Journal of Thermal Analysis, Vol. 29 (1984) 179–192

Special Review

CALORIMETRY FOR THERMOKINETIC DETERMINATIONS*

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(Received July 4, 1983)

The possibilities of using direct calorimetric measurements for the determination of kinetic parameters of processes are discussed in terms of the choice of an appropriate method of reproduction of the course of changes in the heat power generated in time, i.e. thermokinetics. Such methods are presented and it is concluded that many of these methods permit reproduction of the thermokinetics in the same way as if the experimental thermal curve were obtained in a calorimetric system characterized by a time constant 100–200 times as large as that for the thermal inertia of this calorimetric system.

The application of calorimetry for the study of reaction kinetics started a relatively long time ago. A significant date in the history of calorimetric investigations of the kinetics of chemical reactions was 20 January 1908, when M. G. Germez presented the work of Ducleaux [1] at a meeting of the French Academy of Sciences; in this work the possibility was expressly formulated of using calorimetry for the investigation of chemical reactions, e.g. the decomposition of oxygenated water by iron compounds, saccharosis inversion, or the saponification of ethyl and methyl acetates. At nearly the same time [2], the idea of applying calorimetry in kinetic investigations was realized in the Laboratory of Organic and Analytical Chemistry of Moscow University by Tchelintchev and Konovalova, who studied the kinetics of formation of oxonium dibromide from diethyl ether and bromine. Various types of calorimeters are now used to determine the kinetic parameters of chemical reactions. Most experiments have been carried out by means of adiabatic calorimeters [3]. In such calorimeters, the total amount of heat generated during the process studied is accumulated in the calorimeter, and thus its temperature changes. If this change is significant, from the point of view of the process studied, the determination of the reaction rate parameters can be difficult. Nevertheless, as the dynamic development of DSC and DTA for determining kinetic parameters shows [4–6], the lability of the reagent temperature does not diminish the great possibilities of their application.

In many cases it is assumed that the change of the reactant temperature in a chemical reaction can be neglected. It is also assumed that the heat exchange between the

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*Presented at the 2nd Czechoslovak Conference on Calorimetry, Liblice, Czechoslovakia, 1982.

calorimetric vessel and its surroundings is minimized, although the calorimetric shield is kept at a constant temperature. These quasi-adiabatic conditions occur in isoperibol calorimeters [7], often used [8–14] for the determination of rate parameters of chemical reactions, e.g. investigations of polymerization processes [10–14]. Such conditions also occur in flow calorimeters, often used to determine the rate parameters of fast chemical reactions. In this case the method used consists in passing the starting materials of the reaction (liquids or gases) at a constant rate through a suitably long calorimetric vessel placed in a shield. The mean temperature of the vessel's external surface is the basis for determination of the thermal effects of the studied process; the temperature is measured, as is its gradient component, in the direction of the reaction mixture flow axis. This is achieved by means of sensors allowing accurate temperature measurements. In the flow method, time is not measured directly. The distance (from the site of reaction initiation) covered by the reaction mixture, moving at a constant rate, is a measure of that time. In such calorimeters, numerous determinations of the thermokinetics and rate parameters of chemical reactions have been carried out [15–20]. In recent years stopped-flow calorimeters [21–27] have been increasingly utilized for kinetic studies. For example, Berger and Stoddardt [22] constructed a stopped-flow calorimeter with which chemical reactions in solution with a rate constant of 50 s^{-1} or less can be examined.

Minimalization of the temperature changes of the reactants by increasing the amount of heat carried out of the calorimetric vessel in comparison to the amount of heat accumulated in the vessel is achieved in conduction (flux) calorimeters. In this type of calorimeter, good heat conductors are placed between the calorimetric vessel and a constant-temperature shield, in order to intensify the heat exchange. These conduction elements also often serve as temperature sensors. For this purpose, thermistors or semiconductor thermoelements can be used. In many of this type of calorimeter, thousands of thermocouples [28–35] or some semiconductor elements [36–39] are placed between the calorimetric vessel and isothermic shield, a high sensitivity of temperature measurement and a more intensive heat exchange being achieved. In the group of calorimeters with constant-temperature shields, conduction calorimeters are largely used for kinetic investigations in, for example, catalysis and adsorption [6, 40], electrochemistry [37–39], microbiology and medicine [41] and materials engineering [42–43]. Such calorimeters are constructed in many laboratories and are also produced by many firms.

