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# Thermokinetics in conduction calorimetry: method of determination of the lower limits in dynamic heat power resolution

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**Abstract**

A method for determining the lower limit of the dynamic heat power resolution $W_0$ is given. The proposed method enables evaluation of $W_0$ from calibration data of the dynamic calorimeter, with values of the sampling period, the level of noise, and the measured input signal increase.

## INTRODUCTION

Several numerical methods and computer programs for reconstructing thermokinetics functions $W(t)$ [1] from thermograms obtained in conduction calorimeters have been worked out. The application of conduction calorimeters to determination not only of enthalpies but also of the kinetics of reactions has increased. However, in many cases the user of the calorimeter reaches conclusions about the thermokinetics from the thermogram obtained, even though the latter consists of only partial information about the process being studied.

However, the modern methods of reconstruction of thermokinetics allow considerably more information about the course of the reaction to be obtained. For verifying the usefulness of these methods to processes under study in a given calorimeter, a new method for determining the lower limit of dynamic heat power resolution $W_0$ is proposed. A formula for calculation of $W_0$ is given in the form of a modified, simpler and more precise relation than that given in a previous paper [2].

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PROBLEM STATEMENT

We assume that the heat effect of energy $E$ involved is described by a function $f(t)$ and that the response of the calorimeter is described by a function $\Theta(t)$. The equation connecting these two functions has the form [3, 4]

$$\sum_{i=0}^{N} a_i \frac{\mathrm{d}^i\Theta(t)}{\mathrm{d}t^i} = Sf(t) \tag{1}$$

where the coefficients $a_i$ are constant and are functions only of the time constants $\tau_i$ ($i = 1, 2, \ldots, N$); $S$ is the sensitivity of system.

Let us assume that in the conduction calorimeter a constant heat power $W_0$ is involved in a time duration of $\gamma$. Then $E$ is given by

$$E = W_0\gamma \tag{2}$$

Let us assume additionally that this effect can be approximated by the heat impulse of Dirac type

$$f(t) = E\delta(t) \tag{3}$$

The response $\Theta(t)$ of the calorimetric system to this heat effect (at zero initial conditions) is described by [4, 5]

$$\Theta(t) = SE \sum_{i=1}^{N} A_i \mathrm{e}^{-t/\tau_i} \tag{4}$$

where the coefficients $A_i$ are given by

$$A_i = \tau_i^{N-2} \Big/ \prod_{k=1}^{M} (\tau_i - \tau_k) \qquad (k \neq i) \tag{5}$$

For a calorimeter characterized by one time constant $\tau_1$, eqn. (4) takes the form

$$\Theta_1(t) = (ES/\tau_1)\mathrm{e}^{-t/\tau_1} \tag{6}$$

For a calorimeter characterized by two time constants $\tau_1$ and $\tau_2$, eqn. (4) takes the form

$$\Theta_2(t) = [ES/(\tau_1 - \tau_2)](\mathrm{e}^{-t/\tau_1} - \mathrm{e}^{-t/\tau_2}) \tag{7}$$

For a calorimeter characterized by three time constants $\tau_1$, $\tau_2$ and $\tau_3$, eqn.

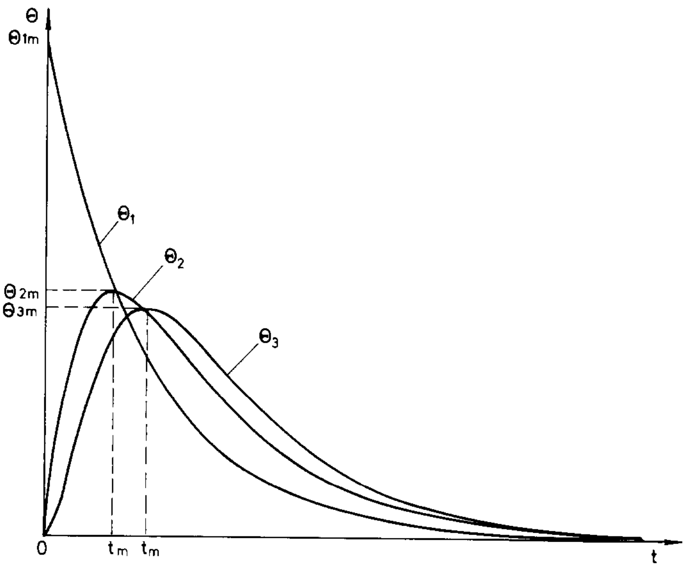


Fig. 1. Plots of eqns. (6)–(8).

(4) takes the form

$$\Theta_3(t) = ES\left[\frac{\tau_1}{(\tau_1-\tau_2)(\tau_1-\tau_3)}\right]e^{-t/\tau_1} + \left[\frac{\tau_2}{(\tau_2-\tau_1)(\tau_2-\tau_3)}\right]e^{-t/\tau_2} + \left[\frac{\tau_3}{(\tau_3-\tau_1)(\tau_3-\tau_2)}\right]e^{-t/\tau_3} \quad (8)$$

Plots of eqns. (6)–(8) are shown in Fig. 1. It can be seen from the curves for $\Theta_1(t)$, $\Theta_2(t)$ and $\Theta_3(t)$ that each of the temperatures reaches the maximal temperature $\Theta_m$ after different times. The calorimeter characterized by only one time constant $\tau_1$ has maximum temperature value $\Theta_{1m}$ at the beginning of the measurements. For calorimeters characterized by more than one time constant, the values $\Theta_m$ are decreasing and $\Theta_m$ appear after increasing periods of time $t_m$. (We note this as important for further considerations.) As a result, in the proposed method we take the value of $t_m$ to be characteristic of the inertial properties of the calorimeter.

