0.019	336.15	243.4	15.47	15.48	−0.062
339.15	1044.6	79.83	79.87	−0.056	333.15	240.7	15.48	15.46	0.122
336.15	1029.1	79.86	79.92	−0.074	330.15	238.5	15.50	15.48	0.073
333.15	1013.2	79.91	79.95	−0.047	327.15	236.2	15.51	15.50	0.086
330.15	998.1	79.97	80.07	−0.127	324.15	234.2	15.53	15.53	−0.001
327.15	982.1	80.04	80.12	−0.102	321.15	232.2	15.54	15.56	−0.087
345.15	826.2	57.46	57.40	0.104	318.15	230.1	15.57	15.58	−0.119
342.15	815.0	57.47	57.35	0.222	345.15	182.4	11.13	11.13	0.018
339.15	804.6	57.49	57.36	0.227	342.15	181.1	11.14	11.16	−0.235
336.15	795.1	57.52	57.45	0.115	339.15	179.3	11.14	11.16	−0.160
333.15	784.6	57.55	57.47	0.145	336.15	177.7	11.14	11.16	−0.159
330.15	774.3	57.59	57.51	0.141	333.15	175.9	11.15	11.16	−0.084
327.15	763.9	57.65	57.55	0.164	330.15	174.3	11.16	11.17	−0.060
324.15	754.0	57.71	57.65	0.094	327.15	172.6	11.17	11.17	0.007
321.15	744.1	57.77	57.76	0.031	324.15	170.9	11.18	11.17	0.087
318.15	734.2	57.85	57.88	−0.053	321.15	169.3	11.20	11.18	0.116
345.15	624.2	41.39	41.44	−0.130	318.15	167.7	11.21	11.19	0.172
342.15	616.9	41.39	41.43	−0.080	345.15	132.5	8.02	8.02	0.003
339.15	609.6	41.40	41.42	−0.032	342.15	131.3	8.02	8.02	−0.006
336.15	602.5	41.42	41.43	−0.014	339.15	130.1	8.02	8.03	−0.049
333.15	595.3	41.45	41.43	0.047	336.15	129.0	8.03	8.03	−0.060
330.15	588.3	41.48	41.45	0.062	333.15	128.0	8.03	8.04	−0.158
327.15	581.5	41.52	41.50	0.038	330.15	126.8	8.04	8.05	−0.140
324.15	574.9	41.56	41.56	0.000	327.15	125.7	8.04	8.06	−0.133
321.15	568.0	41.61	41.61	0.008	324.15	124.4	8.05	8.05	0.021
318.15	561.3	41.67	41.67	−0.020	321.15	123.2	8.06	8.05	0.102
345.15	464.0	29.81	29.82	−0.033	318.15	122.2	8.07	8.07	0.039
342.15	459.3	29.81	29.83	−0.070	330.15	803.6	60.09	60.24	−0.250
339.15	454.4	29.82	29.84	−0.051	330.15	611.2	43.28	43.33	−0.119
336.15	449.1	29.83	29.81	0.082	330.15	457.7	31.17	31.21	−0.128
333.15	444.3	29.85	29.82	0.094	330.15	338.6	22.45	22.46	−0.079
330.15	439.5	29.87	29.84	0.102	330.15	248.3	16.17	16.16	0.068
327.15	434.8	29.90	29.86	0.131	330.15	181.5	11.64	11.65	−0.034
324.15	430.2	29.93	29.90	0.111	330.15	132.0	8.39	8.39	0.004
321.15	425.5	29.97	29.93	0.141	380.15	2832.9	286.34	285.85	0.170
318.15	421.0	30.01	29.97	0.121	380.15	2446.1	206.22	206.50	−0.137
345.15	341.9	21.47	21.47	−0.006	380.15	2004.6	148.52	148.55	−0.020
342.15	338.6	21.47	21.49	−0.040	380.15	1582.9	106.97	106.99	−0.018
339.15	334.9	21.48	21.46	0.064	380.15	1215.9	77.04	76.97	0.084
336.15	331.9	21.49	21.49	−0.033	380.15	918.3	55.48	55.51	−0.049
333.15	328.6	21.50	21.51	−0.041	380.15	683.0	39.96	39.94	0.048
330.15	325.2	21.51	21.51	0.020	380.15	503.4	28.78	28.75	0.083
327.15	321.9	21.53	21.53	0.032	380.15	369.5	20.73	20.76	−0.142
324.15	318.6	21.56	21.53	0.102	380.15	269.4	14.93	14.95	−0.157
321.15	315.4	21.58	21.56	0.110					

