HEAT TRANSFER IN CONDUCTIVE MICROCALORIMETERS

Yu. F. Red'ko, A. V. Mikhailenko,
and O. Ya. Luste

UDC 536.2.083

The process of heat transfer in Calvet-type conductive microcalorimeter has been analysed. The method of reconstructing the true curve of heat liberation from the shape of the thermograms has been presented.

The conductive microcalorimeters of Tien—Calvet type constitute the primary type of instruments that can precisely measure the mild heat flows and study the kinetics of long processes accompanied with micro-generation of heat. Due to the remarkable properties of these devices, particularly sensitivity up to 0.1 μW and high reliability, they are finding wider and wider application in physical, chemical, and biological studies [1], metrology, and measurement techniques [2, 3].

The problems of heat transfer in conductive microcalorimeters have been dealt with in [4-8]. The most comprehensive study of heat transfer in Calvet-type microcalorimeters has been conducted in [8]. The author has examined the thermal processes in simplified models representing a combination of microcalorimetric thermocouple elements. In accordance with the model the thermocouple element is considered as a thermal bridge that join nearly isothermal jackets of a calorimeter. Such a consideration leads to one-dimensional equation of thermal conductivity for a limited thin rod with heat exchange at the lateral surface. An analysis of the solution of a system of equations for active and passive thermal tie-plates confirmed the basic considerations regarding the choice of optimum construction of the thermopile described in [1] and gave a series of practical recommendations for reconstructing the true heat generation curves on the basis of thermograms.

However, the above scheme does not take into account the inhomogeneity of the heat-conducting system, the contact heat resistances at the thermocouple junctions, and the intrinsic convection between the microcalorimeter jackets.

An attempt has been made by us to study the thermal processes in a model which is closer to the actual construction of a thermocouple element than the model suggested by Calvet. In the proposed model the contact heat resistances that are unavoidable in actual construction have been taken into account. The convective heat exchange between the parts of a microcalorimeter has also been considered (Fig. 1). The model takes into account the heat transfer along metallic parts of the thermocouple element, heat resistances at the junction of a thermocouple element with the thermostatic block of the microcalorimeter and its chamber. The heat-conducting system of the construction consisting of a silver plate, inner junction, thermocouple electrode, external junction and a silver plate is considered as a single conductor 2 in Fig. 1.

The heat transfer at the surface of the thermal electrodes and along the silver plates (Fig. 2) attached to the external surface of the copper cylinder takes its own course. On the wire surface a pellicular state of heat transfer is observed, in which the Rayleigh criterion Ra has a value of 0.1 to 0.3 when $\mathrm{Ra} = (\mathrm{Gr} \cdot \mathrm{Pr}) < 1$, $\mathrm{Nu} = 0.5$ and $\alpha = 0.5(k/d)$ [11, 12, 13], where Nu is the Nusselt criterion, α is the heat transfer coefficient, k is the coefficient of thermal conductivity, and d is the diameter.

When there is movement of air along the inner silver plates, a laminar flow takes places with $\mathrm{Gr}_{\mathrm{B}} \cdot \mathrm{Pr}_{\mathrm{B}} < 10^9$. The heat transfer coefficient decreases with height in proportion to $x^{-0.25}$, where x is the

---

Chernovtsy State University. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 27, No. 2, pp. 270-276, August, 1974. Original article submitted October 4, 1973.

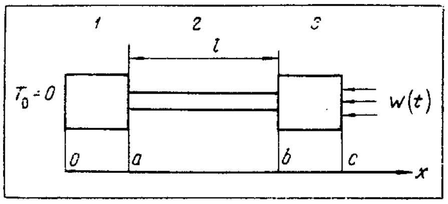

Fig. 1. Model for calculation.

