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Isochoric Specific Heat Capacity of *trans*-1,3,3,3-Tetrafluoropropene (HFO-1234ze(E)) and the HFO-1234ze(E) + CO_2 Mixture in the Liquid Phase

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ABSTRACT: The isochoric specific heat capacity (c_V) of *trans*-1,3,3,3-tetrafluoropropene (HFO-1234ze(E)) and mole fraction x = 0.489 HFO-1234ze(E) + $(1 - x)$ = 0.511 CO_2 in the liquid phase were measured with a twin-cell type adiabatic calorimeter. The sample purity of HFO-1234ze(E) and CO_2 was certified to have a minimum purity of 0.9996 mole fraction and 0.99999 mole fraction respectively by gas chromatographic analysis. The measurements were obtained for temperatures ranging from (270 to 425) K and at pressures up to 30 MPa. Temperatures were measured with a platinum resistance thermometer on the bottom of each cell and were reported based on the International Temperature Scale of 1990 (ITS-90). Sample pressures were measured with a quartz crystal transducer. Densities were calculated from the volume of the calorimeter cell and the sample mass. The expanded uncertainty (with a coverage factor $k = 2$) of temperature measurements is 13 mK and 8 kPa for pressure measurements. The expanded relative uncertainty of density is 0.16 %. As a result, the experimental expanded relative uncertainty of the isochoric specific heat capacity (c_V) is estimated to be from 3.8 % to 4.6 % in the liquid phase. The c_V measurements were almost the same as the values calculated from the proposed equations of state except near the critical isochore.

1. INTRODUCTION

trans-1,3,3,3-Tetrafluoropropene (HFO-1234ze(E)) has generated attention as a candidate of the next generation of refrigerants to replace hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs). Compared with current fluorocarbon refrigerants, its effect on the environment is very low. The ozone depletion potential (ODP) of HFO-1234ze(E) is 0, and the global warming potential (GWP) is 6; the atmospheric lifetime is approximately 2 weeks, and its flammability and toxicity risks are low. Table 1 shows the fundamental physical properties of HFO-1234ze(E)[1] and CO_2.[2] To use HFO-1234ze(E) as an aerosol agent, foaming agent, or refrigerant, thermodynamic research on HFO-1234ze(E) has progressed because of the work of many researchers, for example, *PVT* properties,[3,4,5] equations of state (EOS),[6,7] and isobaric heat capacity.[8] However, the accumulation of experimental measurements of thermodynamic properties of HFO-1234ze(E) is currently insufficient. Various thermophysical property measurements are necessary to develop a reliable equation of state which is required for the use of HFO-1234ze(E).

The inclination and curvature of the pressure—volume—temperature (*PVT*) curved surface vary by substance. It is difficult to reproduce the behavior of $(\partial^2 P/\partial T^{2})_v$ by direct measurement of the *PVT* properties. Therefore, isochoric specific heat capacity (c_V) measurements are important in permitting the calculation of the second derivative of the pressure to temperature relationship accurately. In this study, c_V of HFO-1234ze(E) and the mixture of HFO-1234ze(E) and CO_2 which is environmentally benign in the atmosphere having a low global warming potential were measured in the temperature range from (270 to 425) K at pressures up to 30 MPa.

Table 1. Fundamental Physical Properties for HFO-1234ze(E) and CO_2

	HFO-1234ze(E)	CO_2
chemical formula	$CF_3CH{=}CFH$	$O{=}C{=}O$
critical temperature (K)	382.51	304.128
critical pressure (MPa)	3.632	7.377
critical density ($g \cdot cm^{-3}$)	0.486	0.4676
molar mass ($g \cdot mol^{-1}$)	114.04	44.0098

