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PVT Property Measurements for Difluoromethane

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Experimental vapor pressures and *PVT* data of an important alternative refrigerant, difluoromethane (HFC-32), have been measured by means of a constant-volume method coupled with expansion procedures. Sixty-nine *PVT* data were measured along 10 isochores in a range of temperatures from 322 to 420 K, at pressures from 3.3 to 9.8 MPa, and at densities from 111 to 850 kg·m^{-3}. Twenty-one vapor pressures were also measured at temperatures from 320 K to the critical temperature. The uncertainties of the temperature and pressure measurements are within ±7 mK and ±2 kPa, respectively, while the uncertainty of the density values is within ±0.1%. The purity of the sample used is 99.998 mass %. On the basis of the measurements along each isochore, six saturation densities were determined and the critical pressure was determined by correlating the vapor-pressure measurements. The second and third virial coefficients for temperatures from 340 to 420 K have also been determined.

Introduction

A hydrofluorocarbon, difluoromethane (HFC-32), has zero ozone-depletion potential because it contains no chlorine atoms. It has not been applied to engineering practice due to its flammability, but the expected improvement in performance of a refrigeration system by applying this refrigerant makes it an attractive refrigerant for the replacement of chlorodifluoromethane (HCFC-22).

Information about the thermodynamic properties of HFC-32 is essential for its application as a working fluid in refrigeration systems. Therefore, *PVT* data, vapor pressures, critical pressure, and second and third virial coefficients are presented in this paper.

Experiments

The isochoric method coupled with expansion procedures was used for measuring vapor pressures and *PVT* properties. The apparatus and experimental procedures originally reported by Takaishi et al. (*1*, *2*) have successfully been applied to our series of thermodynamic property measurements of different binary refrigerant mixtures and of pure refrigerants. Some of the recent measurements performed by the present apparatus include the *PVTx* measurements for 1-chloro-1,1-difluoroethane (HCFC-142b) + chlorodifluoromethane (HCFC-22) (*3*) and 1,1-difluoroethane (HFC-152a) + 1,1,2,2-tetrafluoroethane (HFC-134) (*4*) and the *PVT* property measurements for 1-chloro-1,1-difluoroethane (HCFC-142b) (*5*), 1,1-difluoroethane (HFC-152a) (*6*), and 1,1,2,2-tetrafluoroethane (HFC-134) (*7*).

The experimental apparatus is composed of a sample cell, an expansion cell, a differential pressure detector, a platinum resistance thermometer calibrated on ITS-90, a thermostated bath, temperature control/measuring devices, and pressure measuring instruments. The inner volumes of the sample cell and expansion cell have carefully been calibrated by using pure water: they are about 283 and 55 cm^3, respectively. The temperature in the thermostated bath filled with silicone oil was controlled within ±2 mK. After establishing thermal equilibrium between the sample and the heat transfer oil in the bath and confirming the pressure remained constant, the temperature and the pressure of the sample fluid were measured along the prescribed isochore. To obtain another isochore, we expanded the sample fluid in the single phase to the expansion cell after a series of measurements along the initial isochore.

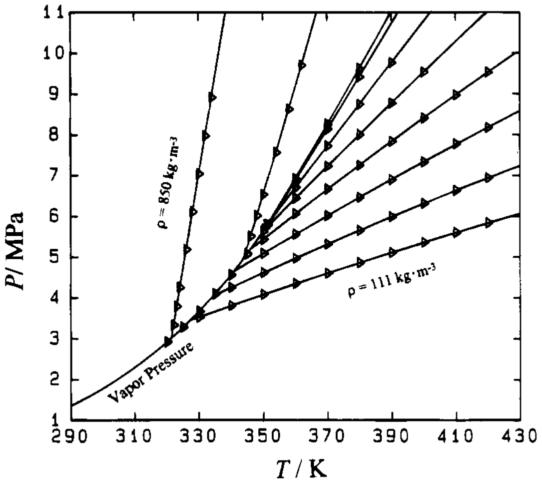

Figure 1. Distribution of the present measurements on the *P−T* plane.

