

THERMOGENESIS: AN APPROACH TO NEARLY EXACT DECONVOLUTION IN TIME-VARYING SYSTEMS

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ABSTRACT

Particular experimental conditions in calorimetry of mixing by continuous injection of a reactant open the possibility of building a simple model to study the performance of such devices. The characteristic equations of the model lead to an exact formulation of a deconvolutive procedure based on variable inverse filtering. The way in which the parameters of the filter may be obtained from experimental work is established.

INTRODUCTION

Detailed study of the thermograms corresponding to continuous injection devices in calorimetry of liquid mixtures has shown a non-negligible evolution of their dynamic characteristics with the quantity of liquid contained in the calorimetric vessel [1,2].

In this sense, RC models (localized constant models) with variable parameters have been considered, and the change in the corresponding thermograms due to the variation has been systematically evaluated in different conditions [3,4].

Additionally, there has been an attempt to propose new deconvolution methods which explicitly take into account the change in the system parameters as the mixture process goes on. In particular, the possibility of using inverse multistage filtering with slightly varying time constants and small modifications in the sensibility has been considered [2,4]. From an experimental point of view, the values of the time constants may be obtained from the decay in the thermogram when the injection comes to a halt. This has to be done at different intermediate levels of the cell contents. A backwards extrapolation to the time origin gives the values of the time constants at the start of the injection [2].

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In this work, heat flux calorimeters with continuous injection of one component are modelled. A multi-body model (RC model) with variable parameters is proposed in accordance with the practical experimental conditions, namely the vigorous stirring of the liquid in the cell and the identification of only a few important dynamic parameters. The theoretical analysis of the heat transport in the model establishes not only the appropriate deconvolution algorithm but also the way in which the identification of the system should be performed. Most of the features encountered in this work are directly related to the calorimeter, Arion-Electronique of BCP type. Nevertheless, the reasoning lines are applicable to equivalent devices and, what is more, they can be made suitable for mass-flow calorimeters devoted to the study of mixtures. In this kind of device the same problems occur, though on a different scale [5].

MODEL DESIGN AND RESULTS

In the Arion-Electronique calorimeter it is clear from the experimental thermograms that the maximum signal-to-noise ratio that may be expected centers around 60 dB. The limited accuracy is mainly due to the combined effects of mixing and stirring. On the other hand, identification in time-invariant experimental conditions clearly shows that two or three poles (two or three time constants) are enough to describe the system [1,2].

One of the simplest models which gives rise to three time constants is a chain-like model of three bodies. In other words, an RC model with three capacitors in line, each one coupled through a thermal resistance only with its nearest neighbours (Fig. 1). The power dissipation (thermogenesis) takes place at the first body and the calorimetric response (thermogram) is the temperature T_3 . Accurate values of the parameters nearly leading to the time constants of the Arion calorimeter may be found in table 1 of ref. 4. The heat balance equations of the model read

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

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

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

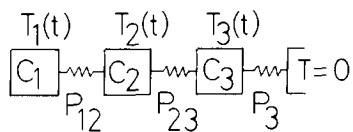


Fig. 1. Schematic representation of the three-body model considered.

This is a coupled system of linear, first-order differential equations. It can be easily transformed into a third-order differential equation of the following kind

$$W_1 = A \frac{d^3 T_3}{dt^3} + B \frac{d^2 T_3}{dt^2} + C \frac{dT_3}{dt} + DT_3$$

In this time-invariant model the thermogenesis will simply be achieved from the experimental thermogram by calculating the three derivatives in the above expression and multiplying them by the appropriate parameters A , B , C and D . This sort of calculation may be performed step-by-step using the set of equations

$$S_2 = T_3 + \tau_1 \frac{dT_3}{dt}$$

$$S_1 = S_2 + \tau_2 \frac{dS_2}{dt}$$

$$W_1 = \left(S_1 + \tau_3 \frac{dS_1}{dt} \right) D$$

where the time constants $\{\tau_i\}$ are related to the physical parameters of the model through the expressions

$$A = \tau_1 \tau_2 \tau_3$$

$$B = \tau_1 \tau_2 + \tau_1 \tau_3 + \tau_2 \tau_3$$

$$C = \tau_1 + \tau_2 + \tau_3 \quad (1)$$

The easiest way to obtain the time constants is to calculate the Laplace transform of the system of differential equations to get a linear algebraic system. The roots in the characteristic polynomial of this system are the poles of the model.

