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COMPUTERIZATION OF CONDUCTION CALORIMETERS BASED ON THE *N*-BODY MODEL

W. ZIELENKIEWICZ, E. MARGAS and J. HATT

Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw (Poland)

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ABSTRACT

A method and microprocessor system for the computerization of conduction calorimeters were developed. The method of construction of the algorithm is based on the multi-body theory. The elaborate program of acquisition and treatment of data enables: (1) precise reproduction of the thermokinetics; (2) registration of the thermogram; (3) determination of the enthalpy of the reaction studied; (4) calibration of the calorimetric system. The algorithm worked out for the reproduction of the thermokinetics enables the change in heat capacity of the object studied to be taken into account.

INTRODUCTION

We have been interested in the development of accurate methods for the determination of heat effects and the reproduction of thermokinetics [1], as well as the range of their application and computerization. Our considerations presented in this paper are based on the multi-body method of determination of thermokinetics [2].

METHOD

Generally, for a conduction calorimeter it is assumed that the heat effect generated can be accumulated in the calorimetric vessel and simultaneously exchanged between this vessel and the calorimetric shield. For this type of calorimeter, according to the multi-body theory [3], the mathematical model of such a system can be represented by the following heat balance equation

$$K_j \mathrm{d}\theta_j(t) + G_{0j}\theta_j(t)\mathrm{d}t + \sum_{\substack{i=1\\ i\neq j}}^{N} G_{ij}\left[\theta_j(t) - \theta_i(t)\right]\mathrm{d}t$$
$$= \mathrm{d}Q_j(t) \quad (j = 1, 2, \ldots, N) \qquad (1)$$

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where N = number of distinguished bodies; K_j = heat capacity of body j; G_{0j} = heat loss coefficient between body j and body i; $\theta_j(t)$ = function describing changes of temperature of body j with respect to environmental temperature, which is constant; $dQ_j(t)$ = quantity of heat generated during time dt in body j. Evaluation of the model demands the mutual configuration of a number of bodies and determination of the physical parameters of the calorimeter. On the basis of the multi-body method described [2] we established an algorithm for $n \leqslant 5$ bodies. This system can be described by the following set of equations

$$K_1 \frac{d\theta_1(t)}{dt} + G_{01}\theta_1(t) + \sum_{i=2}^{5} G_{i1}[\theta_1(t) - \theta_i(t)] = W(t) \tag{2}$$

$$K\theta_j \frac{d\text{-}\theta(t)}{dt} + G_{0j}\theta_j(t) + \sum_{\substack{i=1 \\ i \neq j}}^{5} G_{ij}\left[\theta_j(t) - \theta_i(t)\right] = 0 \quad (j = 2, 3, 4, 5) \tag{3}$$

Equation (2) describes the so-called "changeable" part and (3) the "non-changeable" part of the calorimetric system [3]. K_1 is the heat capacity of the changeable part of the calorimetric system and we assume that it is the heat capacity of the calorimetric vessel with the object studied. The above form of a set of equations indicates that for various heat capacities, K_1, there is no need to change the mathematical model of the calorimetric system, however, a change in the value of K_1 calls for an introduction into the input data of the program. The algorithm established also gives the possibility of applying a model of any configuration of bodies, the number of which can change from five to zero, which also includes a model described by a heat balance equation of a simple body (Tian–Calvet equation)

$$K \frac{d\theta(t)}{dt} + G\theta(t) = W(t) \tag{4}$$

or in the case when the inertial properties of the calorimetric system are negligible (time constant of the calorimeter is very small), heat power $W(t)$ can be described by the relationship

$$W(t) = G\theta(t) \tag{5}$$

and thus corresponds to the recorded thermogram with accuracy up to factor G.

APPARATUS AND RESULTS

The electronic system of acquisition and treatment of data was constructed on the basis of the microprocessor MCY 7880, which cooperates with the calorimeter by an analog-digit transducer. This system consists of: RAM memory, 1 kB; EPROM memory, 4 kB; voltmeter timer; interfaces of the following devices: key board, perforator, registrator, printer and plotter.

