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Vapor Pressure Measurements of 1,1,1,2,3,3-Hexafluoropropane from 300 to 410 K

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We present new vapor pressure measurements for 1,1,1,2,3,3-hexafluoropropane (R-236ea) in the temperature range from 300 to 410 K. The measurements were performed with a static technique, and the uncertainties of the measurements were estimated to be within ±0.6 kPa for pressure and within ±8 mK for temperature. A Wagner-type vapor pressure correlation was developed to represent the measured vapor pressures, and the critical pressure was determined as (3411.6 ± 3.0) kPa corresponding to the critical temperature of 412.375 K. The purity of the R-236ea sample used in the present measurements was 99.9 mol %. The effect of the volatile impurity in the sample on the vapor pressure measurements is discussed and corrected.

Introduction

The production of 1,2-dichloro-1,1,2,2-tetrafluoroethane (R-114), which has been widely used in centrifugal chillers and heat pumps as the working fluid, is scheduled to be discontinued by the end of 1995 along with the production of other fully-halogenated chlorofluorocarbons (CFCs) as agreed by the Montreal Protocol Amendments. 1,1,1,2,3,3-Hexafluoropropane (R-236ea) has virtually zero potential to deplete the stratospheric ozone and low global warming potential. This refrigerant is completely nonflammable over a wide range of concentrations in air at temperatures up to 323 K, and no unusual toxicity has been indicated in limited toxicity testing (Smith, 1993). Through thermodynamic evaluation and experimental tests (Smith, 1993; Kazachki and Gage, 1993; Kazachki et al., 1994), R-236ea has been demonstrated to have high potential as an alternative for R-114.

Accurate information about the vapor pressures for a refrigerant is very important to calculate its thermodynamic properties essential to the cycle analysis and the design of the refrigeration equipment. Up to now, few measurements for the vapor pressures of R-236ea have been published in the literature. Beyerlein et al. (1993) presented vapor pressures for R-236ea in a wide range of temperatures with a sample of 99.5% purity. Defibaugh and Silva (1994) reported vapor pressures for R-236ea below 370 K with a pure (99.9%) sample. However, additional vapor pressure data are needed so as to characterize the thermodynamic properties in more detail.

In this paper, static vapor pressure measurements for R-236ea using one cell of a Burnett apparatus from 300 K to approximately the critical temperature are presented. The Burnett apparatus has been used in the last several years to measure the vapor pressures and compressibility factors of difluoromethane (R-32) (Qian et al., 1993), pentafluoroethane (R-125) (Ye et al., 1995), and 1,1,1-trifluoroethane (R-143a) (Zhang et al., 1995). In order to examine the reproducibility of the vapor pressure measurements for R-236ea, two series of measurements were made as the first set of measurements at approximately the critical density and five measurements were performed as the second set of measurements at densities lower than the critical density.

Experimental Section

The Burnett apparatus used in the present measurements was described in detail in our previous paper (Zhang et al., 1995). The present measurements were performed using the sample cell of the apparatus. The uncertainty of the temperature measurements was estimated to be within ±8 mK, the sum of ±2 mK for the uncertainty of the thermometer, ±1 mK for the uncertainty of the thermometer bridge, and ±5 mK for the possible temperature fluctuation of the thermostated bath. The accuracy of the pressure measuring system was estimated to be better than ±0.5 kPa, which consists of the reproducibility of the differential pressure measurements, ±0.3 kPa, and the accuracy of the pressure gauge, ±2 kPa. Note that it does not include the effect due to the impurity in the sample. The uncertainty of the measured vapor pressures for R-236ea will be discussed in the next section.

The purity of the R-236ea sample used was 99.9 mol % according to the analysis performed by the chemical manufacturer. The sample was not purified further by the present study because of the limitation of the apparatus. Before the R-236ea sample was filled, the sample cell was flushed with the sample gas three times and evacuated to approximately 2 mPa.

Results and Discussion

Two series of vapor pressures were measured as the first set of measurements in the range of 300–410 K with the sample cell filled to approximately the critical density ($\rho = 3.716\ \text{mol·L}^{-1}$). For the purpose of investigating the effect on the vapor pressure measurements due to the possible presence of a volatile impurity in the sample confined in the cell, five points were measured as the second set of measurements at lower filling densities than the critical density, at temperatures of 300, 320, 340, 360, and 380 K, respectively. A total of 38 points were measured.

