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A model for an isoperibol power-compensated twin calorimeter

N. Zucca[a,b,*], G. Erriu[a,b], S. Onnis[a,b], D. Zedda[b], A. Longoni[a]

[a] *Department of Physics, University of Cagliari, 09042 Monserrato (CA), Italy*
[b] *INFM, University of Cagliari, 09042 Monserrato (CA), Italy*

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Abstract

We present a theoretical model of a calorimeter, with particular reference to the Perkin-Elmer DSC-7, with the aim of emulating, in the simplest possible manner, the essential operations of this instrument. The basic idea is to assign a working transfer function to each of its fundamental elements: differential temperature amplifier, average temperature amplifier and programmer. From these transfer functions we get the theoretical output of the calorimeter. This output is used to fit the unbalance that occurs when the calorimeter switches from isothermal to scanning state. Following this, we work out the transfer function of the calorimeter and evaluate it using the parameters obtained from the fitting. We then use this function to deconvolute the melting peak of indium samples and to interpret melting temperature dependence on the scanning rate.

Keywords: DSC; Model; Fitting; Deconvolution

1. Introduction

Many authors have described the general working principles of a differential power scanning calorimeter (DPSC) [1–7], but a theory which enables us to describe the characteristic features of a measured curve is not yet available. In this paper we propose a mathematical model of DPSC, in the limit of linearity, with particular reference to a DSC-7 manufactured by Perkin-Elmer. We use a discrete elements approach, taking into account the inevitable construction differences between the two calorimeters.

The theoretical output of the calorimeter is obtained from the working transfer functions of the three fundamental elements of the DSC-7: average temperature amplifier, differential temperature amplifier and programmer. The number of parameters envisaged in the general model are then critically reduced. To ascertain that this simplified model still meets our main objective (i.e. to emulate, in the simplest possible manner, the essential operations of a DPSC like the DSC-7), it is tested by fitting the unbalance that occurs when the calorimeter switches from the isothermal to the running state.

The positive result of the fitting led us to believe that the model could be used to tackle some problems of interest to calorimeter users, such as that of how to obtain the impulse response of the instrument. This response has already been obtained by numerical differentiation of the unbalance that occurs when the DPSC switches from isothermal to running state [5]. It has also been worked out experimentally, using a very short light flash [8]. Nobody, as far as we know, has provided an analytical expression of the impulse response of the calorimeter. We get it from our model and evaluate it by introducing the parameters obtained

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[*] Corresponding author. Fax: +390-70-510171.
E-mail address: zucca@dsf.unica.it (N. Zucca).

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by the fitting. It is then used to deconvolute the fusion peak of indium samples and to interpret the delay in the onset temperature of fusion with the scan rate.

2. Operating equations

A holder of a DSC-7 is schematically shown in Fig. 1. It is made up of a small wafer-shaped block ABCD over which the compartment for a pan is located. The resistances for heating and measuring the temperature are insulated platinum wires wound around a rectangular aluminum oxide chip, surrounded by powdered aluminum oxide, pressed between two platinum alloy disks. The bottom resistance works as a heater and the top resistance as a temperature sensor.

The problem of heat conduction, taking into account that the distances involved are very small, can be dealt with in a very simple manner by a discrete elements approach. To this end we divided slab ABCD of the holder into two parts, as indicated by the broken line in Fig. 1, and we considered the pan (plus the sample to be studied) as a third part.

