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How do the mathematical models of calorimeters really work?

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Abstract

In the paper methods of the analysis of heat effects occurring in the calorimeter as well as mathematical models applied for the determination heat effects involved in these devices are discussed. It was demonstrated that often mathematical models of the determination of heat effects are rather poor. Whereas, more sophisticated, existing models are relatively rarely used in calorimetric practice. The range of application of thermal–electrical and thermal–dynamic analogy methods were presented.

Keywords: Calorimeters; Models

1. Introduction

Without any doubt in the last decades a great progress in calorimetric techniques was observed. It resulted mainly from the application of modern electronic devices, automation and computerization of measurements, minimalization of sample used and inertia of devices.

Calorimetry has been enriched by the new techniques extending the measurement possibilities for both low and high temperature and pressure ranges.

Several techniques with use of laser technologies have appeared; the number of targets for calorimetric studies has been enlarged including living organisms, drugs, food and environment.

Numerous specialized companies producing the calorimeters causes spreading application of calorimetric methods. It is especially visible in differential scanning calorimetry domain.

It should not be forgotten that at present days calorimetry is not only method, that allows obtaining thermodynamic data. Ribeiro da Silva [1] under the term "molecular thermochemistry" enumerates several non-calorimetric methods concerned with the study of thermodynamic stability and chemical bonds.

The success of non-calorimetric methods in my opinion lies predominantly with sophisticated elaboration of measurement signal.

The progress in calorimetric methods in this way is also possible. It requires undertaking an effort in elaboration and practical applications of more precise methods of description of the heat processes occurring in the calorimetric systems.

The present work is devoted to elaborate on these issues. They are also described in the recently published monograph [2].

2. Calorimetric methods of measurements based on heat balance equation of simple body

Currently in calorimetry, almost all methods for determination of heat effect are based on the mathematical model expressed by the linear, ordinary, first-order differential equation of constant parameters as well as its simplified forms.

Let us describe this equation in the form of the heat balance equation of simple body:

$$C\frac{\mathrm{d}T(t)}{\mathrm{d}t} + G[T(t) - T_0(t)] = \frac{\mathrm{d}Q(t)}{\mathrm{d}t} \tag{1}$$

or after integration in the form

$$C\mathrm{d}T(t) + G[T(t) - T_0(t)]\mathrm{d}t = \mathrm{d}Q(t) \tag{2}$$

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where C is heat capacity of the calorimeter, G is heat losses coefficient, T is temperature of calorimetric cell, T_0 is environmental temperature (temperature of calorimetric jacket/shield) and t is time. The first term of the left-hand of Eq. (1) describes the quantity of heat accumulated throughout the time interval $\mathrm{d}t$ 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 $\mathrm{d}Q(t)$ released throughout the time interval $\mathrm{d}t$ (changes of heat power within time, function called thermokinetics).

It is evident that: (1) the first term of the left side of Eq. (1) constitutes mathematical model applied in adiabatic method of measurements. In this case, it is assumed that only heat accumulation occurs in the proper calorimeter, whereas the second left-hand term of Eq. (1) is neglected; (2) the second term of the left side of Eq. (1) constitutes mathematical model applied in flux method. In this method, it is assumed that quantity of heat accumulated in the calorimetric vessel is extremely small and generated heat effect correspond to the amount of heat exchanged between the calorimetric vessel and the surroundings; (3) both terms of left hand of Eq. (1) constitutes mathematical model applied in dynamic method of measurement. The Eq. (1) is equivalent to the Tian–Calvet equation.

Adiabatic, flux and dynamic methods are applied in isoperibol as well as in scanning calorimeters. In these cases only change is related with the form of the T_0 function (isoperibol calorimeters, $T_0 = \text{constant}$; scanning $T_0 = at$) in Eq. (1).

In the case of total heat effects, Eq. (2) is often used among others in the method of the corrected temperature rise called often Regnault–Phaundler correction method, well known from application in "isoperibol" calorimeters.

There exist other measurement methods based on the described model of the calorimeter. Most of them similarly as in the case of scanning calorimeters, results from the principle of superposition, which is applied to all linear systems.

