SIMULTANEOUS MEASUREMENT OF THERMAL CONDUCTIVITY AND SPECIFIC HEAT OF SHORT-LIVED LIQUID

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The thermal conductivity and specific heat of a short-lived liquid are measured simultaneously by a pulsed version of the probe method. The nonuniformity of the temperature in the body of the probe is taken into account. A block diagram of experimental apparatus realizing the method is described.

The pulsed probe method to be described was developed for the compositive investigation of the thermophysical properties of short-lived (e.g., chemically reacting) liquids. The combined heater and temperature sensor consists of a 0.02-mm-diameter platinum wire of length 100 mm. During the time of measurement ($\tau \sim 10^{-3}$ sec) there is no time for convection to develop in the heater boundary layer; heat transfer is primarily by conduction.

Let us formulate the thermophysical problem for a wire probe located in a liquid and heated by a pulsed current. A uniform metallic cylindrical conductor of radius b and length l with a thermal conductivity λ and a specific heat per unit volume ρc contains a source of heat of constant specific power $\dot{T}_{ad}\rho c$ ($\dot{T}_{ad}$ is the rate of growth of temperature of the completely thermally insulated conductor). Heat exchange takes place at the side surface of the conductor with the surrounding liquid (under investigation), of thermal conductivity λ' and specific heat $\rho'c'$. Massive metal contacts are located at the ends of the conductor.

In the case of an infinitely long cylindrical conductor, the temperature is given by [1]:

$$T(r,\ t) = \frac{8}{\pi^2}\frac{\alpha}{B}\dot{T}_{ad}\int\limits_0^\infty \chi\frac{[1-\exp(-y^2Bt)]\,J_0(yr/\chi b)\,J_1(y/\chi)}{y^4[\psi^2(y)+\varphi^2(y)]}\,dy, \tag{1}$$

where

$$\psi(y) = 2\chi J_1(y/\chi)\,J_0(y) - \alpha J_0(y/\chi)\,J_1(y); \tag{2}$$

$$\varphi(y) = 2\chi J_1(y/\chi)\,N_0(y) - \alpha J_0(y/\chi)\,N_1(y); \tag{3}$$

$$\chi = \sqrt{\frac{a}{a'}};\ \alpha = 2\frac{\rho'c'}{\rho c};\ B = \frac{a'}{b^2}. \tag{4}$$

Since the temperature determined in experiment is the mean over the volume of the probe, we require to take the average over the radius of the wire probe and its length. Firstly, let us average the temperature over the radius:

$$\langle T(t)\rangle_r = \frac{1}{\pi b^2}\int\limits_0^b T(r,\ t)\,2\pi r dr. \tag{5}$$

Utilizing [2], we obtain:

$$\frac{\langle T(t)\rangle_r}{\dot{T}_{ad}} = \frac{16}{\pi^2}\frac{\alpha}{B}\chi^2\int\limits_0^\infty \frac{[1-\exp(-y^2Bt)]J_1(y/\chi)}{y^5[\psi^2(y)+\varphi^2(y)]}\,dy. \tag{6}$$

The temperature field along a cylindrical conductor with metal contacts at the ends is determined by the equation

$$\left(\frac{1}{a}\frac{\partial}{\partial t} - \frac{\partial^2}{\partial x^2}\right)T(x,\ t) = \frac{Q(t)}{\lambda} \tag{7}$$

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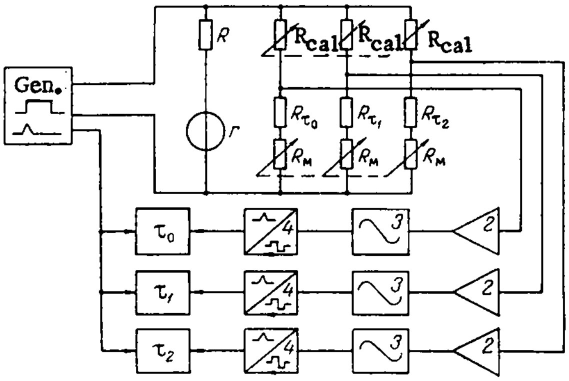

Fig. 1. Block diagram of experimental setup.

