The Thermal Conductivity of CFC Alternatives HFC-125 and HCFC-141b in the Liquid Phase

X. Gao,¹ T. Yamada,¹ Y. Nagasaka,^{1,2} and A. Nagashima¹

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The liquid thermal conductivities of the CFC alternatives, HFC-125, and HCFC-141b measured by a transient hot-wire apparatus with one bare platinum wire are reported in the temperature ranges from 193 to 333 K (HFC-125, $CHF_2 \cdot CF_3$) and from 193 to 393 K (HCFC-141b, $CC1_2F \cdot CF_3$), in the pressure ranges from 2 to 30 MPa (HFC-125) and from 0.1 to 30 MPa (HCFC-141b), respectively. The results have been estimated to have an accurancy of $\pm 0.5\%$. The liquid thermal conductives obtained have been correlated by a polynomial of temperature and pressure which can represent the experimental results within the standard deviations of 0.49% for HFC-125 and 0.46% for HCFC-141b, respectively.

KEY WORDS: CFC- alternatives; HCFC-141b; HFC-125; thermal conductivity; transient hot-wire method.

1. INTRODUCTION

It is an urgent task to search for environmentally safe CFC alternatives after the negotiation of the Montreal Protocol in 1987 to limit the production of certain chlorofluorocarbons. HFC-125 and HCFC-141b are both potential replacements for some working fluids employed in industry. The lack of good-quality experimental thermal conductivity data motivated our efforts to make measurements for these two fluids in the liquid phase.

In the past, we have measured the thermal conductivities of HCFC-123, and HFC-134a in gaseous and liquid phases [1-3] in the wide range of temperatures and pressures. In this paper, we present the results of

¹ Department of Mechanical Engineering, Keio University, 3-14-1 Hiyoshi, Yokohama 223, Japan.

² To whom correspondence should be addressed.

measurement of the liquid thermal conductivities of HFC-125 in the temperature range form 193 to 333 K and in the pressure range from 2 to 30 MPa and HCFC-141b in the temerature range from 193 to 393 K and in the pressure range from 0.1 to 30 MPa, respectively.

2. APPARATUS

A transient hot-wire apparatus with an accurancy of $\pm 0.5\%$ was emloyed in these measurements. The fundamental working equation of the transient hot-wire technique takes the form

$$\lambda(T_{\rm r}, P) = \frac{q}{4\pi} \left| \frac{dT}{d\ln t} \right| \tag{1}$$

in which $\lambda(T_r, P)$ represents the thermal conductivity of the fluid at a reference temperature T_r and at the working pressure P, ΔT is the temperature rise in an ideal condition, q is the rate of heat generation per unit length in the wire, and t is time. The complete working equation for the experimental method, together with a detailed description of all the corrections necessary has been presented elsewhere [4–6].

A schematic diagram describing the hot-wire cell and the pressure vessel is shown in Fig. 1. The platinum wire (4), which is 10 μ m in diameter and about 70 mm in length, is placed between the upper and the lower platinum hooks (7) with an axial stress of predetermined magnitude. To compensate for the end effect, two potential leads of the same platinum wire were spot-welded at the positions about 10 mm from each end of the wire. The resistance-temperature relation of the platinum wire was calibrated *in situ* in the temperature range from 193 to 593 K. A coppercell-holder inserted in the pressure vessel (not shown in Fig. 1) served to reduce both the vertical nonuniformity in the temperature and the volume of the sample. The volume of sample employed in one measurement is about 20 cm³. The pressure vessel made from SUS304 was sealed with a silver-plated hollow metal O-ring (3), and the four electrical leads were brought out through the Conax (1).

