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Determination of thermal conductivity of organic liquids and liquid mixtures by thermal comparator method

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Abstract

A Powell-type direct reading thermal comparator has been fabricated for the determination of thermal conductivity of organic liquids and liquid mixtures and has been calibrated against known thermal conductivities. Thermal conductivities of 28 pure organic liquids and of six binary mixtures of acetone with each of methanol, ethanol, *n*-butanol, *n*-pentanol, *n*-hexanol and *n*-heptanol have been determined, all at room temperature (26–28°C), and compared with the literature data. The agreement is satisfactory.

Key words: Thermal comparator, thermal conductivity, organic liquid, liquid mixture.

1. Introduction

In spite of the rapid advances made in recent years in the understanding of the liquid state, theory is yet inadequate to accurately predict the thermal conductivity of liquids for which experimental determination is still the only alternative. All methods of measuring thermal conductivity can be divided into two classes, namely, steady-state and unsteady-state methods. In the present work, a very simple, versatile, accurate and very rapid thermal comparator method is used. This method is virtually regarded as a steady-state method since it has been proved that the transient term is very small.

The direct reading type of thermal comparator was first developed by Powell[1] devised at first to measure the thermal conductivity of solids; it was subsequently developed to determine the thermal conductivity of gases and liquids.

2. Thermal comparator method

The method is based on the well-known observation that when two materials at different temperatures are brought into contact over a small area, heat transfer, which is a function of the thermal conductivity of the materials, takes place from the hotter to the colder body. As a result, an intermediate temperature is very quickly attained at the point of contact. The contact temperature depends on the thermal conductivity of the two materials. From a simple analysis[2], the following expression connecting the contact temperature V_c with thermal conductivity can be derived by considering the probe (generally a sphere) as a semi-infinite body to be in contact over a small area with the test sample

$$V_c = \frac{K_1}{K_1 + K_2} V_0 \tag{1}$$

where, K_1 and K_2 are the thermal conductivities of the probe and the test material, respectively, and V_0 = initial temperature of the probe, while the test sample is at 0°C.

If now, two thermocouples are attached to this infinite body, one to measure the temperature at the point of contact and the other sufficiently far from this point to remain at the initial temperature, then the difference between these two temperatures, ΔV, is given by

$$\Delta V = V_0 - V_c = \frac{K_2}{K_1 + K_2} V_0. \tag{2}$$

Approximate theoretical analysis[2] shows that provided the area of contact is very small the transient term is only a few per cent of the steady-state term.

Powell's two-ball thermal comparator consists of two matched phosphor-bronze balls mounted in a block of thermal insulating material. These balls are fitted with differentially connected thermocouples which gave the contact temperature. In a subsequent modification[2], the second sphere has been eliminated.

The thermal comparator readings depend on the following factors: (i) area of contact, (ii) surface finish, (iii) size of the sample and (iv) initial temperature difference between probe and test material. These factors should be kept constant both for calibration and in actual run.

To use the thermal comparator for the measurement of thermal conductivity of liquid mixtures[3,4], it is only necessary to fill the liquid in a shallow glass dish and then cover it with a tautly stretched film of plastic material. The sheet being transparent, there is no difficulty in seeing that no air bubbles are entrapped. With the tests on liquids, this membrane serves two purposes. Firstly, it prevents evaporation and the accompanying surface cooling, and secondly, it ensures that the probe and surface make a reproducible contact. The thermal comparator is applied to the surface of the membrane and the test is carried out as for the solid test material.

3. Experimental

3.1 *Apparatus*

The set-up is schematically represented in fig. 1. It mainly consists of a metallic probe, balance, glass vessel for containing liquid, adjustable table, a temperature-controlled oven, D.C. microvoltmeter and a voltage stabiliser.

