

## VARIATIONAL METHODS FOR EXPERIMENTAL INVESTIGATION OF THERMOPHYSICAL PROPERTIES AND THERMAL ANALYSIS OF VARIOUS OBJECTS

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*The methods of automated determination of the thermophysical properties and thermal analysis of various objects (solid bodies, dispersed materials, and liquids) are substantiated. They are based on program variation of thermal fields in the experiment.*

Traditional methods of determining a set of thermophysical properties of various objects (solid bodies, dispersed and fibrous materials, liquids) are laborious, require much time and need various apparatuses and unlike conditions – all adding up to complexity of the analysis and generalization of the data obtained, choice of the field of application, comparison of the theory with experiment, etc. [1–4].

It may be asserted that a certain gap has been formed between the capabilities of the current methods and the growing needs for determining the thermophysical properties of both well-known and newly synthesized substances and materials that have different physicochemical properties, different types of structure, different technologies of manufacture, etc.

It has become possible to shorten considerably the time of measurements and increase their accuracy thanks to the creation of new, variational, methods for experimentally studying the physical properties of objects. These methods are based on discrete changes in the influencing factors that are successively applied to the object of investigation or removed from it and on corresponding recording of the primary information signals that determine the parameters (magnitude, direction of influence, and its duration) of each influencing factor and of the parameters of the response of the object to each separate factor or group of influencing factors; these methods are implemented experimentally with the aid of a system of computer-based automated investigation of a set of thermophysical and thermal properties of objects [5–7].

In what follows, the theory of nonstationary methods of determining thermophysical properties and carrying out a nonstandard differential thermal analysis of various objects of investigation is presented.

**Determination of Thermal Conductivity.** The method considered makes provision for parasitic heat losses (heat exchange of a block and of an object of investigation with the environment and thermal resistances of their contact surfaces), which are the main sources of methodological errors in the means of determining thermophysical properties of materials.

The idea of the proposed method of determining  $\lambda$  is schematically presented in Fig. 1a. A closed isothermal temperature chamber 1, whose walls have the same temperature  $T_0$  fixed in the process of measurement, has inside a mobile block 2 and an object of investigation 3 placed between the mobile block and the base of the temperature chamber. To simplify the solution, the thermal resistance on the end faces of the specimen is represented in the form of one contact layer of doubled thickness. The heat-conduction equations for the block 2, specimen 3, and contact layer 4, respectively (Fig. 1a), are of the form

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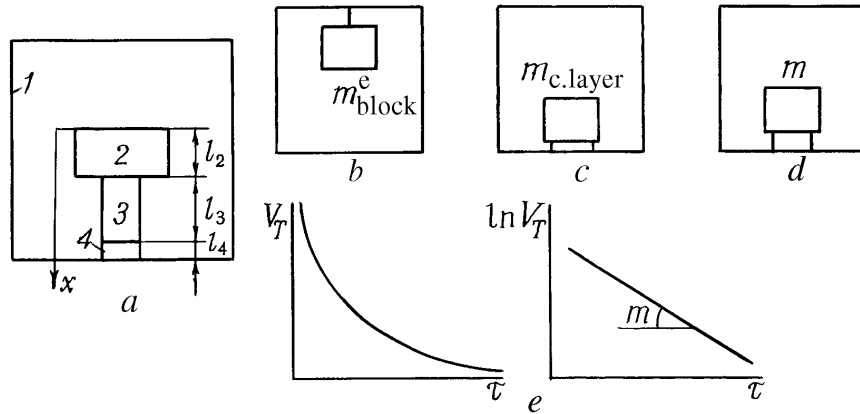


Fig. 1. Basic diagram of the method of determining thermal conductivity [a: 1) temperature chamber; 2) block; 3) object of investigation; 4) contact layer]; techniques of determining the rates of cooling [b)  $m_{\text{block}}^e$  of the block; c)  $m_{\text{c.layer}}$  of contact resistances (block–copper plate–contact layer); d)  $m_{\text{th.st}}$  of the thermal structure (block–object–contact layer)], and the curves of cooling measuring elements (e).

$$\frac{\partial^2 T_2'(x, \tau)}{\partial x^2} - \frac{ad_2}{\lambda_2 s_2} T_2'(x, \tau) = \frac{1}{k_2} \frac{\partial T_2'(x, \tau)}{\partial \tau}, \quad (1)$$

$$\frac{\partial^2 T_3'(x, \tau)}{\partial x^2} - \frac{ad_3}{\lambda_3 s_3} T_3'(x, \tau) = \frac{1}{k_3} \frac{\partial T_3'(x, \tau)}{\partial \tau}, \quad (2)$$

$$\frac{\partial^2 T_4'(x, \tau)}{\partial x^2} - \frac{ad_4}{\lambda_4 s_4} T_4'(x, \tau) = \frac{1}{k_4} \frac{\partial T_4'(x, \tau)}{\partial \tau}. \quad (3)$$

