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THEORETICAL MODELS OF CALORIMETRIC SYSTEMS

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In the present paper the dynamic properties of nonisothermal-nonadiabatic calorimeters have been analysed. In these calorimeters the thermal effect produced is partly accumulated in the calorimetric vessel, and partly transmitted to the shield with constant temperature. The generalized equation of the heat balance and the equation of the dynamics have been given for this type of calorimeter. The dependence between the course of the thermal effect Q in time t as a function of the temperature changes Θ of the calorimeter has been presented. Dependences $Q(t) = f[\Theta(t)]$ for a calorimeter with different domain configurations distinguished in it, and with different mutual locations of heat sources and temperature sensor have been given. Practical application of the considerations presented has been given.

In the past few years a considerable development of the theory of calorimetric systems has taken place. It is the aim of this theory to determine methods of analysis of thermal effects in calorimetric systems; recognize their static-dynamic properties; and describe ways for accurate determination of thermal effects, and above all, of the thermokinetics of the examined processes, i.e. the funtion $W(t)$

$$W(t) = \frac{\mathrm{d}Q(t)}{\mathrm{d}t}$$

where Q is the amount of heat developed in a calorimetric system and t is time. The ability to determine this function accurately considerably enlarges the range of application of calorimetry to the determination of the thermokinetics of the processes examined.

Theoretical models of nonisothermal-nonadiabatic (*n-n*) calorimeters are discussed in this paper. It can be assumed [1] that, in general, every *n-n* calorimeter consists of a calorimetric vessel which is surrounded by a medium bounded by a constant-temperature shield. The thermal effect produced in the calorimetric vessel is partly transferred to the constant-temperature shield and partly accumulated in the vessel.

If the calorimeter is regarded as a uniform, isotropic body of homogeneous temperature Θ, which changes only with time t, and if its coefficients G and K are independent of the range of temperature and time (G is the coefficient of heat losses; K is the heat capacity of the system), then the dependence between $W(t)$ and $\Theta(t)$ can be expressed by the heat balance equation (1) for a single body

$$K\frac{\mathrm{d}\Theta(t)}{\mathrm{d}t} + G\Theta(t) = \frac{\mathrm{d}Q(t)}{\mathrm{d}t}. \tag{1}$$

The first term of the left-hand of Eq. (1) describes the quantity of heat accumulated throughout the time interval dt in the calorimetric vessel, while the second term describes the amount of heat exchanged between the calorimetric vessel and the surroundings. The right-hand term of the equation describes the amount of heat d$Q(t)$ released throughout the time interval dt. For a particular case, when a thermally passive substance is placed in the calorimeter, Eq. (1) becomes

$$\frac{\mathrm{d}\Theta(t)}{\mathrm{d}t} = -(G/K)\,\Theta(t) \tag{2}$$

which is equivalent to the equation of Newton's law of cooling

$$\frac{\mathrm{d}\Theta(t)}{\mathrm{d}t} = -\,\beta\,\Theta(t) \tag{3}$$

provided that K, G. and β are interrelated as follows

$$G = K\beta\,. \tag{4}$$

Thus, a calorimeter can be described in terms of the differential equation (1) and Newton's law of cooling can be used for the determination of the calorimetric system parameters.

Let us now analyse the dynamic properties of the model in terms of calorimetric terminology and also notions taken from the steering and automatic control theory. The dynamic properties of the calorimeter are somehow encoded in the form of the equation representing the formalization of the model. Equation (1) is an ordinary first-order linear differential equation. The principle of superposition is applicable to such equations. This principle can be formulated as follows: the temperature response $\Theta(t)$ of a linear system to several thermal forcing functions $Q_1(t)$, $Q_2(t)$ and $Q_3(t)$ is equal to the sum of the responses to all the individual thermal forcings. This property of the system creates a possibility for a relatively simple means of analysis of complex thermal effects, provided that at least some of the single thermal effects are known and likely to be described in another way.

Another property of the system is also of interest. Namely, it follows from the steering and automatic control theory that a physical system described by this type of equation is characterized by first-order inertial properties, which is a fact easy to recognize, because upon dividing both sides of Eq. (1) by G and putting

$$T = \frac{K}{G} = \frac{1}{\beta}, \qquad f(t) = \frac{1}{G}\,\frac{\mathrm{d}Q(t)}{\mathrm{d}t} = \frac{1}{G}\,W(t)$$

we arrive at the following equation

$$T\frac{\mathrm{d}\,\Theta(t)}{\mathrm{d}t} + \Theta(t) = f(t) \tag{5}$$

which indicates that a knowledge of $\Theta(t)$ and the time constant T suffices to establish the course of thermal effect $f(t)$.