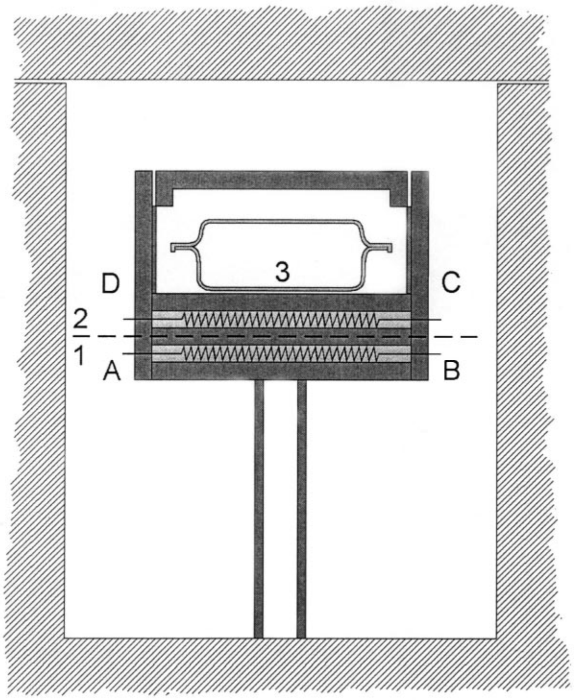

Fig. 1. Schematic representation of a holder in its surroundings. The broken line divides slab ABCD into two parts 1 and 2, where the heater and sensor respectively are embodied. Pan (plus its content) is the third part.

Applying the energy conservation law to the various parts, we get

$$\begin{aligned} P(t) &= C_1\frac{\mathrm{d}T_1(t)}{\mathrm{d}t}+\frac{T_1(t)}{R_1}+\frac{T_1(t)-T_2(t)}{R_{12}}, \\ \frac{T_1(t)-T_2(t)}{R_{12}} &= C_2\frac{\mathrm{d}T_2(t)}{\mathrm{d}t}+\frac{T_2(t)}{R_2}+\frac{T_2(t)-T_3(t)}{R_{23}}, \\ \frac{T_2(t)-T_3(t)}{R_{23}} &= C_3\frac{\mathrm{d}T_3(t)}{\mathrm{d}t}+\frac{T_3(t)}{R_3} \end{aligned} \tag{1}$$

where t is the time, $P(t)$ the power provided to the holder from outside, C_1, C_2, and C_3 are the thermal capacities of the various parts, R_1, R_2 and R_3 are the coupling thermal resistances between the three parts and the holder enclosure block (HEB, hatched in Fig. 1), R_{12} the coupling resistance between parts (1) and (2), R_{23} the coupling resistance between parts (2) and (3), $T_1(t)$, $T_2(t)$ and $T_3(t)$ are the temperatures of the various parts referred to temperature T_∞ of the HEB. Obviously, isotherm temperature T_I, instead of T_∞, can be used as a reference, but in this case power $P(t)$ must also be referred to its isothermal value. In the following, all quantities will be referred to their isothermal values.

We now examine the particular case of an empty holder. In this case $C_3 = 0$ and $R_{23} \to \infty$, consequently the system (1) reduces to

$$\begin{aligned} P(t) &= C_1\frac{\mathrm{d}T_1(t)}{\mathrm{d}t}+\frac{T_1(t)}{R_1}+\frac{T_1(t)-T_2(t)}{R_{12}}, \\ \frac{T_1(t)-T_2(t)}{R_{12}} &= C_2\frac{\mathrm{d}T_2(t)}{\mathrm{d}t}+\frac{T_2(t)}{R_2} \end{aligned} \tag{2}$$

If we eliminate $T_1(t)$ from Eq. (2), we get

$$\begin{aligned} P(t) = {}& R_{12}C_1C_2\frac{\mathrm{d}^2T_2}{\mathrm{d}t^2}+\left(C_1+C_2+\frac{R_{12}C_1}{R_2}+\frac{R_{12}C_2}{R_1}\right) \\ & \times\frac{\mathrm{d}T_2}{\mathrm{d}t}+\left(\frac{1}{R_1}+\frac{1}{R_2}+\frac{R_{12}}{R_1R_2}\right)T_2 \end{aligned} \tag{3}$$

In a DSC-7, temperature control of the two coupled holders is realized in two half-cycles: the average power half-cycle and the differential power half-cycle [9]. These two operations are performed by the average temperature amplifier and by the differential temperature amplifier, respectively [9]. During the power half-period $\tau/2$, the same amount of energy

$P(t)\tau/2$ is supplied to the two holders. The relevant control system operates so that the average temperature $T_A = \frac{1}{2}(T_{2S} + T_{2R})$ increases linearly with time, thus tracking as closely as possible the signal $T_P(t)$ coming from the programmer (letters S and R in the subscripts refer to the sample-holder and the reference-holder, respectively). During the differential half-cycle the difference in temperature of the two holders is controlled and the energy $(P + D/2)\tau/2$ is supplied to the holder with the lower temperature and the energy $(P - D/2)\tau/2$ is supplied to the holder with the higher temperature, in order to decrease their temperature difference.

