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Measurement of Thermal Conductivity of Liquid Fluorocarbons[1]

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The thermal conductivity of ten liquid fluorocarbons, R 11, R 12, R 13, R 13B1, R 22, R 113, R 114, R 115, R 114B2, and R 124, was measured in the temperature range from 204–450 K by using the transient hot wire method. Prior to the measurement of the fluorocarbons, the thermal conductivity of toluene as the reference material was measured. The results for toluene agree with the recommended values by Nagasaka and Nagashima within ±1%. The accuracy of the present results for fluorocarbons is estimated to be better than ±1.5%. The results are compared with the equation by Li and Poole. The equation proves to be unsuitable for some fluorocarbons, and modified Li–Poole equations including the number of fluorine atoms are proposed for the three groups of fluorocarbons based on the smoothed values of this work and are compared with the experimental data.

KEY WORDS: fluorocarbons; liquid; modified Li–Poole equations; thermal conductivity; toluene; transient hot wire method.

1. INTRODUCTION

Fluorocarbons have recently attracted wide attention as the working fluids in various types of power plants. However, knowledge of the thermophysical properties of these fluids is not accurate enough, and more reliable experimental data and equations for prediction are needed. In this paper, the thermal conductivity of the methane series of fluorocarbons (R 11, R

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12, R 13, R 13B1, and R 22) and the ethane series of fluorocarbons (R 113, R 114, R 115, R 114B2, and R 124) is measured in the saturated liquid state in the temperature range 204–450 K. There is no reliable equation for predicting the thermal conductivity of liquids. The equation by Li and Poole, which is said to be suitable for the thermal conductivity of fluorocarbons, is compared with the present results, and modified equations are proposed.

2. EXPERIMENTAL METHOD AND APPARATUS

The principle of the transient hot wire method is described in detail in the literature [1, 2]. The temperature rise of a thin wire, vertically suspended and immersed in a liquid, due to a stepwise input electric current is given as a function of time as follows:

$$\theta = \frac{q}{4\pi\lambda}\left(\ln\frac{4at}{r^2} - \gamma\right) \tag{1}$$

where θ is the temperature rise of the wire; r is the radius of the wire; q is the quantity of heat supplied to the wire per unit length; λ is the thermal conductivity of the liquid; a is the thermal diffusivity of the liquid; t is the time elapsed since the start of heating; and γ is Euler's constant. If the temperature rise of the wire is small, the variation of q and a is negligibly small, and λ is given as follows:

$$\lambda = \frac{q}{4\pi}\frac{1}{\Delta\theta/\Delta(\ln t)} \tag{2}$$

From Eq. (2), λ is calculated from the measured values of q and $\Delta\theta/\Delta(\ln t)$.

Figure 1 gives a schematic view of the potential lead type thermal conductivity cell inserted in the high-pressure vessel. The diameter and the effective length of the platinum wire are approximately 25 μm and 100 mm, respectively. The diameter of the upper and lower potential lead wires is 15 μm. The high-pressure vessel is made of SUS 316 and is 50 ml in volume, and can be used up to 10 MPa. The pressure vessel is inserted in the thermostated bath and the cell is controlled at the prescribed temperatures within ± 10 mK. Figure 2 shows a block diagram of the measuring circuit. The unbalanced potential difference of the double bridge due to the temperature rise of the wire is recorded every 1 or 2 ms by a transient memory (Kawasaki Electronika M-500T, 0.1% precision). Immediately after the recording is finished, the data are transferred to a personal computer (Panafacom C-15E) and the value of the thermal conductivity is

