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Thermal Conductivity of HFC-32, HFC-125, and HFC-134a in the Solid Phase[1]

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Measurements of the thermal conductivity of HFC-32, HFC-125, and HFC-134a were carried out for the first time in both solid and liquid phases at the saturation pressure at room temperature and in the temperature ranges from 120 to 263, from 140 to 213, and from 130 to 295 K, respectively. A transient hot-wire instrument using one bare platinum wire was employed for measurements, with an uncertainty of less than ±2%. The experimental results demonstrated that the thermal conductivity of HFC-32, HFC-125, and HFC-134a in the solid phase showed a positive temperature dependence. For HFC-32 and HFC-125, there were big jumps between the solid and the liquid thermal conductivity at the melting point. But for HFC-134a, the solid and liquid thermal conductivity at the melting point is almost-continuous.

KEY WORDS: HFC-32; HFC-125; HFC-134a; melting point; refrigerant; thermal conductivity; transient hot-wire method.

1. INTRODUCTION

Up to the present, we have measured the thermal conductivity of the pure components HFC-32, HFC-125, and HFC-134a and their mixtures [1–5] in the liquid phase. In the present work, to obtain the solid thermal conductivity of these materials and to investigate the behavior of their thermal conductivity at the melting point, we measured the solid and liquid thermal conductivity of HFC-32, HFC-125, and HFC-134a at their saturation pressures at room temperature, 1.48, 1.29, and 0.61 MPa, and in the

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temperature ranges from 120 to 263, from 140 to 213, and from 130 to 295 K, respectively.

2. EXPERIMENTAL APPARATUS

The measurements were performed with an uncertainty of less than ±2% in a transient hot-wire instrument with a single bare platinum wire. Figure 1 shows a cross-sectional diagram of the hot-wire cell with the pressure vessel. To improve the life span of the hot wire while the sample was solidifying, a relatively thick platinum wire, 15 μm in diameter, was used. In order to compensate for the end effect of the hot wire, two voltage potential leads of the same platinum wire were spot-welded at positions nearly 10 mm from each end of the wire. Between the two potential leads, the transient voltage rise, which corresponds to the temperature increase in the wire, was measured directly with the digital voltmeter. The measuring electrical system used in the present work was the same as that used in previous work [2].

Figure 2 shows a schematic diagram of the experimental apparatus. The temperature-controlled thermostatic bath was composed of double concentric cylinders. The pressure vessel was immersed completely in the inner cylinder of the thermostat. The heat transfer medium was liquid nitrogen, which was contained in the outer cylinder of the thermostat. Two electrical heaters were wound on the upper and lower parts of the pressure vessel. By adjusting both the amount of the liquid nitrogen in the bath and the electrical power of the two heaters, we can regulate the temperature of the sample. To monitor the vertical temperature gradient of the sample, three chromel–alumel thermocouples were placed on the upper, middle, and lower surfaces of the pressure vessel. The temperature of the sample was measured with a platinum–cobalt resistance thermometer calibrated on the ITS-90 with an accuracy of ±0.05 K. In order to prevent the occurrence of the initial natural convection, the temperature in the upper part of the pressure vessel was always adjusted to be 1 to 2 K higher than that in the lower part. During the measurements, the temperature change rate of the heat transfer medium was regulated to be less than 0.002 $\mathrm{K \cdot s^{-1}}$ in order to ensure the high accuracy of the measurements.

The uncertainty of the temperature coefficient of the platinum wire is ±0.3%, the uncertainty of the temperature rise slope of the hot wire is ±0.5%, and the uncertainty of the heat generation of the hot wire is ±0.2%. Taking into account the end effect of the hot wire and the other corrections, the total uncertainty of the thermal conductivity is estimated to be better than ±2%.