This principle can be formulated as follows: the temperature response $T(t)$ of a linear systems to the several heat effects generated $Q_1(t), Q_2(t), \ldots, Q_i(t)$ is equal to the sum of $T_1(t), T_2(t), \ldots, T_i(t)$ responses of the calorimeter to all individual heat effects generated in the calorimetric system. The application of this principle is independent on the place of generation of heat effect. It can be the heat effect (or heat effects) generated in calorimetric cell or on calorimetric shield or both in calorimetric cell and calorimetric shield. Such calorimetric model describes the modulating method used in scanning calorimeters; this method comes from AC isothermal calorimeters.

The principle of superposition is also applied to various methods in which the heat generated during the process examined is compensated by generated heat power (involved by heat-pulses or use proportional compensation, others).

Sum up, the mathematical model presented by Eq. (1) and their simplified forms are used in the following methods of the determinations of heat effects:

Adiabatic	Scanning adiabatic
Dynamic (isoperibol)	Scanning dynamic
Flux	Flux DSC
AC	Modulating
Compensation	DSC compensation

It can be noted, that methods basing on Eqs. (1) and (2) or its simplified forms are used in calorimetry for a very long time: method of corrected temperature rise—since more than hundred years, adiabatic method—since about 100 years. Between presented methods, there are new ones (like modulating method) or those, which became very important, like conduction method, in a period of last 20 or 30 years.

This model is rather poor. As it was shown in [2], the correct use of this equation take place when: (1) the process takes place in isobaric conditions; (2) thermal conductivity coefficient λ, specific heat capacity at constant pressure C_p and density ρ are constants, independent of both pressure and temperature; (3) velocity vector is equal zero; (4) temperature in total volume of the body (proper calorimeter) is homogeneous and only the function of time; (5) temperature on the whole surface of the body (proper calorimeter) is homogeneous and only the function of time; (6) the above temperatures are identically equal one to another, that are the same in each time moment; (7) heat capacity C and heat losses coefficient G are constants and not functions of time and temperature.

Some of those conditions are very difficult or impossible to met. Without doubt, the most hard is the one which requires homogeneity and identity of temperature in total volume and on whole surface. It is hard to assume that in the calorimeter there are no thermal resistances and thermal bridges and that imperfect contact between touching surfaces does not cause the lack of thermal equilibrium and presence of temperature difference.

It has long been known in calorimetry about the difficulties in realizing these conditions. And so, in 1941, King and Grover [3] concluded that according the method of corrected temperature rise evaluated heat capacity of a calorimetric bomb as the sum of the heat capacities of particular parts of the calorimeter was not equal to the experimentally determined heat capacity of the system; Calvet [4] distinguished μ_0 and μ_∞ heat capacities of calorimeter; Madejski, Utzig and Zielenkiewicz demonstrated that applying the model expressed by Eq. (1), it is possible to obtain the relation of the heat capacity to the time of generation of a constant-power Joule's effect [5]; there exist also a great number of papers devoted to the analysis of the sources of errors in the determination of the heat effects in DSC devices based in which the heat effects ate determined using discussed model.

There is one more cause of the poorest of the model described by Eq. (1). This is the existence of temperature difference between the temperature of calorimetric cell and shield temperature. The better is the heat exchange proper calorimeter-surroundings the temperature difference is higher. According to the Boussinesque theorem as well as general solution of Fourier equation [2], in the case of temperature gradient between proper calorimeter and surroundings, the temperature $T(x, y, z, t)$ changes at any point of the proper calorimeter:

$$T(x, y, z, t) = \sum_{n=1}^{\infty} A_n u_n(x, y, z) \mathrm{e}^{-\beta_n t} \tag{3}$$

or

$$T(x, y, z, t) = \sum_{n=1}^{\infty} A_n u_n(x, y, z) \mathrm{e}^{-t/\tau_n} \tag{4}$$

is the sum of infinite number of exponential functions. The sequence of time constants $\tau_1, \tau_2, \tau_3, \ldots, \tau_n$ is the sequence monotonically decreasing. As more accuracy of determination of temperature $T(x, y, z, t)$ is needed, the bigger number of exponential terms must be used. In the limiting case, it is possible to neglect all the exponential terms excluding the one having in the exponent the value of the τ constant.