Eq. (3) written for the two holders, together with the equations for the temperature control of the two half-cycles, are the fundamental equations describing the operation of an empty calorimeter. For generality's sake, we use a PID (proportional, integral, differential) control for both the half-cycles at this stage. We will specialize the system afterwards. We get the following system of equations:

$$\begin{aligned}
&P(t) + \frac{D(t)}{2} = \alpha_2 \frac{\mathrm{d}^2 T_{2S}}{\mathrm{d}t^2} + \alpha_1 \frac{\mathrm{d}T_{2S}}{\mathrm{d}t} + \alpha_0 T_{2S},\\
&P(t) - \frac{D(t)}{2} = \beta_2 \frac{\mathrm{d}^2 T_{2R}}{\mathrm{d}t^2} + \beta_1 \frac{\mathrm{d}T_{2R}}{\mathrm{d}t} + \beta_0 T_{2R},\\
&P(t) = K_P(T_P - T_A) + K_I \int (T_P - T_A)\,\mathrm{d}t\\
&\qquad + K_D \frac{\mathrm{d}(T_P - T_A)}{\mathrm{d}t},\\
&D(t) = -H_P T_D(t) - H_I \int T_D(t)\,\mathrm{d}t - H_D \frac{\mathrm{d}T_D(t)}{\mathrm{d}t},\\
&T_A(t) = \frac{T_{2S}(t) + T_{2R}(t)}{2}, \qquad T_D(t) = T_{2S}(t) - T_{2R}(t)
\end{aligned} \tag{4}$$

where for the sake of brevity we put

$$\begin{aligned}
&\alpha_2 = R_{12S} C_{1S} C_{2S},\\
&\alpha_1 = C_{1S} + C_{2S} + R_{12S}\left(\frac{C_{1S}}{R_{2S}} + \frac{C_{2S}}{R_{1S}}\right),\\
&\alpha_0 = \frac{1}{R_{1S}} + \frac{1}{R_{2S}} + \frac{R_{12S}}{R_{1S}R_{2S}}, \qquad \beta_2 = R_{12R} C_{1R} C_{2R},\\
&\beta_1 = C_{1R} + C_{2R} + R_{12R}\left(\frac{C_{1R}}{R_{2R}} + \frac{C_{2R}}{R_{1R}}\right),\\
&\beta_0 = \frac{1}{R_{1R}} + \frac{1}{R_{2R}} + \frac{R_{12R}}{R_{1R}R_{2R}}
\end{aligned} \tag{5}$$

K_P, K_I, K_D are the constants for the power half-cycle control system and H_P, H_I, H_D are the constants for the differential half-cycle control system. In the temperature control equation for the differential half-cycle we considered the temperature of the reference-holder greater than that of the sample-holder ($T_{2R} > T_{2S}$) and we used the minus sign because, conventionally, $D(t)$ is considered positive in this case. In these equations $T_P(t)$ is the input and all the other quantities, namely: $T_A(t)$, $T_D(t)$, $P(t)$, $D(t)$, $T_{2S}(t)$ and $T_{2R}(t)$ are the outputs. The power difference $D(t)$ is an output provided by the DSC-7 calorimeter.