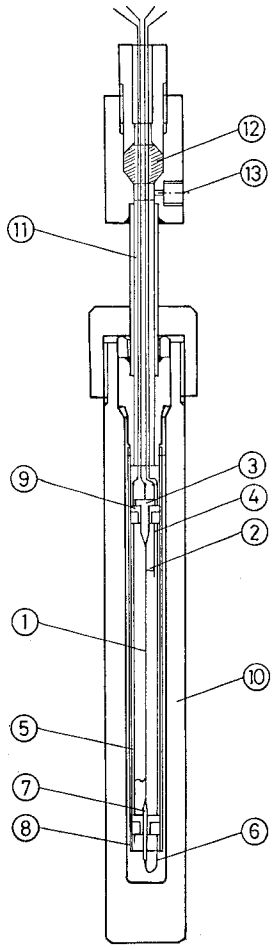

Fig. 1. Hot wire cell in high-pressure vessel. 1, Platinum wire; 2, potential lead wire; 3, upper current tap; 4, upper potential tap; 5, lower potential tap; 6, lower current tap; 7, weight; 8, thin-walled cylinder; 9, alumina insulator; 10, high-pressure vessel; 11, alumina insulator; 12, Teflon packing; 13, liquid inlet.

calculated. The purity of the sample liquids is better than 99.9%, except for that of R 124, which is 99.3%.

3. EXPERIMENTAL RESULTS

In general, it is very important to select appropriate reference materials when studying the thermophysical properties of fluids. Toluene has been

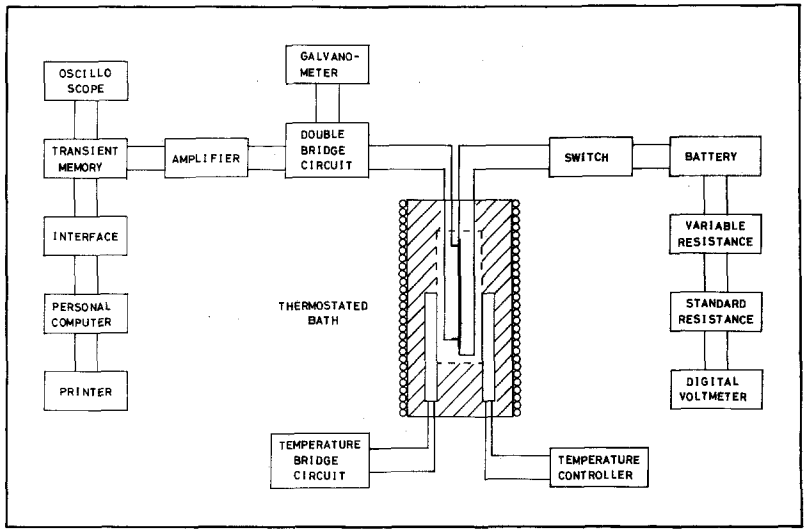

Fig. 2. Block diagram of measuring circuit.

considered to be one of the most promising reference materials with regards to the thermal conductivity of liquids. Thus, prior to measuring the thermal conductivity of fluorocarbons, that of toluene was measured. Many experimentalists have measured the thermal conductivity of toluene very accurately. Recently, Nagasaka and Nagashima [3] have proposed an equation for toluene based on the most reliable recent data. The present results for toluene agree with the recommended equation by Nagasaka and Nagashima within $\pm 1\%$. The measured values are listed in Table I.

The time intervals of the measurement were selected to be between 0.05 and 3 s from the start of heating, to account for the necessary correction for the heat capacity of the wire and the onset time of convection. The amount of the correction for the heat capacity of the wire was limited to less than 1%. The accuracy of the results for fluorocarbons is estimated to be better than $\pm 1.5\%$.

Table I. Experimental Results for the Thermal Conductivity of Liquid Toluene

T (K)	λ ($W \cdot m^{-1} \cdot K^{-1}$)	T (K)	λ ($W \cdot m^{-1} \cdot K^{-1}$)
289.5	0.1348	344.0	0.1184
301.7	0.1308	364.6	0.1127
323.5	0.1243		

