Saturated Pressure and Gas Phase $P-V-T$ Data for 1,1,2,2,3-Pentafluoropropane (R-245ca)

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The vapor pressure and $P-V-T$ properties for 1,1,2,2,3-pentafluoropropane (R-245ca), an ozone-friendly refrigerant, were measured using a constant volume apparatus. Measurements were carried out at temperatures from 258 K to 364 K and at pressures from 16 kPa up to 573 kPa. The 39 measurements in the vapor pressure region were fitted with the Wagner equation. The 34 experimental $P-V-T$ measurements in the superheated vapor region, taken along 5 isochores, were regressed to the virial equation of state in the Leiden form truncated after the second term. Consistency of the derived second virial coefficients was shown with Tsonopoulos' correlating method. The experimental findings were also compared with published data.

Introduction

1,1,2,2,3-Pentafluoropropane (R-245ca) is currently considered as a potential replacement for chlorine-containing compounds used in chillers, such as R-11 (trichlorofluoromethane). Thus, its thermodynamic properties and the compressor characteristics have been studied,[1] as well as its critical temperature, refractive index, surface tension, and liquid and vapor critical densities.[2] Several publications have also dealt with the viscosity,[3] dipole moment,[4] and vapor pressure of a binary system with 338mccp.[5]

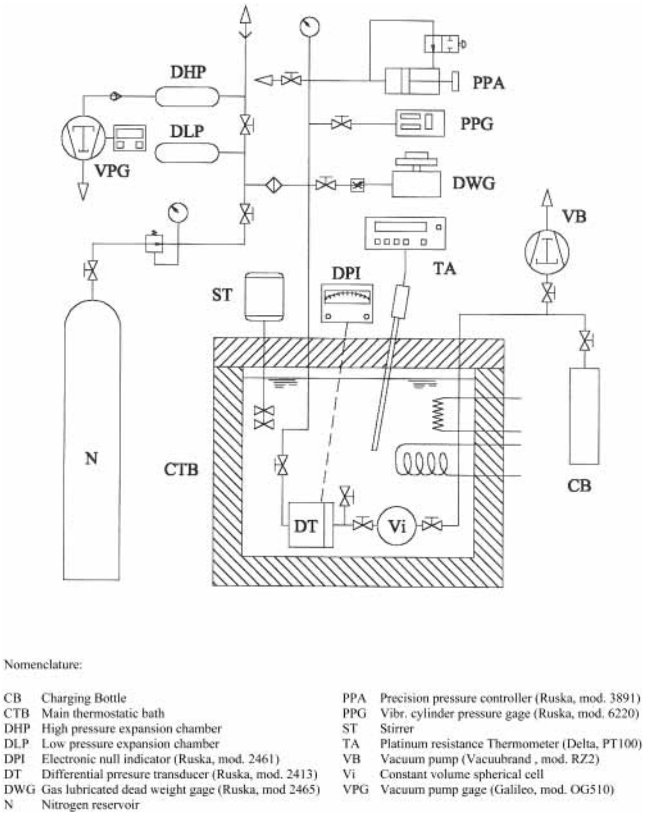
The thermodynamic properties of this refrigerant are collected in ref 6, where 58 saturated vapor pressures were reported, 24 from a comparative apparatus and 34 from a single boiler apparatus. Speed of sound measurements of R-245ca were also performed in ref 7.

To contribute to the current knowledge of the thermophysical properties of R-245ca and continue our analysis of propane derivatives[8−10] and their mixtures,[11,12] this work presents measurements on vapor pressures and in the superheated region.

Experimental Section

Materials. The sample was provided by Lancaster Synthesis Inc. It was deaerated by immersion in liquid nitrogen and evacuation. Its purity was checked by gas chromatography using a thermal conductivity detector and was found to be better than 99.9% by analysis of peak area.