Results

Sixty-nine *PVT* data along 10 isochores at temperatures from 322 to 420 K, pressures from 3.3 to 9.8 MPa, and densities from 111 to 850 kg·m^{-3} were measured. Figure 1 shows the distribution of the data in a pressure−temperature plane. Twenty-one vapor pressures from 320 K to the critical temperature were also measured. Six saturated liquid/vapor densities were determined on the basis of the present *PVT* property data and vapor pressures measured. All measured data are tabulated in Tables 1−3 with temperatures on ITS-90.

The experimental errors of the present *PVT* and vapor-pressure measurements are estimated to be not greater than ±7 mK in temperature, ±2 kPa in pressure, and ±0.1% in density. Saturated liquid/vapor densities are estimated to be accurate within ±0.5% including the

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Table 1. Measured *PVT* Properties of HFC-32

ϱ/(kg·m^{-3})	*T*/K	*P*/MPa	ϱ/(kg·m^{-3})	*T*/K	*P*/MPa
444.60	351.280	5.7863	221.57	380.000	7.2504
444.39	360.000	6.9158	221.46	390.000	7.8321
444.15	370.000	8.2562	221.35	400.000	8.4056
443.91	380.000	9.6157	221.23	410.000	8.9719
			221.12	420.000	9.5315
353.07	360.000	6.6991			
352.88	370.000	7.7225	176.31	350.000	5.0818
352.70	380.000	8.7456	176.22	360.000	5.5556
352.51	390.000	9.7626	176.13	370.000	6.0136
			176.04	380.000	6.4609
280.51	360.000	6.4361	175.96	390.000	6.8941
280.37	370.000	7.2233	175.87	400.000	7.3267
280.22	380.000	8.0032	175.78	410.000	7.7718
280.08	390.000	8.7720	175.69	420.000	8.1733
279.93	400.000	9.5320			
			140.14	340.000	4.2492
424.36	351.260	5.7855	140.07	350.000	4.6160
424.36	351.280	5.7879	140.01	360.000	4.9688
424.17	360.000	6.8679	139.94	370.000	5.3147
423.94	370.000	8.1349	139.87	380.000	5.6509
423.71	380.000	9.4142	139.80	390.000	5.9817
			139.73	400.000	6.3070
850.15	322.000	3.3303	139.66	410.000	6.6279
850.09	323.000	3.7901	139.59	420.000	6.9374
850.03	324.000	4.2540			
849.97	326.000	5.1807	111.39	330.000	3.5261
849.80	328.000	6.1101	111.34	340.000	3.8090
849.69	330.000	7.0398	111.29	350.000	4.0820
849.57	332.000	7.9758	111.23	360.000	4.3468
849.46	334.000	8.9149	111.18	370.000	4.6052
			111.13	380.000	4.8592
674.60	346.000	5.5055	111.07	390.000	5.1090
674.52	348.000	6.0132	111.02	400.000	5.3542
674.44	350.000	6.5282	110.96	410.000	5.5959
674.28	354.000	7.5658	110.90	420.000	5.8342
674.12	358.000	8.6261			
673.96	362.000	9.6994	424.81	351.260	5.7864
			424.81	351.280	5.7891
221.91	350.000	5.4290			
221.80	360.000	6.0567			
221.69	370.000	6.6638			

Table 2. Measured Vapor Pressures of HFC-32

T/K	*P*/MPa	*T*/K	*P*/MPa
320.000	2.9190	320.000	2.9198
330.000	3.6681	330.000	3.6682
340.000	4.5622	340.000	4.5614
350.000	5.6324		
351.240	5.7816	320.000	2.9198
		330.000	3.6692
325.000	3.2781		
335.000	4.0962	320.000	2.9195
345.000	5.0713	325.000	3.2780
351.240	5.7813	335.000	4.0962
		345.000	5.0723
330.000	3.6686	351.240	5.7836
340.000	4.5614		

Table 3. Densities of the Saturated Vapor (ϱ'') and Liquid (ϱ') of HFC-32[a]

ϱ/(kg·m^{-3})	*T*/K	
111.4	327.33	V
140.2	334.48	V
176.4	340.95	V
222.0	346.10	V
674.7	343.78	L
850.2	321.30	L

[a] V = vapor (ϱ''). L = Liquid (ϱ').

estimated uncertainty of ±0.4% due to a graphical extrapolation procedure employed. The purity of the sample which we used was 99.998 mass % according to the analysis performed by the manufacturer. No additional purification and analysis have been performed. The molar mass of HFC-32 is 52.024 g·mol^{-1}.

