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HEAT CAPACITY EVOLUTION IN CALORIMETERS WITH TEMPERATURE PROGRAMMING SIMULATED BY AN RC MODEL

J. FONT, J. MUNTASELL, J. NAVARRO and J.Ll. TAMARIT

Departament de Física, E.T.S.E.I.B., Universitat Politècnica de Catalunya, Diagonal 647, Barcelona 08028 (Spain)

E. CESARI

Departament de Física, Facultat de Ciències, Universitat de les Illes Balears, 07071 Palma de Mallorca (Spain)

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ABSTRACT

Using a one-body RC model, we analyse the output signal of a calorimetric system with temperature programming, simulating different evolutions in the sample heat capacity.

This model allows us to study the influence of the scanning rate β on the system output shape. The calorimetric response signal divided by β reproduces, with good accuracy, the studied heat capacity evolutions for small enough β values.

INTRODUCTION

Simulation of calorimetric systems has been usually carried out through localized constant models (RC models). These studies have generally applied only to isothermal conditions using an invariant formulation (constant parameters) [1–4] as well as non-invariant models [4–8].

In a previous paper [9] the output of a calorimetric system with temperature programming was simulated by means of a one-body RC model. The body, of heat capacity C, was coupled (coupling coefficient P) to a thermostat whose temperature T_b varied at a constant scanning rate β ($T_b(t) = \beta t$).

We analysed heat capacity variations due to either temperature or mass exchange with the exterior. Despite the simplicity of the model, we could obtain the sensitivity expression and analyse the applicability of the standard inverse filtering technique to calorimeters with temperature programming.

In the present study we analyse, using the model described above [9], the influence that different types of heat capacity variations have on the system output when the power released equals zero.

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MODEL

In Fig. 1 we show the model used. The balance equation when the power released equals zero ($W = 0$) is

$$W = 0 = C\frac{\mathrm{d}T}{\mathrm{d}t} + P(T - T_b) = C\beta\frac{\mathrm{d}T}{\mathrm{d}T_b} + P(T - T_b) \tag{1}$$

Below we present the four cases studied.

Discontinuity in heat capacity

Let us suppose that there is a discontinuity in the heat capacity at $T_b = T_1$ defined by

$$\begin{aligned} C &= C_1 \quad \text{for} \quad T_b < T_1 \\ C &= C_2 \quad \text{for} \quad T_b > T_1 \end{aligned} \tag{2}$$

The temperature T for $T_b < T_1$ can be evaluated by solving eqn. (1), previously substituting C for C_1:

$$T = \frac{C_1}{P}\beta \exp\left(-\frac{PT_b}{C_1\beta}\right) - \frac{C_1\beta}{P} + T_b \quad \text{for} \quad T_b < T_1 \tag{3}$$

When the stationary state is reached, i.e. when t is large enough and for $T_b < T_1$, then

$$T = -\frac{C_1\beta}{P} + T_b \tag{4}$$

This equation points out that, if the heat capacity remains constant, the body and the thermostat temperatures evolve in the same way with a constant delay equal to $C_1\beta/P$. The system output ΔT, defined as the difference between T in eqn. (4) and T_b, is

$$\Delta T = -\frac{C_1\beta}{P} \quad \text{for} \quad T_b < T_1 \tag{5}$$

Solving eqn. (1) with $C = C_2$ we can obtain the expression for T for $T_b > T_1$. If we impose a continuity in ΔT at T_1, the output for $T_b \geqslant T_1$ is

$$\Delta T = \frac{C_2 - C_1}{P}\beta \exp\left[\frac{P}{C_2\beta}(T_1 - T_b)\right] - \frac{C_2\beta}{P} \quad \text{for} \quad T_b \geqslant T_1 \tag{6}$$

The evolution of ΔT, when a discontinuity in C occurs at $T_b = T_1$, is

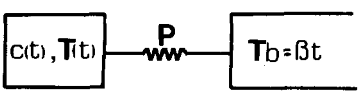

Fig. 1. Scheme of the analysed model.