The probe is the most important part of the set-up as the success of the method depends on the heat flow from the probe to the test material through a very small area of contact. The probe is made of copper and its dimensions are shown in fig. 2. A guard heater is placed around the probe which compensates the heat losses from the probe and is used to keep initial temperature difference constant. Grooves are cut on the surface of

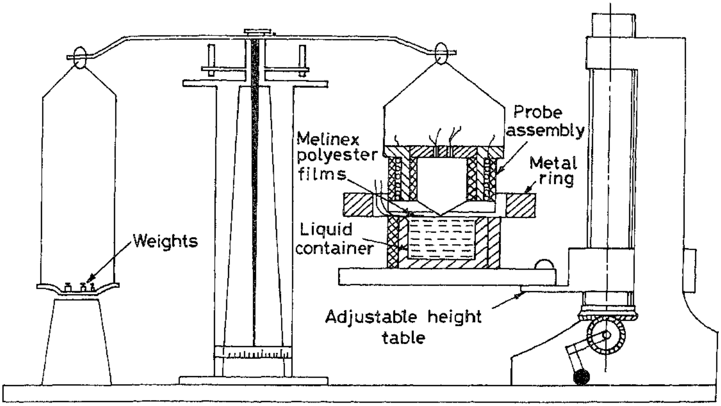


FIG. 1. Apparatus for measurement of thermal conductivity of liquids.

the probe and a Chromel-Alumel thermocouple is inserted in these grooves such that the bead of the thermocouple forms the vertex of the conical portion of the probe. This thermocouple is differentially connected with the thermocouple placed at the top of the probe. This differential arrangement gives the temperature difference between the contact point and the top of the probe. A copper-constantan thermocouple is differentially connected between the probe and the test material. This gives the initial temperature difference between the two and this value has to be kept constant throughout the experiment. The positions of the thermocouples are shown in figs. 3 and 4.

To avoid seriously puncturing the membrane, the probe is suspended from a balance arm and it is counter-balanced by weights on the other arm.

The test liquid is kept in a glass container of 32.5 mm diameter and 22.5 mm height. The test liquid is covered with a tightly stretched film of Melinix which is inert to most liquids and is available in sheets of 0.025 mm thickness. This is mounted in a retaining metal ring of internal diameter larger than that of the container and of sufficient weight to ensure that the film is stretched by appropriate and reproducible amount when placed over the liquid container.

Electrically heated oven having temperature controller is used for the initial heating of the probe to maintain it at the required temperature. D.C. microvoltmeter is used to measure the emfs of the thermocouples.

All chemicals used were of analytical reagent grade quality.

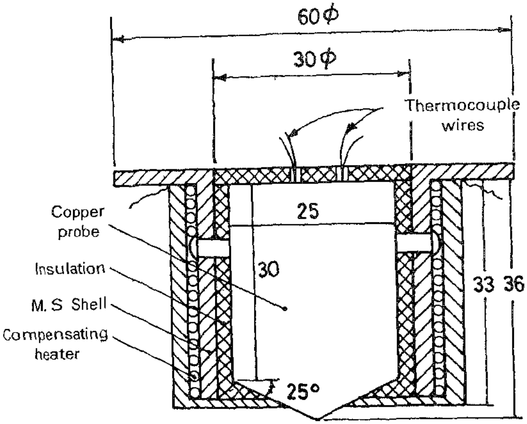


FIG. 2. Probe assembly.

