Liquid Thermal Conductivities

The Apparatus, Values for Several Glycols and Their Aqueous Solutions, and Five High Molecular Weight Hydrocarbons

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An apparatus is described for measuring the thermal conductivities of liquids at temperatures up to 150° C. with a probable error of less than 1%. A thin layer of liquid occupies the annular space between a sphere and a spherical cavity in a surrounding copper block. The thermal conductivity is calculated from the slope of the heat dissipation of the sphere *vs.* the temperature difference between the sphere and the block. Thermal conductivity data are given for mono-, di-, and triethylene glycol; mono and dipropylene glycol; aqueous solutions of these glycols; and for 1-phenyl-3(2-phenylethyl)hendecane (PSU 18), 1-cyclohexyl-3(2-cyclohexylethyl)hendecane (PSU 19), 9-*N*-octylheptadecane (PSU 25), 9-(2-phenylethyl)heptadecane (PSU 87), 1-cyclopentyl-4(3-cyclopentylpropyl)dodecane (PSU 111).

SEVERAL methods have been employed to determine thermal conductivities of liquids involving the measurements of temperature differences between two surfaces while heat is flowing at a measured rate through a liquid between those surfaces. The power dissipation of the warmer surface is a function of the thermal conductivity of the liquid plus energy lost by convection, radiation, and conduction through its solid supports. To obtain accurate conductivity data, power dissipations by all means other than liquid conduction must be minimized, and both temperature differences and power dissipations must be measured with a high degree of accuracy.

In the apparatus used for this work, similar to that described by Riedel (*2*), a $^{3}/_{64}$-inch thick film of liquid occupies the annular space surrounding a 1-inch O.D. nickel-plated copper sphere located at the center of a nickel-plated $1^{3}/_{32}$-inch I.D. spherical cavity in a copper block. Electrical energy supplied to the sphere causes heat to flow radially through the liquid film to the thermostat block. Using a thin film and small temperature differences, the convection heat transfer becomes negligible, and heat loss through the sphere supports can readily be measured.

The power dissipation of the sphere, W, is related to the temperature difference, ΔT, between the sphere and the block by the following equation according to Riedel (*2*):

$$W = kA\Delta T + \Sigma\, k_i b_i \Delta T = (kA + B)\,\Delta T \qquad (1)$$

where k is the thermal conductivity of the liquid, A is a geometry constant for the apparatus, and $B = \Sigma k_i b_i$ is the heat loss by means other than conduction through the liquid. Differentiating Equation 1 gives:

$$dW/d\Delta T = Ak + B \qquad (2)$$

from which it is apparent that k is obtained directly from the slope of a plot of W *vs.* ΔT, when the constants are known.

EXPERIMENTAL

Apparatus. The details of the conductivity cell are shown in Figure 1. The copper sphere F, contains a central cavity, J, for a heater and a cylindrical cavity, G, for a platinum resistance thermometer. The sphere is fixed at the center of the cavity in the copper block, E and I, by four tetrahedrally located supports, the top support being a thin-walled stainless steel tube containing eight lead wires, and the other three being pointed glass rods, H. Into close fitting holes in the block are placed five 9-ohm heaters, a 12- and a 1-junction thermocouple, and a platinum resistance thermometer, N.

A $^{1}/_{16}$-inch hole, D, in the block, E, connects the annular space to the inlet hole, B. A $^{1}/_{8}$-inch diameter stainless steel tube connects the block inlet hole to a vacuum valve and sample reservoir.

The temperature of the block when located in a thermos flask can be maintained at any temperature from 0° to 150° C. with temperature fluctuations of ±0.001° C. by using a 12-junction thermopile, and adjustable bucking potential, a d.c. amplifier, and a Brown "Electronik" Continuous Balance Unit to turn on and off a portion of the block heating current.

The block temperature is measured with a 25-ohm platinum resistance thermometer calibrated by the National Bureau of Standards. The platinum resistance thermometer in the sphere was calibrated by comparing it with the block thermometer at many temperatures between 0° and 150° C. The resistances of the 25-ohm thermometers are measured with a Mueller bridge with a precision of ±0.00005 ohm. Thus the reproducibility of the temperature difference between the block and sphere is ±0.001° C. Since the measured temperature differences are on the order of 0.2° to 1.0° C., the error in ΔT is less than 0.5%. This is the largest source of measurement error. Consequently, the thermal conductivities are precise to better than 1%.

Current to the sphere heater is obtained from Everready air cell batteries and adjusted with a series of coarse and fine controls. The sphere power dissipation is determined by measuring with a potentiometer the voltage drop across the heater and across a calibrated series resistance with a precision of one part per thousand.

