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Note

Determination of the thermal conductivity of liquids in a constant temperature environment calorimeter

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The thermoconductivity (k) of any substance is defined by the fundamental law of conduction given by Eqn. (1):

$$dQ/d\theta = -kA\ (dT/dx) \tag{1}$$

where dQ is the heat transmitted in time $d\theta$ along a temperature gradient, dT/dx, perpendicular to an area A. Thus any method for determining absolute values of k requires the establishment of a known temperature distribution and the simultaneous measurement of the heat flux through the known temperature gradient. Previously used steady state and transient methods have been summarized[1]. The most commonly used transient method, the hot wire method[1], measures the temperature gradient produced when a thin wire of low thermal capacity is heated. Grassman and Straumann[2], and Turnbull[3] have used a thin platinum wire in a wheatstone bridge circuit to determine liquid thermal conductivities from measurements upon the heat source alone. The accuracy of such measurements is about 1%. In a similar manner relative thermal conductivities of liquid samples may be accurately and rapidly determined using a constant temperature environment calorimeter. The method uses a small bead-in-glass thermistor immersed in the sample liquid to monitor temperature changes caused by the application of a small current to the thermistor. Problems associated with convection of the liquid can be minimized since the large temperature coefficient of resistance for thermistors reduces the amount of heat which must be introduced to obtain a significant resistance change.

METHOD

When a current is passed through a thermistor in a static medium, the resistance of the thermistor will vary due to IR^2 heating. The rate at which the resistance will vary is dependent on the rate at which the surrounding medium can dissipate the heat produced. Small bead-in-glass thermistors, having a time constant of less than a half of a second, will equilibrate rapidly and the rate of resistance change of the thermistor should be inversely proportional to the thermal conductivity of the liquid in which the thermistor is immersed.

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Measurements were made by recording the temperature of the thermistor (measured as voltage unbalance of the calorimeter wheatstone bridge) as a function of time following the introduction of a current through the thermistor. A Tronac Inc., constant temperature environment titration calorimeter utilizing a Veco 5000 Ω, 0.060 inch, bead-in-glass thermistor probe was used in the measurements. Runs were made using reagent grade samples of glycerol, ethylene glycol, methanol, isopropanol, toluene, cyclohexane, carbon tetrachloride and distilled water. A 50-ml sample of the liquid to be measured was placed in the calorimeter reaction vessel and the temperature of the sample brought to the temperature of the bath in which the reaction vessel was immersed. The calorimeter stirrer and thermistor were then turned off and the liquid allowed to stand for about 15 min. The thermistor bridge was then turned on and measurements taken for about 30 sec, at which point the stirrer was turned on and the reaction vessel sample equilibrated. The initial temperature of the solution was obtained by extrapolation of the stirring slope to the time when the stirrer was first turned on. The heat introduced to the liquid due to IR^2 heating of the thermistor during the time period when the thermistor bridge was on but the stirrer was off could be neglected in this extrapolation. The process was then repeated. Consecutive measurements were found to be reproducible to better than 1%.

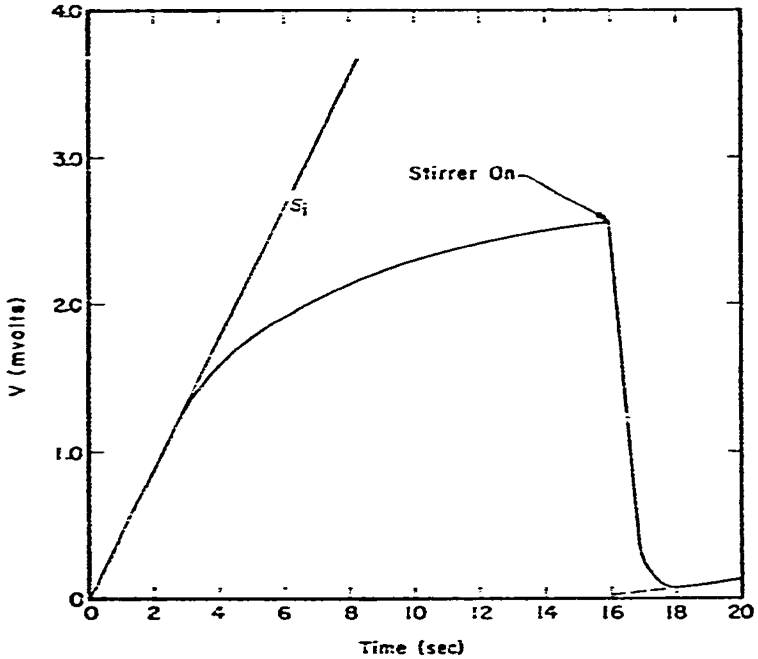

Fig. 1. Sample run for ethylene glycol.