The time constant T is the parameter decisive for the inertial properties of the system. This also means that the values of the time constant determine whether the experimental conditions approach more closely either the isothermal or the adiabatic type, and the resulting observed temperature course follows more or less closely the course of the function $f(t)$, which corresponds to the thermokinetics of the transformation investigated. Simply, the values of T control the inertial or damping properties of the system. Equally simple in this method is the procedure for the determination of $W(t)$, because it is not difficult to get information on numerical values of G and K [1, 2].

The common application of this model in *n-n* calorimetry is generally familiar. Most corrections applied to an ordinary calorimeter, for example the Regnault-Pfaundler correction [3], are based on this method. It underlies the static-dynamic method od Świętosławski and Salcewicz [4, 5]. This model has also been used for evaluation of long-duration thermal effects in Calvet microcalorimeters [6], LKB calorimeters, and other calorimeters. However, this model is rather poor. When thermal inertia takes place, or when temperature gradients occur between particular elements of the calorimetric system and in the elements themselves, this dynamic model does not always show clearly enough the real properties of calorimetric systems. It does not fully explain the influences of external disturbances on the investigated calorimetric system, either. Numerous experimental facts are by no means explicable in terms of the one-body model. By way of illustration, these include the heat capacities μ_0 and μ_∞ discovered by Calvet [5] and the relation of the heat capacity to the time of generation of a constant-power Joule's effect established by Madejski, Utzig and Zielenkiewicz [7]. The dependence between $W(t)$ and $\Theta(t)$ given by the one-body model does not precisely describe the thermokinetics of short-duration or quickly-changeable thermal processes in the *n-n* calorimetric systems.

These facts resulted in research for other models of calorimetric systems. Numerous authors have employed the "black box" notion, known in the steering and automatic theory, to develop a number of methods for determining unknown $W(t)$ from the measured transmittance of the calorimetric systems and the observed course of temperature changes $\Theta(t)$. It is assumed at the same time that a calorimeter constitutes a dynamic linear system with lumped parameters, which is described by means of an ordinary differential equation of the n-th-order. The input function of such a dynamic system is the termal power developed in the calorimeter, whereas the output function is the course of the temperature changes. If the thermal effect, usually constant in time, developed in the process of testing a calorimeter is known and the temperature changes caused by this effect measured, the transfer function of the calorimetric system is determined by different means. For determination of the thermokinetics Navarro, Rojas and Torra [8, 9] use the method of harmonic analysis through determination of the transfer function on the basis of spectrum transmittance. In the dynamic optimization method Gutenbaum, Utzig, Wiśniewski and Zielenkiewicz [10, 11] base the transformation equation on application of convolution and then the method of the conjugate gradient. Brie, Petit and Gravelle [12] determine the thermokinetics by the methods of state variables. It is assumed in all these works that the transmittance of the calorimetric system is invariable.

A separate group of works considers the calorimetric models based on distributed parameters of the calorimetric system. The technique applied in these papers resolves itself to solving the Kirchhoff-Fourier partial equation. Laville [13] formulated the fundamentals of the theory of the Calvet microcalorimeter on this basis. Calvet and Camia [14] and Camia [15, 16] presented principles of the method of determining short-duration thermal effects in calorimeters of this type. Oleinik [17] carried out analysis of thermal effects in a calorimetric bomb. Hattori, Amaya and Tanaka [18] assumed an idealized, one-dimensional model of a calorimeter and proved that in a particular case the total thermal effect developed in a conductive calorimeter is proportional to the area between the course of the temperature changes and the time axis. There are few works on this problem. This may be due to the fact that dynamic models based directly on detailed solution of the Kirchhoff-Fourier equation have, in general, too complicated a form to be used at present to solve practical problems.

Development of methods of determining dynamic properties of calorimetric systems is carried out on the basis of simplified models, which allow obtaining of the transformation equation in a limited set of parameters and are based on consideration of the thermal balance equations of the calorimeter, treated as a system of several distinguished bodies. This method was used for the first time to determine the total thermal effects in a calorimetric bomb by King and Grover [19], Jessup [20], and then by Armstrong, West, Churney [21, 22]. It was the aim of these works to determine accurately the total thermal effect developed in a calorimetric bomb.

On the basis of the theory of thermal exchange and the theory of control, the fundamentals of the multi-body theory [23, 24] were determined. The method has been widely used for the investigation of dynamic properties of calorimetric systems and for the determination of the thermokinetics of the examined thermal effects. The assumptions of this theory are as follows [24].