Here  $T'(x, \tau) = T(x, \tau) - T_0$ . The boundary-value conditions are presented by the expressions

$$aT_2'(0, \tau) = \lambda_2 \frac{\partial T_2'(0, \tau)}{\partial x}, \quad (4)$$

$$T_2'(l_2, \tau) = T_3'(l_2, \tau), \quad (5)$$

$$\lambda_2 s_2 \frac{\partial T_2'(l_2, \tau)}{\partial x} = \lambda_3 s_3 \frac{\partial T_3'(l_2, \tau)}{\partial x}, \quad (6)$$

$$T_3'(l_2 + l_3, \tau) = T_4'(l_2 + l_3, \tau), \quad (7)$$

$$\lambda_3 s_3 \frac{\partial T_3'(l_2 + l_3, \tau)}{\partial x} = \lambda_4 s_4 \frac{\partial T_4'(l_2 + l_3, \tau)}{\partial x}, \quad (8)$$

$$T'_3(x, 0) = 0, \quad T'_4(x, \tau) = 0. \quad (9)$$

Equations (1)–(3) under boundary-value conditions (4)–(9) are solved by the method of operational calculus [8]. Omitting the intermediate calculations, we obtain that on the object of investigation at any time instant

$$\Delta T = \frac{T'_0}{1 + \beta} \exp(-m_{\text{th.st}} \tau), \quad (10)$$

$$\beta = \frac{C_3}{3C_2} + \frac{m_{\text{block}}^e}{m_0} \left( \frac{C_3}{C_2} + \frac{S_3^s}{S_2^{\text{tot}}} \right), \quad (11)$$

$$m(1 + \beta) = \frac{1}{\frac{C_2 l_3}{\lambda_3 s_3} + \frac{C_2 l_4}{\lambda_4 s_3}} + \frac{aS_2^{\text{tot}}}{C_2} \left( 1 - \frac{s_3 - \frac{d_3 l_3}{3}}{S_2^{\text{tot}}} \right). \quad (12)$$

From expression (10) it is seen that with time the cooling of the block follows a strictly exponential law. The power of the exponent  $m_{\text{th.st}}$  characterizes the rate (tempo) of cooling the thermal structure "block–object of investigation–contact layer." The quantity  $m_{\text{th.st}}$  can be represented as an algebraic sum of the rates of cooling:

$$m_0 = \frac{\lambda_3 s_3}{l_3 C_2}, \quad (13)$$

$$m_{\text{block}} = m_{\text{block}}^e \left( 1 - \frac{s_3 - \frac{d_3 l_3}{3}}{S_2^{\text{tot}}} \right), \quad (14)$$

$$m_{\text{block}}^e = \frac{aS_2^{\text{tot}}}{C_2}, \quad (15)$$

$$m_{\text{c.layer}} = \frac{\lambda_4 s_3}{l_4 C_2}, \quad (16)$$

and then expression (12) takes the form

$$m_{\text{th.st}}(1 + \beta) = \frac{1}{\frac{1}{m_0} + \frac{1}{m_{\text{c.layer}}}} + m_{\text{block}}. \quad (17)$$

Equation (17) can easily yield an equation for determining the thermal conductivity of the object of investigation:

$$\lambda_3 = C_2 \frac{l_3}{s_3} (1 + \beta) m_0, \quad (18)$$

in which

$$m_0 = \frac{m_{\text{th.st}} (1 + \beta) - m_{\text{block}}}{1 - \frac{m_{\text{th.st}} (1 + \beta) - m_{\text{block}}}{m_{\text{c.layer}}}}. \quad (19)$$

The quantity  $m_0$  is attributable to the change in the heat content of the upper block due to the heat flux through the specimen ( $a \rightarrow 0$ ,  $\lambda_4$  and  $\lambda_2 \rightarrow \infty$ , i.e., when heat losses are equal to zero); the rates of cooling  $m_{\text{block}}$  and  $m_{\text{c.layer}}$  result from heat exchange of the block inside the isothermal chamber and from heat conduction between the block and the contact layers at the boundaries of the object with the block and the base of the temperature chamber.

On the whole, the considered process of cooling the thermal system "block-object of investigation-contact layer" can be considered as a result of variation of three independent influencing factors: heat exchange of the block with the walls of the isothermal temperature chamber, the heat flux through the specimen, and the heat flux through the contact layer. In accordance with these statements, the total rate of cooling  $m$  is determined in three stages by finding the rates  $m_{\text{block}}^{\text{c}}$ ,  $m_{\text{c.layer}}$ , and  $m_{\text{th.st}}$  following the schemes presented in Fig. 1b, c, and d, respectively. Practically,  $m_{\text{c.layer}}$  is determined from the curve of cooling the block through a thin copper plate ( $< 0.001$  m), both sides of which are covered by a contacting liquid whose thermal conductivity greatly exceeds that of the air in the pores of the contacting surfaces (for example, glycerin, silicone oil, an In-Ga eutectic solution, etc.). To reduce the thermal resistance, the block and the plate are fabricated from a highly conductive material (copper), and the end faces of the block and the specimens are polished beforehand. The rates of cooling ( $m_{\text{block}}^{\text{c}}$ ,  $m_{\text{c.layer}}$ , and  $m_{\text{th.st}}$ ) are determined from the curves that show the change in time of the temperature of the measuring elements (Fig. 1e):

$$m = \frac{\ln V_{T_1} - \ln V_{T_2}}{\tau_2 - \tau_1}. \quad (20)$$

Thus, it is shown that the main sources of errors in measuring thermophysical properties (heat losses) can be represented in the experiment as constants of the setup for the given block and contact layer in terms of the rates of cooling  $m_{\text{block}}^{\text{c}}$  and  $m_{\text{c.layer}}$  and correspondingly can be eliminated.

