

COMBINED SHORT-TIME MEASUREMENTS OF THE THERMOPHYSICAL PROPERTIES
OF ORGANIC LIQUIDS

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A short-time heated-wire method is used to measure the thermal conductivity, thermal diffusivity, and thermal activity of organic liquids.

The heated-wire method is now the most widely used method for studying the thermal conductivity of liquids [1-4]. The method consists essentially of recording, as a function of time, measured from the start of the current pulse, the increase of the temperature of a probe submerged in the liquid of interest. The thermal conductivity λ is determined from the slope of the straight line $\Delta T = f(\ln t)$ in accordance with the relation

$$\Delta T = \frac{q_l}{4\pi\lambda} \ln \frac{4at}{r_0^2\gamma}, \quad (1)$$

which holds for $t \gg r_0^2/4a$, and $\gamma = 1.781$ is Euler's constant. The advantages of the method, which make it so popular, are high accuracy, speed, relative simplicity, and the smallness of the measuring cell. It is significant that in the case of measuring times of 0.1 sec the method gives information about purely molecular thermal conductivity, undistorted by radiation transfer.

Together with the thermal conductivity this method in principle makes it possible to perform measurements of the thermal diffusivity $a = \lambda/(c_p\rho)$, and therefore to determine the heat capacity $c_p\rho$ per unit volume and the thermal activity $\varepsilon = \sqrt{\lambda c_p\rho}$. However a number of difficulties arise in the practical implementation of combined measurements, and if these difficulties cannot be overcome, the errors of measurement of a and $c_p\rho$ are large.

The combined nature of the method greatly expands its possibilities and makes the investigations more efficient, so that persistent efforts are made to find the optimal method for performing combined measurements.

There exist several methods for measuring the complex of thermophysical properties by the heated-probe method. One such method is based on combining the measurements performed with the help of flat and linear probes, which make it possible to obtain data on ε and λ , respectively. Another method employs narrow strips of foil and combines measurements with short ($t \ll d^2/a$) and long ($t \gg d^2/a$) times (d is the width of the foil).

The third method is based on the relation (1), which contains, in addition to the thermal conductivity λ , the thermal diffusivity a and therefore it incorporates the possibility of measuring them simultaneously. In order to perform such measurements it is necessary to measure especially accurately the temperature increment ΔT and the time t . This can be achieved by combining a number of measures: balancing very accurately the bridge circuit containing the probe and controlling the temperature of the liquid of interest, preventing drift of the amplifying and measuring apparatus, and suppressing electric interferences as much as possible [5-7].

In [8, 9] the relative variant of the heated-wire method for measuring thermal conductivity using a compensation scheme was developed. This significantly simplifies the apparatus and increases its sensitivity.

The basic idea of the compensation scheme is balancing the measured signal by changing the resistances of the bridge circuit, but not the entire signal - only the part that is governed by the difference of the thermophysical properties of the liquid of interest and

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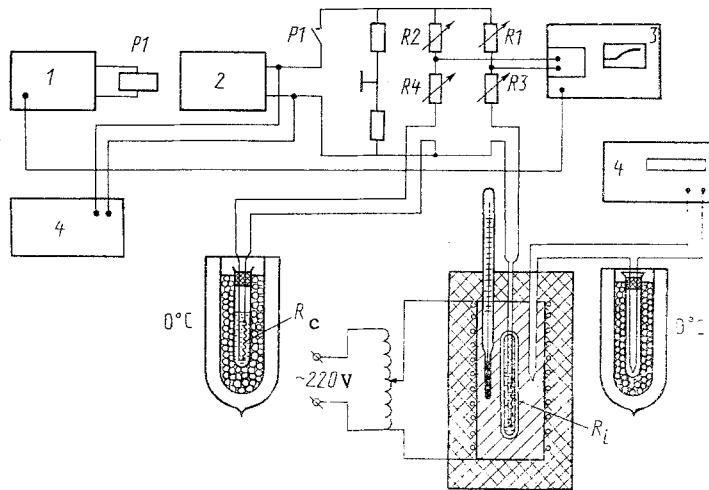


Fig. 1. Electric layout of the apparatus: 1) pulse generator; 2) power supply; 3) oscillograph; 4) voltmeter.

the liquid into which the compensation probe is submerged. The compensation scheme makes it possible to perform easily combined measurements.