To correlate the vapor pressures of R-236ea, the Wagner-type vapor pressure equation was used:

$$\ln P_r = (a\tau + b\tau^{1.5} + c\tau^3 + d\tau^6)/T_r \qquad (1)$$

where $T_r = T/T_c$, $P_r = P/P_c$, $\tau = 1 - T_r$, $T_c = 412.375$ K is the critical temperature measured by Aoyama et al. (1995), and the numerical constants a through d and the critical pressure P_c were determined by a least-squares analysis.

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Table 1. Numerical Constants in Eq 1

coefficient	uncorrected (300–412.375 K)	corrected (248–412.375 K)
a	−7.77054	−7.75671
b	1.48833	1.41434
c	−4.49436	−4.05869
d	15.9952	−2.35003
P_c/kPa	3411.8	3411.6

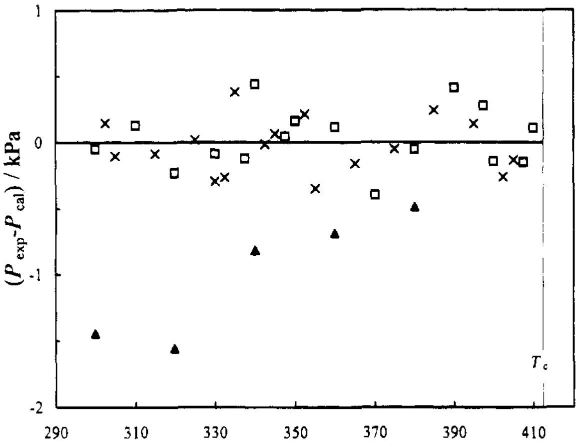

Figure 1. Absolute deviations of the original vapor pressure values (uncorrected) from eq 1 with the coefficient listed in column 2 in Table 1: ×, first set of measurements (series 1, ρ = 3.716 mol·L^{-1}); □, first set of measurements (series 2, ρ = 3.716 mol·L^{-1}); ▲, second set of measurements (ρ = 0.373 mol·L^{-1} at 300, 320, and 340 K, ρ = 0.993 mol·L^{-1} at 360 and 380 K).

In order to examine the self-consistence of the original measurements, the first set of measurements (uncorrected for the impurity effect) were correlated using eq 1, and the numerical constants are given in Table 1. As shown in Figure 1, the two series of measurements at the same density (ρ = 3.716 mol·L^{-1}) are self-consistent and the deviations from eq 1 with the coefficients given in column 2 in Table 1 do not exceed ±0.5 kPa which is not more than the uncertainty of the pressure measuring system. In addition, the second set of measurements are also plotted in Figure 1. The second set of measurements are considerably lower than the first set of measurements at the same temperatures. The sample cell was approximately half-full of sample liquid in the first set of measurements, while only a small fraction of the cell was filled with the sample liquid in the second set of measurements. This fact suggests that there was a volatile impurity, possibly the air, in the filling sample since the measured vapor pressure obviously depends on the average density within the cell, especially at the low temperatures.

Kabata et al. (1991) studied the effect of an air impurity, nitrogen, on their vapor pressure measurements of 2,2,2-trifluoroethanol. They used the Peng–Robinson equation of state to calculate the vapor–liquid equilibrium. They presented the results for the bubble-point curve, where they showed that an impurity of only 6 ppm would cause a pressure increase of about 1.6 kPa for temperatures of 320–380 K and that an impurity level of 35 ppm caused an error of 8 kPa. Weber (1994) and Boyes and Weber (1994) reported an approach to estimate the effect due to an impurity on their vapor pressure measurements of 1-chloro-1,2,2,2-tetrafluoroethane (R-124). They indicated that the increase in the static pressure due to the volatile impurity depends mainly on the average density of the sample within the cell, the mole fraction of the impurity, and Henry's constant for the impurity dissolved in the refrigerant. In most cases, however, the mole fraction of an impurity and Henry's constant are not known.