with boundary and initial conditions:

$$T(x=0,\ l;\ t)=0,\ T(x,\ t=0)=0. \tag{8}$$

In terms of Green's function of the first kind for a segment [3], its solution has the form

$$T(x,\ t)=\int_0^t dt'\int_0^l dx' Q(t')\,G(x-x',\ t-t'). \tag{9}$$

The temperature averaged over the length of the conductor can then be written:

$$\langle T(t)\rangle=\frac{1}{l}\int_0^l T(x,t)\,dx=\int_0^t dt' Q(t')\,s(t-t'), \tag{10}$$

where

$$s(\tau)=\frac{1}{l}\int_0^l dx\int_0^l dx' G(x-x',\ \tau). \tag{11}$$

In measurements we have that $\sqrt{at'}/l \ll 1$ (in the present method the time t ∿ 1 msec, l ∿ 10 cm). Utilizing the asymptotic expansion of the function s(τ) in this small parameter, we obtain

$$s(\tau)\approx\frac{1}{\rho c}\left(1-\frac{4}{\sqrt{\pi}}\frac{\sqrt{a\tau}}{l}\right). \tag{12}$$

We model the power of the heat dissipation in the conductor by the quantity

$$Q(t)=\rho c\frac{\partial}{\partial t}\langle T(t)\rangle_r. \tag{13}$$

Inserting $\langle T(t)\rangle_r$ from (6) into (13) and then the resulting expression together with formula (12) into the integrand in (10), we obtain the following relationship for the temperature of the conductor averaged over the radius and the length:

$$\frac{T(r,\ t)}{\dot{T}_{ad}}=\frac{16}{\pi^2}\frac{\alpha}{B}\chi^2\int_0^\infty\frac{J_1^2(y/\chi)\,dy}{y^5[\psi^2(y)+\varphi^2(y)]}\Big[1-\exp(-y^2Bt)-$$

$$-\frac{8}{3\sqrt{\pi}}\frac{\sqrt{at}}{l}y^2Bt\Phi(1,\ 5/2;\ -y^2Bt)\Big]\equiv f(\alpha,\ B,\ t,\ \chi,\ \sqrt{a},\ l) \tag{14}$$

or, remembering that $\chi=(1/b)\sqrt{a/B}$, we can write

$$T(t)/\dot{T}_{ad}=f(\alpha,\ B,\ t,\sqrt{a},\ b,\ l). \tag{15}$$

Here the parameters α and B characterize the investigated liquid; the parameters a, b, l characterize the measuring probe and are constant at a given temperature. Integral (14) is subsequently found by means of numerical calculation.

Let us return directly to the method of measurement. At the measurement durations

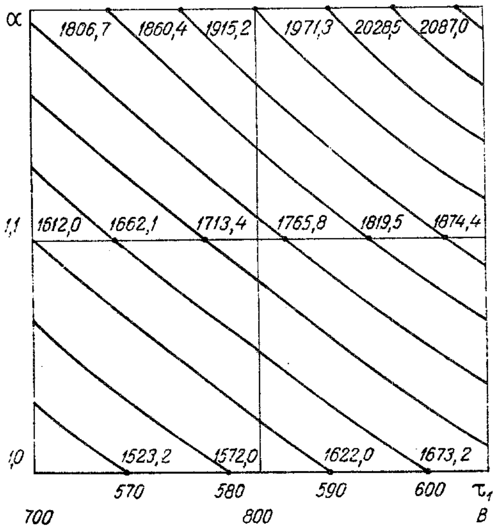

Fig. 2. Fragment of nomogram of dependence of α and B on τ_1 and τ_2. The numbers in the field of the nomogram equal the values of τ_2 at these points. τ_1, τ_2 are in μsec, B in sec^{-1}.

encountered in the present experimental setup, only the thermal conductivity and the specific heat of the liquid can affect the thermophysical process, which can be seen from (14). Accordingly, the system of equations

$$f(\alpha,\ B,\ t=\tau_1) = f_1,\ f(\alpha,\ B,\ t=\tau_2) = f_2, \tag{16}$$

where f_1 and f_2 are constants, is a complete system, i.e., in principle, for known constants f_1 and f_2 (and also parameters a, b, l), the quantities α and B (λ' and $\rho'c'$) are uniquely determined by the quantities τ_1 and τ_2 and conversely. The method described here has both absolute and relative versions. In practice the relative version is more convenient, as it does not require exact knowledge of the quantity $\dot{T}_{ad}$, which is indispensible in the absolute variant. In the relative version of measurement described below, the following condition is satisfied

$$f_1 = \frac{T_1 - T_0}{\dot{T}_{ad}} = \text{const}_1,\quad f_2 = \frac{T_2 - T_0}{\dot{T}_{ad}} = \text{const}_2. \tag{17}$$

This enables the necessary calculations to be done in advance and nomograms, e.g., to be constructed of the dependence of α and B on τ_1 and τ_2.

