Mathematical modeling and numerical realization of direct calorimetry problem

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Abstract. The object of research is the process of heat generation in the calorimetric system. The subject of the study is a mathematical model of the process of heat generation in the calorimetric system, computational methods for finding the temperature distribution by the density of heat sources in the capsule. The aim of the work is to develop mathematical support for the process of processing measurement results by calorimetric systems to increase the accuracy and speed of determining the calorific value of fuel and automation of the measurement process. The field of application is calorimetry data, which are used to calculate the thermodynamic properties of substances, compiling thermal balances of technological processes, calculating chemical equilibrium, establishing a relationship between thermodynamic characteristics of substances and their properties, structure, stability, reactivity. Calorimetry is also used to study the kinetics and determine the enthalpies of slow processes of dissolution, mixing, gelation, etc. Mathematical model of the calorimetric system is built. A direct problem of calorimetry is formulated with investigating it for correctness. An integrate-interpolation method is used to construct a finite-difference scheme for a system of differential equations of a mathematical model of a calorimetric system to solve a direct problem of calorimetry, given that the capsule and the outer cylinder are built of different materials. Software implementation of the numerical method and conduct numerical experiments is induced for the direct problem in order to study the influence of the parameters of the calorimetric system on the solution of the problem.

1. Intoduction

Calorimetry is one of the main experimental methods of thermophysics and thermochemistry, which measures the energy effects of processes (including combustion) and studies the thermal properties of substances. The introduction of new non-traditional fuels, the creation and research of new materials, the improvement of heat technologies requires the widespread introduction of calorimetric measurement methods, i.e. methods for determining the heat released or absorbed in the process.

Polymer composite materials are widely used to create aircraft products. Reference to international standards confirms the effectiveness of thermal methods for studying samples of binding materials in polymer composite materials, according to ASTM E 698–05 - Standard Test Method for Arrehenius Kinetic Constants for Thermally Unstable Materials and ASTM E 2041–04 - Standard Test Method for Heat of Reaction of Thermally Reactive Materials by Differential Scanning Calorimetry (DSC).

Film adhesives are used in the manufacture of large-sized units for aerospace engineering, providing an increased resource and reliability of adhesive structures during operation. Differential scanning calorimetry is one of the ways to study the properties of such materials. Modeling of a real calorimeter begins with consideration of its thermal model (thermal scheme), which reflects the thermal properties of interest to the researcher. Then the simulation is performed and the model is compared with the analytical solution [1-10].

Actually calorimeter, as a rule, means a vessel in which the measured thermal phenomena occur. The heat released or absorbed in this vessel causes a change in the temperature of the calorimeter, resulting in heat exchange with the environment. Heat exchange takes place between the surface of the calorimetric vessel (inner shell) and the surface of the cavity (outer shell) in which this vessel is placed. The heat flux that is established between the two shells, the greater the temperature difference and the greater the thermal conductivity of the medium that separates them.

The direct problem of calorimetry: according to the known dependence of the density of heat sources in the capsule on time to find the dependence of time on the temperature on the outer surface of the capsule. The inverse problem of calorimetry: according to the known dependence of the temperature on the outer surface of the capsule to find the dependence on time of the density of heat sources in the capsule.

2. Mathematical modelling of the heat distribution process in the calorimeter

For mathematical modeling of the heat distribution process in the calorimeter capsule and in the outer cylinder, we use the one-dimensional equation of thermal conductivity in the cylindrical coordinate system. In addition, take into account the heat transfer conditions on the axis of the calorimeter, on the border of the capsule and the outer cylinder and on the side of the outer cylinder. To construct the boundary condition, we use the differential consequence of the thermal conductivity equation. On the side of the outer cylinder, under the condition of the experiment, the temperature is always equal to 0. It is also necessary to set the initial condition (the temperature of the calorimeter is initially equal to 0). As a result, we obtain an initial-boundary value problem for a system of two differential equations in partial derivatives of parabolic type [4].