height [14]. The maximum value of heat transfer coefficient corresponds to $\alpha = 0.5(k/d)$ as in the case of a thermocouple electrode. When the height of the cylinder is 8 cm the coefficient for the upper silver plate is approximately half as much as for the lower one. The heat transfer from the surface of the microcalorimeter elements has been taken care of by means of introducing a coefficient H of heat transfer in the equation. The analysis and evaulations show that, without diminishing the generality of the problem, the quantity H can be considered as constant and not dependent on temperature. The equation of thermal conductivity and the boundary conditions in the present case have the form

$$\frac{\partial T_i}{\partial t} = \varkappa_i \frac{\partial^2 T_i}{\partial x^2} - \nu_i T_i, \tag{1}$$

Here i = 1, 2, and 3 for the three fields shown in Fig. 1

$$\begin{gathered} T_1(a,\ t) - T_2(b,\ t) = \theta(t), \\ S_3 k_3 \left.\frac{\partial T_3}{dx}\right|_{x=c} = W(t), \\ T_1(a,\ t) = T_2(a,\ t),\ T_2(b,\ t) = T_3(b,\ t),\ T_1(0,\ t) = 0, \\ S_1 k_1 \left.\frac{\partial T_1}{\partial x}\right|_{x=a} = S_2 k_2 \left.\frac{\partial T_2}{\partial x}\right|_{x=a}, \\ S_2 k_2 \left.\frac{\partial T_2}{\partial x}\right|_{x=b} = S_3 k_3 \left.\frac{\partial T_3}{\partial x}\right|_{x=b}, \end{gathered} \tag{2}$$

where T_i is the difference of temperatures at the point with coordinate x and in the thermostatic block, t is the time, W(t) is the capacity of heat liberation in the microcalorimeter chamber, θ(t) is the difference of temperatures at the points x = a and x = b, $\varkappa_1$, $\varkappa_3$, and $\varkappa_2$ are the thermal conductivities of the insulating and thermocouple materials respectively. By W(t) one understands the heat flow that reaches the inner jacket of a microcalorimeter (i.e., the surface of the microcalorimeter chamber 5 in Fig. 2). The contents of the microcalorimeter chamber can be extremely different. Heat capacity of the chamber contents is often variable due to the occurrence of phase transformtions. Additional investigation of the effect of heat capacity of the chamber contents on W(t) offers the possibility of studying the dynamics of heat liberation inside the chamber.

In the present study the object for microcalorimetric measurement along with its heat capacity has not been defined concretely. Further the insulating material in the fields 1 and 3 (Fig. 1) will be considered as one and the same. The quantity $K_1 = K_3$ and K_2, which denote the thermal conductivities of insulation and thermocouple. The quantity $S_1 = S_3$ and S_2, which denote the cross sectional areas of the insulation stack and thermocouple:

$$\nu_i = \frac{H_i \Pi_i}{c_i \rho_i S_i};$$

where Π_i are the perimeters of the cross-section, c_i are the specific heat capacities, and ρ_i are the densities of the substance of respective fields. The initial temperature difference in the system is assumed to be equal to zero. Integration of (1) and (2), after Laplace's transformations, leads to the solution of the system of common differential equations of the following form

$$\varkappa_i \frac{d^2 \overline{T}_i(x,\ p)}{dx^2} - (\nu_i + p)\overline{T}_i(x,\ p) = 0, \tag{3}$$

where the corresponding Laplace forms have been denoted by a bar over the variables. The solution of Eqs. (3) with respect to the form of heat liberation function $\overline{W}$(p) under the given boundary conditions is given by

$$\overline{W}(p) = \frac{\overline{\theta}(p)}{\operatorname{sh}(a\mu_1)[1 - \operatorname{ch}(l\mu_2)] + \gamma \frac{\mu_1}{\mu_2} \operatorname{ch}(a\mu_1)\operatorname{sh}(l\mu_2)} \times$$

$$\times \left\{ S_1 k_1 \mu_1 \operatorname{ch}(l\mu_2)[\operatorname{sh}^2(a\mu_1) + \operatorname{ch}^2(a\mu_1)] + \right.$$