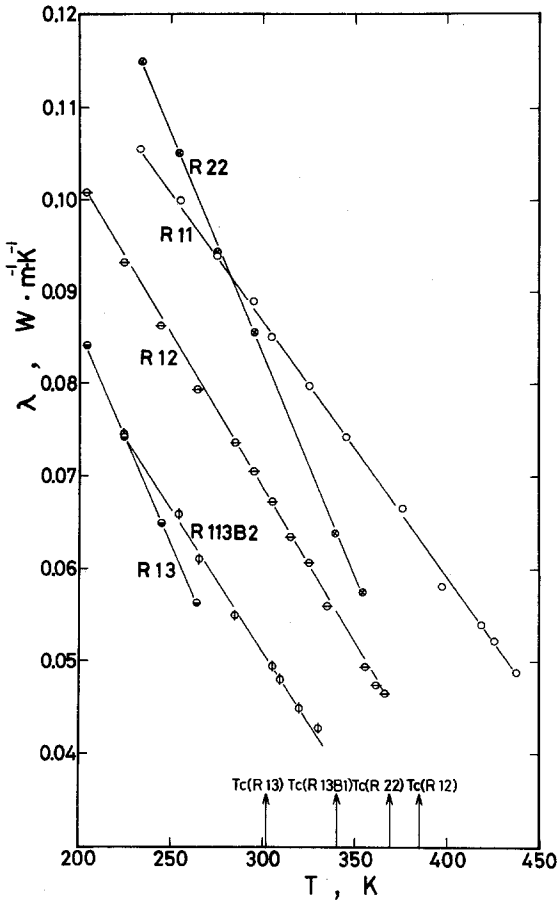

Fig. 3. Experimental results for the thermal conductivity of the methane series of fluorocarbons.

Figures 3 and 4 show the experimental results for the thermal conductivity of the methane series and the ethane series of fluorocarbons, respectively. The results are also shown in Table II. As shown in Figs. 3 and 4, the thermal conductivity λ of fluorocarbons in the liquid state decreases almost linearly with increasing temperature T. Thus the thermal conductivity can be expressed by the equation

$$\lambda = A + BT \tag{3}$$

The numerical values of the coefficients A and B in Eq. (3) for the fluids

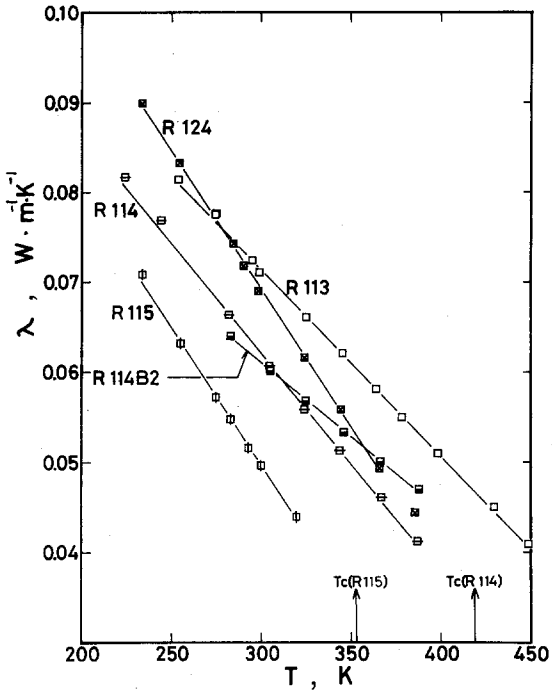

Fig. 4. Experimental results for the thermal conductivity of the ethane series of fluorocarbons.

measured have been determined and are shown in Table III, together with the applicable temperature ranges and the average deviations of the measured values from the equations.

4. MODIFIED LI–POOLE EQUATIONS

Li and Poole [4] derived a theoretical expression for the thermal conductivity of liquids as follows:

$$S = f(T/T_B) \tag{4}$$

where the quantity S is defined as

$$S = \lambda\left[V_B^{2/3}\left(\frac{M}{T_B}\right)^{1/2}\left(\frac{V_c}{V_B}\right)^2\right] \tag{5}$$

where T_B is the normal boiling point; V_B is the molar volume at the normal boiling point; V_c is the molar volume at the critical point; and M is the

Table II. Experimental Results for the Thermal Conductivity of Liquid Fluorocarbons