Let us assume that the calorimetric system accommodates n bodies having the properties of linear first-order inertial objects. Therefore, each body has a uniform temperature throughout its total volume, which varies only with the time t, and its heat capacity is constant. Let temperature gradients occur only in the media separating the bodies, the heat capacities of these media being assumed to be negligible. Further, let us assume that the heat exchanged by the bodies through the media is proportional to the temperature difference between the bodies concerned, the corresponding coefficients of heat losses being the coefficients of proportionality. Furthermore, each body may comprise a source of thermal power and temperature can be measured in each body. A system of these bodies is contained within a medium of constant temperature. With these assumptions it proved possible to develop a generalized equation for the heat balance on n bodies. This equation was derived by several methods; among others it can be derived from the Kirchhoff–Fourier equation by a procedure similar to the one used to derive the heat balance on one body. This equation is

$$K_j \, d\Theta_j(t) + G_{0j} \Theta_j(t) \, dt + \sum_{\substack{i=1 \\ i \neq j}}^{n} G_{ij} [\Theta_j(t) - \Theta_i(t)] \, dt = dQ_j(t) \tag{6}$$

$$j = 1, 2, \ldots, n$$

where n is the number of bodies; K_j is the heat capacity of the body j; G_{0j} is the coefficient of heat losses between the body j and the surroundings; G_{ij} is the coefficient of heat losses between bodies i and j; $\Theta_j(t)$ is the function describing changes in the temperature of the body j in time with respect to the surroundings; $dQ_j(t)$ is the amount of heat evolved within the time dt in the body j; $G_{0j}\Theta_j(t)dt$ is the amount of heat exchanged between the body j and the surroundings within a period of time dt; and $G_{ij}[\Theta_j(t) - \Theta_i(t)]dt$ is the amount of heat exchanged between bodies i and j within the time dt.

Next, Eq. (6) was normed in the dimension of temperature and the result is

$$T_j \frac{d\Theta_j(t)}{dt} + \Theta_j(t) = \sum_{\substack{i=1 \\ i \neq j}}^{n} k_{ij} \Theta_i(t) + \lambda_j f_j(t). \tag{7}$$

$$j = 1, 2, \ldots, n$$

In the derivation of the above equation the following quantities have been introduced.

The overall coefficient of heat losses for any body, defined as

$$G_j = \sum_{\substack{i=0 \\ i \neq j}}^{n} G_{ij}; . \qquad j = 1, 2, \ldots, n \tag{8}$$

This coefficient accounts for the heat exchange occurring not only between the body j and the surroundings, but also between the body j and other bodies.

The time constant T_j was defined as the ratio of the heat capacity K_j to the overall heat loss coefficient G_j

$$T_j = K_j / G_j; \qquad j = 1, 2, \ldots, n. \tag{9}$$

The time constant of the body j, that is T_j, is a measure of the thermal lag of the body j in the n-body system.

The coefficient of interaction was also introduced, defined as the ratio of the heat loss coefficient to the overall heat loss coefficient

$$k_{ij} = G_{ij} / G_j. \tag{10}$$

This is a measure of the thermal interaction between bodies i and j in respect to the interaction of the remaining bodies and the surroundings with the body j. The interaction coefficients affect essentially the thermal lag of the calorimeter and allow us to establish the structure of the dynamic model of a given calorimeter.

Furthermore, the notion of the forcing function $f_j(t)$ – taken from the steering theory – was introduced into these considerations. The function $f_j(t)$ has the dimension of temperature and is proportional to the thermal power evolved.

The equations for the heat balance in the system of n bodies are quite general equations, and most frequently they are reduced to a model involving two or three bodies. Also, the assumptions adopted are general enough to include systems of any configuration. For example (Fig. 1), it can be assumed that in a calorimeter

