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EXPERIMENTAL STUDY OF THE THERMAL CONDUCTIVITY OF WEAKLY ABSORBING LIQUIDS IN LAYERS TRANSPARENT TO INFRARED RADIATION

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The thermal conductivities of a number of organic liquids are determined by a transient method under irregular thermal conditions.

A great deal of experimental work has been carried out in the last few years in connection with the influence of radiation on thermal-conductivity measurements in semitransparent media, a category including the majority of liquids. Measurements have most frequently been based on the most widely accepted steady-state methods (plane layers, coaxial cylinders, heated filaments). Theoretical analysis [1-5] and a considerable number of experimental investigations [3, 5-8] show that the influence of radiation expresses itself as a dependence of the thermal conductivity on the thickness of the layer used for the measurements. The molecular thermal conductivity is approximately obtained on extrapolating this relationship to zero layer thickness.

There are certain possible ways of eliminating the effect of radiation on the results of thermal-conductivity measurements; these include the so-called transient methods, especially those involving irregular thermal conditions. These methods are most frequently realized by the transient heating of a metal filament immersed in the liquid, with simultaneous recording of its temperature. The use of very thin filaments with a low intrinsic heat capacity enables the thermal conductivities to be measured quite rapidly, so that the region (layer) over which the measurement is carried out may be relatively small. For a broad class of weakly absorbing liquids, the thickness of this layer may be smaller than the mean free path of the photons characterizing infrared radiation. The radiative mechanism of heat transfer may then be almost entirely neglected, and the value of the thermal conductivity obtained under these specific conditions may be identified with the molecular thermal conductivity. The influence of radiative heat transfer then only appears as a loss of some of the heat from the surface of the heater and from the interior of the layer into which the transient temperature field penetrates. The total extent of these losses is small in the case of brief measurements and need not be taken into account.

The criterion of "transparency" as regards thermal radiation may be written in the form

$$\bar{l} > l^*, \tag{1}$$

where

$$\bar{l} = \int \frac{1}{k_\nu} \cdot \frac{\partial u}{\partial T}\, d\nu \Big/ \int \frac{\partial u}{\partial T}\, d\nu, \quad l^* = (at)^{1/2}.$$

In order to estimate $\bar{l}$ it is sufficient to limit consideration to monochromatic radiation of frequency ν_0 corresponding to the maximum of the Planck distribution function at the particular temperature. In this case $\bar{l} = 1/k_{\nu_0}$, and inequality (1) may be expressed in the form

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$$t < \frac{1}{k_{\nu_0}^2 a}. \tag{2}$$

Thus, subject to the condition that the layer should be "transparent" with respect to infrared radiation, the choice of the period of measurements is determined by the parameter $1/k_{\nu_0}^2 a$. For example, the numerical value of the parameter is 34 msec for toluene and 840 msec for CCl_4.

The filament placed in the test liquid is heated by an electric current. On using rectangular current pulses, creating a steady thermal flux q_l in unit length of the filament, the law of temperature variation in the filament is determined [10] by the relationship

$$\Delta T = \frac{q_l}{4\pi\lambda} \ln \frac{4at}{r^2 c}, \tag{3}$$

valid for fairly small values of the parameter $r^2c/4at$. From Eq. (3) we derive an expression for the temperature increment of the filament between the instants t and t_0:

$$\Delta T_{(t)} - \Delta T_{(t_0)} = \frac{q_l}{4\pi\lambda} \ln \frac{t}{t_0}. \tag{4}$$

The thermal flux was generated in a platinum filament ($r = 2\ \mu$). The type of filament regularly produced by industry was rolled into a copper sheath of 25-μ radius. In order to create a probe, this was set in a special glass base (Fig. 1). The points of soldering the filament to the current lead and the contact between the filament and the base were covered with paraffin, and then the base and filament were immersed in a solution of nitric acid. After etching away the copper sheath from the open parts of the filament and washing in acetone, the probe so prepared was placed in toluene in order to dissolve the paraffin. The total length of the open platinum filament was about 150 mm.

