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DYNAMIC MODELS FOR RECONSTRUCTION OF THERMOKINETICS

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The dynamic models of the calorimetric system used for the reconstruction of thermokinetics were evaluated on the basis of the multi-body theory. Special attention was given to the fundamentals of each of the methods and the resulting consequences for the range of application of these methods (problem of initial conditions, localization of heat sources and temperature sensors, etc.).

The total heat effects and the thermokinetics of a heat process examined by means of a calorimeter are always determined by measuring a quantity directly in the calorimeter, e.g. temperature. Let us consider heat power $W(t)$ as the input function, and temperature $\theta(t)$ as the output function. Determination of the function $W(t)$ on the basis of $\theta(t)$ is equivalent to defining an operator which transforms the values of $\theta(t)$ into the values of $W(t)$. There are now several numerical and analog methods for reconstructing the thermokinetics [1]. Implementation of the international program [2, 3] permitted a comparison for the first time of results obtained by these methods. A marked improvement has occurred in this field.

Application of such numerical methods allows reproduction of the thermokinetics in a manner as if the experimental thermal curve were obtained in a calorimetric system with a time constant 100–200 times smaller than that for the thermal inertia of this calorimetric system. The results obtained by using various methods differ little between each other, encouraging a more general analysis of the conditions for application of these methods. This analysis is based on the multi-body theory [4].

1 The multi-body theory

The multi-body theory is based on distinguishing in each of the calorimetric systems a system of bodies characterized by precisely defined properties and

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parameters. Each of the bodies has a uniform temperature throughout its volume and its heat capacity is constant. The temperature gradients occur only in the media which separate these bodies, and the heat capacities of the media are taken to be negligibly small. The amount of heat exchanged between the bodies through these media is proportional to the difference between their temperatures. The proportionality factors are the corresponding heat loss coefficients, and a heat source as well as a temperature sensor can be located in each of them. The system of bodies is placed in an environment having a constant temperature, which is treated as a reference temperature. With these assumptions, the overall heat balance equation takes the form [4]:

$$K_j\,\mathrm{d}\theta_j(t)+G_{0j}\theta_j(t)\,\mathrm{d}t+\sum_{\substack{i=1\\ i\neq j}}^{N} G_{ij}[\theta_j(t)-\theta_i(t)]\,\mathrm{d}t=\mathrm{d}Q_j(t) \qquad j=1,2,\ldots,N \tag{1.1}$$

where N = number of distinguished bodies, K_j = heat capacity of body j, G_{ij} = heat loss coefficient between body j and body i, G_{0j} = heat loss coefficient between body j and the environment, $\theta_j(t)$ = function describing the change in temperature of body j at time t with reference to the environment temperature, and $\mathrm{d}Q_j(t)$ = amount of heat generated in body j during time $\mathrm{d}t$.

The system of differential equations (1.1) normalized by the dimension of temperature takes the following form:

$$T_j\frac{\mathrm{d}\theta_j(t)}{\mathrm{d}t}+\theta_j(t)=\sum_{\substack{i=1\\ i\neq j}}^{N} k_{ji}\theta_i(t)+c_jf_j(t) \qquad j=1,2,\ldots,N \tag{1.2}$$

The system of differential equations (1.2) is called the equations of dynamics of the calorimetric system. The following concepts have been employed in the derivation of (1.2).

The overall heat loss coefficient, G_j, for each of the distinguished bodies was described as

$$G_j=\sum_{\substack{i=0\\ i\neq j}}^{N} G_{ji} \qquad j=1,2,\ldots,N \tag{1.3}$$

The overall heat loss coefficient takes into account the heat exchange between body j and the environment, as well as the heat exchange between this body and other bodies.

The time constant T_j of body j is defined as the ratio of heat capacity K_j to the overall heat loss coefficient G_j of this body:

$$T_j=K_j/G_j \qquad j=1,2,\ldots,N \tag{1.4}$$

The time constant T_j is a measure of the inertia of the body in the system of bodies.