2. MEASUREMENTS

2.1. Experimental Procedures. A twin-cell type adiabatic calorimeter was used for these measurements; it has been described previously in detail by Kuroki et al.[9] and Kitajima et al.[10] A spherical cell (approximately 33 cm^3) contains the sample, and a second identical cell serves as a reference. The calorimeter is capable of reaching 470 K. For the heat-capacity measurements, precisely measured electrical energy (Q) is continuously applied, and the resulting temperature rise ($\Delta T = T_2 - T_1$) is measured. c_V is obtained from

$$c_V \left(\frac{\partial U}{\partial T}\right)_V \cong \frac{\alpha(\Delta Q - \Delta Q_0) - W_{PV}}{m \Delta T} \tag{1}$$

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Table 2. Experimental Data for HFO-1234ze(E) and $x = 0.489$ HFO-1234ze(E) + $(1 - x) = 0.511$ CO_2[a]

T	p	ρ	c_V	T^*	p^*	ρ^*	$c_V{}^*$
K	MPa	$g \cdot cm^{-3}$	$J \cdot g^{-1} \cdot K^{-1}$	K	MPa	$g \cdot cm^{-3}$	$J \cdot g^{-1} \cdot K^{-1}$
270.15	5.540	1.2666	0.941	270.15	10.302	1.1918	0.951
275.15	7.679	1.2662	0.940	275.15	14.848	1.1910	0.956
280.15	9.813	1.2657	0.947	280.15	19.370	1.1901	0.963
285.15	11.937	1.2653	0.946	285.15	23.857	1.1892	0.964
290.15	14.055	1.2649	0.942	286.15	24.752	1.1890	0.993
295.15	16.163	1.2644	0.940	290.15	28.318	1.1883	0.968
295.15	2.684	1.1850	0.968	290.15	7.501	1.1157	0.981
300.15	4.324	1.1847	0.975	295.15	11.107	1.1150	0.995
305.15	5.963	1.1843	0.977	300.15	14.713	1.1142	1.002
310.15	7.598	1.1840	0.984	301.15	15.434	1.1141	1.004
315.15	9.231	1.1836	0.982	302.15	16.154	1.1140	1.001
320.15	10.858	1.1833	0.990	303.15	16.872	1.1138	0.992
325.15	12.483	1.1829	0.986	306.15	19.026	1.1133	0.979
330.15	14.103	1.1825	0.992	310.15	21.888	1.1127	1.017
335.15	15.720	1.1822	0.982	315.15	25.455	1.1120	1.011
335.15	3.368	1.0482	1.077	320.15	28.987	1.1112	0.999
340.15	4.423	1.0479	1.066	320.15	9.139	1.0038	0.966
345.15	5.477	1.0477	1.069	325.15	11.633	1.0032	0.976
350.15	6.529	1.0474	1.061	330.15	14.125	1.0027	0.971
355.15	7.582	1.0471	1.052	335.15	16.616	1.0021	0.956
360.15	8.633	1.0469	1.042	340.15	19.103	1.0016	0.956
365.15	9.684	1.0466	1.039	345.15	21.584	1.0010	0.982
370.15	10.734	1.0463	1.043	350.15	24.061	1.0004	0.977
375.15	11.784	1.0461	1.044	355.15	26.532	0.9999	0.978
380.15	12.833	1.0458	1.060	360.15	28.998	0.9993	1.007
385.15	13.882	1.0456	1.061	361.15	7.303	0.6489	1.262
390.15	14.930	1.0453	1.056	365.15	7.938	0.6487	1.247
395.15	15.976	1.0450	1.071	370.15	8.742	0.6485	1.287
385.15	4.344	0.7175	1.717	375.15	9.557	0.6483	1.320
390.15	4.695	0.7174	1.691	380.15	10.380	0.6481	1.340
395.15	5.051	0.7173	1.667	385.15	11.211	0.6479	1.335
400.15	5.410	0.7171	1.626	390.15	12.047	0.6476	1.356
405.15	5.772	0.7170	1.589	395.15	12.887	0.6474	1.379
410.15	6.137	0.7169	1.546	400.15	13.731	0.6472	1.328
415.15	6.503	0.7168	1.529	405.15	14.576	0.6470	1.307
420.15	6.872	0.7167	1.501	410.15	15.424	0.6468	1.241
425.15	7.243	0.7166	1.469	415.15	16.273	0.6466	1.197
				420.15	17.122	0.6463	1.182
				425.15	17.972	0.6461	1.173