Such a course of temperature changes occurs, e.g. in conduction calorimeters. The assumption, that $T(t)$ function represents the course of heat power in time is not always correct. This occurs only in the case of slow enough heat changes. Generally, calorimeter can not be treated as a device in which the measure “heat flow” which if often suggested nowadays.

3. Methods of determination of heat effects based on linear differential equation of *N*-order

For the first time for description of the short duration heat processes, investigated in the Calvet microcalorimeter, Camia [4] proposed the following equation:

$$T = \Delta Q (a_1 \mathrm{e}^{-\omega_1 t} + a_2 \mathrm{e}^{-\omega_2 t} + \ldots) \tag{5}$$

This equation demonstrate, that the Calvet microcalorimeter was described by the linear differential equation of second or higher order.

Then, several mathematical models of calorimeters based on linear differential equations of higher that first-order have been subsequently created. The common basis of the elaborated models is the acceptance of a number of general assumptions, which are as follows.

Generally, calorimeter is treated as an object described by N-order linear differential equation.

$$A_N \frac{\mathrm{d}^N T(t)}{\mathrm{d}t^N} + \ldots + A_1 \frac{\mathrm{d}T(t)}{\mathrm{d}t} + A_0 T(t) = b_0 P(t) + b_1 \frac{\mathrm{d}P(t)}{\mathrm{d}t} + \ldots + b_m \frac{\mathrm{d}^m P(t)}{\mathrm{d}t^m} \tag{6}$$

where t is time, T is temperature, P is heat power, and $A_N, \ldots, A_0, A_1, b_0, b_1, \ldots, b_m$ are coefficients. It is assumed that the calorimeter is a linear and stationary object; and object of exactly defined initial conditions.

As can be seen, mathematical model expressed by Eq. (6) is a model of an infinite order. In fact, it is necessary to limit the order of this equation. Generally, this is due to the compromise between the available information and the possibility of applying it.

The way in which the equation is applied while the transformation equation of a calorimeter is being formulated differs depending on the methods used. There are the mathematical models based: (1) on physical parameters of the calorimetric system, e.g. method of finite elements [6], multidomains method; (2) on neglecting the physical parameters of the system, e.g. harmonic analysis method [7–9], optimalization method [10–12], method of state variable [13–15], the inverse filter method [16,17].

The evaluation of the presented methods was made more than 20 years ago [2]. It was stated “it is clear that the objective is not complete reconstruction of thermokinetics, but rather decrease of the influence of thermal lags in calorimetric data; thus after reconstruction, the residual time constant which appears in the data is ∼200 times smaller than actual 1st order time constant of the instrument used”.

In others words, it means that in the conduction calorimeter having the time constant of 60 s, the use of discussed methods allows to apparently lower the time constant to $60/200 = 0.3$ s.

Despite undoubful advantages of these numerical methods, they did not find enough wide applications in the determinations of thermokinetics, particularly, kinetic investigations of fast reactions. Also the advantages of the multibody method [8,9] based on knowledge of physical parameters of particular distinguishing parts of the calorimeter, treated as a system of various configuration were not widely applied. This method should be enormously useful in the determinations, in which there takes place a change of physical parameters of the calorimeter during the calorimetric measurements, e.g. in titration calorimeters. So far the biggest practical application in the reconstruction of thermogram has the inverse filter method. This method is based on the assumption that the time constants of the calorimeter being inertial object have been determined previously. For example, when the calorimeter is treated as a object of second order, the relation between $P(t)$ and $T(t)$ can be expressed according to Eq. (6) in the form of the following differential equation:

$$A_2 \frac{\mathrm{d}^2 T(t)}{\mathrm{d}t^2} + A_1 \frac{\mathrm{d}T(t)}{\mathrm{d}t} + T(t) = bP(t) \tag{7}$$