$T_P(t)$, the reference signal for the average temperature amplifier, is generated by the programmer, which is the third fundamental device of a DSC-7 calorimeter in addition to the average temperature amplifier and differential temperature amplifier [9]. $T_P(t)$ must increase linearly with time at rate u_P. The input of the programmer is the so-called programmed temperature, $\vartheta(t) = u_P(t + q)$, which is the abscissa of the measured curve and is generated by the timing source of the instrument. We, of course, do not know the exact transfer function of the programmer; we know only what it must perform. So we approximate this transfer function by a linear second-order equation. We put

$$t_P(L) = \frac{\omega^2 u_P}{L^2 + 2\zeta\omega L + \omega^2}\left(\frac{1}{L^2} + \frac{q}{L}\right) \tag{6}$$

The three parameters ω, ζ and q are to be determined by the fitting. The terms in the round brackets $T_P(t)$ is the Laplace transforms of $T_P(t)$. According to Eq. (6), we have the following initial values: $T_P(0) = T'_P(0) = 0$, and $T''_P(0) = q\omega^2 u_P$. Moreover, for the steady state, we get

$$T_{P,\infty}(t) = (t + q)u_P - \frac{2\zeta}{\omega} u_P \tag{7}$$

$T_{P,\infty}(t)$ has then a delay $(2\zeta/\omega)u_P$ with respect to input $\vartheta(t)$. It follows then, that not only heat-transfer, as envisaged in Eq. (4), but also the action of the programmer is to be considered in the total delay with respect to $\vartheta(t)$.

In order to have the outputs as functions of the input, we must solve system (4). In the limits of linearity, all parameters are constants and this integro-differential system can be more easily solved using Laplace transforms. If we suppose momentarily all initial conditions equal to zero, system (4) becomes

$$
\begin{aligned}
&p(L)+\tfrac{1}{2}d(L)=[\alpha_2L^2+\alpha_1L+\alpha_0]t_{2\mathrm{S}}(L),\\
&p(L)-\tfrac{1}{2}d(L)=[\beta_2L^2+\beta_1L+\beta_0]t_{2\mathrm{R}}(L),\\
&p(L)=K_{\mathrm{P}}[t_{\mathrm{P}}(L)-t_{\mathrm{A}}(L)]+\frac{K_{\mathrm{I}}}{L}[t_{\mathrm{P}}(L)-t_{\mathrm{A}}(L)]\\
&\qquad+K_{\mathrm{D}}L[t_{\mathrm{P}}(L)-t_{\mathrm{A}}(L)],\\
&d(L)=-H_{\mathrm{P}}[t_{2\mathrm{S}}(L)-t_{2\mathrm{R}}(L)]-\frac{H_{\mathrm{I}}}{L}[t_{2\mathrm{S}}(L)-t_{2\mathrm{R}}(L)]\\
&\qquad-H_{\mathrm{D}}L[t_{2\mathrm{S}}(L)-t_{2\mathrm{R}}(L)],\\
&t_{\mathrm{A}}(L)=\tfrac{1}{2}[t_{2\mathrm{S}}(L)+t_{2\mathrm{R}}(L)],\\
&t_{\mathrm{D}}(L)=[t_{2\mathrm{S}}(L)-t_{2\mathrm{R}}(L)]
\end{aligned}
\tag{8}
$$

In these formulas L is a complex variable and the small letters stand for the Laplace transforms of the functions indicated by capital letters in the time domain. System (8) can now be treated as an algebraic system with p, d, $t_{2\mathrm{S}}$, $t_{2\mathrm{R}}$, t_{A}, t_{D} unknown. The outlines of the solution of this system are reported in Appendix A.

In the case of a pan placed in a holder, solving system (1) in the complex domain with respect to $t_2(L)$, we get

$$
\begin{aligned}
p(L)=\Bigg\{&R_{12}C_1C_2L^2+\Bigg(C_1+C_2+\frac{C_1R_{12}}{R_2}+\frac{C_2R_{12}}{R_1}\\
&+\frac{C_1R_{12}}{R_{23}}\left[\frac{C_3L+1/R_3}{C_3L+1/R_3+1/R_{23}}\right]\Bigg)L+\frac{1}{R_1}\\
&+\frac{1}{R_2}+\frac{R_{12}}{R_1R_2}+\frac{R_{12}}{R_{23}}\left(\frac{1}{R_1}+\frac{1}{R_{12}}\right)\\
&\times\left[\frac{C_3L+1/R_3}{C_3L+1/R_3+1/R_{23}}\right]\Bigg\}t_2(L)
\end{aligned}
\tag{9}
$$