[a] The symbols (T, p, ρ, c_V) represent that for HFO-1234ze(E), and symbols ($T^*, p^*, \rho^*, c_V{}^*$) represent that for mole fraction $x = 0.489$ HFO-1234ze(E) + mole fraction $x = 0.511$ CO_2.

where U is the internal energy, ΔQ_0 is the energy difference between the sample cell and the reference cell when both cells are empty, ΔQ refers to the energy added during an experiment with a sample in the cell and a blank (vacuum) in the reference cell, W_{PV} is the change-of-volume work due to the slight dilation of the cell, α (determined to be 0.940) is the available electrical energy supplied to the heater wire, and m is the mass of sample in the sample cell. To calculate the c_V, the value of temperature rise ΔT was used as $\Delta T = 1$ K.

To prepare for measurements, the sample cell was cooled to about 263 K and completely evacuated. The sample was charged into the calorimeter by a cryopump method. Then, measurements were performed by raising the temperature until either the upper temperature or the pressure (30 MPa) was reached on the quasi-isochore. At the completion of the run, a portion of the sample in the cell was filled into a light cylinder so as to obtain the next filling density. Then it was weighed with an electronic balance. The next run was started with a lower density. After all of these runs are completed, the remaining sample in the cell was filled and weighed. The measurement were carried out by heating the sample cell whose temperature will follow the temperature of the reference cell heated with a constant current.

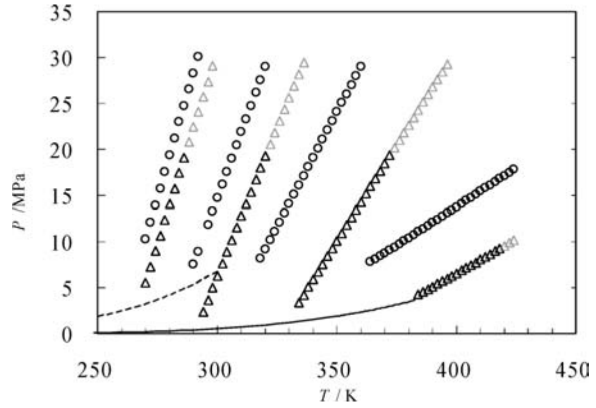

Figure 1. Distributions of the experimental measurements spaced by 2 K for pressure and temperature at the temperature range from (270 to 425) K and for pressures up to 30 MPa. The symbols correspond to the experimental data obtained by this work (△, HFO-1234ze(E); ○, x = 0.489 HFO-1234ze(E) + (1 − x) = 0.511 CO_2; —, saturated vapor pressure for HFO-1234ze(E);[5] - - -, saturated vapor pressure for CO_2[2]). The light-colored symbols show the outside of the available range of the EOS by McLinden et al.[6]

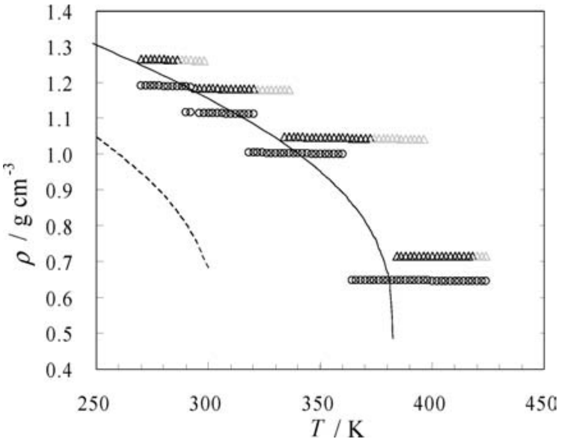

Figure 2. Distributions of the experimental measurements for density and temperature obtained by this work. The symbols correspond to the experimental data obtained by this work (△, HFO-1234ze(E); ○, x = 0.489 HFO-1234ze(E) + (1 − x) = 0.511 CO_2; —, saturated liquid density for HFO-1234ze(E);[5] - - -, saturated liquid density for CO_2[2]). The light-colored symbols show the outside of the available range of the EOS by McLinden et al.[6]