A block diagram of an appropriate apparatus is shown in Fig. 1. The signal from a pulse generator 1 is fed to a measuring bridge consisting of four branches, one of which contains the probe r [4]. The resistance bridges consisting of the outermost branch rR together with each of the three remaining branches are brought alternately into balance, the bridge $rRR_{cal}R_{\tau_0}R_M$ being brought to a state of balance at the initial moment of time by adjusting the variable resistor R_M. The signal from the bridge diagonal is fed via a null detection circuit (a low-noise amplifier 2, an amplifier-limiter 3, a comparator 4) to time measuring circuits (τ_0, τ_1, τ_2). Resistors R_{cal}, R_M, R, R_{τ_i} are low-inductance types. As the probe is being heated, its resistance in the linear approximation is given by:

$$r(\tau = \tau_0) \equiv r_0 = r_0^0(1 + \beta T_0), \tag{18}$$

$$r(\tau = \tau_1) \equiv r_1 = r_0^0(1 + \beta T_1) = r_0 + r_0^0\beta(T_1 - T_0), \tag{19}$$

$$r(\tau = \tau_2) \equiv r_2 = r_0^0(1 + \beta T_2) = r_0 + r_0^0\beta(T_2 - T_0), \tag{20}$$

where r_0^0 is the resistance of the probe at 0°C. Also,

$$RR_M = R_{cal}r_0,\ R(R_M + R_{\tau_i}) = R_{cal}[r_0 + r_0^0\beta(T_i - T_0)], \tag{21}$$

where i = 1,2;

$$R_{\tau_i} = \frac{R_{cal}r_0^0\beta(T_i - T_0)}{R}. \tag{22}$$

It can be seen from (22) that the temperature through which the probe heats up, $T_i - T_0$, does not depend on T_0 but depends on the constant resistors R, R_{τ_i}, the probe material (r_0^0, β), and the variable resistor R_{cal}. The calibration R_{cal} are functions of the temperature of measurement T_0. In order to realize conditions (17) it is necessary and sufficient to make one single determination of the dependence of R_{cal} on T_0. This dependence is found for a standard liquid with known α and B. Using the found values of $R_{cal}(T_0)$ one measures the times τ_1 and τ_2 of heating of the probe in the investigated liquid, and then finds α and B (λ' and $\rho'c'$) for this liquid using the previously constructed nomograms of the dependence of α and B on τ_1 and τ_2.

The total time of measurement τ_2 is prescribed by choosing the constant f_2, which has the significance of the minimum possible value of τ_2. For organic liquids the real time of total measurement is around two times greater than f_2. The constant f_1 is determined from the condition that the error of solution of system (16) be minimal. Machine experiments show that the optimum $f_1 \sim 0.5f_2$. A fragment of the nomogram is shown in Fig. 2. The calculation was performed on a computer for values

$$f_1 = 3.5\cdot 10^{-4}\,\text{sec}, f_2 = 7\cdot 10^{-4}\,\text{sec}. \tag{23}$$

We note that a calculation ignoring the nonuniformity of the temperature field in the body of the probe gives a deviation $\delta\alpha \sim 3\%$, $\delta B \sim 5\%$.

Apparatus error is determined mainly by error in the measurement of the moments at which the bridge is balanced. In the tested version of the device, the quantities τ_0, τ_1, and τ_2 could be determined to within ±0.2 μsec.

The pulse generator (output impedance ∿0.1 Ω) produced a heating pulse of duration 2 msec and amplitude 10 V; the pulse summit was flat to within 0.1%.

An error in the determination of the parameters of the probe (in our case a platinum wire of radius 10 μm and length 10 cm) of 20% in the thermal conductivity, 20% in the radius of the wire, and 10% (1 cm) in the length of the wire, gives a contribution to the measurement error of λ' and $\rho'c'$ of less than 1%. The total computational error is less than 5%. The instrument was calibrated using CCl_4 and used to measure the properties of toluene. In the temperature interval 15-60°C the discrepancy with reference data [5] was less than 1% for the specific heat and less than 1% for the thermal conductivity.

The above method has been used to investigate chemically aggressive liquids and has proved to be convenient in operation.

NOTATION

a, thermal diffusivity; b, probe radius; f_i, time for completely thermally insulated probe to heat up; $J_\nu(z)$, Bessel function; l, length of probe; $N_\nu(z)$, Neumann function; r, radius; T, temperature; $\dot{T}_{ad}$, rate of rise of temperature of completely thermally insulated probe; λ, thermal conductivity; ρc, specific heat per unit volume; τ_i, time for probe to heat up in investigated liquid; $r(\tau)$, r_i, r_0^0, probe resistance; R_{cal}, R_M, R_{τ_i}, resistors; β, temperature coefficient of resistance of platinum; x, y, coordinates; t, time; $\Phi(a, c, x)$, degenerate hypergeometric function.

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