Measurements of the Vapor Pressures and $p\rho T$ Properties for *trans*-1,3,3,3-Tetrafluoropropene (HFO-1234ze(E))

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The vapor pressures and $p\rho T$ properties for *trans*-1,3,3,3-tetrafluoropropene (HFO-1234ze(E)) are measured using a metal-bellows cell. As for the vapor pressure, eight data points are obtained in the temperature range from (310 to 380) K and pressure range from (703 to 3458) kPa. The data of the vapor pressure is correlated by the Wagner type equation with the absolute average deviation of 0.02 %. By extrapolating the vapor-pressure correlation to the critical temperature, the critical pressure is determined to be 3632 kPa. The acentric factor is also determined to be 0.296 by using the vapor-pressure correlation. As for the $p\rho T$ properties, 26 data points are obtained in the temperature range from (310 to 370) K and pressure range from (2000 to 5000) kPa. The data of the $p\rho T$ properties are correlated by the Sato equation with the absolute average deviation of 0.04 %. Seven data points of the saturated liquid density are obtained by extrapolating the correlation of the $p\rho T$ properties to the vapor pressure.

Introduction

Regarding the refrigerants of automobile air conditioners, hydrofluorocarbons (HFCs) having great global warming potentials (GWP) values will be shifting toward low GWP substances. Hydrofluoro-olefins (HFOs) such as HFO-1234ze(E) (*trans*-1,3,3,3-tetrafluoropropene)[1] and HFO-1234yf (2,3,3,3-tetrafluoropropene)[2−4] having low GWP values are expected as alternatives for HFCs. However, there are a few experimental data of thermodynamic properties for HFO-1234ze(E) with which to evaluate refrigeration cycles. Grebenkov et al.[1] have recently reported the experimental data of vapor pressure in the temperature range from (237 to 380) K and pressure range from (41 to 3439) kPa and of the $p\rho T$ properties in the temperature range from (282 to 371) K and pressure range from (643 to 9203) kPa.

In this work, the vapor pressures and $p\rho T$ properties of HFO-1234ze(E) are measured using a metal-bellows cell. On the basis of the present results, the correlations of the vapor pressure and $p\rho T$ properties are formulated. The critical pressure and the acentric factor are determined from the correlation of the vapor pressure. The saturated liquid densities are obtained from the correlation of $p\rho T$ properties.

Experimental Section

Sample. HFO-1234ze(E) is manufactured by Central Glass Co. Ltd., Japan. Its purity is better than 99.96 %. This sample is degassed by freeze−thaw cycling with liquid nitrogen before use.

Apparatus. The schematic diagram of the apparatus is shown in Figure 1. The principles of measurements for the vapor pressures and $p\rho T$ properties are based on the apparatus by Kabata et al.[5,6] and Miyamoto et al.[7,8] The sample container is a cylindrical cell with a metal bellows whose volume can be varied from (34 to 44) cm^3. A sample of known mass is loaded inside the sample container, and nitrogen gas is filled outside the sample container. Nitrogen gas is used as pressure medium. The pressure of nitrogen gas is measured by a digital pressure gauge (Paroscientific, 43K) with the uncertainty of 1 kPa. By increasing or decreasing the pressure of nitrogen gas, the metal bellows of the sample container is compressed or expanded. The displacement of the metal bellows is detected by a linear variable differential transformer. The sample container is

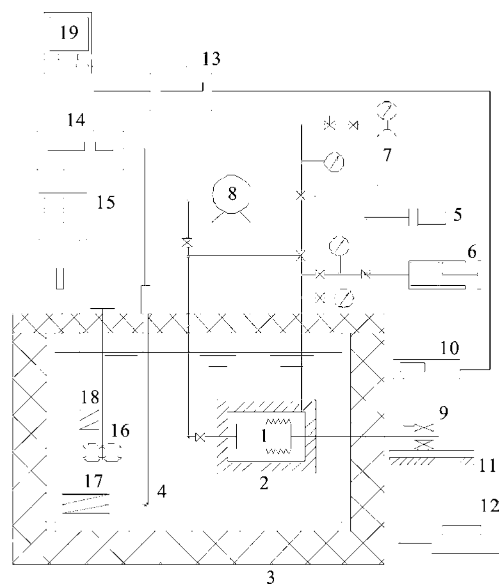

Figure 1. Schematic diagram of the apparatus. 1, metal-bellows cell; 2, pressure vessel; 3, thermostatted silicone-oil bath; 4, platinum resistance thermometer; 5, digital pressure gauge; 6, pressure controller; 7, nitrogen gas bomb; 8, vacuum pump; 9, linear variable differential transformer; 10, displacement indicator; 11, linear stage; 12, linear gauge; 13, digital multimeter; 14, thermometer bridge; 15, proportional, integral, derivative (PID) controller; 16, stirrer; 17, main heater; 18, subheater; 19, computer.