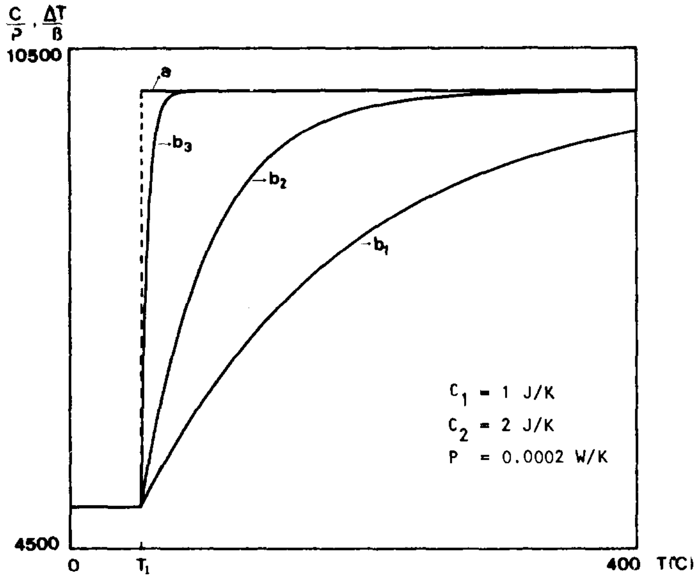

Fig. 2. C/P (line a) and $\Delta T/\beta$ (curves b) values for a discontinuity in the heat capacity as a function of the thermostat temperature for a change of 400 K: curve b_1, $\beta = 15 \times 10^{-3}$ K s^{-1}; curve b_2, $\beta = 5 \times 10^{-3}$ K s^{-1}; curve b_3, $\beta = 0.5 \times 10^{-3}$ K s^{-1}.

obtained from eqns. (5) and (6). We observe in eqn. (6) that ΔT tends towards $-C_2\beta/P$ when T_b increases. Thus, the difference in the stationary levels of ΔT above and below the temperature at which the capacity varies, is directly proportional to $C_2 - C_1$, to the scanning rate β and to the sensitivity ($S = 1/P$).

In Fig. 2 we represent the $\Delta T/\beta$ signal as well as the evolution with T_b of the heat capacity divided by P in order to have the same units. This figure shows that $\Delta T/\beta$ tends more quickly towards C/P when β diminishes, since the relaxation constant $\beta C_2/P$ in eqn. (6) is directly proportional to β.

Linear variation of the heat capacity with temperature

Let us consider a heat capacity variation in the form:

$$\begin{aligned} C &= C_1 && \text{for} \quad T_b \leqslant T_1 \\ C &= mT_b + n && \text{for} \quad T_1 \leqslant T_b \leqslant T_2 \\ C &= C_2 && \text{for} \quad T_b \geqslant T_2 \end{aligned} \tag{7}$$

In order to simulate the linear variation of the heat capacity we accept an evolution of the value of C with the thermostat temperature T_b. This assumption simplifies the resolution of the balance equations and will be more acceptable for lower values of the scanning rates because, under these conditions, T approaches T_b. Substituting in (eqn. 1) the expressions for the capacity given in eqn. (7) we obtain the balance equations for this case.

If we impose the continuity in ΔT at $T_b = T_1$ and $T_b = T_2$, we can write the equations that correspond to the output evolution with the thermostat temperature:

$$\Delta T = -\frac{C_1 \beta}{P} \quad \text{for} \quad T_b \leqslant T_1 \tag{8}$$

$$\Delta T = -\frac{C_1 \beta^2 m}{P(P+\beta m)} \left(\frac{m T_b + n}{C_1} \right)^{-P/m\beta} - \frac{\beta}{P+\beta m}(m T_b + n)$$

$$\text{for} \quad T_1 \leqslant T_b \leqslant T_2 \tag{9}$$

$$\Delta T = \frac{\beta^2 m}{P(P+\beta m)} \left[C_2 - C_1 \left(\frac{C_1}{C_2} \right)^{P/\beta m} \right] \exp\left[\frac{P}{C_2 \beta}(T_2 - T_b) \right] - \frac{C_2 \beta}{P}$$

$$\text{for} \quad T_b \geqslant T_2 \tag{10}$$

In Fig. 3 we represent the values of $\Delta T/\beta$ and C/P in front of T_b. This figure shows the influence of β on the system response. This representation reveals that, when the scanning rate diminishes, the $\Delta T/\beta$ signal follows more clearly the evolution of C/P with the temperature because the relaxation constant increases linearly with β as in the former case.