Discussion

Critical Pressure and Vapor-Pressure Measurements. Table 4 summarizes the critical parameters of HFC-32 reported in the literature *(8–13)* besides the present study. We used the critical temperature and density values determined by Kuwabara et al. *(10)* since they are the most reliable directly-measured values with the same sample as that used in the present work. We measured the vapor pressures along two isochores which are very close to the critical density, and then the critical pressure was determined as the vapor-pressure value at the critical temperature, i.e., $T_c = 351.255 \pm 0.010$ K *(10)*. The value of the critical pressure thus determined is

$$P_c = 5.7840 \pm 0.0025\ \text{MPa} \tag{1}$$

We developed a vapor-pressure correlation based on the present vapor-pressure measurements, experimental data reported by Qian et al. *(12)* and Weber and Goodwin *(14)*, and the normal-boiling-point temperature, $T_b = 221.4$ K, reported by Malbrunot et al. *(8)* using a functional form proposed by Wagner *(15)* with the aid of the least-squares fitting procedure accompanying the statistical analysis developed by Kubota et al. *(16)*:

$$\ln P_r = (1/T_r)\{A(1 - T_r) + B(1 - T_r)^{1.5} + C(1 - T_r)^3\} \tag{2}$$

with

$$P_r = P/P_c, \quad T_r = T/T_c$$

$$P_c = 5.7840\ \text{MPa}, \quad T_c = 351.255\ \text{K}$$

$$A = -7.435\,00, \quad B = 1.527\,26, \quad C = -2.909\,36$$

Figure 2 shows the pressure deviations of the reported vapor-pressure data from eq 2 which reproduces the present measurements and the data of Qian et al. *(12)*, Weber and Goodwin *(14)*, Defibaugh et al. *(17)*, and Baroncini et al. *(18)* within ± 0.2%. The data by Widiatmo et al. *(19)* and by Malbrunot et al. *(8)* show systematic deviations from the present correlation. Equation 2 is expected to be effective from 208 K to the critical temperature and to be reliable within ±0.15%.

Saturated-Liquid Densities. Figure 3 shows the deviations of the saturated-liquid densities from the correlation reported by Widiatmo et al. *(19)*. The saturated-liquid density measurements of this study are systematically higher than the correlation by 0.2% at 321 K and 0.4% at 344 K. The saturated-liquid densities reported by Kuwabara et al. *(10)* and Oliveira dn Wakeham *(20)* are within ±0.2% except a point near the critical temperature. The data of Defibaugh et al. *(17)* and Holcomb et al. *(21)* are also higher than the correlation of Widiatmo et al. by about 0.2%, and are in good agreement with the data of this study at the overlapping temperatures.

PVT Data. Figure 4 shows the pressure deviations of the *PVT* data from an equation of state developed by Piao et al. *(22)* in the vapor phase and the critical region. The Piao equation reproduces the present measurements and the data of Qian et al. *(12)* and Defibaugh et al. *(17)* within ±0.5%, while the *PVT* data of Malbrunot et al. *(8)* always show a significant scatter from the Piao equation. This fact suggests a lack of reliability in this earlier measurement.

