Measurements of the Isobaric Specific Heat Capacities for *trans*-1,3,3,3-Tetrafluoropropene (HFO-1234ze(E)) in the Liquid Phase

Katsuyuki Tanaka,*,† Gen Takahashi,‡ and Yukihiro Higashi†

Department of Mechanical Systems and Design Engineering, Iwaki Meisei University, Iwaki, Fukushima 970-8551, Japan, and Graduate School of Iwaki Meisei University, Iwaki, Fukushima 970-8551, Japan

The isobaric specific heat capacity of *trans*-1,3,3,3-tetrafluoropropene (HFO-1234ze(E)) in the liquid phase was measured using a metal-bellows calorimeter. Twenty-six data points were obtained in the temperature range from (310 to 370) K and pressure range from (2 to 5) MPa. The relative experimental uncertainty of the isobaric specific heat capacity was estimated to be 5 %. On the basis of the present data, the correlation of the isobaric specific heat capacity in the liquid phase was formulated as functions of temperature and pressure. The heat capacities of saturated liquid were derived from this correlation by substituting the vapor pressure.

Introduction

F-gas regulation in Europe[1] suggests that *trans*-1,3,3,3-tetrafluoropropene (HFO-1234ze(E)) as well as 2,3,3,3-tetrafluoropropene (HFO-1234yf) could be an alternative refrigerant to HFC-134a for automobile air conditioners.[2] The authors have investigated the thermophysical properties of HFO-1234ze(E) by measurements of the critical parameters,[3] saturated liquid densities,[3] vapor pressure,[4] and $p\rho T$ properties.[4] The isobaric specific heat capacity is useful not only in applications such as heat transfer calculations but also for the development of the equation of state. However, there is no literature data of the isobaric specific heat capacity for HFO-1234ze(E).

In this work, measurements of the isobaric specific heat capacity of HFO-1234ze(E) in the liquid phase were carried out, and a correlation as functions of temperature and pressure was developed. The heat capacity of saturated liquid was also derived from this correlation.

Experimental Section

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

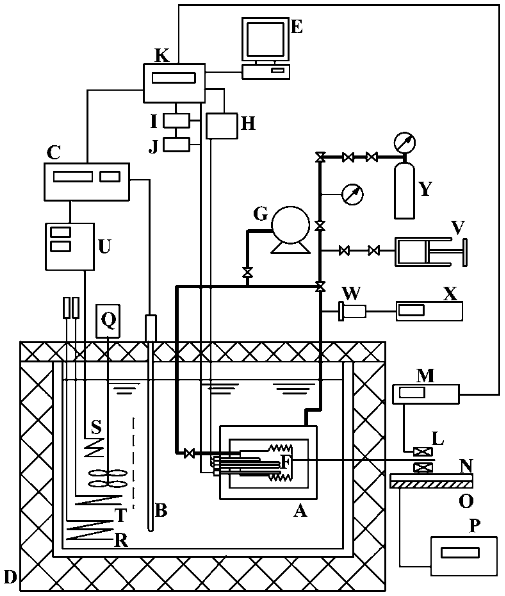

Figure 1. Schematic diagram of the apparatus. A, pressure vessel; B, standard platinum resistance thermometer; C, thermometer bridge; D, thermostatted silicone-oil bath; E, computer; F, calorimeter; G, vacuum pump; H, resistance-measurement circuit; I, standard resistance; J, regulated direct current power supply; K, digital multimeter; L, linear variable differential transformer; M, displacement meter; N, linear stage; O, linear gauge; P, indicator; Q, stirrer; R, main heater; S, supplemental heater; T, cooler; U, proportional integral derivative (PID) controller; V, pressure controller; W, pressure transducer; X, pressure indicator; Y, nitrogen gas bomb.