$$c_1\rho_1 \frac{\partial T}{\partial t} = \lambda_1 \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T}{\partial r}\right) + F(r,t), \quad 0 < r < R_1, \tag{1}$$

$$r\frac{\partial T}{\partial r}\bigg|_{r=0} = 0, \quad \lambda_1 \frac{\partial T}{\partial r}\bigg|_{r=R_1-0} = \lambda_2 \frac{\partial T}{\partial r}\bigg|_{r=R_1+0}, \tag{2}$$

$$T(R_1,t) = T^*(t), \tag{3}$$

$$c_2\rho_2 \frac{\partial T}{\partial t} = \lambda_2 \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T}{\partial r}\right), \quad R_1 < r < R_2, \tag{4}$$

$$T(R_2,t) = 0, \quad t \geq 0, \tag{5}$$

$$T(r,0) = 0, \quad 0 \leq r \leq R_2, \tag{6}$$

where

$$F(r,t) = \begin{cases} f(t), & 0 \leq r < r_1, \\ 0, & r_1 \leq r < R_1. \end{cases} \tag{7}$$

c_1 is specific mass heat capacity (dimension $[J/kgK]$) of the substance in the capsule of the calorimeter;
c_2 is specific mass heat capacity (dimension $[J/kgK]$) of the substance from which the second (outer) calorimeter cylinder is constructed;
ρ_1 is density (dimension $\left[kg/m^3\right]$) of the substance contained in the calorimeter capsule;
ρ_2 is density (dimension $\left[kg/m^3\right]$) of the substance from which the second (outer) cylinder of the calorimeter is constructed;
$c_1\rho_1$ is specific volumetric heat capacity (dimension $\left[J/m^3 K\right]$), the substance in the calorimeter capsule;
$c_2\rho_2$ is specific volume heat capacity (dimension $\left[J/m^3 K\right]$), the substance from which the second (outer) calorimeter cylinder is constructed;
λ_1 is thermal conductivity (dimension $[Wt/mK]$) of the substance contained in the calorimeter capsule;
λ_2 is thermal conductivity (dimension $[Wt/mK]$) of the substance from which the second (outer) calorimeter cylinder is constructed;
$k_1 = \dfrac{\lambda_1}{c_1\rho_1}$ is the coefficient of thermal conductivity of the substance contained in the capsule of the calorimeter;
$k_2 = \dfrac{\lambda_2}{c_2\rho_2}$ is the coefficient of thermal conductivity of the substance from which the second (outer) cylinder of the calorimeter is constructed;
t - time (minutes), r - the distance (centimeters) between the center of the calorimeter and the point where the temperature is measured;
$T(r,t)$ is temperature (in Celsius) at a point distant from the center of the calorimeter at a distance r at time t;
$F(r,t)$ is the density of heat sources (or drains) located in the calorimeter (in the capsule it is equal to $f(t)$ and independent of r, in the second (outer) cylinder of the calorimeter it is zero).

The system of equations (1) - (7) and is a mathematical model of the calorimeter, provided that the heat sources are located uniformly in both length and radius of the capsule, and energy equivalent.

3. Finite-difference scheme for the direct calorimetry problem

The system of equations (1) – (7) for the direct problem of calorimetry takes the following form:

$$\begin{aligned}
&\frac{\partial T}{\partial t} = k_1 \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T}{\partial r}\right) + F_1(r,t), \qquad 0 < r < R_1, \quad t > 0,\\
&\frac{\partial T}{\partial t} = k_2 \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T}{\partial r}\right), \qquad R_1 < r < R_2, \quad t > 0,\\
&\frac{\partial T}{\partial t} = 2k_1 \frac{\partial^2 T}{\partial r^2} + F_1(r,t), \qquad r = 0, \quad t > 0,\\
&T(R_2,t) = 0, \quad t \ge 0, \quad T(r,0) = 0, \quad 0 \le r \le R_2,
\end{aligned} \tag{8}$$

where

$$k_1 = \frac{\lambda_1}{c_1\rho_1}, \quad k_2 = \frac{\lambda_2}{c_2\rho_2}, \quad Q(r,t) = \frac{F(r,t)}{c_1\rho_1} = \begin{cases} f_1(t), & 0 \le r < r_1, \\ 0, & r_1 \le r < R_1. \end{cases}, \quad f_1(t) = \frac{f(t)}{c_1\rho_1}.$$

We introduce a uniform spatial grid $\omega_h = \{r_i = ih,\ i = \overline{0, N_2}\}$, where $h = R_2 / N_2$, and uniform grid over time $\omega_\tau = \{t_n = n\tau,\ \ n = \overline{0, M}\}$. Denote by the T_i^n desired approximate value of the temperature $T(r_i, t_n)$ in the node of the grid (r_i, t_n), by N_1 - integer part of the number R_1 / h, and by $r_{i-0.5} = (i-0.5)h$, $r_{i+0.5} = (i+0.5)h$ - intermediate nodes of the spatial grid.