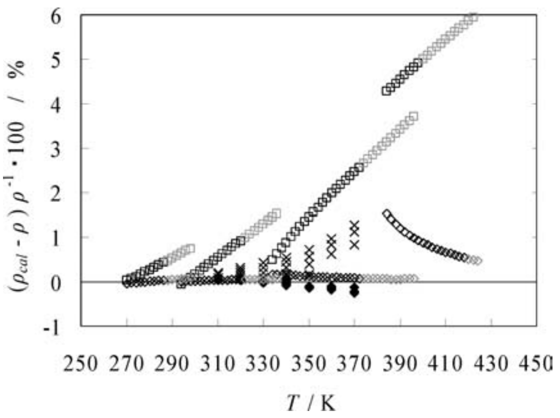

Figure 3. Percentage deviations of the values calculated with the EOS by McLinden et al.[6] and Akasaka[7] from the experimental density data for HFO-1234ze(E) obtained by this work and Tanaka et al.[5] This work: ◇, the calculated values from the EOS by McLinden et al.;[6] □, the calculated values from the EOS by Akasaka.[7] Tanaka et al.:[5] ◆, the calculated values from the EOS by McLinden et al.;[6] ×, the calculated values from the EOS by Akasaka.[7]

2.2. Materials. High-purity samples of HFO-1234ze(E) were used for this measurement. The HFO-1234ze(E) was certified to have a minimum purity of 0.9996 mole fraction that was obtained by gas chromatographic analysis carried out by the sample's manufacturer, and the minimum purity of CO_2 was 0.99999 claimed by it is manufacturer. The mixture used in this study was prepared inside the calorimeter cell. A quantity of each pure gaseous component was filled into its own lightweight cylinder (75 cm^3) and was weighed with a digital balance having 0.1 mg uncertainty. After both components were introduced into the cell from its cylinder, the cell was cooled below 278 K by a mini-cooler. The remaining mass in each cylinder was weighed, and the composition of the sample in the cell was calculated from the mass charged to the cell. The sample composition of the mixture consisted of x = 0.489 HFO-1234ze(E) + (1 − x) = 0.511 CO_2. To ensure complete homogenization prior to measurement, the sample temperature was rapidly increased until the sample pressure reached 20 MPa; then it was cooled, and this process was repeated two or three times.

2.3. Assessment of Uncertainty. The experimental expanded uncertainty (with a coverage factor k = 2) of the absolute temperature measurement is 13 mK by considering the calibration report of the PRTs (± 2 mK), temperature gradients in the cell, and the accuracy of each instrument. The value for the pressure measurement for k = 2 is ± 8 kPa, based on the pressure transducer's specifications and the accuracy of the instruments. The standard uncertainty of the inner volume of the cell is 0.025 cm^3, estimated by calibration with distilled water, and that of the mass measurement is 0.15 mg, based on balance specifications and the standard uncertainty of the air buoyancy effect. The estimated expanded uncertainty of the density is 0.16 %, as derived from the standard uncertainties of the inner volume of the cell and the mass measurement. The expanded uncertainty of c_V is estimated from a combination of the standard uncertainty of the elapsed time required for a 1 K temperature rise (0.65 %), that of the change-of-volume work (20 %) which contributes 0.3 % to the uncertainty of c_V, the experimental standard deviation of α of 0.6 %, the uncertainty of the density, and the temperature fluctuation of the adiabatic shields which contribute an amount of $0.4/(mc_V)$ $J \cdot g^{-1} \cdot K^{-1}$ to the uncertainty of c_V. The resulting expanded uncertainty (k = 2) of c_V is estimated to be from 3.8 % to 4.6 % in the liquid phase. The value of the expanded uncertainty changes with the value of the density and temperature. The lower density or the higher temperature will lead to the higher expanded uncertainty of c_V.

