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SIGNAL PROCESSING IN TIME-VARYING CALORIMETERS FOR THE STUDY OF CONTINUOUS LIQUID MIXTURES

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ABSTRACT

An analysis of the time-varying calorimetric systems used in the study of molecular mixtures obtained by continuous injection is presented from the point of view of signal processing. A complete recipe to perform the identification and deconvolution of the thermal output is given, which enables rather complex systems to be dealt with, i.e. calorimeters whose time-invariant transfer function presents not only real poles but non-negligible zeros as well. The recipe has been deduced following a theoretical study of a model which represents rather accurately the actual behaviour of a heat-conduction calorimeter used in the study of continuous liquid mixtures.

INTRODUCTION

Coupling a mechanism for continuous injection of liquids to a highly sensitive heat-conduction calorimeter has opened the possibility of studying thermal properties of solutions at very low concentrations ($x \leqslant 0.001$). New and sometimes unexpected results have been found in certain molecular mixtures [1], in the study of micellar solutions and in the investigation of miscibility regions in systems exhibiting separation of phases.

Accurate experimental tests have shown, in turn, that the coupling of the continuous injection device to the calorimeter results in a slightly time-varying calorimetric system [2]. As a consequence, one is faced with the problem of developing new signal-processing algorithms which take into account explicitly the breakdown of the time-invariancy and enable the actual thermal power released inside the calorimeter to be recovered from the thermal output signal. Much effort has been directed towards generalizing classical inverse filtering to the new situation, simulated by very simple models. Up to now the generalization has been carried out only for models

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which, in the time-invariant state, only exhibit poles in their transfer function [3,4].

As a step forward, the objective of the present paper is to extend the generalization of inverse filtering to a situation in which the time-invariant transfer function of the device does present non-negligible zeros. This is the case, for example, when dissipation takes place near the detection system [5].

The plan of the paper is as follows: in part 1 the theoretical framework of the problem is presented; thus, in section 1.1 an elaborate time-varying calorimetric model is developed which, with high generality, resembles the actual behaviour of calorimeters with continuous injection systems. In section 1.2 we discuss the kind of information that is actually available from calorimetric experiments, relating it to the equations of the model. In section 1.3, finally, we establish the correspondence between the experimental information and the solutions to the signal-processing problem suggested by the equations of the model. This is done after a formal rearrangement of the transport equations, resulting in what we have called "fictitious equations". An example for a very simple model is explained in full detail. In part 2 a rather complete ensemble of numerical calculations and results is presented: section 2.1 describes different particularities of the general model to the different possible experimental situations. In section 2.2 the corresponding numerical results obtained by means of the "fictitious equations" are given; from the pattern of behaviour which results, a detailed rule of experimental and numerical procedure is designed, which is believed to be of general applicability for heat conduction calorimeters with continuous injection devices.

1. THEORETICAL FRAMEWORK

In a previous work [3] we have shown that the continuous injection of a liquid inside the laboratory cell of a heat-conduction calorimeter results in a double effect: on one side the thermal and geometrical properties of the calorimeter change with time and therefore the calorimeter, considered as an input–output system, ceases to be time-invariant. Or, in other words, the deformation produced on the thermal power signal released in it is continuously changing throughout the experiment. On the other side, there is a modification in the energy balance inside the calorimeter because part of the heat released (or absorbed) in the process under study has to be devoted to raise (or lower) the temperature of the liquid which is being injected.

In order to recover the thermogenesis, i.e. the input signal representing the evolution of the thermal power with time, in these situations, a new algorithm has been proposed. It essentially consists of a typical inverse filtering using parameters which vary with time to account for the first of the above-mentioned effects, followed by an extra-correction proportional to the rate of injection of liquid to account for the second effect [3].

The algorithm is also of application when there is an appreciable variation of the thermal couplings with time, which results in a dependence of the calorimetric sensitivity on the level of liquid contents in the cell [4].

1.1. Model of the time-varying calorimeter

All the analyses leading to such conclusions were performed on heat-conduction models which represent a calorimeter by means of an electrical analogy to an RC circuit, and which are called "localized constants models". The study was restricted to the situation in which the invariant system obtained from the model by neglecting the temporal dependence of the parameters had only poles in its transfer function. Consequently, the linear differential equation relating the thermogenesis to the thermogram did not contain any derivative of the thermal power. The models resembled the thermal behaviour of an actual system (Arion-Electronique calorimeter of the BCP type) and presented only three thermal capacities. Therefore the thermogram was identified with the temperature of the third element.

