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Vapor Pressure of 1,1,1,2,2-Pentafluoropropane

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We have used a comparative ebulliometer to measure the vapor pressure of 1,1,1,2,2-pentafluoropropane (HFC245cb) in the temperature range (248 to 326) K. Pressures ranged from (74 to 995) kPa. The data were adjusted for impurities in the sample. The temperature of the normal boiling point was found to be (255.11 ± 0.10) K, and the Pitzer acentric factor was calculated to be 0.297. An estimate for the critical pressure is given, $P_c = (3148 \pm 15)$ kPa.

Introduction

Fluorinated propanes vary widely in volatility and thus offer a variety of possibilities as alternatives to chlorofluorocarbons. One of the more volatile ones is 1,1,1,2,2-pentafluoropropane (known as HFC245cb in the refrigeration industry). Like some of the other pentafluoropropanes, it is marginally flammable (Smith, 1995). Therefore, it would probably be used as a component in a mixture, possibly an azeotropic mixture.

The vapor pressure of HFC245cb has been the subject of two previous studies. Shank (1967) published measurements from 232 K to 380 K, and recently, DesMarteau and Beyerlein (1995) reported measurements in the range (235 to 381.6) K. Those two works agree within about 1% at the higher temperatures, but they exhibit larger disagreement at temperatures below 270 K.

The following section gives a brief description of the apparatus and describes the technique used to adjust the results in order to compensate for the presence of impurities. The final section presents the results of this study and compares them with the earlier data.

Experimental Section

The vapor pressures were measured in a metal comparative ebulliometer, which has been described by Weber and Silva (1996). Weber and Silva (1994) and Weber and Defibaugh (1996) have reported other vapor pressure results obtained with this apparatus.

Briefly, two identical boilers with reflux condensers are connected through a manifold, which is filled with helium gas at a carefully controlled pressure (±20 Pa). One boiler contains the fluid of interest and the other one contains a reference fluid whose vapor pressure is accurately known. A platinum resistance thermometer in each boiler measures the boiling temperature on the ITS-90 temperature scale with a reproducibility of 5−10 mK. The temperature in the reference boiler provides an accurate measure of the system pressure. In this case, 1,1,1,2-tetrafluoroethane (HFC134a) was used as the reference fluid. Its vapor pressure curve had been previously determined relative to that of water (for $P < 213$ kPa) in a glass ebulliometer and, for higher pressures, with the laboratory gas dead-weight pressure balance; see Goodwin et al. (1992).

Table 1. Concentrations and K_i at 294 K for the Impurities (t_i = Retention Time in Minutes; $\Delta Z_{lv} \simeq 0.826$)

i	t_i	$10^2 x_i$	K_i	$10^3(K_i - 1)x_i$
1	0.62	0.22	2.19	2.6
2	0.70	2.1	1.05	1.1
3	0.90	0.006	1.8	0.05
4	0.99	0.13	0.92	−0.10
5	1.12	0.36	1.36	1.3
6	1.21	0.26	1.13	0.34
				5.3 (total)

$\delta P/P \cdot 10^3 = 5.3/0.826 = 6.4$

The sample of HFC245cb used contained no measurable quantity of air (<0.01 mol %), but it was relatively impure. A gas chromatograph indicated that impurities, which produced peaks with a total area equal to 0.031 of the main peak, were present in the sample as received. Weber and Silva (1994) showed how vapor pressure measurements made in an ebulliometer like this one can be corrected for the effects of dilute impurities. If there are several impurities, we assume that the effect of each impurity is independent of the presence of others. The relative error in pressure is given approximately by