Apparatus. The experimental apparatus is schematically illustrated in Figure 1. A classical constant volume apparatus with a volume of 254.8 cm^3 was used. The apparatus has been described in detail elsewhere.[13,14] A stainless steel spherical cell contains the refrigerant sample and is connected to a differential-diaphragm pressure transducer, coupled to an electronic null indicator. The spherical cell and pressure transducer are immersed in the main thermostatic bath containing a mixture of water and glycol and controlled with a proportional integrative derivative (PID) device. An auxiliary bath, also controlled with a PID device, helps the system to keep the temperature constant. A platinum resistance thermometer is immersed near the cell and is connected to a digital indicator. The instrument is calibrated on the ITS-90 scale, and its uncertainty is certified as being within ±15 mK. The pressure measurement is obtained with a dead weight gauge with an experimental uncertainty in the pressure measurements of ±0.5 kPa.



Nomenclature:

CB	Charging Bottle	PPA	Precision pressure controller (Ruska, mod. 3891)
CTB	Main thermostatic bath	PPG	Vibr. cylinder pressure gage (Ruska, mod. 6220)
DHP	High pressure expansion chamber	ST	Stirrer
DLP	Low pressure expansion chamber	TA	Platinum resistance Thermometer (Delta, PT100)
DPI	Electronic null indicator (Ruska, mod. 2461)	VB	Vacuum pump (Vacuubrand , mod. RZ2)
DT	Differential prresure transducer (Ruska, mod. 2413)	Vi	Constant volume spherical cell
DWG	Gas lubricated dead weight gage (Ruska, mod 2465)	VPG	Vacuum pump gage (Galileo, mod. OG510)
N	Nitrogen reservoir		

Figure 1. Schematic illustration of the apparatus.

The charging procedure for a one-component system has been described elsewhere.[8] The uncertainty in the measurement of the mass inside the cell is estimated in the same way, amounting to ±10 mg for this sample. The

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Table 1. Experimental Saturation Pressures for R-245ca

T_{90}/K	P/kPa	T_{90}/K	P/kPa	T_{90}/K	P/kPa
258.27	15.7	290.58	74.7	323.31	243.2
260.28	17.5	293.01	82.4	326.22	266.3
262.92	20.3	295.57	91.2	328.19	283.1
265.40	23.2	298.08	100.7	331.79	315.6
267.46	25.7	300.55	110.6	333.63	333.3
270.40	29.8	304.14	126.4	336.12	358.5
273.04	34.0	306.52	137.9	338.03	378.7
275.63	38.6	309.06	150.9	341.25	414.8
278.11	43.4	311.41	164.0	343.32	439.4
280.63	48.6	313.85	178.3	346.15	474.7
283.11	54.3	315.95	191.4	348.58	506.8
285.53	60.3	318.42	207.6	350.91	539.1
288.07	67.2	321.26	227.7	353.26	573.3

volume of the cell, piping, and pressure transducer cavity is measured with an uncertainty of ± 0.0003 dm^3. From the uncertainties in the mass and volume measurements, the uncertainty in the calculated molar volume was estimated to be always lower than ± 0.08 dm^3·mol^{-1}.

The overall experimental uncertainty in terms of pressure, calculated using the laws of error propagation, was estimated to be lower than ± 0.7 kPa for measurements along the saturation line and lower than ± 1.2 kPa in the superheated vapor region.

Results and Discussion

Vapor Pressure. The experimental vapor pressures in the temperature range from 258 K to 353 K are given in Table 1. Experimental data were fitted with one of the most popular equations, that is, the four-parameter Wagner equation,

$$\ln\frac{P}{P_c} = \frac{T_c}{T}[A_1\tau + A_2\tau^{1.5} + A_3\tau^{2.5} + A_4\tau^5] \tag{1}$$

where $\tau = (T_c - T)/T_c$; the critical temperature $T_c = 447.57$ K and the critical pressure $P_c = 3925.23$ kPa were taken as fixed values from ref 2.

The following values were found for the parameters: $A_1 = -7.340\,079\,2$, $A_2 = 0.376\,361\,5$, $A_3 = -0.148\,095\,7$, and $A_4 = -12.361\,423\,6$ with d$P = -0.02\%$ and abs(dP) $= 0.07\%$.

Deviations in pressure are defined as

$$\mathrm{d}P = \frac{1}{n}\sum_{i=1}^{n}[(P_{\mathrm{exp}} - P_{\mathrm{calc}})/P_{\mathrm{exp}} \times 100] \tag{2}$$

$$\mathrm{abs}(\mathrm{d}P) = \frac{1}{n}\sum_{i=1}^{n}[\mathrm{abs}(P_{\mathrm{exp}} - P_{\mathrm{calc}})/P_{\mathrm{exp}} \times 100] \tag{3}$$

where n is the number of experimental points. The error distribution is shown in Figure 2.