Procedure. Ten to 15 ml. of liquid are placed in the inverted sample reservoir attached at A, and dissolved gases are removed by boiling under reduced pressure. The liquid is frozen in the reservoir attached to the inverted conductivity cell, which is then evacuated, and the vacuum valve is closed. The liquid is heated to a temperature above that of the block, and the evacuated cell and sample bulb are turned right side up, which allows the liquid to flow down into the annular space in the cell by gravity with no trapped gas bubbles. Only a small fraction of the 10- to 15-ml. sample enters the cell, while the remainder in the bulb is maintained at a temperature above that of the block so that the pressure in the bulb is great enough to prevent vaporization of the liquid in the annular space. If necessary, the apparatus can be used with considerably less than the normal amount of liquid, the only requirement being that the annular space be filled during the measurements.

The block temperature is adjusted to the desired level; and then the sphere power dissipation (W) and temperature difference (ΔT) are measured at zero and three or more different currents in the sphere heater. All measurements are repeated several times to assure that the data apply to steady state conditions. The slope of W *vs.* ΔT is determined by the least squares method. The block temperature is then changed and the measurements are repeated.

Calibrations. The value of the constant B in Equation 2 was obtained from the slope of W *vs.* ΔT when the cell was highly evacuated (7×10^{-5} mm.) and $k = 0$ and was 21.776 mw. per °C. The value of A was determined from measurements on distilled water at four temperatures between 0° and 90°C. and a smooth curve obtained from data for water from Sakiadis and Coates (*3*), using only those references claiming an error of less than 5%. The value of A was 77.271×10^4 mw. second cm. per cal. Since the literature data for water exhibited a spread of about ±1%, experimentally determined thermal conductivities may be in error by as much as 1%, even though the precision of the measurements is better than that. Using helium at atmospheric pressure and three temperatures, the measured thermal conductivities agreed within 2% of those given by Hilsenrath and Touloukian (*1*), which are claimed to be reliable within 3%. Measurements on aqueous solutions of ethylene glycol and propylene glycol using the apparatus and procedure described here agreed within 2% of thermal conductivity data published by Riedel (*1*).

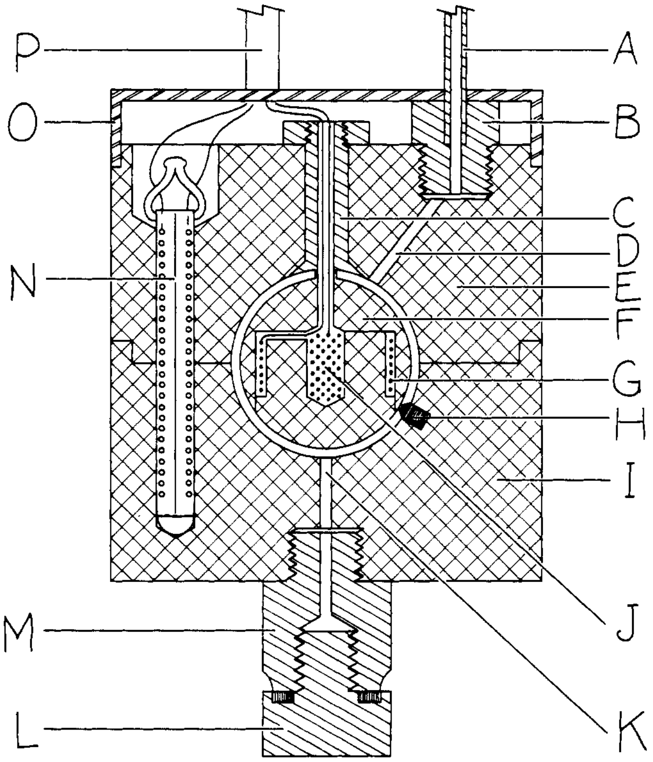

Figure 1. Conductivity cell

A. Stainless steel tube to sample reservoir
B. Stainless hex connector
C. Stainless steel sphere support
D. Sample entrance passage
E. Upper half of copper thermostating block
F. Copper sphere
G. Platinum resistance thermometer
H. Tetrahedrally located glass positioner
I. Lower half of copper thermostating block
J. Electric sphere heater
K. Sample exit passage
L. Sample drain hex plug of stainless steel
M. Stainless steel drain port
N. Platinum resistance thermometer
O. Protective cover of brass
P. Stainless tube for wire conduit

Material. Samples of the glycols were obtained from the Dow Chemical Co. production plants. These materials have a purity of greater than 98% with the impurities being other glycols and a trace of water. Since such impurities will affect the thermal conductivity by only a small fraction of 1%, no further purification was necessary. The five high molecular weight hydrocarbon samples were supplied through the courtesy of American Petroleum Institute Project 42 at Pennsylvania State University, and were of high enough purity to be used as received.