The interaction coefficient k_{ji} is defined as the ratio of the heat loss coefficient G_{ji} to the overall heat loss coefficient G_j:

$$k_{ji} = G_{ji}/G_j; \; i = 0, 1, \ldots, N; \; j = 1, 2, \ldots, N; \; i \neq j \tag{1.5}$$

and is a measure of the heat interaction of body j with body i with respect to the interactions of the remaining bodies and of the environment on body j. The value of the interaction coefficient k_{ji} has an important influence on the inertia of the calorimetric system, and permits a description of the structure of the dynamic model for the examined calorimetric system.

The forcing function $f_j(t)$ is defined as follows:

$$f_j(t) = \frac{1}{c_j G_j} \frac{dQ_j(t)}{dt} = \frac{1}{c_j G_j} W_j(t) \; j = 1, 2, \ldots, N \tag{1.6}$$

We may conclude from (1.6) that the course of the generated heat power $W_j(t)$ is proportional to the forcing function $f_j(t)$, which has the dimension of temperature. Coefficients c_j are defined by

$$c_j = |D|/|D_{jj}| \; j = 1, 2, \ldots, N \tag{1.7}$$

where $|D|$ is the determinant of matrix D:

$$D = \begin{vmatrix} 1 & -k_{12} & \ldots & -k_{1N} \\ -k_{21} & 1 & \ldots & -k_{2N} \\ . & . & \ldots & . \\ . & . & \ldots & . \\ . & . & \ldots & . \\ -k_{N1} & -k_{N2} & \ldots & 1 \end{vmatrix} \tag{18}$$

and $|D_{jj}|$ is the corresponding minor of this matrix. Coefficients c_j are dimensionless and are chosen so that the rise in temperature $\theta_j(t)$ in a steady-state (in the state of stationary heat exchange) is equal to the increase in the value of the forcing function $f_j(t)$. The coefficients c_j defined in this way are particularly useful in application of the superposition principle to the examined body-system.

The system of differential equations (1.2) may be presented in a matrix form as follows:

$$T \cdot \dot{\theta}(\tau) + D \cdot \theta(t) = C \cdot f(t) \tag{1.9}$$

where matrix D is given by (1.8) and matrices T and C are diagonal matrices of the form

$$T = \begin{vmatrix} T_1 & 0 & \dots & 0 \\ 0 & T_2 & \dots & 0 \\ . & . & \dots & . \\ . & . & \dots & . \\ . & . & \dots & . \\ 0 & 0 & \dots & T_N \end{vmatrix} \qquad C = \begin{vmatrix} c_1 & 0 & \dots & 0 \\ 0 & c_2 & \dots & 0 \\ . & . & \dots & . \\ . & . & \dots & . \\ . & . & \dots & . \\ 0 & 0 & \dots & c_N \end{vmatrix}$$

The state vector $\theta(t)$ and the forcing vector $f(t)$ are defined as

$$\theta(t) = \begin{vmatrix} \theta_1(t) \\ \theta_2(t) \\ . \\ . \\ . \\ \theta_N(t) \end{vmatrix} \qquad f(t) = \begin{vmatrix} f_1(t) \\ f_2(t) \\ . \\ . \\ . \\ f_N(t) \end{vmatrix}$$

and $\dot{\theta}(t)$ is treated as a derivative of state vector $\theta(t)$ with respect to time t.

2. Calorimetric models

Let us use the relationships given above to characterize the dynamic models applied for reconstruction of the thermokinetics. The method based on Eq. (1.1) is called the multi-body method [5]. This equation may be applied for reproduction of the thermokinetics when the number of bodies, their mutual localization, parameters K_j, G_{ji} and G_{0j} of the calorimetric system and the initial temperature conditions are known. The dependences which form the basis of the multi-body method also include the finite element method [6, 7], the method of lumped parameters [8–11] and the techniques of analog and numerical correction [12–15]. For a single-body case ($j = 1$), Eq. (1.1) takes the form of the heat balance equation of a simple body—known in the calorimetric literature as the Tian–Calvet equation [16].

