Measurement of Isobaric Heat Capacity of Gaseous Trans-1,3,3,3-tetrafluoropropene (HFO 1234ze (E))

Noboru KAGAWA *†, Atsushi MATSUGUCHI *, Koichi WATANABE **

* Department of Mechanical Systems Engineering, Faculty of Systems Engineering, National Defense Academy (1-10-20 Hashirimizu, Yokosuka 239-8686, Japan)
** Department of System Design Engineering, Faculty of Science and Technology, Keio University (3-14-1 Hiyoshi, Yokohama 223-8522, Japan)

Summary

The specific isobaric heat capacity ($c_p$) was measured for HFO-1234ze(E) (trans-1,3,3,3-tetrafluoropropene) in the gas phase. HFO-1234ze(E) has a lower GWP value of 6 and is one of new environment-friendly refrigerants. Nineteen measurements for HFO-1234ze(E) were obtained at temperatures from 303 K to 363 K and at pressures from 0.35 MPa to 1.3 MPa. The expanded uncertainty ($k=2$) of the temperature measurements is estimated to be less 22 mK, and that of the pressure measurements is less 4.4 kPa. The expanded uncertainty for $c_p$ is estimated to range from 14 to 21 J kg$^{-1}$ K$^{-1}$.

Key words: Heat capacity, Refrigerant, Trans-1,3,3,3-tetrafluoropropene, Isobar, Gas phase, Ideal-gas heat capacity, Thermodynamics

1. Introduction

HFO-1234ze(E) (trans-1,3,3,3-tetrafluoropropene, CHF$_2$=CHF) is considered as one of new environment-friendly refrigerants and has a potential to replace conventional refrigerants, e.g., HFC-125 (pentafluoroethane, CHF$_2$CF$_3$) and HFC 134a (1,1,2-tetrafluoroethane, CH$_2$FCF$_3$). Ozone depletion potential (ODP) of HFO-1234ze(E) is zero, and global warming potential (GWP) is 6, which is much smaller than that of hydrofluorocarbons currently used as refrigerants.

In order to use a new refrigerant, the thermophysical property information about the refrigerant is required. Among the information, isobaric heat capacity ($c_p$) is one of the fundamental thermophysical property data which are used to design application systems. However, available thermophysical property data for HFO-1234ze(E)$^{1-5}$ are currently very limited, especially for caloric properties. For $c_p$ of the liquid HFO-1234ze(E), Takahashi et al.$^4$ obtained 26 data at temperatures from 310 K to 370 K and at pressures from 2 MPa to 5 MPa. However, there are no available $c_p$ data in the gas phase.

In Table 1, the fundamental thermophysical property data for HFO-1234ze(E)$^{1-3}$ are tabulated. For comparison, the corresponding data of HFC-125 and HFC-134a obtained from a reliable compilation$^6$ are listed in Table 1. The thermophysical property data of HFO-1234ze(E), HFC-125 and HFC-134a are almost identical.

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Mukoyama et al.\textsuperscript{7)}, and Yasumoto and Watanabe\textsuperscript{8)} of Keio University obtained \(c_p\) data of HFC-143a (1,1,1-trifluoroethane, CH\textsubscript{3}CF\textsubscript{3}) in the gas phase by using a flow calorimeter. After the apparatus was transferred to the National Defense Academy in 2003, additional 10 \(c_p\) data for HFC-143a were obtained. The measurements and the previous 17 \(c_p\) data for HFC-143a which had been obtained at Keio University were evaluated with available equations of state\textsuperscript{9)}. Furthermore, \(c_p\) data in the gas phase of HFC-134a\textsuperscript{10)}, carbon dioxide (CO\textsubscript{2})\textsuperscript{10)}, HFE-347pfc\textsubscript{2} (1,1,2,2-tetrafluoroethyl-2,2,2-trifluoroethylether, CH\textsubscript{2}CF\textsubscript{3}OCHF\textsubscript{2}CF\textsubscript{2})\textsuperscript{11)}, and HFC-125\textsuperscript{12)} were obtained and reported by the authors.

In this work, \(c_p\) data of HFO-1234ze(E) in the gas phase was obtained by using the flow calorimeter. The measurements are obtained at temperatures from 303 K to 363 K and at pressures from 0.35 MPa to 1.3 MPa.