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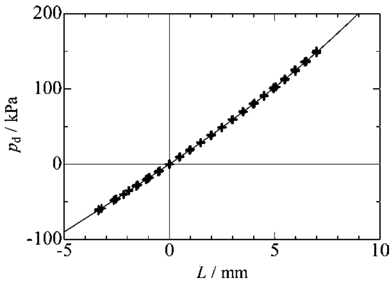

Figure 2. Relationship between the differential pressure and the displacement of the metal bellows.

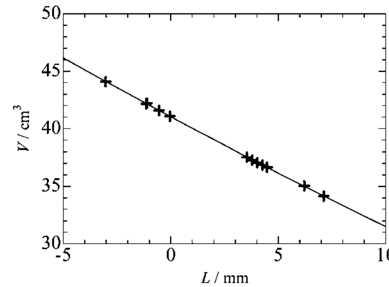

Figure 3. Relationship between the volume of the sample container and the displacement of the metal bellows.

Table 1. Coefficients in Equation 2

a_0	19.346
b_0	0.41897
c_0	0.018245
a_1	−0.0015726
b_1	−0.00052842
c_1	−0.0000052760

immersed in a thermostatted silicone-oil bath to keep the temperature constant. The temperature of the silicone oil is measured by a 25 Ω standard platinum resistance thermometer (Chino, R800-2) and precise thermometer bridge (Tinsley 5840) with the uncertainty of 5 mK.

The vapor pressure p_s of the sample is obtained from eq 1.

$$p_s = p_n - p_d \tag{1}$$

where p_n is the nitrogen gas pressure and p_d is the differential pressure caused by the elastic force of a metal bellows. Differential pressure is calibrated by using nitrogen gas. The calibration is conducted in the differential pressure range from (−60 to 150) kPa and in the bellows displacement range from (−3 to 7) mm as shown in Figure 2. The calibration data for the differential pressure are correlated as functions of temperature T and the displacement L of the metal bellows as follows:

$$p_d = (a_0 + a_1T)L + (b_0 + b_1T)L^2 + (c_0 + c_1T)L^3 \tag{2}$$

The coefficients in eq 2 are listed in Table 1. The deviation of the calibration data from eq 2 is within 1 kPa. Actually, measurement of the vapor pressure is conducted when the displacement of the metal bellows is near zero so as to make the differential pressure less than 1 kPa.

The density ρ of the sample is obtained from eq 3.

$$\rho = \frac{m}{V} \tag{3}$$

where m is the mass of sample and V is the volume of the sample container. The mass of the sample is measured by a precision analytical balance with the uncertainty of 2 mg. The volume of the sample container is calibrated by using HFC-134a whose properties are calculated by REFPROP.[11] The calibration is conducted in the volume range from (34 to 44) cm^3 and in the bellows displacement range from (−3 to 7) mm as shown in Figure 3. The calibration data are correlated as a function of the displacement of the metal bellows as expressed as follows:

$$V = d_0 + d_1L + d_2L^2 \tag{4}$$

The coefficients in eq 4 are listed in Table 2. The standard deviation of the calibration data from eq 4 is 0.028 cm^3. The uncertainty of the density measurement is less than 0.2 %.

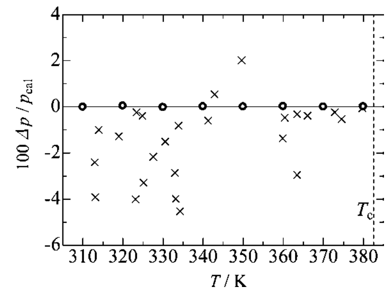

Figure 4. Deviation plots of the vapor-pressure data from eq 5. ○, present work; ×, Grebenkov et al.[1]

Table 2. Coefficients in Equation 4

d_0	41.033
d_1	−1.0014
d_2	0.0047255

Table 3. Experimental Results of the Vapor Pressure for HFO-1234ze(E)

T/K	p_s/kPa
310.000	703 ± 1
320.000	920 ± 1
330.000	1183 ± 1
340.000	1500 ± 1
350.000	1876 ± 1
360.000	2320 ± 1
370.000	2841 ± 1
380.000	3458 ± 1

