THERMAL-DYNAMIC ANALOGY METHOD IN CALORIMETRY

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The paper describes the fundamentals and applications of the thermal-dynamic analogy method to analyze the course of heat effects occurring in calorimeters. The method is based on introduction to the heat effect analysis of the terms, notions and mathematical procedures used in the steering theory. It was pointed out that this method can well be applied for elaboration of mathematical models of various types of calorimeters. These models determine both the heat properties of calorimeters as well as the dynamic ones.

Keywords: *analysis of the course of thermal effects in calorimeters, mathematical models of calorimeters, thermal-dynamic analogy method*

Introduction

During over 200 years of the existence of calorimetry a great number of instruments have been constructed for determination of various heat effects. Along with the development of this measurement technique, also a number of mathematical models of calorimeters have appeared. They consist in presenting, in the form of an equation based on distinguished parameters of the system, of the dependence between a quantity measured in the calorimeter (e.g. temperature) and a quantity which is the aim of the measurement (heat power, total thermal effect). The latter form a basis for calculation of the generated heat effects. Mathematical models have been constructed to analyze the course of heat effects in time.

One of the most frequently used methods of analysis of heat effects occurring in the calorimeters is the thermal-electrical analogy method [1–10] based on similarity of the equations describing the heat conduction and electrical conduction. Such a study generally involves both the use of circuit theory and the principle of dimensional similarity. In order to analyze the course of heat effects (according to this model) in the calorimetric system it is necessary to determine the number of elements, their arrangement and the existing mutual interactions. In this way the so-called Beuken model [11] is constructed. Consequently, in this way the suitable system of heat balance equations was formulated.

During the last years the foundations were established for the use in calorimetry of another analogy method [12], namely the thermal-dynamic analogy method based on introduction into the heat effect analysis of the terms, notions and mathematical procedures used in the steering theory [13]. By using this method we obtain considerable information about calorimeters as dynamic objects. It also offers a possibility of analyzing the course of heat effects in time.

This work presents the fundamentals and way of applications of thermal-dynamic analogy in calorimetry, especially for analyzing the heat effects occurring in closed ('batch') calorimeters.

Fundamentals of thermal-dynamic analogy method

From the point of view of the heat transfer theory a calorimeter can be treated as a physical object with active sources of heat that act in it. The basis of description of thermal phenomena is the Fourier law and the Fourier-Kirchhoff equation. The mathematical models of calorimeters that are created are the result of detailed, usually very simplified, forms of this equation.

In the steering theory the calorimeter is treated as a dynamic object in which the generated heat effects characterized by the input signal {input signals, functions $y_1(t)$, $y_2(t)$, $\ldots y_n(t)$} can be transformed to the quantity measured directly in the calorimeter, e.g. temperature {output signals, functions $x_1(t)$, $x_2(t) \ldots x_n(t)$}. The relationship between input and output functions is accepted as the mathematical model of the calorimeter. To solve an adequate equation expressing the model the Laplace or Fourier transforms are used, whereas the transmittance is defined as a quotient of the transforms of output and input functions. In the transmittance the dynamic properties are encoded. The form of transmittance depends on the type of the dynamic object studied. Let us distinguish

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the following types of dynamic objects called open dynamic objects [13]:

- proportional, when the input function $y(t)$ is proportional to the output function $x(t)$:

$$kx(t) = y(t) \tag{1}$$

where: k – proportionality coefficient, whereas Laplace transmittance has the form

$$H(s) = \frac{1}{k} \tag{2}$$

- integrating, when the input function is proportional to the derivative of the output function

$$C\frac{\mathrm{d}x(t)}{\mathrm{d}t} = y(t) \tag{3}$$

whereas

$$H(s) = \frac{1}{Cs} \tag{4}$$

first order inertial, when the input function is the linear combination of the output function and its derivative

$$C\frac{\mathrm{d}x(t)}{\mathrm{d}t} + kx(t) = y(t) \tag{5}$$

whereas

$$H(s) = \frac{1}{Cs + k} \tag{6}$$

Let us ascribe the above-mentioned models of open dynamic objects to the groups of calorimeters distinguished in the classification, assuming the heat balance equation of a simple body (Eq. (7)) as a general mathematical model of calorimeters,

$$C\frac{\mathrm{d}T(t)}{\mathrm{d}t} + G[T(t) - T_0(t)] = \frac{\mathrm{d}Q(t)}{\mathrm{d}t} = P(t) \tag{7}$$

in which C is heat capacity, G is a heat loss coefficient, T is the temperature of the proper calorimeter (calorimetric vessel with contents), T_0 is the temperature of the shield which is a part that is functionally distinct from the proper calorimeter, $P(t)$ is heat power in time.