**Determination of Thermal Diffusivity.** The schematic representation of the method of determining the value of  $k$  is given in Fig. 2. Placed in the isothermal chamber 1 (Fig. 2a) are: a thermal block 2 and an object of investigation 3 (a solid body and a cell with dispersed material or liquid). The object 3 is placed on a thin copper plate 4 fastened at the base of the chamber by heat-insulating pillars 5.

At the initial time instant  $\tau = 0$  and during the whole experiment, the upper block is kept at a constant temperature of  $T_2'(l_2, \tau) = T_m$ . At the time  $\tau = 0$ , the block is placed on the object 3 and then, when  $\tau > 0$  (Fig. 2b), the process of measuring is started. For  $\tau > 0$ , the problem concerning the change in the temperature  $\Delta T(\tau)$  of its lower end face in time relative to  $T_0$  of the temperature chamber is reduced to the solution of heat-conduction equation (2) under the boundary-value conditions

$$T'(0, \tau) = T_0'; \quad T'(x, 0) = 0; \quad \partial T'(\infty, \tau) / \partial x = 0. \quad (21)$$

Taking into account the fact that the surface of the block is much larger than the side surface of the specimen, the solution of this problem is governed by the expression

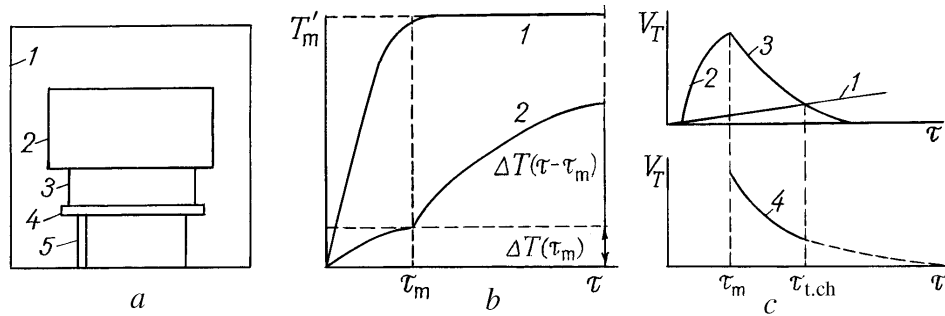


Fig. 2. Basic diagram of the methods of determining thermal diffusivity (a, b) and of the temperature behavior of thermal conductivity (c); a) placement of the elements of the thermal structure [1] temperature chamber; 2) block; 3) object of investigation; 4) plate; 5) heat-insulating pillars]; b) heating of the elements of the thermal structure [1] heating of the block to the temperature  $T_m(\tau_m)$ ; 2) increase of the temperature of the lower end face of the object by  $\Delta T(\tau_m)$  and thereafter by  $\Delta T_m(\tau - \tau_m)$  in measuring  $k$ ]; c) diagrams of the change in  $T(\tau)$  [1] chamber; 2) thermal structure "block-object-contact layer" on heating, and 3) cooling, respectively; 4) predicted curve].

$$\Delta T(\tau) = T_m \operatorname{erfc} \left[ \frac{l_3}{2\sqrt{k\tau}} \left( 1 + \frac{2k\tau}{l_3^2} \sqrt{\frac{m_{\text{block}}}{m_0}} \right) \right], \quad (22)$$

in which  $\operatorname{erfc}(x)$  is the tabulated integral of probability; therefore, the value of  $k$  can easily be found at the prescribed values of  $l_3$  and  $T_m$  and at the values of  $\Delta T(\tau)$  and  $\tau$  measured in the experiment.

If the block is installed on the object of investigation prior to the start of measurements, then for the period of its heating (Fig. 2b) to the temperature  $T_m(\tau_m)$  the temperature of the lower face of the object also rises by the value  $\Delta T(\tau_m)$ . Then expression (22) will not be exact already, and this will result in an error in determining the true value of  $k$ . With this fact being taken into account, the boundary conditions will have the form

$$T'(l_2, 0) = T'(l_2 + l_3, 0) = 0; \quad T'(l_2, \tau) = \nu\tau; \quad T'(\infty, \tau) = 0. \quad (23)$$

Solving Eq. (2), we obtain (omitting, for simplicity, the intermediate calculations and limiting the discussion to the terms of the second order of smallness) the following expression for the time-varying temperature of the lower end face of the object under investigation:

$$\frac{\Delta T(\tau - \tau_m)}{T_m \left( 1 + \sqrt{\frac{\tau_m}{\tau - \tau_m}} \right)} = \operatorname{erfc} \left[ \frac{l_3}{2\sqrt{k(\tau - \tau_m)}} \left( 1 + \frac{2k}{l_3^2} \sqrt{\frac{m_{\text{block}}}{m_0}} \tau(\tau - \tau_m) \right) \right]. \quad (24)$$

Thus, taking account of the duration of the heating  $\tau_m$  of the block that results in the change in the temperature of the lower face of the object by the value  $\Delta T(\tau_m)$  leads to the elimination of the methodological error introduced by this effect into the determination of the value of  $k$ . Numerical values of the  $\operatorname{erfc}$  function in Eq. (24) at measured values of  $T_m$ ,  $\Delta T(\tau - \tau_m)$ ,  $\tau_m$ , and  $\tau$  makes it possible to find its argument and correspondingly the value of  $k$  of the object from the tables given in [8].