Thermokinetics

Most techniques used in kinetic measurements involve determination of the changes in concentration of the compounds in the reaction mixture. Calorimetric measurements do not, in principle, give any information about the instant values of concentration. As a result of calorimetric measurements, changes in enthalpy of the reaction can be determined. The evaluation of kinetic parameters from this type of thermochemical data [44] is one of the important investigative possibilities. Calorimetric measurements also provide a possibility for the determination of thermokinetics, i.e. the course of heat power W in time t:

$$W(t) = \frac{dQ(t)}{dt} \tag{1}$$

The determination of this function is the source of kinetic information. The simultaneous occurrence of the studied chemical reaction and the accompanying thermal effect is assumed for all calorimetric measurements in which $W(t)$ is determined.

Determination of thermokinetics yields information on the usefulness of calorimetry for kinetic investigations. The most important role here is played by conduction calorimetry. Nevertheless, the theoretical basis and calculation methods are common for the whole group of nonisothermal–nonadiabatic (n–n) calorimeters, in which two processes are involved heat generation; accumulation of heat in the calorimetric vessel, and heat transfer to the isothermal shield. The theoretical basis of the themokinetic interpretation of measurements was given by Swietoslawski and Salcewicz [45] and Calvet and Prat [46]. The works of Laville [47], Calvet and Camia [48], Camia [49], Łaźniewski [50, 51], and Zielenkiewicz and coworkers [52–56] give the recent theoretical basis for numerical and analogue methods of determination of thermokinetics. The main aim of these works in an appropriate determination of mathematical models of the calorimetric system. It is well known that the overall heat effect, and the thermokinetic function $W(t)$, are always determined by measuring a quantity directly in the calorimeter, e.g. temperature θ. Let us call $W(t)$ the input function, and $\theta(t)$ the output function. In practice, the output function never reproduces $W(t)$ directly. The calorimeter transforms and distorts it. Thus, in order to reproduce $W(t)$ with the required accuracy on the basis of $\theta(t)$, dependence between those two functions should be determined:

$$W(t) = M\{\theta(t)\}$$

and a respective procedure should be selected for it to be possible to carry out an inverse operation, i.e.

$$\theta(t) = M^{-1}\{W(t)\}$$

so as to be able to determine the input function of the calorimeter on the basis of a given course of the output function of the calorimeter. This is the aim of all work connected with the reproduction of thermokinetics. Generally, the common basis of the elaborated methods of reproduction of $W(t)$ in n–n calorimeters is the acceptance of a number of general assumptions, which are as follows. The calorimetric system is treated as an object described by an N-order differential equation:

$$\begin{aligned} &A_N \frac{d^N\theta(t)}{dt^N} + \dots + A_1 \frac{d\theta(t)}{dt} + A_0\theta(t) = \\ &= b_0W(t) + b_1 \frac{dW(t)}{dt} + \dots + b_m \frac{d^mW(t)}{dt^m} \end{aligned} \tag{2}$$

where t is time, θ is temperature, W is heat power, and $A_N, \ldots, A_1, A_1, b_0, b_1, \ldots$ $\ldots, b_m$ are coefficients. It is assumed that the calorimeter is a linear and stationary object; and object of exactly defined initial conditions; and an invariant object, i.e. with the same parameters values during calibration and determination of the input function $W(t)$. The way in which the equation is applied while the transformation equation of a calorimeter is being formulated differs depending on the methods used and the dynamic properties of the calorimeter, resulting from its mathematical model. Let us describe the principles of these methods.