Our experimental results were also compared with published data. To our knowledge, only ref 6 reports a wide range of vapor pressures for this compound. In ref 6, the authors reported 24 pressures from the comparative apparatus and 34 from the single boiler apparatus. Comparing the literature data with eq 1 in our temperature range, a good consistency was found with ref 6, the deviations always being lower than 1 kPa. The distribution of deviations is shown in Figure 3.

A further comparison of our vapor pressure experimental results was made with pressures calculated using REFPROP 6.01,[15] and the following deviations were obtained: d$P = -0.44\%$ and abs(dP) $= 0.80\%$.

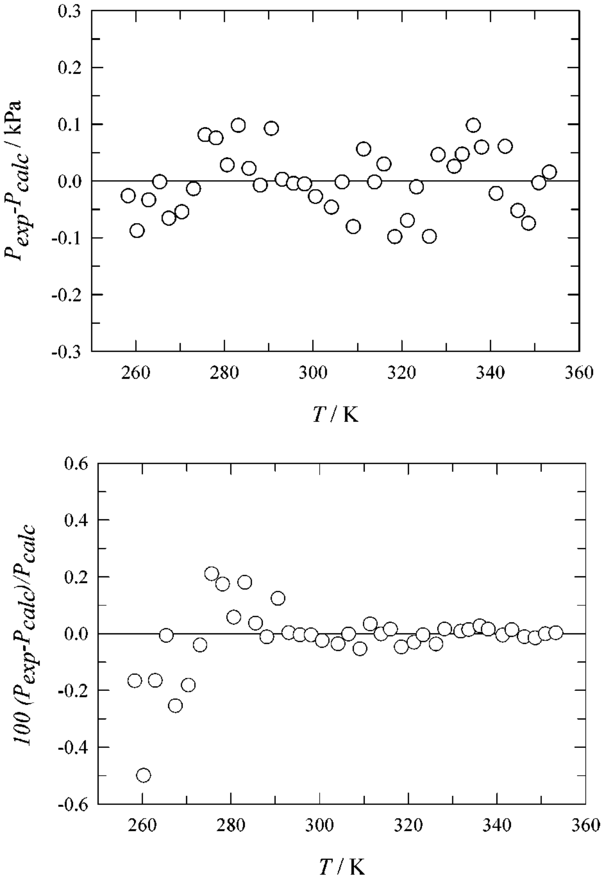

Figure 2. Scatter diagram of the saturated pressure deviations from the fit with the Wagner equation, eq 1.

P−V−T. The 38 experimental $P-V-T$ measurements in the superheated vapor region along 5 isochores are presented in Table 2. The measurements were taken in the temperature range from 334 K to 364 K, for pressures from 301 kPa to 551 kPa and for densities from (0.12 to 0.21) mol·dm^{-3}.

Second Virial Coefficients. The experimental $P-V-T$ measurements were used to derive coefficients of the virial equation of state in the Leiden form,

$$P = \frac{RT}{V}\left(1 + \frac{B}{V} + \frac{C}{V^2}\right) \tag{4}$$

where B and C are the second and third virial coefficients.

Because of our narrow reduced temperature range ($0.75 < T_r < 0.81$), where $T_r = T/T_c$ and $T_c = 447.57$ K[2], the virial equation of state was truncated after the second term in the calculations.

The temperature dependence of the second virial coefficient can be described by

$$B = B_0 + B_1/T + B_2\exp(1/T_r) \tag{5}$$

where the coefficients B_i are $B_0 = -0.036\,568$, $B_1 = 1486.476$, and $B_2 = -1.3565$. The fit gives d$P = -0.005\%$ and abs(dP) $= 0.444\%$. The deviations between the second virial coefficients derived by eq 5 and those derived from experimental data are shown in Figure 4. Using eq 5 with the experimental temperature and volume data, and with the coefficients specified above for B, the deviations from the experimental pressure defined as

$$\mathrm{d}P_i = (P_{i,\mathrm{exp}} - P_{i,\mathrm{calc}})/P_{i,\mathrm{exp}} \times 100 \tag{6}$$