Figure 5 shows the density deviations of the *PVT* data from the Piao equation in the liquid phase. The Piao equation reproduces the present measurements and the data of Qian et al. *(12)* and Defibaugh et al. *(17)* within ±0.5%, except in the critical region. Again, the *PVT* data

Table 4. Available Critical Parameters of HFC-32

ref	year	T_c/K	P_c/MPa	ϱ_c/(kg·m^{-3})	purity
8	1968	351.56 ± 0.20	5.83	430	99.95 mol %
9	1991	351.56 ± 0.02	5.814	429.61	
10	1992	351.255 ± 0.010		424 ± 1	99.998 mass %
11	1992	351.26 ± 0.02		427 ± 5	99.98 mol %
12	1992		5.780 ± 0.002		99.98 mass %
13	1993	351.26 ± 0.03	5.778 ± 0.003	425 ± 5	99.998 mass %
this work	1992		5.7840 ± 0.0025		99.998 mass %

Table 5. Second and Third Virial Coefficients

T/K	B/(cm^3·mol^{-1})	C/(dm^6·mol^{-2})	T/K	B/(cm^3·mol^{-1})	C/(dm^6·mol^{-2})
340.000	−207.9	0.016 25	390.000	−144.7	0.010 34
350.000	−191.4	0.014 31	400.000	−135.6	0.009 646
360.000	−178.2	0.013 25	410.000	−128.1	0.009 418
370.000	−166.2	0.012 26	420.000	−119.5	0.008 480
380.000	−155.2	0.011 33			

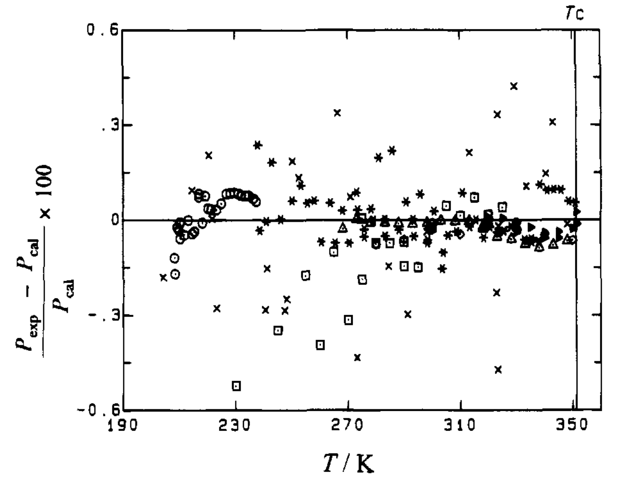

Figure 2. Deviation of vapor-pressure measurements from eq 2: (▸) this work, (◇) Qian et al. (*12*), (⊡) Widiatmo et al. (*19*), (⊙) Weber and Goodwin (*14*), (×) Malbrunot et al. (*8*), (▲) Defibaugh et al. (*17*), (*) Baroncini et al. (*18*).

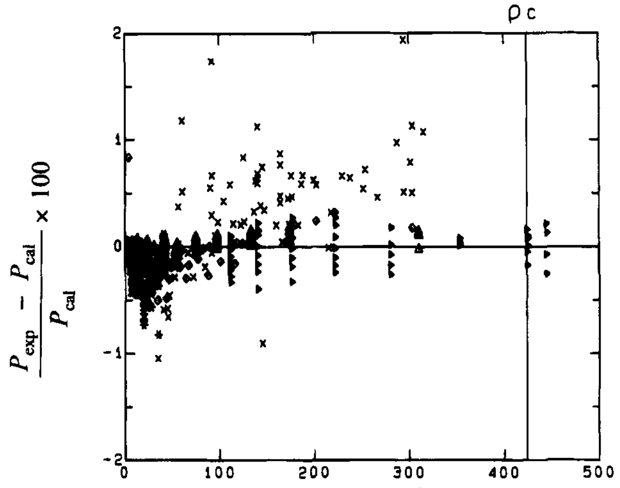

Figure 4. Pressure deviations from the equation of state by Piao et al. (*22*): (▸) this work, (◇) Qian et al. (*12*), (×) Malbrunot et al. (*8*), (▲) Defibaugh et al. (*17*), (*) Baroncini et al. (*18*).