Table 4. Coefficients in Equation 5

e_1	−7.60109
e_2	2.00169
e_3	−3.85312
e_4	21.2611

Results and Discussion

Vapor Pressures. Eight data points of the vapor pressure are obtained in the temperature range from (310 to 380) K and in the pressure range from (703 to 3458) kPa. The experimental data of the vapor pressure are listed in Table 3. On the basis of the present data, the Wagner type correlation of the vapor pressure is formulated as follows:

$$\ln\left(\frac{p}{p_c}\right) = \frac{T_c}{T}[e_1\tau + e_2\tau^{1.5} + e_3\tau^{2.5} + e_4\tau^5] \tag{5}$$

where τ is $1 - T/T_c$ and critical temperature T_c is 382.51 K determined by Higashi et al.[9] The exponential values in eq 5 are the same as those adopted for HFO-1234yf.[2] The coefficients in eq 5 are listed in Table 4. The deviation plots of the present data and the data by Grebenkov et al.[1] in the effective temperature range from eq 5 are shown in Figure 4. This equation is able to represent the present data with the absolute average deviation of 0.02 % and a maximum deviation of 0.04

Table 5. Key Properties of HFO-1234ze(E)

molar mass M (g·mol^{-1})[10]	144.0416
critical temperature T_c (K)[9]	382.51 ± 0.01
critical density ρ_c (kg·m^{-3})[9]	486 ± 3
critical molar volume V_c (cm^3·mol^{-1})[9]	234.7 ± 1.5
critical pressure p_c (kPa)	3632 ± 3
acentric factor ω	0.296

Table 6. Experimental Results of $p\rho T$ Properties for HFO-1234ze(E)

T/K	p/kPa	ρ/kg·m^{-3}
310.000	5000	1147.7 ± 1.8
310.000	4000	1142.1 ± 1.7
310.000	3000	1136.3 ± 1.7
310.000	2000	1130.2 ± 1.7
320.000	5000	1114.7 ± 1.7
320.000	4000	1108.0 ± 1.6
320.000	3000	1100.9 ± 1.6
320.000	2000	1093.3 ± 1.6
330.000	5000	1080.0 ± 1.7
330.000	4000	1072.2 ± 1.7
330.000	3000	1063.6 ± 1.7
330.000	2000	1054.2 ± 1.6
340.000	5000	1042.4 ± 1.6
340.000	4000	1032.2 ± 1.6
340.000	3000	1021.0 ± 1.5
340.000	2000	1008.1 ± 1.5
350.000	5000	1000.5 ± 1.6
350.000	4000	987.6 ± 1.5
350.000	3000	972.3 ± 1.5
350.000	2000	953.6 ± 1.4
360.000	5000	952.9 ± 1.4
360.000	4000	934.2 ± 1.4
360.000	3000	910.5 ± 1.3
370.000	5000	896.7 ± 1.4
370.000	4000	867.6 ± 1.3
370.000	3000	821.5 ± 1.2

%. On the other hand, the data by Grebenkov et al.[1] are very scattered. Their absolute average deviation is 1.7 %, and the maximum deviation is 4.6 %. The data by Grebenkov et al.[1] are not adopted for formulating the correlation.

The critical pressure p_c is also determined as one of fitting parameters in eq 5. Its value is 3632 kPa. The uncertainty of the critical pressure is estimated to be 3 kPa as an expanded uncertainty consisting of 1 kPa of the uncertainty of the vapor-pressure measurement, 1 kPa of the uncertainty of the vapor-pressure correlation, and 1 kPa of the uncertainty from the vapor-pressure correlation by 0.01 K of the critical-temperature uncertainty. The acentric factor ω is also determined to be 0.296 from eq 6.

$$\omega = -\log\left(\frac{p}{p_c}\right)_{T_r=0.7} - 1 \tag{6}$$

where p in eq 6 is calculated by substituting the reduced temperature $T_r = 0.7$ in eq 5 and p_c determined in this work is used. The key properties of HFO-1234ze(E) are summarized in Table 5.

