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Measurements of the Isobaric Specific Heat Capacity for 1,1,1-Trifluoroethane (R143a), Pentafluoroethane (R125), and Difluoromethane (R32) in the Liquid Phase

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Measurements of the isobaric specific heat capacity for the hydrocarbons 1,1,1-trifluoroethane (R143a), pentafluoroethane (R125), and difluoromethane (R32) were carried out in the liquid phase at a pressure of 5 MPa by using a batch type calorimeter equipped with a metal bellows. Ten data points of the isobaric specific heat capacity for R143a, 11 data points for R125, and seven data points for R32 were obtained in the temperature range from (310 to 350) K and at a pressure of 5 MPa. The experimental uncertainties are estimated to be 5 mK for temperature, 3 kPa for pressure, and 5.2 % for isobaric specific heat capacity. The present results were compared with the literature data and the values calculated from the equation of state. The correlations of the isobaric specific heat capacity were formulated as a function of temperature at a pressure of 5 MPa. Maximum deviations of the present results from correlations were 1.4 % for R143a, 1.5 % for R125, and 0.9 % for R32, respectively.

Introduction

Caloric properties such as enthalpy and heat capacity are important for the performance evaluation of a refrigeration cycle. These values can be calculated from the equation of state. However, most of equations of state are developed without the experimental data for these caloric properties because of the lack of sufficient data. As refrigerants are used under high pressure, caloric properties under high pressure such as the compressed liquid phase are required.

1,1,1-Trifluoroethane (R143a), pentafluoroethane (R125), and difluoromethane (R32) are components of widely used refrigerants R507A, R410A, and R407C. The equation of state for R143a was developed by Lemmon and Jacobsen.[1] However, no heat capacity data including the isobaric specific heat capacity was used in the fit. The isobaric specific heat capacity of the liquid phase was reported only by Yamamura et al.[2] They obtained 30 data points in the temperature range from $T = (285$ to $330)$ K and pressure range from (1.5 to 3.0) MPa. Lemmon and Jacobsen stated that additional experimental information on the isobaric heat capacity of the liquid phase is needed. As for R125, its equation of state was also developed by Lemmon and Jacobsen,[3] and no heat capacity data was used, similar to R143a. There were only two data sets for the isobaric specific heat capacity of the liquid phase for R32 by Wilson et al.[4] and by Kan et al.[5] Wilson et al. obtained five data points in the temperature range from $T = (285$ to $325)$ K and pressure range from (1.5 to 3.0) MPa. As for R32, its equation of state was developed by Tillner-Roth and Yokozeki,[6] and the isochoric heat capacity in the liquid phase and saturated heat capacity data by Lüddecke and Magee[7] were used in the fit. Data of the isobaric specific heat capacity in the liquid phase was reported by Yomo et al.,[8] but there was no data table in their paper.

Experimental Apparatus

The calorimeter for measuring the isobaric specific heat capacity by the thermal relaxation method was reported previously.[9] The calorimeter is a cylindrical vessel with metal bellows whose volume is variable from (33 to 43) cm^3. A heater and four platinum resistance thermometers (100 Ω) were put into the calorimeter. The calorimeter is inserted into the pressure vessel, and nitrogen gas as a pressure medium is filled between the calorimeter and the pressure vessel. The sample was loaded into the calorimeter from the sample bottle. The sample can be pressurized through the metal bellows by pressurizing nitrogen gas, and the sample pressure is kept constant at a selected value of pressure. The pressure of nitrogen gas is measured by a precise digital pressure gauge, and the pressure of the sample is set in consideration of the pressure due to the elastic deformation of the metal bellows with an uncertainty of 3 kPa. The pressure vessel is immersed in the thermostat in silicone oil, and the temperature of the pressure vessel is kept constant at a selected value of temperature. The temperature of the silicone oil in the thermostat is measured by a 25 Ω standard platinum resistance thermometer and a precise thermometer bridge with an uncertainty of 5 mK.

When a constant heat flow is supplied to the sample by a heater, the record of the temperature change is obtained as an average value of the four thermometers. The isobaric specific heat capacity c_p is determined by the following relation:

$$c_p = \left(k\frac{EI}{\Delta T_{\max}}\tau - C_{\mathrm{a}}\right)/m \qquad (1)$$

where E, I, and k are the voltage, electrical current, and coefficient of a heater, respectively. τ is a thermal relaxation time, and $\Delta T_{\max}$ is a maximum temperature change. m is the mass of the sample, and C_{a} is the heat capacity of the calorimeter. E and I are measured by a digital multimeter. τ and $\Delta T_{\max}$ are obtained from a record of the temperature change. m is determined from the mass difference of the sample bottle.