The algorithm for the determination of thermokinetics is given in Fig. 1. As a criterion of the quality of reproduction of thermokinetics, a mean squared error of reproduction of the model course of $W(t)$ is taken. On the basis of the analysis of numerical properties of this algorithm [4] the

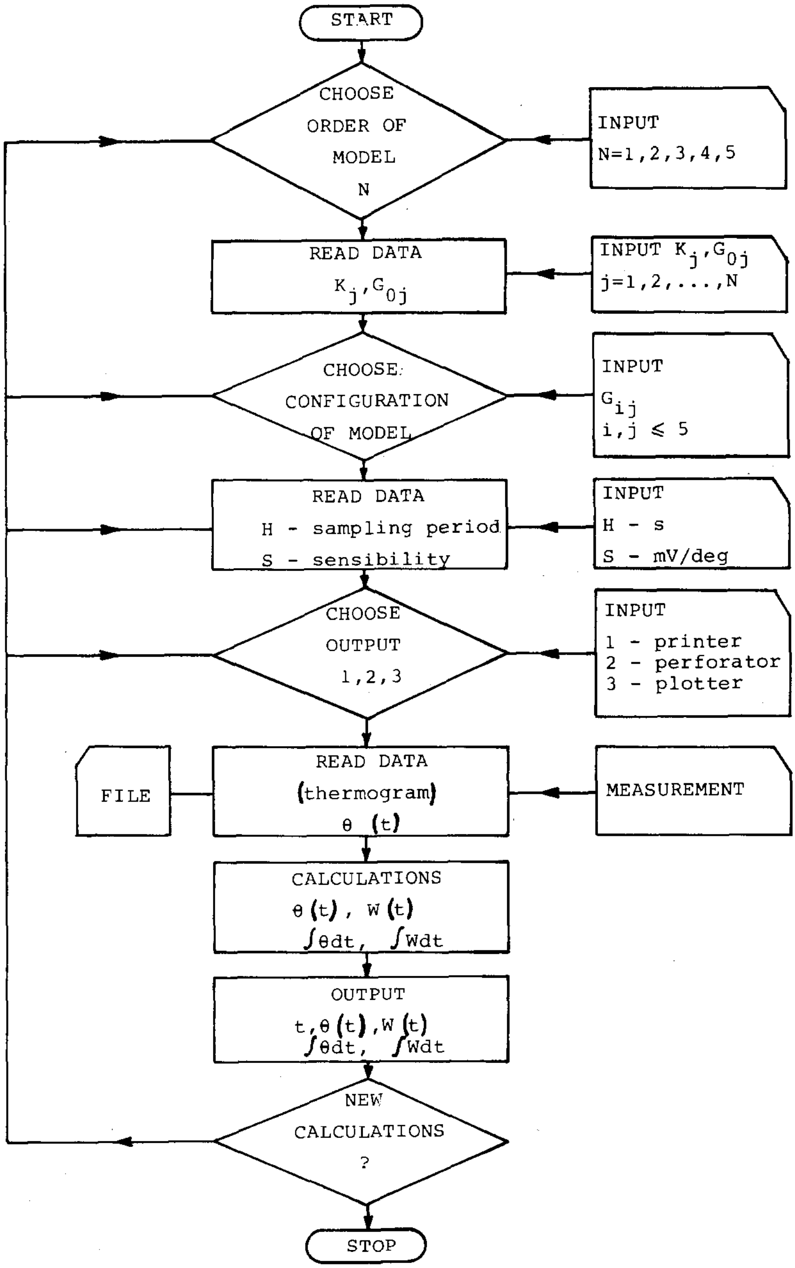

Fig. 1. Flow diagram of the algorithm.

following were determined: functional processor parameters; sampling parameters; measurement accuracy and level of the system noise desired; accuracy of model parameters needed. It was taken that the sensibility of the algorithm to systematic perturbations of coefficients G_{0j} is two or three times smaller than to perturbations of the remaining parameters of the model. Assuming an equal contribution of components of errors in the total error of reconstruction of thermokinetics, it was taken that the relative variance of measurement noise should be less than 10^{-3} and a microprocessor of precision of 24 bites should be used.

The important advantages of the present method of computerization of conduction calorimeters are: the possibility of taking into account different inertial properties of the calorimetric system; the possibility of changing the heat capacity, K_1; the possibility of applying to various types of commercial and "home-made" conduction calorimeters.

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