However, in a continuous-mixing device the heat capacity of the calorimetric vessel changes at the time the second component is being injected. The system of equations must be modified to take this fact into account, and should therefore read

$$W_1 = \frac{d(C_1 T_1)}{dt} + P_{12}(T_1 - T_2) = C_1(t) \frac{dT_1}{dt} + P_{12}(T_1 - T_2) + \dot{C}_1 T_1$$

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

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

It is no longer possible to apply the Laplace transform to this system, in order to obtain the time constants of the model, since it still has time-variable coefficients. However, we are able, by systematically substituting each

equation in the one above, to get a general equation of the form

$$W_1 = A' \frac{d^3 T_3}{dt^3} + B' \frac{d^2 T_3}{dt^2} + C' \frac{dT_3}{dt} + D' T_3 \quad (2)$$

Of course, this can only be used for those cases where there are no zeros in the transfer function of the model. As we are not interested in solving the system of differential equations, but in obtaining the power, $W_1(t)$, from the experimental thermogram, we may solve the problem by formally writing

$$S_2 = T_3 + \tau'_1 \frac{dT_3}{dt}$$

$$S_1 = S_2 + \tau'_2 \frac{dS_2}{dt}$$

$$W_1 = \left(S_1 + \tau'_3 \frac{dS_1}{dt} \right) D'$$

In these expressions, the parameters $\{\tau'_i(t)\}$ should be considered to have their values at time t , but not to participate in the derivatives. With this convention it is very simple to see that we obtain the third-order differential equation (2) again. Now the $\{\tau'_i\}$ parameters are functions of time. They exactly verify the equivalents of the expressions (1). In other words, they are, in every instant of time, the time constants of the time-invariant model modified with an additional coupling, \dot{C}_1 between the first body and the thermostat. Correspondingly, as they are modified by the presence of the injection, the values of $\{\tau'_i\}$ cannot be obtained from the experimental records when the injection is cut off. The same applies to the sensibility, D' , which is now a function of \dot{C}_1 , and consequently it is no longer measurable from time-invariant experiments.

To avoid the difficulty of obtaining the values of $\{\tau'_i\}$ and D' experimentally, it is possible to define a new power dissipation, W^* . This explicitly considers the power necessary to heat the liquid coming into the calorimetric vessel, $\dot{C}_1 T_1$.

$$W^* = W_1 - \dot{C}_1 T_1 = C_1(t) \frac{dT_1}{dt} + P_{12}(T_1 - T_2)$$

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

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

Again it is possible to reorganize the system in the form

$$W^* = W_1 - C_1 T_1 = A \frac{d^3 T_3}{dt^3} + B \frac{d^2 T_3}{dt^2} + C \frac{dT_3}{dt} + D T_3 \quad (3)$$

where the coefficients A , B and C , though being functions of time, have

exactly the same functional dependence with the parameters of the model as they had in the time-invariant case. Equation (3) gives the power W^* from the thermogram T_3 . Formally, it may be imagined as the sequence

$$S_2 = T_3 + \tau_1 \frac{dT_3}{dt}$$

$$S_1 = S_2 + \tau_2 \frac{dS_2}{dt}$$

$$W^* = \left(S_1 + \tau_3 \frac{dS_1}{dt} \right) D$$

The values of $\{\tau_i\}$ are now functions of time but correspond instantaneously to the values of time constants in an equivalent time-invariant system with the same value of C_1 , that is, the same quantity of liquid in the cell. They may be evaluated in practice from the corresponding time-invariant experimental conditions. The parameter D stands for the static sensibility of the time-invariant device, in order to convert the result into power units.

The power W_1 is obtained from W^* using the correction $\dot{C}_1 T_1$.

This last step is not experimentally feasible, because the temperature T_1 cannot be directly measured. The equations of the model, whether time invariant or not, show that T_1 can be obtained from T_3 as

$$T_1 = \alpha \left(\tau_1^* \frac{d}{dt} + 1 \right) \left(\tau_2^* \frac{d}{dt} + 1 \right) T_3$$

$$\alpha = 1 + \frac{P_3}{P_{12}} + \frac{P_3}{P_{23}}$$

The values of τ_1^* and τ_2^* cannot, again, be obtained experimentally. Considering that the correction in the power to be made with $\dot{C}_1 T_1$ is very small [2], we may simply suppose that both values are zero and take the temperature T_1 to be proportional to T_3 .

EXPERIMENTAL PROCEDURE

The experimental procedure to obtain the power as a function of time in non-invariant calorimetric systems may be summarized as follows.

Dynamic parameters

Several identifications at different levels of cell contents are necessary. They may be performed on the experimental thermograms corresponding to several breaks in the injection. The variable time constants obtained should be extrapolated backwards to guess their value at $t = 0$.

Sensibility

Only two measurements have to be made.

First, a permanent Joule effect showing the influence of the injection on

the steady-state temperature (see, for example, Fig. 2). From this measurement it is possible in practice to evaluate the term $\dot{C}_1 T_1$ in the steady state.

