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PLENARY LECTURES

CALORIMETRIC MODELS

Theory and application

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The basis of the determination of mathematical models of calorimetic systems is presented. Examples of applications of these models are given for the elaboration of a classification of calorimetric systems; the analysis of the course of heat effects in calorimeters; the analysis of dynamic properties: and the analysis of total heat effects and thermokinetics. Special attention is paid to the application of the multi-body method for the construction of mathematical models of calorimetic systems.

This work concerns mathematical models of calorimetric systems. It will deal with theoretical work from the field of calorimetry and thermal analysis; the search for the relations between the function describing the examined heat effect and the function describing the system response to a given applied effect; and the search for this relation by determining the set of parameters which decide the formalization of the mathematical model, and the dependences between them. In order to locate these notions

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in calorimetric problems, let us consider the process of introducing experimental facts into the theory, in the case of the calorimetric system, a physical system. In general, we can assume that the calorimeter is a device for the determination of heat effects of various transformations. With respect to the fact that heat energy is not a directly measured physical magnitude, the calorimetric measurement does not give a direct measure of the energetic transformation, and treatment of the calorimetric data is necessary. The fundamental condition for the proper treatment of the data is the knowledge of the calorimeter behavior, that is the changes of state due to energetic transformations. A set of statements about the possible behavior (changes of the calorimetric state), which gives the theory of calorimetric measurements, can be obtained from an analysis of the relations binding together the state variables – measurable parameters which characterize the calorimetric properties. The quantitative determination of the relation between the state variables is the domain of thermodynamics. The only possibility for the determination of heat energy on the basis of the first law of thermodynamics is when the remaining forms of energy are known. Therefore, it is necessary to formulate a thermodynamic description between the heat and inner energy based on the theory of heat exchange. Furthermore, if we are interested in the course of the changes of heat processes within time, it is important to learn the dynamics of the processe.

Formalization of calorimetic model

The dependence which in the most general way describes the relation between the efficiency of heat sources, the measured temperature and the heat parameters of the system is the Fourier-Kirchhoff equation, complemented, with respect to mass transport, by the Navier-Stokes equation and the continuity of flux equation. With the initial and boundary conditions determined, this equation gives more information about the system. The Fourier-Kirchhoff equation is the basis of a number of calorimetric publications; for example, the papers by Laville [1] and Camia [2] treat general problems of calorimetry, while from the other side the papers by Tanaka, Amaya and Hattori [3, 4] treat the problems of the determination of particular heat effects. Such work is now not at the centre of interest of articles on mathematical models of calorimetric systems. When determining the particular forms of solutions of the Fourier-Kirchhoff equation, we have to deal with strictly mathematical problems (the solution of nonlinear equations), which in many cases makes analysis of the problem complicated or even impossible. In this situation, the arbitrary contraction to a set of parameters which are the most important from the point of view of the process studied is possible and is often used [5]. These types of models are mostly constructed on the basis of sets of heat balance equations [6]. From the heat parameters of the system, the following are distinguished; heat capacities, heat loss coefficientes; the input function is heat power; the output function which is measured is the temperature. It is assumed then that the calorimetric system is a system of several bodies (domains) of uniform temperature; temperature gradients occur only between bodies and are characterized by heat loss coefficients. It is also assumed that in each of these bodies a heat effect can be generated and the temperature can be determined. In the simplest case we use the heat balance equation of the simple body. In other cases, in many problems of modern calorimetry, we are dealing with a system of equations of several bodies. Application of these equations is very convenient, because the possibility of the experimental identification of domains in the calorimetric system can be shown [5]; the set of physical parameters is not large and can be determined [5]: according to the circuit theory, the electric-heat analogy allows [7] the identification of accumulation terms and terms describing the heat exchange giving the pendants of resistance and heat capacity.

The third way to construct mathematical models of calorimetric systems (the most simplified and poorest) is to use the "black box" notion, in which it is assumed that the calorimeter is a linear and stationary object with exactly defined conditions; a stationary object with the same values of parameters during the calibration as during the determination of the output function. Identification of the physical parameters of the system is neglected. This manner of constructing calorimetric models has mostly been used for the determination of thermokinetics. Practically, it is not useful for the analysis of heat courses.