Table 2. Vapor Pressures for R-236ea

T/K (ITS-90)	P/kPa (corrected)	T/K (ITS-90)	P/kPa (corrected)
300.000	219.6	350.001	929.2
300.000	219.7[a]	352.500	987.0
302.499	239.3	355.000	1046.9
305.000	259.8	360.000	1176.7
310.000	305.8	360.000	1176.7[a]
315.000	357.2	365.000	1317.5
320.000	415.2	370.000	1470.5
320.000	415.2[a]	375.000	1637.7
325.001	480.6	380.001	1818.5
330.000	552.8	380.000	1818.7[a]
330.001	553.0	385.001	2014.7
332.500	592.1	390.000	2226.8
335.000	634.0	395.001	2455.8
337.501	677.0	397.500	2577.5
340.000	723.2	400.001	2703.6
340.000	723.1[a]	402.502	2835.2
342.500	770.7	405.000	2972.2
345.000	821.1	407.501	3114.9
347.500	873.8	410.000	3264.0

[a] Second set of measurements.

Since the dew-point curve is defined as the minimum limit of the effect of the volatile impurities at any given temperature, we developed a correlation between the static vapor pressure and the average density within the sample cell in the present study so as to correct the original measurements by extrapolating the correlation to dew points. The correlation for a specified temperature was assumed to be given as a linear function:

$$\Delta P = (P_1 - P_2)\frac{\rho - \rho''}{\rho_1 - \rho_2} \tag{2}$$

where ΔP is the pressure difference between the point with a density ρ and the dew point, P_1 is the measured vapor pressure at point 1 with a higher density ρ_1, P_2 is the measured vapor pressure at a lower density ρ_2 and ρ'' denotes the saturated vapor density at the dew point. For the first set of measurements (ρ_1 = 3.716 mol·L^{-1}), the pressure differences ΔP in eq 2 are correlated as the following function of temperature:

$$\Delta P/\mathrm{kPa} = 8.7032\tau - 11.037\tau^2 \tag{3}$$

where $\tau = 1 - T/T_c$. For the second set of measurements, however, we can directly use eq 2 to obtain the pressure differences ΔP. The effect of the volatile impurity decreases with increasing temperature, and at the critical temperature it becomes the minimum because the dew curve and the bubble curve merge at the critical point. Thus, as shown by eq 3, we neglected the effect of the volatile impurities at the critical temperature. Using eqs 2 and 3, all the original values were corrected, and the corrected results are given in Table 2. The saturated vapor densities were calculated using REFPROP (Gallagher et al., 1994). We took our corrected vapor pressure values for temperatures of 300–410 K and the values measured using ebulliometric techniques by Defibaugh and Silva (1994) for temperatures of 248–370 K as a set of input data to establish a vapor pressure correlation for R-236ea which can be used for a wide temperature range. The functional form of the developed correlation is shown as eq 1, and the numerical constants are also given in Table 1. The critical pressure was determined by the regression analysis as P_c = (3411.6 ± 3.0) kPa corresponding to the critical temperature T_c = 412.375 K mentioned above.

In consideration of the effect of the volatile impurity, the uncertainty of the correlated vapor pressure values are

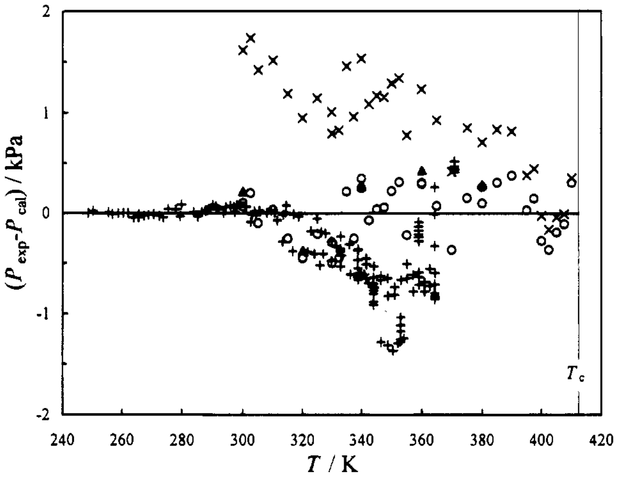

Figure 2. Absolute vapor pressure deviations from eq 1 with the coefficients listed in column 3 in Table 1: ×, uncorrected first set of measurements; ▲, uncorrected second set of measurements; ○, corrected measurements; +, Defibaugh and Silva (1994).