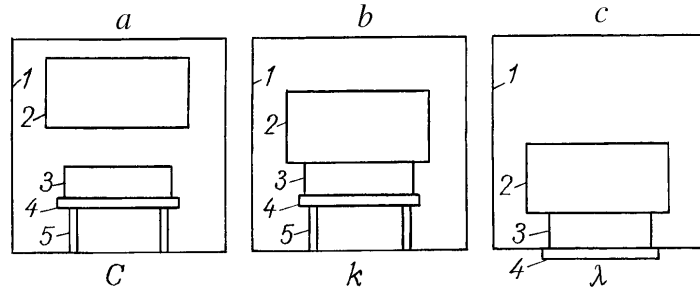


Fig. 3. Basic diagram of the method of determining a set of thermophysical properties of objects in a single experiment; a) of heat capacity  $C$ ; b) thermal diffusivity  $k$ ; 1, 2, 3, 4, 5) elements similar to those presented in Fig. 2a.

**Determination of the Heat Capacity.** The schematic representation of the nonstationary method of determining the  $C$  value is given in Fig. 3a. The object of investigation 3 (solid materials in the form of disks, dispersed and liquid substances in a closed cylindrical copper cell with a thin heat-insulating side wall of height no more than 0.005 m) is preliminarily heated to the temperature  $T(\tau)$  by 8–10° above the  $T_0$  of chamber 1, and then with block 2 fixed above it is placed on the copper plate 4, and thereafter the process of its cooling in time is recorded continuously:

$$T'(\tau) = T_0 \exp(-m_3\tau). \quad (25)$$

The value of  $m_3$  is determined similarly to the scheme shown in Fig. 1e. It can easily be seen that

$$m_3 = \frac{aS_3^{\text{tot}}}{C_3}. \quad (26)$$

Measuring separately  $m_{\text{cell}}$  and noting that  $C_3 = C_{\text{cell}} + C_{\text{sam}}$ , we respectively obtain the values

$$m_{\text{sam}} = \frac{m_3}{1 - \frac{m_3}{m_{\text{cell}}}}, \quad (27)$$

$$C_{\text{sam}} = \frac{m_{\text{block}}}{m_3} \frac{S_3^{\text{tot}}}{S_2^{\text{tot}}} C_2 \left( 1 - \frac{m_3}{m_{\text{cell}}} \right). \quad (28a)$$

Formula (28a) allows one to determine easily the mass of water (or of any other liquid) in different materials, keeping in mind that

$$C_{\text{sam}} = C_{\text{sp.w}} M_w + C_{\text{sp.d.m}} M_{\text{d.m}}. \quad (28b)$$

For this purpose, it is only necessary that the specific heat of a dry mass of dispersed material be measured preliminarily in the cell.

**Determination of the Temperature Behavior of the Thermal Conductivity.** Consider now the measurement of the thermal conductivity in a wide temperature range. The case of the temperature of the environment changing in a stepwise fashion from one fixed value to another is of no interest, since this method of measuring the behavior of the temperature  $\lambda(T)$  entails a large expenditure of time and hinders the

possibility of subsequently automating the process of measurement of the thermal conductivity. Therefore, we will keep in mind that the temperature of the environment undergoes changes and assume for simplicity that it does so following the linear law

$$T'(\tau) = T(\tau) - T_0(0) = \nu\tau. \quad (29)$$

This is the condition under which continuous variation in time of two independent influencing factors occurs (heat fluxes in the object of investigation): that of the external linear and internal (heat flux from the block) exponential. It is evident that the resulting character of the change in the heat flux in the sample only under certain conditions can be represented in the form of the additive sum of acting heat fluxes. The heat-conduction equation and boundary-value conditions for the object of investigation with allowance for heat transfer to the environment (to simplify, the contact thermal resistances on the end faces of the sample are considered to be equal to zero) have the form

$$\frac{\partial^2 T'_3(x, \tau)}{\partial x^2} - \frac{ad_3}{\lambda_3 s_3} T'_3(x, \tau) = \frac{1}{k_3} \frac{\partial T'_3(x, \tau)}{\partial \tau}, \quad (30)$$

$$C_2 \frac{\partial T'_2(l_2, \tau)}{\partial \tau} = -a(S_2^{\text{tot}} - s_3) T'_2(l_2, \tau) + \lambda_3 s_3 \frac{\partial T'_3(l_2, \tau)}{\partial x}, \quad (31)$$