A more realistic approach, however, should consider that the detection system in a heat conduction calorimeter is usually a battery of thermocouples, and consequently the resulting signal or thermogram is related to a difference of temperatures between their ends. And also that there is a stirring device inside the fluid which has to be simulated by inert elements of the model. This will produce zeros in the transfer function of the time-invariant version of the model. The presence of intense stirring enables the hypothesis to be made that the power dissipation takes place in the bulk of the liquid in the calorimetric vessel. But, as the liquid injected enters the vessel at the temperature of the thermostat, an extra contribution has still to be added in the heat balance equations of the vessel.

Taking all these elements into account, and assuming that the dissipation takes place in the L-th element, which will therefore represent the vessel, the heat-balance equations for a general model consisting of N elements read:

$$
\begin{aligned}
0 &= C_1 \frac{\mathrm{d}T_1}{\mathrm{d}t} + \sum_{k \neq 1} P_{1k}(T_1 - T_k) + P_1 T_1 \\
W &= C_L \frac{\mathrm{d}T_L}{\mathrm{d}t} + \sum_{k \neq L} P_{Lk}(T_L - T_k) + P_L T_L + T_L \frac{\mathrm{d}C_L}{\mathrm{d}t} \qquad (1) \\
0 &= C_N \frac{\mathrm{d}T_N}{\mathrm{d}t} + \sum_{k \neq N} P_{Nk}(T_N - T_k) + P_N T_N
\end{aligned}
$$

where C_i represents the heat capacity of the i-th element, P_i the inverse of the thermal resistance between the i-th element and the thermostat and P_{ik} the inverse of the thermal resistance between the i-th and the k-th elements. Generally speaking, due to the variation of volume of liquid inside the

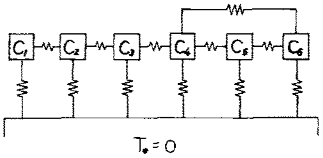

Fig. 1. Diagram of the calorimetric model used in the numerical simulations.

laboratory cell, any of these parameters can be a function of the level of cell contents $x(t)$, and hence a function of time. The term $\dot{C}_L T_L$ represents the power absorbed to change the temperature of the liquid which is being injected, from the temperature of the thermostat ($T_0 = 0$) to the temperature of the mixture (T_L).

The equations of the general model will be reduced to account for the particular conditions of each model. For example, as in the vicinity of the laboratory cell every element almost surrounds the one before, only couplings to the immediate neighbours have to be considered in this part. Moreover, when the level of liquid in the cell influences the thermal couplings, only the couplings connected to the element of variable capacity will have to be considered as variable. The rest of the device will not change with time. Finally, as the thermocouples measure temperature differences, the thermogram of the model will be obtained as the difference between the temperatures T_i and T_j.

As it will be detailed in section 2.1, we have restricted our numerical applications and results to a specific model with only six thermal capacities, which is presented in Fig. 1. On the one side, the model exceedingly covers the experimental possibilities: in an actual calorimeter with injection the signal-to-noise ratio on the thermogram is rarely greater than 60 dB and therefore the possibilities of identifying six time constants, corresponding to the six poles of the model in the time-invariant situation, and one or more zeros, are practically null. On the other side, the simplified model of Fig. 1 still represents the main features we demanded of the general model to perform a very general study, namely:

(a) a detection based on a difference of temperatures;
(b) a complete separation between the variable and invariant parts of the device;
(c) the explicit possibility of zeros in the dynamic response of the corresponding time-invariant system.

1.2. Information that can be experimentally achieved

From the analysis of time-varying calorimetric models we attempt to design a working procedure which enables the thermogenesis to be recovered with the greatest possible accuracy and, at the same time, be experimentally feasible. From an experimental point of view, three kinds of measurements can be performed which will help to study the behaviour of the system:

(1) Studying the output decay from a Heaviside input signal at different levels of cell contents, in two cases: (a) in a process without injection in which the heat released by means of the Joule effect is cut off; (b) stopping the injection of a liquid A into another liquid B once a nearly steady state in the thermogram has been reached.

(2) Studying the output decay from a Heaviside input signal released by means of the Joule effect while, during the whole process, a liquid A is being injected into the same liquid A.

(3) Studying the differences between the permanent regimes in the thermogram of a constant Joule effect dissipation when the system is kept invariant (there is no injection) and when a liquid identical to the liquid filling the vessel is being injected. In this last situation a permanent regime is reached only if the thermal couplings with the laboratory cell show a null or very small variation during the process of injection and in contrast with the change in the heat capacity of the vessel (see fig. 2 from ref. 2).