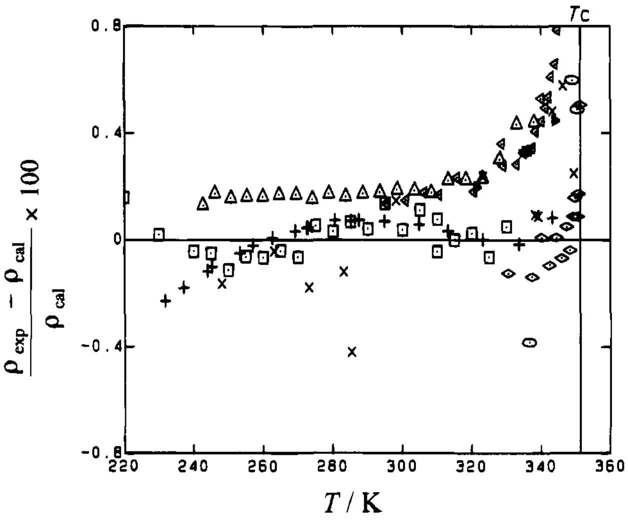

Figure 3. Deviation of measured saturated-liquid densities from Widiatmo's correlation: (▸) this work (extrapolated), (⊡) Widiatmo et al. (*19*), (×) Malbrunot et al. (*8*), (◇) Kuwabara et al. (*10*), (⊖) Higashi et al. (*16*), (▲) Defibaugh et al. (*17*), (◀) Holcomb et al. (*21*), (+) Oliveria and Wakeham (*20*).

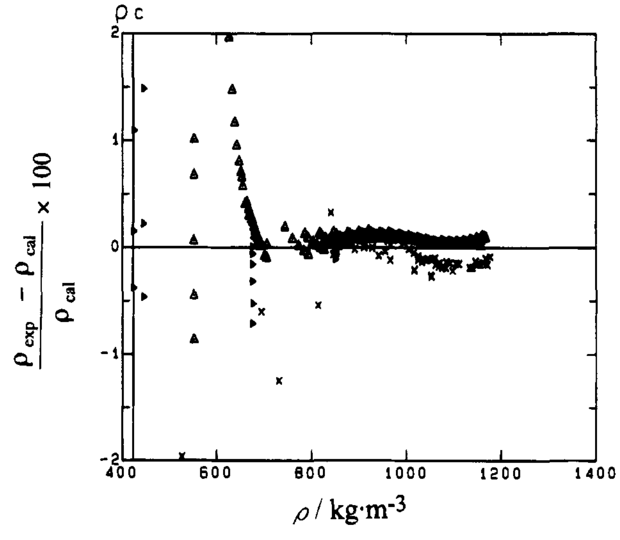

Figure 5. Density deviation from the equation of state by Piao et al. (*22*): (▸) this work, (◇) Qian et al. (*12*), (×) Malbrunot et al. (*8*), (▲) Defibaugh et al. (*17*), (*) Baroncini et al. (*18*).

of Malbrunot et al. (*8*) show somewhat different behavior even at higher densities.

Virial Coefficients. The compressibility factors of HFC-32 in the superheated vapor region have been deduced from the measurements as

$$Z = P/\varrho RT \qquad (3)$$

where R is the gas constant.

In Figure 6, $(Z - 1)/\varrho$ values calculated from the present *PVT* data are plotted along 10 isotherms with 10 K intervals between 330 and 420 K, together with the reported data of Qian et al. (*12*) for temperatures of 290–370 K. As shown in this figure, each isotherm by the present measurements can be represented by a straight line.

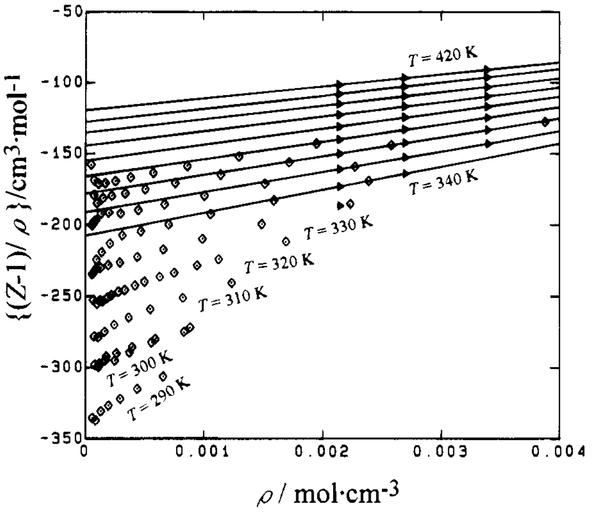

Figure 6. $(Z - 1)/\varrho$ values from the *PVT* measurements in the gaseous phase: (▸) this work, (◇) Qian et al. (*12*).