$$T'_3(l_2 + l_3 \tau) = \nu\tau, \quad (32)$$

$$T'_2(x, 0) = 0. \quad (33)$$

The solution of Eq. (30) under the boundary-value conditions (31)–(33) is performed by the method of operational calculus [8]. Omitting intermediate calculations, write the final expression in the space of inverted transforms for the change in the pressure drop on the sample:

$$\begin{aligned} \Delta T = & \frac{T'_0}{1 + \beta} \exp(-m_{\text{th.st}}\tau) - \nu \left\{ \left[ 1 - \frac{m_0}{\left(1 + \frac{C_3}{2C_2}\right)B} \right] \tau - \frac{m_0}{\left(1 + \frac{C_3}{2C_2}\right)B^2} \times \right. \\ & \times \left[ \frac{(1 - \sqrt{1 - 4BD})^2}{4\sqrt{1 - 4BD}} \left( 1 - \exp\left(-\frac{2B\tau}{1 - \sqrt{1 - 4BD}}\right) \right) - \right. \\ & \left. \left. - \frac{(1 + \sqrt{1 - 4BD})^2}{4\sqrt{1 - 4BD}} \left( 1 - \exp\left(-\frac{2B\tau}{1 + \sqrt{1 - 4BD}}\right) \right) \right] \right\}, \quad (34) \end{aligned}$$

where

$$B = \frac{m_0 + m_{\text{block}}^e \left( 1 + \frac{S_3^s}{S_2^{\text{tot}}} \right)}{1 + \frac{C_3}{2C_2}}; \quad D = \frac{1}{6} \frac{l_3^2}{k_3} \left( 1 - \frac{C_3}{4C_2} \right).$$

The second term in formula (34) can be represented in a simpler form if it is taken into account that the powers of exponents can always be restricted to a value smaller than unity. Then, expanding the exponents into a Taylor series and limiting the discussion to terms of the first order of smallness yield

$$\Delta T = \frac{T'_0}{1 + \beta} \exp(-m_{\text{th.st}}\tau) - \nu\tau \left( 1 - \frac{m_{\text{th.st}}k_3}{l_3^2} \tau^2 \right). \quad (35)$$

From this expression it is seen that the change in the temperature drop  $\Delta T$  on the sample at each given instant of time is the result of the variation of opposite heat fluxes caused by exponential cooling of the thermal system "block-object of investigation"  $\Delta T_{\text{th.st}}$  and linear increase in the temperature of the temperature chamber  $\Delta T_{\text{t.ch}}$ . This process is terminated by the time instant at which the temperature of the block and of the sample become equal to the temperature of the chamber; thereafter they are heated jointly.

Figure 2c presents the distribution of the electromotive forces that are proportional to the change in the temperature of the chamber  $\Delta T_{\text{t.ch}}$  (curve 1) and also to the change in the temperature  $\Delta T_{\text{th.st}}$  in the period of fast heating (curve 2) and subsequent cooling (curve 3). In the experiment, the temperature of the block is raised several degrees above the temperature of the chamber by switching-on a heater placed inside the block; the curves  $\Delta T$  and  $\Delta T_{\text{t.ch}}$  are continuously recorded on the screen of a monitor. Curve 4 over the time interval from  $\tau = \tau_m$  to  $\tau = \tau_{\text{t.ch}}$  characterizes the change in the temperature of the object of investigation  $\Delta T = \Delta T_{\text{th.st}} - \Delta T_{\text{t.ch}}$  as though the temperature of the chamber did not change at that time instant. The unknown quantity  $m_{\text{th.st}}$  is determined precisely from this curve. The constants of the device  $m_{\text{block}}^e(T_{\text{t.ch}})$  and  $m_{\text{c.layer}}(T_{\text{t.ch}})$  are determined similarly to the method described above.

**Determination of a Set of Thermophysical Properties in a Single Experiment.** The essence of the method of determining the set of thermophysical properties of objects in a single experiment consists of successive specification in time of the initial and boundary conditions of the process of heating and cooling the thermal structure "block-object-plate" inside an isothermal chamber.

Measurements are made in the sequence  $C, k, \lambda$ , in which their overall duration and errors of determination of the set of thermophysical properties are at a minimum (Fig. 3):

a) to determine the value of  $C$ , the object of investigation is preliminarily heated to a temperature 8–10° higher than the temperature of the chamber and then is installed on a thin copper plate; thereafter, the process of change in time of the mean volumetric temperature of cooling of the object is fixed. The value of  $C$  is determined from Eqs. (28a) and (28b);

b) to find the thermal diffusivity, the upper block is automatically descended on the object of investigation and is heated to a fixed temperature following a program prescribed by a computer. Thereafter, the change in time of the temperature of the lower end face of the object  $\Delta T$  is recorded. The value of  $k$  is determined from formula (24);

c) to determine the thermal conductivity, the thermal structure "block-object of investigation-plate" is automatically descended until a complete contact is reached with the base of the chamber, after which the process of cooling-off of the thermal structure in time relative to the constant temperature of the chamber is recorded; the value of  $\lambda$  is determined from Eq. (18).