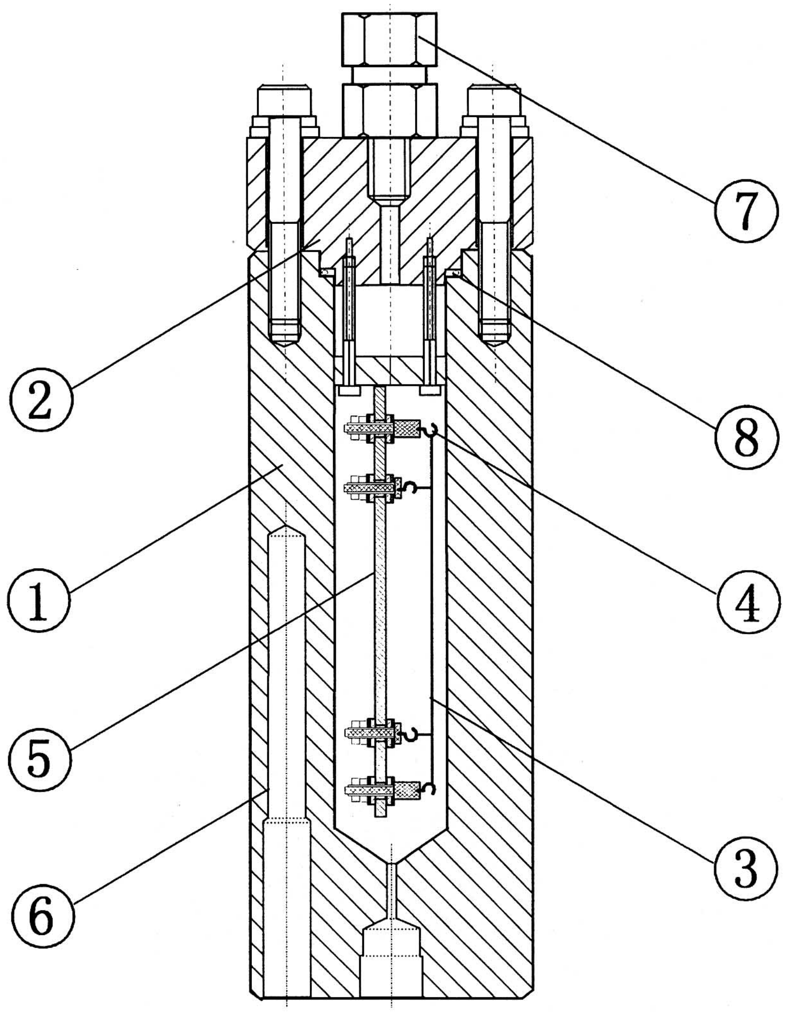

Fig. 1. Sectional diagram of the hot-wire cell with the pressure vessel: (1) pressure vessel (duralumin), (2) pressure vessel cap, (3) platinum wire (15-μm diameter), (4) platinium hook (0.5-mm diameter), cell frame (titanium), (6) Pt–Co resistance thermometer well, (7) sealing unit (Conax), and (8) metal O-ring.