Equation (7) found a wide application in calorimetry and is well-known in the form of Tian-Calvet equation.

The first left-hand side term of Eq. (7) describes the quantity of heat accumulated throughout the time interval dt in the calorimetric vessel and constitutes a mathematical model applied in adiabatic calorimetry. It corresponds to the form of Eq. (3) describing the dynamic properties of integrating objects.

The second term of Eq. (7) describes the amount of heat exchanged between the calorimetric vessel and the surroundings. This term constitutes a mathematical model applied in the flux method. In this method it is assumed that the quantity of heat accumulated in the calorimetric vessel is extremely small and can be neglected. This term of Eq. (7) corresponds to the form of Eq. (1) describing the dynamic properties of proportional objects.

A mathematical description of the calorimeter expressing the first and second left-hand side terms of Eq. (7) corresponds to calorimeters in which the generated heat effect is partly accumulated in the proper calorimeter and is partly transmitted to the shield. One can easily notice that Eq. (7) has the same form as Eq. (5) describing the dynamic properties of inertial objects.

As can be noticed, the function $y(t)$ in Eqs (1), (3), (5) corresponds to the function $P(t)$ in Eq. (7), which is linear, ordinary, differential equation. For this kind of equations the principle of superposition can be applied. According to this principle the temperature response $T(t)$ of a calorimeter to the several heat powers generated $P_1(t)$, $P_2(t)$ …. $P_i(t)$ is equal to the sum of $T_1(t)$, $T_2(t)$ …. $T_i(t)$ temperature responses. It is independent on the place of generation of heat effect. That means that function $P(t)$ in Eq. (7) can express heat power (or heat powers) generated in calorimetric cell, or on calorimetric shield, or both. The $P(t)$ function can also be equal to the sum of: 1) the heat power generated by transformation studied, 2) the heat power involved in the calorimetric shield, causing the conditions of the process to be different from isothermal. In this last case the particular forms of function $P(t)$ (and similarly $y(t)$) describe the heat processes occurring the calorimeters of variable temperature of calorimetric shield e.g. scanning calorimeters.

Thereby it was demonstrated that open dynamic objects described the dynamic properties of considerable groups of calorimeters.

Of course not only the properties of open dynamic objects can be used in the consideration of dynamic properties of the calorimeters. For example, in the case of compensation calorimeters in $P(t)$ function, the compensating heat power causing that the difference of temperature between the calorimetric vessel is zero or constant in time, should be taken into account. In this case the dynamic objects in feed-back system are considered.

For the calorimeters in which external mass is introduced to the calorimetric vessel during the calorimetric determination, the heat balance equation is different from Eq. (7). Also, the dynamic properties for these systems are unlike those described above. This does not constitute an obstacle in using the thermal-dynamic analogy method. The terms, notions and mathematical procedures used in the steering theory and consequently in thermal-dynamic analogy method can be undoubtedly used for these purposes.

Dynamics equation

In calculations performed with the use of the thermal-dynamic analogy method very often the equations expressing the mathematical model of calorimeter are given in temperature dimension. These equations are called dynamic equations. In the case of Eq. (7) for this purpose one should divide both sides of this equation by G and put

$$\tau = \frac{C}{G} \qquad \frac{\mathrm{d}Q(t)}{\mathrm{d}t} = P(t) \qquad f(t) = \frac{1}{G}P(t) \tag{8}$$

where τ is a time constant, a decisive parameter for characterizing inertial properties of the calorimeter. Taking into account relations (8) in Eq. (7) it becomes

$$\tau\frac{\mathrm{d}[T(t)]}{\mathrm{d}t} + T(t) = f(t) + T_0(t) \tag{9}$$

The use of the Laplace transformation for Eq. (9)

$$L\left[\frac{\mathrm{d}[T(t)]}{\mathrm{d}t} + T(t)\right] = L[f(t) + T_0(t)] \tag{10}$$

gives the solution of Eq. (9) in the complex domain

$$(\tau s + 1)T(s) - \tau T(0) - T_0(s) = F(s) \tag{11}$$

which can be presented in the form

$$T(s) = \frac{\tau T(0)}{(\tau s + 1)} + \frac{F(s)}{(\tau s + 1)} + \frac{T_0(s)}{(\tau s + 1)} \tag{12}$$

Equation (12) is called the subsidiary solution of Eq. (9), where $T(s)$ is the response transform of output function, $F(s)$ and $T_0(s)$ are driving forces, $1/(\tau s+1)$ is the characteristic function of the object. Function $1/(\tau s+1)$ characterizes the dynamic properties of inertial objects. The first and third right-hand side terms of Eq. (12) being the function of initial conditions are the transforms of a transient solution. The second term, which is independent of initial conditions, represents the transforms of a steady-state solution.