**The Method of Nonstandard Differential Thermal Analysis.** An example of the use of a thermophysical mechanism to investigate the physicochemical properties of materials with the aid of variation of two heat fluxes, of which one is external and the other internal, is the well-known [9] method of differential thermal analysis. The internal heat flux directed opposite to the external one or co-flowing with it originates within the sample itself in a certain definite temperature interval attributable to the appearance of endo- or exothermal effects in it and is fixed by the difference of temperatures  $\Delta T_{1,2}$  between the substance investigated A (Fig. 4c, curve 3, at the zone of the point C) and some standard substance B in which these effects



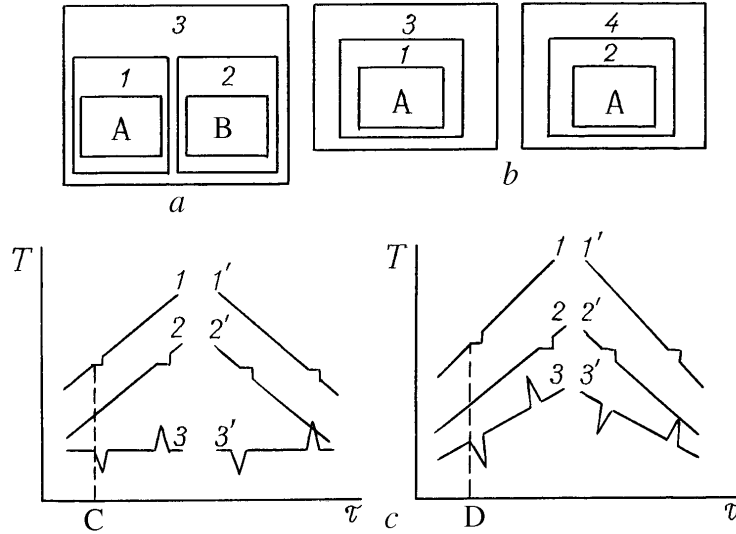


Fig. 4. Scheme of the methods of thermal analysis: differential thermal analysis (a) and nonstandard differential thermal analysis (b): a) the differential thermal analysis, ampoules A (object of investigation) and B (standard) in crucibles 1 and 2 inside a single temperature chamber 3; b) the nonstandard differential thermal analysis, ampoules A (objects of investigation) in crucibles 1 and 2 in separate chambers 3 and 4; c) curves of the temperatures of heating 1 and 2, cooling 1' and 2' of ampoules A and temperature difference 3 and 3' between them; C and D, zones of thermal effects at  $v_1 = v_2$  and  $v_1 \neq v_2$ , respectively.

are absent in the given temperature range. Both substances are placed in special crucibles 1 and 2 installed inside one chamber 3 (Fig. 4a). The temperatures and magnitudes of thermal effects appearing in the substance investigated are found from simultaneous analysis of curves 1 and 3 (Fig. 4c) that depict the changes in time of the quantities  $T_1(\tau)$  and  $\Delta T_{1,2}(\tau)$  in the process of heating or cooling of the sample and the standard. It is obvious that the accuracy of recording thermal conversions in the substance under investigation will depend on the properties of the standard, the constancy of the rate of change in the temperature of the chamber, the geometry, and the thermophysical characteristics of experimental crucibles or ampoules and also on the place of disposition and identity of measuring thermocouples.

If ampoules with a substance have the form of a cylinder for which  $L \gg R$ , then the distribution of temperature over the cylinder radius (provided that at  $r = 0$  the temperature is finite and at  $r = R$  the surface temperature is equal to the environmental one) will be described by the equation

$$\frac{\partial^2 T_{1,2}(r, \tau)}{\partial r^2} + \frac{1}{r} \frac{\partial T_{1,2}(r, \tau)}{\partial r} = \frac{1}{k_{1,2}^{\text{am}}} \frac{\partial T_{1,2}(r, \tau)}{\partial \tau} + \frac{q_{1,2}(r, T_{1,2})}{\lambda_{1,2}^{\text{am}}}. \quad (36)$$

The subscripts 1 and 2 relate to the substance under investigation and the standard, respectively. The solution of this equation at  $q_{1,2} = 0$  (when there are no endo- and exothermal effects) has the form

$$T_{1,2}(r, \tau) = T_0 + v_{1,2}\tau - \frac{v_{1,2}(R^2 - r^2)}{4k_{1,2}^{\text{am}}} + \frac{v_{1,2}R^2}{k_{1,2}^{\text{am}}} \sum_{n+1}^{\infty} \frac{A_n}{\mu_n^2} J_0\left(\mu_n \frac{r}{R}\right) \exp\left(-\frac{\mu_n^2 \tau}{R^2}\right), \quad (37)$$

where  $A_n = r/[\mu_n J_1(\mu_n)]$  are the initial thermal amplitudes;  $J_0\left(\frac{\mu_n}{R} r\right)$  is the Bessel function of the first-kind and zero order of the argument  $\mu_n \frac{r}{R}$ , and  $\mu_n$  are the roots of the equation  $J_0(\mu_n) = 0$ .