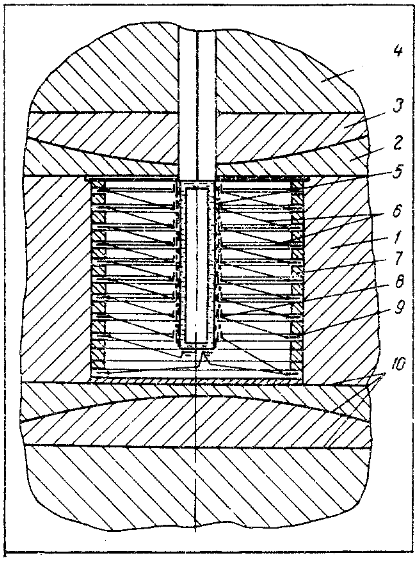

Fig. 2

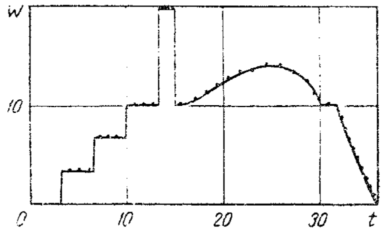

Fig. 3

Fig. 2. Thermopile of the microcalorimeter: 1) copper block; 2) copper lense; 3) correcting steel lense; 4) copper casing; 5) microcalorimetric chamber; 6) thermopile electrodes; 7) fixing ring; 8) glue, insulator, silver plate, glue, insulator, and inner junction; 9) glue, insulator, silver plate, and external junction; 10) heat-conductive grease.

Fig. 3. Comparison of the true and computed heat liberation curves. The continuous line represents the true curve and the dots represent the computed values. (W in μW and t in minutes).

$$+\left[\gamma S_1 k_1 \frac{\mu_1^2}{\mu_2} + S_2 k_2 \mu_2\right] \mathrm{ch}\,(a\mu_1)\,\mathrm{sh}\,(a\mu_1)\,\mathrm{sh}\,(l\mu_2)\Bigg\} ,$$

where

$$\gamma = \frac{S_1 k_1}{S_2 k_2}; \quad \mu_i = \sqrt{\frac{p + \nu_i}{\varkappa_i}} .$$

By inverse Laplace's transformation we obtain

$$W(t) = \sum_{n=1}^{\infty} \Bigg\{ \frac{2S_1 k_1 \alpha_n \cos(2a\alpha_n)\cos(l\delta_n)}{\zeta(\alpha_n)} -$$

$$- \frac{\left(S_1 k_1 \gamma \dfrac{\alpha_n^2}{\delta_n^2} + S_2 k_2 \delta_n\right) \sin(2a\alpha_n)\sin(l\delta_n)}{\zeta(\alpha_n)} \Bigg\} \cdot \tag{4}$$

$$\cdot \exp\{-(\nu_1 + \varkappa_1 \alpha_n^2)\, t\} \int_0^t \theta(\tau) \exp(\nu_1 + \varkappa_1 \alpha_n^2)\, \tau d\tau,$$

where

$$\delta_n = \left(\frac{\varkappa_1}{\varkappa_2}\alpha_n^2 + \frac{\nu_1 - \nu_2}{\varkappa_2}\right)^{1/2} ;$$

$$\zeta(\alpha_n) = \frac{\sin(l\delta_n)}{\varkappa_1 \delta_n}\left\{\cos(a\alpha_n) + \left(a\gamma - \frac{\varkappa_1}{\varkappa_2} l\right)\sin(a\alpha_n)\right\} -$$

$$- \frac{\cos(a\alpha_n)}{\varkappa_1 \alpha_n}\left\{\gamma l \frac{\varkappa_1}{\varkappa_2} \frac{\alpha_n^2}{\delta_n^2} \sin(l\delta_n) + \alpha\,[1 - \cos(l\delta_n)]\right\};$$

Here α_n are the roots of the transcendental equation

$$\frac{\delta_n}{\alpha_n}\,\mathrm{tg}\,(a\alpha_n) = - \frac{\gamma \sin(l\delta_n)}{1 - \cos(l\delta_n)} .$$