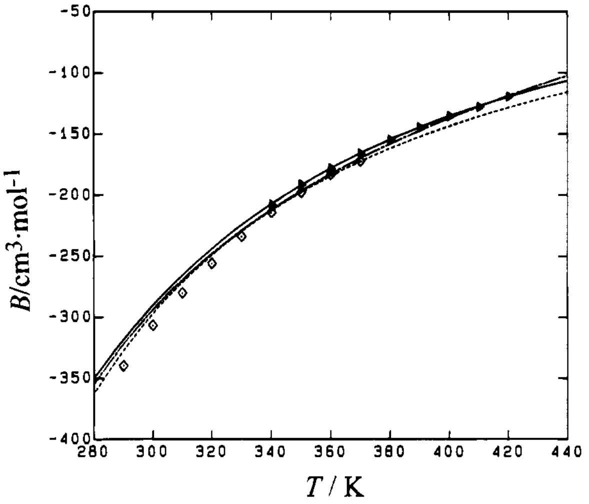

Figure 7. Second virial coefficient of HFC-32 as a function of temperature: (▸) this work, (◇) Qian et al. (*12*), (- - -) Sato et al. (*23*, *24*); (—) Qian et al. (*12*), (- · · -) Defibaugh et al. (*17*).

The second and third virial coefficients for temperatures from 340 to 420 K were determined by fitting the following truncated virial expression to the present data along a different isotherm, except 330 K along which we have measured a single data point:

$$(Z - 1)/\varrho = B + C\varrho \qquad (4)$$

The second and third virial coefficients thus determined are shown in Figures 7 and 8, respectively. We have estimated that the uncertainty of the B and C values is not greater than ±1% and ±3%, respectively. The present second virial coefficients, those of Qian et al. (*12*), and those of Defibaugh et al. (*17*) show a reasonable temperature dependence from a physical point of view and agree with the equation of state reported by us (*23*, *24*) within 0.984 $\mathrm{cm^3{\cdot}mol^{-1}}$. The third virial coefficients also agree with our equation within 4.14×10^{-4} $\mathrm{dm^6{\cdot}mol^{-2}}$.

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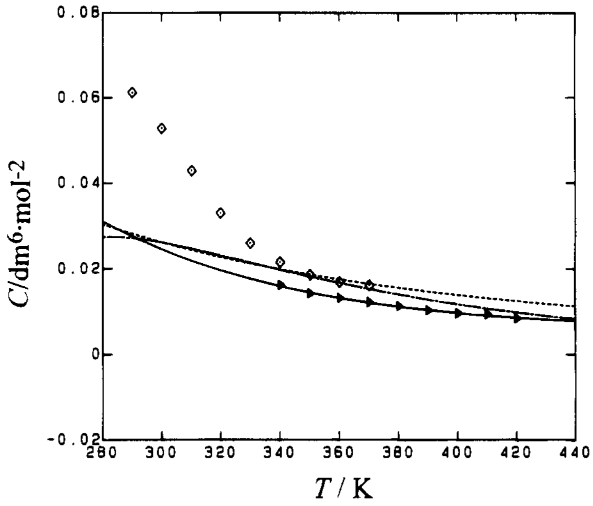

Figure 8. Third virial coefficient of HFC-32 as a function of temperature: (▸) this work, (◇) Qian et al. (*12*), (- - -) Sato et al. (*23*, *24*); (—) Qian et al. (*12*), (- · · -) Defibaugh et al. (*17*).

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