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A new calorimeter for measuring rapidly the thermal conductivity of liquids

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Abstract

A new calorimeter for measuring the thermal conductivity of liquids has been constructed. It is a totally automatic instrument utilizing computer control. The time of measurement is 1 s and the temperature rise due to heating is within 1°C. The instrument has been calibrated at 25°C using six reference liquids. The accuracy is better than 1% and the precision is about 0.2%. The thermal conductivities of nine normal alcohols were measured at 25°C and the results are satisfactory.

Keywords: Calorimeter; Conductivity; Liquid; Novel

1. Introduction

The measurement of the thermal conductivity of liquids is very important in both practical applications and theoretical research. However, it is quite difficult to measure accurately the thermal conductivity of liquids because of the presence of convection and radiation accompanying the experimental process.

The thermal conductivity λ of any substance is defined by

$$dQ/dt = -\lambda A(dT/dx) \quad (1)$$

where dQ is the heat transmitted in time dt along a temperature gradient, dT/dx, perpendicular to an area A. It is now known that the convection and radiation

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caused by the temperature gradient and measurement time tend to make the experimental values too high.

Mallan et al. [1] have collected the experimental values of the thermal conductivity of toluene at 20°C reported over the past 44 years. From 1923 to 1967, the experimental values decreased, year by year. The decrease is due to improvements in the measuring method and experimental techniques. Reid et al. [2] pointed out that many investigators have contributed notably to the measurement of λ of liquids, but their results often do not agree well, the deviation being as large as 5–10%. When these results are reviewed, we conclude that in general the lower values are more acceptable.

In order to overcome the effects of convection and radiation, the authors have constructed the apparatus described. In the experiments, the measuring time is 1 s and the temperature rise due to heating is within 1°C.

2. Apparatus

The apparatus is shown schematically in Fig. 1. The thermal conductivity cell is cylindrical in form, 40 mm in length and 15 mm in inner diameter. A specially made small bead in the glass thermistor is used as the heating element; it is immersed in the liquid to be investigated. The thermistor is connected to the electric circuit of an unbalanced bridge. R_1, R_2 and R_3 are standard resistances, 1000 Ω each. R_T is the resistance of the thermistor.

A steady current is passed through the thermistor which is immersed in static liquid. Because the conductivity is different for every liquid, the rate of temperature change of the thermistor when immersed in different liquids is also different. It has been found that the rate of temperature change dT/dt is inversely proportional to the thermal conductivity λ of the liquid [3]; the following equations are valid

$$R_T = R_0 e^{B/T} \tag{2}$$

$$V = E\left(\frac{R_1}{R_1 + R_3 + R_T} - \frac{R_2}{R_2 + R_4}\right) \tag{3}$$

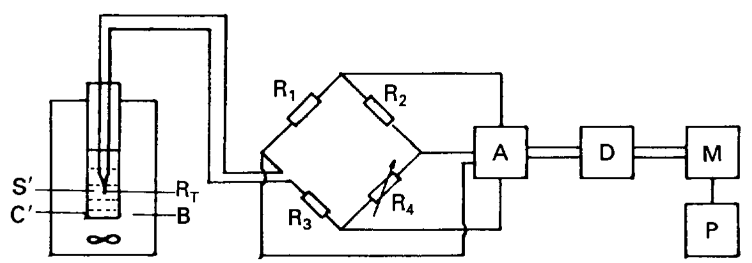

Fig. 1. Schematic graph of apparatus: C, thermal conductivity cell; S, liquid sample; R_T, thermistor; B, thermostatic water bath; R_1, R_2, R_3; standard resistors; R_4, adjustable resistor; A, amplifier and d.c. mains; D, diskette and fixed disk system; M, computer; P, printer.

where V is the voltage of the unbalanced bridge, and E is the stable d.c. current. Substituting Eq. (2) into Eq. (3) and differentiating it with respect to temperature T, we obtain

$$\frac{dV}{dT} = \frac{EBR_1}{T^2}\left(\frac{R_T}{R_1 + R_3 + R_T}\right) \tag{4}$$

the dV/dT is a function of temperature T and thermistor resistance R_T. E, R_1 and B are constants. Eq. (4) shows that if R_T is about 3 kΩ and T is 298.15 K, then dV/dT shows a maximum value, and if the temperature rise due to heating in experiment is within 1°C, dV/dT can be considered as a constant. Thus

$$S_i = dV/dt = (dV/dT)(dT/dt) = k\ dT/dt \tag{5}$$

where S_i is a rate of voltage change of the bridge and is determined by experiment. Because dV/dT is constant, S_i will also be inversely proportional to the thermal conductivity of the liquid [4,5].

3. Experimental and results

The sample liquid is poured into the thermal conductivity cell. A stable current of 0.041 mA is passed through the thermistor bridge; adjusting R_4 to keep the bridge balance, the heating current of 1.000 mA is then passed through the thermistor. The time constant of the small thermistor immersed in the liquid is less than 0.5 s. S_i is measured, 0.5 s after the heating current has been switched on, and the measuring time is 1 s.