Measurements of types (1) and (2) will be useful to evaluate the change in the dynamic parameters of the calorimeter during injection, while measurements of type (3) will give information about the change in sensitivity.

Generally speaking, we may say that by means of the Joule effect we are able to study the system in the time-invariant situation at different levels of filling and the system in the variable situation as well. On the contrary, in a typical experiment of mixture we only get information from the output decays after stopping the injection, i.e. in time-invariant situations.

To relate the time-invariant and the variable regimes in the actual experiments it is therefore necessary to relate, previously, both regimes in the Joule effect measurements. The natural way to establish the relation between the parameters of the system in the time-invariant and the variable regimes is to compare and analyse the equations of the calorimetric model in both situations. This is done in the following section.

1.3. Time-invariant and variable models: "fictitious equations"

The system of linear differential equations (1) may be rewritten, after successive substitutions, as a linear differential equation of the form:

$$\sum_{i=0}^{M} a_i'(t)\frac{\mathrm{d}^i W(t)}{\mathrm{d}t^i} = \sum_{i=0}^{N} A_i'(t)\frac{\mathrm{d}^i s(t)}{\mathrm{d}t^i} \tag{2}$$

where the coefficients a_i' and A_i' will in general depend on $C_i(t)$, $P_i(t)$ and $P_{ik}(t)$ and on their derivatives which will have appeared in the process of substitution.

In the time-invariant situation, i.e. for a certain fixed level of contents $x(t_i)$, we get a differential equation with constant coefficients of the form:

$$\sum_{i=0}^{M} a_i(x)\frac{\mathrm{d}^i W(t)}{\mathrm{d}t^i} = \sum_{i=0}^{N} A_i(x)\frac{\mathrm{d}^i s(t)}{\mathrm{d}t^i} \tag{3}$$

The coefficients $a_i(x)$ and $A_i(x)$ correspond to the coefficients $a_i'(t)$ and $A_i'(t)$, respectively, for a fixed level of cell contents $x(t)$. As there is no change of the level with time, all the dependence on temporal derivatives of capacities and coupling vanishes; this is the reason why the coefficients a_i and A_i do not coincide with a_i' and A_i' at any time and, in particular, are different for the level reached at $t = t_i$.

At this point it is important to stress the fact that only the coefficients a_i and A_i can be experimentally determined from the decay of the thermogram after stopping the injection. Hence, although in eqn. (2) a formal relation between the thermogenesis $W(t)$ and the thermogram $s(t)$ has already been established, and will enable the deconvolution of the thermogram to be performed we still lack a method of deducing the coefficients a_i' and A_i' from a_i and A_i. It should be noted, however, that if the flow of injected fluid progressively decreases to zero the coefficients in eqn. (2) tend towards the coefficients in eqn. (3) until, at zero flow, they are equal.

To relate one group of coefficients to the other we introduce a new set of differential equations which we call "fictitious equations" in a sense that will be made clear below. The equations must satisfy two conditions at once: firstly, for a given level of contents $x(t)$ they must be equations with constant coefficients so that in the process of substituting an equation in the preceding ones no derivatives of capacities and couplings appear; and, secondly, the coefficients must coincide with the coefficients a_i' and A_i' in eqn. (2) for the different levels of cell contents.

Generally speaking, the "fictitious equations" are obtained from eqn. (2) of the variable system by adding all the dependence in the temporal derivatives of capacities and couplings to the actual capacities and couplings appearing in eqn. (2).

Example

To clear up the process, let us consider a simple example of a calorimetric model with two capacities where the heat is released at element 1 and where C_1, P_1 and P_{12} vary with time.

The equivalent of eqns. (1) for this model are:

$$W = C_1\dot{T}_1 + P_{12}(T_1 - T_2) + P_1 T_1 + \dot{C}_1 T_1$$
$$0 = C_2\dot{T}_2 + P_{12}(T_2 - T_1) + P_2 T_2$$

From the second equation we get for the temperature T_1:

$$T_1 = T_2 + \frac{1}{P_{12}}(C_2\dot{T}_2 + P_2 T_2)$$

and therefore

$$\dot{T}_1 = \dot{T}_2 + \frac{1}{P_{12}}(C_2\ddot{T}_2 + P_2\dot{T}_2) + \left[\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{1}{P_{12}}\right)\right](C_2\dot{T}_2 + P_2T_2)$$