### 2. Measurements

#### 2.1 Experimental Procedure

A flow calorimeter (D in Fig. 1) was used for these measurements; it has been described previously in detail by Mukoyama et al.\textsuperscript{7)} and the authors\textsuperscript{10)}. A stable and steady flow of sample gas is provided, and heat flux is generated by a microheater inserted in the calorimeter tube. The calorimeter tube is surrounded with an evacuated thermal shield. The tube and shield are placed in a

\begin{table}[h]
\centering
\begin{tabular}{|l|c|c|c|}
\hline
\textbf{Refrigerant} & \textbf{HFO-1234ze(E)} & \textbf{HFC-125} & \textbf{HFC-134a} \\
\textbf{Chemical Formula} & CH\textsubscript{3}CF\textsubscript{3}=CHF & CHF\textsubscript{3}CF\textsubscript{3} & CH\textsubscript{2}CF\textsubscript{3} \\
\hline
Molar mass (kg·kmol\textsuperscript{-1}) & 114.042 & 120.021 & 102.031 \\
Normal boiling point temperature (K) & 254 & 225.07 & 247.08 \\
Critical temperature (K) & 382.51 & 339.165 & 374.083 \\
Critical pressure (kPa) & 3647 & 3618 & 4048 \\
Critical density (kg·m\textsuperscript{-3}) & 486 & 568 & 509 \\
\hline
ODP (R 11=1)* & 0 & 0 & 0 \\
GWP (CO\textsubscript{2}=1, ITH=100 year)** & 6 & 3500 & 1430 \\
\hline
\end{tabular}
\caption{Fundamental thermophysical property data, ODP and GWP values for HFO-1234ze(E)\textsuperscript{1,3)}, HFC-125 and HFC-134a obtained from a reliable compilation\textsuperscript{6)}.}
\end{table}

* ODP values are those adopted under the Montreal Protocol on Substances that Deplete the Ozone Layer.
**GWP values were taken from the IPCC fourth Assessment Report.

![Fig. 1 Apparatus](image-url)
well-stirred water bath which is controlled at the target temperature within ±10 mK. Each \( c_p \) datum is determined by measuring the temperature increment, \( \Delta T \), and mass flow rate, \( \dot{M} \), of HFO-1234ze(E).

To measure the temperature increment, two calibrated standard platinum resistance thermometers (PRTs) \((P_1, P_2)\) are located at both ends of the microheater in the sample flow. To measure the mass flow rate, a three-way solenoid valve \((K)\), a timer \((L)\), and a sampling cylinder \((I)\) were used. During one minute, the sample is permitted to flow into the cylinder that was cooled by liquefied nitrogen. The cylinder mass was measured with an electronic balance with an uncertainty of 0.1 mg.

To establish a stable sample flow in the calorimeter tube during measurements, a condenser \((M)\) with a liquid pump \((N)\), an evaporator \((B)\), and a nozzle (needle valve) \((G)\) are used for the apparatus. The liquid pump is a bellows type and is driven by a stepping motor. A mass flow meter \((R)\) was inserted after the needle valve to observe the flow conditions. The mass flow can be adjusted by the needle valve. The sample pressure at the calorimeter outlet was measured with a quartz crystal pressure transducer \((\text{Paroscientific, Model 31K-101})\) \((F)\).

By measuring the heat input to the heating element, \( \dot{Q}_s \), and mass flow rate, \( \dot{M} \), experimental values of \( c_{p,\text{app}} \) are obtained from

\[
c_{p,\text{app}} = \frac{\dot{Q}_s}{\dot{M} \Delta T} = \frac{\dot{Q}_s}{\dot{M} \Delta T} + \frac{\dot{Q}_L}{\dot{M} \Delta T} = c_p + \frac{\dot{Q}_L}{\dot{M} \Delta T} . \tag{1}
\]

Part of the heating energy, \( \dot{Q}_L \), is released from the sample and the calorimeter to the surroundings even though the calorimeter is thermally shielded. In order to determine the value of \( \dot{Q}_L \), more than four \( c_{p,\text{app}} \) data were measured by changing the mass flow rate from 2.3 to 4.7 g min\(^{-1}\) with \( \Delta T = 2 \) K at the same temperature and pressure. By plotting a \( c_{p,\text{app}} \) curve versus \( \dot{M}^{-1} \) and extrapolating the curve to \( \dot{M}^{-1} \rightarrow 0 \), the actual \( c_p \) value can be determined. For example, the points at 303.15 K and 343.15 K, both under 0.35 MPa were determined as shown in Fig. 2. Vertical error bars in the figure indicate the expanded uncertainties (with a coverage factor \( k = 2 \)) of the experimental data.