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Table 1. Experimental Isobaric Specific Heat Capacity for R143a, R125, and R32

	R143a		R125			R32
	ser. 1	ser. 2	ser. 1	ser. 2	ser. 3	ser. 1
	m/g					
	30.715	24.649	40.611	37.073	31.179	32.160
T/K	c_p/(kJ·kg^{-1}·K^{-1})					
310.00	1.62 ± 0.08		1.29 ± 0.07			2.05 ± 0.11
315.00	1.67 ± 0.09		1.33 ± 0.07			2.11 ± 0.11
320.00	1.73 ± 0.09		1.36 ± 0.07			2.18 ± 0.11
325.00	1.79 ± 0.09		1.43 ± 0.07			2.30 ± 0.12
330.00	1.85 ± 0.10		1.52 ± 0.08	1.53 ± 0.08		2.42 ± 0.13
335.00	1.93 ± 0.10			1.61 ± 0.08		2.67 ± 0.14
340.00	2.07 ± 0.11			1.77 ± 0.09	1.81 ± 0.09	3.16 ± 0.16
345.00	2.26 ± 0.12	2.29 ± 0.12			2.02 ± 0.11	
350.00		2.67 ± 0.14			2.35 ± 0.12	

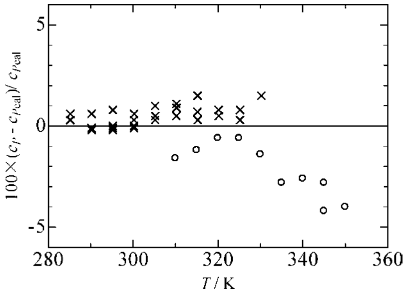

Figure 1. Deviations between the values calculated according to the equation of state of Lemmon and Jacobsen and the experimental data obtained for the isobaric specific heat capacities of R143a at several temperatures. ○, present work; ×, Yamamura et al.

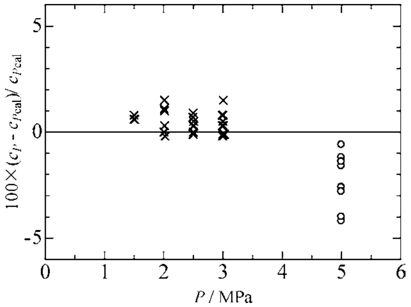

Figure 2. Deviations between the values calculated according to the equation of state of Lemmon and Jacobsen and the experimental data obtained for the isobaric specific heat capacities of R143a at several pressures. ○, present work; ×, Yamamura et al.

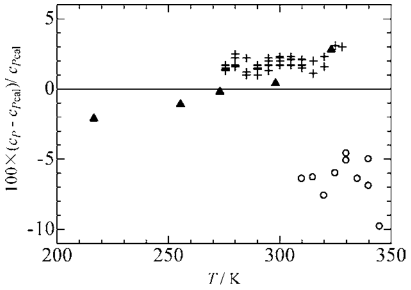

Figure 3. Deviations between the values calculated according to the equation of state of Lemmon and Jacobsen and the experimental data obtained for the isobaric specific heat capacities of R125 at several temperatures. ○, present work; +, Kan et al.; ▲, Wilson et al.

The mass of the sample bottle is measured by a precision analytical balance with an uncertainty of 2 mg. The terms k and C_a are apparatus constants and were evaluated in advance by using water, methanol, and R134a. The relative standard deviation of the isobaric specific heat-capacity measurements for water, methanol, and R134a was 2.6 %. The uncertainty of the measurements of the isobaric specific heat capacity was estimated to be 5.2 % as the coverage factor $k = 2$.

The sample of R143a and R125 were supplied from Asahi Glass Co. Ltd., Japan, and their purities were better than 99.99 in mass fraction. The sample of R32 was supplied from Daikin Industrial Co. Ltd., Japan, and its purity was better than 99.9999 in mole fraction.

Results and Discussion

Ten data points of the isobaric specific heat capacities for R143a, 11 data points for R125, and seven data points for R32 were obtained in the temperature range from $T = (310\text{ to }350)$ K and at a pressure of 5 MPa. The present results are listed in Table 1.

R143a. Figures 1 and 2 show relative deviations of the existing data of the isobaric specific heat capacity including the present data from the equation of state developed by Lemmon and Jacobsen.[1] No c_p data was used in their fit. The data from Yamamura et al.[2] show systematically positive deviations from the equation of state of about 1 %. The deviations of the present data increase with the increase of temperature having values from (−0.5 to −4) %. Since the temperature dependence of the isobaric specific heat capacity becomes larger near the critical temperature of 345.88 K and critical pressure of 3.764 MPa reported in our previous work,[10] the present data will be used in the improvement of the equation of state.