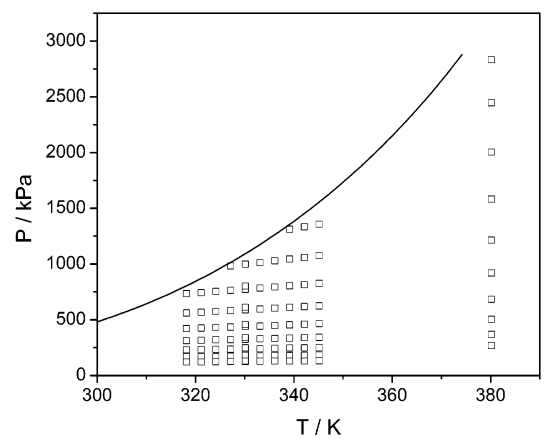

Figure 2. Distribution of gaseous phase *PVT* measurements for HFC-227ea.

in the pressure measurements of this system can be estimated to be within ±1.5 kPa, and at 3.0 MPa it was about 0.75 kPa. The uncertainty in density values is estimated to be ±0.15%.

The cell system is composed of two heavy-walled vessels, a sample cell (A1) and an expansion sell (A2), made of 1Cr18Ni9Ti stainless steel, and an expansion valve (V10). Before an experiment, the cells, pipes, and valves are rinsed with acetone to remove any residue from previous experiments and placed under vacuum to 1×10^{-4} Pa.

Procedure. A Burnett−isochoric coupled method similar to that of Hall et al.[4] was used in this measurement. Before an experiment, the cells were rinsed and placed under vacuum. The relatively high temperature, 345.15 K, was chosen as a base, and the sample gas was filled in the sample cell controlled at a slightly lower pressure than the saturated vapor pressure at the same temperature. After equilibrium was established, the temperature and pressure of the sample were measured. The temperature was then lowered in successive steps to the minimum desired value; that is, an isochoric run was made. Then the temperature was raised to 345.15 K and a Burnett expansion was made to the next pressure. After that, the process was repeated until the expansion pressure was low enough.

Calibration. The Burnett cell constant, which is the volume ratio $N = (V_1 + V_2)/V_1$, can be determined from the pressure ratio with $N = \lim_{P_i \to 0}(P_{i-1}/P_i)$. The apparatus constant is determined to be =1.3885 ± 0.0001 from the calibration measurements with high purity nitrogen with a stated purity of 99.999 mol % (Nan Jing Special Gas Factory, China). The experimental densities of nitrogen calculated from the expansion pressure using $N = 1.3885$

Table 3. Coefficients of Eq 2

B_0/m^3·kg^{-1}	B_1/m^3·kg^{-1}	B_2/m^3·kg^{-1}	B_3/m^3·kg^{-1}	B_4/m^3·kg^{-1}
5.236 865 4 × 10^{-2}	−0.187 334 9	0.236 627 9	−0.111 324 0	8.933 554 3 × 10^{-3}
B_5/m^3·kg^{-1}	C_0/m^6·kg^{-2}	C_1/m^6·kg^{-2}	D_0/m^9·kg^{-3}	D_0/m^9·kg^{-3}
−1.411 609 9 × 10^{-3}	5.314 908 2 × 10^{-6}	−3.830 939 8 × 10^{-6}	−6.136 459 8 × 10^{-10}	8.503 745 0 × 10^{-10}

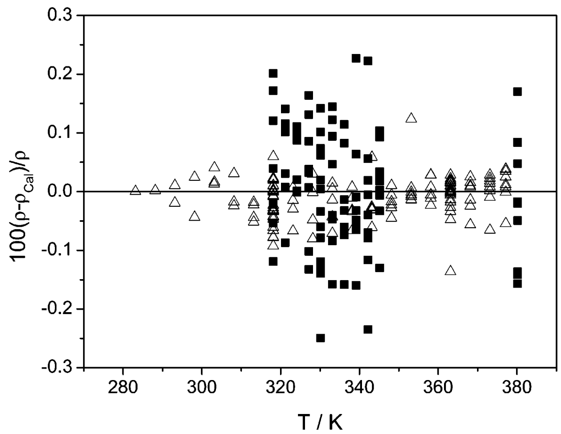

Figure 3. Density deviations of measured *PVT* data for HFC-227ea from values calculated using eq 2: (■) this work; (□) Lin Shi et al.[2]