The inverse Laplace's function defines function $T(t)$ characterizing the course of temperature changes of the calorimeter.

Models of calorimeters

The heat balance equation of a simple body is the basis of most methods of determining heat effects. However, in order to analyze the heat effects proceeding in calorimeters we have to use some more complicated models. The mathematical model expressed by Eq. (7) as it was shown in [12] is too simplified. And so: in 1941 King and Grover [14] and then Jessup [15] concluded that when using the mathematical model based on Eq. (7) the evaluated heat capacity of a calorimetric bomb as the sum of heat capacities of particular parts of the calorimeter was not equal to the experimentally determined heat capacity of the system. In calculations of heat capacity of a calorimetric bomb a dependence called the energetic equivalent was used. This dependence was introduced as a result of distinguishing in the calorimeter of two parts (domains) and of working out a mathematical model expressed by the heat balance equation of the second degree. Calvet and Prat [16] summarizing the works done in the Centre de Microcalorimétrie CNRS stated that the course of temperature of the short heat effect processes investigated in the Calvet microcalorimeter is multiexponential. Madejski *et al*. [17], demonstrated that when applying the heat equation of a simple body the relation of heat capacity to the time of generation of heat power was obtained. This effect was named the 'apparent heat capacity'. In all these cases there is more than one domain distinguished in the calorimeter. It can be assumed that each of those domains is described by the heat balance equation of a simple body. They were the subject of works applying the thermal-dynamic analogy method. In many cases it is sufficient to analyze a model of two or three domains. Thus for instance the basis for consideration was a calorimeter (Fig. 1) in which the following parts were distinguished: a calorimetric vessel containing a substance as one domain; an internal shield containing the vessel or thermopile junctions fixed to the vessel as the second domain; the whole device placed in an external shield, which is taken as the environment of a temperature T_0. In such a case the following parameters were distinguished: the heat capacity C_2 of the calorimetric vessel with its contents; the temperature of

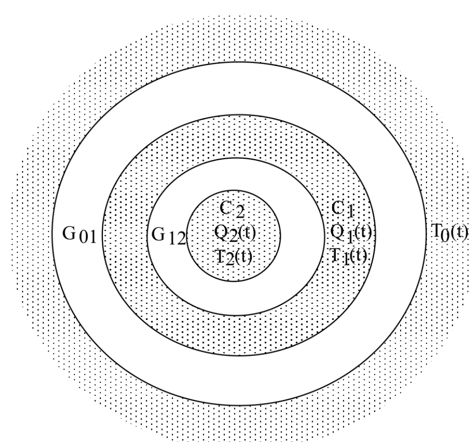

Fig. 1 Calorimeter as a system of two bodies of concentric configuration

this body $T_2(t)$; heat capacity of internal shield C_1 and temperature T_1. It is assumed that in the calorimetric vessel and in the internal shield there can exist heat sources, expressed by Q_2 and Q_1, respectively. The heat exchange between the calorimetric vessel and the internal shield of temperature $T_0(t)$ is characterized by the heat loss coefficient G_{12}, whereas the heat exchange between the internal shield and external shield – by the heat loss coefficient G_{01}. The performed calculations resulted in a dependence showing in what conditions it is necessary to use the energetic equivalent of the calorimeter instead of the method of corrected temperature rise in order to determine the total heat effects. It was also pointed out [12] that if temperature gradients occur in the calorimeter then the relation $T(t)=f[P(t)]$ is dependent on mutual distribution of heat sources and temperature sensors, and moreover it is not always enough to measure the temperature in one of the distinguished bodies. For this reason Zielenkiewicz and Tabaka [18–21] proposed a new method of reconstruction of $P(t)$ function using a multipoint temperature measurement in the calorimetric vessel.

While analyzing the course of heat effects in a calorimeter it is necessary to distinguish many domains in it. It is a great advantage of the thermal-dynamic analogy method that it allows one to determine heat effects and analyze the course of thermal effects in calorimeters with complex structures using the n-domains method. The method comprises procedures necessary to determine mathematical models of calorimeters with a significant number of parameters.

