OPTIMIZATION OF THE METHOD OF SCANNING ADIABATIC CALORIMETRY

M. E. Gurevich, L. N. Larikov,
and A. I. Nosar'

UDC 535.629

The problem of optimizing the measurements of the temperature dependence of heat capacity, thermal effects, and thermal conductivity in a scanning calorimeter is examined.

In improving instruments for scanning adiabatic calorimetry, the greatest effort is directed toward increasing the accuracy of the measurements.

In the present article, we examine the problem of optimizing the measurements of the temperature dependence of the heat capacity, thermal effects, and thermal conductivity. In order to obtain an undistorted value of the quantities indicated, we propose that at the time the measurements are recorded, a correction, taking into account the thermal inertia of the system, be introduced into the signal, modulating their temperature and time dependence. We also carry out a calculation of the distortions related to the nonuniformity of the temperature field in the specimen and breakdown in the regularity of the regime.

In determining the heat capacity by recording the intensity with which a specimen is heated by an internal microheater placed under quasiadiabatic conditions in the regular regime of the second kind [1] (heating at constant programmed rate $b_p = \text{const}$), distortions related to the thermal inertia of the specimen arise. Thermal inertia causes the rate at which the specimen is heated to deviate from the given rate and heats to the appearance of errors in determining the heat capacity [2].

We will examine a hollow cylindrical specimen with an internal microheater, surrounded by a protective shell, whose temperature, in order to create quasiadiabatic conditions, is maintained equal to the temperature of the surface of the specimen, programmed to vary according to $T_p = T_p + b_p t$. Under the conditions mentioned, all of the thermal power $p_p(t)$, introduced into the specimen, goes into heating it.

When the regular regime is strictly observed, if the specimen is heated uniformly over the entire volume (e.g., by the passage of a constant current through the specimen), the temperature dependence of the heat capacity of the specimen is modeled by the heating power according to the expression

$$c_p(T_p) = \frac{p_p(t)}{b_p}. \tag{1}$$

In an actual experiment following the scheme being examined, since the heat source does not coincide spatially with the specimen, a certain amount of time is required to transfer heat from the heater to the specimen, which is determined by the thermal inertia of the specimen $\tau = c_p/\alpha$ (where α is the heat-transfer coefficient from the heater to the specimen). This leads to a time shift that modulates the heat capacity of the electrical power liberated by the heater by an amount τ [3, 4]. This distortion can be avoided when recording the measurements by correcting the measured temperature of the specimen by an amount $b_p\tau$.

The thermal inertia of the specimen, in addition, causes its temperature (and heating rate) to deviate from the programmed value, which also distorts the recorded function $c_p(T)$. These distortions are most significant when processes accompanied by liberation (absorption) of heat or a sharp change in the heat capacity, e.g., with phase transitions of the second kind, occur in the specimen. These distortions can be corrected in two ways.

The first method consists of correcting the recorded quantity $p(t)/b_p$ by determining the true heating rate $b = b_p + (d\Delta T/dt)$ (where $\Delta T = T - T_p$ is the deviation of the measured temperature of the specimen from the programmed temperature) and operationally dividing the instantaneous value $p(t)$ by b:

Institute of Metal Physics, Academy of Sciences of the Ukrainian SSR, Kiev. Translated from Inzhenerno-Fizicheski Zhurnal, Vol. 41, No. 1, pp. 129-135, July, 1981. Original article submitted June 10, 1980.

$$c_p(T + b_p\tau) = \frac{p(t)}{b} = \frac{p(t)}{b_p + \dfrac{d\Delta T}{dt}}. \qquad (2)$$

The correction $b\tau$ is replaced, in the linear approximation with respect to ΔT, by $b_p\tau$. Here, and in what follows, we do not take into account the fact that when the temperature deviates from the programmed value, there not only arises a dependence b(t), but also b depends on the coordinates inside the specimen [5], since the technique developed was specialized primarily to materials with quite high thermal conductivity. In this case, the errors related to the coordinate dependence of b are much less than the change in b(t) related to the inaccuracy in maintaining the regular regime.