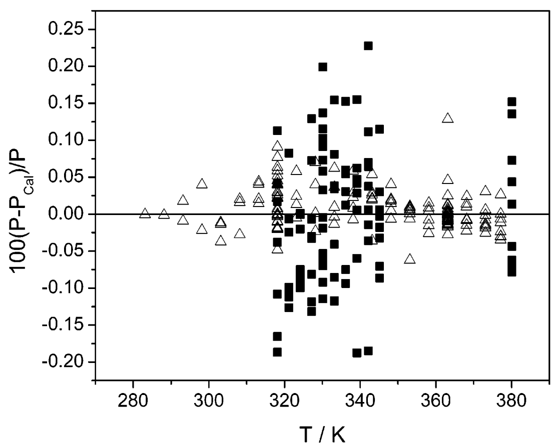

Figure 4. Pressure deviations of measured *PVT* data for HFC-227ea from values calculated using eq 2: (■) this work; (□) Lin Shi et al.[2]

Table 4. Values of Virial Coefficient *B*

no.	*T*/K	*B*/cm^3·mol^{-1} this work	*B*/cm^3·mol^{-1} calc from eq of Shi[2]
1	318.15	−560.3	−558.6
2	323.15	−538.1	−536.5
3	328.15	−517.0	−515.7
4	333.15	−497.0	−496.1
5	338.15	−478.1	−477.5
6	343.15	−460.1	−459.9
7	348.15	−443.0	−443.1
8	380.15	−350.9	−352.2

were listed in Table 1. The average absolute deviation of experimental densities from the values calculated using the equation of state for nitrogen[5] is only 0.003%.

Measured *PVT* Data and Discussion

A total of 97 *PVT* data for HFC-227ea have been measured. Burnett method measurements were made at 345.15 K, at 330.15 K, and at 380.15 K. Isochoric method measurements were made at temperatures from 318.15 K to 342.15 K. Because the volume of the vessels underwent a small change at different temperatures, the densities of the isochores were amended according to eq 1:

$$\rho_{i,v}(T) = \frac{\rho_i}{1 + 3\alpha(T - T_0)} \qquad (1)$$

where α is the average linear expansibility; for 1Cr18Ni9Ti $\alpha = 16.6 \times 10^6$ K^{-1} between 293.15 K and 373.15 K.[6] The results were listed in Table 2. Figure 2 shows the location in pressure and temperature of the present data.

On the basis of the present data and the results of Shi,[2] a virial equation was correlated:

$$\frac{P}{\rho RT} = 1 + B\rho + C\rho^2 + D\rho^3 \qquad (2)$$

where

$$B = B_0 + B_1 T_r^{-1} + B_2 T_r^{-2} + B_3 T_r^{-3} + B_4 T_r^{-6} + B_5 T_r^{-8}$$

$$C = C_0 T_r^{-5} + C_1 T_r^{-6}$$

$$D = D_0 + D_1 T_r$$

$$T_r = T/T_c$$

the critical temperature $T_c = 375.04$ K,[7] the gas constant $R = 48.9001$ J·K^{-1}·kg^{-1}, and the molecular weight is 170.03 g·mol^{-1}. In this equation, the units of T, P, and ρ are kelvin, kilopascal, and kilogram per cubic meter, respectively. The coefficients of eq 2 were listed in Table 3, and the values of virial coefficient B were given in Table 4. The temperature range of eq 2 is from 283.15 K to 380.15 K, and the density range is up to 286 kg·m^{-3}. The maximum and average absolute pressure deviations of this work from eq 2 were 0.23% and 0.073%, respectively, and 0.13% and 0.021% for the results of Lin Shi et al.[2] The maximum and average absolute density deviations of this work from eq 2 were 0.25% and 0.083%, respectively, and 0.057% and 0.026% for the results of Lin Shi et al.[2] The deviations for density and pressure were shown in Figures 3 and 4, respectively. Obviously, the deviations of our data are higher than those produced by the data of Shi et al.,[2] the main reason being that the accuracy of the pressure-measurement apparatus of Shi[2] is higher than that of ours.

Conclusion

A total of 97 gaseous phase *PVT* data for HFC-227ea were measured at temperatures from 318.15 K to 348.15 K using the Burnett−isochoric coupled method and at 330.15 K and at 380.15 K using the Burnett expansion method, respectively. The maximum uncertainties of these measurements were estimated to be within ±1.5 kPa for pressure and within ±5 mK for temperature. A virial equation for HFC-227ea was developed, and the results calculated using this equation agree well with the experimental data.

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Received for review July 12, 2002. Accepted January 19, 2003. This work is supported by the National Science Foundation of China (Grant No. 59976040) and the Youth Foundation of the University of Science and Technology of China.

JE025582+