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SIMULATION OF A DTA SYSTEM BY THE RC MODEL

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ABSTRACT

In this communication we present the elaboration of an RC model and its application to a differential thermal analysis system. The model is simple and has been developed for isothermal conditions. Despite these simplifications we have analysed the influence of temperature on several experimental parameters and their evolution on the thermograms.

The first two or three time constants of the calorimetric system have been determined by the dissipation of a certain amount of energy known from Joule's law and correcting the experimental result with standard inverse filtering.

INTRODUCTION

Models of calorimetric systems have been successfully used on different and diverse systems. They have allowed the influence of some parameters on the result to be evaluated, particularly on the calibration factor, the system to be characterized and deconvolution methods to be developed [1–4]. More recently, a study of the effects of non invariance on heat [5,6] and mass flux [7] calorimeters has been started.

Several models in DTA based on the application of the Fourier equation [8–10] or using balance equations exist [11–16], which are also called RC models or localized-constant models. Both of these are basically oriented to justify the proportionality between the peak's area and the total energy related to the process, and to the study of particular thermal effects such as so-called invariant processes.

In this paper we expose the development of an RC model that, despite its simplicity, permits the study of several experimental parameters, sensibility changes and time constants, all as a function of the temperature of the process and through simulation of the real system's behaviour.

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DEFINITION OF THE MODELS

Knowing that development through the Fourier equation becomes very mathematically complex, we have chosen treatment through balance equations.

Model of three bodies

For the simplest model we have considered the sample (element 1), the crucible (element 2) and the thermocouples (element 3) as three bodies that form a linear chain (Fig. 1).

The temperature of the thermostat, T_0, has been considered a constant because of the small temperature ranges in which DTA peaks typically occur (a few degrees only). In order to study the evolution of the model for different values of T_0, different parameter sets have been used. We have tried invariant formulation of the model for each T_0 value.

The linear structure is very simple and does not show the reference-holder assembly, which is included with the thermostat. Our DTA system has a slow thermal coupling between crucibles and we therefore think that the thermal effects generated in the sample do not affect the reference. Furthermore, our model corresponds to isothermal conditions, under which the temperatures of the thermostat and the reference are always equal.

The signal given by the DTA corresponds to T_3, while all the thermal effects occur in the sample (element 1 in Fig. 1).

Under these conditions, and given that $T_0 = 0$, the balance equations are

$$W_1 = C_1 \frac{dT_1}{dt} + P_{12}(T_1 - T_2)$$

$$0 = C_2 \frac{dT_2}{dt} + P_{12}(T_2 - T_1) + P_{23}(T_2 - T_3)$$

$$0 = C_3 \frac{dT_3}{dt} + P_{23}(T_3 - T_2) + P_3 T_3$$

where C_i is the heat capacity of element i, P_{ij} is the thermal coupling between elements i and j, and P_k is the direct thermal coupling of element k with the thermostat. Working out these equations gives

$$K = 1/P_3 = S/Q$$

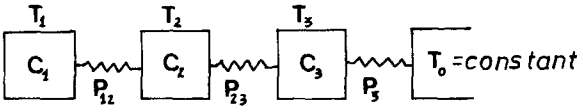

Fig. 1. Schematic representation of three-body RC model.

where S is the area of the thermogram ($S = \int_0^\infty T_3 \mathrm{d}t$), Q is the generated thermal effect, and K is the system's sensibility.

The parameters C_i, P_{ij} and P_k were chosen by adjusting the model as closely as possible to the real system. This is relatively easy for the capacities, but the indetermination in the couplings is important. We have worked with two values of C_2, corresponding to crucibles made of aluminium and nickel-coated copper. The heat capacity of an electrical resistance placed in the crucible with SiC was the value used for C_1.

With this configuration, several signals generated at the electrical resistance and known from Joule's law of heating were used to contrast the predictions of the model with the real DTA signal. The change of C_i with temperature T_0 is linear because the specific heats of the constitutive materials of each element vary linearly with temperature.

The values adopted for P_{ij} and P_k were those that determined the time constants and sensibility to be as close as possible to the values obtained by standard inverse filtering of the Joule signals. They were found to increase linearly with T_0. The basic parameters chosen and their evolution with temperature are shown in Table 1.

With this configuration the evolution of the real system's sensibility with temperature was observed by varying P_3, and it was compared to the corresponding evolution of the time constants.

Model of four bodies

In some studies with metallic samples the crucible has been substituted by a layer of mica, placed between the sample and the thermocouples. In order to simulate the effect of the mica, but still work with the crucible, we have imagined a four-element model (Fig. 2). Elements 1, 2, 3 and 4 are the contents of the crucible, the crucible, the layer of mica and the thermocouples, respectively.