For the initial-boundary value problem (8) we construct an implicit two-layer finite difference scheme:

$$\frac{T_0^{n+1} - T_0^n}{\tau} = \frac{4k_1}{h^2}\left(T_1^{n+1} - T_0^{n+1}\right) + Q_0^n,$$

$$\frac{T_i^{n+1} - T_i^n}{\tau} = \frac{k_1}{r_i h}\left(r_{i+0.5}\frac{T_{i+1}^{n+1} - T_i^{n+1}}{h} - r_{i-0.5}\frac{T_i^{n+1} - T_{i-1}^{n+1}}{h}\right) + Q_i^n, \quad i = 1, 2, \ldots, N_1,$$

$$\frac{T_i^{n+1} - T_i^n}{\tau} = \frac{k_2}{r_i h}\left(r_{i+0.5}\frac{T_{i+1}^{n+1} - T_i^{n+1}}{h} - r_{i-0.5}\frac{T_i^{n+1} - T_{i-1}^{n+1}}{h}\right), \quad i = N_1 + 1, N_1 + 2, \ldots, N_2 - 1, \quad (9)$$

$$T_{N_2}^{n+1} = 0, \quad T_i^0 = 0, \quad i = 0, 1, \ldots, N_2, \quad n = 0, 1, \ldots, M-1.$$

Find the error of the approximate solution of problem (8) according to scheme (9). By definition, in a grid node (r_i, t_n) it has the form $z_i^n = T(r_i, t_n) - T_i^n$, where $T(r_i, t_n)$ - the exact solution of the differential problem (3.1). From the difference scheme (9) it follows that this error satisfies the system of equations:

$$\frac{z_0^{n+1} - z_0^n}{\tau} = \frac{4k_1}{h^2}\left(z_1^{n+1} - z_0^{n+1}\right) + \psi_0^n,$$

$$\frac{z_i^{n+1} - z_i^n}{\tau} = \frac{k_1}{r_i h}\left(r_{i+0.5}\frac{z_{i+1}^{n+1} - z_i^{n+1}}{h} - r_{i-0.5}\frac{z_i^{n+1} - z_{i-1}^{n+1}}{h}\right) + \psi_i^n, \quad i = 1, 2, \ldots, N_1,$$

$$\frac{z_i^{n+1} - z_i^n}{\tau} = \frac{k_2}{r_i h}\left(r_{i+0.5}\frac{z_{i+1}^{n+1} - z_i^{n+1}}{h} - r_{i-0.5}\frac{z_i^{n+1} - z_{i-1}^{n+1}}{h}\right) + \psi_i^n, \quad i = N_1 + 1, N_1 + 2, \ldots, N_2 - 1, \quad (10)$$

$$z_{N_2}^{n+1} = 0, \quad z_i^0 = 0, \quad i = 0, 1, \ldots, N_2, \quad n = 0, 1, \ldots, M-1,$$

where ψ_i^n is scheme approximation error. We decompose the function $T(r, t)$ according to Taylor's formula around a point $\left(r_i, t_{n+0.5}\right)$. That is $\psi_i^n = O(\tau + h^2)$.

Therefore, scheme (9) has the first order of approximation in τ and the second in h. From the system of equations (10) it follows that the error of the approximate solution of the differential problem (8) by the difference scheme (9) is equal to solution with the first order on τ and the second on h.

We study the stability of the difference scheme (9) by the Fourier harmonic method. We look for a partial solution of the system of equations (10) in the form $z_i^n(\alpha) = q^n e^{jih\alpha}$, where j is an imaginary unit, α is any real number, and q is the transition factor from the n-th to $(n+1)$-st time layer. The inequality $|q| \le 1$ holds for all real numbers α. This means that the finite-difference scheme (9) is absolutely stable.