2.2 Materials A sample of HFO-1234ze(E) of a minimum purity of 99.96 mol% was obtained for this study. The sample supplied in a bottled cylinder was filled into the apparatus. The total mass of the charged sample was about 1 kg.

2.3 Assessment of Uncertainties The experimental expanded uncertainty has been described previously in detail\(^{10}\). The expanded uncertainty according to the ISO guideline (with a coverage factor \( k = 2 \)) of the temperature measurement is from 6 mK to 22 mK, by considering the calibration test of the PRTs (the expanded uncertainty is 3.5 mK), the temperature fluctuation and distribution in the calorimeter (<22 mK), and the accuracy of each instrument. That of the pressure measurement is less than 4.5 kPa, based on the pressure transducer’s specifications (0.6 kPa) and pressure fluctuations (<2.2 kPa).

The expanded uncertainty of \( c_p \) is estimated from a combination of the standard uncertainty of the mass flow rate during 1 minute (<0.30 mg s\(^{-1}\)), that of the supplied heat quantity (<19 mW), and that of the temperature increment (<18 mK). The resulting expanded uncertainty of \( c_p \) ranges from 14 to 21 J kg\(^{-1}\) K\(^{-1}\) depending on the conditions of each
3. Results and Discussion

Figure 3 shows the $c_p$-$T$ diagram of the present measurements for HFO-1234ze(E). Vertical error bars in the figure indicate the uncertainties of the experimental data. The experimental $c_p$ values and the expanded uncertainties are tabulated in Table 2. In Fig. 3, the isobaric data along 0.35, 0.7, 1.0, and 1.3 MPa are smoothly connected with four lines. The behavior of the isobars seems to be reasonable.

The present measurements along isotherms of 318 K, 333 K, and 353 K are plotted and are connected with three lines in Fig. 4. The values correspond to 0.832, 0.871, and 0.923 of reduced temperature, $T_r = T/T_c$, respectively. In this figure, calculated isotherms of HFC-125 and HFC-134a in terms of virial equations of state by Sato et al. are included. From the figure, it becomes clear that the gaseous $c_p$ values for HFO-1234ze(E) are almost 17% larger than those for HFC-125 and are 5% larger than HFC-134a. The behavior of the present measurements along each isotherm is quite similar to that of HFC-125 and HFC-134a although the absolute values differ at the same reduce pressure value.

At present, there is no equation of state formulated with calorimetric property data for HFO-1234ze(E) in the gas phase. Therefore, the ideal-gas heat capacity information obtained from the present measurements is useful to present the thermodynamic surface. Based on the behavior of the present measurements and the plotted isotherms of HFC-125 and HFC-134a in Fig. 4, five data of the isobaric ideal-gas heat capacity, $c_{p,0}$ of

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$p$ (kPa)</th>
<th>$c_p$ (J·kg$^{-1}$·K$^{-1}$)</th>
<th>Expanded uncertainty ($k = 2$)</th>
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<td></td>
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<td>$T$ (mK)</td>
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<tr>
<td>303.15</td>
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HFO-1234ze(E) were graphically determined (Table 3). Vertical error bars in the figure indicate the uncertainties of the experimental data. The $c_{p,0}$ data were correlated with an equation.

$$c_{p,0} = \frac{3.151 + 12.08 T_r - 1.4147 T_r^2}{R}.$$  \hspace{1cm} (2)

where, $R$ is the universal gas constant, 8.314472 kJ·kmol$^{-1}$·K$^{-1}$. The applicable temperature range of the correlation is from 303 K to 363 K corresponding to the measurement range. The uncertainty in the calculated results with Eq. (2) is estimated to be about 2 % because the maximum deviation of the values from the $c_{p,0}$ data is 0.03 % and the estimated uncertainty of the $c_{p,0}$ data is about 2 % as shown in Table 3. The calculated $c_{p,0}$ values with Eq. (2) are also shown in Fig. 3.

### 4. Conclusions

Measurements of $c_p$ were reported for HFO-1234ze(E) in the gas phase. Based on the measurements, a correlation of the isobaric ideal-gas heat capacity for HFO-1234ze(E) was formulated.
The present measurements show reasonable behavior. Also, the isobaric heat capacity behavior along isotherms for HFO-1234ze(E) is compared with that of HFC-125 and HFC-134a.

From the comparison, it became clear that $c_p$ values of HFO-1234ze(E) are approximately 17% higher than those of HFC-125. This is an advantage to use this environment-friendly substance for refrigeration systems. The present measurements will contribute to establish thermodynamic models for designing the applications so as to represent thermodynamic properties of HFO-1234ze(E).

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