N-domains method

The basic postulates of the multi-domains (bodies) method are as follows. Each of the separate bodies has a uniform temperature in its entire volume; the temperature is a function of time t only, and the heat capacity of the body is constant. Temperature gradients appear only in the media separating the bodies, and the heat capacities of these media are by assumption negligibly small. The amount of heat exchanged between bodies through these media is proportional to the difference in the temperatures of the bodies; the proportionality constants are the appropriate heat loss coefficients. Furthermore, a heat source or a temperature sensor may be positioned in any of the bodies. The system of bodies is placed in a medium with a constant temperature. The generalized heat balance equation derived from these assumptions is:

$$C_{\mathrm{j}}\frac{\mathrm{d}T_{\mathrm{j}}(t)}{\mathrm{d}t}+G_{\mathrm{j}}^{0}[T_{\mathrm{j}}(t)-T_{0}(t)]+ \\ +\sum_{\mathrm{i}=1}^{\mathrm{N}}G_{\mathrm{j}}^{\mathrm{i}}[T_{\mathrm{j}}(t)-T_{\mathrm{i}}(t)]=P_{\mathrm{j}}(t) \tag{14}$$

$i\neq j$, j=1, 2, ..., N

Equation (14) in the temperature dimension has the form

$$\tau_{\mathrm{j}}^{0}\frac{\mathrm{d}T_{\mathrm{j}}(t)}{\mathrm{d}t}+T_{\mathrm{j}}(t)=\sum_{\mathrm{i}=1}^{\mathrm{N}}k_{\mathrm{ij}}T_{\mathrm{j}}(t)+\lambda_{\mathrm{j}}f_{\mathrm{j}}(t) \tag{15}$$

$i\neq j$, j=1, 2, ..., N

The set of differential Eq. (15) are called the general equation of dynamics, which assumptions are sufficiently to allow the calorimeter to have different configuration.

The following notions have been introduced in Eq. (14): an overall coefficient of heat loss, time constant of the domain, interaction coefficient, forcing function.

The overall coefficient of heat loss G_{j} for each of the domains is defined as

$$G_{\mathrm{j}}=\sum_{\mathrm{i}=0,\,\mathrm{i}\neq\mathrm{j}}^{\mathrm{N}}G_{\mathrm{ij}};\ j=1,2,...,\mathrm{N} \tag{16}$$

This coefficient characterizes the heat exchange between domain j and the surroundings but also between domains j and other domains.

The time constant τ_{j}^{0} of domain j is defined as the ratio of heat capacity C_{j} and overall coefficient of heat loss G_{j} of the domain.

$$\tau_{\mathrm{j}}^{0}=C_{\mathrm{j}}/G_{\mathrm{j}};\ j=1,2,...,\mathrm{N} \tag{17}$$

The time constant τ_{j}^{0} of domain j that is τ_{j}^{0}, is a measure of the thermal inertia of this domain in the system of domains.

The interaction coefficient k_{ij} is defined as the ratio of the heat loss coefficient G_{ij} to the overall coefficient of heat loss G_{j}

$$k_{\mathrm{ij}}=G_{\mathrm{ij}}/G_{\mathrm{j}};\ i=1,...,\mathrm{N};\ j=1,2,...,\mathrm{N} \tag{18}$$

This is a measure of heat interaction between the domain i and the domain j in relation to the interactions between the remaining domains and surroundings and the domain j. The interaction coefficients affect essentially the thermal inertia of the calorimeter and allow us to establish the structure of the dynamic model of a given calorimeter. If the value of the interaction coefficient k_{ij} is negligibly small, it may be assumed that there is no thermal interaction between domains i and j or, more exactly, that the thermal interaction between domains i and j is small enough to be ignored in comparison with the interaction between domains *i* and *j* and other domains and the surroundings.

Furthermore, the notion of the forcing function $f_j(t)$ – taken from the steering theory – was introduced into these considerations. This function is defined as

$$f_j(t) = \frac{1}{\lambda_j G_j} \frac{dQ_j(t)}{dt}; \quad j = 1, 2, ..., N \qquad (19)$$