Given the experimental sensibility change, this model includes new direct losses from the crucible and the mica to the thermostat. The sensibility of this system is worse than that of a system without the layer of mica working at the same temperatures. As the coupling thermocouples–thermostat group

TABLE 1

Values of the parameters of the model ($\times 10^4$) between the two extreme working temperatures. All the values evolve linearly with temperature (T (K), C (J K^{-1}), P (W K^{-1}))

T	C_1	C_2		C_3	P_{12}		P_{23}		P_3	
		Al	Cu		Al	Cu	Al	Cu	Al	Cu
320	360	452	1170	50	38	45	41	80	89	87
570	416	514	1590	60	56	56	69	169	130	130

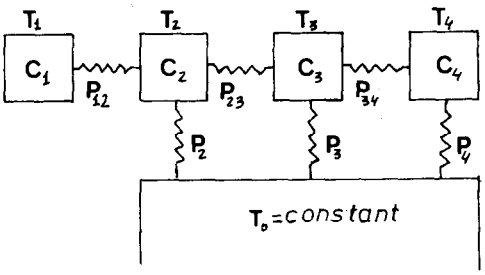

Fig. 2. Schematic representation of four body RC model.

P_4 (P_3 for the three bodies model) is not changed by the existence of the layer of mica between the crucible and the thermocouples, the equation $K = 1/P_4$ for this sensibility is no longer valid. This accounts for the inclusion of the direct losses to the thermostat group. The balance equations of this new formulation are ($T_0 = 0$)

$$W_1 = C_1 \frac{dT_1}{dt} + P_{12}(T_1 - T_2)$$

$$0 = C_2 \frac{dT_2}{dt} + P_{12}(T_2 - T_1) + P_{23}(T_2 - T_3) + P_2 T_2$$

$$0 = C_3 \frac{dT_3}{dt} + P_{23}(T_3 - T_2) + P_{34}(T_3 - T_4) + P_3 T_3$$

$$0 = C_4 \frac{dT_4}{dt} + P_{34}(T_4 - T_3) + P_4 T_4$$

Here $Q = P_4 \int_0^\infty T_4 dt + \text{losses} = P_4 S' + \text{losses}$, where S' is the area of the new thermogram. S' is less than the area S obtained from the measurements made without the mica element. This equation explains the decrease in sensibility without changing the coupling thermocouples–thermostat group.

We have studied the results of the model with two different thicknesses of the layer of mica (0.03 and 0.25 mm) and, for each thickness, with the two kinds of crucible (Al and Cu) already used in the three-body model.

The parameters of the four-body model are given in Table 2, where it can be seen that the heat capacities, coupling and losses that are common to both systems were kept unchanged. We found that the values of P_{ij} and P_k that better simulate the answer obtained from Joule signals evolve linearly with temperature, as for the previous model.

EXPERIMENTAL

A constantan electrical resistance (0.05 mm diameter) placed in the crucible with SiC was used to calibrate the DTA system through Joule's law.

TABLE 2

Values of the parameters of the model ($\times 10^4$) between the two extreme working temperatures. All the values, except the heat capacity of mica that is considered a constant, evolve linearly with temperature (T (K), C (J K^{-1}), P (W K^{-1}), M1 = mica 0.03 mm, M2 = mica 0.25 mm)

T	C_1	C_2		C_3		C_4	P_{12}		P_{23}			
		Al	Cu	M1	M2		Al	Cu	Al		Cu	
									M1	M2	M1	M2
320	360	452	1170	4	32	50	38	45	45	43	120	100
570	416	514	1590	4	32	60	56	56	63	70	260	240

T	P_{34}		P_2				P_3		P_4
	M1	M2	Al		Cu		M1	M2	
			M1	M2	M1	M2			
320	110	95	2	3	4	4	6	6	82
570	240	162	5	4	6	8	8	9	120

It was covered with layers of Cu or Al depending on the kind of crucible. The resistance was about 120 Ω and the intensity of the current was 10 mA during 100 s, which represents an energy dissipation close to 1.2 J.

The differential signal was amplified by a factor of 5×10^3, digitalized with an HP3478A voltmeter and acquired by a microcomputer with sampling periods equal to 0.6 or 2 s.

All the experiments were done under static air atmosphere between 320 and 570 K in steps of 50 K always under isothermal conditions. 570 K is the maximum allowable temperature for the thin constantan wire.

The time constants may be calculated from returns to the baseline by inverse filtering of these Joule generated dissipations when the current is cut off. We used thermograms with sampling every 0.6 s in the case where three time constants were to be found. We assumed their uncertainty to be ± 1 s.

We have to remark that the values of sensibility that we obtained from Joule signals and those obtained from standard reference materials differ by 0.4 mV W^{-1} at all temperatures, which represents 10% at most. This difference is reasonable because the contents of the crucibles were different in both cases, but the important fact is that the evolution of sensibility with temperature from Joule signals is correct.