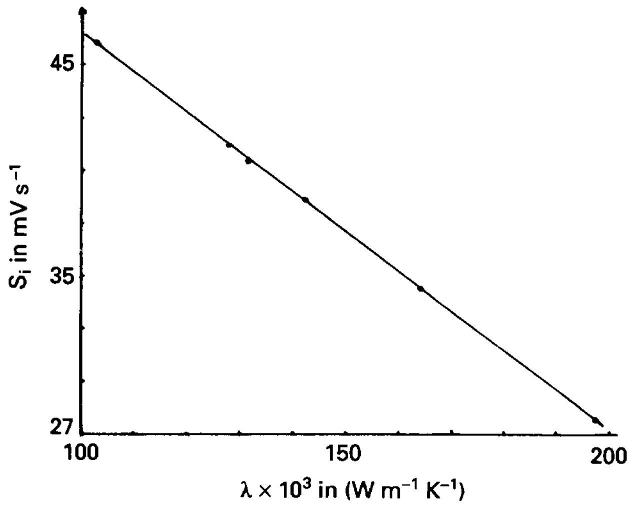

Fig. 2. The plot of λ vs. S_i for six reference liquids.

The experimental control, data acquisition and analysis are accomplished using a computer under software control.

The values of λ for the most common organic liquids range between 100 and 200 mW m^{-1} K^{-1} at temperatures below the normal boiling point. In order to measure organic liquids, six liquids, methanol, ethanol, benzene, toluene, *n*-heptane and carbon tetrachloride, were taken as reference samples. The apparatus was calibrated at 25°C using these six liquids. Fig. 2 shows a typical plot of λ versus S_i.

The corresponding data were calculated by means of a least squares fit. The calibration equation of the apparatus was obtained

$$\lambda \text{ (in mW m}^{-1}\text{ K}^{-1}) = 391.80 - 6.589 S_i \tag{6}$$

Table 1
The comparison of experiment λ_{exp} and literature λ_{lit} values

Sample	S_i/mV s^{-1}	λ_{lit}/mW m^{-1} K^{-1}	λ_{exp}/mW m^{-1} K^{-1}	Dev. %
Methanol	29.504	197.2 [6]	197.4	0.1
Ethanol	34.528	164.2 [7]	164.3	0.1
Benzene	37.928	142.1 [8]	141.9	0.1
Toluene	39.445	131.6 [9]	131.9	0.2
n-Heptane	40.280	127.5 [10]	126.4	0.8
Carbon tetrachloride	43.800	102.5 [11]	103.2	0.7

Table 2
Six S_i values for toluene and their mean

No.	1	2	3	4	5	6	Mean
S_i/mV s^{-1}	39.504	39.452	39.429	39.427	39.453	39.453	39.453

Table 3
S_i and λ of alcohols at 25°C

Alcohol	Purity/wt%	S_i/mV s^{-1}	λ/mW m^{-1} K^{-1}
Methanol	99.5	29.504	197.4
Ethanol	99.7	34.528	164.3
1-Propanol	98.0	35.458	158.3
1-Butanol	98.0	35.545	157.7
1-Pentanol	99.0	35.616	157.2
1-Hexanol	98.0	35.652	157.0
1-Octanol	98.0	35.122	160.5
1-Nonanol	97.0	35.092	160.7
1-Decanol	97.0	34.622	163.8

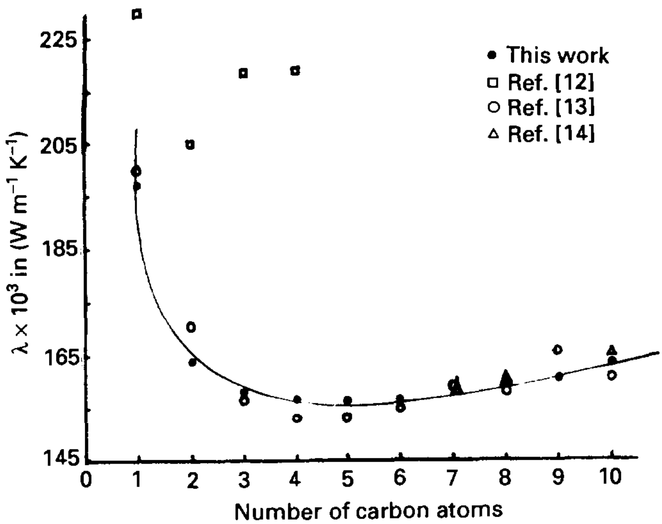

Fig. 3. Thermal conductivity λ vs. the number of carbon atoms.

Table 1 shows the comparison between values predicted by Eq. (6) and corresponding literature values. The accuracy is better than 1%. The S_i is the mean value of six measurements. Six S_i values for toluene are given in Table 2.

The thermal conductivities of nine normal alcohols have been measured by means of the calibrated apparatus. The results are shown in Table 3.

The plot of λ versus the number of carbon atoms is shown in Fig. 3, together with the data of other investigators.

4. Discussion

Because this is a comparative method, its accuracy will depend on the uncertainty of the thermal conductivity values of the reference liquids. In order to reduce this effect, six reference liquids are used to calibrate the apparatus and corresponding data are calculated by means of the least squares method.

The measurement time is 1 s and the temperature rise is within 1°C; therefore, the effect of convection and radiation may be neglected.

The stability of the thermistor is not very good. The change in resistance is about 0.1% over a year. If an obvious change in resistance is discovered, the apparatus must be recalibrated.

From the measured values of S_i of toluene (in Table 2), the precision of measurement is better than 0.2%, i.e. the apparatus is also applicable in conductive theory research.

The measurement results of nine alcohols are considered to be reliable. The smooth change of λ with the number of carbon atoms merits further study.

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