Substituting in the first equation we get the equivalent of eqn. (2) for this model:

$$W = C_1\left\{\dot{T}_2 + \frac{1}{P_{12}}(C_2\ddot{T}_2 + P_2\dot{T}_2) + \left[\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{1}{P_{12}}\right)\right](C_2\dot{T}_2 + P_2T_2)\right\}$$
$$+ (C_2\dot{T}_2 + P_2T_2) + (P_1 + \dot{C}_1)\left[T_2 + \frac{1}{P_{12}}(C_2\dot{T}_2 + P_2T_2)\right]$$

Formally, the same equation could have been obtained from the following system:

$$W = C_1\dot{T}_1 + \left\{P_{12} + C_1P_{12}\left[\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{1}{P_{12}}\right)\right]\right\}(T_1 - T_2) + P_1T_1 + \dot{C}_1T_1$$
$$0 = C_2\dot{T}_2 + P_{12}(T_2 - T_1) + P_2T_2$$

if we consider now that for every level of contents, and therefore at every instant of time, the parameters C_1, P_1 and P_{12} have fixed values and in the substitution of one equation into the other they do not bring new derivatives (which have already been introduced ad hoc).

The new system obtained in this way is only a mathematical tool. It has no direct physical meaning and, in many instances, it cannot be associated with an invariant model; in the example presented, for instance, the matrix of thermal couplings becomes non-symmetric. Non-physical situations, such as the transfer of heat from low to high temperatures, can also appear.

The important feature is that the new system coincides with the variable system of the type (1) for every level of liquid in the cell and at the same time it is time-invariant. Hence, it is possible to obtain the parameters defining the impulse response of the model (poles $-1/\tau_i'$, zeros $-1/\tau_i^{*\prime}$, and the sensitivity S') by simply applying the standard methods to solve linear systems with constant coefficients. In particular, the Laplace transform turns the system of differential equations into an algebraic system whose solution is the ensemble of values $\{\tau_i', \tau_i^{*\prime}\}$. If this solution is calculated at different times $t_1, \ldots, t_k$ corresponding to increasing quantities of substance in the vessel, a polynomial fit $\tau_i'(t)$ and $\tau_i^{*\prime}(t)$ can be found for every pole and zero of the model, and, along similar lines, for the sensitivity S'. Then, the coefficients $a_i'(t)$ and $A_i'(t)$ in eqn. (2) can directly be obtained because the values $a_i'(t)$ and $A_i'(t)S'(t)$ are exactly the coefficients of the polynomials whose roots are, respectively, $-1/\tau_i^{*\prime}(t)$ and $-1/\tau_i'(t)$. Once this process is accomplished, eqn. (2) can be solved and the dissipation $W(t)$ recovered from the thermogram $S(t)$.

2. CALCULATIONS AND RESULTS

The fictitious equations are helpful in calculating the values of $\tau_i'(t)$, $\tau_i^{*\prime}(t)$ and $S'(t)$ once we have a variable model of the calorimeter, but they do not tell us how to obtain these values from actual measurements if such a model, as it is most often the case, is missing. In this section the fictitious equations are used to show that, in a wide variety of cases, $\tau_i'(t)$, $\tau_i^{*\prime}(t)$ and $S'(t)$ have the same temporal behaviour as $\tau_i(t)$, $\tau_i^*(t)$ and $S(t)$, respectively, their homologues for the invariant eqn. (3) which can actually be obtained from experiments, and are only shifted from them by certain constant quantities. The way in which these constant quantities can be experimentally ascertained is also explained, and this completes our systematic treatment.

2.1. Particular models considered

The model studied has six different capacitive elements coupled in the form shown in Fig. 1. The coupling between elements 4 and 6 gives a zero in the transfer function of the invariant model. The numerical values assigned to heat capacities and couplings are summarized in Table 1.

The following situations have been studied:

(1) Dissipation in element 1 with C_1, P_{12} and P_1 as time-varying elements. The variation of P_{12} makes the sensitivity of the model variable too.

(2) Dissipation in element 2, with C_2 variable. This simulates the presence of the stirrer, represented by element 1, as an inert part of the vessel, in axial position.

(3) Dissipation in element 2, with C_2, P_{12}, P_{23} and P_2 varying with time. In this case the effects of the stirrer and the injection are taken into account. The model will have a sensitivity variable with time.