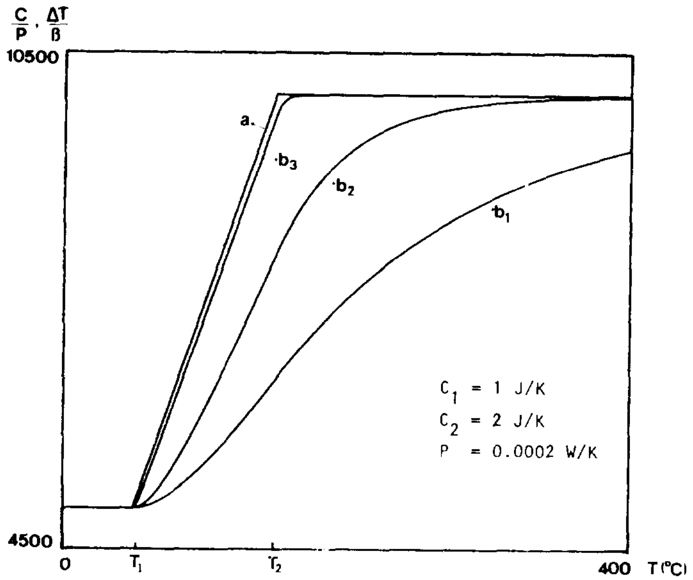

Fig. 3. C/P (line a) and $\Delta T/\beta$ (lines b) values for a linear variation of the heat capacity as a function of the thermostat temperature for a change of 400 K: curve b_1, $\beta = 15 \times 10^{-3}$ K s^{-1}; curve b_2, $\beta = 5 \times 10^{-3}$ K s^{-1}; curve b_3, $\beta = 0.5 \times 10^{-3}$ K s^{-1}.

Heat capacity variation in a triangular form

Let us suppose a variation of the heat capacity defined by

$$\begin{aligned}
C &= C_1 && \text{for} \quad T_b \leqslant T_1 \\
C &= mT_b + n && \text{for} \quad T_1 \leqslant T_b \leqslant T_2 \\
C &= -mT_b + n' && \text{for} \quad T_2 \leqslant T_b \leqslant T_3 \\
C &= C_1 && \text{for} \quad T_b \geqslant T_3
\end{aligned} \tag{11}$$

The balance equations corresponding to this case will be obtained by substitution in eqn. (1) of the expressions given in eqn. (11). Solving these balance equations and imposing the continuity in ΔT at T_1, T_2 and T_3 we obtain

$$\Delta T = -\frac{C_1\beta}{P} \text{ for } T_b \leqslant T_1 \tag{12}$$

$$\Delta T = -\frac{C_1\beta^2 m}{P(P+\beta m)}\left(\frac{mT_b+n}{C_1}\right)^{-P/m\beta} - \frac{\beta}{P+\beta m}(mT_b+n)$$
$$\text{for} \quad T_1 \leqslant T_b \leqslant T_2 \tag{13}$$

$$\Delta T = \left(\frac{C_2}{-mT_b+n'}\right)^{-P/m\beta}\left[\frac{2m\beta^2 C_2}{P^2-m^2\beta^2} - \frac{C_1\beta^2 m}{P(P+m\beta)}\left(\frac{C_2}{C_1}\right)^{-P/m\beta}\right]$$
$$-\frac{\beta}{P-m\beta}(-mT_b+n') \quad \text{for} \quad T_2 \leqslant T_b \leqslant T_3 \tag{14}$$

$$\Delta T = \left[\frac{-mC_1\beta^2}{P(P-m\beta)} + \frac{2m\beta^2 C_2}{P^2-m^2\beta^2}\left(\frac{C_2}{C_1}\right)^{-P/m\beta} - \frac{C_1\beta^2 m}{(P+m\beta)P}\left(\frac{C_2}{C_1}\right)^{-2P/m\beta}\right]$$
$$\times \exp\left(\frac{P}{C_1\beta}(T_3-T_b)\right) - \frac{C_1\beta}{P} \quad \text{for} \quad T_b \geqslant T_3 \tag{15}$$

where C_2 is the heat capacity value at $T_b = T_2$.