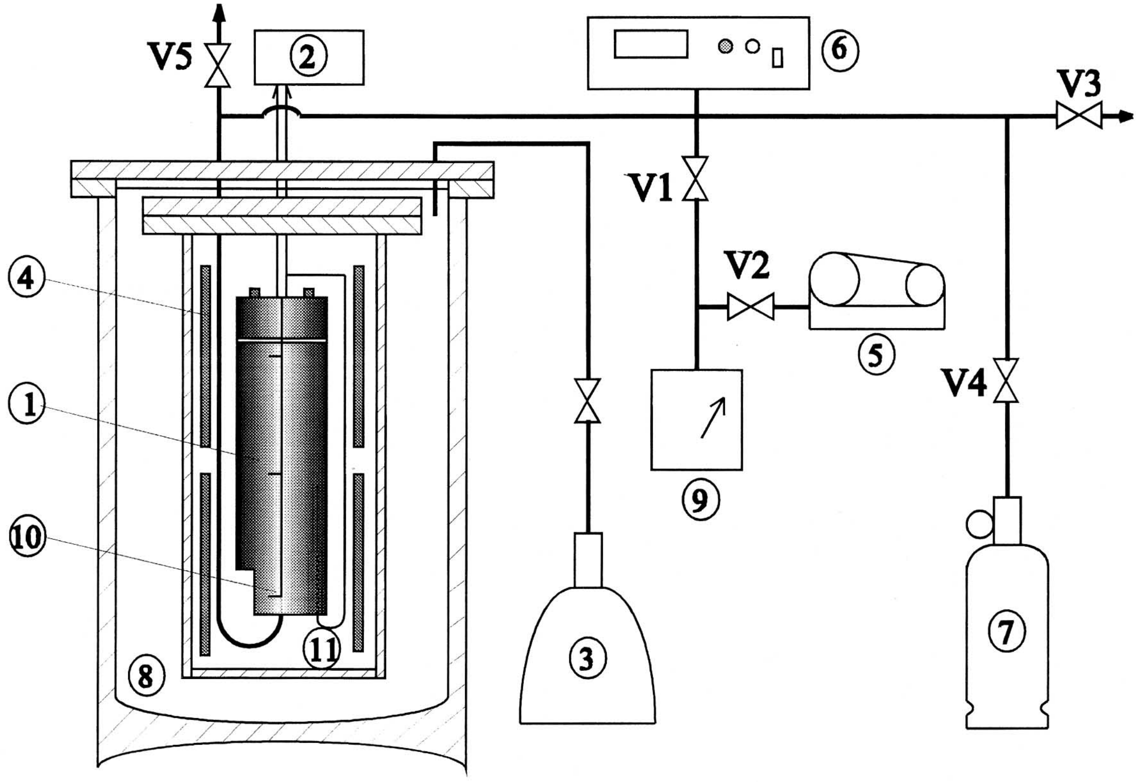

Fig. 2. Schematic diagram of the experimental apparatus: (1) pressure vessel, (2) digital voltmeter, (3) liquid N_2, (4) heater, (5) vacuum pump, (6) pressure gauge, (7) sample bomb, (8) cryostat, (9) vacuum gauge, (10) thermocouples, and (11) Pt–Co resistance thermometer.

3. RESULTS AND DISCUSSION

The performance of the experimental apparatus was tested by performing measurements of the liquid thermal conductivity of toluene, which agreed with IUPAC recommended values [6] within a deviation of 2 to 3%. During the experiments for HFC-32, HFC-125, and HFC-134a, the pressure vessel was always connected to the sample cylinder, which remained at the saturation pressure associated with room temperature. The measurements started at room temperature, and the solid thermal conductivity was measured in succession following the measurements in the liquid phase. Near the melting point, the sample was cooled for about 5 h to ensure complete solidification.

3.1. HFC-32

The measurements of the thermal conductivity of HFC-32 were performed two times using two hot-wire cells at the saturation pressure at room temperature (1.48 MPa) over the temperature ranges from 120 to 135 and from 136 to 263 K in the solid and liquid phases, respectively. A sample of HFC-32 with a purity of better than 99.98% by mass was supplied by Showa Denko Co., Ltd.. The experimental results for HFC-32 in the solid phase are listed in Table I. The thermal conductivity of HFC-32 in the solid and liquid phases is plotted as a function of temperature in Fig. 3. Above 193 K, the present results in the liquid phase agree very well with

Table I. Thermal Conductivity of HFC-32 in the Solid Phase at the Saturation Pressure at Room Temperature (1.48 MPa)

Temperature (K)	Thermal conductivity, λ ($W \cdot m^{-1} \cdot K^{-1}$)
135.0	0.2805
134.2	0.2882
133.1	0.2897
132.9	0.2882
133.0	0.2859
128.9	0.2872
128.6	0.2881
127.4	0.2845
127.6	0.2876
127.6	0.2881
120.3	0.2583
120.4	0.2523
120.5	0.2593

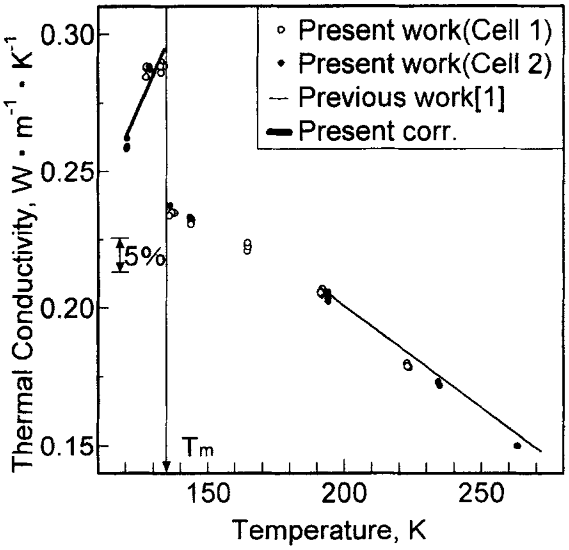

Fig. 3. Thermal conductivity of HFC-32 in the solid and liquid phases as a function of temperature.