4. Software implementation of finite-difference scheme

For the numerical implementation of the difference scheme (9), we write it as a system of linear algebraic equations with respect to unknowns T_i^{n+1}:

$$T_0^{n+1}\left(1 + \frac{4k_1\tau}{h^2}\right) - \frac{4k_1\tau}{h^2}T_1^{n+1} = T_0^n + \tau Q_0^n,$$

$$-\frac{k_1\tau r_{i-0.5}}{h^2 r_i}T_{i-1}^{n+1}+\left(1+\frac{k_1\tau r_{i-0.5}}{h^2 r_i}+\frac{k_1\tau r_{i+0.5}}{h^2 r_i}\right)T_i^{n+1}-\frac{k_1\tau r_{i+0.5}}{h^2 r_i}T_{i+1}^{n+1}=T_i^n+\tau Q_i^n\,,\quad i=1,2,\ldots,N_1\,,\qquad (11)$$

$$-\frac{k_2\tau r_{i-0.5}}{h^2 r_i}T_{i-1}^{n+1}+\left(1+\frac{k_2\tau r_{i-0.5}}{h^2 r_i}+\frac{k_2\tau r_{i+0.5}}{h^2 r_i}\right)T_i^{n+1}-\frac{k_2\tau r_{i+0.5}}{h^2 r_i}T_{i+1}^{n+1}=T_i^n\,,$$

$$i=N_1+1,N_1+2,\ldots,N_2-1\,,\quad T_{N_2}^{n+1}=0\,.$$

The system of linear algebraic equations (1.1) is tridiagonal with a diagonal advantage. An effective method of solving such systems is the run method. In the general case, this method is used for systems of the form:

$$y_0=\chi_1 y_1+\mu_1\,,\quad y_N=\chi_2 y_{N-1}+\mu_2\,,$$
$$a_i y_{i-1}-c_i y_i+b_i y_{i+1}=-f_i\,,\quad i=1,2,\ldots,N-1\,,\qquad (12)$$

The algorithm of the run method consists of two stages - direct and inverse run. At the first stage, the auxiliary coefficients are calculated according to the formulas:

$$\alpha_1=\chi_1\,,\quad \beta_1=\mu_1\,,\quad \alpha_{i+1}=\frac{b_i}{c_i-\alpha_i a_i}\,,\quad \beta_{i+1}=\frac{a_i\beta_i+f_i}{c_i-\alpha_i a_i}\,,\quad i=1,2,\ldots,N-1\,.$$

The formulas of the inverse run are as follows:

$$y_N=\frac{\chi_2\beta_N+\mu_2}{1-\chi_2\alpha_N}\,,\quad y_i=\alpha_{i+1}y_{i+1}+\beta_{i+1}\,,\quad i=N-1,N-2,\ldots,0\,.$$

Comparing systems (4.1), (4.2) we find that

$$\chi_1=\frac{4\xi_1}{1+4\xi_1}\,,\quad \mu_1=\frac{T_0^n+\tau Q_0^n}{1+4\xi_1}\,,\quad \chi_2=0\,,\quad \mu_2=0\,,$$

$$a_i=\left(1-\frac{1}{2i}\right)\xi_1\,,\quad b_i=\left(1+\frac{1}{2i}\right)\xi_1\,,\quad f_i=T_i^n+\tau Q_i^n\,,\quad i=1,2,\ldots,N_1\,,$$

$$a_i=\left(1-\frac{1}{2i}\right)\xi_2\,,\quad b_i=\left(1+\frac{1}{2i}\right)\xi_2\,,\quad f_i=T_i^n\,,\quad i=N_1+1,N_1+2,\ldots,N_2-1\,,\quad c_i=1+a_i+b_i\,,$$

where

$$\xi_1=\frac{k_1\tau}{h^2}\,,\quad \xi_2=\frac{k_2\tau}{h^2}\,.$$

Thus, the algorithm for solving the system of linear algebraic equations (11) is given by the formulas:

1) direct run

$$\alpha_1=\frac{4\xi_1}{1+4\xi_1}\,,\quad \beta_1=\frac{T_0^n+\tau Q_0^n}{1+4\xi_1}\,,$$

$$\alpha_{i+1}=\frac{\left(1+\frac{1}{2i}\right)\xi_1}{1+2\xi_1-\alpha_i\left(1-\frac{1}{2i}\right)\xi_1}\,,\quad \beta_{i+1}=\frac{\left(1-\frac{1}{2i}\right)\xi_1\beta_i+T_i^n+\tau Q_i^n}{1+2\xi_1-\alpha_i\left(1-\frac{1}{2i}\right)\xi_1}\,,\quad i=1,2,\ldots,N_1\,,$$

$$\alpha_{i+1}=\frac{\left(1+\frac{1}{2i}\right)\xi_2}{1+2\xi_2-\alpha_i\left(1-\frac{1}{2i}\right)\xi_2}\,,\quad \beta_{i+1}=\frac{\left(1-\frac{1}{2i}\right)\xi_2\beta_i+T_i^n}{1+2\xi_2-\alpha_i\left(1-\frac{1}{2i}\right)\xi_2}\,,\quad i=N_1+1,N_1+2,\ldots,N_2-1\,.$$

2) reverse run

$$T_{N_2}^{n+1}=0\,,\quad T_i^{n+1}=\alpha_{i+1}T_{i+1}^{n+1}+\beta_{i+1}\,,\quad i=N_2-1,N_2-2,\ldots,0\,.$$

The algorithm for solving the finite-difference scheme (11) was implemented in the computer system MATLAB R2015b. The following is a program for solving a direct calorimetric problem.

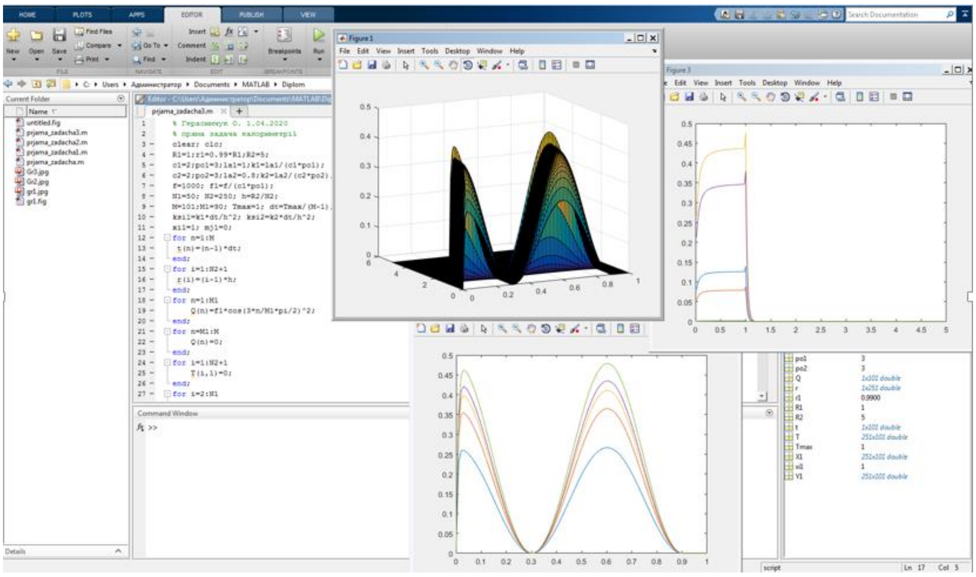

Figure 1. Working window of the MATLAB R2015b system with a fragment of the program for solving the direct calorimetry problem

With the help of the developed computer program computational experiments on the mathematical model of the calorimeter were carried out.

5. Computational experiments on the mathematical model of the calorimeter

The purpose of these experiments was to determine the influence of the input parameters of the model on the nature of the temperature distribution both in time and in space. Particular attention was paid to the study of the influence of the density function of heat sources in the calorimeter capsule $f(t)$ on temperature $T(r,t)$. The input parameters of the system are as follows:

$$R_1 = 1,\ r_1 = 0.99R_1,\ R_2 = 5,\ c_1 = 2,\ \rho_1 = 3,\ \lambda_1 = 1,\ k_1 = \frac{\lambda_1}{c_1\rho_1},\ c_2 = 1,\ \rho_2 = 4,\ \lambda_2 = 0.8,\ k_2 = \frac{\lambda_2}{c_2\rho_2}.$$

Experiment №1. Function $f(t) = 1000$ for a period of time from 0 to 0.9 minutes, and then equal to 0.