RESULTS

A typical run is shown in Fig. 1 where the sample is ethylene glycol. Correlations were made between known conductivities[4] and the initial rate of temperature rise, S_i.

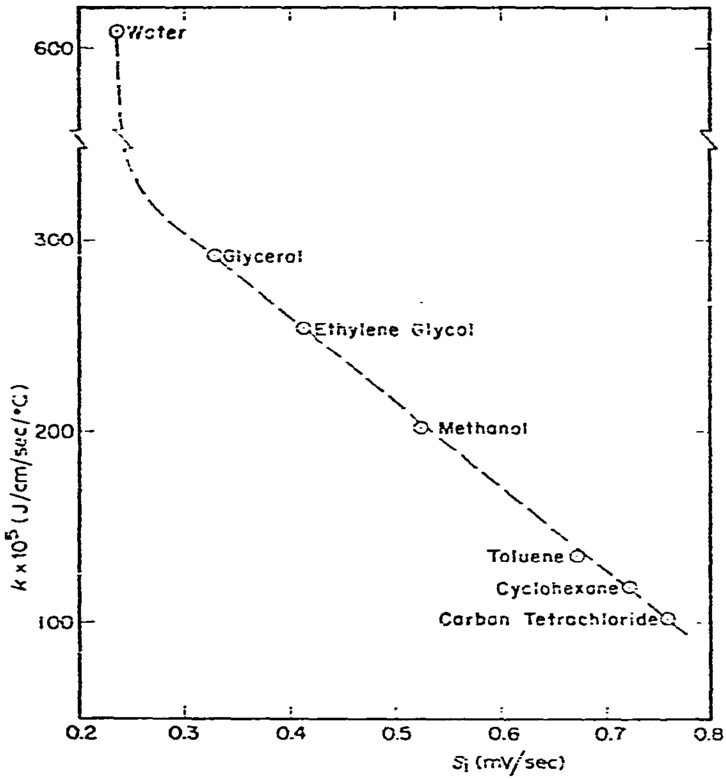

Fig. 2. Plot of k *versus* S_i for several compounds having known thermoconductivity.

TABLE I

DATA USED IN FIG. 2

Liquid	S_i (*mV/sec*)	$k \times 10^5$ (*J/cm/sec/°C*)[a]
Water	0.238	607
Glycerol	0.330	291
Ethylene glycol	0.416	253
Methanol	0.526	201
Toluene	0.675	135
Cyclohexane	0.725	119
Carbon tetrachloride	0.760	103

[a] Data are from Ref. 4.

The results are given in Fig. 2 and the data from which Fig. 2 was constructed are given in Table I. The S_i values are the average of from two to four determinations and in all cases values for a given sample were consistent to better than ±1%. For k values less than 300 J/cm/sec/°C, the results given in Fig. 2 are described by the least squares straight line

$$k \times 10^5 = 435 - 439 \times S_i \qquad (2)$$

with an average deviation of ±1% and a standard deviation of $\pm 2 \times 10^{-5}$ J/cm/sec/°C.

CONCLUSIONS

The results of this study indicate that thermal conductivities of liquids may be accurately and rapidly measured using a thermistor in an adiabatic calorimeter reaction vessel if reference materials of known conductivities are available. The consistence of the data given in Fig. 2 would indicate that convection is not a serious problem in the present method and the accuracy is about ±1%. The maximum thermal conductivity which can be determined with the present apparatus is just above 300×10^{-5} J/cm/sec/°C. At this point, the response of the thermistor is too slow to measure k. This problem could be overcome by using thermistors having a higher resistance, by passing more current through the thermistor, or by using bare thin film resistors having a smaller time constant than the thermistor used in the present study. How far such changes would extend the useful range of the technique is not now known.

The calibration line given in Fig. 1 may then be used to rapidly obtain k values for other liquid samples. Thus for example, measurements may be made on either pure samples of unknown conductivity, or mixtures, and the k value obtained, using the experimental S_i value and calibration curve given in Fig. 2.

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