pρT Properties. Twenty-six data points of $p\rho T$ properties are obtained along with seven isotherms in the temperature range from (310 to 370) K and in the pressure range from (2000 to 5000) kPa. The experimental data of $p\rho T$ properties are listed in Table 6 and shown in Figure 5. The present data is correlated by the following equation:

$$\rho = \rho_c \frac{(p/p_c + F(T/T_c))^{G(T/T_c)}}{H(T/T_c)} \tag{7}$$

where $F(T/T_c) = \sum_{i=0}^{2} f_i(T/T_c)^i$, $G(T/T_c) = \sum_{i=0}^{2} g_i(T/T_c)^i$, $H(T/T_c) = \sum_{i=0}^{2} h_i(T/T_c)^i$. The functional form in this work is used as the same that by Kayukawa et al.[12,13] adopted for some HFCs and hydrocarbons (HCs). Its original function was proposed by Sato.[14] The coefficients in eq 7 are listed in Table 7. The deviation plots of the experimental data from eq 7 are shown in Figure 6. This equation is able to represent the present data with the absolute average deviation of 0.04 % and the maximum deviation of 0.12 %. The data by Grebenkov et al.[1] with eq 7 are compared in the effective temperature range. All of the data by Grebenkov et al.[1] is lower than that of eq 7. The absolute average deviation of the data by Grebenkov et al.[1] is 0.6 %, and their maximum deviation is 1.4 %.

Seven data points of the saturated liquid densities are estimated by extrapolating eq 7 to the vapor pressure and listed in Table 8. The present data are compared with the data by Higashi et al.[9] and the data by Grebenkov et al.[1] Higashi et al.[9] formulated the correlation of the saturated liquid density using their data near the critical temperature and the data by Grebenkov et al.[1] in the wide temperature range from (250 to 380) K. The deviation plots of the saturated liquid-density data from the correlation by Higashi et al.[9] is shown in Figure 7. The behavior of the present data is similar to the data by Grebenkov et al.[1] The absolute average deviation of the present

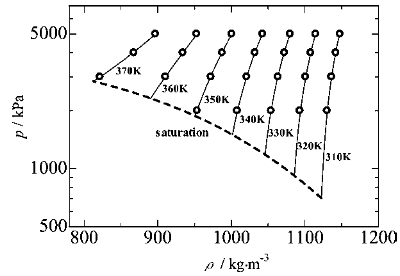

Figure 5. Pressure−density plane. ○, present work; —, isotherms.

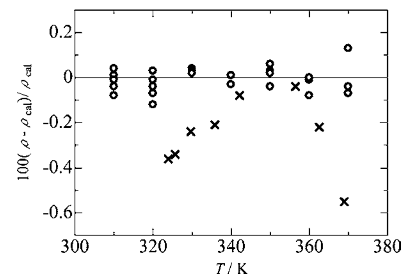

Figure 6. Deviation plots of the experimental density data from eq 7. ○, present work; ×, Grebenkov et al.[1]

Table 7. Coefficients in Equation 7

f_0	69.76524
f_1	−126.57363
f_2	55.85617
g_0	0.20460
g_1	−0.37841
g_2	0.28459
h_0	0.36448
h_1	0.00013
h_2	0.18734

Table 8. Estimated Values of the Saturated Liquid Density for HFO-1234ze(E)

T/K	ρ'/kg·m^{-3}
310.000	1122.6
320.000	1085.7
330.000	1045.8
340.000	1001.5
350.000	950.9
360.000	890.5
370.000	812.4

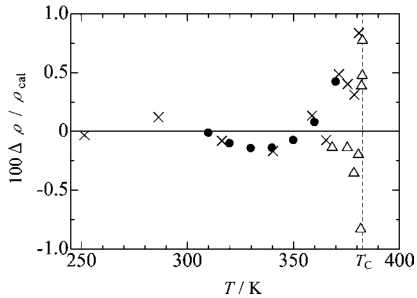

Figure 7. Deviation plots of the saturated liquid-density data from the correlation by Higashi et al.[9] ●, present work; ×, Grebenkov et al.;[1] △, Higashi et al.[9]

data from the correlation is 0.14 %, and the maximum deviation is 0.41 %. The present data is in good agreement with the correlation by Higashi et al.[9]

Conclusion

The measurements of the vapor pressures and $p\rho T$ properties for HFO-1234ze(E) are conducted using a metal-bellows cell. The experimental data of the vapor pressure are obtained in the temperature range from (310 to 380) K and in the pressure range from (703 to 3458) kPa. The experimental data of the $p\rho T$ properties are obtained in the temperature range from (310 to 370) K and in the pressure range from (2000 to 5000) kPa. Correlation of the vapor pressure is formulated as a function of temperature. As for key properties of HFO-1234ze(E), the critical pressure and acentric factor are determined using the vapor-pressure correlation. Correlations of $p\rho T$ properties are formulated as functions of temperature and pressure. The saturated liquid densities are obtained from the correlation of $p\rho T$ properties. The experimental data and correlations of the vapor pressure and $p\rho T$ properties and the estimated values of critical pressure, the acentric factor, and saturated liquid density will be useful to the development of the thermodynamic model for estimating the refrigeration cycle.

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