This equation coincides with the transform of Eq. (3), apart from the two fractional terms in square brackets. C_3, the thermal capacity of the pan plus the sample, is about $2.5\times10^{-2}\,\mathrm{J\,K^{-1}}$, i.e. an order of magnitude smaller than the thermal capacity of a holder. We can therefore approximate the fractional term by its power expansion in C_3:

$$
\begin{aligned}
\frac{C_3L+1/R_3}{C_3L+1/R_3+1/R_{23}}=&\frac{R_{23}}{R_{23}+R_3}+\frac{R_{23}R_3^2}{(R_{23}+R_3)^2}LC_3\\
&-\frac{R_{23}^2R_3^3}{(R_{23}+R_3)^3}L^2C_3^2+\cdots
\end{aligned}
\tag{10}
$$

Substituting this equation in (9) and using positions (5) concerning the sample-holder, we have

$$
\begin{aligned}
p(L)=\alpha_2L^2+\Bigg[&\alpha_1+\frac{C_{1\mathrm{S}}R_{12\mathrm{S}}}{R_{23\mathrm{S}}}\Bigg(\frac{R_{23\mathrm{S}}}{R_{23\mathrm{S}}+R_{3\mathrm{S}}}\\
&+\frac{R_{23\mathrm{S}}R_{3\mathrm{S}}^2}{(R_{23\mathrm{S}}+R_{3\mathrm{S}})^2}LC_{3\mathrm{S}}+\cdots\Bigg)\Bigg]L+\alpha_0+\frac{R_{12\mathrm{S}}}{R_{23\mathrm{S}}}\\
&\times\left(\frac{1}{R_{1\mathrm{S}}}+\frac{1}{R_{12\mathrm{S}}}\right)\Bigg(\frac{R_{23\mathrm{S}}}{R_{23\mathrm{S}}+R_{3\mathrm{S}}}+\frac{R_{23\mathrm{S}}R_{3\mathrm{S}}^2}{(R_{23\mathrm{S}}+R_{3\mathrm{S}})^2}\\
&\times LC_{3\mathrm{S}}-\frac{R_{23\mathrm{S}}^2R_{3\mathrm{S}}^3}{(R_{23\mathrm{S}}+R_{3\mathrm{S}})^3}L^2C_{3\mathrm{S}}^2+\cdots\Bigg)
\end{aligned}
\tag{11}
$$

In this substitution we neglected the terms in L which would generate an equation of an order higher than two; in this way we get an equation which can easily be compared with the transform of Eq. (3) for an empty holder. Reordering and using the explicit form of α_1, α_2 and α_3, we see that these expressions can be redefined in the following manner:

$$
\begin{aligned}
\alpha_2=&R_{12\mathrm{S}}C_{1\mathrm{S}}\left[C_{2\mathrm{S}}+\frac{R_{3\mathrm{S}}^2}{(R_{23\mathrm{S}}+R_{3\mathrm{S}})^2}C_{3\mathrm{S}}\right]\\
&-\left(1+\frac{R_{12\mathrm{S}}}{R_{1\mathrm{S}}}\right)\frac{R_{3\mathrm{S}}^3}{(R_{23\mathrm{S}}+R_{3\mathrm{S}})^3}R_{23\mathrm{S}}C_{3\mathrm{S}}^2,\\
\alpha_1=&C_{1\mathrm{S}}+\left[C_{2\mathrm{S}}+\frac{R_{3\mathrm{S}}^2}{(R_{23\mathrm{S}}+R_{3\mathrm{S}})^2}C_{3\mathrm{S}}\right]\\
&+\frac{R_{12\mathrm{S}}}{R_{1\mathrm{S}}}\left[C_{2\mathrm{S}}+\frac{R_{3\mathrm{S}}^2}{(R_{23\mathrm{S}}+R_{3\mathrm{S}})^2}C_{3\mathrm{S}}\right]\\
&+R_{12\mathrm{S}}C_{1\mathrm{S}}\left(\frac{1}{R_{2\mathrm{S}}}+\frac{1}{R_{23\mathrm{S}}+R_{3\mathrm{S}}}\right),\\
\alpha_0=&\frac{1}{R_{1\mathrm{S}}}+\left(1+\frac{R_{12\mathrm{S}}}{R_{1\mathrm{S}}}\right)\left(\frac{1}{R_{2\mathrm{S}}}+\frac{1}{R_{23\mathrm{S}}+R_{3\mathrm{S}}}\right)
\end{aligned}
\tag{12}
$$