our previous work [1]. Because there are no previous measurements in the solid phase, no comparison is possible. The experimental results between the measurements of the first and those of the second series agree well with each other within an accuracy of ±2%. In the vicinity of the melting point, the solid and the liquid thermal conductivity of HFC-32 is not continuous. The thermal conductivity of HFC-32 in the solid phase is higher than that in the liquid phase at the melting point. The thermal conductivity of HFC-32 in the solid phase shows a positive temperature slope. During the measurements near the melting point, we observed that the reproducibility became worse sometimes, and the measured data were about 10 to 40% higher than the expected values. It is assumed that this is due to the latent heat generation during the liquid–solid phase transition. Therefore, these data were removed in the present work. The solid thermal conductivity of HFC-32 can be represented as a function of temperature in the range 120 to 136 K by

$$\begin{aligned}\lambda_S &= \lambda_m + a(T - T_m)\\ &= 0.2987 + 2.25 \times 10^{-3}(T - 136)\end{aligned} \qquad (1)$$

Here λ_S is the solid thermal conductivity $(\mathrm{W \cdot m^{-1} \cdot K^{-1}})$, λ_m is the solid thermal conductivity at the melting point $(\mathrm{W \cdot m^{-1} \cdot K^{-1}})$, and T_m is the estimated temperature of the melting point according to the present measurements.

3.2. HFC-125

Measurements of the liquid and solid thermal conductivity of HFC-125 were carried out at the saturation pressure at room temperature (1.29 MPa) over the temperature range from 140 to 213 K. A sample of HFC-125 with a purity of 99.6%, by mass, was supplied by Du Pont–Mitsui Fluorochemicals Co., Ltd.. Table II lists the experimental results for HFC-125 in the solid phase. The experimental results of HFC-125 in the solid and liquid phases are shown in Fig. 4. Previously we have measured the liquid thermal conductivity in the temperature range from 193 to 333 K [2]. As shown in Fig. 4, the present results in the liquid phase above 193 K agree with our previous work within ±2%. Contrary to the situation for HFC-32, though there is a big jump between the solid and the liquid thermal conductivity of HFC-125 at the melting point, the thermal conductivity of HFC-125 in the solid phase is lower than that in the liquid phase. The solid thermal conductivity of HFC-125 also shows a positive temperature slope, similar to HFC-32. For the same reason as in the case for HFC-32, the measured data near the melting point were removed for

Table II. Thermal Conductivity of HFC-125 in the Solid Phase at the Saturation Pressure at Room Temperature (1.29 MPa)

Temperature (K)	Thermal conductivity, λ ($W \cdot m^{-1} \cdot K^{-1}$)
169.1	0.1034
169.0	0.1031
169.1	0.1021
162.2	0.1028
162.2	0.1007
160.4	0.1009
160.4	0.0996
160.5	0.1015
150.8	0.0997
151.0	0.0972
151.0	0.0991
140.7	0.0991
140.6	0.1004

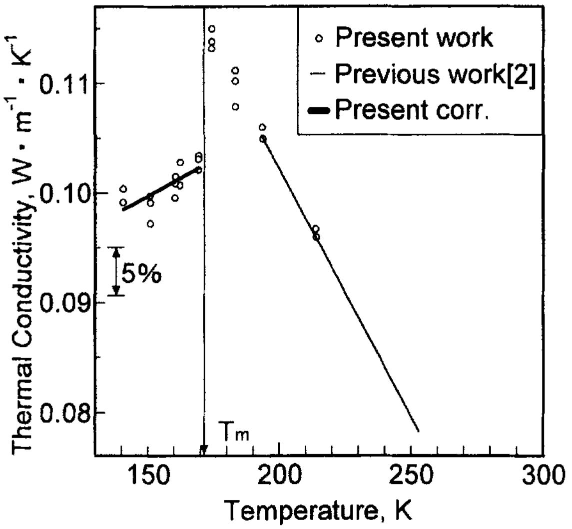

Fig. 4. Thermal conductivity of HFC-125 in the solid and liquid phases as a function of temperature.