3. RESULTS

Isochoric specific heat capacity (c_V) of HFO-1234ze(E) and x = 0.489 HFO-1234ze(E) + (1 − x) = 0.511 CO_2 have been measured in the liquid phase for temperatures ranging from (270 to 425) K and at pressures up to 30 MPa. Table 2 presents the experimental data (T, P, ρ, c_V) at temperatures spaced by 5 K for HFO-1234ze(E) and x = 0.489 HFO-1234ze(E) + (1 − x) = 0.511 CO_2, respectively. Figure 1 shows the pressure and temperature distributions of the experimental measurements

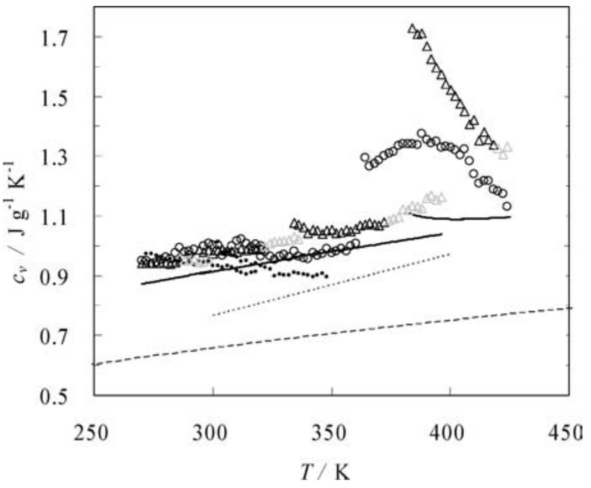

Figure 4. Isochoric specific heat capacity (c_V) for HFO-1234ze(E) and $x = 0.489$ HFO-1234ze(E) + $(1 - x) = 0.511$ CO_2 in the liquid phase (△, c_V for HFO-1234ze(E); ○, c_V for $x = 0.489$ HFO-1234ze(E) + $(1 - x) = 0.511$ CO_2; ●, c_V for CO_2;[11] · · ·, the calculated isochoric specific heat capacity c_{V0} of the ideal gas for HFO-1234ze(E);[8] - - -, the calculated isochoric specific heat capacity of the ideal gas for CO_2;[2] —, the calculated c_V values from the EOS by McLinden[6]). The light-colored symbols show the outside of the available range of the EOS by McLinden et al.[6]

obtained by this work. The data are plotted in each figure spaced by 2 K. The solid line represents the calculated values of saturated vapor pressure for HFO-1234ze(E) from the correlation by Takahashi et al.[5] The broken line represents the calculated values of saturated vapor pressure for CO_2 calculated with an EOS established by Span and Wagner.[2] The light-colored symbols show the outside of the available range of the EOS by McLinden et al.[6] Each measurement was made along four isochores.

Figure 2 shows the density and temperature distributions of the experimental measurements obtained by this work. The solid line represents the calculated values of saturated liquid density for HFO-1234ze(E).[5] The broken line represents the calculated values of saturated liquid density of CO_2.[2] The light-colored symbols show the outside of the available range of the EOS by McLinden et al.[6]

Figure 3 shows the percentage deviations of the values calculated with EOS proposed by McLinden et al.[6] and Akasaka[7] from the experimental density data for HFO-1234ze(E) obtained by this work and Tanaka et al.[5] The available range of the EOS reported by Akasaka[7] is from (240 to 400) K for temperature, below 20 MPa for pressure, and below 1.527 g·cm^{-3} for density. As for the EOS by McLinden et al.[6] is from (168 to 420) K, below 20 MPa, and 1.5053 g·cm^{-3}. The deviations of the values are also presented outside of the available range of the equations by using the light-colored symbol. The calculated values from the EOS by McLinden et al.[6] indicate very good agreement with the measurements below 375 K, but the deviations of density increase to 1.5 % near the critical temperature. As for the calculated values from the EOS by Akasaka,[7] the deviations of density tend to be large as the temperature increases at each isochore and approaches 5 % near the critical temperature.