The second method is realized by introducing a correction into the temperature dependence of $c_p(T)$ together with a correction to $b_p\tau$. In this case, the magnitude of the heat capacity is determined by the ratio $p(t)/b_p$, while the temperature displacement δT is found from the following simple transformations of the recorded quantity $p(t)/b_p$ using (1) and (2):

$$\begin{aligned} \frac{p(t)}{b_p} &= \frac{p(t)}{b}\frac{b}{b_p} = c_p[T(t) + b_p\tau]\frac{b}{b_p}, \\ \frac{p(t)}{b_p} &= \frac{p_p(t+\Delta t)}{b_p} = c_p[T_p(t+\Delta t) + b_p\tau], \end{aligned} \qquad (3)$$

where Δt is the time shift between the instantaneous value of p(t), determining the true heating rate b and the measured temperature T(t), and the value $p_p(t + \Delta t)$ equal to it, ensuring that the programmed heating rate b_p and the programmed temperature $T_p(t + \Delta t)$ are maintained.

Since the shift sought is $\delta T = T_p(t + \Delta t) - T_p(t)$, from (3) we obtain a relation for determining its magnitude at time t:

$$c_p(T + b_p\tau)\frac{b}{b_p} = c_p(T_p + \delta T + b_p\tau). \qquad (4)$$

In order that δT be expressed in terms of the measured quantity ΔT, we will represent ΔT approximately within the limits of unit deviation of T from T_p as a broken line consisting of two segments, whose beginning and end coincide with points where $\Delta T = 0$. Along the first segment, at the beginning of the deviation, $b = \text{const} \neq b_p$ (for definiteness, e.g., $b > b_p$, i.e., $\Delta T > 0$). Let us locate the origin for measuring time t' and temperature T' at the point where $\Delta T = 0$. Since it may be assumed that the heat capacity is a linear function of temperature in a small temperature interval (outside singular points), in the system of coordinates chosen, we can write $c_p = c_{p0}(1 + \beta T')$ and (4) takes the form

$$(1 + \beta T')\frac{b}{b_p} = 1 + \beta(T'_p + \delta T'), \qquad (4a)$$

where

$$\beta = \frac{1}{c_p}\frac{dc_p}{dT'} = \frac{1}{bp}\frac{dp}{dt}.$$

Since, also, $T_p' = b_p t'$, $T' = bt'$, $\Delta T' = T' - T'_p = \Delta T$, we find from (4a), in a linear approximation with respect to ΔT, the correction to the programmed temperature T_p sought:

$$\delta T = 2\Delta T + \frac{1}{\beta T_p}\frac{d\Delta T}{dt}. \qquad (5)$$

Similar reasoning for the second segment leads to the same type of expression.

In the absence of anomalies in the heat capacity, usually $\beta \sim 10^{-3}\ \text{K}^{-1}$, and maintaining the heating rate with an error in the range of 0.1% (massive specimens do not permit changing the rate sharply) gives for the second term in (5) a quantity of the order of several degrees. The quantity ΔT in this case is of the same order of magnitude. In regions with anomalies, β can increase by an order of magnitude and the role of the first term increases.

Thus, the temperature dependence of the heat capacity, in general, must be corrected according to (5), both with respect to the deviation of the temperature, as well as that of the heating rate, from the given program values. If, on the other hand, the operational determination of the correction presents difficulties, then the programmed temperature is partially corrected by the amount $2\Delta T$ (or the measured temperature by the amount ΔT). Thus, taking into account this correction, for the correction method being examined, the temperature dependence of the heat capacity is found from the expression

$$c_p(T+\Delta T+b_p\tau)=\frac{p(t)}{b_p}. \tag{6}$$

In determining the thermal effects of the transformations in solids by the differential method (with respect to a standard specimen, whose temperature is maintained equal to the temperature of the specimen being studied, while their heat capacities are equal) by recording the supplementary heating power of one of the specimens, the heat balance equations taking into account the thermal inertia have the form