Apparatus. A metal-bellows calorimeter for measuring the isobaric specific heat capacity for fluids and fluid mixtures was developed by Tanaka and Uematsu.[5] Its data processing with a thermal relaxation method was modified to use a heater coefficient instead of the thermal conductance of the calorimeter for an apparatus constant and described in detail by Tanaka et al.[6] The schematic diagram of the apparatus is shown in Figure 1. The calorimeter is a cylindrical cell with a metal bellows whose volume can be varied from (34 to 44) cm^3. Four stainless-sheathed platinum resistance thermometers and one stainless-sheathed heater were installed in the calorimeter. The calorimeter was inserted in the pressure vessel. A sample of known mass was loaded into the calorimeter, and nitrogen gas as a pressure medium was filled outside of the calorimeter. The pressure of nitrogen gas was 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 calorimeter was compressed or expanded. The pressure of the sample was determined from the measurement of the nitrogen-gas pressure with a consideration of the differential pressure caused by the elastic force of a metal bellows. The differential pressure was calibrated as a function of the displace-

---

* To whom correspondence should be addressed. E-mail: ktanaka@iwakimu.ac.jp. Tel.: +81-246-29-7026. Fax: +81-246-29-0577.

† Department of Mechanical Systems and Design Engineering, Iwaki Meisei University.

‡ Graduate School of Iwaki Meisei University.

10.1021/je900799e

ment of the metal bellows with the uncertainty of 1 kPa. The displacement was detected by a linear variable differential transformer. The pressure vessel with the calorimeter was immersed in a thermostatted silicone-oil bath to keep the temperature constant. The temperature was measured by a 25 Ω standard platinum resistance thermometer (Chino, R800-2) and precise thermometer bridge (Tinsley 5840) with the uncertainty of 5 mK. As this calorimeter is a batch type and has a variable volume cell, measurements can be conducted in wide temperature and pressure ranges by a small sample in comparison with a flow-type calorimeter.[7]

The measurement of the isobaric specific heat capacity was conducted by supplying a constant heat flow to the sample. Then, the energy-balance equation is given in eq 1.

$$\dot{Q} = C\frac{d\Delta T}{dt} + \alpha\Delta T \tag{1}$$

where $\dot{Q}$ is the constant heat flow supplied to the sample, C is the heat capacity of the calorimeter with sample, ΔT is the temperature change of the sample, t is time, and α is the thermal conductance of the calorimeter. Equation 1 can be integrated with an initial condition $\Delta T = 0$ at $t = 0$ as follows.

$$\Delta T = \frac{\dot{Q}}{\alpha}\left[1 - \exp\left(-\frac{\alpha}{C}t\right)\right] \tag{2}$$

Maximum temperature difference $\Delta T_{\max}$ and time constant τ can be expressed as follows.

$$\frac{\dot{Q}}{\alpha} = \Delta T_{\max} \tag{3}$$

$$\frac{C}{\alpha} = \tau \tag{4}$$

Equation 2 can be rewritten by substituting eqs 3 and 4.

$$\Delta T = \Delta T_{\max}\left[1 - \exp\left(-\frac{t}{\tau}\right)\right] \tag{5}$$

The temperature change of the sample ΔT was recorded as an average value of four thermometers in the calorimeter, and the thermal relaxation time τ and maximum temperature change $\Delta T_{\max}$ were obtained. By combining eq 3 with eq 4, the heat capacity of the calorimeter with the sample is obtained.

$$C = \frac{\dot{Q}}{\Delta T_{\max}}\tau \tag{6}$$

The heat capacity of the calorimeter with sample can be written as follows.

$$C = mC_p + C_a \tag{7}$$

where m is the mass of the sample, C_p is the isobaric specific heat capacity of the sample, and C_a is the heat capacity of the calorimeter. Meanwhile, the constant heat flow can be written as follows.

$$\dot{Q} = kEI \tag{8}$$

where E and I are the voltage and the electrical current of the heater, respectively. k is the heater coefficient. The isobaric specific heat capacity C_p was obtained.

$$C_p = \left(k\frac{EI}{\Delta T_{\max}}\tau - C_a\right)/m \tag{9}$$

The mass of the sample filled into the calorimeter was determined from the mass difference of the sample bottle between before and after filling. The mass of the sample bottle was measured by a precision analytical balance with the uncertainty of 2 mg. The heater coefficient k and the heat capacity of the calorimeter C_a were determined by using water, methanol, and HFC-134a in the temperature range from (310 to 370) K and pressures up to 5 MPa. Water was produced by the deionized water unit and degassed four or five times by freeze−thaw cycling with liquid nitrogen before it was loaded into the calorimeter. Methanol was supplied from Kanto Chemical Co., Inc., Japan. Its purity was stated better than 99.8 %. Methanol was dried using a molecular sieve of 0.3 nm for more than 24 h and degassed using the same procedure as that for water. HFC-134a was supplied from Asahi Glass Co., Ltd., Japan, and its purity was stated better than 99.99 % in mass fraction. The values of the isobaric specific heat capacities are used from the literature for water,[8] methanol,[9] and HFC-134a,[10] respectively. The heater coefficient k was determined as a constant value, and the heat capacity of the calorimeter C_a was determined as functions of temperature T and pressure p as follows:

Table 1. Determination of the Heat Capacity of the Calorimeter: Coefficients in Equation 11

$\frac{a}{\mathrm{J \cdot K^{-1}}}$	$\frac{b}{\mathrm{J \cdot K^{-1}}}$	$\frac{c}{\mathrm{J \cdot K^{-1} \cdot MPa}}$
37.059	0.12062	11.522

$$k = 0.6116 \tag{10}$$

$$C_a = a + bT + \frac{c}{p} \tag{11}$$

Coefficients in eq 11 are listed in Table 1. The relative deviation plots of the isobaric specific heat capacities of the calibration fluids are shown in Figure 2 in relation to temperature and in Figure 3 in relation to pressure. The relative uncertainty of the measurement for the isobaric specific heat capacity was estimated to be within 5 %.

Results and Discussion

Twenty-six data points of the isobaric specific heat capacity were obtained in the temperature range from (310 to 370) K

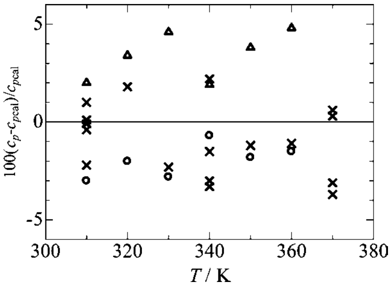

Figure 2. Relative deviation plots of the isobaric specific heat capacities for the calibration fluids in relation to temperature. ○, water; △, methanol; ×, HFC-134a.

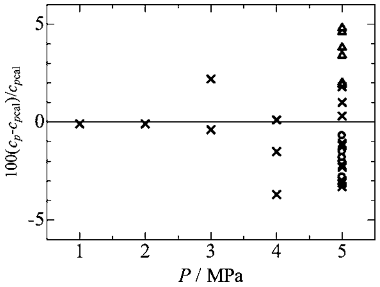

Figure 3. Relative deviation plots of the isobaric specific heat capacities for the calibration fluids in relation to pressure. ○, water; △, methanol; ×, HFC-134a.

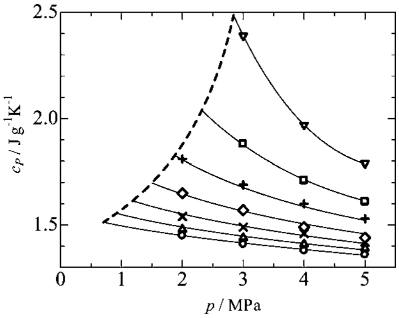

Figure 4. C_p—pressure diagram of HFO-1234ze(E): ○, 310 K; △, 320 K; ×, 330 K; ◇, 340 K; +, 350 K; □, 360 K; ▽, 370 K; —, isothermal line calculated from eq 12; ---, saturated liquid line calculated from eq 12.

Table 2. Experimental Results of the Isobaric Specific Heat Capacity for HFO-1234ze(E)

T / K	p / MPa	C_p / J·g^{-1}·K^{-1}
310.000	5.00	1.36 ± 0.07
310.000	4.00	1.38 ± 0.07
310.000	3.00	1.41 ± 0.07
310.000	2.00	1.45 ± 0.07
320.000	5.00	1.39 ± 0.07
320.000	4.00	1.41 ± 0.07
320.000	3.00	1.44 ± 0.07
320.000	2.00	1.48 ± 0.07
330.000	5.00	1.42 ± 0.07
330.000	4.00	1.46 ± 0.07
330.000	3.00	1.49 ± 0.07
330.000	2.00	1.54 ± 0.08
340.000	5.00	1.44 ± 0.07
340.000	4.00	1.49 ± 0.07
340.000	3.00	1.57 ± 0.08
340.000	2.00	1.65 ± 0.08
350.000	5.00	1.53 ± 0.08
350.000	4.00	1.60 ± 0.08
350.000	3.00	1.69 ± 0.08
350.000	2.00	1.81 ± 0.09
360.000	5.00	1.61 ± 0.08
360.000	4.00	1.71 ± 0.09
360.000	3.00	1.88 ± 0.09
370.000	5.00	1.79 ± 0.09
370.000	4.00	1.97 ± 0.10
370.000	3.00	2.39 ± 0.12

