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Measurement of the Thermal Conductivity of Liquids by Transient Hot-Wire Method

I: Measurement at Atmospheric Pressure*

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In this first report in a series of studies to measure the thermal conductivity of fluids at high temperature and high pressure, preliminary studies on the reliability of a transient hot-wire method and measured results of eight liquids are described. Measurements were performed for water, methanol, ethanol, benzene, acetone, glycerin, refrigerants R11 and R113 at atmospheric pressure in the temperature range $-90 - +80^{\circ}\text{C}$. Empirical correlations were established for each liquid. Comparisons with available data in literatures showed reasonably good agreement for most of liquids.

1. Introduction

Existing data on the thermal conductivity of liquids often show large discrepancies with one another. Although a clear explanation of these discrepancies is rarely given, in many cases the biggest source of the error is supposed to be convection in the fluid layer. Most of the measurements were performed with a steady-state method in which the thickness of the fluid layer and/or the magnitude of the temperature gradient had to be adjusted in order to minimize the convection error. If the measurement is completed in very short time before convection starts, the error due to convection will be eliminated. Although the idea of this transient method is not new, refinements of the method for precision measurement has been tried recently.

The present series of studies were performed to improve the reliability of the transient hot-wire method and to use it for the measurement of the thermal conductivity of liquids at high temperature and pressure. In this first report, the present state of our knowledge on this method is summarized and measurements are performed for water, methanol, ethanol, glycerin, benzene, acetone, refrigerants R11 and R113 at atmospheric pressure and from -93°C to -80°C with a precision of about 1.5%.

2. Symbols and units

- a: thermal diffusivity m^2/s
- I: current A
- k: ratio of heat capacities of fluid to wire
- ℓ: length of the wire m
- Q: heat W/m
- r: radius of the wire μm
- γ: Euler's constant
- δ: thickness of the fluid layer m
- λ: thermal conductivity of the fluid W/mK
- λ_w: thermal conductivity of the wire W/mK

- t: time s
- t_c: time of the start of convection s
- V: voltage V
- α: temperature coefficient of resistance
- σ: electrical conductivity of the fluid
- σ_w: electrical conductivity of the wire
- θ: temperature $^{\circ}\text{C}$
- Δθ: temperature rise $^{\circ}\text{C}$
- ε: emissivity

3. Theory of the transient hot-wire method

We consider the case that an infinite cylindrical heat source of radius r is immersed in an infinite fluid. Following conditions are assumed: (i) the rate of heat Q generated per unit length of the heating wire is constant, (ii) temperature distribution on the cross-section of the wire is uniform, (iii) temperature rise of the wire is small, (iv) properties of the wire and the fluid are constant, and (v) there is no convection, then the temperature rise of the heat source, Δθ, can be given as a solution of Fourier's equation by Carslaw and Jaeger⁽¹⁾;

$$\Delta\theta = \frac{Q}{4\pi\lambda} \left[\ln\left(\frac{4at}{r^2}\right) - \gamma + \frac{r^2}{2at} - \frac{k-1}{k} \frac{r^2}{2at} \ln\left(\frac{4at}{r^2}\right) - \gamma \right] \dots \quad (1)$$

where γ is Euler's constant. If $r^2/(4at)$ is small enough, terms of higher order can be neglected and,

$$\Delta\theta = \frac{Q}{4\pi\lambda} \left[\ln\left(\frac{4at}{r^2}\right) - \gamma \right] \quad (2)$$

Differentiating it, we obtain

$$\lambda = \left(\frac{Q}{4\pi} \right) / \left(\frac{d\Delta\theta}{d\ln t} \right) \quad (3)$$

The thermal conductivity λ is calculated from the ratio of heat Q to the ratio of the temperature rise $d\Delta\theta/d\ln t$.

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Fig.1 An example of temperature rise of the heating wire

The transient hot-wire method was used for liquid in 1931 by Stalhane and Pyk⁽²⁾ in order to check the reliability of the method by comparing with the parallel plate method. Since then a number of authors⁽³⁾⁻⁽¹⁹⁾ published reports on this method. Many of them described more about improvements of the method than about studying the behavior of the thermal conductivity. Reliability and the limit of the transient hot-wire method are not yet fully investigated. Present state of our knowledge on this method can be summarized as follows.