Figure 4 includes the representation of $\Delta T/\beta$ and C/P as a function of T_b for the evolution of the heat capacity defined by eqn. (11). In this figure one observes a displacement in the temperature of the peak tips corresponding to the input (fixed evolution of heat capacity) and the output signals. This displacement diminishes with β. However, though ΔT increases with the scanning rate (without dividing by β), the rounding-off effect is more evident for greater β values. A widening of the peak corresponding to the output signal when β increases is also observed.

Potential variation in the heat capacity

In this case the evolution of the heat capacity is defined by

$$C = C_1 \quad \text{for} \quad T_b \leqslant T_1$$

$$C = A\left(\frac{T_P - T_b}{T_P}\right)^{-\alpha} \quad \text{for} \quad T_1 \leqslant T_b < T_P \tag{16}$$

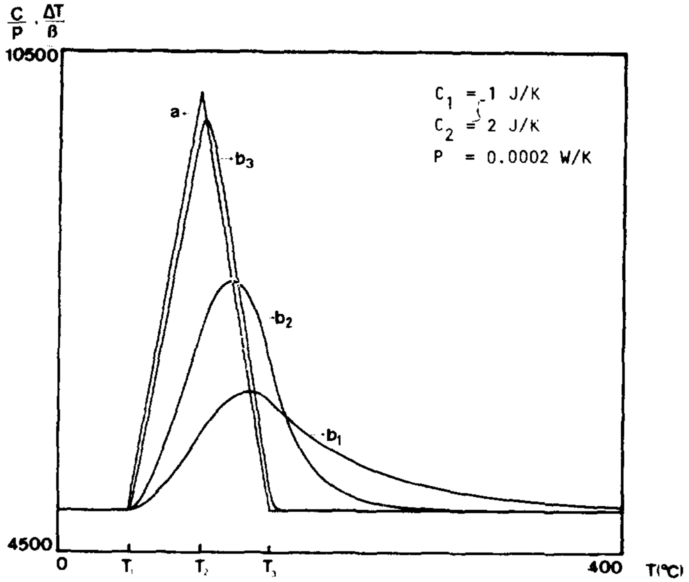

Fig. 4. C/P (line a) and $\Delta T/\beta$ (curves b) values for a triangular variation of the heat capacity as a function of the thermostat temperature for a change of 400 K; curve b_1, $\beta = 15 \times 10^{-3}$ K s^{-1}; curve b_2, $\beta = 5 \times 10^{-3}$ K s^{-1}; curve b_3, $\beta = 0.5 \times 10^{-3}$ K s^{-1}.

where A and α are constants and T_P is the thermostat temperature at which $C \to \infty$.

Through this evolution in the heat capacity we attempt to simulate a second-order transition with a critical exponent α.

Substituting C for C_1 in eqn. (1) and solving the balance equation we get the ΔT expression for $T_b \leqslant T_1$:

$$\Delta T = -\frac{C_1 \beta}{P} \quad \text{for} \quad T_b \leqslant T_1 \tag{17}$$

We solve numerically the balance equation corresponding to a potential variation in C for $T_1 \leqslant T_b < T_P$ by the Runge–Kutta method.

The evolution of $\Delta T/\beta$ and C/P as a function of T_b is represented in Fig. 5 for $\alpha = 0.3$ and $\alpha = 0.5$ values that are included in the critical exponents interval typical for second-order transitions. This figure indicates that $\Delta T/\beta$ values are nearer to those of C/P when β decreases.