A group of methods exists which "a priori" use a model of a calorimetric system in the form of a convolution function. Let us derive equations which are mathematical models of these methods. Laplace transformation of Eq. (1.1) in its matrix form (1.9) gives

$$(s \cdot T + D) \cdot \theta(s) = C \cdot f(s) + T \cdot \theta_0 \tag{2.1}$$

where s = Laplace operator, θ_0 = initial state vector (initial temperature condition in the bodies), and $\theta(s)$ and $f(s)$ = Laplace transforms of state vector $\theta(t)$ and forcing vector $f(t)$, respectively. The solution of Eq. (2.1) in the complex domain s is

$$\theta(s) = H(s)\cdot C\cdot f(s)+H(s)\cdot T\cdot \theta_0 \tag{2.2}$$

where

$$H(s) = (s\cdot T+D)^{-1} \tag{2.3}$$

is the transfer matrix; in the frequency domain ω the solution is

$$\theta(j\omega) = H(j\omega)\cdot C\cdot f(j\omega)+H(j\omega)\cdot T\cdot \theta_0 \tag{2.4}$$

and in the time domain t the solution is

$$\theta(t) = \int_0^t H(t-\tau)\cdot C\cdot f(\tau)\,\mathrm{d}\tau+H(t)\cdot T\cdot \theta_0 \tag{2.5}$$

where $H(t)$ is the matrix of fundamental solutions. Assuming that

$$f(t) = \sum_{n=0}^{\infty} f(nh)\delta(t-nh) \tag{2.6}$$

where h = sampling period and $\delta(t)$ = Dirac function, (2.5) can be rewritten as

$$\theta(t) = \sum_{n=0}^{\infty} H(t-nh)\cdot C\cdot f(nh)+H(t)\cdot T\cdot \theta_0 \tag{2.7}$$

Assuming, additionally, that the heat source is located in one body only (for example, in body r), that the temperature is measured in one body only (for example, in body j) and under the condition of zero initial temperature, Eqs (2.4), (2.5) and (2.7) define the mathematical model for reconstruction of the thermokinetics. Equation (2.4) becomes

$$\theta_j(j\omega) = H_{jr}(j\omega)c_r f_r(j\omega) \tag{2.8}$$

representing the mathematical model of the harmonic analysis method [17]; Eq. (2.5) becomes

$$\theta_j(t) = \int_0^t H_{jr}(t-\tau)c_r f_r(\tau)\,\mathrm{d}\tau \tag{2.9}$$

representing the mathematical model of the dynamic optimization method [18]; and Eq. (2.7) becomes

$$\theta_j(t) = \sum_{n=0}^{\infty} H_{jr}(t-nh)c_r f_r(nh) \tag{2.10}$$

representing the mathematical model of the thermal curve interpretation method [19].

Techniques using analog and numerical correction of the dynamic properties of the system, compensating transmittance zeros and poles, are also treated as component methods for reconstruction of the thermokinetics. According to relationship (2.3), the transmittance $H_{jr}(s)$ has the form

$$H_{jr}(s) = S^{jr}\frac{\prod\limits_{p=1}^{m}(L_p s+1)}{\prod\limits_{l=1}^{N}(M_1 s+1)} \tag{2.11}$$

where S^{jr} = gain factor. Thus, the dependence between the generated heat effect $f_r(t)$ and temperature changes $\theta_j(t)$ can be written as

$$\theta_j(s) = H_{jr}(s)c_r f_r(s) \tag{2.12}$$

The following set of differential equations is assigned to (2.12) in the time domain:

$$M_1\dot{\theta}_j(t)+\theta_j(t) = x_1(t) \tag{2.13}$$

$$M_l\dot{x}_{l-1}(t)+x_{l-1}(t) = x_l(t);\quad 1 = 2, 3, \ldots, N \tag{2.14}$$

$$L_1\dot{y}_1(t)+y_1(t) = x_N(t) \tag{2.15}$$

$$L_p\dot{y}_p(t)+y_p(t) = y_{p-1}(t);\quad p = 2, 3, \ldots, m \tag{2.16}$$

$$y_m(t) = S^{jr}c_r f_r(t) \tag{2.17}$$

where $x_1(t), x_2(t), \ldots, x_N(t), y_1(t), y_2(t), \ldots, y_m(t)$ = state variables. According to dependences (2.13) and (2.14), the poles of transmittance in the numerical correction method [14, 20] are compensated, and on the basis of Eqs (2.15) and (2.16) the zeros of transmittance are compensated. In the analog correction method [12, 13, 15], the zeros and poles of the transmittance are compensated by means of operational amplifiers. The form of the set of Eqs (2.13)–(2.17) corresponds to the method of state variables [21], and variables $\{x_1(t)\}$, $\{y_p(t)\}$ are canonic variables. Initial conditions for state variables $\{x_l(t)\}$, which are obtained by compensating poles, can be calculated by an iterative method on the basis of the temperature changes in the calorimetric system. The question arises as to what initial conditions must be taken into account for state variables $\{y_p(t)\}$, which are obtained by the compensation of zeros, in order to reconstruct the course of the thermokinetics uniquely. The above discussion shows that in a general case there can be m degrees (degree of numerator of transmittance) of indetermination in the reconstruction of the thermokinetics.

3 Kinetic and frequency limits

It results from a detailed solution of Fourier's heat conduction equation that the impulse response $H_{jr}(t)$ of the calorimetric system is described by an infinite sum of exponential functions:

$$H_{jr}(t) = \sum_{n=1}^{\infty} a_{jr,n} e^{-b_n t} \tag{3.1}$$

Thus, an ideal model for reconstruction of the thermokinetics would be a model of an infinite order. This assumption is accepted as the basis of methods using the convolution function. Mathematical models with an assumed order of the differential equation give poorer results. Thus, a paradox of obtaining practically identical results of reconstructing the thermokinetics by means of various methods exists [22].

This is due to the compromise between the available information and the possibility of applying it. The harmonic analysis method can be given as an example of this. In this method the transmittance is obtained numerically using the Fast Fourier Transform. This procedure uses $N = 2^n$ points, where $n = 10, 11, 12$, and $N = 1024, 2048, 4096$, respectively. The number of data used for calculations must cover the whole interval of time from "initial zero" to "final zero" of the temperature calorimetric response. The discrete measurement of temperature limits the upper bounds of frequency which can be applied for reconstruction of the thermokinetics. The value of this frequency, ν_{sh}, resulting from Shannon's theorem is a function of the sampling period and can be expressed by the relation $\nu_{sh} = 1/h$ ($\nu = \omega/2\pi$). It is therefore impossible to use the complete spectrum of the frequency. There also exists a boundary frequency ν_p:

$$\frac{|H(j\omega)|_{\nu=\nu_p}}{|H(j\omega)|_{\nu=0}} = \frac{\text{noise amplitude}}{\text{maximum amplitude of thermogram}} \tag{3.2}$$

which is related to the measurement noise. The boundary frequency ν_p is the second limitation of the frequency spectrum, which can be applied in reconstruction of the thermokinetics for a given calorimetric system, and $\nu_p < \nu_{sh}$.

The high precision of calorimetric measurements today permits a less strict description of the calorimetric system itself. The comparison of reconstructions of the thermokinetics obtained with the multi-body method and with other methods shows the convergence of the results [3] when the calorimetric system is described by a linear differential equation with constant coefficients of the third to sixth order. Conclusions may be drawn, too, about some of the limitations of these methods.

4 Calibration of the calorimeter

The multi-body method and the other methods based on heat balance equations involve modelling of the process by a set of ordinary differential equations with coefficients which are functions of the physical parameters of the calorimetric system. When the body configuration and the mutual localization of the heat source and the temperature sensor are changed, it is possible to introduce corresponding changes in the equations describing the model on the basis of which the thermokinetics and the integral heat effect of the examined process are determined.

In the methods based on the "black box" notion (convolution function), it is assumed that during the calibration, as well as during the calorimetric measurement, we are dealing with the same dynamic system, i.e. with a time-invariant system. This assumption is not always true, and may sometimes introduce errors in reconstruction of the thermokinetics [23]. At certain positions of the heat source and temperature sensor, under particularly unfavourable conditions of measurement, a paradox may appear where reconstruction of the thermokinetics requires some information about the unknown heat power being reconstructed.

This whole discussion emphasizes the great importance of a proper calibration of the calorimetric system. The equivalence of the heat source during the calibration and the measurement proper is a necessity; otherwise, even the best reconstruction methods may lead to false results.