After a certain time  $\tau$ , the last term in Eq. (37) tends to zero and a quasistationary regime develops in the ampoules, in which the temperature at any point  $r$  over the section of the ampoules has the form

$$T_{1,2}(r, \tau) = T_0 + v_{1,2}\tau - \frac{v_{1,2}}{4k_{1,2}^{\text{am}}}(R^2 - r^2). \quad (38)$$

The difference between the temperatures  $\Delta T_{1,2} = T_1 - T_2$  of the object and the standard at  $v_1 = v_2$  is determined by the expression

$$\Delta T_{1,2}(\tau) = \frac{v}{4\pi L} \left( \frac{C_2^{\text{am}}}{\lambda_2^{\text{am}}} - \frac{C_1^{\text{am}}}{\lambda_1^{\text{am}}} \right). \quad (39)$$

From Eq. (39) it follows that  $\Delta T_{1,2}(\tau) = 0$  within the entire temperature interval only when  $C_2^{\text{am}}/\lambda_2^{\text{am}} = C_1^{\text{am}}/\lambda_1^{\text{am}}$ , i.e., the principal condition of the differential thermal analysis is the preservation of the zero temperature difference between the object and the standard in the absence of thermal conversions in them. However, in practice it is very difficult to satisfy the condition  $\Delta T_{1,2}(\tau) = 0$ , since the thermophysical parameters of the substance and standard ( $\lambda_1^{\text{am}}, C_1^{\text{am}}, \lambda_2^{\text{am}}, C_2^{\text{am}}$ ) depend differently on temperature. Moreover, essential here are the conditions of heat exchange of the sample and the standard with the environment. In the latter case, it should be kept in mind that the temperature of the sample and standard is

$$T_{1,2}(r, \tau) = T_0 + v_{1,2}\tau - \frac{v_{1,2}R^2}{4k_{1,2}^{\text{am}}} \left( 1 + \frac{2\lambda_{1,2}^{\text{am}}}{a_{1,2}^{\text{am}}R} - \frac{r^2}{R^2} \right), \quad (40)$$

and the quantity  $\Delta T_{1,2}(\tau)$  at  $v_1 = v_2$  has the form

$$\Delta T_{1,2}(\tau) = \frac{vR^2}{4} \left[ \frac{1 + \frac{2\lambda_2^{\text{am}}}{a_2^{\text{am}}R}}{k_2^{\text{am}}} - \frac{1 + \frac{2\lambda_1^{\text{am}}}{a_1^{\text{am}}R}}{k_1^{\text{am}}} - \frac{r^2}{R^2} \left( \frac{1}{k_2^{\text{am}}} - \frac{1}{k_1^{\text{am}}} \right) \right]. \quad (41)$$

From Eq. (41) it is evident that  $\Delta T_{1,2}(\tau)$  may substantially be varied in the process of thermal analysis at different values of  $a_1^{\text{am}}$  and  $a_2^{\text{am}}$  from the surface of the object and standard. The factors considered above (the difference in thermophysical parameters, conditions of heat exchange, rates of heating, geometries of the objects and standards, etc.) is one of the main sources of error in the determination of temperatures and heat of conversion of thermal effects.

We suggested [10] a different technique of nonstandard differential thermal analysis. This technique is based on variation of two homogeneous pairs of heat fluxes (external and internal) in separate, but identical in geometry and properties, objects of investigation. For this purpose, the technique involves two identically changing in time external heat fluxes, each of which is localized in two identical ampoules 1 and 2 with the same substance A (Fig. 4b) located in two identical temperature chambers 3 and 4. Naturally, of importance for thermal analysis is the design of the ampoules, whose geometry must be selected so that the length of the cylinder be at least larger than its doubled diameter; for distinct recording of the beginning and end of thermal effects, the thickness of the substance placed in the cylindrical ampoule must not exceed several hun-

dredths of a fraction of the cylinder length. The process of measurement consists of simultaneous recording of the temperatures of both substances and of the difference between them on the computer screen. Then, as can easily be seen (since  $\lambda_1^{\text{am}} = \lambda_s^{\text{am}}$  and  $k_1^{\text{am}} = k_2^{\text{am}}$ ), the expression for the temperature drop at  $a_1^{\text{am}} = a_2^{\text{am}}$  is

$$\Delta T_{1,2}(\tau) = T_1 - T_2 - (v_1 - v_2) \tau. \quad (42)$$

On the condition that the character of changes of heat fluxes is kept linear but the velocities  $v_1 \neq v_2$  (though they are invariable in time), the value of  $T$  changes according to Eq. (42). But if the chambers are heated so that  $v_1 = v_2$ , then there is a quasistationary regime, for which, in the absence of thermal effects in the substance,

$$\Delta T_{1,2}(\tau) = T_1 - T_2 = \text{const}. \quad (43)$$

The character of the representation of the measured quantities  $T_1$ ,  $T_2$ , and  $\Delta T_{1,2}(\tau)$  in the case of  $v_1 = v_2$  and  $v_1 \neq v_2$  is shown in Fig. 4a. When thermal conversion occurs in the first ampoule with a higher temperature, the changes in the linear character of increase in temperature appear on curves 1 and 3 (in the zone of the points C and D); the temperature in the second ampoule in these time intervals does not alter its slope, since it does not attain the value corresponding to the start of the endothermal effect. In this case, the substance in the second ampoule plays the role of a standard. Thereafter, as the temperature rises, the effect appears in the second ampoule, and the slope of the  $T_2(\tau)$  curve is changed; the curve of recording of the temperature of the substance in the first ampoule in this time interval does not change its slope, because thermal conversion in it was already completed earlier. Accordingly, a thermal effect in the second ampoule will be fixed on the  $\Delta T(\tau)$  curve. Thus, the same effect is recorded twice in the same test, since the same substance is contained in both ampoules.