R125. Figures 3 and 4 show deviations of the existing data of the isobaric specific heat capacity including the present data from the equation of state developed by Lemmon and Jacobsen.[3] No c_p data was used in their fit. The data by Kan et al.[5] shows systematically positive deviations from the equation of state with the values from (1 to 3) %. The data by Wilson et al.[4] crossed at about 280 K. The present data have systematically negative deviations from the equation of state with the values between −4 % and −10 %. As the data for R125 was also obtained near critical temperature (339.17 K) and critical pressure (3.616 MPa) in a previous work,[11] it will be incorporated to improve the equation of state.

R32. Figure 5 shows the deviation of the present data of the isobaric specific heat capacity for R32 from the equation of state developed by Tillner-Roth and Yokozeki.[6] No data was used in their fit. There are no data in the liquid phase. As far as the data near critical temperature (351.26 K) and critical pressure (5.785 MPa) for R32 have been published in a previous work,[11] this data and the present data will be incorporated to improve the equation of state.

Correlation. The temperature dependence of the values of the isobaric specific heat capacity is shown in Figure 6. The present data was correlated as follows,

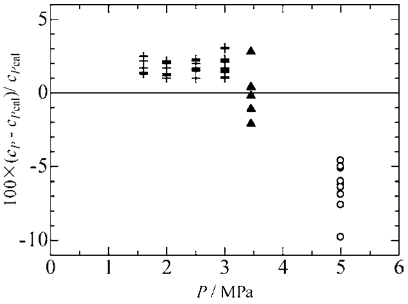

Figure 4. Deviations between the values calculated according to the equation of state of Lemmon and Jacobsen and the experimental data obtained for the isobaric specific heat capacities of R125 at several pressures. ○, present work; +, Kan et al.; ▲, Wilson et al.

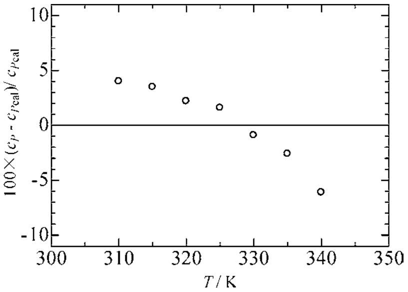

Figure 5. Deviations between the values calculated according to the equation of state of Tillner-Roth and Yokozeki and the experimental data obtained for the isobaric specific heat capacities of R32 at several pressures. ○, present work.

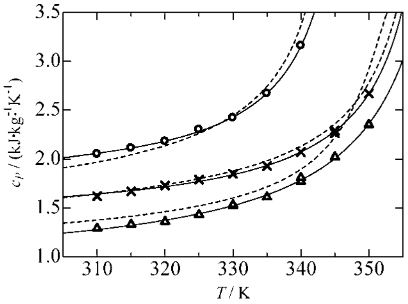

Figure 6. Plot of the values of the isobaric specific heat capacities at 5 MPa of pressure versus temperature. ×, R143a; △, R125; ○, R32; solid line indicates the correlation; dashed line indicates the equation of state.

Table 2. Numerical Values of Adjustable Parameters in Equation 2

	a / kJ·kg^{-1}·K^{-1}	b / kJ·kg^{-1}	c / K
R143a	1.320	16.97	362.6
R125	0.826	25.60	366.7
R32	1.679	15.20	350.3

$$c_{p,5\mathrm{MPa}} = a + \frac{b}{c - T} \tag{2}$$

where a, b, and c are adjustable parameters. The numerical values of adjustable parameters are summarized in Table 2. Calculations by these correlations are also drawn in Figure 6 as solid lines. The relative deviation of the present data from eq 2 is shown in Figure 7. The maximum relative deviations were 1.4 % for R143a, 1.5 % for R125, and 0.9 % for R32.

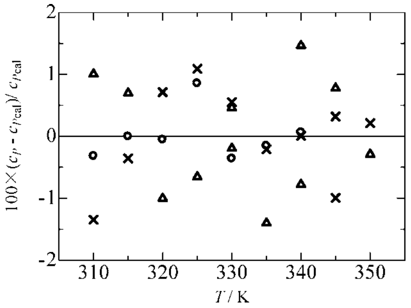

Figure 7. Deviations between the values calculated according to the correlation equation and the experimental data obtained for the isobaric specific heat capacities at several temperatures. ×, R143a; △, R125; ○, R32.

Conclusion

Measurements of the isobaric specific heat capacity for R143a, R125, and R32 were carried out in the temperature range from (310 to 350) K and at a pressure of 5 MPa in the liquid phase. On the basis of the measurements, correlations for the isobaric specific heat capacity were formulated. Since the present work provides data in new regions of temperature and pressure, the data will be incorporated to improve the equation of state.

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