The obtained solution contains infinite sum of exponents and, at first glance, agrees with the results of Laville [4]. However, after interpolating the function $\theta(t)$ by Lagrange's polynomial in an arbitrary section and then integrating the expression (4) term-wise it is not difficult to make sure of the reverse. The reason for this disagreement should be found in the fact that in the formula (7) in [4] the time dependence was ignored for the quantities

$$g_\nu = A_\nu(p)(\lambda_\nu + p) \equiv g_\nu(p).$$

The microcalorimeter under consideration is a sensitive isothermal instrument. In measuring thermal values of less than 1 μW the temperature fluctuation does not exceed 0.1°C. Therefore, the thermoelectric parameters of the material of thermocouples can be considered as invariable with time. With such assumptions the thermocouple emf E is determined by the expression

$$E = \sum_{m=1}^{s} \theta(t)\, \Delta\alpha_m, \tag{5}$$

where $\Delta\alpha_m$ is the differential thermo-emf of m-th thermocouple and s is the number of thermocouples.

The expression (4) permits the analysis of a basic problem of microcalorimetric measurements, i.e., the reconstruction of the true form of heat liberation curve from the recorded thermograms.

Such an analysis was carried out by Calvet, Calvet and Camia (graphical method) [1, 6] and Laville [4, 5]. However, by using the first method in a number of cases sufficient accuracy (5%) could not be achieved by us. This method does not enable one to carry out a general analysis of the degree of disagreement between the true curve of heat liberation and the recorded thermogram. The processing of one recorded curve by the graphical method usually takes comparatively longer time (7 to 8 h). It has been already mentioned that the second method does not have entirely correct mathematical calculations, as a result of which certain results in [4] could not be accepted to have been sufficiently generalised.

From the Eqs. (4) and (5) it foolows that the scale factor ξ determined by the ratio $\xi = W(t)/E(t)$ is the functional of $\theta(t)$ and is a function of the parameters of the microcalorimeter chamber

$$\xi(t) = \sum_{n=1}^{\infty} A_n \exp(-\nu_1 + \varkappa_1 \alpha_n^2)t \,\frac{1}{\theta(t)} \int_0^t \theta(\tau) \exp(\nu_1 + \varkappa_1 \alpha_n^2)\tau\, d\tau, \tag{6}$$

where A_n are the coefficients depending on the parameters of the microcalorimeter chamber. During the experiments on the basis of the relation $\xi(t)$ for a number of standard $\theta(t)$ (rectangular pulse and linear dependence) the coefficient A_n have been determined with an accuracy of 0.15%.

The formula (6) makes it possible to determine the true curve of heat liberation on the basis of microcalorimetric experiments by means of integration which can be easily carried out with the help of calculating machines. The analysis of the expression (6) also shows that the main causes of time dependence of the scale factor are the heat exchange from the thermocouple surface, heat capacity of the microcalorimeter elements, and dissimilarily of the thermopile components.

The experimental varification of the obtained theoretical relations and the analysis of the basis of the given model were carried out in the Calvet-type microcalorimeter constructed by us with cones equalizing the heat flows [1]. The microcalorimeter (Fig. 2) enclosed in a multijacket thermostat, was placed in a special thermostat of large volume. This arrangement is, in fact, similar to setting a microcalorimeter in a place with rigid conditioning but it is more compact. For a volume of 1.6 m^3 the temperature is maintained in the interval of 15° to 40°C with an accuracy of up to 0.001°C. Therefore, the temperature requirements of the laboratory where the big thermostat is located are not so rigid as in the set-up of Calvet. Simple conditioning and an air-mixing system of certain planning than ensures the stability of air temperature in the laboratory within 0.1°C were sufficient for us.

The microcalorimeter consisted of two copper constantan thermopiles with 95 thermocouples in each pile connected in a differential circuit. The division of the thermopiles into large and small was the same as in the Calvet's system.