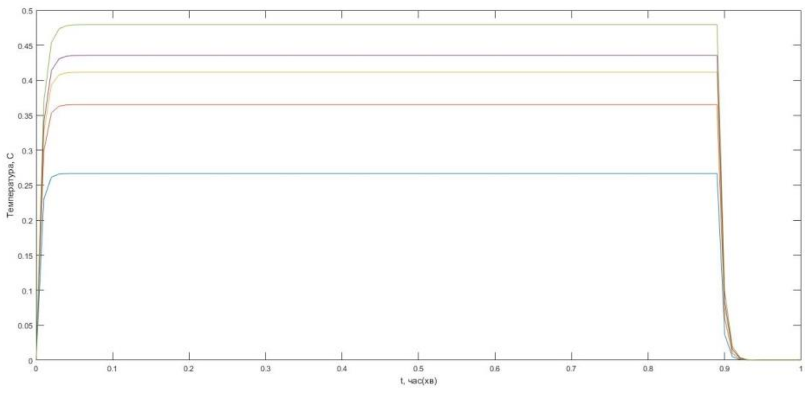

Figure 2. $f(t) = 1000$, temperature distribution over time in 5 different points of the capsule: *1) r=0.02 sm; 2) r=0.1 sm; 3) r=0.2 sm; 4) r=0.6 sm; 4) r=1 sm.*

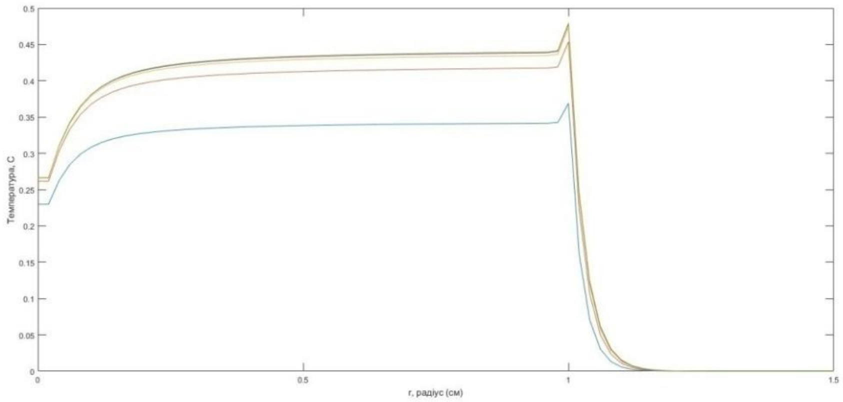

Figure 3. $f(t) = 1000$, temperature distribution by radius at 5 different points in time: *1) t=0.02 min; 2) t=0.03 min; 3) t=0.04 min; 4) t=0.05 min; 4) t=0.08 min.*

Experiment №2. Function $f(t) = 1000\cos^2(\pi t / 1.8)$ for a period of time from 0 to 0.9 minutes, and then equal to 0.

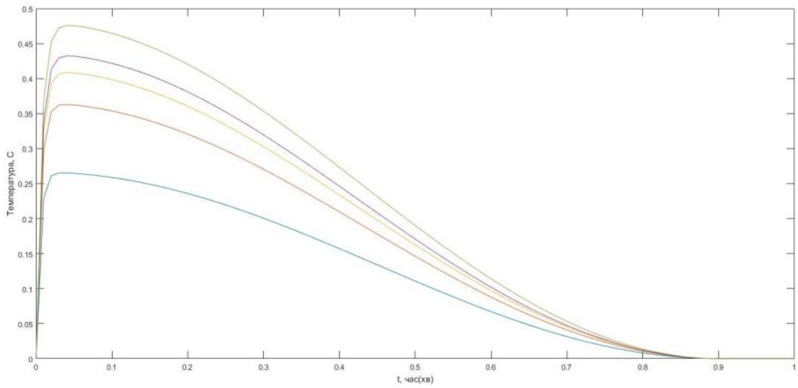

Figure 4. $f(t) = 1000\cos^2(\pi t / 1.8)$, temperature distribution over time in 5 different points of the capsule: *1) r=0.02sm; 2) r=0.1sm; 3) r=0.2sm; 4) r=0.6sm; 4) r=1sm;*