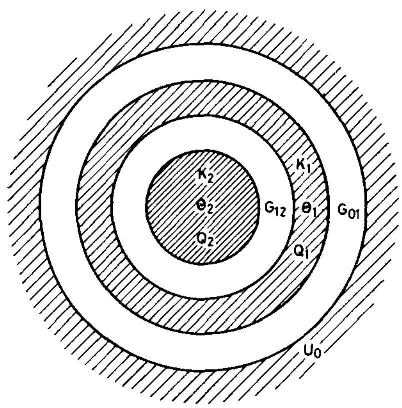

Fig. 1. Sketch of the two-body model

the vessel and its contents constitute one body; the internal shield containing the vessel or the thermocouples attached to the external surface of the vessel or another body; and the whole is placed in an external shield which is regarded as the medium (surroundings) of a constant uniform temperature U_0. In this case the following parameters may be distinguished: the heat capacity K_2 of the calorimetric vessel and its contents; and the temperature of this body with reference to the external shield temperature, U_0, expressed as $\Theta_2(t) = U_2(t) - U_0$. Similarly, for the internal shield, K_1 is the heat capacity and $\Theta_1(t)$ is the temperature with respect to the external shield temperature U_0. The heat exchange between the calorimeter and the isothermal shield is characterized by the heat loss coefficient G_{01}; whereas the heat exchange between the bodies distinguished is characterized by the coefficient G_{12}. For a two-body system of configuration as presented in Fig. 1, the heat balance equations are as follows

$$K_2\,\mathrm{d}\Theta_2(t) + G_{12}[\Theta_2(t) - \Theta_1(t)]\,\mathrm{d}t = \mathrm{d}\,Q_2(t) \tag{11}$$

$$K_1\,\mathrm{d}\,\Theta_1(t) + G_{12}[\Theta_1(t) - \Theta_2(t)]\,\mathrm{d}t + G_{01}\,\Theta_1(t)\,\mathrm{d}t = \mathrm{d}\,Q_1(t)\,. \tag{12}$$

Conveniently, these heat balance equations can be normed in the dimension of temperature and then they become

$$T_2 \frac{d\,\Theta_2(t)}{dt} + \Theta_2(t) = \Theta_1(t) + k f_2(t) \tag{13}$$

$$T_1 \frac{d\,\Theta_1(t)}{dt} + \Theta_1(t) = (1 - k)\,\Theta_2(t) + k f_1(t) \tag{14}$$

In this form the equation are referred to as the equations of system dynamics. Time constants T_1 and T_2 and the coefficient k are expressed as follows

$$T_1 = K_1/(G_{01} + G_{12}); \qquad T_2 = K_2/G_{12}; \qquad k = G_{01}/(G_{01} + G_{12}) \tag{15}$$

and also

$$f_1(t) = W_1(t)/G_{01}; \qquad f_2(t) = W_2(t)/kG_{12}.$$

Investigation of the heat balance equations (11) and (12), and the dynamics equations (13) and (14) constituted a basis for the analysis of numerous calorimetric problems. It appears that different forms of dependencies combining the function $W(t)$ with the function $\Theta(t)$ are obtained according to relative locations of heat sources and temperature sensors in bodies *1* and *2*. Thus – if the thermal effect is produced in body *1* and the temperature of body *1* is taken, the relation has the form

$$\left\{M_1 M_2 \frac{d^2\,\Theta_1(t)}{dt^2} + (M_1 + M_2)\frac{d\,\Theta_1(t)}{dt} + \Theta_1(t)\right\} G_{01} = W_1(t) + T_2 \frac{d\,W_1(t)}{dt} \tag{16}$$

– if the thermal effect is produced in body *2* and the temperature of body *1* is taken, the relation has the form

$$\left\{M_1 M_2 \frac{d^2\,\Theta_1(t)}{dt^2} + (M_1 + M_2)\frac{d\,\Theta_1(t)}{dt} + \Theta_1(t)\right\} G_{01} = W_2(t) \tag{17}$$

– if the thermal effect is produced in body *1* and the temperature of body *2* is taken, the relation has the form

$$\left\{M_1 M_2 \frac{d^2\,\Theta_2(t)}{dt^2} + (M_1 + M_2)\frac{d\,\Theta_2(t)}{dt} + \Theta_2(t)\right\} G_{01} = W_1(t) \tag{18}$$

– if the thermal effect is produced in body *2* and the temperature of body *2* is taken, the relation has the form

$$\left\{M_1 M_2 \frac{d^2\,\Theta_2(t)}{dt^2} + (M_1 + M_2)\frac{d\,\Theta_2(t)}{dt} + \Theta_2(t)\right\} G_{01} =$$

$$= (1 + G_{01}/G_{12}) \left\{ W_2(t) + T_1 \frac{W_1(t)}{\mathrm{d}t} \right\} \tag{19}$$

where

$$(M_1 + M_2)k = T_1 + T_2; \qquad M_1 M_2 k = T_1 T_2 \,. \tag{20}$$

Thus, as has been shown by dependencies (16) – (19) relative locations of heat sources and temperature sensors in a calorimetric system are of essential importance for the choice of an adequate form of the transmittance [25].