Figure 2 shows the electrical system used in the present research. Because the circuit is substantially simplified without the Wheatstone bridge, the automation procedure and data processing became more straightforward. The experimental procedure is as follows. (1) The initial resistance of the platinum wire is measured by a high-resolution, 8.5-digits, digital voltmeter (DVM HP3458A). (2) The switch S_2 is switched to the side of a low-noise constant current power supply (HP3245A). (3) After a run

Fig. 1. Hot-wire cell with pressure vessel: (1) Conax; (2) thrust ring; (3) hollow metal O-ring; (4) platinum wire, $10-\mu$ m diameter; (5) platinum resistance thermometer well; (6) pressure vessel plug; (7) platinum hook, 0.5 mm diameter; (8) titanium strut; (9) pressure vessel; (10) ceramic disk.

is initiated by S_1 , the transient voltage rise, which corresponds to the temperature increase of the wire, is measured by the DVM with an integration time of 20 ms. The electrical current through the wire is measured by another DVM (TR6877) which measures the voltage across a 1- Ω standard resistor, R_{st} . All the data acquisition and instrument control was performed by a computer via the IEEE-488 interfaces.

The pressure vessel was immersed completely in a temperature-controlled thermostatic bath. The heat transfer medium in the bath was methanol for the low-temperature range (193–293 K), water for the midletemperature range (293–333 K), and silicone oil for the high-temperature range (293–393 K). The temperature of the sample was measured with a

Fig. 2. Block diagram of electrical system.

platinum resistance thermometer calibrated on the ITS-90 with an accuracy of ± 0.1 K. The sample was pressurized with a hand pump through a mercury separator. The pressure was measured with a precise digital pressure gauge of accuracy ± 0.07 MPa.

3. RESULTS AND DISCUSSION

3.1. HFC-125

A transient hot-wire apparatus with one bare platinum wire was used to measure the thermal conducitivity of HFC-125 in the liquid phase in the temperature range from 193 to 333 K and the pressure range from 2 to 30 MPa with an estimated accuracy of $\pm 0.5\%$. The sample employed here was supplied by Du Pont-Mitsui Fluorochemicals Co. Ltd. The purity of the sample was confirmed to be better than 99.6%. The experimental results for HFC-125 in the liquid phase are listed in Table I. These values are the averages of three measurements, whose reproducibility was less than $\pm 0.5\%$, at the same T and P. The influence of current leakage and polarization is negligible because there is no clear distortion of the linearity between ΔT and the logarithm of time during the measurement. The thermal conductivity of HFC-125 is plotted as a function of temperature in Fig. 3. Figure 4 illustrates the experimental results of HFC-125 as a function of pressure. Moreover, the liquid thermal conductivity of HFC-125 is correlated by a polynomial of temperature and pressure:

$$\lambda = \sum_{n=0}^{2} a_n P^n + \sum_{n=0}^{2} (b_n P^n) T + \sum_{n=0}^{2} (c_n P^n) T^2$$
(2)

Fig. 3. The thermal conductivity of HFC-125 in the liquid phase as a function of temperature.

with λ in W · M⁻¹ · K⁻¹, T in K, and P in MPa. The coefficients of Eq. (2) for HFC-125 are listed in Table II. This equation can represent the entire experimental data within a standard deviation of 0.49% as shown in Fig. 5. Table III summarizes all the previous measurements for HFC-125 and HCFC-141b.

Based on the correlation of Eq. (2), Fig. 6 shows plots of the deviations of the results of all the measurements for HFC-125. A transient hotwire instrument with two platinum wires was employed by Fellows et al. [7], Wilson et al. [8], Yata et al. [9], and Gross and Song [10] with $\pm 2-3$, ± 2 , ± 1 , and $\pm 1.6\%$ uncertainties, respectively. It is clear from Fig. 6 that the results obtained by Fellows et al. and Yata et al. agree with our present work within the mutual accuracy ranges. The measurements of Fellows et al. lie uniformly 2-3% below the present work, and the results of Yata et al. shows a different temperature slope although the deviation never exceeds 3%. There are only four data points in the work reported by

Fig. 4. The thermal conductivity of HFC-125 as a function of pressure.