Figure 4 shows the experimental behavior of c_V. The dotted line in the figure represents calculated isochoric specific heat capacity of the ideal-gas, c_{V0}, for HFO-1234ze(E) derived from the gaseous isobaric specific heat capacity measured by Kagawa et al.[8] The broken line represents the c_{V0} for CO_2 reported by Span and Wagner.[2] The solid line represents the calculated values for HFO-1234ze(E) from the EOS by McLinden et al.[6] Also shown in Figure 4 are results of Fujita et al.,[11] whose data have been measured previously with the same apparatus used in this work at over the temperature range from $T = (270$ to $350)$ K. The light-colored symbols show the outside of the available range of the EOS by McLinden et al.[6] While the c_V measurements for HFO-1234ze(E) increase at almost same rate as c_{V0} and the calculated values from the EOS by McLinden et al.[6] below 380 K, they significantly increase and indicate discontinuous values near the critical isochore between (380 and 430) K. Then, they decrease rapidly with the rise of the temperature. As for $x = 0.489$ HFO-1234ze(E) + $(1 - x) = 0.511$ CO_2, the c_V values are the almost the same as with HFO-1234ze(E) below 325 K. On the other hand, the values are on the average between HFO-1234ze(E) and CO_2 above 325 K. Figure 5 shows the percentage deviations of the calculated values with the equations of state by McLinden et al.[6] and Akasaka[7] from the experimental c_V data for HFO-1234ze(E) obtained in this work and the measurements of the isobaric specific heat capacity c_P by Tanaka et al.[12] The deviations of the values are also presented at the outside of the available range of the equations. The deviations of c_V from the measurements were within ± 10 % below 380 K, which covers the available range of the equations; however, the deviations increase suddenly above 380 K.

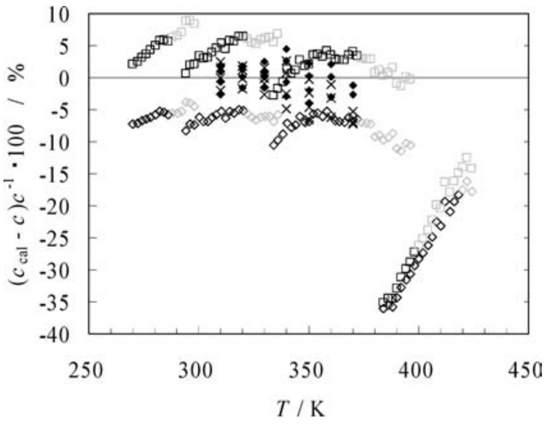

Figure 5. Percentage deviations of the values calculated with the EOS by McLinden et al.[6] and Akasaka[7] from the experimental isochoric specific heat capacity data for HFO-1234ze(E) obtained by this work and the measurements of the isobaric specific heat capacity c_P by Tanaka et al.[12] This work: ◇, the calculated values from the EOS by McLinden et al.;[6] □, the calculated values from the EOS by Akasaka.[7] Tanaka et al.:[12] ◆, the calculated values from the EOS by McLinden et al.;[6] ×, the calculated values from the EOS by Akasaka.[7]

4. CONCLUSIONS

Isochoric specific heat capacity (c_V) for HFO-1234ze(E) and $x = 0.489$ HFO-1234ze(E) + $(1 - x) = 0.511$ CO_2 were reported in the temperature range of $T = (270$ to $425)$ K with an uncertainty ranging from 3.8 % to 4.6 %. At present, other experimental c_V information for HFO-1234ze(E) is not available, which can be compared to this work. It is expected that the measured values would be useful for the development of new equations of state and also for industrial applications.

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