or in the dimension of temperature

$$f_j(t) = \frac{1}{\lambda_j G_j} P_j(t); \quad j = 1, 2, ..., N \qquad (20)$$

As it results from the above considerations for the elaboration of the dynamic model it is necessary to calculate the heat capacities of the defined domains, heat loss coefficients and to determine the structure of the model. The elaboration of the model allows determination of the set of heat balance equations or the set of equations of dynamics. Determination of the transmittance for such a system is equivalent to the determination of a mathematical model of the calorimeter. It is assumed to be properly determined only when the optimization and stability conditions of the numerical solution are fulfilled. These conditions require admission of value of a sampling period which is obtained from the amplitude characteristics of the calorimeter, taking into account the noise-signal ratio. The optimal sampling period limits the smallest value of time constants. If any number of time constants of the calorimeter does not satisfy the stability condition, then the new model of the system must be worked out, decreasing the number of domains and calculating new parameters. The maximum order of the new model is limited by the number of time constants which satisfy the stability condition. N-body method was successfully applied to determine a mathematical model of the BMR [22, 23] calorimeter as well as the UNIPAN calorimeter [24]. The advantage of this manner of elaborating mathematical models of calorimeters is the determination of system parameters as the result of the determination of their values and relations between them and consequently, the possibility to optimize the construction of a calorimeter. Moreover, the knowledge of the structure and parameters of the calorimeter allows to distinguish in the mathematical model of parameters and structure the ‘changeable’ and ‘unchangeable’ parts of the calorimeter and ascribe the equations respectively. Let us assume that in our experiments the ‘unchangeable’ part of the calorimeter corresponding to an empty calorimeter remains constant. Whereas in the ‘changeable’ part there can occur changes in the heat capacity C_m. The form of a set of equations determined in these conditions indicates that for various heat capacities C_m, there is no need to change the mathematical model of the calorimeter, however, a change in the C_m calls only for introduction of new data in deconvolution program. This can be extremely useful when heat capacities of the calorimetric vessel contents change during the experiment, e.g. in the titration process.

References

1 J. Rouquerol and P. Boivinet, Calorimetric Measurements in Differential Thermal Analysis, Vol. 2, Ed. R.C. Mackenzie, London, New York, 1972.
2 H. Maurus and C. R. Hebd, Séance. Acad. Sci., Paris, 261 (1965) 3103.
3 R. A. Arndt and F. E. Fujita, Rev. Sci. Instrum., 34 (1963) 868.
4 E. Calvet, J. Chim. Phys., 59 (1962) 319.
5 F. W. Wilburn, J. R. Hesford and J. R. Flower, Anal. Chem., 40 (1968) 777.
6 M. M. Nicolaus, Thermochim. Acta, 151 (1989) 345.
7 T. Ozawa and K. Kanari, Thermochim. Acta, 288 (1996) 39.
8 P. Claudy, J. Commercon and J. M. Letoffe, Thermochim. Acta, 65 (1983) 245.
9 P. Claudy, J. Commercon and J. M. Letoffe, Thermochim. Acta, 68 (1983) 305.
10 P. Claudy, J. Commercon and J. M. Letoffe, Thermochim. Acta, 68 (1983) 317.
11 C. L. Beuken, Dissertation, Saechs, Berakademie Freiberg, Berlin, 1936.
12 W. Zielenkiewicz and E. Margas, Theory of Calorimetry, Kluwer Academic Publishers B. V., 2002.
13 D. P. Campbell, Process Dynamics, John Wiley and Sons Inc., New York, 1958.
14 A. King and H. Grover, J. Appl. Phys., 13 (1941) 129.
15 R. S. Jessup, J. Appl. Phys., 13 (1942) 29.
16 E. Calvet and H. Prat, Microcalorimétrie, Applications Physico-chimiques et biologiques, Masson, Paris, 1956.
17 J. Madejski, E. Utzig and W. Zielenkiewicz, Bull. Acad. Polon. Sci., Ser. Sci. Chim., 16 (1970) 275.
18 W. Zielenkiewicz and A. Tabaka, Bull. Acad. Polon. Sci., Ser. Sci. Chim., 28 (1980) 727.
19 W. Zielenkiewicz and A. Tabaka, Bull. Acad. Polon. Sci., Ser. Sci. Chim., 29 (1981) 41.
20 W. Zielenkiewicz and A. Tabaka, Bull. Acad. Polon. Sci., Ser. Sci. Chim., 29 (1981) 51.
21 W. Zielenkiewicz and A. Tabaka, Bull. Acad. Polon. Sci., Ser. Sci. Chim., 29 (1981) 61.
22 A. Zielenkiewicz., Bull. Acad. Polon. Sci., Ser. Sci. Chim., 21 (1973) 333.
23 E. Cesari, J. Hatt, E. Margas, J. Navarro, E. Utzig and W. Zielenkiewicz, Bull. Acad. Polon. Sci., Ser. Sci. Chim., 28 (1980).
24 J. Hatt, E. Margas and W. Zielenkiewicz, Thermochim. Acta, 64 (1983) 305.

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