Analysis of heat effect courses

Calorimetric models based on heat balance equations for multi-body systems are used for the analysis of heat effect courses in calorimeters, especially in nonisothermal-nonadiabatic calorimeters [8, 9]. These are the systems in which the calorimetric vessel containing the examined object is placed in the shield of constant temperature. For this type of system, the method of quantitative analysis of the influences of external disturbances on the accuracy of the calorimetric measurement has been elaborated. This analysis has been carried out for simple and differential calorimetric systems [10, 11]. Analysis of the mutual localization of the heat sources and temperature sensors for the calorimeter treated as a system of two or of three bodies [12, 13] with a concentric configuration has been performed. It has been considered to what degree the time characteristics of the calorimetric systems depend on the mutual localization of the heat sources and temperature sensors [14, 15]. Depending on the mutual localization of the heat sources and temperature sensors, various measuring curves are obtained. The relationships between the temperatures of the distinguished bodies the generated heat effects take various forms [12, 16]. For some cases of the mutual localization of the source and sensor it is impossible to determine the heat power on the basis of the temperature measurement of only one body. Because of this, a new method for the reconstruction of heat power [17] was proposed. It was shown that for these systems the heat capacity must not be the algebraic sum of the heat capacities of the distinguished bodies, but their linear combination [18]. This surprising conclusion explains the phenomenon of the change of heat capacity, which was experimentally observed by King and Grover [19], Jessup [20], West and Churney [21], Calvet and Prat [22] and Madejski, Utzig, Zielenkiewicz [23]. Mathematical models of calorimetric systems have been elaborated for several calorimeters [24–27] and used for the optimization of calorimetric construction and the determination of thermokinetics.

Reconstruction of thermokinetics

The important domain of the application of calorimetric models is the determination of thermokinetics, i.e. the function describing the changes of heat power in time [5]. The determination of this function involves the fact that each calorimetric measurement in which thermokinetics is determined is a source of kinetic information. The need to determine this function is closely related to particular interests of many fields of science: physical chemistry; biology, biochemistry, medical science and materials science. The determination of this function is used for the determination of the kinetic parameters of different chemical reactions; it is applied to examine the metabolism of various living systems; the growth of bacteria and plants; and thermal changes in human blood. Practically, various types of calorimeters are used to determine the thermokinetics. A large number of publications concern conduction calorimeters. A mathematical model based on the simple body heat balance equation has been used for the reconstruction of thermokinetics by Swietosławski an Salcewicz, Calvet and others. A great number of articles relate to mathematical models based on the "black box" notion. This type of model gives the basis for the method of reconstruction of thermokinetics, e.g. the harmonic analysis method [28], state variable method [29], dinamic optimization method [30], inverse filter method [31], automatic compensation method [32] and finite elements method [33].

One of the most useful methods of reconstruction of thermokinetics is the multi-body method [25]. This is based on the knowledge of the physical parameters of the calorimetric system. As demonstrated experimentally [34], this method is very convenient and allows a distinction between the changeable and nonchangeable parts of calorimeters; this indicates that, for various capacities of the calorimetric vessel, there is no need to change the mathematical model of the calorimetric system, but a change in the value of the heat capacity of the calorimetric vessel calls for an introduction into the input data of the program. This method is computerized and used for the determination of various heat effects. It has been successfully applied to determine the thermokinetics in calorimetric systems in which changes in heat capacities take place.

Evaluation of numerical methods of reconstruction of thermokinetics is the subject of many papers [35]. By carrying out the same type of measurement series or an investigation of the kinetic limits [36] and the signal-to-noise ratio one can determine the dynamic possibilites of a calorimetric system.