Mica [1], fluoroplastic [9], and lavsan [10] were used as electrical insulators of thermocouple junctions. The thermal conductivity of the transition layer glue-insulator-glue was studied in a specially prepared set-up for different types of glue and insulating materials. The maximum value of thermal conductivity was obtained with a triacetate film and a special synthetic glue. The assembled thermopile had high strength, reliable electric insulation, and minimum thermal resistance of the transition layer between the copper cylinder and silver plate. In assembling the external junctions the same materials were used.

The thermopiles were located in two holes in the central copper block which is fixed between the thermally correcting lenses and cones that equalize the heat flows [1]. The central block and the cones are made of electro-technical copper and the lenses are made of steel Kh18N9T. The adjacent surfaces were polished to match each other and were lubricated with a fine layer of grease with high thermal conductivity of the transition layer. The selection of grease that would ensure minimum thermal resistance of the transition layer between the two metal surfaces was done with the help of a special set-up made for this purpose. Loading of samples, introduction of standard heaters and thermometers, and pouring of oil in the vessels were carried out through holes in the cones, lenses, covers, and jackets with the help of polyethylene tubes joining a laboratory area with the microcalorimeter. During measurements these holes and connecting tubes were sealed with multilayer porolon stoppers which were put in and taken out with the help of special devices.

The above mentioned relations among the heat transfer coefficients and other experimentally determined thermal parameters of the microcalorimeter were used to compute the heat liberation curve by means of Eq. (6). The microcalorimeter was calibrated in the same way as in [1] with the help of a standard axial heater. The amount of liberation of Joule's heat in the microcalorimeter chamber was determined with an accuracy of 0.03% potentiometrically by measuring the current and voltage of the heater.

The comparisin of the calculated and true heat liberation curves is given in Fig. 3. The agreement between the curves is good with an accuracy that lies in the range of the experimental precision. In [1, 4, 5, and 6] a very high accuracy has been claimed in matching the true and computed curves. The achievement of this accuracy depends on the assumption that all the mathematical calculations are correct. This is not wholly true. The accuracy of 1.0 to 0.1% shown in [1, 6] is doubtful. According to our experiments and evaluations the methods employed in the above studies give an accuracy that is five times lower.

The proposed method of processing the results of a microcalorimetric experiment provides a sufficient accuracy of 2%. The processing of results of one experiment in accordance with the proposed method does not require more than 2 h, when the calculations are made with the help of a calculating machine of the type BÉSM-4.

LITERATURE CITED

1. E. Calvet and H. Prat, Microcalorimetrie, Application Physicochimiques et Biologiques, Masson and Cie, Paris (1956).
2. J. L. Petit and C. Brie, Compt., Rend., Acad, Sci., 267, No. 26, B, 1380-1382 (1968).
3. P. Gravelle, Rev. Gen. Therm., 8, No. 93, 873 (1969).
4. G. Laville, Compt., Rend., Acad. Sci., 240, No. 10, 1060 (1955).
5. G. Laville, Compt., Rend., Acad. Sci., 240, No. 10, 1195 (1955).
6. E. Calvet and F. Camia, J. Chim. Phys. et Phys.-Chim. Biol., 55, No. 10, 818 (1958).
7. L. Benjamin and G. Benson, Canad. J. Chem., 40, No. 4, 601 (1962).
8. P. Calvet, J. Phys., 26, No. 10, 207 (1965).
9. R. Attree, R. Cushing, J. Ladd, and J. Pieroni, J. Rev. Sci. Inst., 29, No. 6, 491 (1958).
10. E. K. Zavidovskaya, E. M. Golovchanskii, and A. V. Kuz'mina, PTÉ, No. 5, 217 (1966).
11. M. V. Kirpichev, M. A. Mikheev, and L. S. Éigenson, Heat Trasnfer [in Russian], Gosénergoizdat (1940).
12. L. S. Éigenson, Modelling [in Russian], Sovetskaya Nauka (1952).
13. V. N. Serebryanskii and A. I. Logvinenko, Inzh. Fiz. Zh., 21, No. 1, 182 (1971).
14. I. M. Pchelkin, in: Convection and Radiation Heat Transfer [in Russian], Izd. Akad. Nauk SSSR, 56 (1960).