5 Initial state and initial conditions

In the majority of reconstruction methods (methods based on the convolution function, analog and numerical correction), zero initial conditions for the measured temperature of the calorimetric system are assumed. This assumption in some cases makes thermokinetic reconstruction difficult or impossible. It will be proved now that it is necessary to derive a relationship between the initial state of the calorimetric system and the initial conditions for the temperature of the body.

The set of differential equations (1.2) has an equivalent N-th-order equation:

$$\sum_{l=0}^{N} A_1 \frac{\mathrm{d}^1\theta_j(t)}{\mathrm{d}t^1} = c_r \sum_{p=0}^{m} a_p^{jr} \frac{\mathrm{d}^p f_r(t)}{\mathrm{d}t^p}, \quad m<N \tag{5.1}$$

when the heat effect is generated in body r and the temperature changes in body j are measured. Applying the Laplace transformation to Eq. (5.1), we obtain

$$\sum_{l=1}^{N} A_l s^l \theta_j(s) - \sum_{q=0}^{l-1} s^{l-1-q}\theta_{j0}^{(q)} = c_r\left(\sum_{p=0}^{m} a_p^{jr} s^p f_r(s) - \sum_{k=0}^{p-1} s^{p-1-k} f_{r0}^{(k)} \right) \tag{5.2}$$

where $\theta_{j0}^{(q)}$ = value of the q-th derivative of temperature $\theta_j(t)$ with respect to time at the initial moment, and $f_{r0}^{(k)}$ = value of the k-th derivative of the forcing function $f_r(t)$ with respect to time at the initial moment. Relationship (5.2) can be written in the form

$$\theta_j(s) \sum_{l=0}^{N} A_l s^l = c_r f_r(s) \sum_{p=0}^{m} a_p^{jr} s^p + \sum_{l=0}^{N} A_l \sum_{q=0}^{l-1} s^{l-1-q} \theta_{j0}^{(q)} + \\ - c_r \sum_{p=0}^{m} a_p^{jr} \sum_{k=0}^{p-1} s^{p-1-k} f_{r0}^{(k)} \tag{5.3}$$

or

$$\theta_j(s) = H_{jr}(s) c_r f_r(s) + \sum_{i=0}^{N} H_{ji}(s) T_i \theta_{i0} \tag{5.4}$$

where $H_{jr}(s)$ is determined by (2.4) and

$$\sum_{i=0}^{N} H_{ji}(s) T_i \theta_{i0} = \left(\sum_{l=0}^{N} A_l \sum_{q=0}^{l-1} s^{l-1-q} \theta_{j0}^{(q)} + \right. \\ \left. - c_r \sum_{p=0}^{m} a_p^{jr} \sum_{k=0}^{p-1} s^{p-1-k} f_{r0}^{(k)} \right) \Big/ \sum_{l=0}^{N} A_l s^l \tag{5.5}$$

According to (2.2), the Laplace transform $\theta_j(s)$ of the temperature $\theta_j(t)$ for body j has the form

$$\theta_j(s) = \sum_{i=1}^{N} H_{ji}(s) c_i f_i(s) + \sum_{i=1}^{N} H_{ji}(s) T_i \theta_{i0} \tag{5.6}$$

In the special case when the heat effect is generated only in body r, we have

$$\theta_j(s) = H_{jr}(s) c_r f_r(s) + \sum_{i=1}^{N} H_{ji}(s) T_i \theta_{i0} \tag{5.7}$$

It can readily be seen that (5.4) and (5.7) are identical.

To find the relationship between the initial conditions $\theta_{j0}^{(n)}$ ($n = 0, 1, \ldots, N$) for temperature $\theta_j(t)$ and the vector $\underline{\theta}_0$ of the initial state of the calorimetric system, we can write Eq. (1.9) for the initial moment in the form

$$T \cdot \underline{\theta}_0^{(n+1)} + D \cdot \underline{\theta}_0^{(n)} = C \cdot \underline{f}_0^{(n)}, \quad n = 0, 1, 2, \ldots \tag{5.8}$$