Wilson et al. The maximum deviation of their measurements from our work is about 13%. The experimental results of Gross and Song are uniformly 9% higher than ours. A modified hot-wire method was used by Bivens et al. [11] with ± 1 % uncertainty. At around 250 K, the results of Bivens et al. are 2% higher than those of the present work. And in the 320 K region, the difference rises to 10%. Two measurements have been performed with a transient hot-wire apparatus making use of electrically insulated tantalum wires by Papadaki and Wakeham [12], and Assael and Karagiannidis [13] with an accuracy of ± 1 %. In the low-temperature range, the data of Papadaki and Wakeham are nearly the same as ours. But as the temperature increases, the difference between their values and ours becomes larger. In the temperature region near 310 K, the data of Papadaki and Wakeham are nigher than the present values by 5%. The results of Assael and Karagiannidis are uniformly higher than our results by 2% with little variation. This is an acceptable difference in view of both

Thermal Conductivity of HFC-125 and HCFC-141b

| Temperature, T (K) | Pressure, P (MPa) | Thermal conductivity, λ (W · m ⁻¹ · K ⁻¹) |
|-----------------------|----------------------|---|
| 193.5 | 2.0 | 0 1059 |
| 193.5 | 10.0 | 0 1090 |
| 193.6 | 20.0 | 0.1125 |
| 193.6 | 30.0 | 0.1160 |
| 213.4 | 2.0 | 0.0961 |
| 213.4 | 10.0 | 0.0998 |
| 213.3 | 20.0 | 0.1040 |
| 213.4 | 30.0 | 0.1077 |
| 233.4 | 2.0 | 0.0870 |
| 233.3 | 10.0 | 0.0913 |
| 233.3 | 20.0 | 0.0959 |
| 233.3 | 30.0 | 0.1002 |
| 253.0 | 2.0 | 0.0784 |
| 253.1 | 10.0 | 0.0831 |
| 253.1 | 20.0 | 0.0883 |
| 253.1 | 30.0 | 0.0927 |
| 272.9 | 2.0 | 0.0703 |
| 272.9 | 10.0 | 0.0762 |
| 273.0 | 20.0 | 0.0817 |
| 273.1 | 30.0 | 0.0863 |
| 292.9 | 2.0 | 0.0627 |
| 292.9 | 10.0 | 0.0696 |
| 292.9 | 20.0 | 0.0761 |
| 292.9 | 30.0 | 0.0812 |
| 313.7 | 3.0 | 0.0545 |
| 313.7 | 10.0 | 0.0625 |
| 313.7 | 20.0 | 0.0701 |
| 313.7 | 30.0 | 0.0757 |
| 333.9 | 5.0 | 0.0496 |
| 333.9 | 10.0 | 0.0562 |
| 333.8 | 20.0 | 0.0648 |
| 333.9 | 30.0 | 0.0714 |

Table I. Thermal Conductivity of HFC-125

Table II. Optimum Values of the Coefficients a_i , b_i , and c_i in Eq. (2) for HFC-125.

| i | а | b | с |
|---|---------------------------|--------------------------|---------------------------|
| 0 | 2.0347×10^{-1} | -5.5302×10^{-4} | 2.1755×10^{-7} |
| 1 | 1.7779 × 10 ⁻³ | -1.5417×10^{-5} | 4.3340×10^{-8} |
| 2 | -2.4433×10^{-5} | 2.5675×10^{-7} | -7.0531×10^{-10} |

Fig. 5. Deviations of the present data for HFC-125 from Eq. (2).

Fig. 6. Comparison of the Eq. (2) for HFC-125 with other previous measurements.