We now examine the possibility of using the compensation scheme for performing temperature measurements of the thermal conductivity and thermal diffusivity of organic liquids (Fig. 1).

Two probes, a compensation probe R_C and the measuring probe R_i , are inserted into the parallel arms of the bridge. One of the probes (the compensation probe) is kept under constant temperature conditions throughout the entire period of the measurement; its temperature is kept constant by placing it in a Dewar flask with melting ice. The second probe (the measuring probe) is placed in a beaker together with the liquid being studied; the temperature of this probe can be arbitrary.

Initially, before the warming pulse is switched on, the bridge is balanced, so that

$$\frac{R_2}{R_1 + R_C} = \frac{R_1}{R_3 + R_i} = 1. \quad (2)$$

In practice this balancing is achieved with the help of the ballast resistance introduced into the circuit powering the bridge. This prevents the voltage pulse U_0 from heating the measuring and compensation probes.

The warming pulse U_0 heats up the wire probes. The increase of their temperature can be represented as a sum of variable (time dependent) and constant components:

$$\Delta T = \frac{q_l}{4\pi\lambda} \ln t + \frac{q_l}{4\pi\lambda} \ln \frac{4a}{r_0^2 \gamma}. \quad (3)$$

As the probe heats up its resistance changes by the amount

$$\Delta R = [\alpha + 2\beta(T - T_0)] R(T) \Delta T, \quad (4)$$

where the coefficients α and β determine the temperature dependence of the resistance of the wire $R(T) = R(T_0)[f + \alpha(T - T_0) + \beta(T - T_0)^2]$. The heating of the probes and the change of their resistances ΔR_i and ΔR_C in the general case throws the bridge out of balance. It is easy to verify that if $R_1 = R_3 + R_i$ it is impossible to achieve complete balancing of the bridge - simultaneous vanishing of the variable and constant components of the output signal - by varying the resistances R_1 and R_3 . Balance is possible if an additional change is introduced, for example, the resistance R_1 is varied, and the condition $R_1 + \delta R_1 = R_3 + R_i$ is satisfied.

In this case, in the linear approximation the strength e of the unbalanced signal is equal to

$$e = \frac{U_0}{4} \left(\frac{\Delta R_i}{R_1} - \frac{\delta R_1}{R_1} - \frac{\Delta R_C}{R_2} \right) \quad (5)$$

and the equality

$$\frac{\Delta R_i}{R_1} - \frac{\delta R_1}{R_1} = \frac{\Delta R_c}{R_2}, \quad (6)$$

is the condition of balance of the bridge.

The experiment is performed so that the function of time $\Delta R_c/R_2$ remains constant in all measurement procedures – the compensation probe is located in the same liquid at fixed temperature $t = 0^\circ\text{C}$, the resistances R_2 and R_4 remain constant, and the constancy of the voltage U_0 is checked with a voltmeter. Balance ($e = 0$) is achieved by manipulating the resistance R_1 and R_3 . If the bridge was balanced in two cases, when the probe was placed in the standard liquid with the starting (prior to the warming pulse) temperature T_0 and in the liquid under study at temperature T , then the following equality is satisfied:

$$\frac{\Delta R_{i\text{st}}}{R_{i\text{st}}} - \frac{\delta R_{1\text{st}}}{R_{1\text{st}}} = \frac{\Delta R_i}{R_1} - \frac{\delta R_1}{R_1}, \quad (7)$$

or, substituting Eqs. (3) and (4) and using the expressions for the power of the electric current $q_i = U_0^2 R_i / [(R_i + R_1 + R_3)^2 t]$,