Identification of model parameters

Application of the mathematical model allows the treatment of calorimetric systems as dynamic objects. For this purpose it is necessary to determine the dynamic parameters, precisely i.e. the time constants of the calorimetric system. In the past few years, a significant development can be observed in the field of identification methods, which permit:

1. the determination of the zeros and poles of the transmittance on the basis of the assumed form of the pulse response and the accepted criterion of fitting it to the "experimental" pulse response;
2. the determination of the poles and zeros of the transmittance on the basis of the equation describing the system and the corresponding equation of the pulse response by the modulating function method;

3. the approximation of the transmittance by the rational function by the Pade method;

4. the determination of the poles and zeros of the transmittance on the basis of frequential characteristics.

For the methods of determining the model parameters, the following should be considered: Pades approximation method [37], the modulating function method [38], the frequential analysis method [39, 40], the time analysis method [15, 27, 41], the least squares method [42] and the multi-body method [6, 24, 43]. Additionally, different techniques of calculating the values of the parameters are elaborated in each of these methods.

References

1 G. Laville, C. R. Acad. Sci., 240 (1955) 1060; ibid., 240 (1955) 1195.
2 F. M. Camila, Traité de thermocinétique impulsionelle, Dunod, Paris, 1967.
3. S. Tanaka and K. Amaya, Bull. Chem. Soc., Japan. 43 (1970) 1032.
4 M. Hattori, K. Amaya and S. Tanaka, Bull. Chem. Soc., Japan, 43 (1970) 1027.
5 W. Zielenkiewicz, J. Thermal Anal., 29 (1984) 179.
6 E. Margas and W. Zielenkiewicz, Bull. Acad. Polon. Sci., Ser. Sci. Chim., 26 (1978) 503.
7 C. L. Beuken, Wärmeverluste bei periodisch betriebenen elektrischen Öfen; eine neue Methode zur Vorausbestimmung, Triltsch und Hunter, Berlin 1936.
8 J. Rouquerol and W. Zielenkiewicz, Thermochim Acta, 109 (1986) 121.
9 W. Zielenkiewicz and E. Margas, Naucznaja Apparatura-Scientific Instrumentation, 1 (1986) 55.
10 W. Zielenkiewicz, Analysis of the thermal processes occurring in nonisothermal-nonadiabatic calorimeter, PWN, Warsawa, 1966.
11 E. Margas, W. Zielenkiewicz and A. Zielenkiewicz, Bull. Acad. Polon. Sci., Ser. Sci. Chim., 18 (1970) 271; ibid., 18 (1970) 277.
12 W. Zielenkiewicz, E. Margas and A. Tabaka, Coll. Intern de Thermochimie, Marseille, 1971, Thermochimie CNRS, Nr 201, 153.
13 E. Margas, A. Tabaka and W. Zielenkiewicz, Bull. Acad. Polon. Sci., Ser. Sci. Chim., 20 (1972) 323; ibid., 20 (1972) 329.
14 E. Margas and W. Zielenkiewicz, Bull. Acad. Polon. Sci., Ser. Sci. Chim., 28 (1980) 89.
15 E. Margas and W. Zielenkiewicz, Proc. of III. Intern. Conf. on Chemical Thermodynamics, Baden, Austria, 1973, 1 (1973) 92.
16 W. Zielenkiewicz and E. Margas, Bull. Acad. Polon. Sci., Ser. Sci. Chim., 21 (1973) 247; ibid., 21 (1973) 251.
17 W. Zielenkiewicz and A. Tabaka, Bull. Acad. Polon. Sci., Ser. Sci. Chim., 28 (1980) 727; ibid., 29 (1981) 41; ibid., 29 (1981) 51; ibid., 29 (1981) 61.
18 W. Zielenkiewicz and A. Tabaka, Bull. Acad. Polon. Sci., Ser. Sci. Chim., 21 (1973) 327.
19 A. King and H. Grover, J. Appl. Phys., 12 (1941) 560.
20 R. S. Jessup, J. Appl. Phys., 13 (1942) 129.
21 E. D. West and K. L. Churney, J. Appl. Phys., 39 (1968) 4206.
22 E. Calvet and H. Prat, Microcalorimetrie, Mason, Paris 1956.
23 J. Medejski, E. Utzig and W. Zielenkiewicz, Bull. Acad. Polon. Sci. Ser. Sci. Chim., 16 (1968) 275.
24 E. Cesari, J. Hatt, E. Margas, J. Navarro, V. Torra, E. Utzig and W. Zielenkiewicz, Bull. Acad. Polon. Sci. Ser. Sci. Chim., 28 (1980) 297.
25 J. Hatt, E. Margas and W. Zielenkiewicz, Thermochim. Acta, 64 (1983) 305.
26 E. Cesari, J. Ortin, J. Vinals, J. Hatt, W. Zielenkiewicz and V. Torra, Thermochim. Acta, 71 (1983) 351.