When Eq.(3) is applicable, it means that when the third term and successive terms in Eq.(1) are negligible, the relation between the temperature rise and the logarithmic time is linear. If convection occurs, this relation deviates from the straight line. Thus measurement affected by convection can be eliminated. A typical example of the recording is shown in Fig. 1. The deviation from the straight line up to A means a difference between Eq.(1) and Eq.(3). Deviation after B shows the occurrence of convection. Therefore, section A-B can be used to calculate the thermal conductivity. If the heating current, resistance of the wire and the thermal conductivity of the fluid is not adequately matched, the linear section A-B will be very small or may not appear at all. It is known that the time to the start of convection is much shorter with the heating wire in horizontal position⁽¹¹⁾. There is a report saying that convection starts with Rayleigh number $Ra > 1800$ ⁽⁸⁾. In the case of a thin wire, the surface area is smaller and so the wire with less radiation loss is more advantageous than other types of heating surface. Effect of finite thickness of fluid is small for normal setting and can be estimated⁽¹⁾⁽¹⁸⁾. Temperature profile on the cross section of the wire is not uniform, strictly speaking, but the difference of the surface temperature from the mean temperature on the cross section $\bar{\theta}$,

$$\bar{\theta} - \theta_0 = \frac{Q}{8\pi\lambda_0} \quad (4)$$

can be neglected in the case of a platinum wire of about 50 μm diameter.⁽¹⁰⁾ So-called "temperature jump" at the surface of the thin wire is negligible for liquid. The

end effect due to the finite length of the wire can either be corrected theoretically⁽⁷⁾ or be eliminated experimentally using voltage taps on both ends of the wire. The change in the thermal conductivity of the wire and the fluid due to the temperature rise during a run can be neglected, if the temperature rise is less than 1 - 2 °C. For an electrically conducting liquid, the ratio of current I through the wire to the total current I_0 can be estimated⁽¹⁰⁾ as,

$$\frac{I}{I_0} = 1 + 0.261 \frac{\sigma}{\sigma_0} \left(\frac{l}{r} \right)^{1.863} \quad (5)$$

where the ratio of the length to the radius of the wire l/r is assumed to be about 10^3 .

Recently, an interesting method of recording the temperature rise against time has been proposed and used by Kestin and co-workers⁽¹⁸⁾⁽¹⁹⁾.

To sum up, we can see that the transient hot-wire method can be used for high precision measurement, if the factors are adequately considered such as dimensions of the wire, the current as well as the design of the recording system. The most important advantages of this method include the elimination of convection error, the small radiation loss, the possibility of absolute measurement without any complicated apparatus and a simple test section suitable for high pressure measurement.

4. Experimental apparatus and procedures

Fig.2 shows an experimental set-up for temperature range above 0 °C. The diameter of the wire is 50 μm and the length between voltage junction is 0.12865 m. The temperature of upper part of the cell is adjusted by a heater 8. The apparatus in Fig.3 was used for measurements at lower

1 platinum wire	8 heater
2 test cell	9 thermometer
3 current leads	10 controller
4 potential leads	11 agitator
5 spacer(Teflon)	12 heater
6 rubber cap	13 bath
7 insulator	

Fig.2 Experimental set-up I (above 0 °C)

temperatures. The temperature of the cell was controlled with dry ice 4 in a double container 2,3 and a heater 5 with a fan 6. Although the sublimation temperature of dry ice at atmospheric pressure is -78.5°C , the temperature of the cell can be lowered with subcooled dry ice. At the lowest temperature, the largest variation of the temperature of the cell was within 0.5°C in several hours, which means that the temperature change during a run was negligible. The volume of the test cell is 300 cm^3 and the inner diameter is 40 mm . The electrical circuit with a double bridge is shown in Fig.4. The resistance X corresponds to the test section of the wire. The lower part in Fig.4 is a dummy circuit for stabilizing the discharge of the battery before the start of a run. Measuring procedure of the temperature rise of the platinum wire was as follows. The resistance X of the platinum wire was determined by a double

Fig.3 Experimental set-up II
(for low temperature)

bridge. Change of the uncompensated voltage due to the temperature rise after the start of a run was recorded with an X-Y recorder. As the input of X axis(time) of the X-Y recorder, the charging curve of a capacitance was used after calibration. Since the temperature rise $\Delta\theta$ was detected as the uncompensated voltage V , $d\Delta\theta/d\ln t$ in Eq.(3) had to be converted to $dV/d\ln t$. When the temperature rise is not large, the change in X can be expressed as

$$X = X_{00}(1 + \alpha\Delta\theta) \quad (6)$$

where X_{00} is the resistance at 0°C and α is the temperature coefficient of resistance. For the circuit with double bridge shown in Fig.4, Eq.(3) is rewritten as

$$\lambda = \frac{s\alpha X_{00}}{4\pi l} \frac{XI^3}{X+s} \frac{dV}{d\ln t} \quad (7)$$

and the following equation is obtained,

SW switch
GA Galvanometer
PM potentiometer
Es standard cell

Fig.4 Electrical circuit

$$\lambda = 3.1605 \times 10^{-3} \frac{XI^3}{X+s} \frac{dV}{d\ln t} \quad (8)$$

with $s = 20.0074\Omega$, $l = 0.12865\text{m}$ and $X_{00} = 6.4040\Omega$.