$$\begin{aligned} & \frac{1}{R_1} \frac{[\alpha + 2\beta(T - T_0)]}{4\pi\lambda l_i} \frac{U_0^2 R_i(T)}{[R_1 + R_3 + R_i(T)]^2} \left[\ln t + \ln \frac{4a}{r_0^2 \gamma} \right] - \frac{\delta R_1}{R_1} = \\ & = \frac{1}{R_{1\text{st}}} \frac{\alpha}{4\pi\lambda l_i} \frac{U_0^2 R_{\text{st}}(T_0)}{[R_{1\text{st}} + R_{3\text{st}} + R_{i\text{st}}(T_0)]^2} \left[\ln t + \ln \frac{4a_{\text{st}}}{r_0^2 \gamma} \right] - \frac{\delta R_{1\text{st}}}{R_{1\text{st}}}. \end{aligned} \quad (8)$$

The latter equality decomposes into two equalities: for the variable and constant components. From the fact that the coefficients in front of $\ln t$ are equal in the approximation $R_1 \approx R_3 + R_i$ (in this case it introduces into the resulting formula an error not exceeding 0.1-0.2%) we obtain an expression which is the working formula used in measurements of the thermal conductivity:

$$\lambda = \lambda_{\text{st}} \frac{R_{\text{st}}^3(T_0)}{R_1^3(T)} \frac{R_i(T)}{R_{i\text{st}}(T_0)} \left[1 + \frac{2\beta}{\alpha} (T - T_0) \right]. \quad (9)$$

From the fact that the constant components are equal we obtain

$$K \ln \frac{4a}{r_0^2 \gamma} - \frac{\delta R_1}{R_1} = K \ln \frac{4a_{\text{st}}}{r_0^2 \gamma} - \frac{\delta R_{1\text{st}}}{R_{1\text{st}}}. \quad (10)$$

The structure of the coefficient K can be easily reconstructed by comparing the relations (10) and (8). This coefficient remains constant during all measurements by virtue of the fact that the function of time $\Delta R_c/R_2$ does not change and because the bridge is balanced.

From the relation (10) it follows that

$$a = a_{\text{st}} \exp \left[\frac{1}{K} \left(\frac{\delta R_1}{R_1} - \frac{\delta R_{1\text{st}}}{R_{1\text{st}}} \right) \right]. \quad (11)$$

The value of the coefficient K is most easily determined experimentally with the help of additional calibration in one other liquid, for example, perfluorooctane, at one temperature, for example, at 20°C . If toluene (t) and perfluorooctane (f) are used as the standard liquids, then

$$K = \left(\frac{\delta R_{1f}}{R_{1f}} - \frac{\delta R_{1t}}{R_{1t}} \right) \ln \frac{a_t}{a_f}.$$

In order to produce short-time temperature fields for probing the liquid, we employed platinum filaments with a radius of $4 \mu\text{m}$ and length of 40-50 mm. The width of the pulses fed to the bridge circuit did not exceed 50 msec and the pulse repetition frequency was chosen from the condition that the temperature field vanish almost completely in the intervals between pulses – the repetition frequency is usually equal to 0.5-1.0 Hz.

The liquid of interest was placed into a cylindrical cavity of a constant-volume bomb. A metal plug with insulated current output leads, to which a wire was welded, was screwed into the cavity.

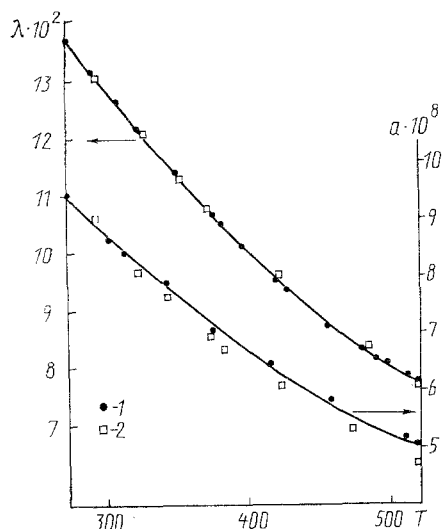


Fig. 2. Results of measurements of the thermal conductivity and thermal diffusivity of toluene: 1) experimental result; 2) published data. T, K; λ , W/(m·K); a , m²/sec.