Comparing Eq. (12) with their analog (5) we see that, apart from the quadratic term in $C_{3\mathrm{S}}^2$, in the first-order approximation, placing a pan in an empty holder is the same as increasing its capacity C_2 and its thermal conductance $1/R_2$ by the respective amounts:

$$
C_2+\frac{R_3^2}{(R_{23}+R_3)^2}C_3\to C_2,\qquad \frac{1}{R_2}+\frac{1}{R_{23}+R_3}\to\frac{1}{R_2}
\tag{13}
$$

These positions allow us to consider a holder with a pan as if it were empty, but of course the best fitting parameters must be recalculated. When we put a pan in a holder an RC-term is added in series with the holder and consequently an extra exponential should appear in the general solution. This is quite clear if we inspect Eq. (9). It turns out to be a third-order equation, while Eq. (2), concerning an empty holder, is of the second order. In the empty holder approximation (EHA) the number of exponentials is still that of an empty calorimeter, nevertheless the measured curves can always be fitted quite well. We considered two fundamentally different experimental situations: (a) when the calorimeter is well balanced (e.g. a pan is placed in both holders), in this case the EHA should apply to both holders and (b) when the calorimeter is unbalanced (e.g. a pan is placed in the sample-holder and the reference-holder is empty). In this case the EHA should apply only to the sample-holder. In both experimental situations the measured curves can be fitted quite well. This gives us confidence that the EHA is a good approximation adequate to describe the output of the instrument.

3. Fitting of the experimental curve

The theoretical output $D(t)$ is given in the complex domain by Eq. (A.10) of the appendix and its coefficients are given by (A.6) and (A.9). Taking into account Eq. (6) for $t_P(L)$ and the initial condition $T''_P(0) = q\omega^2 u_P$, we can rewrite Eq. (A.10) in the following form, which is that used for the fitting:

$$d(L) = \frac{P_{D3}L^3 + P_{D2}L^2 + P_{D1}L + P_{D0}}{A_5L^5 + A_4L^4 + A_3L^3 + A_2L^2 + A_1L + A_0} \times \frac{\omega^2 u_P}{L^2 + 2\zeta\omega L + \omega^2}\left(\frac{1}{L^2} + \frac{q}{L}\right) - \frac{P_{D3}q\omega^2 u_P}{A_5L^5 + A_4L^4 + A_3L^3 + A_2L^2 + A_1L + A_0} \tag{14}$$

In the programme there is the option to introduce a delay between the start of scanning and the end of the isotherm. Calling X_P this dead time, the function to minimize turns out to be

$$\chi^2(C_{1S}, C_{1R}, C_{2S}, C_{2R}, R_{1S}, R_{1R}, R_{2S}, R_{2R}, R_{12S}, R_{12R}, K_I, K_P, K_D, H_I, H_P, H_D, \zeta, \omega, q, X_P) = \sum [D(t) - Y(t)]^2 \tag{15}$$

where $Y(t)$ is the experimental output. The general function of fitting depends on 20 parameters, but in fitting the measured curves of our DSC-7 we always worked with a smaller number.

The DSC-7 output is usually reported to be proportional to the difference in temperature of the two holders [6,8]. Accordingly, for the differential half-cycle we put: $H_I = H_D = 0$. As a further simplification we also put: $K_D = 0$.