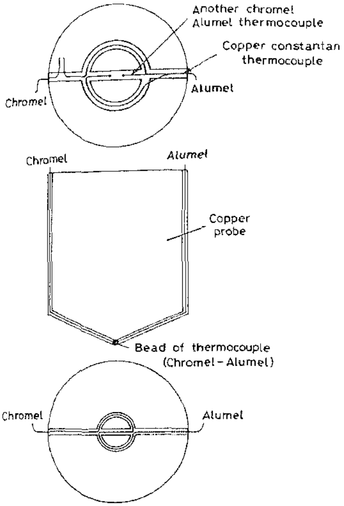
3.2 *Procedure*

The probe is placed inside the oven to raise its temperature and is kept for a period till the initial temperature difference between the probe and the test liquid reads 1000 μV in the microvoltmeter (approximately equivalent to 25°C). After the initial temperature difference is attained, the probe is removed from the oven and suspended from the arm of a balance. Compensating heater current is adjusted to keep the initial temperature difference (*i.e.*, the reading in the microvoltmeter) constant. Test liquid is taken in a glass cell and is covered with polyester film. It is placed on an adjustable platform which is raised to make the contact of the probe tip with the polyester film. Counter weights are put such that there is a positive load of 2 g on the arm of the balance having the probe. This ensures proper contact of the probe tip with the polyester film. Corresponding to the observed comparator reading for the liquid, the thermal conductivity is obtained from the calibration curve given in fig. 5. Thermal conductivity data for eight liquids each at 28°C taken from the literature[5-7] were used to make the calibration curve. A second-order polynomial by least square fitting of the calibration curve gives the following equation:

$$K \times 10^6 = 54.0025 - 2.2032 \times 0.0287X^2 \tag{4}$$

where K = thermal conductivity in cal/cm sec °C, and
X = thermal comparator reading in μV.

All thermal comparator readings were taken at a constant difference of 16°C between the probe and the sample temperatures. This ensures the elimination of any effect of temperature difference between probe and sample on the thermal conductivity.



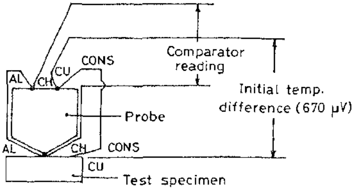


FIG. 3. Position of thermocouples on probe.

FIG. 4. Differential arrangement of thermocouples.

3.3 Precautions

The following precautions were taken to get reliable results:

(i) The tension in the thermocouple was maintained not to disturb the balance and the probe position.

(ii) Initial temperature difference between the probe and the test liquid was kept constant at the designed value.

(iii) The film used for covering the liquids was of uniform thickness and good surface finish.

(iv) No air bubbles were entrapped below the film.

4. Results and discussion

The thermal conductivities of 28 different organic liquids at room temperature (27° ± 2°C) have been determined. The liquids have been so chosen as to include a wide variety of aliphatic acids, alcohols, esters and cyclic compounds. The results obtained are given in Table I.

Table I
Thermal conductivity of organic liquids

Organic liquids	Liquid temperature °C	Comparator reading μV	Thermal conductivity k × 10^6 cal/(cm sec °C)		% Deviation*
			Present work	Filippov[6] data (30°C)	
Alcohols					
Methanol	26.0	171.33	518.75	447.80	+ 15.8
Ethanol	26.4	158.0	422.36	397.25	+ 6.32
Propanol	24.5	152.67	386.15	375.03	+ 2.97
n-Butanol	27.0	146.0	329.18	361.14	− 8.849
n-Amyl alcohol	26.8	134.3	263.95	325.03	− 18.784
Isoalcohols					
i-Propanol	26.4	137.0	290.85	333.34	− 12.74
i-Butanol	26.4	152.6	386.15	325.06	+ 18.80
i-Amyl alcohol	24.0	136.0	285.22	316.69	− 9.94
Aliphatic acids					
Formic acid	26.1	192.67	694.32	638.94	+ 8.67
Acetic acid	25.5	156.0	408.77	405.88	+ 0.71
Propionic acid	25.2	142.0	319.88	337.78	− 5.08
Butyric acid	25.8	153.67	392.71	352.80	+ 11.31
Hexanoic acid	26.0	136.0	285.22	–	–
Esters					
Ethyl acetate	27.0	154.0	395.39	341.69	+ 15.71
Propyl acetate	26.1	138.0	296.55	330.58	− 10.29
Amyl acetate	26.8	130.6	255.80	305.55	− 16.28
Cyclic compounds					
Cyclohexamine	26.2	134.67	277.43	327.80	− 15.37
Cyclohexanol	26.1	143.33	327.84	–	–
Cyclohexone	25.6	134.0	274.13	344.47	− 16.37
Miscellaneous					
Benzene	23.9	148.6	360.39	344.47	+ 4.62
Furfuryl alcohol	25.4	144.0	331.89	427.80	− 22.40
Ethyl methyl ketone	23.8	142.67	323.80	–	–
Nitrobenzene	25.8	154.0	395.38	358.36	+ 10.33
Chlorobenzene	24.7	132.0	263.27	302.80	− 13.05
Dioxane	25.4	146.67	348.28	–	–
Acetone	25.2	154.66	399.78	375.03	+ 6.50
Ethanolamine	26.0	155.0	402.05	–	–
Propylene glycol	24.0	168.67	489.78	475.03	+ 2.95
p-cresol	24.6	138.0	296.55	361.16	− 17.89