The resistance of the filament was incorporated into a bridge circuit (Fig. 2). Voltage pulses of specified amplitude and length were shaped by means of a key based on a KT-802 transistor. The pulse length was specified by means of a rectangular pulse generator G of the G5-6A type. In order to "decouple" the circuit from the ground, transformer coupling was employed between the generator output and the base–emitter junction of the transistor. An S1-15 oscillograph was used to indicate the signals from the bridge diagonal. Between the generator and the oscillograph was a delay line DL creating a time displacement between the tripping of the oscillograph and the instant at which the voltage pulse acted upon the bridge circuit.

Let us consider the measurement of the instantaneous values of filament resistance during transient heating. Before the onset of the measurements the bridge resistances were chosen in such a way that the following relationship was satisfied:

$$R_1/R_{i0} = R_2/R_3 = 1. \tag{5}$$

As soon as the pulse operates, the filament temperature rises and the bridge circuit loses balance. Because of the delay line between the generator and the oscillograph, the oscillograph screen only records part of the temperature signal from the filament. When pulses arrive periodically (at a frequency chosen subject to the condition that the temperature field created by the previous pulse should vanish almost completely in the

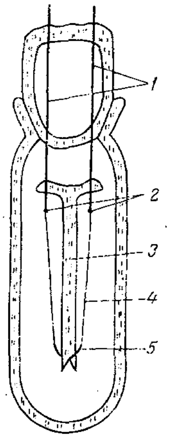

Fig. 1. Experimental cell: 1) current leads; 2) soldering points; 3) glass base; 4) working part of filament; 5) section of filament in copper sheath.

TABLE 1. Thermal Conductivity of a Number of Organic Liquids

Liquid and temperature range of measurement	λ 20 °C, W/m·deg		$\frac{\lambda_{20°}\text{lit.}-\lambda_{20°}\text{exp.}}{\lambda_{20°}\text{exp.}}$	$\frac{d\lambda}{dT}\cdot\frac{1}{\lambda_{20°}}\times 10^3$, deg^{-1}		$\frac{d\lambda}{dT}\cdot 10^4$, W/m·deg^2	
	exp.	lit.	%	exp.	lit.	exp.	lit.
Toluene (20—90 °C)	0,129	0,132	—2,3	2,0	1,9	2,6	2,5
Carbon tetrachloride (20—70 °C)	0,098	0,104	—5,7	2,5	2,1	2,4	2,2
Cyclohexane (20—70 °C)	0,118	0,122	—3,3	2,3	1,8	2,7	2,2
Isoamyl alcohol (20—90 °C)	0,134	0,135	—0,7	0,8	1,0	1,0	1,3

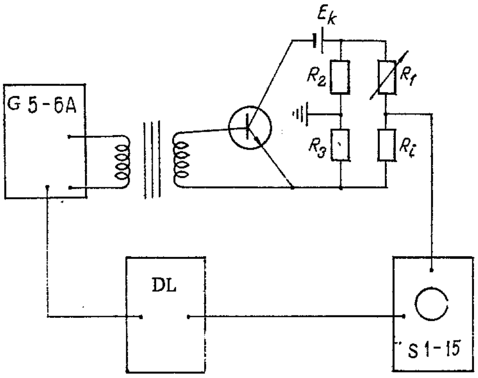

Fig. 2. Arrangement of the apparatus.

pause between the pulses ~ 0.2-0.5 Hz), by varying the resistance R_1 the beginning of the signal recorded on the oscillograph screen may be made to coincide with its zero line. It follows from (5) that in this case $R_1 = R_{i(t)}$, i.e., the value of R_1 coincides with the resistance of the filament at the instant of time t (delay time). For a more reliable indication of the bridge balance at the maximum sensitivity of the oscillograph, the beam traveling time was restricted to 50 μsec. The indeterminacy of the indication of the "instantaneous" bridge balance was governed by the minimum step through which the resistance R_1 could be varied (0.01 Ω) (R-517M resistance box). From the value of the electrical signal corresponding to the minimum step the value of R_1 was determined to an error of no greater than 0.003 Ω, i.e., no more than 0.5% of the total disbalance resistance.