$$\delta P/P = \sum_i (K_i - 1)x_i/\Delta Z_{lv} \tag{1}$$

where δP is the error in pressure and $K_i = y_i/x_i$ with x_i and y_i the mole fractions of the impurity in the liquid and vapor phases, respectively. Z_{lv} is the compressibility factor difference between the saturated vapor and liquid sample; it was estimated from the experimental vapor pressure and estimated virial coefficients from the model of Weber (1994). The compositions of both phases in the sample cylinder were estimated with a gas chromatograph. The identities of the impurities were unknown. However, appropriate ratios of the peak areas for the two phases allowed the accurate determination of the K_i without the necessity of calibrating the chromatograph. The mole fractions, x_i, were assumed to be proportional to the ratios of the areas of the impurity peaks to that of the main peak, with a probable uncertainty of about 10%. This approximation should be sufficiently accurate for the small adjustments required for the pressures. Six impurities were found, and the data for each are given in Table 1. Table 1 shows that the impurities raised the measured vapor pressure by approximately 0.64% at ambient temperature (∼294 K), the temperature of the sample cylinder. The K_i are functions of temperature; the values of K_i are estimated to vary with temperature according to the relationship

$$K_i = \exp[a_i(T_c - T)^{1/3}/T] \tag{2}$$

which is an approximation of the expression given by Japas and Levelt-Sengers (1989). In eq 2 we assume that no

S0021-9568(95)00312-8

Table 2. Vapor Pressure Dta for HFC245cb from the Comparative Ebulliometer

T/K	P/kPa	T/K	P/kPa
248.004	74.26	269.326	178.03
249.432	79.23	269.363	178.49
250.820	84.28	272.196	197.93
252.021	88.57	272.208	198.45
252.144	89.31	278.505	248.37
253.402	94.28	283.916	297.87
254.470	98.50	283.926	297.79
254.611	99.27	288.690	347.60
255.634	103.49	292.955	397.36
256.745	108.46	300.413	496.84
258.880	118.40	300.453	496.78
258.945	118.88	306.812	596.44
260.863	128.34	312.445	696.01
262.727	138.26	317.520	795.54
262.784	138.69	322.201	895.17
266.186	158.15	326.443	994.80
266.227	158.59		

azeotropes are formed. Here, T_c is the critical temperature of the HFC245cb. All of the K_i approach the value unity $_c$. Equation 2, with the a_i evaluated from the data in Table 1, indicates that the relative change in the pressure, P, due to impurities increases to 0.94% at 248 K, and it decreases to 0.57% at 326 K. These estimates of $\delta P/P$ have fairly large uncertainties because the x_i were estimated, because of the possible formation of azeotropes, and because eqs 1 and 2 are approximate. However, the effects are considerably larger than the uncertainty in the pressure measurements, and thus adjustments to the data are justified.

Results and Comparisons

A total of 33 pressure/temperature measurements were made in the temperature range (248 to 326) K. Experimental pressures ranged from (74 to 995) kPa, and the results are reported in Table 2. The data in Table 2 have been adjusted with eqs 1 and 2. The data were represented with a four-term Wagner type equation

$$\ln P = \ln P_c + (T_c/T)(a_1\tau + a_2\tau^{1.5} + a_3\tau^{2.5}) \qquad (3)$$

where T_c and P_c are the critical parameters and $\tau = (1 -$). The critical temperature was obtained from Schmidt (1995), $T_c = 380.38$ K. Measurement of T_c was made on a purified sample, and thus it is not subject to uncertainty due to impurities. The other parameters were found to be $= -7.675\,09$, $a_2 = 2.382\,05$, and $a_3 = -3.652\,20$. The critical pressure was calculated to be 3148.3 kPa with a statistical uncertainty of ±100 kPa (1σ), due primarily to the long extrapolation beyond the maximum experimental temperature. Other considerations—experience with other fluids and comparison with other results near the critical temperature of HFC245cb—lead us to estimate that the uncertainty in P_c is no greater than ±15 kPa. Apparently, the impurities affected the experimental precision, however. The standard deviation of the fit of eq 3 is 0.09% in pressure. This imprecision is several times larger than that obtained previously for measurements on purer samples in the same apparatus, normally (0.015 to 0.025)%. Equation 3 gives the normal boiling temperature to be (255.11 ± 0.02) K. The stated uncertainty is the statistical value derived from the imprecision of the data on this sample. Approximations in the correction for the impurities lead to additional uncertainty in this value, probably about ±0.1 K. The Pitzer acentric factor was calculated to be $\omega = 0.297$.