T (K)	λ (W · m^{-1} · K^{-1})	T (K)	λ (W · m^{-1} · K^{-1})	T (K)	λ (W · m^{-1} · K^{-1})	T (K)	λ (W · m^{-1} · K^{-1})
R 11		R 13		R 113		R 115	
233.1	0.1055	204.4	0.0844	254.3	0.0814	234.4	0.0715
254.9	0.1007	224.4	0.0742	275.0	0.0776	254.8	0.0632
275.2	0.0939	244.7	0.0649	295.0	0.0724	275.3	0.0572
295.2	0.0896	264.4	0.0566	298.8	0.0710	282.8	0.0544
304.4	0.0844	R 13B1		325.2	0.0660	295.3	0.0516
324.8	0.0798			345.7	0.0624	299.8	0.0497
354.2	0.0742	204.1	0.0814	363.9	0.0579	320.4	0.0439
376.1	0.0657	224.2	0.0746	378.7	0.0549	R 114B2	
397.3	0.0581	244.6	0.0659	398.8	0.0510		
418.9	0.0540	264.6	0.0599	430.1	0.0453	282.8	0.0640
426.2	0.0523	284.8	0.0545	449.3	0.0412	304.7	0.0603
437.8	0.0489	305.4	0.0495			325.2	0.0565
		309.6	0.0480	R 114		345.9	0.0533
R 12		319.7	0.0449	223.9	0.0818	366.6	0.0499
203.7	0.1008			243.8	0.0774	387.7	0.0470
224.1	0.0932	R 22		282.4	0.0663		
244.3	0.0863	234.0	0.1149	303.8	0.0602	R 124	
264.4	0.0794	254.4	0.1051	324.1	0.0559	234.2	0.0901
284.6	0.0736	275.1	0.0943	344.2	0.0513	254.5	0.0833
294.8	0.0706	295.2	0.0856	366.9	0.0461	274.5	0.0776
305.1	0.0673	339.2	0.0638	386.9	0.0414	285.0	0.0746
314.7	0.0634	354.4	0.0575			290.4	0.0712
325.2	0.0607					298.5	0.0685
334.6	0.0557					324.4	0.0616
355.6	0.0494					345.2	0.0558
361.4	0.0474					366.2	0.0493
366.4	0.0465						

Table III. Numerical Values of the Coefficients in Eq. (3) and Applicable Temperature Ranges and Average Deviations

Substance	Temperature range (K)	A	$B \times 10^4$	Average deviation (%)
R 11	233–438	0.1717	− 2.8193	0.90
R 12	204–366	0.1702	− 3.3941	0.85
R 13	204–264	0.1700	− 4.2790	1.00
R 13B1	233–320	0.1295	− 2.6303	0.70
R 22	234–354	0.2268	− 4.7877	1.00
R 113	254–449	0.1336	− 2.0630	0.85
R 114	263–387	0.1336	− 2.3838	0.98
R 115	234–320	0.1379	− 2.9358	0.66
R 114B2	284–388	0.1098	− 1.6276	0.80
R 124	234–366	0.1588	− 2.9774	0.60

molecular weight. By using the available experimental values, they determined a single expression for the thermal conductivity of fluorocarbons as follows:

$$S = 17.5947 - 3.81013 T/T_B \tag{6}$$

They claimed that Eq. (6) is applicable to fluorocarbons with an uncertainty of ±5%. Figure 5 shows the relation between S and T/T_B from Eq. (6) together with the smoothed values of this work. Equation (6) seems to be good enough for R 11, R 113, etc. However, it is not suitable for some

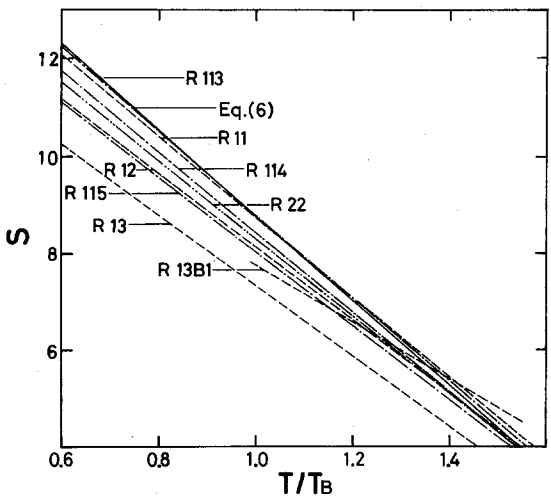

Fig. 5. Relation between S and T/T_B from Eq. (6) and smoothed values from this work.

fluorocarbons, for instance, for R 13, where the discrepancy between Eq. (6) and the experimental values is of the order of 15%.