From measurements of $R_{i(t)}$ for the relaxation times t_0 and t we may convert Eq. (4) into a computing relationship for determining λ:

$$\lambda = \frac{u_0^2\alpha}{16\pi l}\cdot\frac{1}{\operatorname{tg}\varphi},\qquad (6)$$
$$\operatorname{tg}\varphi = \Delta R_i/\ln\frac{t}{t_0}\quad(\Delta R_i = R_{i(t)} - R_{i(t_0)}).$$

The results of the experiments were expressed in the form of a relationship between ΔR_i and $\ln(t/t_0)$, determining tan φ. The delay times in the experiments were $t_0 = 3$ msec, $t = 5$, 10, 15 msec, for a voltage pulse length of 15.5 msec. The experimental points gave a good reproduction of a linear relationship (the maximum deviation of the points from the straight line was no greater than 0.5%), which indicated due satisfaction of the logarithmic law (3). The test tube containing the liquid under consideration (with the probe inserted into it) was placed in a TS-16A thermostat. The maximum heating of the filament in the pulse was no greater than 2.5°C. The liquids were of the analytically and chemically pure types.

The results of the investigations into the thermal conductivity of a number of liquids are presented in Table 1.

The main error in the measurements was due to apparatus errors in measuring the quantities indicated in Eq. (4); to these must be added a number of errors due to differences between the real physical model and the idealized model corresponding to the solution of Eq. (3). The maximum apparatus error equals

$$\frac{\Delta\lambda}{\lambda} = 2\frac{\Delta u_0}{u_0} + \frac{\Delta l}{l} + \frac{\Delta\alpha}{\alpha} + \frac{\Delta\operatorname{tg}\varphi}{\operatorname{tg}\varphi}.$$

For measuring the voltage we used a certified Shch1412 digital voltmeter (reading error 0.03%, scale error 0.02%). We measured the static voltage in the voltage source, which exceeded u_0 by an amount equal to the voltage drop in the internal resistance of the source and the transistor. The total extent of the latter discrepancies was very slight (not more than 1% of u_0); nevertheless, it was taken into account when calculating u_0. The time required to form the pulse in the load was less than 5 μsec; the constancy of the pulse amplitude and its reproducibility were solely determined by the voltage source, hardly depending at all on the parameters of the transistor, which operated under saturation conditions. Allowing for the foregoing factors, the error in measuring the voltage $\Delta u_0/u_0 = 0.2\%$.

For measuring the length of the filament we used an MIM-7 microscope; the measuring error $\Delta l/l = 0.7\%$.

The temperature coefficient of the resistance of the filament material was measured in a thermostat of the TS-16 A type. The filament was immersed in Vaseline oil, the temperature of the latter being measured to within 0.1°C. The error in measuring α was $\Delta\alpha/\alpha = 0.5\%$.

The error associated with tan φ is determined by the partial errors involved in measuring the delay time and the instantaneous values of the resistances. The delay line was calibrated with a frequency meter of the TF1417/3M1 type, the calibrating error being no greater than 0.3%. The error in measuring the resistance was discussed earlier. The resultant maximum error was $\Delta\tan\varphi/\tan\varphi = 1\%$.

The error associated with the change in thermal flux during the pulsed heating of the filament was small, subject to the satisfaction of condition (5), and was not taken into account.

The maximum apparatus error was accordingly 2.6%.