It is possible to extend the present study to differential calorimetric systems having a weak thermal coupling between sample and reference. If the reference heat capacity C_r remains unvarying, there will be a constant difference $(C_r\beta/P)$ between the differential signal $(T_s - T_r)$ and $T_s - T_b$ where T_s, T_r and T_b are the sample, reference and thermostat temperatures respectively. This difference has no influence on the output signal shape.

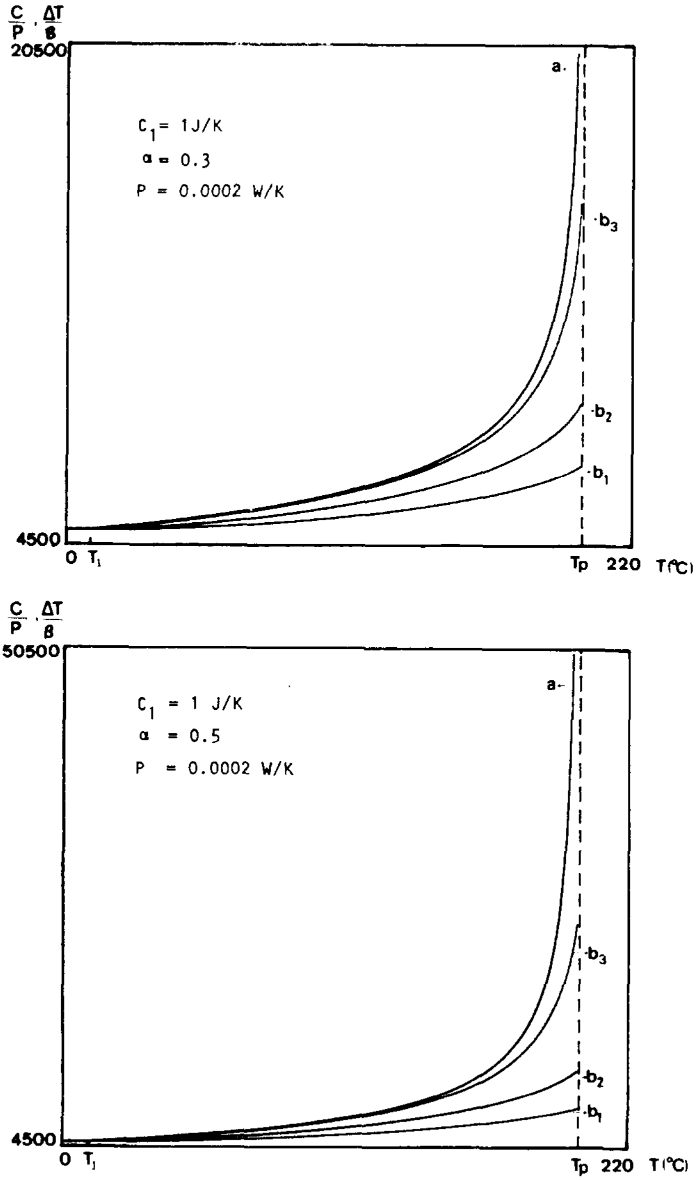

Fig. 5. C/P (curve a) and $\Delta T/\beta$ (curves b) values for a potential variation of the heat capacity as a function of the thermostat temperature for a change of 200 K: curve b_1, $\beta = 15 \times 10^{-3}$ K s^{-1}; curve b_2, $\beta = 5 \times 10^{-3}$ K s^{-1}; curve b_3, $\beta = 0.5 \times 10^{-3}$ K s^{-1}.

CONCLUSIONS

We have studied the output of a calorimetric system with temperature programming using a one-body RC model, considering different types of heat capacity variations.

The model, in spite of its simplicity, has allowed us to analyse the influence of the scanning rate β on the system output shape. In the different cases studied this simulation justifies the possibility of following the evolution of the heat capacity by using a reduced representation (system response divided by β) with low enough scanning rates. Under these conditions, the $\Delta T/\beta$ signal reproduces accurately the heat capacity evolution with temperature.

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