A simple transformation of Eq. (17) gives

$$K_{12}(t) \frac{\mathrm{d}\, \Theta_1(t)}{\mathrm{d}t} + G_{01}\, \Theta_1(t) = W_2(t) \tag{21}$$

where

$$K_{12}(t) = \left\{ M_1 + M_2 + M_1 M_2 \frac{\mathrm{d}^2\, \Theta_1(t)}{\mathrm{d}t^2} : \frac{\mathrm{d}\, \Theta_1(t)}{\mathrm{d}t} \right\} G_{01} \tag{22}$$

which indicates that the consideration of the equation in terms of the one-body model leads to the values of the heat capacity K_{12} of the calorimetric system as a variable with time [26]. Similarly, as a result of the works of Jessup [20], King and Grover [19], Oetting [27], West and Churney [21] and Churney, West and Armstrong [22], it was pointed out, using the same model, that the equivalent energy of a calorimetric bomb depends upon the heat capacities of the distinguished bodies and the location of heat sources and temperature sensors.

The discussed two-body model of a concentric configuration, as well as more complicated models, were used for the determination of the static-dynamic properties of a number of calorimetric systems [1, 28, 29], and for the investigation of problems of thermostating calorimetric systems [30–33]. Among other things, the importance attached to the differential coupling of calorimetric systems [1, 34, 35] has been analyzed at full length. It was found out that if temperature fluctuations occur in the isothermal shield, even small differences in time constants for the calorimeters I and II can give rise to gross measurement errors if the temperature is taken by the differential method. This leads to the conclusion that the only correct method for using the differential calorimeter is that in which the calorimeter together with the thermally passive substance is nothing more than a passive witness of the temperature change in the surroundings.

The development of the multi-body theory, and creation of dynamic models of calorimeters by different means, will certainly contribute to the development of the theory of calorimeters. The theory, however, is not the aim in itself. Apart from the purity of the substance, the accuracy of choice of the object of thermochemical research and the application of measuring devices of high precision, it has become a topical question as to how to raise the accuracy of measurement through the choice of appropriate dependencies between the observed values in the course of calorimetric measurement and the thermal effect developed.

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RÉSUMÉ — Les propriétés dynamiques des calorimètres appelés non-isothermes/non-adiabatiques sont examinées dans cet article. Dans ces calorimètres, l'effet thermique étudié est, en partie, accumulée dans la cellule calorimétrique et, en partie, transmis à la gaine à température constante. On donne l'équation générale du bilan thermique et l'équation de la thermocinetique pour ce type de calorimètre. L'évolution de l'effet thermique Q pendant le temps t est exprimée en fonction des variations de température Θ du calorimètre en temps t. Les relations $Q(t) = f[\Theta(t)]$ sont données pour un calorimètre avec différentes configurations et différentes altérations mutuelles des sources de chaleur et des détecteurs de température. On donne également une application pratique des considérations présentées.

ZUSAMMENFASSUNG — Die Eigenschaften der sog. nicht-isotherm-nicht-adiabatischen Kalorimeter werden analysiert. In diesen Kalorimetern wird der ausgelöste thermische Effekt teils im Kalorimetergefäß gespeichert und teils dem Konstanttemperaturschild übertragen. Die verallgemeinerte Gleichung des Wärmegleichgewichts und die Gleichung der Dynamik werden für diesen Kalorimetertyp mitgeteilt. Die Abhängigkeit zwischen dem Verlaufe des thermischen Effektes Q in der Zeit t als Funktion der Temperaturänderungen Θ des Kalorimeters werden ebenfalls mitgeteilt. Die Abhängigkeiten $Q(t) = f[\Theta(t)]$ werden für ein Kalorimeter mit verschiedenen Bereichskonfigurationen, verschiedenen gegenseitigen Störungen der Wärmequelle und des Temperatursensors angegeben. Es wird auch die praktische Anwendung der beschriebenen Anordnungen gezeigt.

Резюме — Проанализированы динамические свойства так называемых неизотермических-неадиабатических калориметров. В таких калориметрах полученный термический эффект частично аккумулируется в калориметрическом сосуде, частично передается экрану с постоянной температурой. Для этого типа калориметров даны обобщенные уравнение теплового баланса и уравнение динамики. Зависимость хода термического эффекта Q за время t представлена как функция температурных изменений Θ калориметра. Приведены зависимости $Q(t) = f[\Theta(t)]$ для калориметра с различными конфигурациями сферы и с-различным взаимным нарушением тепловых источников и температурного сенсора. Приведено практическое применение представленных соображений.