$$\begin{gathered}p_s(t)=c_p(T_s+b_p\tau)\frac{dT_s}{dt}=c_p(T_s+b_p\tau)\,b,\\ p_o(t)+q(T_o+b_o\tau)=c_p(T_o+b_o\tau)\frac{dT_o}{dt},\end{gathered} \tag{7}$$

where T_s and T_o are the measured temperatures of the standard and the specimen, respectively; $b=b_p+d\Delta T/dt$, true heating rate of the standard; $b_o=p_o/c_p$, rate at which the specimen is heated by an internal heater ($b_o \neq dT_o/dt$, since the specimen is also heated by the heat of internal transformations); q, thermal power liberated in the specimen, e.g., as a result of a phase transformation; $\Delta T_s=T_s-T_p$, deviation of the temperature of the standard from the programmed temperature.

Since the quantities recorded in the experiment are T_s, T_o, p_s and p_o, as well as

$$\Delta p=p_s-p_o,\ \Delta T=T_o-T_s, \tag{8}$$

while b_p enters as a constant, which determines the operational regime of the instrument, then the measured quantity q is corrected, in the same way as above, by two methods. In making the correction by determining the true heating rate from (7), we obtain in the linear approximation with respect to small quantities ΔT, $b_p\tau$, and $b_o\tau$

$$q\left(T_o+\frac{p_o}{p_s}b_p\tau\right)=\left(1-\frac{\tau}{p_s}\frac{dp_s}{dt}\right)\Delta p(t)+\frac{1}{b_p}\frac{d(p_s\Delta T)}{dt}. \tag{9}$$

Thus, the recorded quantity Δp is corrected in accordance with the expressions $1-\tau/p_s\,dp_s/dt$ and $(1/b_p)\cdot d(p_s\Delta T)/dt$, while the temperature dependence is corrected by the quantity $p_ob_p\tau/p_s$.

If the correction is made with the help of the shift in temperature relative to the programmed value, then, according to (5), Eqs. (7) take the form

$$\begin{gathered}p_s(t)=c_p(T_p+\delta T_s+b_p\tau)\,b_p,\\ p_o(t)+q(T_p+\delta T_o+b_o\tau)=c_p(T_p+\delta T_o+b_o\tau)\,b_p,\end{gathered} \tag{9a}$$

where

$$\delta T_s=2\Delta T_s+\frac{1}{\beta b_p}\frac{d\Delta T_s}{dt};\ \delta T_o=2\Delta T_o+\frac{1}{\beta b_p}\frac{d\Delta T_o}{dt}, \tag{10}$$

while $\Delta T_o=T_o-T_p$ is the deviation of the temperature of the specimen from the programmed value, and in addition, according to (8), $\Delta T_o-\Delta T_s=\Delta T$.

From (8) and (9), setting $\beta=1/c_p\,dc_p/dT \simeq 1/p_sb_p\,dp_s/dt$, we obtain in the linear approximation with respect to small quantities ΔT and $b_p\tau$

$$q\left(T_p+\delta T_o+\frac{p_o}{p_s}b_p\tau\right)=\left(1-\frac{\tau}{p_s}\frac{dp_s}{dt}\right)\Delta p+\frac{1}{b_p}\left[\Delta T\frac{dp_s}{dt}+\frac{d(p_s\Delta T)}{dt}\right]. \tag{11}$$

When it is impossible to correct the heating rate in (11), it is necessary to set $d(\Delta T)/dt=0$. In this case, taking into account the fact that $T_p+\Delta T_o=T_o$, we obtain

$$q\left(T_0+\Delta T_0+\frac{p_0}{p_s}b_p\tau\right)=\left(1-\frac{\tau}{p_s}\frac{dp_s}{dt}\right)\Delta p+\frac{2\Delta T}{b_p}\frac{dp_s}{dt}\,. \tag{12}$$

In this case, if the heat capacity varies smoothly within the limits of the experiment, so that the temperature of the standard can be maintained with sufficient degree of accuracy at the programmed level, i.e., $\Delta T_s = 0$, then in (12) it is necessary to set $\Delta T_0 = \Delta T$ and to use only measured quantities in (12).