| Investigator and reference | Year | Method of Measurement ^a | Temperature range (K) | Pressure range (MPa) | State | Accuracy (%) | Purity (wt%) |
|-------------------------------|------|---------------------------------------|--------------------------|----------------------------|-------|-----------------|-----------------|
| | | | HFC-125 | | | | |
| Fellows [7] | 1990 | THW | 307.35331.75 | 1.7-3 | Lia. | +2-3 | |
| Wilson [8] | 1992 | THW | 216.48-333.15 | Sat. | Liq. | +2 | |
| | | | 238.71-333.15 | 0.1 | Gas | ±2 | |
| Yata [9] | 1993 | THW | 257305 | - 30 | Liq. | ±١ | |
| Bivens [11] | 1993 | THW | 253.25-338.15 | Sat. | Liq. | ±1 | |
| Papadaki [12] | 1993 | THW | 225.47-306.03 | Sat. | Liq. | ±1 | 99.9 |
| Assael [13] | 1994 | THW | 273.11-313.15 | 0.34-16 | Liq. | ±1 | |
| Tsvetkov [14] | 1994 | TCCM | 159.15-293.15 | -10 | Liq. | ± 2–3 | 99.83 |
| Gross [10] | 1994 | THW | 233.15-263.15 | 0.1-6 | Liq. | <u>+</u> 1.6 | 99.8 |
| | | | | | Gas | <u>+</u> 2 | |
| Tanaka [18] | 1994 | THW | 283-333 | - Sat. | Gas | <u>+</u> 1 | 99.8 |
| Present work | 1994 | THW | 193–333 | 2-30 | Liq. | ±0.5 | 99.6 |
| | | | HCFC-141b | | | | |
| Richard [19] | 1989 | THW | 284.15-333.15 | Sat. | Gas | ±3 | |
| Tanaka [20] | 1991 | ССМ | 293.15-353.15 | 0.1 | Gas | ±1 | 99.9 |
| Gurova [16] | | THW | 205-300 | Sat. | Liq. | ±0.5 | |
| Yata [15] | 1992 | THW | 251.76-392.15 | 0.1-30.4 | Liq. | ±1 | 99.5 |
| Yamamoto [21] | 1993 | THW | 313.15-373.15 | 0.1-0.6 | Gas | ±0.5 | |
| Papadaki [17] | 1993 | THW | 248.6-303.9 | Sat. | Liq. | ±1 | 99.6 |
| Assael [13] | 1994 | THW | 253.25-313.33 | 0.01-21.71 | Liq. | ±1 | |
| Present work | 1994 | THW | 193-393 | 0.1-30 | Liq. | ±0.5 | 99.88 |

Table III. Previous Measurements of Thermal Conductivity of HFC-125 and HCFC-141b

"THW, transient hot-wire method; TCCM, transient coaxial cylinder method; CCM, coaxial cylinder method.

the different purities of the samples and the different types of wire. A transient coaxial cylinder apparatus was employed by Tsvetkov et al. [14] with an uncertainty of less than ± 2 -3%. It can be seen that in the high-temperature region their experimental results are up to 9% above ours. On the other hand, in the low-temperature region ther results are lower than our values by about 3%. The results of Tsvetkov et al. also show a behaviour similar to those of Papadaki and Wakeham.

3.2. HCFC-141b

The thermal conductivity of HCFC-141b in the liquid phase was measured in the temperature range from 193 to 393 K and the pressure range from 0.1 to 30 MPa with the same apparatus as HFC-125. The

purity of the sample, also supplied by Du Pont-Mitsui Fluorochemicals Co. Ltd., was better than 99.88%. Table IV shows the experimental results for HCFC-141b in the liquid phase. These values are also the averages of three measurements, whose reproducibility was less than $\pm 0.5\%$, at the same T and P. The influence of current leakage and polarization is also negligible in this measurement. Both Figs. 7 and 8 illustrate the thermal conductivity of HCFC-141b in the liquid phase as functions of temerature and pressure, respectively. The thermal conductivity of HCFC-141b has also been represented by Eq. (2). The coefficients obtained for HCFC-141b has also been represented by Eq. (2). The coefficients obtained for HCFC-141b has reshown in Table V. This equation can reproduced the total experimental data of HCFC-141b within a standard deviation of 0.46% as shown in Fig. 9.

The deviations of the results of all measurements available for HCFC-141b from those calculated by Eq. (2) are illustrated in Fig. 10. A transient hot-wire method with two platinum wires was employed by Yata et al.

Fig. 7. The thermal conductivity of HCFC-141b in the liquid phase as a function of temperature.