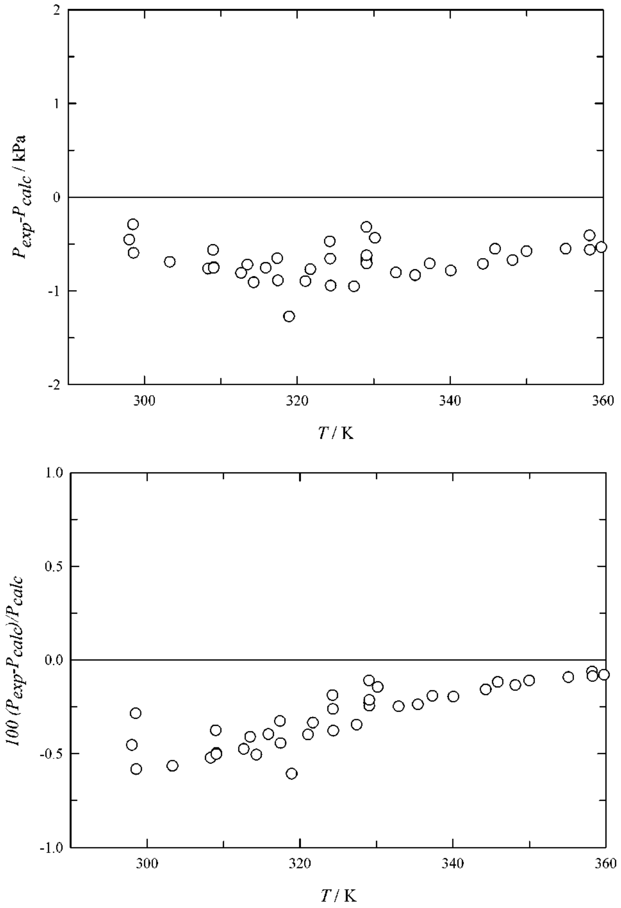

Figure 3. Vapor pressure deviations of R-245ca from eq 1: (○) Defibaugh et al.[6]

Table 2. Experimental $P-V-T$ Data for R-245ca

T_{90}/K	P/kPa	V/dm^3·mol^{-1}	T_{90}/K	P/kPa	V/dm^3·mol^{-1}
333.76	300.8	8.382	353.07	423.8	6.209
338.28	306.0	8.383	355.69	427.7	6.210
342.80	311.4	8.385	358.37	431.7	6.211
348.24	317.4	8.387	361.66	436.7	6.212
353.23	323.0	8.389			
358.63	328.9	8.391	348.29	478.8	5.266
361.73	332.3	8.393	350.39	484.3	5.266
			353.13	490.0	5.267
338.39	341.9	7.414	355.47	494.6	5.267
342.90	348.0	7.415	357.70	498.6	5.268
347.62	354.2	7.417	359.60	502.4	5.268
351.40	359.0	7.418	362.03	507.0	5.269
354.45	363.0	7.419			
357.68	367.1	7.420	353.27	529.0	4.811
360.22	370.3	7.421	355.24	533.0	4.812
			357.36	537.9	4.812
343.48	407.8	6.207	359.19	541.4	4.812
346.74	413.6	6.208	361.17	545.7	4.813
349.33	417.6	6.208	363.59	550.5	4.813

were calculated for each data point and are shown in Figure 5.

Among the empirical methods describing the second virial coefficients as a universal function of temperature in terms of compound parameters (critical parameters, dipole moment, acentric factor, polarizability), the Tsonopoulos method[16] was chosen to compare our second virial coefficients.