27 W. Zielenkiewicz and E. Margas, Proc. of II. National Conf. on Calorimetry and Thermal Analysis, Zakopane, Poland, 1976.
28 J. Navarro, V. Torra and E. Rojas, An. Fis. 67 (1971) 367.
29 C. Brie, J. L. Petit and P. C. Gravelle, Journées de Calorimétrie at d'A. T. D., Mulhouse, France, 1971.
30 J. Gutenbaum, E. Utzig, J. Wisniewski and W. Zielenkiewicz, Bull. Acad. Polon. Sci., Ser. Sci. Chim., 24 (1976) 193.
31 R. Point, J. L. Petit and P. C. Gravelle, J. Thermal Anal., 11 (1977) 431.
32 J. P. Dubes, M. Barres and H. Tachoire, Thermochim. Acta, 19 (1977) 101.
33 N. Davids and R. L. Berger, Currents in Modern Biology, 3 (1969) 169.
34 W. Zielenkiewicz, E. Margas and J. Hatt, Thermochim. Acta, 88 (1985) 387.
35 E. Cesari, P. C. Gravelle, J. Gutenbaum, J. Hatt, J. Navarro, J. L. Petit, R. Point, V. Torra, E. Utzig and W. Zielenkiewicz, J. Thermal Anal., 20 (1981) 47.
36 V. Torra, E. Margas and W. Zielenkiewicz, Naucznaja Apparatura-Scientific Instrumentation, (in press).
37 J. Ortin, V. Torra, E. Cesari and J. Vinals, Thermochim. Acta, 70 (1983) 113.
38 J. Ortin, V. Torra, T. Castan and E. Cesari, Thermochim. Acta, 70 (1983) 123.
39 J. Navarro, E. Rojas and V. Torra, Rev. Gen. Therm. Fr., 12 (1973) 1137.
40 E. Cesari, J. Ortin J. Vinals, J. Hatt, W. Zielenkiewicz and V. Torra, Thermochim. Acta, 71 (1983) 351.
41 H. Tachoire, J. L. Macqueron and V. Torra, Thermochemistry and its applications to chemical and biochemical systems, NATO ASI series C, 119, Reidel Dordrecht, 1984, p. 77.
42 J. Rodriguez, C. Rey, V. Perez-Villar, J. P. Dubes, H. Tachoire and V. Torra, Thermochim. Acta, 75 (1984) 51.
43 W. Zielenkiewicz and E. Margas, Proc. of I. National Conf. on Calorimetry, Zakopane, Poland, 1973.

Zusammenfassung — Die Grundlage zur Ableitung mathematischer Modelle von kalorimetrischen Systemen wird vorgestellt. Für diese Modelle werden folgende Anwendungsbeispiele ausgeführt: Fortgeschrittene Klassifizierung kalorimetrischer Systeme, Analyse des Verlaufs von Wärmeeffekten in Kalorimetern, Analyse der dynamischen Eigenschaften, Analyse der vollständigen Wärmeeffekte, Thermokinetik. Besondere Aufmerksamkeit gilt der Anwendung der Vielkörpermethode zur Aufstellung eines mathematischen Modells für kalorimetrische Systeme.

РЕЗЮМЕ — Представлены основы определения математических моделей для калориметрических систем. Даны примеры применения таких моделей для хорошо продуманной классификации калориметрических систем, анализа тепловых эффектов в калориметрах, анализа динамических свойств, анализа общих тепловых эффектов и термокинетики. Особое внимание уделено применению метода множеств при создании математических моделей калориметрических систем.