## METHOD OF DETERMINATION OF $W_{0,\min}$

In order to reconstruct thermokinetics it is necessary to obtain an observed change in the output function $\Theta$ in the thermogram. We assume that the smallest value of $\Theta$ corresponds to $\Theta_m$ and that

$$\Theta_m \geqslant Kb \quad (9)$$

where $b$ is the noise level and $K$ is the multiplicity of the noise level.

As mentioned above, when the calorimeter is characterized as a

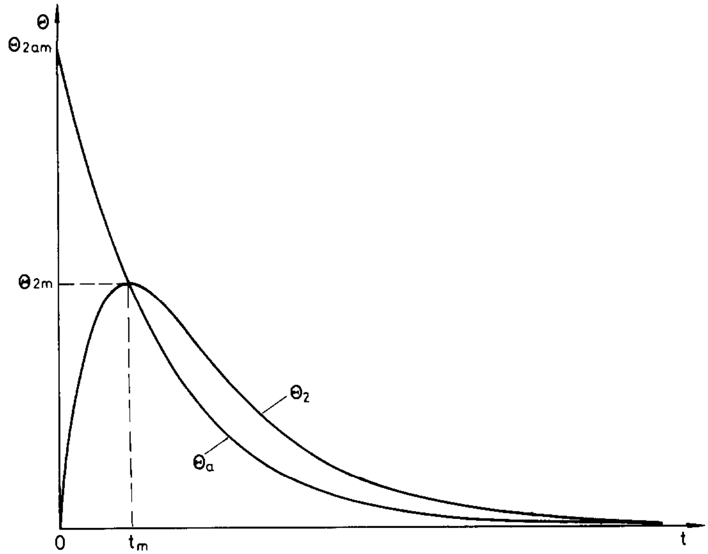


Fig. 2. Plots of eqns. (7) and (14).

first-order inertial system, the response $\Theta$ expressed by eqn. (6) has the maximum value $\Theta_{1m}$ at the beginning. We assume that among $\Theta_1(t)$ values, $\Theta_{1m}$ fulfils the condition

$$\Theta_{1m} = SE/\tau_1 \geqslant Kb \tag{10}$$

It follows that $E_{min}$ is given by

$$E_{min} = Kb\tau_1/S \tag{11}$$

and that using eqn. (2), the minimal heat power $W_{0,min}$ is given by

$$W_{0,min} = Kb\tau_1/S\gamma \tag{12}$$

For the second-order system the response of $\Theta_2(t)$ (Fig. 2) has the form of eqn. (7), and for $t \geqslant t_m$ it can be described by the function [4]

$$\Theta_2(t) = [\Theta_{2m}/(\tau_1 - \tau_2)][\tau_1 e^{-(t-t_m)/\tau_1} - \tau_2 e^{-(t-t_m)/\tau_2}] \tag{13}$$

where $\Theta_{2m}$ is the maximum value of $\Theta_2$ and can be approximated by the function

$$\Theta_{2a}(t) = \Theta_{2m} e^{-(t-t_m)/\tau_1} \tag{14}$$

Extrapolating eqn. (14) to $t = 0$, we obtain a maximum value of $\Theta_2$ expressed by

$$\Theta_{2am} = \Theta_{2m} e^{t_m/\tau_1} \tag{15}$$

Taking eqn. (9) into consideration gives

$$\Theta_{2m} \geqslant Kb \tag{16}$$

and from eqn. (15), we have

$$\Theta_{2am} \geqslant Kb e^{t_m/\tau_1} \tag{17}$$

According to eqn. (10)

$$\Theta_{2am} = SE/\tau_1 \tag{18}$$

and then

$$SE/\tau_1 \geqslant Kb e^{t_m/\tau_1} \tag{19}$$

and $W_{0,min}$ is given by

$$W_{0,min} = (Kb\tau_1/S\gamma)e^{t_m/\tau_1} \tag{20}$$

Equation (20) can be applied to systems of any order where $t_m$ is the time after which the pulse response reaches a maximum. It follows from eqn. (20) that the lower limit $W_{0,min}$ depends on the sensitivity $S$ of the calorimeter, the sampling period $\gamma$, the assumed values of $K$ and $b$, the maximum time constant $\tau_1$, and the time $t_m$.

The choice of the time of duration $\gamma$ of the calibrating pulse and of the sampling period $\Delta t$ is determined by the user of calorimeter and depends on the properties of the calorimeter and the nature of the process being studied. The relationship given in ref. 2, i.e.

$$\Delta t = \gamma = \tau_1/300 \tag{21}$$

results from the following considerations. Assuming that the ratio of the noise amplitude $A_n$ to the amplitude $A_s$ of the calorimetric signal is expressed by the relationship [5]

$$A_n/A_s = (1 + \omega^2\tau_1^2)^{1/2} \approx 1/\omega\tau_1 \tag{22}$$

where $\omega$ is frequency of the noise and is equal to 1/1000, and assuming that the sampling period $\Delta t = \pi/\omega$, we obtain the relationship (21) in the form

$$\Delta t = 0.001\pi\tau_1 \approx \tau_1/300 \tag{23}$$

## CONCLUSIONS

The dynamic criterion obtained enables determination of the possibilities of reconstruction of the smallest heat effects liberated during the heat reaction in the calorimeter. The relationship proposed by us has a general character and does not depend on the complexity of the calorimetric system. It is a valuable advantage of this relationship that it characterizes to a better degree than the static resolution or dynamic resolution previously given [2] the capabilities of the calorimeter in thermokinetics studies.

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