or

$$\underline{\theta}_0^{(n+1)} + T^{-1} \cdot D \cdot \underline{\theta}_0^{(n)} = T^{-1} \cdot C \cdot \underline{f}_0^{(n)}, \quad n = 0, 1, 2, \ldots \tag{5.9}$$

where $\underline{\theta}_0^{(n)}$ and $\underline{f}_0^{(n)}$ are the values of the n-th-order derivatives with respect to time of the state vector $\underline{\theta}(t)$ and the forcing vector $\underline{f}(t)$ at the initial moment, respectively. Applying the Z-transformation [24] to Eq. (5.9), we obtain

$$(I+z^{-1}\cdot T^{-1}\cdot D)\cdot \underline{\theta}_0(z) = \underline{\theta}_0^{(0)}+z^{-1}\cdot T^{-1}\cdot C\cdot \underline{f}_0(z) \tag{5.10}$$

where I is a unit matrix. From (5.10), we have

$$\begin{aligned}\underline{\theta}_0(z) &= (I+z^{-1}\cdot T^{-1}\cdot D)^{-1}\cdot \underline{\theta}_0^{(0)}+\\ &+z^{-1}\cdot(I+z^{-1}\cdot T^{-1}\cdot D)^{-1}\cdot T^{-1}\cdot C\cdot \underline{f}_0(z)\end{aligned} \tag{5.11}$$

Applying the inverse Z-transformation to (5.11), we obtain

$$\begin{aligned}\underline{\theta}_0^{(n)} &= (-1)^n\cdot(T^{-1}\cdot D)^n\cdot \underline{\theta}_0^{(0)}+\\ &+\sum_{k=1}^{n}(-1)^{k-1}\cdot(T^{-1}\cdot \mathrm{D})^{k-1}\cdot T^{-1}\cdot C\cdot \underline{f}_0^{(n-k)}\\ n &= 1, 2,\ldots, N-1\end{aligned} \tag{5.12}$$

Relationship (5.12) links together the initial conditions $\underline{\theta}_0^{(n)}$ for the temperature of any body with vector $\underline{\theta}_0$ of the initial state for a system of bodies and the initial conditions $\underline{f}_0^{(k)}$ for the forcing vector $\underline{f}(t)$. This relationship reveals that zero initial conditions for a system of bodies do not directly imply zero initial conditions for the temperature of each of these bodies. These conditions depend, however, on the initial conditions of the generated heat effect.

6 Conclusions

The comparison of methods for reconstructing the thermokinetics shows that the multi-body method including the physical parameters of the calorimetric system is better than other methods and techniques based on the assumption that the calorimeter can be treated as an inertial object described by a higher-order differential equation without considering its physical parameters. This treatment often permits elimination of the effect of changing the dynamic properties of a calorimetric system as well as the initial conditions. This also refers to calorimetric systems in which the heat loss coefficient is a function of temperature (free convection, radiation), i.e. when the capacity of the calorimetric vessel changes. Approximate solutions are applied in these cases.

It is shown that several of the models used for reconstruction of the thermokinetics are equivalent, if appropriate conditions are fulfilled. The multi-body model and the convolution function model are equivalent if the initial state of the calorimetric system is zero. If, instead of a continuous model, we use its discrete approximation, several differences in the reconstruction of the thermokinetics can occur, due to the approximation and choice of the sampling period. The other sources of differences in reconstructing the thermokinetics may be the quality of the experimental data (measurement precision, noise, drift of zero) and the choice of a model which does not completely describe the process taking place in the calorimetric system.

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Zusammenfassung — Die dynamischen Modelle des zur Rekonstruktion der Thermokinetik benutzten kalorimetrischen Systems werden auf der „multi-body"-Theorie basierend bewertet. Besondere Beachtung wird den Grundlagen jeder dieser Methoden und den sich für die Anwendung ergebenden Konsequenzen (Problem der Anfangsbedingungen, Anordnung der Wärmequellen und Temperaturfühler usw.) gewidmet.

Резюме — На основе теории многих тел определены динамические модели калориметрической системы, используемой для воспроизведения термокинетики. Особое внимание уделено основам каждого метода и конечным выводам отн сительно области применения этих методов (проблема исходных условий, местонахождения тепловых источников и температурных датчиков и другие).