Using Laplace transformation and replacing the coefficients A_1 and A_2 by the time constants τ_1 and τ_2 of the calorimeter: $\tau_1 + \tau_2 = A_1$; $\tau_1 \tau_2 = A_2$, Eq. (8) becomes:

$$T(s) = \frac{1}{\tau_1 s + 1} \frac{1}{\tau_2 s + 1} bP(s) \tag{8}$$

The purpose of the inverse filter method is the application of a procedure which allows elimination of the influence of inertia units in the determination of the relation between $T(s)$ and $P(s)$, and thus, that between $T(t)$ and $P(t)$. It consists in the introduction (by the numerical or analogue method) of terms $\tau s + 1$ providing inverse function to the terms $1/(\tau s + 1)$. In the case, an individual corrector becomes:

$$T'(s) = \frac{b(\tau' + 1)}{(\tau_1 s + 1)(\tau_2 s + 1)} P(s) \tag{9}$$

In the case of two correctors becomes:

$$T''(s) = \frac{b(\tau' s + 1)(\tau'' s + 1)}{(\tau_1 s + 1)(\tau_2 s + 1)} \tag{10}$$

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

$$T'' \cong P(s) \tag{11}$$

In practical application of the inverse filter method on numerical way thermal, electrical analogy method is often used.

4. Thermal–electrical analogy method

This method analogy is based on the similarity of the equations describing the heat conduction and electrical conduction. Such a study generally involves both the use of circuit theory and principle of dimensional similarity.

In a corresponding network analogue the thermal resistances and capacities are simulated respectively by electrical resistors and capacitors. In constructing such circuits, it is considered that there is an equivalence between the quantities: electric current and heat flow; electric voltage difference and temperature difference; electric resistance and thermal resistance; electric capacity and heat capacity.

For example: (1) J. Rouquerol and P. Boivinet in book “Differential Thermal Analysis” [18] presented analogues of electric circuits for following heat-flux and power compensation devices: the conventional DTA instrument of Mauras, differential scanning microcalorimeter of Arndt and Fujita, the Tian–Calvet microcalorimeter; (2) Wilburn et al. [19] use both passive and active analogs to investigate the effect of holder design on the shape of DTA peaks; (3) thermal–electrical analogy for analyzing the problem of reconstruction of heat flux curve was applied Nicolaus [20]; (4) Ozawa and Kanari in [21] illustrate the discussed heat balance equations for constant heating rate DSC by an equivalent electrical circuit; (6) The method of analogy is used in the paper of Claudy et al. [22–24].

The thermal-electric analogy method is useful to represent the accepted structures, that distinguish the domains and way of their connection with themselves and the environment. Simultaneously, it is also useful to formulate the suitable system of the balance equations for the bodies (domains). The increase of the number of its applications has been related to the development of the analogue computer calculation methods.

5. Thermal–dynamic analogy method

There is another method allowing the relatively simple analysis of the course of heat effects within time. This is thermal–dynamic analogy method. It has advantage to apply the known from theory of steering terms and relations applied in the analysis of the course of heat effects involved. The similarity of the terms and equations used in heat transfer theory and steering theory was demonstrated in the presented “dictionary” of thermal–dynamic analogy method (Table 1).

Thermal–dynamic analogy method find the large application for analysis of heat effects of calorimeters based on multibody method, in which physical parameters of distinguished parts of device were distinguished. In this way the simple calorimetric system weres analysed, in which

Table 1
Dictionary of thermal–dynamic analogy method

Calorimetry	Steering theory
Calorimeter	Dynamic object
Heat Q generated in the calorimeter in the time t	Input function $y(t)$
Quantity directly measured in the calorimeter, e.g. temperature in time T	Output function $x(t)$
$Q(t) \rightarrow$ equation$\rightarrow$ $T(t)$	$y(s) \rightarrow$ transmittance $\rightarrow$ $x(s)$ transmittance $H(s) = x(s)/y(s)$
Heat balance equation of simple body $C(\mathrm{d}T(t)/\mathrm{d}t) + G[T(t) - T_0(t)] = \mathrm{d}Q(t)/\mathrm{d}t$ (dynamic method)	Inertial object $C(\mathrm{d}x(t)/\mathrm{d}t) + k(x) = y(t)$ of transmittances: $H(s) = 1/(Cs + 1)$ or $H(j\omega) = 1/(Cj\omega + 1)$
Accumulation term of heat balance equation $C(\mathrm{d}(T)/\mathrm{d}t) = \mathrm{d}Q(t)/\mathrm{d}t$ (adiabatic method)	Integrating type object $C(\mathrm{d}(x)/\mathrm{d}t = y(T)$ $H(s) = 1/Cs$ or $H(j\omega) = 1/Cj\omega$
Heat exchange term of heat balance equation $G[T(t) - T_0(t)] = \mathrm{d}Q(t)/\mathrm{d}t$ (flux method)	Proportional object $kx(t) = y(t)$ $H(s) = 1/k$ or $H(j\omega) = 1/k$
Short duration heat effect of relatively high amplitude	Unit pulse function (impulse function, Dirac function)
Constant heat effect in time	Unit step function
Heat effect that is constant in time over a determined interval of time	Input step function
Heat effect rising linear in time	Ramp function
Heat effect of periodically change	Period input function