TABLE 1

Values of the heat capacities (J K^{-1}) and thermal couplings (W K^{-1}) of the calorimetric model used to perform the numerical simulations in the three situations detailed in the text. The values between parentheses are the initial value of the time-varying parameters in each situation

	Situation							
	1	2 and 3		1	2 and 3		1	2 and 3
C_1	(40)	5	P_1	(0.075)	0.02	P_{12}	(0.25)	(0.45)
C_2	20	(40)	P_2	0.075	(0.075)	P_{23}	0.35	(0.8)
C_3	20	60	P_3	0.25	0.1	P_{34}	0.55	0.4
C_4	18	40	P_4	0.75	0.6	P_{45}	0.75	1.75
C_5	18	18	P_5	0.08	0.08	P_{56}	1.25	1.25
C_6	18	18	P_6	1.25	1.25	P_{46}	0.1	1.0

TABLE 2

Rates of evolution (in SI units) of the variable thermal parameters in the three different situations considered in the text. The numbers (1), (2), (3) and (4) are to identify the curves in Figs. 2, 3 and 4. The values of this table have been selected in a way that (4) simulates a double rate of injection to that of (3), and (3), in turn, simulates a rate of injection four times greater than (2).

Curve	Situation		
	1	2	3
(1)	Time-invariant	Time-invariant	Time-invariant
(2)	$\dot{C}_1 = 0.2778E-2$ $\dot{P}_1 = 0.1764E-5$ $\dot{P}_{12} = 0.1736E-5$	$\dot{C}_2 = 0.2778E-2$ $\dot{P}_2 = 0.0$ $\dot{P}_{12} = 0.0$ $\dot{P}_{23} = 0.0$	$\dot{C}_2 = 0.2778E-2$ $\dot{P}_2 = 0.2084E-5$ $\dot{P}_{12} = 0.3125E-4$ $\dot{P}_{23} = 0.2778E-4$
(3)	$\dot{C}_1 = 0.1111E-1$ $\dot{P}_1 = 0.7056E-5$ $\dot{P}_{12} = 0.6944E-5$	$\dot{C}_2 = 0.1111E-1$ $\dot{P}_2 = 0.0$ $\dot{P}_{12} = 0.0$ $\dot{P}_{23} = 0.0$	$\dot{C}_2 = 0.1111E-1$ $\dot{P}_2 = 0.8336E-5$ $\dot{P}_{12} = 0.1250E-3$ $\dot{P}_{23} = 0.1111E-3$
(4)	$\dot{C}_1 = 0.2222E-1$ $\dot{P}_1 = 1.4112E-5$ $\dot{P}_{12} = 1.3888E-5$	$\dot{C}_2 = 0.2222E-1$ $\dot{P}_2 = 0.0$ $\dot{P}_{12} = 0.0$ $\dot{P}_{23} = 0.0$	$\dot{C}_2 = 0.2222E-1$ $\dot{P}_2 = 1.6672E-5$ $\dot{P}_{12} = 0.2550E-3$ $\dot{P}_{23} = 0.2222E-4$

In all cases the thermogram has been obtained as the difference between temperatures T_5 and T_6. The variation of the thermal parameters has been taken as linear, with different rates of evolution summarized in Table 2.

2.2. *Results and conclusions*

The values of τ_i, τ_i^*, S and τ_i', $\tau_i^{*\prime}$, S' for different levels x in the cell contents and for the three situations considered are given, respectively, in Tables 3, 4 and 5. For a given value of the heat capacity of the laboratory vessel we notice that

$$\begin{aligned} &\tau_i(x) \simeq \tau_i'(x) \qquad \forall_i \neq 1 \\ &\tau_i^{*\prime}(x) \simeq \tau_i^*(x) \quad \forall_i \end{aligned} \tag{4}$$

Figures 2, 3 and 4 show τ_1 and S' as a function of the heat capacity for different rates of variation in the parameters. In particular, the case of zero rate, corresponding to the invariant model at every level of vessel contents, has also been considered. From this figures we conclude that

$$\begin{aligned} &\tau_1'(x) \simeq \tau_1(x) + \Delta\tau \\ &S'(x) \simeq S(x) + \Delta S \end{aligned} \tag{5}$$

TABLE 3

Evolution of τ_i, τ_i', τ_i^*, $\tau_i^{*\prime}$ (s) and S, S' (K W^{-1}) with the evolution of the heat capacity C_1 of the model in situation 1