Prior to the measurements the liquid was cooled in an atmosphere of liquid nitrogen up to the melting point, after which measurements were performed on the saturation line in the dynamic regime of heating of the substance up to temperatures close to critical temperatures.

The dynamic measurement regime is possible owing to the difference of the rates of heating of the entire liquid as a whole together with the ampul and the heater and probed layer in a pulse. For example, with an overall heating rate of 1 K/min the ratio of the rates is equal to $\sim 2 \cdot 10^{-4}$.

Thus the thermal conductivity and thermal diffusivity of organic compounds are investigated simultaneously by using a linear heat source (platinum wire) as a probe. The thermal activity $\varepsilon = \lambda/\sqrt{a}$ and the volume isobaric heat capacity $c_p\rho = \lambda/a$ are calculated based on the experimental data [3].

Analysis of the errors of the relative measurements shows that the basic sources of relative error are associated with the effect of the specific heat capacity of the filament on the result of the determination of the thermal conductivity, the instrumental errors in measuring R_1 and R_i , and the uncertainty in the indication of the complete balance of the bridge. According to our estimates, the resulting error of the relative measurements does not exceed 1% for the thermal conductivity and $\sim 5\%$ for the thermal diffusivity. In order to check the reliability of the data, we measured the thermal conductivity and thermal diffusivity of toluene in the temperature range 273-523 K (Fig. 2).

The values of the thermal conductivity of toluene agree to within 1% with the results of Nefedov [14], obtained by the method of periodic heating. The values of the thermal conductivity agree to within 4% with the calculations of $a = \lambda/(c_p\rho)$ in [10], where the values for the isobaric heat capacity were taken from [11], the values of the density were taken from [13], and the values of the thermal conductivity were taken from [14].

This method was used to investigate the thermophysical properties of a number of fluorocarbon compounds. The temperature dependences of the thermal conductivity and thermal diffusivity obtained from the experimental data are presented in Table 1. The values for the thermal conductivity and volume isobaric heat capacity can be easily calculated from data on the thermal conductivity and thermal diffusivity.

We now examine the possibility of using the compensation scheme for measuring the thermal activity of a substance.

It is easy to obtain the asymptotic expansion of the exact solution of the problem of the increment to the temperature of a cylinder heated by a current with a constant power q_0 for short times $t \ll r_0^2/4a$, assuming that all points of the cylinder have the same temperature:

$$\Delta T = \frac{q_0 t}{r_0^2 \pi \rho_1 c_{p1}} \left[1 - \frac{8}{3\sqrt{\pi}} \frac{\varepsilon_2}{r_0 c_{p1} \rho_1} \sqrt{t} - \frac{1}{4} \frac{a_2}{r_0^2} \left(\frac{1}{32} + \frac{c_{p2} \rho_2}{c_{p1} \rho_1} \right) t + \dots \right], \quad (12)$$

where the indices 1 and 2 refer to the probe and the medium surrounding the probe, respectively.

TABLE 1. Polynomials Approximating the Experimental Data on the Thermal Conductivity and Thermal Diffusivity of a Number of Fluoroorganic Compounds

Compound	T, K	λ , W/(m·K)	$a \cdot 10^8$, m ² /sec
C ₈ F ₁₈	263—463	$6,59 \cdot 10^{-2} - 0,142 \cdot 10^{-3}(T-273)$	$4,79 - 4,96 \cdot 10^{-3}T$
C ₉ F ₁₇ OCH ₃	213—500	$7,84 \cdot 10^{-2} - 1,41 \cdot 10^{-5}T - 1,08 \cdot 10^{-7}T^2$	$4,57 - 3,87 \cdot 10^{-3}T$
C ₅ F ₁₂ O	213—473	$8,31 \cdot 10^{-2} - 4,96 \cdot 10^{-5}T - 9,46 \cdot 10^{-8}T^2$	$4,41 - 3,59 \cdot 10^{-3}T$
[CF ₃ O (CF ₂ O) ₃ CF ₂] ₂	223—473	$6,50 \cdot 10^{-2} + 1,63 \cdot 10^{-4}T - 3,92 \cdot 10^{-7}T^2$	$4,60 - 9,54 \cdot 10^{-4}T$
[CF ₃ O (CF ₂ O) ₄ CF ₂] ₂	193—500	$6,14 \cdot 10^{-2} + 1,89 \cdot 10^{-4}T - 3,91 \cdot 10^{-7}T^2$	$4,85 - 5,06 \cdot 10^{-4}T$
[CF ₃ O (CF ₂ O) ₅ CF ₂] ₂	213—500	$8,68 \cdot 10^{-2} - 0,104 \cdot 10^{-4}(T-273) - 0,361 \cdot 10^{-6}(T-273)^2$	$3,98 + 4,04 \cdot 10^{-4}T$