The presence of a nonuniform temperature field in the specimen leads, as is well known, to the fact that the temperature measured at some point in the specimen, e.g., on the surface, does not coincide with the average temperature of the specimen. On the other hand, the instantaneous value of the heat capacity must be related precisely to the average temperature. For example, for a hollow long cylindrical specimen in the regular regime the temperature field is determined by the equation

$$T(\rho,\ t)=T_i+b_p t+\theta(\rho), \tag{13}$$

where $\theta(\rho)$ is the temperature differential over the distance ρ from the center of the specimen. With the boundary conditions $\theta(R) = d\theta(R)/d\rho$ (where R is the external radius of the specimen), i.e., when quasiadiabatic conditions are satisfied, the solution of the heat-conduction equation gives [6]

$$\theta(\rho)=\frac{h}{4\varkappa}\left[2R^2\ln\frac{R}{\rho}+\rho^2-R^2\right], \tag{14}$$

where $\varkappa$ is the thermal diffusivity.

Expression (14) was obtained by solving the heat-conduction equation for a regular regime under the condition that the thermal conductivity does not depend on temperature. However, for materials with high thermal conductivity, expression (14) can also be used in cases when the thermal conductivity depends on temperature, imposing in this case limitations on the heating rate. As follows from an analysis of the exact solution (see, e.g., [1]), for metallic specimens with R = 1 cm, the time for establishing a regular regime varies over the range 1-10 sec. In this case, heating rates less than 0.17 K/sec give an error, in determining the temperature dependence of $\varkappa$, on the order of 2°K or less.

For the average temperature $\bar{T}$ of the specimen, we obtain from (13) and (14)

$$\begin{gathered}\bar{T}(t)=T_i+b_p t+\bar{\theta},\\ \bar{\theta}=\frac{1}{R-r}\int_r^R\theta(\rho)\,d\rho=\frac{b}{\varkappa}f(r,\ R),\end{gathered} \tag{15}$$

$$f(r,\ R)=\frac{4R^3+r(3R^2-r^2)-6R^2r\left(1-\ln\dfrac{r}{R}\right)}{12(R-r)} \tag{16}$$

(r is the inner radius of the specimen).

Thus, the overall correction to the temperature dependence of measured quantities is determined by the sum $\delta T + h_p\tau + \bar{\theta}$. In this case, as follows from (14) and (15),

$$\bar{\theta}=\theta(r)\varphi(r,\ R), \tag{17}$$

$$\varphi(r,\ R)=\frac{4R^3+r(3R^2-r^2)-6R^2r\left(1-\ln\dfrac{r}{R}\right)}{3(R-r)\left(2R^2\ln\dfrac{R}{r}-R^2+r^2\right)}, \tag{18}$$

where $\theta(r)$ is the measured temperature differential between the inner and outer surfaces of the cylindrical specimen.

Starting from the calculations presented, it is possible to determine the thermal conductivity λ. Indeed, for the hollow cylindrical specimens examined, the flux through the inner surface with area S equals the power introduced into the specimen

$$p(t) = -\lambda(T + \Delta T + b_p\tau)\, S\frac{d\theta(r)}{d\rho} = \lambda S\psi(r,\ R), \tag{19}$$

$$\psi(r,\ R) = \frac{R^2 - r^2}{2r},\ \lambda = \varkappa c_p d, \tag{20}$$

where d is the density. As follows from (15), (16), (19), and (20), the temperature dependence of the thermal conductivity corrected for thermal inertia has the form

$$\lambda(T + \Delta T + b_p\tau + \bar{\theta}) = \frac{p(t)}{\theta(r)} F(r,\ R), \tag{21}$$

where

$$F(r,\ R) = \frac{1}{4V}\left(2R^2 \ln\frac{R}{r} + r^2 - R^2\right), \tag{22}$$

and V is the volume of the specimen.