Among the sources of error due to the difference between the idealized and physical measuring models, the errors associated with the finite length of the filament, the limited volume of liquid, convection, and radiation from the surface of the filament are negligibly small. The error associated with neglect of the intrinsic heat capacity of the filament may be appreciable; however, an estimate based on the arguments of [11] indicates that under the conditions envisaged the upper limit should be 0.5%.

An additional source of error may be nonuniformity in the filament diameter. However, study of a large number of samples with different lengths of the etched sections (1-15 cm) showed that the resistivity of the filament was reproduced to the same accuracy as the length measurement, and this source of error was therefore also omitted.

Thus, the maximum error committed in measuring the thermal conductivity is $\Delta\lambda/\lambda = 3.1\% \approx 3\%$. The scatter in the experimental values of the thermal conductivity is, in general, no greater than 2% and for measurements with a single probe, 1%.

Table 1 includes the measured thermal conductivities of two weakly absorbing liquids (toluene and carbon tetrachloride) and two stronger absorbents (cyclohexane and isoamyl alcohol). The distinction is made on a qualitative basis. In particular, strongly absorbing liquids include those for which the absorption spectra are based on an uncontrollable thickness of the layer of liquid (flattened drop).

It is well known that toluene and carbon tetrachloride are among the most comprehensively studied liquids and are often used as standards. The thermal conductivities and temperature coefficients of the thermal conductivities of these liquids $d\lambda/dT \cdot 1/\lambda$ at 20°C are given in Table 1 on the basis of results presented in the monograph [12], which correlates the data of a large number of research workers. For toluene the effect of radiation is taken into account, i.e., the data reflect the molecular thermal conductivity to a fair degree of reliability. Cyclohexane and isoamyl alcohol have been less studied; in this case the table represents the results presented in [13].

Our own experimental values of the thermal conductivity at 20°C are lower than the published values for all the liquids studied, and have different relative "underestimation" coefficients $(\lambda_{lit} - \lambda_{exp})/\lambda_{lit}$. Allowing for the fact that in the case of liquids studied here, the error in order of increasing thermal conductivity was no greater than 1%, we may justifiably speak of a correlation between $(\lambda_{lit} - \lambda_{exp})/\lambda_{lit}$ and the degree of absorption of the thermal radiation; for weakly absorbing liquids the relative underestimate of the experimental data by comparison with the results of steady-state measurements was greater than for strongly absorbing liquids (for toluene without the radiation correction $(\lambda_{lit} - \lambda_{exp})/\lambda_{lit} \cdot 100\% = 3.7\%$).

It is interesting to compare the data relating to the derivative $d\lambda/dT$. The experimental values of the derivative (except for the measurements in isoamyl alcohol) exceed the values calculated from published data, which, as already indicated, were obtained by steady-state measurements. It is well known that for steady-state measurements the influence of radiation increases with increasing temperature of the liquid, and the overestimated $d\lambda/dT$ derived from our own measurements confirms that this influence is reduced or entirely eliminated under the conditions envisaged. As regards the measurements in isoamyl alcohol, the indeterminacy of the published data should be taken into account as well as the measuring error for comparison purposes. In particular, according to [14] for isoamyl alcohol $d\lambda/dT = 1.0 \cdot 10^{-4}$ W/m · deg^2, in satisfactory agreement with our own data.

NOTATION

$\bar{l}$, mean free path of a photon; l^*, diffusion length of the temperature field; k_ν, absorption coefficient for radiation of frequency ν; u, volumetric density of radiant energy; t, time; a, thermal diffusivity of the liquid; g_l, thermal flux per unit length of filament; T, filament temperature; ΔT, filament temperature difference; λ, thermal conductivity of the liquid; r, filament radius; c, Euler's constant; R_1, R_2, R_3, resistance in bridge circuit; R_{l0}, initial resistance of filament; $R_{l(t)}$, resistance of filament at time t; u_0, voltage pulse amplitude; l, length of filament; α, temperature coefficient of the resistance of the filament material. Indices: exp, experimental values; lit., published values.

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