Measurement was performed after about two hours of stabilization at constant temperature. Current was supplied to the dummy circuit whose resistance was adjusted to that of the test circuit. A run was started after adjusting the voltage at the test section to 100 mV with a potentiometer. Recording continued about 4 seconds although about one second was enough for determining the thermal conductivity. Current and resistance were again measured right after each run.

5. calibration and estimation of error

The optimum value of the electrical current for the heating wire was determined experimentally after several trials considering the following conditions. Time to the point A in Fig.1 was about 0.06 seconds for water. If we assume that properties of the wire and fluid are constant, heat Q is constant for constant current until the start of convection. Therefore the product of the thermal conductivity of the fluid and the temperature rise is constant. And, since $\ln(4at/r^2)$ changes

Fig.5 Effect of stabilizing time

with $4\pi\lambda\Delta\theta/Q$, the product at is constant for constant $\lambda\Delta\theta$. First approximation of the optimum current was determined considering various factors such as the time up to the start of convection, temperature rise of the wire, approximate value of the thermal conductivity and the aimed precision. Then, after several trials we decided to use a current of about 95 - 100 mA for the present set-up. The temperature coefficient of the resistance of the platinum wire was measured as $3.8661 \times 10^{-3}/^{\circ}\text{C}$. Temperature of the fluid was measured with a standard mercury-in-glass thermometer. Although convection was easily detected by the present method, the critical Rayleigh number to show the criteria at convection was calculated with the equivalent dimension suggested by van der Held et al. (3). It appeared to be about 100 which was lower enough than the ordinarily accepted value of 1000 for steady state on the cylindrical surface. The time to the start of convection, t_c , is shorter at higher temperature and is independent of pressure. Dependence of t_c on the stabilizing time of fluid layer before each run was measured. One of the examples is shown in Fig. 5 for water at 0°C , where abscissa shows the time interval between successive measurements. Deviation of each run from the final average becomes less than $\pm 1\%$ for stabilizing time of more than 20 minutes. Results in the present report were obtained with stabilizing time of about 50 minutes. Radiation loss between solid surface is less than 0.01% of the total heat, for example, transferred at 100°C with a temperature difference of 1°C and emissivity of plati-

num surface $\varepsilon \approx 0.036$. With the aid of Eq. (5), effect of the electrical conductivity of fluid was estimated to be,

$$I/I_0 - 1 \approx 4 \times 10^{-10}$$

where $\sigma = 4.15 \times 10^{-8} \Omega^{-1}\text{cm}^{-1}$ for water. For finite thickness of the fluid layer, estimation of error by Vos is given in Horrock's report (7), in which Fisher's solution for fluid layer of thickness and the solution for infinite thickness are compared. In the present case, $2t/\delta^2 \approx 5 \times 10^{-3}$ and this error is less than 0.01% .

Purities of specimens were: 99.991 wt% for R113 (the balance being R123) and 99.998 wt% for R11 (the balance being R12); other specimens were of laboratory grade and water was a twice-distilled one.

In conclusion, major part of experimental error came from errors in temperature coefficient α of the wire resistance (0.50%), in voltage reading on X-Y recorder (0.83%), in logarithmic time (0.40%). Therefore the error in the final result of the thermal conductivity is estimated to be about 1.5% . Standard deviation of measured data from the average value was 0.5% .

6. Results and comparisons

Measured results of the thermal conductivity of eight fluids in the temperature range from -93°C to $+80^{\circ}\text{C}$ and at atmospheric pressure are listed in Table 1. These values can be expressed by the following correlation;

$$\lambda = A_0 + A_1\theta + A_2\theta^2 \quad (10)$$

where A_0, A_1, A_2 are constants given in

Table 1 Experimental data of the thermal conductivity (in W/mK)

$\theta^{\circ}\text{C}$	water	ethanol	glycerin	acetone	methanol	benzene
0	5.70	1.74		1.75	2.06	
10	5.89	1.71		1.70	2.03	1.50
20	6.13	1.70	2.91	1.62	2.01	1.49
30	6.29	1.66	2.92		1.97	1.48
40	6.38	1.65	2.94			1.47
50	6.53	1.65	2.95			
60	6.65		2.96			
70	6.67		2.97			
80	6.79					

$\theta^{\circ}\text{C}$	ethanol	R11	R113
-93.6		1.17	
-83.1		1.15	
-82.4	1.97		
-73.5		1.13	
-64.5	1.92		
-63.4		1.11	
-53.7		1.08	
-48.8	1.84		
-43.5		1.06	
-30.3			0.87
-28.5	1.82		
-10.1	1.75		
-9.7			0.85
+7.4			0.77