Method of dynamic optimalization

Applying the Laplace transformation to Eq. (2) under zero initial conditions we obtain

$$(A_N s^N + \cdots + A_1 s + A_0)\theta(s) = (b_m s^m + \cdots + b_1 s + b_0) W(s) \tag{3}$$

where s is a Laplace operator, and $\theta(s)$ and $W(s)$ are Laplace transforms of temperature $\theta(t)$ and heat power $W(t)$, respectively. Relationship (3) can be written in the form

$$\theta(s) = H(s) W(s) \tag{4}$$

where

$$H(s) = \frac{b_m s^m + \cdots + b_1 s + b_0}{A_N s^N + \cdots + A_1 s + A_0} \tag{5}$$

Transmittance $H(s)$ characterizes the dynamic properties of the calorimetric system in a complex plane. The inverse Laplace transform $h(t)$

$$h(t) = L^{-1}\{H(s)\} \tag{6}$$

of the transmittance $H(s)$ is called the impulse response of the calorimetric system, and characterizes its dynamic properties in the time domain. Relationship (4) in the time domain corresponds to a convolution of functions:

$$\theta(t) = h(t) W(t) = \int_0^t h(t-\tau) W(\tau)\, d\tau = \int_0^t h(\tau) W(t-\tau)\, d\tau \tag{7}$$

In the dynamic optimalization method, relationship (7) is taken as a mathematical model of calorimeter, and thus appropriate zero initial conditions are assumed. This method assumes the existence of one input function $\theta(t)$ and one output function $W(t)$. The impulse response $h(t)$ (6) is determined as a derivative with respect to time of the response of the calorimetric system to a unit step. As a criterion of accordance between the measured temperature change $\theta(t)$ and the estimated course of temperature $x(t)$, the integral of the square of the difference between these two course is taken:

$$q[x(t)] = \int_0^u [\theta(t) - x(t)]^2\, dt \tag{8}$$

or, substituting the convolution of functions (7), we obtain

$$q[W(t)] = \int_0^u \left[\theta(t) - \int_0^t h(\tau) W(t-\tau)\, d\tau\right]^2 dt \tag{9}$$

The task of dynamic optimalization consists in the selection of the unknown thermal power $W(t)$ so that the function (9) attains a minimum. Such a task can be solved, provided that the temperature response $\theta(t)$ and the impulse response $h(t)$ of the calorimeter are known in the analytical form. However, in calorimetric measurements numerical values $\theta_0, \theta_1, \ldots, \theta_N$ are usually available on the course of the temperature changes $\theta(t)$ of the calorimeter. Because of this, the integrals in function (9) are approximated by sums, and thus the function becomes a function of multi-variables:

$$q = q(W_0, W_1, \ldots, W_{n-1}, W_1) \tag{10}$$

In the search for the minimum of function (10), a conjugate gradient method is used.

The dynamic optimalization method for the determination of thermokinetics was proposed by Gutenbaum and coworkers [57]. This method has been applied [57–60] for the determination of thermokinetics in thermochemical studies of clathration reactions [61] and in the thermochemical analysis of cements [43].

Harmonic analysis method

In this method the convolution recorded in the frequency domain is accepted as the transformation equation (11) of the calorimeter:

$$\theta(j\omega) = H(j\omega) W(j\omega) \tag{11}$$

where $\theta(j\omega)$ and $W(j\omega)$ are Fourier transforms of the output function $\theta(t)$ and input function $W(t)$, respectively; and $H(j\omega)$ is the spectrum transmittance. The description of function $H(j\omega)$ corresponds to the determination of the dynamic properties of the calorimeter. The spectrum transmittance $H(j\omega)$ is determined on the basis of the response of the calorimeter to a known heat effect. After determination of the spectrum transmittance $H(j\omega)$ and the calorimeter response $\theta_x(t)$, the thermokinetics $W_x(t)$ is obtained as to inverse Fourier transform

$$W_x(t) = F^{-1}\left\{\frac{\theta_x(j\omega)}{H(j\omega)}\right\} \tag{12}$$

where $\theta_x(j\omega)$ is the Fourier transform of the response $\theta_x(t)$. As a criterion of the possibility of reproduction, Shannon's theorem is applied. In practice, a frequency is used which is obtained on the basis of the transfer function calculated. The practical frequency ν_p is determined on the basis of the dependence

$$\frac{|FT|_{\nu=\nu_p}}{|FT|_{\nu=0}} = \frac{\text{noise}}{\text{maximum impulse response}}$$

where $|FT|_{\nu=0}$ is the value of the spectrum transmittance amplitude for $\nu = 0$;

$|FT|_{\nu=\nu_p}$ is the value of the amplitude for the practical frequency, and noise is the noise amplitude.