In the calculations, an acentric factor of $\omega = 0.3182$ was derived from our vapor pressure data by means of eq 1; the dipole moment was kept as a constant value $\mu = 1.74$ from ref 15. Thus, the calculated value for the reduced dipole moment was

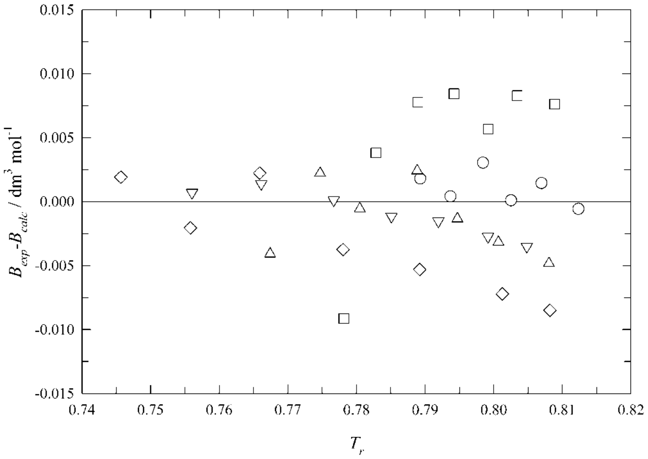

Figure 4. Scatter diagram of the second virial coefficients from the fit with eq 5: (◇) 8.387 dm^3·mol^{-1} isochore; (▽) 7.418 dm^3·mol^{-1} isochore; (△) 6.209 dm^3·mol^{-1} isochore; (□) 5.267 dm^3·mol^{-1} isochore; (○) 4.812 dm^3·mol^{-1} isochore.

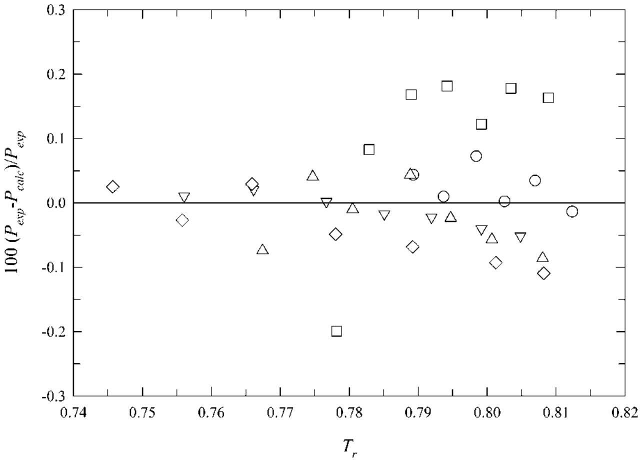

Figure 5. Scatter diagram of pressure deviations produced by the virial equation of state: (◇) 8.387 dm^3·mol^{-1} isochore; (▽) 7.418 dm^3·mol^{-1} isochore; (△) 6.209 dm^3·mol^{-1} isochore; (□) 5.267 dm^3·mol^{-1} isochore; (○) 4.812 dm^3·mol^{-1} isochore.

$$\mu_r = (1 \times 10^5)\mu^2(P_c)/(T_c^{\,2}) = 58.7 \tag{7}$$

where P_c is the critical pressure expressed in atmospheres and μ is in Debyes.

Considering the volumetric properties, the deviation in molar volume was calculated by truncating eq 4 after the second term for each ith point and taking experimental P, V, and T values as follows

$$dV = \left(\frac{PV}{RT} - 1\right)V - B \tag{8}$$

where B was calculated according to the Tsonopoulos correlating method.[16]

Absolute average deviations (AADs) in volume were calculated as

$$\mathrm{AAD} = \sum_{i=1}^{n} \mathrm{abs}(dV_i)/n \tag{9}$$

AAD values of 0.005 dm^3·mol^{-1} for Tsonopoulos' method[16] were obtained.

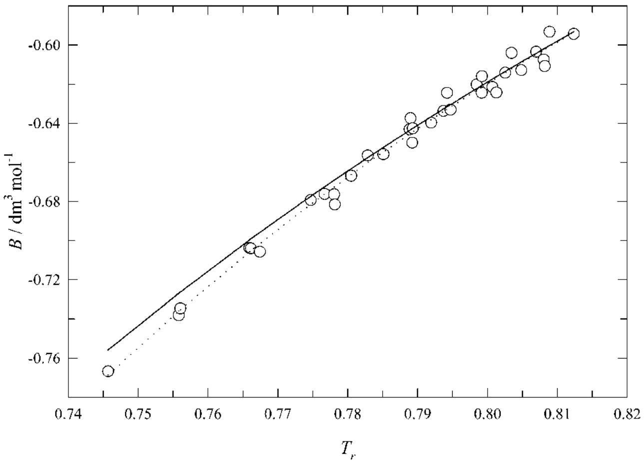

Figure 6. Second virial coefficients as a function of reduced temperature $T_r = TT_{c-1}$ with $T_c = 447.57$ K[2]: (○) derived from the $P-V-T$ data; (dotted line) their representation with the coefficients of eq 5; (solid line) predicted by Tsonopoulos' method.[16]