Thermal Conductivity of HFC-125 and HCFC-141b

| Temperature, T (K) | Pressure, P (MPa) | Thermal conductivity, λ (W · m ⁻¹ · K ⁻¹) |
|-----------------------|----------------------|---|
| 193.6 | 0.1 | 0.1205 |
| 193.7 | 10.0 | 0.1223 |
| 193.7 | 20.0 | 0.1242 |
| 193.7 | 30.0 | 0.1260 |
| 212.9 | 0.1 | 0.1151 |
| 212.9 | 10.0 | 0.1175 |
| 212.9 | 20.0 | 0.1195 |
| 212.9 | 30.0 | 0.1217 |
| 232.9 | 0.1 | 0.1097 |
| 232.9 | 10.0 | 0.1127 |
| 232.9 | 20.0 | 0.1151 |
| 233.0 | 30.0 | 0.1175 |
| 252.8 | 0.1 | 0.1039 |
| 252.8 | 10.0 | 0.1069 |
| 252.8 | 20.0 | 0.1100 |
| 252.8 | 30.0 | 0.1118 |
| 272.6 | 0.1 | 0.0981 |
| 272.5 | 10.0 | 0.1016 |
| 272.5 | 20.0 | 0.1045 |
| 272.5 | 30.0 | 0.1074 |
| 292.9 | 0.1 | 0.0926 |
| 292.9 | 10.0 | 0.0963 |
| 292.9 | 20.0 | 0.0996 |
| 292.9 | 30.0 | 0.1027 |
| 314.1 | 0.2 | 0.0870 |
| 314.1 | 10.0 | 0.0910 |
| 314.0 | 20.0 | 0.0947 |
| 314.5 | 30.0 | 0.0982 |
| 333.5 | 0.4 | 0.0813 |
| 333.5 | 10.0 | 0.0858 |
| 333.6 | 20.0 | 0.0899 |
| 333.0 | 30.0 | 0.0939 |
| 353.7 | 0.6 | 0.0764 |
| 353.6 | 10.0 | 0.0809 |
| 353.5 | 20.0 | 0.0851 |
| 353.2 | 30.0 | 0.0893 |
| 374.0 | 0.9 | 0.0718 |
| 373.8 | 10.0 | 0.0766 |
| 373.7 | 20.0 | 0.0810 |
| 373.5 | 30.0 | 0.0852 |
| 394.0 | 1.2 | 0.0663 |
| 393.9 | 10.0 | 0.0723 |
| 393.9 | 20.0 | 0.0776 |
| 393.7 | 30.0 | 0.0819 |

Table IV. Thermal Conductivity of HCFC-141b

| i | а | b | С |
|---|---------------------------|--------------------------|---------------------------|
| 0 | 1.8145 × 10 ⁻¹ | -3.3233×10^{-4} | 9.8070×10^{-8} |
| 1 | 5.0168×10^{-4} | -2.7791×10^{-6} | 8.0261×10^{-9} |
| 2 | -1.6401×10^{-5} | 1.1339×10^{-7} | -2.1036×10^{-10} |

Table V. Optimum Values of the Coefficients a_i , b_i , and c_i in Eq. (2) for HCFC-141b

[15] for the measurement of HCFC-141b with an uncertainty of $\pm 1\%$. In Figure 10 we see that the results of Yata et al. follow a completely different behaviour compared with the results of our work. The experimental data of Yata et al. in the high-temperature region are 10% below our present values, while in the low-temperature region they rise to 5% above the present results. A polarized transient hot-wire technique was performed by Gurova et al. [16] with an uncertainty of $\pm 0.5\%$. The data of Gurova et al. are the same as our present work within $\pm 1\%$. A transient hot-wire

Fig. 8. The thermal conductivity of HCFC-141b as a function of pressure.

Fig. 9. Deviations of the present data of HCFC-141b from Eq. (2).

Fig. 10. Comparison of the Eq. (2) for HCFC-141b with other previous measurements.

apparatus with two electrically insulated tantalum wires was employed by Papadaki et al. [17], and Assael and Karagiannidis [13]; estimated accuracy is of $\pm 1\%$. It can be seen that the experimental results of Papadaki et al. lie almost uniformly 4% above our present data. The results of Assael and Karagiannidis agree with those of our work within the mutual uncertainties.

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