It is obvious from the relation (12) that at the initial stage of heating of a wire probe the change in the temperature of the probe is determined by the characteristic heat capacity of the probe and the thermal activity of the medium. The manifestation of thermal activity is related with the fact that the condition $t \ll r_0^2/4a$ is equivalent to the assertion that the thermal disturbance penetrates into the medium to a depth that is small compared with the radius of the probe, i.e., it is the condition under which the cylindrical problem can be replaced by a planar problem.

The thermal activity can be measured when the third and subsequent terms in Eq. (12) are small compared with the second term, but when this requirement is satisfied the second term is usually small compared with unity. In order to eliminate the influence of the characteristic heat capacity of the probe the compensation probe is made of the same wire as the measuring probe and the bridge was balanced in the interval $\sim 10-100$ μ sec, when both probes are located in the same liquid and have the same temperature.

The probe is then placed in the liquid being studied or the standard liquid, and in so doing the resistances R_1 and R_3 , the initial temperature of the liquid, and the temperature of the probe itself remain constant. In this case the unbalanced signal varies in time as

$$e = \frac{U_0^3}{16} \frac{1}{r_0^2 \pi c_{p1} \rho_1} \left\{ - \frac{8D}{3 \sqrt{\pi} r_0 c_{p1} \rho_1} (\varepsilon_c - \varepsilon_i) t \sqrt{t} - \frac{D}{4r_0^2} \left[a_c \left(\frac{1}{32} + \frac{c_{pi} \rho_c}{c_{p1} \rho_1} \right) - a_i \left(\frac{1}{32} + \frac{c_{pi} \rho_i}{c_{p1} \rho_1} \right) \right] t^2 \right\}, \quad (13)$$

where

$$D = \frac{R_i^2}{R_1^3 l_i} = \frac{R_c^2}{R_2^3 l_c}.$$

In the case when the unbalanced signal varies in time, balance can be achieved at some fixed moment in time (in our case $t = 100$ μ sec) if

$$\frac{\Delta R_i}{R_1} - \frac{\delta R_1}{R_2} = \frac{\Delta R_c}{R_2}.$$

Neglecting $1/32$ compared with $c_{p2} \rho_2 / (c_{p1} \rho_1)$, we arrive at the relation

$$D' [(\varepsilon_c - \varepsilon_i) + (\delta \varepsilon_c - \delta \varepsilon_i)] = \frac{\delta R_1}{R_1}, \quad (14)$$

where

$$D' = \frac{U_0^2}{4} \frac{1}{r_0^2 \pi^{3/2} (c_{p1} \rho_1)^2}; \quad \delta \varepsilon_{c,i} = \frac{3 \sqrt{\pi}}{32} \frac{\lambda_{c,i}}{r_0} \sqrt{t}.$$

The method of measuring the thermal activity of a substance is based on the use of the relation (14). From two expressions of the type (14), corresponding to measurements in the standard liquid (st) and the liquids studied (i), we obtain a working relation for determining the thermal activity of the substance under study. This relation has the form