Second, the mixing of a standard binary mixture (say, for instance, benzene–cyclohexane) through a wide range of concentrations, in order to determine the static sensibility of the calorimeter.

Once these two steps have been accomplished the power is obtained by means of the following expression

$$W = S \left\{ \text{IF}[s] + \left(\frac{\Delta s}{s} \right)_{\text{Joule}} \cdot \frac{(\rho c \dot{V})}{(\rho c \dot{V})_{\text{Joule}}} \cdot s \right\} \quad (4)$$

where:

(a) the ratio $(\Delta s/s)_{\text{Joule}}$ is the relative decrease in the thermogram of the permanent Joule effect measurement (Fig. 2) due to the injection of a certain liquid with a rate of change in its specific heat of $(\rho c \dot{V})_{\text{Joule}}$; ρ is the density of the liquid, c its specific heat and \dot{V} the volume injected per unit time.

(b) s corresponds to the experimental thermogram.

(c) $\text{IF}[s]$ symbolizes the result of inverse filtering the thermogram with the

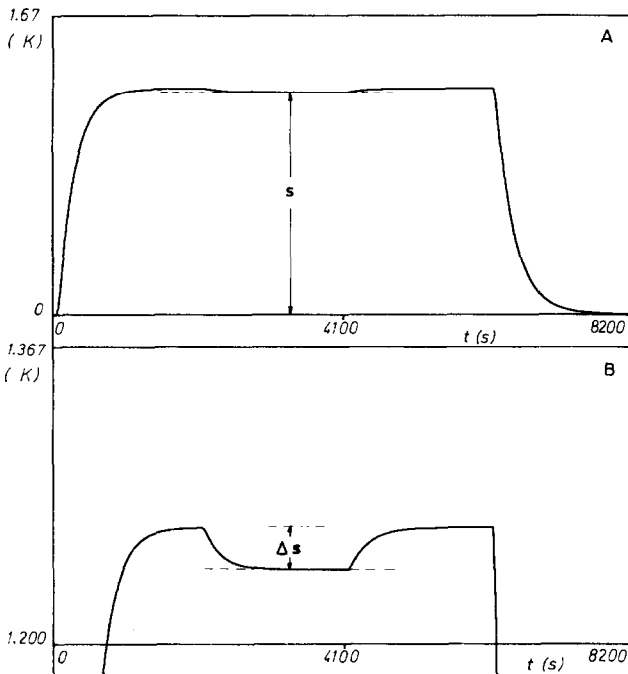


Fig. 2. (A) Simulated thermogram T_3 corresponding to a constant input power lasting 6150 s. Between $t = 2100$ and 4150 s there is a simulated liquid injection inside the cell which increases the heat capacity C_1 of the model by 20% of its initial value. (B) The steady-state interval of T_3 enlarged ten times to show the effect of injection. The figure shows the way of experimentally obtaining, from the recorded thermogram, the relative value $(\Delta s/s)_{\text{Joule}}$.

parameters $\{\tau_i(t)\}$, namely

$$\text{IF}[s] = \left(\tau_1(t) \frac{d}{dt} + 1 \right) \left(\tau_2(t) \frac{d}{dt} + 1 \right) \left(\tau_3(t) \frac{d}{dt} + 1 \right) s$$

(d) $(\rho c \dot{V})$ is the change in heat capacity of the calorimetric vessel due to the component injected into the mixture.

(e) S is the static sensibility of the device in the absence of injection. S could be directly measured from the Joule effect, but the presence of the heater and the thermal conduction through the wires modify the heat balance. It is generally acknowledged that a calibration based on standard mixtures may give the value of S with greater accuracy. Equation (4) again applies, with the power W replaced by $(h_i^E \dot{n}_i)$. Here h_i^E is the semiempirical polynomial of the excess partial molar enthalpy as a function of concentration corresponding to the standard mixture developed in the cell, and \dot{n}_i gives the number of moles of liquid injected per unit time.

CONCLUSIONS

A way of identifying the dynamic properties of a time-varying calorimetric system has been proposed. The experimental device is used in the study of binary mixtures by continuous injection of a component. The useful parameters $\{\tau_i(t)\}$, generalization of the time constants to the time-varying systems, are obtained by cutting off the injection and identifying the corresponding thermograms. This is done for different concentrations. It is also necessary to make an extrapolation of these values to the origin to get the initial parameters.

The injection affects the dynamic sensibility. By means of a permanent Joule effect, and injecting at a constant rate to reach the new steady state, it is feasible to measure the sensibility change for a certain density, specific heat, input power and volume rate.

Deconvolution in non-invariant calorimeters can finally be achieved by a variable inverse filtering with the parameters previously obtained, and a correction, measured from a permanent Joule effect, accounting for the power taken in by the injection.

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