$C_1 =$	40	44	48	52	56	60
τ_1	217.74	233.11	284.09	262.70	276.97	290.90
τ_1'	215.18	230.15	244.75	259.04	272.93	286.46
τ_2	42.94	43.27	43.52	43.70	43.84	43.94
τ_2'	42.93	43.26	43.51	43.70	43.84	43.94
τ_3	24.95	24.96	24.97	24.98	24.97	24.97
τ_3'	24.95	24.96	24.97	24.98	24.98	24.97
τ_4	15.44	15.44	15.43	15.43	15.43	15.43
τ_4'	15.44	15.44	15.43	15.43	15.43	15.43
τ_5	7.22	7.22	7.22	7.22	7.22	7.22
τ_5'	7.22	7.22	7.22	7.22	7.22	7.22
τ_6	4.82	4.82	4.82	4.82	4.82	4.82
τ_6'	4.82	4.82	4.82	4.82	4.82	4.82
S ($\times 10^{-5}$)	6004	5950	5897	5846	5795	5746
S' ($\times 10^{-5}$)	5931	5873	5817	5763	5710	5658
τ_1^*	12.59	12.59	12.59	12.59	12.59	12.59
$\tau_1^{*\prime}$	12.59	12.59	12.59	12.59	12.59	12.59

where $\Delta\tau$ and ΔS have constant values which depend on the rate of injection, i.e. the rate at which the vessel is filled. This pattern of behaviour is believed to be of general applicability; then, the following experimental

TABLE 4

Evolution of τ_i, τ_i', τ_i^*, $\tau_i^{*\prime}$ (s) and S, S' (K W^{-1}) with the evolution of the heat capacity C_2 of the model in situation 2

$C_2 =$	40	44	48	52	56	60
τ_1	222.10	231.72	241.45	251.29	261.23	271.26
τ_1'	220.70	230.20	239.89	249.65	259.51	269.45
τ_2	37.47	38.07	38.66	39.26	39.84	40.41
τ_2'	37.47	38.06	38.66	39.25	39.84	40.41
τ_3	26.69	27.29	27.80	28.21	28.56	28.85
τ_3'	26.68	27.29	27.80	28.21	28.56	28.85
τ_4	9.25	9.39	9.50	9.60	9.68	9.74
τ_4'	9.24	9.38	9.49	9.59	9.67	9.74
τ_5	5.66	5.66	5.66	5.66	5.66	5.66
τ_5'	5.66	5.66	5.66	5.66	5.66	5.66
τ_6	3.92	3.92	3.92	3.92	3.92	3.92
τ_6'	3.92	3.92	3.92	3.92	3.92	3.92
S ($\times 10^{-5}$)	9309	9309	9309	9309	9309	9309
S' ($\times 10^{-5}$)	9239	9238	9238	9238	9238	9238
τ_1^*	10.64	10.64	10.64	10.64	10.64	10.64
$\tau_1^{*\prime}$	10.64	10.64	10.64	10.64	10.64	10.64
τ_2^*	6.41	6.41	6.41	6.41	6.41	6.41
$\tau_2^{*\prime}$	6.41	6.41	6.41	6.41	6.41	6.41

TABLE 5

Evolution of τ_i, τ_i', τ_i^*, $\tau_i^{*\prime}$ (s) and S, S' (K W^{-1}) with the evolution of the heat capacity C_2 of the model in situation 3

	$C_2 = 40$	44	48	52	56	60
τ_1	222.10	229.61	237.00	244.27	251.41	258.42
τ_1'	220.77	228.26	235.62	242.87	249.99	256.99
τ_2	37.48	37.55	37.60	37.62	37.62	37.61
τ_2'	37.48	37.55	37.60	37.62	37.62	37.61
τ_3	26.69	26.47	26.24	26.00	25.74	25.47
τ_3'	26.69	26.48	26.25	26.00	25.75	25.48
τ_4	9.25	8.57	7.98	7.46	7.00	6.59
τ_4'	9.25	8.58	7.98	7.46	7.00	6.59
τ_5	5.66	5.66	5.66	5.66	5.66	5.66
τ_5'	5.66	5.66	5.66	5.66	5.66	5.66
τ_6	3.92	3.92	3.92	3.92	3.92	3.92
τ_6'	3.92	3.92	3.92	3.92	3.92	3.92
S ($\times 10^{-5}$)	9310	9271	9232	9193	9153	9113
S' ($\times 10^{-5}$)	9258	9222	9184	9146	9107	9068
τ_1^*	10.64	9.71	8.93	8.26	7.69	7.19
$\tau_1^{*\prime}$	10.64	9.71	8.93	8.26	7.69	7.19
τ_2^*	6.41	6.41	6.41	6.41	6.41	6.41
$\tau_2^{*\prime}$	6.41	6.41	6.41	6.41	6.41	6.41

procedure is to be considered in order to perform the deconvolution of the thermograms:

(i) To determine the value of $\Delta\tau$ for each injection rate it is necessary to calculate τ_1' once, by means of an identification using a variable inverse filtering [4]. In this calculation, the slope of τ_1' is taken equal to the slope of

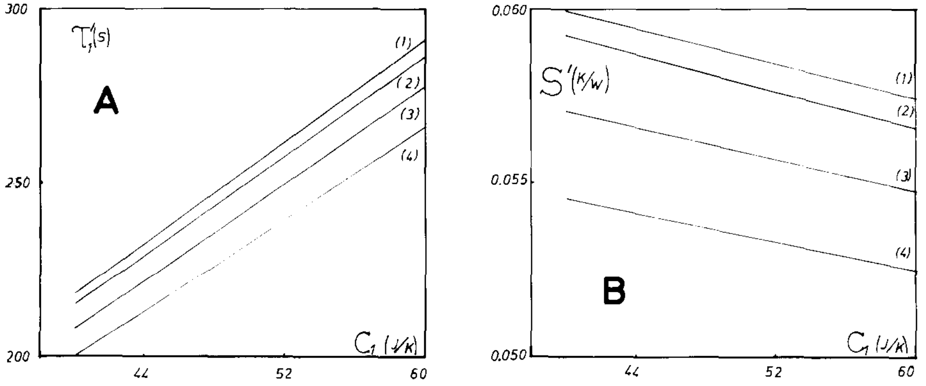

Fig. 2. Variation of (A) the main time constant τ_1' and (B) the sensitivity S' of the variable model as a function of the heat capacity C_1. The dissipation takes place in element 1, and C_1, P_{12} and P_1 vary with time. The different curves (1), (2), (3) and (4) correspond to different rates of variation of these parameters as detailed in Table 2 (situation 1).

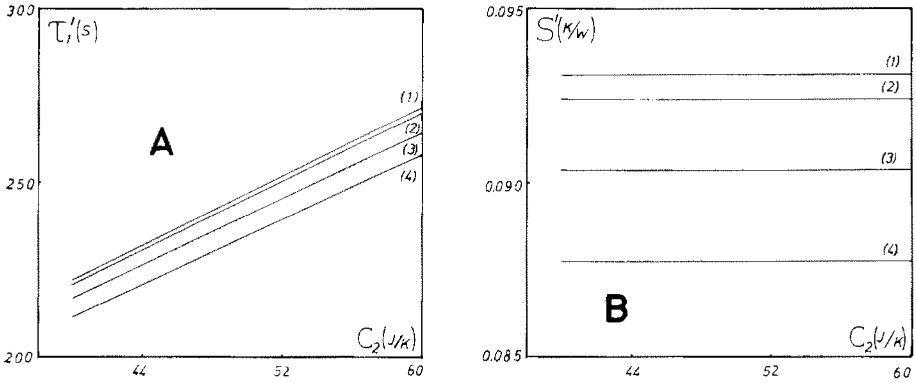

Fig. 3. Variation of (A) the main time constant τ_1' and (B) the sensitivity S' of the variable model as a function of the heat capacity C_2. The dissipation takes place in element 2, and C_2 is the only parameter varying with time. The different curves (1), (2), (3) and (4) correspond to different rates of variation of C_2, detailed in Table 2 (situation 2).

τ_1. The thermogram to be analysed is the decay obtained when a constant Joule effect is switched off while, for the whole process, liquid A is injected into liquid A.

To determine ΔS two ways are possible:

(a) If the thermal couplings between the vessel and the rest of the calorimeter do not appreciably change when the liquid is injected, the following experiment gives ΔS directly for a given injection rate and for a given injected substance: initially the system is at a homogeneous temperature and there is no output signal. Then a constant power is released by means of the Joule effect and an invariant steady state is reached. If