TABLE 2. Comparison of Measurements of the Thermal Activity with Published Data

Compound	$\varepsilon_{\text{exp}}, \text{W} \cdot \text{sec}^{1/2} / (\text{m}^2 \cdot \text{K})$	$\varepsilon_{\text{publ}} [11,14,15,16]$	$\varepsilon_{\text{calc}} = \lambda / t \bar{a}$
CCl ₄	377	367	369
H-C ₆ H ₁₈	449	441	439
C ₆ H ₁₂	419	416	
H-C ₆ F ₁₈	340	345	344
N(C ₄ F ₉) ₃	349		346
H-C ₆ H ₁₄	429	422	
C ₁₄ O ₄ F ₂₈	349		346
CF ₃ O(CF ₂ CF ₂ O) ₄ CF ₃	355		353
[CF ₃ O(CF ₂ O) ₄ CF ₂] ₂	397		393
[CF ₃ O(CF ₂ O) ₅ CF ₂] ₂	421		419

$$\varepsilon_i = \varepsilon_c + (\varepsilon_{\text{st}} - \varepsilon_c) \frac{\delta R_{1i}}{\delta R_{1\text{st}}} + C,$$

where

$$C = (\delta \varepsilon_c - \delta \varepsilon_i) - (\delta \varepsilon_c - \delta \varepsilon_i) \frac{\delta R_{1i}}{\delta R_{1\text{st}}}.$$

The correction C can be calculated using the known and measured values of the thermal conductivities λ_i and λ_c . The correction ranges from 1 to 3%, depending on the ratio of the thermal conductivities of the liquids.

The thermal activity of a number of organic liquids at T = 293 K was investigated experimentally. The results of the measurements, the published data [12], and the values of ε obtained based on calculations from the experimental data on a and λ , are presented in Table 2.

Comparing the experimental, computed, and published data shows that at room temperatures the method of determining the thermal activity with a linear source of heat gives satisfactory results. The experimental values agree to within 3% with the computed values and the published values.

Thus the heated-wire method, realized in the variant employing the compensation principle, makes it possible to use a simple, inexpensive apparatus to perform instantaneous measurements of the thermal conductivity and thermal diffusivity a of liquids on the basis of the relation (1), which is valid for $t \gg r_0^2 / (4a)$.

The direct measurement of the thermal activity ε on a different time scale ($t \ll r_0^2 / (4a)$) is a more complicated and laborious procedure and is recommended only for performing additional tests and for checking the consistency of experimental data at room temperatures and as an element for developing the electric scheme of the apparatus.

NOTATION

Here q_l is the heat flux per unit length of the filament; λ is the thermal conductivity; a is the thermal diffusivity; t is the time; r_0 is the radius of the wire; c_p is the specific isobaric heat capacity; ρ is the density; R is the resistance; and T is the temperature.

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RAPID METHODS FOR DETERMINATION OF THERMAL CONDUCTIVITY COEFFICIENTS
OF THERMOELECTRIC MATERIALS IN SEMICONDUCTOR THERMOBATTERIES

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Methods are developed for absolute and relative determination of the thermal conductivity coefficient of specimens of semiconductor material, with the only measurements required being determination of the relative temperature heads between the external medium and the specimen faces when controlled heat exchange is created at the external surface.

The net temperature-energy efficiency of a semiconductor cooler, especially a multi-stage one, depends to a significant degree on the correspondence of the semiconductor thermoelectric properties - thermo-emf coefficient, thermal conductivity, and electrical conductivity, used in calculations, to the real properties of the materials in the semiconductor stages.

Refinement of the temperature dependences of material thermoelectric properties at the temperature realized in semiconductor stages is also of great importance for the purpose of correcting data used to perform calculations.

When high efficiency batch methods are used to prepare thermobattery micromodules, or with use of high efficiency semiconductor materials produced by directed crystallization causing significant radial and axial anisotropy, the parameters of individual elements can differ greatly from the standard specifications of the billet from which they were cut. Therefore a necessary stage which must be included in the design of semiconductor coolers is rapid determination of material thermoelectric properties directly in the devices, refinement of their actual temperature dependences, and rejection of specimens whose properties do not correspond to those used in the calculations. The problem of developing high speed methods for determining the thermal conductivity coefficient of large quantities of semiconductor specimens is especially complex.

The major source of error in existing absolute and comparative methods for measuring thermal conductivity of semiconductor specimens is the complexity of precisely determining the thermal flux passing through the specimen and thermal losses from lateral surfaces [1,

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