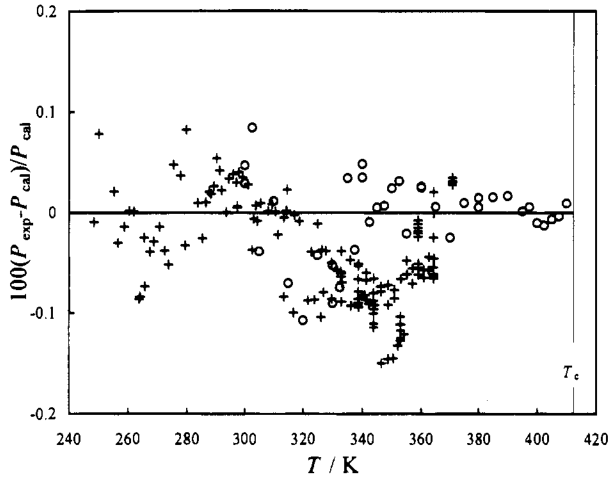

Figure 3. Relative vapor pressure deviations from eq 1 with the coefficients listed in column 3 in Table 1: +, Defibaugh and Silva (1994); ○, this work (corrected data).

estimated to be no more than ±0.6 kPa, ±0.5 kPa for the pressure measurement scheme and ±0.1 kPa due to the correction of the original measurements.

The absolute pressure deviations of the present corrected results and those measured using ebulliometer apparatus by Defibaugh and Silva (1994) from the correlation are shown in Figure 2, where the reference standard is eq 1 with the numerical constants in column 3 in Table 1. All our results agree with eq 1 within ±0.5 kPa, and the standard deviation is 0.3 kPa. The values by Defibaugh and Silva (1994) are also in good agreement with eq 1. As shown in Figure 3, the relative deviations of the measurements by Defibaugh and Silva from eq 1 are almost within ±0.1%. The standard deviation for both the present data and those by Defibaugh and Silva is 0.055% in pressure. We have also compared the vapor pressures measured by a static technique by Beyerlein et al. (1993) and the vapor pressure correlation by Defibaugh and Silva with the present results in Figure 4. From 370 K to the critical temperature, the correlation by Defibaugh and Silva shows a temperature dependence different from that of eq 1. This may be due to the fact that no measured values from 370 K to the critical temperature were available when Defibaugh and Silva developed their vapor pressure correlation. The vapor pressure data reported by Beyerlein et al. differ significantly (from −3.5% to +2%) from eq 1.

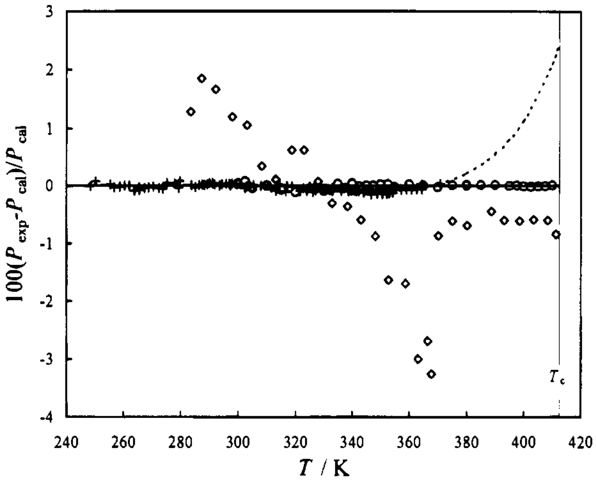

Figure 4. Relative vapor pressure deviations from eq 1 with the coefficients listed in column 3 in Table 1: +, Defibaugh and Silva (1994); ○, this work (corrected data); ◇, Beyerlein et al. (1993); - - -, correlation by Defibaugh and Silva (1994).

Table 3. Critical Pressure and Temperature of R-236ea

ref	T_c/K	P_c/kPa
Beyerlein et al. (1993)	414.25	3533
Defibaugh and Silva (1994)	412.44^a	3502.0
this work	412.375^b	3411.6 ± 3.0

^{a} Measured by Schmidt, J., NIST, Gaithersburg, MD (see Defibaugh and Silva, 1994). ^{b} Measured by Aoyama et al. (1995).

The critical pressures, P_c, determined in this work, determined by Defibaugh and Silva, and measured by Beyerlein et al. are listed in Table 3 along with the corresponding critical temperatures, T_c. The critical temperature used by Defibaugh and Silva is 65 mK greater than that used in the present study, while P_c determined by Defibaugh and Silva is greater than ours by about 90 kPa. Beyerlein et al. observed higher T_c and P_c values than those found in the present study.