The method of harmonic analysis for the determination of thermokinetics was proposed by Navarro and coworkers [62]. This method was applied in the works [63–66].

Thermal curve interpretation method

The thermal curve interpretation method by spectral resolution into the basic set of rectangular pulse curves [67, 68] is also based on harmonic analysis. In this method it is assumed that the course of the temperature changes $\theta(t)$ can be presented in the form

$$\theta(t) = \sum_{i=0}^{N} W_i B_i(t) \tag{13}$$

of the set of orthogonal and orthonormal functions $\{B_i(t)\}$, which satisfy the following conditions:

$$\begin{aligned} &\int_0^T B_i^2(t)\,dt = 1 \\ &\int_0^T B_i(t)B_j(t)\,dt = 0 \quad \text{for} \quad j \neq i \end{aligned} \tag{14}$$

where $W_i = W(i\Delta)$, which corresponds to the heat power $W(t)$ at instant i. For the generation of this set of functions, the procedure proposed by Löwdin was used [67]. This procedure is often applied in quantum chemistry calculations, since it gives a set of orthogonal functions which maximally resembles the set of orthogonalized functions, i.e. the quantity

$$\sum_{j=1}^{M} \int_0^{T=N\Delta} B_j(t)\theta_j(t)\,dt = \sum_{j=1}^{M} \sum_{i=1}^{N} B_j(i\Delta)\theta_j(i\Delta)\Delta \tag{15}$$

The values of the heat power in particular time periods can then be expressed by the following relationship:

$$W_j = \int_0^T \theta(t)B_j(t)\,dt \qquad (j = 1, 2, \ldots, N) \tag{16}$$

or

$$W_j = \sum_{i=0}^{N} \theta(i\Delta)B_j(i\Delta)\Delta \tag{17}$$

This method, like that described before, does not require a knowledge of the physical parameters of the system. The advantage of this method, in comparison with method presented before, is the possibility of its application for any initial conditions of the system.

Method of state variables

In the method of state variables a certain set of parameters is distinguished

$$x_1(t), x_2(t), \ldots, x_n(t) \tag{18}$$

which characterize the calorimetric system. These values are referred to as state variables. Three types of state variables are distinguished: physical variables, canonical variables and phase variables. The vector

$$x(t) = \begin{vmatrix} x_1(t) \\ x_2(t) \\ \cdot \\ \cdot \\ \cdot \\ x_n(t) \end{vmatrix} \tag{19}$$

the components of which are state variables, is referred to as the state vector. Thus, the calorimeter transformation equation combines the state variables with the parameters of the calorimetric system and the thermal power produced:

$$\dot{x}(t) = Ax(t) + BW(t) \tag{20}$$

The state equation (20) written in this way is a system of first-order equations. Due to the available calorimetric information, the state variables should be transformed in such a way as to obtain a relationship between one input function $W(t)$ and one output function. The relationship between the state variables and the output function has the following form:

$$\theta(t) = c^T x(t)$$

The method of state variables for the determination of thermokinetics was proposed by Brie and coworkers [69]. The method was applied in the following works [70–72].

Method of a multi-body system

The method of a multi-body system was proposed by Zielenkiewicz et al. [52, 73]. The bases of this method are as follows. In the calorimetric system, N domains are distinguished; each of them is characterized by a constant heat capacity K_i, a homogeneous temperature $T_i(t)$ and a heat source of power $W_i(t)$. The heat balance equation for such a domain system can then be given as a set of ordinary linear equations according to [73]:

$$K_i \frac{\mathrm{d}\theta_i(t)}{\mathrm{d}t} + \sum_{\substack{j=1 \\ j \neq i}}^{N} G_{ij}[\theta_i(t) - \theta_j(t)] + G_{i0}\theta_i(t) = W_i(t) \qquad (i = 1, 2, \ldots, N) \tag{21}$$

where G_{ij} is the heat loss coefficient between the i-th and j-th distinguished domains, and G_{i0} is the heat loss coefficient between the i-th domain and the environment. The calorimetric system is placed in a thermostat (environment) at constant temperature