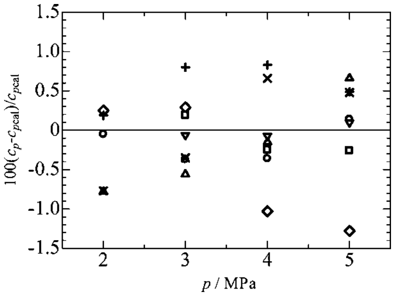

Figure 5. Deviation plots of the present data for the isobaric specific heat capacity from eq 12: ○, 310 K; △, 320 K; ×, 330 K; ◇, 340 K; +, 350 K; □, 360 K; ▽, 370 K.

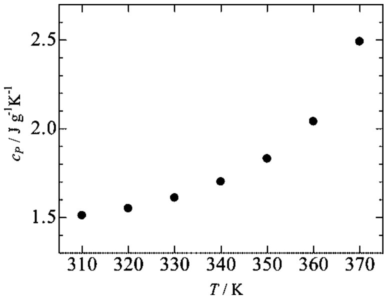

Figure 6. Temperature dependence of the saturated liquid heat capacity for HFO-1234ze(E).

Table 4. Heat Capacity of Saturated Liquid C_p' of HFO-1234ze(E)

T / K	p_s / MPa	C_p' / J·g^{-1}·K^{-1}
310	0.703	1.51
320	0.920	1.56
330	1.183	1.61
340	1.500	1.70
350	1.876	1.83
360	2.320	2.04
370	2.841	2.49

and in the pressure range from (2 to 5) MPa. The experimental data is listed in Table 2 and shown in Figure 4. On the basis of the present data, the correlation was formulated as follows:

$$C_p = A + Bp_r^{0.5} + Cp_r \tag{12}$$

where

$$A = A_1 + \frac{A_2}{(1 - T_r)^2} \tag{13}$$

$$B = B_1 + B_2(1 - T_r) + \frac{B_3}{(1 - T_r)} + \frac{B_4}{(1 - T_r)^2} \tag{14}$$

$$C = \frac{C_1}{(1 - T_r)^{1.5}} + \frac{C_2}{(1 - T_r)^2} \tag{15}$$

$p_r = p/p_c$, and $T_r = T/T_c$. The fundamental functional form of eq 12 used is the same as that by Nakagawa et al.[11,12] and Yomo et al.[13] adopted for the liquid C_p of some refrigerants. Critical pressure p_c is 3.632 MPa determined by Tanaka et al.,[4] and critical temperature T_c is 382.51 K determined by Higashi et al.[3] The coefficients in eqs 13 to 15 are listed in Table 3. The deviation plots of the present data from eq 12 are shown in Figure 5. This equation is able to represent the present data with the average relative deviation of 0.6 % and the maximum relative deviation of 1.3 %. Isotherms calculated from eq 4 are drawn as solid lines in Figure 4.

Saturated liquid heat capacities were calculated from eq 4 by substituting the vapor pressures calculated from the correlation developed by Tanaka et al.[4] These values are listed in Table 4. The calculations of the heat capacities of the saturated liquid were drawn as a broken line in Figure 4. The temperature dependence of the saturated liquid heat capacities is shown in Figure 6.

Conclusions

The measurements of the isobaric specific heat capacity for HFO-1234ze(E) were conducted using a metal-bellows cell. A correlation of the isobaric specific heat capacity was formulated as functions of temperature and pressure on the basis of the

Table 3. Correlation of the Isobaric Specific Heat Capacity for HFO-1234ze(E): Coefficients in Equations 13 to 15

A_1 / J·g^{-1}·K^{-1}	A_2 / J·g^{-1}·K^{-1}	B_1 / J·g^{-1}·K^{-1}	B_2 / J·g^{-1}·K^{-1}	B_3 / J·g^{-1}·K^{-1}	B_4 / J·g^{-1}·K^{-1}	C_1 / J·g^{-1}·K^{-1}	C_2 / J·g^{-1}·K^{-1}
1.3270	0.0098620	−0.43584	0.59944	0.12266	−0.018711	−0.025367	0.010689

present results. The heat capacities of saturated liquid were obtained from the correlation by substituting the vapor pressure.