$$\% \text{ Deviation}^* = \frac{\text{Present data} - \text{Filippov}^6 \text{ data}}{\text{Filippov data}} \times 100$$

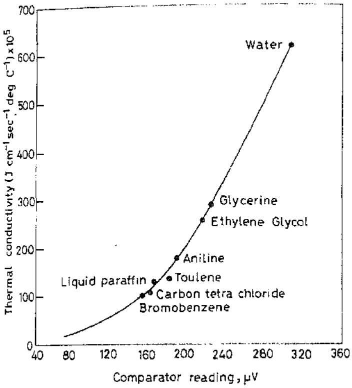


FIG. 5. Calibration curve (Comparator reading *vs* thermal conductivity).

A study of the published literature shows that the thermal conductivities reported by various authors differ by as much as 20% and sometimes even more. However, the values recommended by Filippov (as reported by Tsederberg[6]) are considered to be the most reliable. Results of this study, therefore, are compared with the corresponding values recommended by Filippov.

Table II

Thermal conductivity (K) of the binary mixtures of acetone + aliphatic alcohol systems

Sl. no.	The second component in the binary mixture	Composition of acetone in the binary mixture (W/W %)									
		0		25		50		75		100	
		K × 10^6 in cal. $cm^{-1}.s^{-1}.°C^{-1}$									
		I	II	I	II	I	II	I	II	I	II
1.	Methanol	447.6	500.6	427.1	471.7	411.3	452.1	390.3	430.2	375.5	408.9
2.	Isopropanol	300.5	337.9	313.6	347.1	335.3	366.4	355.4	388.8	375.5	408.9
3.	*n*-Butanol	330.8	369.0	337.3	375.5	346.8	385.5	353.5	392.2	375.5	408.9
4.	Isobutanol	295.0	328.9	315.0	344.4	332.5	361.6	338.7	372.1	375.5	408.9
5.	Tertiary butanol	239.0	273.0	266.9	300.7	311.2	342.3	346.8	380.3	375.5	408.9
6.	*n*-Pentanol	331.8	365.2	331.5	365.0	341.8	375.2	353.3	386.7	375.5	408.9
7.	*n*-Hexanol	331.0	364.5	328.9	362.3	342.3	375.7	351.3	384.8	375.5	408.9
8.	*n*-Heptanol	332.7	336.3	336.3	367.4	340.8	374.3	353.5	386.4	375.5	408.9

I: 28°C (present work); II: 0°C (Ref. 8)

Table I also shows the deviation of the thermal conductivities obtained in this work from those reported by Filippov. It is noted that the deviation rarely exceeds 15%. This agreement supports the reliability of the thermal comparator method used in this work.

The thermal conductivities of eight binary liquid mixtures of acetone with each of the eight aliphatic alcohols of the homologous series, C_nH_{2n+1} OH (for n = 1 to 7) have been determined at 28°C for various compositions. They are tabulated in Table II along with Jamieson's data[8] for the same systems at the corresponding compositions taken at 0°C. The correspondence between the two sets of data is well within the experimental error generally encountered.

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