T_0, which is accepted as the reference temperature, so that $\theta_j(t) = T_j(t) - T_0$. The set of equations can be given as

$$K_i \frac{d\theta_i(t)}{dt} + G_i\theta_i(t) - \sum_{\substack{j=1 \\ j \neq i}}^{N} G_{ij}\theta_j(t) = W_i(t) \qquad (i = 1, 2, \ldots, N) \tag{22}$$

where

$$G_i = \sum_{\substack{j=0 \\ j \neq i}}^{N} G_{ij} \qquad (i = 1, 2, \ldots, N) \tag{23}$$

Applying the Laplace transformation to Eq. (22) and assuming zero initial conditions, one can write

$$(K_i s + G_i)\theta_i(s) - \sum_{\substack{j=1 \\ j \neq i}}^{N} G_{ij}\theta_j(s) = W_i(s) \qquad (i = 1, 2, \ldots, N) \tag{24}$$

or in a matrix form

$$A(s)\theta(s) = W(s) \tag{25}$$

The particular elements of the matrix $A(s)$ are $a_{ij}(s) = -G_{ij}$ $(i \neq j)$, $a_{ii}(s) = K_i s + G_i$. $\theta(s)$ is the Laplace transform of the state vector, the components of which are the temperatures of the distinguished domains. $W(s)$ is the Laplace transform of the heat power vector, the components of which are the heat powers generated in the distinguished domains. The solutions of the set of equations (25) are

$$\theta(s) = A^{-1}(s)W(s) \tag{26}$$

where $A^{-1}(s)$ is the inverse matrix of the matrix $A(s)$. From the dependence (26), it results that the Laplace transform $\theta_i(s)$ of the temperature $\theta_i(t)$ of the i-th distinguished domain is given as

$$\theta_i(s) = \sum_{j=1}^{N} a_{ij}^{-1}(s)W_j(s) \qquad (i = 1, 2, \ldots, N) \tag{27}$$

where $a_{ij}^{-1}(s)$ is the element of the inverse matrix and the transfer function of the calorimeter, when the measured temperature $\theta_i(t)$ is the temperature of the i-th domain and the heat effect $W_j(t)$ is generated in the j-th domain. This transfer function can be written in the form

$$H_{ij}(s) = a_{ij}^{-1}(s) = \frac{|A_{ij}(s)|}{|A(s)|} \tag{28}$$

where $|A(s)|$ is the determinant of the matrix $A(s)$, and $|A_{ij}(s)|$ is the corresponding minor of the matrix.

The determinant $|A(s)|$ involves a power series with respect to a polynomial s of degree N:

$$|A(s)| = \sum_{n=0}^{N} a_n s^n = f(s) \tag{29}$$

The determinant $|A_{ji}(s)|$ involves a power series with respect to a polynomial s of degree m:

$$|A_{ji}(s)| = \sum_{k=0}^{m} b_k s^k = g_{ji}(s) \tag{30}$$

where $0 \leqslant m \leqslant N - 1$. The determination of the transmittance $H_{ij}(s)$ of the calorimetric system in form (28) is equivalent to calculations of coefficients of polynomials $f(s)$ and $g_{ij}(s)$. The determined transmittance has a form

$$H_{ij}(s) = \frac{b_0}{A_0} \prod_{k=1}^{m} (L_k s + 1) : \prod_{n=1}^{N} (M_n s + 1) \tag{31}$$

where $0 \leqslant m \leqslant N - 1$. The determination of the transmittance $H_{ij}(s)$ of the calorimetric system in form (28) is equivalent to calculations of coefficients of polynomials nominator of the transmittance).