Literature Cited

(1) European Parliament & Council. Emissions from air conditioning systems in motor vehicles and amending Council Directive 70/156/EEC. *Off. J. Eur. Union* **2006**, *L161*, 12–18.

(2) Spatz, M. W. *Latest Developments in Refrigerants for A/C&R Applications*, Presentation of the International Symposium on New Refrigerants and Environmental Technology, Kobe, Japan, Nov 20−21, 2008.

(3) Higashi, Y.; Tanaka, K.; Ichikawa, T. Critical parameters and saturated densities in the critical region for trans-1,3,3,3-tetrafluoropropene (HFO-1234ze(E)). *J. Chem. Eng. Data* **2009**; DOI: 10.021/je900696z.

(4) Tanaka, K.; Takahashi, G.; Higashi, Y. Measurements of the Vapor Pressures and $p\rho T$ properties for trans-1,3,3,3-tetrafluoropropene (HFO-1234ze(E)). *J. Chem. Eng. Data* **2010**; DOI: 10.021/je900756g.

(5) Tanaka, K.; Uematsu, M. Calorimeter for measuring the isobaric specific heat capacity of fluids and fluid mixtures by the thermal relaxation method. *Rev. Sci. Instrum.* **2006**, *77*, 035110.

(6) Tanaka, K.; Takahashi, G.; Kitayama, A.; Higashi, Y. *Calorimeter for measuring the isobaric specific heat capacity of natural refrigerants*, Proceedings of the 8th IIF/IIR Gustav Lorentzen Conference on Natural Working Fluids, Copenhagen, Denmark, Sept 7−10, 2008; CD-ROM.

(7) Saitoh, A.; Nakagawa, S.; Sato, H.; Watanabe, K. Isobaric heat capacity for liquid HFC-134a. *J. Chem. Eng. Data* **1990**, *35*, 107–110.

(8) Wagner, W.; Pruss, A. The IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use. *J. Phys. Chem. Ref. Data* **2002**, *31* (2), 387–535.

(9) de Reuck, K. M.; Craven, R. J. B. *Methanol: International Thermodynamic Tables of the Fluid State-12*; Blackwell Science Publications: London, 1993.

(10) Tillner-Roth, R.; Baehr, H. D. An International Standard Formulation of the Thermodynamic Properties of 1,1,1,2-Tetrafluoroethane (HFC-134a) for Temperatures from 170 to 455 K at Pressures up to 70 MPa. *J. Phys. Chem. Ref. Data* **1994**, *23*, 657–729.

(11) Nakagawa, S.; Sato, H.; Watanabe, K. Isobaric heat capacity data for liquid HCFC-123 ($CHCl_2CF_3$, 2,2-dichloro-1,1,1-trifluoroethane). *J. Chem. Eng. Data* **1991**, *36*, 156–159.

(12) Nakagawa, S.; Hori, T.; Sato, H.; Watanabe, K. Isobaric heat capacity for liquid 1-chloro-1,1-difluoroethane and 1,1-difluoroethane. *J. Chem. Eng. Data* **1993**, *38*, 70–74.

(13) Yomo, M.; Sato, H.; Watanabe, K. Measurements of isobaric heat capacity for liquid difluoromethane (HFC-32). *High Temp. High Pressures* **1994**, *26*, 267–272.

Received for review October 2, 2009. Accepted January 29, 2010. The authors are grateful to Central Glass Co. Ltd., Japan, for furnishing the sample and analyzing the purity of the sample. This work was conducted as a joint research in Japan with Kyusyu University, Saga University, Iwaki Meisei University, National Institute of Advanced Industrial Science and Technology, The Kansai Electric Power Co., Inc., Hokkaido Electric Power Co., Inc., Hitachi Appliances, Inc., Toshiba Carrier Co., Ltd., Central Glass Co., Ltd., and Showa Tansan Co., Ltd.

JE900799E