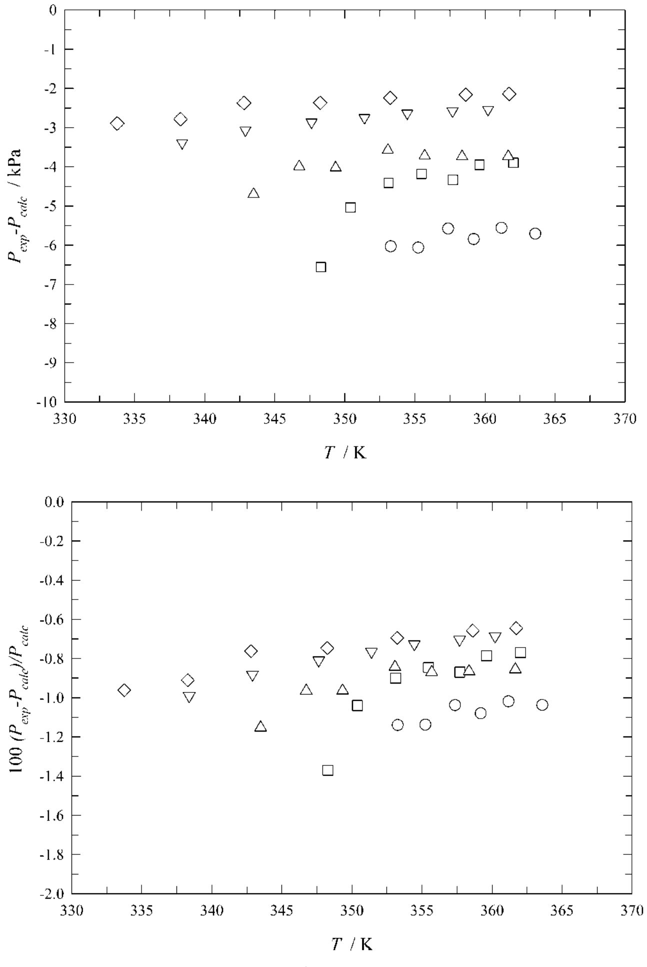

Figure 7. Scatter diagram of deviations between experimental $P-V-T$ data and values calculated from ref 7: (◇) 8.387 dm^3·mol^{-1} isochore; (▽) 7.418 dm^3·mol^{-1} isochore; (△) 6.209 dm^3·mol^{-1} isochore; (□) 5.267 dm^3·mol^{-1} isochore; (○) 4.812 dm^3·mol^{-1} isochore.

Figure 6 shows the second virial coefficients calculated by means of the correlating method together with those derived from the experimental measurements. The good consistency between the calculated second virial coefficients and the experimental results is particularly evident at higher reduced temperatures.

The experimental results were also compared with the speed of sound measurements reported in ref 7. Adopting the second, third, and fourth virial coefficients calculated by the author,[7] the pressure values were calculated at our experimental conditions. Deviations between the experimental and the calculated pressures are given in Figure 7 and averaged around 1%.

Finally, the $P-V-T$ results were compared with REFPROP 6.01[15] and the following deviations were obtained: d$P = -0.02$% and abs(dP) = 0.06%.

Conclusions

This work presents 83 experimental points for saturated pressure and the superheated vapor region of R-245ca. The measurements were obtained using a constant-volume apparatus. The experimental points taken within the VLE boundary were fitted with the Wagner equation. The experimental $P-V-T$ measurements in the superheated vapor region were regressed to the virial equation of state in the Leiden form truncated after the second term.

The derived second virial coefficients proved consistent with the Tsonopoulos correlating method calculations. The experimental results were also compared with recently published data, and the consistency was found to be better than 1% for the VLE data and around 1% by average for the $P-V-T$ data.

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