RESULTS AND DISCUSSION

The sensibility and the first two or three time constants for Al and Cu crucibles (without mica for the three-body model and with two thicknesses of mica for the four-body model) as a function of temperature were calculated with the experimental configuration above exposed.

Table 3 shows the experimental values and those obtained from the corresponding models. It can be seen how the models follow the evolution of the experimental sensibility at the different temperatures studied. The differences in sensibility produced when varying the experimental conditions (such as the kind of crucible and the absence or presence of mica of different thicknesses) are also manifested in the theoretical results of the simulation. Both models respond to the decrease of the time constants for increasing temperature. This result is coherent with the increase of direct losses to the thermostat group at higher temperatures.

The Cu crucible presents a greater heat capacity than the Al crucible, fundamentally because its mass is greater (Cu, 175 mg; Al, 50 mg). This fact results in the time constants measured with the Cu crucible being greater than those measured with the Al crucible. The two formulated models confirm these phenomena.

As the agreement between the theoretical and the experimental results is so great, we think that these two models may be valid for a broad set of working conditions, at least up to 600 K, at which point the constantan

TABLE 3

Values of time constants and sensibility obtained from experimental measurements and from the theoretical models (T (K), τ (s), k (mV W^{-1}))

T	Al crucible									Cu crucible								
	Model					Filtering				Model					Filtering			
	τ_1	τ_2	τ_3	τ_4	k	τ_1	τ_2	τ_3	k	τ_1	τ_2	τ_3	τ_4	k	τ_1	τ_2	τ_3	k
Three-body model																		
320	34.1	4.5	0.4		4.49	35	5		4.5	39.2	5.8	0.3		4.60	39	6	2	4.6
370	31.9	4.3	0.4		4.21	33	5		4.2	37.3	5.8	0.3		4.30	37	6	2	4.3
420	29.9	4.1	0.4		4.00	31	4		3.9	35.2	5.7	0.3		4.00	35	6	2	4.0
470	28.3	3.9	0.3		3.64	29	4		3.6	33.3	5.7	0.2		3.64	33	6	2	3.7
520	26.5	3.7	0.3		3.33	27	4		3.3	31.4	5.7	0.2		3.33	31	6	2	3.3
570	24.8	3.5	0.3		3.08	25	4		3.0	29.5	5.5	0.2		3.08	29	6	2	3.0
Four-body model (mica M1)																		
320	35.9	4.6	0.4		4.00	36	5	1	4.0	40.0	5.8	0.4		3.90	40	7	2	3.9
370	33.9	4.4	0.4		3.71	34	5	2	3.7	38.0	5.8	0.3		3.66	38	6	2	3.7
420	31.8	4.2	0.4		3.45	32	5	2	3.4	36.0	5.7	0.3		3.46	36	7	2	3.5
470	30.1	3.9	0.4		3.24	30	5	1	3.2	34.4	5.7	0.3		3.29	34	6	2	3.3
520	28.1	3.7	0.4		2.94	28	5	1	2.9	32.2	5.7	0.3		3.03	32	5	2	3.0
570	26.4	3.5	0.4		2.68	26	4	1	2.7	30.2	5.5	0.2		2.79	30	6	2	2.8
Four-body model (mica M2)																		
320	36.3	4.6	0.6	0.2	3.80	36	6	2	3.8	43.7	5.8	0.5	0.1	3.83	44	8	2	3.9
370	34.3	4.4	0.6	0.1	3.56	34	5	2	3.6	41.4	5.8	0.4	0.1	3.57	42	7	2	3.6
420	32.3	4.2	0.5	0.1	3.34	32	5	2	3.4	39.0	5.8	0.4	0.1	3.33	39	7	3	3.4
470	30.8	4.0	0.5	0.1	3.15	31	6	2	3.1	37.1	5.7	0.4	0.1	3.13	37	6	3	3.1
520	28.8	3.7	0.5	0.1	2.88	29	5	2	2.9	34.8	5.7	0.3	0.1	2.84	35	7	2	2.8
570	26.9	3.6	0.5	0.1	2.66	27	4	2	2.7	32.5	5.6	0.3	0.1	2.61	32	6	2	2.6

resistance fails to work properly. The linear evolution of the parameters of the model with temperature therefore seems enough to account for the variation of the sensibility and time constants of the system, at least under 600 K. The variation of each parameter gives information about its influence on the change in the result with temperature.

At present we are studying the influence of several experimental configurations (covered or uncovered crucibles, greater or less mass, etc.) on measurements of real processes such as the transition II → I in KNO_3 at atmospheric pressure. We intend to compare the kinetic parameters obtained by direct and filtered thermograms.

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