two or three domains of differently located heat sources and temperature sensors were distinguished as well as the calorimetric systems of great numbers of domains The application of this analogy method in the multibody method of the determination of heat effects in elaboration of various types of calorimetrers was in detail demonstrated in monograph “Theory of Calorimetry” [2]. May be its application will be helpful in development of new calorimetric methods of heat determinations.

References

[1] M.A.V. Ribeiro da Silva, IUPAC Provisional Recommendations for the Terminology of the Thermochemistry of Chemical Reaction: Nomenclature, Symbols and Experimental Methods for the Determination of Bond Energies, 2002.

[2] M.W. Zielenkiewicz, E. Margas, Theory of Calorimetry, Kluwer Academic Publishers, Dordrecht/Boston/London, 2002.

[3] A. King, H. Grover, J. Appl. Phys. 13 (1941) 129.

[4] E. Calvet, H. Prat, Microcalorimetrie, Masson et C^{ie}, Paris, 1956.

[5] J. Madejski, E. Utzig, W. Zielenkiewicz, Bull. Acad. Polon. Sci. 16 (1968) 275.

[6] N. Davis, R.L. Berger, Biochem. Biophys. Methods 6 (1982) 205.

[7] W. Zielenkiewicz (Ed.), Thermokinetics, Signal Processing in Calorimetric System, Ossolineum, Wroclaw, 1990.

[8] J. Hatt, E. Margas, W. Zielenkiewicz, Thermochim. Acta 64 (1983) 305.

[9] W. Zielenkiewicz, E. Margas, J. Hatt, Thermochim. Acta 88 (1985) 387.

[10] J. Gutenbaum, E. Utzig, J. Wiśniewski, W. Zielenkiewicz, Bull. Acad. Polon. Sci. Ser. Sci. Chim. 24 (1976) 193.

[11] J. Gutenbaum, E. Utzig, J. Wiśniewski, W. Zielenkiewicz, IV Conference Internationale de Thermodynamique Chimique, Montpellier 9 (1975) 144.

[12] J. Gutenbaum, E. Utzig, J. Wiśniewski, W. Zielenkiewicz, in: Proceedings of the First. National Conference on Calorimetry, Zakopane, Poland, 1973.

[13] C. Brie, M. Guivarch, J.L. Petit, in: Proceedings of the First International Conference on Calorimetry and Thermodynamics, Warsaw, Poland, 1969 (PWN (1971) 73).

[14] C. Brie, J.L. Pelit, P.C. Gravelle, J. Chim. Phys. 70 (1973) 1107.

[15] R. Point, J.L. Pelit, P.C. Gravelle, J. Therm. Anal. 11 (1977) 431.

[16] R. Point, These, Nr. 327, Lyon, France, 1978.

[17] Y. Thouvenin, C. Hinnen, A. Rousseau, Actes du Colloque CNRS 156, CNRS ed., Paris, vol. 65, 1967.

[18] J. Rouquerol, P. Boivinet, in: R.C. Mackenzie (Ed.), Calorimetric Measurements in Differential Thermal Analysis, vol. 2, London, New York, 1972.

[19] F.W. Wilburn, J.R. Hesford, J.R. Flower, Anal. Chem. 40 (4) (1968) 777.

[20] M.M. Nicolaus, Thermochim. Acta 151 (11989) 345.

[21] T. Ozawa, K. Kanari, Thermochim. Acta 288 (1996) 39.

[22] P. Claudy, J. Commercon, J.M. Letoffe, Thermochim. Acta 65 (1983) 245.

[23] P. Claudy, J. Commerconm, J.M. Letoffe, Thermochim. Acta 68 (1983) 305.

[24] P. Claudy, J. Commercon, J.M. Letoffe, Thermochim. Acta 68 (1983) 317.