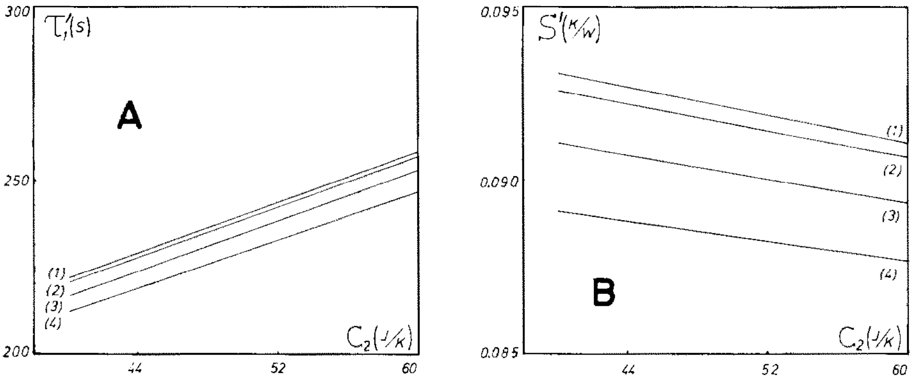

Fig. 4. Variation of (A) the main time constant τ_1' and (B) the sensitivity S' of the variable model as a function of the heat capacity C_2. The dissipation takes place in element 2, and C_2, P_{12}, P_{23} and P_2 vary with time. The different curves (1), (2), (3) and (4) correspond to different rates of variation of these parameters, as detailed in Table 2 (situation 3).

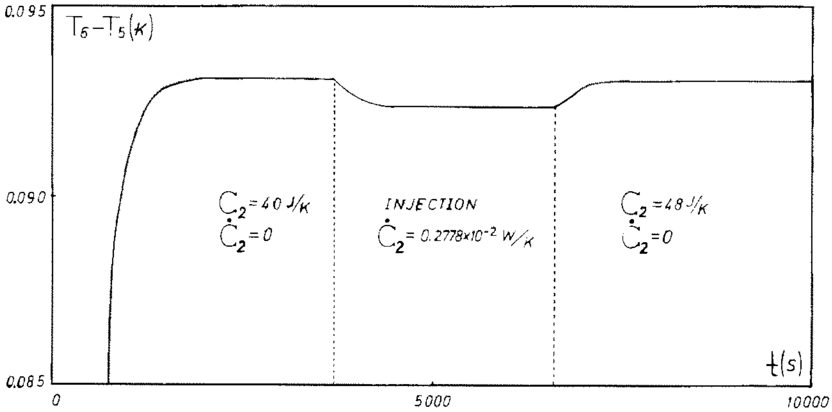

Fig. 5. Simulation of the change in the sensitivity of the calorimeter when the heat capacity C_2 of the vessel increases linearly with time, due to the injection of liquid. The simulation has been carried out with a model in which C_2 is the only time-varying parameter, corresponding to situation 2 in Table 2.

liquid A is now injected into liquid A, after a certain time another permanent state will be reached with a lower signal than the one before, because the liquid injected absorbs part of the heat released. Halting the injection leads to a recovery of the preceding steady state, which will now correspond to a different level in the cell contents. The difference between the two permanent states is ΔS, as shown in Fig. 5.

The value of ΔS for other injection rates and other substances can then be obtained directly, as described in ref. 3, by considering the ratio between the products $\rho c \dot{V}$ (density × specific heat × injection rate) corresponding to the experiment described above and to the experiment in which ΔS is searched for, respectively.

(b) If the conditions in (a) do not hold, a thermogram corresponding either to a Joule effect with injection of A into A or to a standard mixture will be used. This thermogram has to be filtered using the values τ_i', $\tau_i^{*\prime}$ and the sensitivity $S(t)$. If we call $z(t)$ the resulting signal and $W(t)$ the actual thermogenesis we are able to write:

$$[S(t)+\Delta S]\,W(t)=[S(t)]\,z(t)$$

and therefore

$$\Delta S = S(t)\left[\frac{z(t)}{W(t)}-1\right]$$

(ii) From the knowledge of $\tau_i(x)$, $\tau_i^*(x)$ and $S(x)$, which can be obtained from time-invariant experiments, and $\Delta\tau$ and ΔS, expressions (4) and (5) give $\tau_i'(x)$, $\tau_i^{*\prime}(x)$ and $S'(x)$ as functions of the level of vessel contents and, hence, $x(t)$ being known, as functions of time.

(iii) As explained in section 1.3, $\tau_i'(t)$, $\tau_i^{*\prime}(t)$ and $S'(t)$ determine in a unique way the coefficients $a_i'(t)$ and $A_i'(t)$, i.e. a differential equation of the kind (2) describing the time-varying experimental system.

The differential equation, once its coefficients are known, can be solved numerically to get the actual thermal power $W(t)$ released in the calorimeter from the experimental thermogram $S(t)$.

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