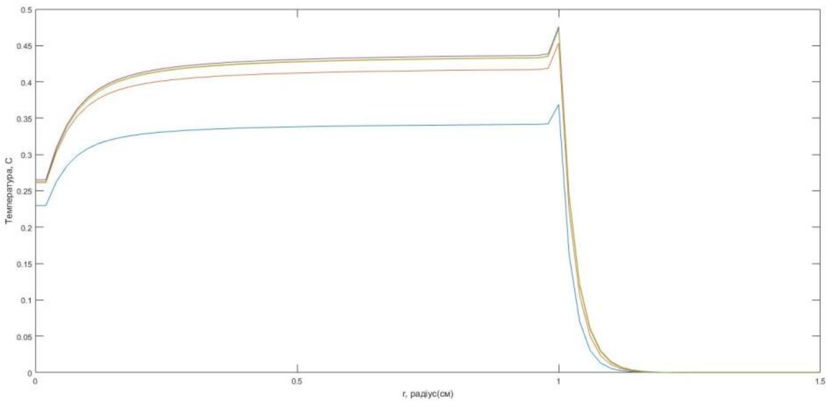

Figure 5. $f(t) = 1000\cos^2(\pi t / 1.8)$, temperature distribution by radius at 5 different points in time: *1) t=0.02 min; 2) t=0.03 min; 3) t=0.04 min; 4) t=0.05 min; 4) t=0.08 min;*

Experiment №3. Function $f(t) = 1000\cos^2(2\pi t / 1.8)$ for a period of time from 0 to 0.9 minutes, and then equal to 0.

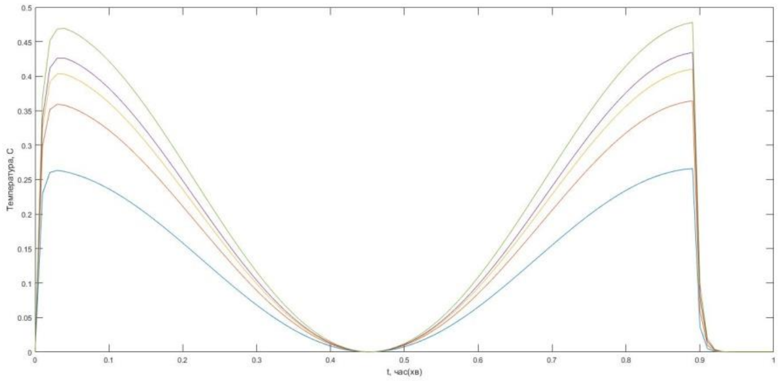

Figure 6. $f(t) = 1000\cos^2(2\pi t / 1.8)$, temperature distribution over time in 5 different points of the capsule: *1) r=0.02 sm; 2) r=0.1 sm; 3) r=0.2 sm; 4) r=0.6 sm; 4) r=1 sm;*

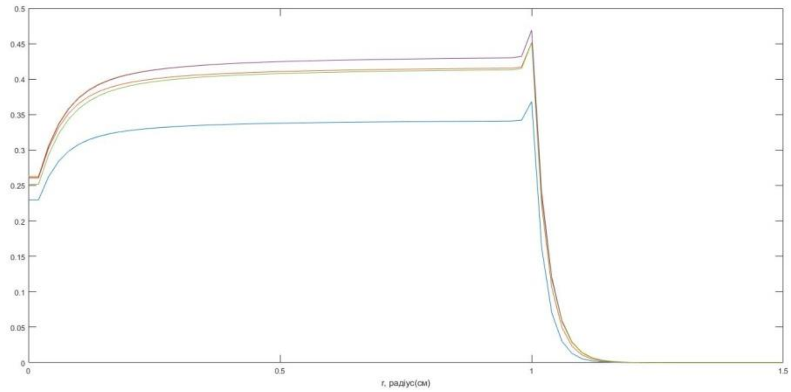

Figure 7. $f(t) = 1000\cos^2(2\pi t / 1.8)$, temperature distribution by radius at 5 different points in time: *1) t=0.02 min; 2) t=0.03 min; 3) t=0.04 min; 4) t=0.05 min; 4) t=0.08 min;*

Experiment №4. Function $f(t) = 1000\cos^2(3\pi t / 1.8)$ for a period of time from 0 to 0.9 minutes, and then equal to 0.