Simultaneous recording of the temperatures in both ampoules and of the temperature drop between them makes it possible to separate the main effects from parasitic ones attributable to the difference in the conditions of heat exchange between the ampoules. For example, if the change in the character of heating on one curve is not repeated on the other, this effect cannot be considered as reliable. A substantial advantage of the method of a nonstandard differential thermal analysis is that the interval of time needed for heating the chambers and the temperature drop between them can easily be selected such that the thermal effects in the ampoules would not overlap.

It is important to note that the recording, in one experiment by the method of nonstandard differential thermal analysis, of thermal graphs of heating and cooling of the substance investigated makes it possible to establish the degree of the identity and reversibility of thermal effects, to record the effects of overcooling in solidification of substances, to study the influence of a gaseous medium and ultimately to obtain additional information on its physicochemical and thermophysical properties that is inaccessible by standard methods of thermal analysis.

## NOTATION

$a$ ,  $k$ ,  $C$ ,  $\lambda$ ,  $M$ ,  $d$ ,  $l$ ,  $s$ ,  $S^s$ , and  $S^{\text{tot}}$ , coefficient of heat transfer, thermal diffusivity, total heat capacity, thermal conductivity, mass, perimeter, height, cross-sectional areas of the side and total surface of the elements of the thermal structure;  $T$ , temperature;  $T_0$ , fixed temperature of the temperature chamber;  $\tau$ , time;  $m_{\text{block}}^e$ ,  $m_{\text{c.layer}}$ , and  $m_{\text{th.st}}$  are the experimentally determined rates of cooling the block, contact layer, and the thermal structure "block-object-contact layer";  $m_0$ , true rate of cooling the object;  $\Delta T = T_2(l_2, \tau) - T_3(l_2 + l_3, \tau)$ , temperature drop on the object;  $(V_{T_1} - V_{T_2})$ , analog difference of temperatures on the end faces of the object in the temperature interval  $\tau_2 - \tau_1$ ;  $v$ , rate of heating of the elements of the thermal structure;  $C_2$ ,  $C_3$ ,

$C_{\text{sam}}$ , and  $C_c$ , total heat capacities of the block, the thermal structure "cell-sample," the sample, and the cell;  $M_w$ ,  $M_{\text{d.m}}$ ,  $C_{\text{sp.d.m}}$ , mass of water, mass and specific heat of dry dispersed material;  $L$ ,  $r$ , and  $R$ , length and internal and external radii of ampoules, respectively;  $q$ , rate of absorption or evolution of heat in endo- or exothermal effects in a substance;  $a_1^{\text{am}}$  and  $a_2^{\text{am}}$ , heat-transfer coefficients of ampoules 1 and 2;  $k_{1,2}^{\text{am}}$ ,  $\lambda_{1,2}^{\text{am}}$ , and  $C_{1,2}^{\text{am}}$ , thermal diffusivity, thermal conductivity, and total heat capacity of substances in ampoules 1 and 2.

## REFERENCES

1. A. V. Luikov, *Theory of Heat Conduction* [in Russian], Moscow (1952).
2. A. G. Blokh, *Fundamentals of Radiative Heat Exchange* [in Russian], Moscow (1962).
3. B. M. Mogilevskii and A. F. Chudnovskii, *Thermal Conductivity of Semiconductors* [in Russian], Moscow (1972).
4. V. P. Kozlov, *Two-Dimensional Axisymmetric Problems of Heat Conduction* [in Russian], Minsk (1986).
5. I. S. Lisker and M. B. Pevzner, *Inzh.-Fiz. Zh.*, **34**, No. 3, 470–476 (1978).
6. I. S. Lisker and M. B. Pevzner, *Inzh.-Fiz. Zh.*, **37**, No. 4, 662–667 (1979).
7. I. S. Lisker, in: *Agrophysical Methods and Devices* [in Russian], Vol. 3, St. Petersburg (1998), pp. 299–312.
8. V. A. Ditkin and A. P. Prudnikov, *Reference Book on Operational Calculus* [in Russian], Moscow (1965).
9. G. O. Piloyan, *Introduction to the Theory of Thermal Analysis* [in Russian], Moscow (1964).
10. I. S. Lisker and S. P. Bardeeva, "A Technique of Carrying out a Differential Thermal Analysis", Inventor's Certificate No. 18384, *Byul. Izobr.*, No. 20 (1966).