If the values of the parameters K_i, G_{ij} and G_{i0}, of the model are known [74], and values L_k and M_n are determined, one can obtain a description of the thermokinetics. For this purpose, two methods can be used: (1) determination of $W(t)$ numerically or by analogue correction on the basis of the transmittance; (2) on the basis of a particular form of a set of heat balance equations. With the second possibility, the differential equations (22) are approximated by difference equations. The iteration procedure of solving the set of equations (22) calculates step by step the temperatures of the neighbouring bodies to the sensor, and then the temperatures of the bodies neighbouring to the bodies the temperatures of which are determined in the first step. The procedure leads to the calculation of the temperature of the bodies in which the heat source is situated. On the basis of this temperature, the value of $W_i(t)$ is calculated. The algorithm of the calculations is given in [74].

Methods of analogue and numerical correction

The methods of analogue and numerical correction are bàsed on the assumption that a calorimetric system can be characterized as an n-order inertial object, provided that the time constants of this system have been determined previously. The application of these methods is usually restricted to the case in which the calorimeter is treated as a linear inertial object of second order. Then, according to Eq. (2), the relation between $W(t)$ and $\theta(t)$ can be expressed in the form of the following differential equation:

$$A_2 \frac{d^2\theta(t)}{dt^2} + A \frac{d\theta(t)}{dt} + \theta(t) = bW(t) \tag{32}$$

Using Laplace transformation and replacing the coefficients A_1 and A_2 by the time constants T_1 and T_2 of the calorimeter according to the dependence: $T_1 + T_2 = A_1$; $T_1 T_2 = A_2$, Eq. (32) becomes

$$\theta(s) = \frac{1}{T_1 s + 1} \frac{1}{T_2 s + 1} bW(s) \tag{33}$$

The purpose of the correction methods is the application of a procedure which allows elimination of the influence of inertia units in the determination of the relation between $\theta(s)$ and $W(s)$, and thus that between $\theta(t)$ and $W(t)$. It consists in the introduction (by the numerical or analogue method) of terms $Ts + 1$ providing inverse functions to the terms $1/(Ts + 1)$. In the case of an individual corrector, it corresponds to the following relationship:

$$\theta'(s) = \frac{b(T's + 1)}{(T_1 s + 1)(T_2 s + 1)} W(s) \tag{34}$$

In the case of two correctors, this corresponds to the following relationship:

$$\theta''(s) = \frac{b(T's + 1)(T''s + 1)}{(T_1 s + 1)(T_2 s + 1)} \tag{35}$$

For an ideal correction, this would lead to the case when the input function corresponds to the output function, as represented by the relationship

$$\theta''(s) \cong W(s) \tag{36}$$

The practical attainment of analogue correction is different in different systems [75–81], but advantage is always taken of electronic elements active under the form of an operational amplifier and impedance divider of feedback, by which the required function $1 + Ts$ is achieved.

Another way of achieving the differential correction is numerically [82]. Taking into account Eq. (34), it is intended to calculate numerically the functions corresponding to terms $1 + Ts$. To each of these terms there corresponds a linear differential equation of first order of the form

$$T \frac{d\theta(t)}{dt} + \theta(t) = \theta_1(t) \tag{37}$$

Thus, for an inertial object of second order the following equations can be noted:

$$\begin{aligned} \theta'(t) &= \theta(t) + T' \frac{d\theta(t)}{dt} \\ \theta''(t) &= \theta'(t) + T'' \frac{d\theta'(t)}{dt} \end{aligned} \tag{38}$$

When the time constants T' and T'' and $\theta(t)$ are known, it is possible to determine the $\theta'(t)$ and $\theta''(t)$ values consecutively, and thus $W(t)$.

Dynamic method

Many calorimetric determinations are based on the heat balance equation

$$K \frac{d\theta(t)}{dt} + G\theta(t) = W(t) \tag{39}$$

where G is the heat loss coefficient, and K is the heat capacity of the calorimeter. After integration, Eq. (39) can be given in the form

$$Q\Big|_{t'}^{t''} = K\int_{t'}^{t''} \mathrm{d}\theta(t) + G\int_{t'}^{t''} \theta(t)\,\mathrm{d}t \tag{40}$$

where $\int_{t'}^{t''} \mathrm{d}\theta(t)$ is the difference in response of $\theta(t'')$ and $\theta(t')$, and $\int_{t'}^{t''} \theta(t)\,\mathrm{d}t$ is the area between the determined course of change θ and time t axis. The values of the area and θ result from the calorimetric measurement. The values K and G are determined on the basis of the calibration of the calorimeter.