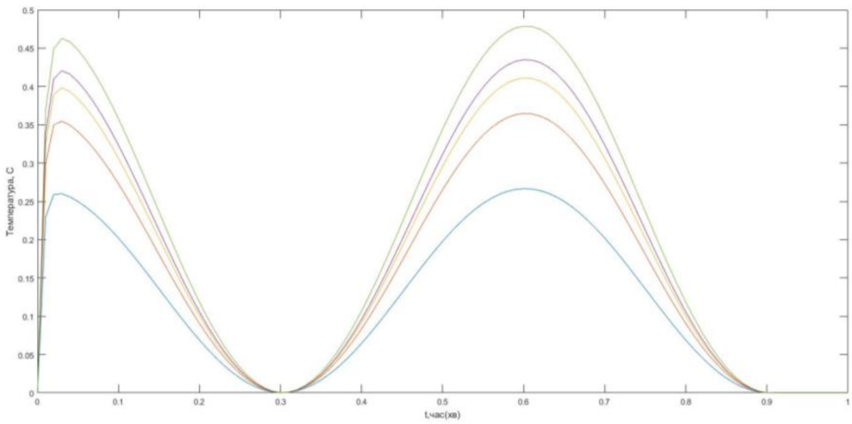

Figure 8. $f(t) = 1000\cos^2(3\pi t / 1.8)$, temperature distribution over time in 5 different points of the capsule: *1) r=0.02 sm; 2) r=0.1 sm; 3) r=0.2 sm; 4) r=0.6 sm; 4) r=1 sm;*

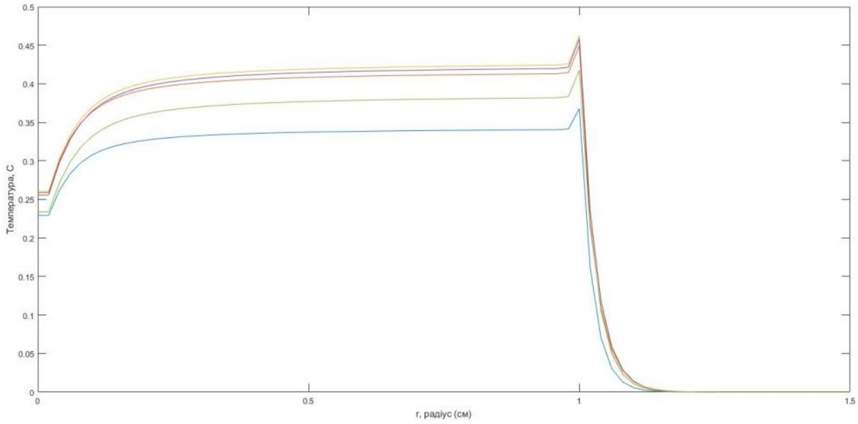

Figure 9. $f(t) = 1000\cos^2(3\pi t/1.8)$, temperature distribution by radius at 5 different points in time: *1) t=0.02 min; 2) t=0.03 min; 3) t=0.04 min; 4) t=0.05 min; 4) t=0.08 min;*

Thus, the graphs of sections of the temperature function $T(r,t)$ at fixed values *r* of time *t* (or fixed values *t* of the distance *r* of the point from the center of the calorimeter) significantly depends on the function of the density of heat sources in the calorimeter capsule $f(t)$.

And from figures 3, 5, 7, 9 it follows that the nature of the behavior of the graphs of sections of the temperature function $T(r,t)$ at fixed values *r* of time *t* almost does not change depending on the choice of function: they first grow monotonically with increasing distance *r*, and then on the border between the capsule and the outer to 0. In contrast, graphs from figures 2, 4, 6, 8 sections of the temperature function $T(r,t)$ at fixed values *t* of the distance *r* of the point from the center of the calorimeter show qualitative changes depending on the choice of function $f(t)$: if the function $f(t)$ is periodic, then the section function is periodic. This allows the use of harmonic analysis methods and Fourier series to reproduce the density function.

Conclusions

For mathematical modeling of the heat distribution process in the calorimeter capsule and in the outer cylinder, we use the one-dimensional equation of thermal conductivity in the cylindrical coordinate system. A finite-difference scheme for a direct calorimetry problem is drawn up. For the numerical implementation of the difference scheme, it is written as a system of linear algebraic equations and solved by the run method.

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