Since accurate values of V_c are not known, we used the number of fluorine atoms to obtain new equations for three different series of fluorocarbons based on the smoothed values of this work. The equations are as follows:

$$\lambda\left[V_B^{2/3}(M/T_B)^{1/2}(1.059)^{n_f-1}\right] = 2.374 - 1.151\,T/T_B \qquad \text{for R 11–R 13} \tag{7}$$

$$\lambda\left[V_B^{2/3}(M/T_B)^{1/2}(1.054)^{n_f-1}\right] = 2.174 - 1.054\,T/T_B \qquad \text{for R 21–R 23} \tag{8}$$

$$\lambda\left[V_B^{2/3}(M/T_B)^{1/2}(1.038)^{n_f-1}\right] = 2.638 - 1.305\,T/T_B \qquad \text{for R 113–R 115} \tag{9}$$

where n_f denotes the number of fluorine atoms. Since we did not measure R 21 and R 23, we used the results by Djalalian [5] and Geller *et al.* [6].

As shown in Fig. 6, the smoothed values of this work and the results by Djalalian and Geller *et al.* agree well with Eqs. (7)–(9).

Figure 7 compares the experimental results by Djalalian [5], Geller *et al.* [6], Riedel [7], Tsvetkov [8], Tauscher [9], and Tree and Leidenfrost [10] as well as values from the JAR Tables [11] with Eqs. (7)–(9). Reasonable agreement between the calculated and the experimental values is observed.

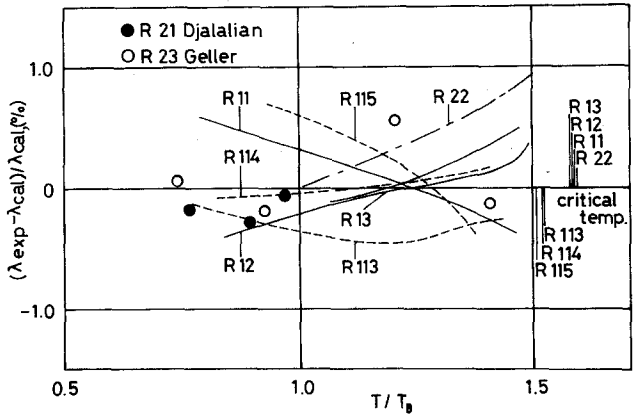

Fig. 6. Comparison of smoothed values from this work with Eqs. (7)–(9).

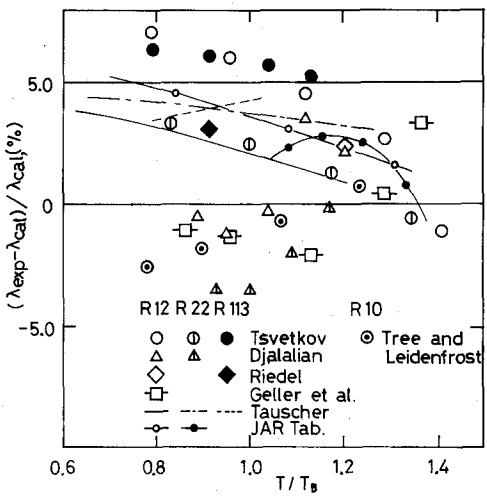

Fig. 7. Comparison of reported experimental values with Eqs. (7)–(9).

In particular, it is worth mentioning that the values by Tree and Leidenfrost for R 10 (CCl_4) agree well with Eq. (7), which was determined based on the data for R 11, R 12, and R 13.

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