Equation (39) for the heat balance of a simple body is generally called the Tian—Calvet equation. A wide range of application of the dynamic method for the determination of thermokinetics and rate parameters of chemical reactions have been demonstrated in the book of Calvet and Prat [46] and many other publications.

Flux method

The flux method is based on the assumption that the amount of heat exchanged between the calorimeter and the shield is directly proportional to the temperature difference. Thus, the course of $\theta(t)$ obtained from the measurement resembles that of $W(t)$, and its value is determined on the basis of the second term on the left-side of Eq. (39):

$$W(t) = G\theta(t)$$

The integral effect of the studied reaction is determined on the basis of

$$Q_I = G\int_{t_0}^{t_k} \theta(t)\,\mathrm{d}t$$

which results from Eq. (40) provided that the measurement is carried out so that the responses at initial time t_0 and final time t_k are equal: $\theta(t_0) = \theta(t_k)$ [83].

The flux method is widely used for the determination of thermokinetics and rate parameters of chemical reactions. Johnson and Biltonen [84], using the alkaline hydrolysis of ethyl acetate as a model reaction, showed the applicability of a conduction calorimeter to measure bimolecular reaction rates with half-times in the range of at least 5 sec to several hours. Beezer and Tyrrel [85] have established the relations between the calorimeter response and the reaction parameters for reactions with zero and first-order kinetics, with particular reference to the kinetics of enzyme-catalyzed reactions. Belaich et al. [86—87] have demonstrated a way to obtain kinetic data on the growth of a culture of Saccharomyces in a synthetic medium and the maximum rate of metabolism: the data of Michaelis—Menten kinetics. Prosen et al. [37], Hansen et al. [38] and Schaft [39] use conduction microcalorimeters for the determination of thermokinetics, and study the electrochemical reaction in cardiac pacemakers.

Conclusions

The methods presented above show a possibility of choosing various means of reproduction of thermokinetics. As shown in papers [67, 74, 88, 89], it is possible to reproduce the thermokinetics in a manner as if the experimental thermal curve were obtained in a calorimetric system characterized by the time constant 100–200 times as large as the constant T for the thermal inertia of this calorimetric system. This indicates clearly how large a development has been made in new calculative methods of determination of thermokinetics. On the other hand, it is now possible to construct a calorimetric system of small inertia, with a time constant of the order of a few seconds or a few hundred seconds. Thus, calorimetry is becoming a useful technique for the determination of the thermokinetics of various, slow and also very short-duration processes.

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Zusammenfassung — Die Möglichkeiten zur Benutzung direkter kalorimetrischer Messungen zur Bestimmung kinetischer Parameter von Prozessen werden hinsichtlich der Wahl geeigneter Methoden zur Reproduzierung des Verlaufs der Änderungen der Wärmekraft mit der Zeit, d.h. zur Reproduzierung der Thermokinetik diskutiert. Solche Methoden werden angeführt und es wird die Schlussfolgerung gezogen, dass viele dieser Methoden die Reproduzierung der Thermokinetik auf gleiche Weise wie in den Fällen erlauben, in denen die thermische Kurve mit einem kalorimetrischen System erhalten wird, dessen Zeitkonstante um 100–200mal grösser als die des diskutierten Systems ist.

Резюме — Возможности использования прямых калориметрических измерений обсуждены в плане выбора соответствующего метода воспроизводимости хода изменения выделяющегося тепла во времени т. е. термокинетики. Представлены эти методы и сделан вывод, что многие из этих методов позволяют воспроизвести термокинетику тем же самым путем, как если бы экспериментальные термические кривые были получены в калориметрической системе, характеризующейся постоянной времени в 100–200 раз выше по сравнению с термической инерционностью такой калориметрической системы.