Figure 1 shows the deviation of the data from eq 3, as well as the deviations of the data of Shank (1967) and of DesMarteau and Beyerlein (1995). At temperatures greater than about 270 K all three data sets agree with the equation to within ±0.5%, except for the data of DesMarteau and Beyerlein near the critical point where the deviations approach 1%. Our extrapolated equation agrees with the data of Shank within 0.1% or less near the critical point. Below 270 K the data of DesMarteau and Beyerlein begin to depart rapidly from eq 3, and the deviation reaches about −2.5% near the normal boiling point at 255 K. Both of the other data sets appear to exhibit discontinuities near 255 K. Shank reported using a different apparatus (an ebulliometer) for subambient pressures, and those results exhibit deviations of about −2.5%. On the other hand, the results of DesMarteau and Beyerlein agree relatively well with the present work at those low temperatures and pressures. Shank reproted that his sample had a purity of 99.9 mol %. Figure 1 also shows the locus of our unadjusted data and our estimated uncertainty in the adjusted results.

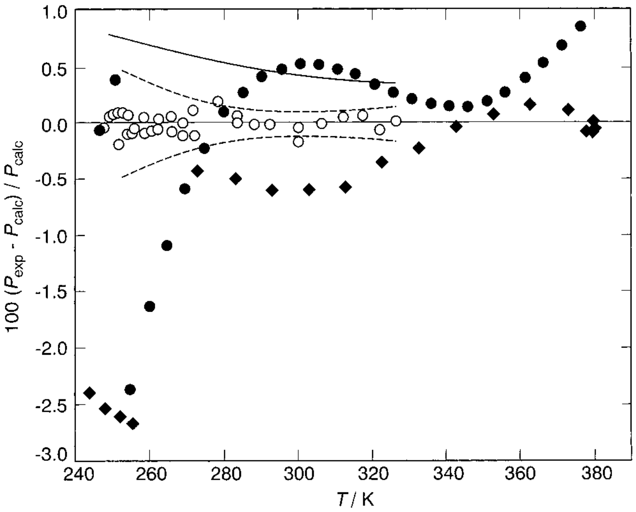

Figure 1. Deviations of the data from eq 3: (○) this work; (◆) Shank (1967); (●) DesMarteau and Beyerlein (1995); (—) locus of unadjusted data; (- - -) estimated uncertainty in these results.

Shank also made PVT measurements, and from those he derived critical parameters. He reported $T_c = 380.08$ K (converted to the ITS-90 scale) and $P_c = 3137$ kPa. From Schmidt's value of 380.38 K for T_c we found $P_c = 3148$ kPa. These two (T_c,P_c) pairs fall on the same vapor pressure curve (within 0.25%), indicating that the two vapor pressure curves show a high degree of consistency near the critical point. Therefore the statistical uncertainty in our value for P_c, ±100 kPa given earlier, is probably much too conservative. DesMarteau and Beyerlein reported somewhat higher values for both parameters, $T_c = 381.6$ K and $P_c = 3264$ kPa, which are inconsistent with the other two data sets by about 0.8%.

Summary

We have made vapor pressure measurements on HFC245cb in the temperature range (248 to 326) K. Although the sample had approximately 3 mol % impurity, we have made appropriate adjustments, based on the most likely behavior of the impurities. We have estimated the residual uncertainties. The adjusted results fall midway between the only other two sets of reported data for this fluid.

Acknowledgment

The authors are indebted to J. Schmidt for the use of his data prior to publication.

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Received for review December 12, 1995. Accepted April 1, 1996. This work was supported in party by the U.S. Environmental Protection Agency, Contract No. EPA DW13935432-01-4. Apparatus development was supported by the Division of Engineering and Geosciences, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract No. DE-A105-88ER13823.[⊗]

JE950312V

[⊗] Abstract published in *Advance ACS Abstracts,* May 1, 1996.