Fig. 6 Thermal conductivity of water

Table 2 Constants in Eq. (10)
Units: λ W/cmK
 $\theta^{\circ}\text{C}$

Substance	A_0	A_1	A_2	Range $^{\circ}\text{C}$
water	5.7002×10^{-3}	2.1480×10^{-5}	-9.9825×10^{-8}	0 ~ 100
methanol	2.0599×10^{-3}	-2.7300×10^{-6}		-10 ~ 40
ethanol	1.7450×10^{-3}	-2.5040×10^{-6}		-114 ~ 78
benzene	1.5077×10^{-3}	-8.7000×10^{-7}		6 ~ 50
glycerin	2.8945×10^{-3}	1.0180×10^{-6}		18 ~ 100
acetone	1.7520×10^{-3}	-6.4250×10^{-6}		0 ~ 50
R11	9.7010×10^{-4}	-2.1233×10^{-6}		-111 ~ 0
R113	8.1010×10^{-4}	-2.1950×10^{-6}		-47 ~ 35

Symbols in Figs.7 - 13

- present study
 △ Mason(23)
 + Dittman(27)
 □ Baxter(26)
 ◇ Riedel(29)
 ○ Tufeu(22)
 ▲ Tomanovskaya(31)
- △ Horrocks(7)
 ☆ Byron(24)
 ▽ Challoner(21)
 □ Poltz(28)
 ▽ Jobst(25)
 ---- Bates(30)

Fig.7 Thermal conductivity of methanol

Fig.8 Thermal conductivity of ethanol

Table 2. Effective region of Eq.(10) for each fluid is also given in Table 2. The estimated error of Eq.(10) is about 1.5%. Results for water are compared with the recommended values of the International Conference on the Properties of Steam (ICPS)⁽²⁰⁾ as shown in Fig.6, which are consistent with an extensive review by Challoner and Powell⁽²¹⁾ on existing data. Present results are slightly higher than those of ICPS but are within the specified tolerances.

As seen in Figs.7-13, present results for other fluids show a linear relationship of the thermal conductivity with the temperature. Fig.7 shows a comparison with

methanol. Tufeu's value⁽²²⁾ shows a deviation of 5% and the values by Mason⁽²³⁾ and Byron⁽²⁴⁾ show better agreement. Over the entire temperature range of Fig.8, present results of ethanol agree fairly well with other authors' except those by Mason⁽²³⁾ and by Baxter⁽²⁶⁾ at 40°C and by Dittman⁽²⁷⁾ at 30°C. Results of benzene agree very well with those by Riedel⁽²⁹⁾ at 20°C, but show systematic deviation from those by Horrock⁽⁷⁾ and by Poltz⁽²⁸⁾ at higher temperatures. Horrock et al. used a transient hot-wire method while Poltz et al. used a parallel plate method. Fig.10 shows comparison of data on glycerin. Glycerin has the highest boiling point among these eight fluids and is one of the liquids most stable against convection. Present results agree well with other authors'. Calculated value by Bates⁽³⁰⁾ has no temperature dependence and so shows a larger deviation at higher temperature. In the case of acetone shown in Fig.11, good ag-

Fig.9 Thermal conductivity of benzene

Fig.10 Thermal conductivity of glycerin

Table 3 Thermal conductivity calculated with Eq.(10) (in 10⁻¹ W/mK)

θ °C	water	methanol	ethanol	glycerin	acetone	benzene	R11	R113
-90			1.97				1.16	
-80			1.95				1.14	
-70			1.92				1.12	
-60			1.90				1.10	
-50			1.87				1.08	
-40			1.85				1.06	
-30			1.82				1.03	0.876
-20			1.80				1.01	0.854
-10		2.09	1.77				0.991	0.832
0	5.70	2.06	1.75		1.75		0.970	0.810
10	5.91	2.03	1.72		1.69	1.50		0.788
20	6.11	2.01	1.70	2.92	1.62	1.49		0.766
30	6.25	1.98	1.67	2.93	1.56	1.48		0.744
40	6.40	1.95	1.65	2.94	1.50	1.47		
50	6.52		1.62	2.95	1.43	1.46		
60	6.63		1.60	2.96				
70	6.71		1.57 ₆	2.97				
80	6.78			2.98				
90	6.82			2.99				
100	6.85			3.00

Fig.11 Thermal conductivity of acetone

reement is found among data by different authors except those by Baxter⁽²⁶⁾. Results of refrigerants R11 and R113 are shown in Figs.12 and 13, respectively. Tomanovskaya's correlated value⁽³¹⁾ for R113 showed very good agreement with present results.

The thermal conductivity data on eight liquids calculated with Eq.(10) are given in Table 3.

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Fig.12 Thermal conductivity of R11

Fig.13 Thermal conductivity of R113