Conclusion

In the range of temperatures from 300 to 410 K, 38 vapor pressures have been measured and the effect of the volatile impurity in the sample has also been taken into account. In combination with the experimental data by Defibaugh and Silva, a vapor pressure correlation for R-236ea, which is effective from 248 K up to the critical temperature, has been developed and the critical pressure has been determined by regression as P_c = (3411.6 ± 3.0) kPa corresponding to the critical temperature of 412.375 K. For static vapor pressure measurements, the effect of a volatile impurity depends on the average density of the sample within the cell. Therefore, if a small amount of sample liquid is maintained in the sample cell, better results will be obtained.

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Literature Cited

Aoyama, H.; Sato, H.; Watanabe, K. To appear in the *Proceedings of the 16th Japan Symposium on Thermophysical Properties*, Hiroshima, Japan, Nov 7–9, 1995; Japan Society of Thermophysical Properties.

Beyerlein, A. L.; Desmartean, D. D.; Hwang, S. H.; Smith, N. D.; Joyner, P. A. Physical Properties of Fluorinated Propane and Butane Derivatives as Alternative Refrigerants. *ASHRAE Trans.* **1993**, *99*, 368–379.

Boyes, S. J.; Weber, L. A. Vapor Pressures and Gas-Phase PVT Data for 1-Chloro-1,2,2,2-Tetrafluoroethane (R124). *Int. J. Thermophys.* **1994**, *15* (3), 443–459.

Defibaugh, D. R.; Silva, A. M. Compressed Liquid Densities, Saturated Liquid Densities and Vapor Pressures of 1,1,1,2,3,3-Hexafluoropropane (HFC-236ea). Paper presented at the 12th Symposium on Thermophysical Properties, Boulder, CO, June 19–24, 1994.

Gallagher, J.; McLinden, M.; Morrison, G.; Huber, M.; Ely, J. NIST Standard Reference Database 23, Thermodynamic Properties of Refrigerants and Refrigerant Mixtures (REFPROP), 1994.

Kabata, Y.; Yamaguchi, S.; Takiguchi, Y.; Uematsu, M. Measurements of the vapor pressure of 2,2,2-trifluoroethanol in the temperature range from 320 K to 400 K. *J. Chem. Thermodyn.* **1991**, *23*, 671–678.

Kazachki, G. S.; Gage, C. L. Thermodynamic Evaluation and Compressor Characteristics of HFC-236ea and HFC-245ca as CFC-114 and CFC-11 Replacements in Chillers. *Proceedings of the 1993 International CFC and Halon Alternatives Conference*, Washington, DC, Oct 20–22, 1993; The Alliance for Responsible CFC Policy: Frederick, MD; pp 167–176.

Kazachki, G. S.; Gage, C. L.; Hendriks, R. V.; Rhodes, W. J. Investigation of HFC-236ea and HFC-236fa as CFC-114 Replacements in High-Temperature Heat Pumps. *Proceedings of the International Conference, CFCs, The Day After, Joint Meeting of IIR Commissions B1, B2, E1 and E2*, Padova, Italy, Sept 21–23, 1994; Int. Inst. of Refrig.: Paris, France; pp 155–162.

Qian, Z.-Y.; Nishimura, A.; Sato, H.; Watanabe, K. Compressibility Factors and Virial Coefficients of Difluoromethane (HFC-32) Determined by Burnett Method. *JSME Int. J.* **1993**, *36* (4), 665–670.

Smith, N. D. HFC-236ea: A Potential Alternative for CFC-114. *Proceedings of the 1993 International CFC and Halon Alternatives Conference*, Washington, DC, Oct 20–22, 1993; The Alliance for Responsible CFC Policy: Frederick, MD; pp 150–157.

Weber, L. A. Criteria for establishing accurate vapor pressure curves. *Int. J. Refrig.* **1994**, *17* (2) 117–122.

Ye, F.; Sato, H.; Watanabe, K. Gas-Phase *PVT* Properties and Vapor Pressures of Pentafluoroethane (HFC-125) Determined According to the Burnett Method. *J. Chem. Eng. Data* **1995**, *40* (1), 148–152.

Zhang, H.-L.; Sato, H.; Wanatabe, K. Vapor Pressures, Gas-Phase *PVT* Properties, and Second Virial Coefficients for 1,1,1-Trifluoroethane. *J. Chem. Eng. Data* **1995**, *40* (4), 887–890.

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