HFC-125. The solid thermal conductivity of HFC-125 is correlated as a linear function of temperature in the range 140 to 172 K according to

$$\begin{aligned}\lambda_S &= \lambda_m + a(T - T_m)\\ &= 0.1027 + 1.34 \times 10^{-4}(T - 172) \qquad (2)\end{aligned}$$

3.3. HFC-134a

Measurements for HFC-134a have been carried out at the saturation pressure at room temperature (0.61 MPa) in the liquid phase from 179.8 to 295 K and in the solid phase from 130 to 166.5 K. The sample of HFC-134a used here was supplied by ICI Chemicals and Polymers, and its purity was confirmed to be better than 99.9%, by mass. Table III lists the experimental results for HFC-134a in the solid phase. Figure 5 shows the temperature dependence of the solid and liquid thermal conductivity for HFC-134a. It is clear from Fig. 5 that the present results in the liquid phase above 193 K agree with our previous work [3] within the mutual uncertainties. No comparison is possible in the solid phase because no previous work is available. Contrary to the situation for HFC-32 and HFC-125, the solid and liquid thermal conductivity of HFC-134a at the melting point is

Table III. Thermal Conductivity of HFC-134a in the Solid Phase at the Saturation Pressure at Room Temperature (0.61 MPa)

Temperature (K)	Thermal conductivity, λ ($\mathrm{W \cdot m^{-1} \cdot K^{-1}}$)
166.5	0.1304
166.0	0.1310
166.1	0.1303
160.7	0.1282
160.9	0.1277
160.8	0.1269
150.9	0.1242
151.1	0.1240
150.4	0.1242
150.5	0.1242
151.0	0.1244
130.3	0.1168
130.6	0.1192
130.2	0.1182
130.8	0.1193
130.1	0.1187

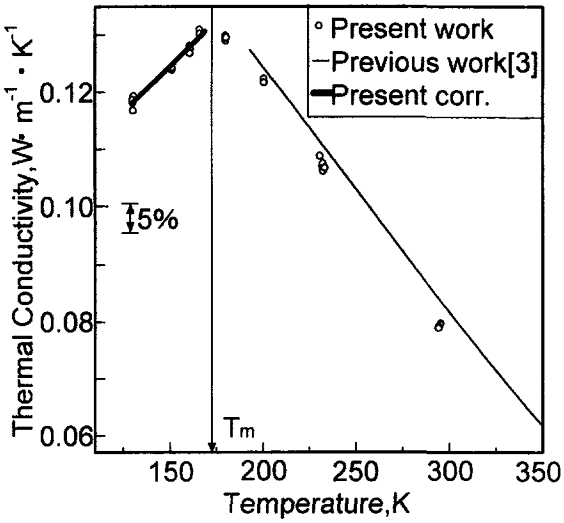

Fig. 5. Thermal conductivity of HFC-134a in the solid and liquid phases as a function of temperature.

almost-continuous. Like HFC-32 and HFC-125, the solid thermal conductivity of HFC-134a also shows a positive temperature slope. During the liquid–solid transition at the melting point, the measured data were removed in the present work because of the poor reproducibility due to the latent heat generation. The experimental data in the solid phase have been represented in the range 130 to 170 K as a function of temperature by the following equation:

$$\begin{aligned}\lambda_S &= \lambda_m + a(T - T_m)\\ &= 0.1310 + 3.21 \times 10^{-4}(T - 170)\end{aligned} \tag{3}$$

For nonmetallic materials, the ratio of the solid to the liquid thermal conductivity at the melting point is approximately expressed as [7]

$$\frac{\lambda_S}{\lambda_L} \cong \left(\frac{\rho_S}{\rho_L}\right)^{g_L} \tag{4}$$

where λ_S and λ_L represent the solid and liquid thermal conductivity at the melting point, respectively, and ρ_S and ρ_L are the solid and liquid density at the melting point, respectively. The exponent g_L, which depends only on the thermal properties of the liquid phase, is defined as the variation of the liquid thermal conductivity λ_L with the volume at constant temperature near the melting point. For most of the nonmetallic substances, g_L is estimated to be in the range from 1 to 4. It can be assumed that the different behavior of the thermal conductivity of HFC-32, HFC-125, and HFC-134a at the melting point indicates a different change in density during the solid–liquid phase transition. As no solid and liquid density data are available at the melting point for HFC-32, HFC-125, and HFC-134a, the above-mentioned assumption remains to be verified by measuring the solid and liquid densities at the melting point in the near-future.

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