Analysis of the errors in the method shows that the corrections presented strongly affect the results of measurements in the scanning regime. Estimates were made for a vacuum (10^{-5} torr) adiabatic calorimeter using standard specimens, heated by an internal microheater with heating rates of 0.017-0.17 K/sec, scanning from 300 to 1200°K, with second-order accuracy in maintaining a regular regime with respect to the maximum deviation of temperature from the programmed value $(\Delta T/T)_{\max} = 0.1\%$, and with respect to the maximum deviation of the heating rate from the given rate of $(\Delta b/b)_{\max} = 0.1\%$. Pure nickel and iron were used as standard substances. For nickel, $\tau_0 = 6 \cdot 10^3\ c_p$ ($T_0 = 300°K$), which for $b_p = 0.08$ K/sec gives an error in determining the temperature dependence of $b_p\tau_0 = 54°K$. For iron $\tau_0 = 7 \cdot 10^3\ c_p$ and, correspondingly, $b_p\tau_0 = 70°K$. In view of the high thermal conductivity, the error stemming from the temperature field in the specimen, for metals with good heat conduction, constitutes 10^{-1}-10^{-2} K/sec (for the heating rates indicated, much less than the error due to thermal inertia). At low temperatures, the error caused by the inaccuracy in maintaining the program temperature is relatively small: $\Delta T = 10^{-3}T \simeq 0.3°K$, but at high temperatures it increases to several degrees.

Since the vacuum in the calorimeter constitutes 10^{-5} torr and heat transfer from the heater to the specimen occurs primarily by radiation, we can approximately assume that $\tau = \tau_0\ (1 + (T - T_0)/b_p p\ dp/dt)(T_0/T)^3$, i.e., as the temperature increases, the error in determining the temperature dependence, caused by thermal inertia, decreases and becomes comparable to the error stemming from the inaccuracy in maintaining the temperature. Thus, for $T = 1200°K$ $b_p\tau \simeq 1°K$, and $\Delta T \simeq 1.5°K$.

In the absence of anomalies, and in view of the smallness of $1/c_p\ dc_p/dT$ ($\sim 10^{-4}$ for nickel and $\sim 10^{-3}$ for iron), deviations in the heating rate from the programmed value make the main contribution to the total error in determining the magnitude of the heat capacity $\Delta C_p/C_q = (\Delta T + b_p\tau)/c_p\ dc_p/dT + \Delta b/b$. However, in a region with anomalies, due to the increase in $1/c_p\, dc_p/dT$, these errors become comparable. Thus, in the vicinity of a phase transition of the second kind (magnetic transition) for nickel $b_p\tau/c_p\, dc_p/dT \simeq 9\%$ and for iron 6%. At the same time, in the region with these transformations, $b_p\tau = 12°K$ for nickel and 6°K for iron.

Thus, the proposed optimization of the method permits avoiding a number of significant errors, which is especially important in identifying physical processes in materials from the change in their thermal properties and in determining critical points.

LITERATURE CITED

1. A. V. Lykov, Theory of Heat Conduction [in Russian], Vysshaya Shkola, Moscow (1967).
2. L. N. Larikov, V. T. Cherepin, and M. E. Gurevich, Automation in Monitoring and Research [in Russian], Tekhnika, Kiev (1971).
3. M. M. Popov, Thermometry and Calorimetry [in Russian], Moscow State Univ. (1954).
4. B. N. Oleinik, Precision Calorimetry [in Russian], Standartov, Moscow (1973).
5. E. S. Platunov, Thermophysical Measurements in the Monotonic Regime [in Russian], Énergiya, Leningrad (1973).
6. M. E. Gurevich, L. N. Larikov, and A. I. Nosar', Heat Exchange and Hydrodynamics [in Russian], Naukova Dumka, Kiev (1977).