RESULTS

The apparatus and procedure described above were used to measure the thermal conductivities of five glycols and their aqueous solutions. Table I shows the experimental results obtained for the various experimental conditions. Table II presents thermal conductivity values for the aqueous solutions at three temperatures. The values for the solutions of ethylene glycol and for the other pure glycols were obtained by graphical interpolation of the experimental data. The remainder of the solution data was calculated using the known 0 and 100% intercepts data and assuming

Table I. Thermal Conductivities of Glycols and Their Aqueous Solutions—Experimental Data

Glycol	Wt. of Glycol	Temp., °C.	Thermal Cond., Cal./Cm. Sec. °C.
Ethylene	100	0.0	6.08×10^{-4}
		51.1	6.20
		105.1	6.35
		132.9	6.43
	79.95	0.0	7.01
		107.6	7.51
	59.98	0.0	8.12
		54.1	8.93
		93.0	9.17
	20.02	0.0	11.37
		47.7	12.66
		91.4	13.43
Water	0.0	0.0	13.50
		50.0	15.31
		75.0	15.92
		100.0	16.32
Diethylene	100.0	0.0	4.86×10^{-4}
		59.3	5.13
		125.4	5.12
Triethylene	100.0	0.0	4.66×10^{-4}
		77.6	4.73
		132.7	4.65
Propylene	100.0	0.0	4.80×10^{-4}
		64.9	4.75
		131.9	4.69
Dipropylene	100.0	0.0	3.83×10^{-4}
		77.7	3.89
		136.0	3.79
	25.0	0.0	10.29

Table II. Thermal Conductivities of Aqueous Solutions of Glycols—Interpolated Data

Glycol	Temp., °C.	Glycol, % 0	20	40	60	80	100
		Thermal Cond. × 10^4, Cal./Cm. Sec. °C.					
Ethylene	0	13.50	11.37	9.59	8.13	7.00	6.08
	50	15.30	12.73	10.58	8.82	7.33	6.20
	100	16.32	13.54	11.14	9.21	7.63	6.34
Diethylene	0	13.50	11.13	9.10	7.40	6.02	4.86
	50	15.30	12.51	10.14	8.17	6.46	5.11
	100	16.32	13.30	10.66	8.50	6.68	5.15
Triethylene	0	13.50	11.09	9.02	7.28	5.86	4.66
	50	15.30	12.44	9.99	7.94	6.16	4.73
	100	16.32	13.21	10.49	8.23	6.33	4.71
Propylene	0	13.50	11.11	9.08	7.36	5.98	4.80
	50	15.30	12.44	10.01	7.96	6.19	4.77
	100	16.32	13.22	10.50	8.24	6.34	4.73
Dipropylene	0	13.50	10.92	8.69	6.78	5.20	3.83
	50	15.30	12.27	9.66	7.44	5.49	3.90
	100	16.32	13.04	10.15	7.72	5.65	3.86

Table III. Thermal Conductivities of Five High Molecular Weight Hydrocarbons

1-Phenyl-3(2-phenylethyl)-hendecane (PSU 18)

T, °C.	k, cal./cm. sec. °C.
41.2	2.98×10^{-4}
92.3	3.02×10^{-4}
146.9	2.93×10^{-4}

1-Cyclohexyl-3(2-cyclohexyl-ethyl)hendecane (PSU 19)

T, °C.	k, cal./cm. sec. °C.
41.2	2.75×10^{-4}
93.4	2.94×10^{-4}
141.3	3.13×10^{-4}

9-*N*-Octylheptadecane (PSU 25)

T, °C.	k, cal./cm. sec. °C.
41.3	3.15×10^{-4}
91.3	3.14×10^{-4}
139.5	3.13×10^{-4}

9-(2-Phenylethyl)heptadecane (PSU 87)

T, °C.	k, cal./cm. sec. °C.
39.8	2.77×10^{-4}
92.6	3.00×10^{-4}
142.8	2.98×10^{-4}

1-Cyclopentyl-4(3-cyclopentyl-propyl)dodecane (PSU 111)

T, °C.	k, cal./cm. sec. °C.
40.8	3.26×10^{-4}
91.5	3.21×10^{-4}
146.2	3.05×10^{-4}

that the shape of the thermal conductivity *vs.* concentration curves was the same as that of ethylene glycol. The validity of this method for calculating solution data was checked by measuring the thermal conductivity of a 25% solution of dipropylene glycol at 0° C. The experimental value (10.29×10^{-4}) agreed within 0.3% of the calculated one (10.32×10^{-4}).

Since the hydrocarbon samples were in a high state of purity, precautions were taken in cleaning and flushing the sample chamber of the apparatus to avoid contamination. Some difficulty was experienced in filling the spherical annular space in the cell and in keeping it filled at the higher temperatures, since the amount of sample supplied (ca. 2 to 3 ml.) was small. These measurements were repeated sufficiently to obtain consistent data, indicating that the annular space was filled with liquid and did not contain vapor bubbles. Some discoloration was noted in the 1-phenyl-3(2-phenylethyl)hendecane sample (PSU 18) after the measurements at 147° C. The experimental results are listed in Table III and should be reliable within 2%.

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