To have a rough evaluation of the thermal capacity of a holder, we used an old measuring head of our calorimeter. We obtained for block ABCD a value of $\simeq 0.5$ and then $\simeq 0.25\,\mathrm{J\,K^{-1}}$ for its two half-parts. In the fitting we set $C_{1S} = C_{1R} = C_{2R} = 0.25\,\mathrm{J\,K^{-1}}$, leaving only C_{2S} to vary. A rough evaluation of resistances R_1 and R_2 was performed by calculating the thermal flux between a holder and the HEB. For the HEB at 200 K and the holder at 273 K we get $R_1 \simeq 130\,\mathrm{K\,W^{-1}}$, $R_2 \simeq 320\,\mathrm{K\,W^{-1}}$. Also in this case we set constants $R_{1S} = R_{1R} = 130\,\mathrm{K\,W^{-1}}$ and $R_{2R} = 320\,\mathrm{K\,W^{-1}}$, leaving only R_{2S} to vary. Values of C_{1S}, C_{1R}, C_{2R}, R_{1S}, R_{1R}, R_{2R} within 10% of the quoted values practically provide fittings with the same standard deviation. Resistance R_{12} has instead a value of few units. In the process of fittings we kept R_{12R} as a constant and R_{12S} as a variable parameter. The best fittings were obtained with $R_{12R} \simeq 2.3\,\mathrm{K\,W^{-1}}$. These positions, while reducing the number of parameters, still account for the asymmetries between the two coupled holders. In fact, their differences in thermal capacity and conductance are all incorporated in the fitting parameters C_{2S}, R_{2S} and R_{12S}.

At this point, the parameters left free to vary in the process of fitting are therefore: K_I, K_P, H_P, C_{2S}, R_{2S}, R_{12S}, ζ, ω, q, X_P. This number can be further reduced by two by imposing that the steady state solution of Eq. (14) should coincide with the asymptotic behavior of the experimental curve. If we denote by $Z_1t + Z_2$ the straight line that fits the experimental curve when the initial transient is over, then from Eq. (14), we get

$$Z_1A_0 = P_{D0}u_P, \qquad Z_1(A_1\omega + 2\zeta A_0) + Z_2A_0\omega = (P_{D0}q + P_{D1})\omega u_P \tag{16}$$

In our fitting programme these equations are used to get R_{2S} and C_{2S}.

Eq. (14) and their coefficients (A.6) and (A.9) show that the function is not linear in its fitting parameters and consequently the error function can have more than one minimum in the parameter hypersurface. It is therefore necessary, at the beginning of the process of fitting, to localize one of these minima, either tentatively or by using one of the searching techniques in the parameter space [10]. In reality, we tentatively determined a point near a minimum, then we optimized the parameters by the Marquardt method [10].

>From Eq. (A.11) and taking into account what has been said before concerning Eq. (14), we get for $t_{2S}(L)$:

$$t_{2S}(L) = \frac{T^*_{S3}L^3 + T^*_{S2}L^2 + T^*_{S1}L + T^*_{S0}}{A_5L^5 + A_4L^4 + A_3L^3 + A_2L^2 + A_1L + A_0} \times \frac{\omega^2 u_P}{L^2 + 2\zeta\omega L + \omega^2}\left(\frac{1}{L^2} + \frac{q}{L}\right) - \frac{T^*_{S3}q\omega^2 u_P}{A_5L^5 + A_4L^4 + A_3L^3 + A_2L^2 + A_1L + A_0} \quad (17)$$

whose coefficients, (A.6) and (A.12), can be calculated using the parameters obtained from the fitting of the measured curve $D(t)$.

The second of Eq. (2) allows us to get temperature $t_{1S}(L)$. This equation, using the symbols relating to the sample-holder and resolved with respect to temperature $T_{2S}(t)$, becomes in the complex domain:

$$t_{1S} = \left[R_{12S}C_{2S}L + \left(\frac{R_{12S}}{R_{2S}} + 1\right)\right]t_{2S}(L) \quad (18)$$

where all the parameters are known from the fitting of $D(t)$. The third of Eq. (1) written in the complex domain becomes:

$$t_{3S}(L) = \frac{1/C_{3S}R_{23S}}{L + (1/C_{3S}R_{3S} + 1/C_{3S}R_{23S})}t_{2S}(L) \quad (19)$$

and may allow us to evaluate temperature $t_{3S}(L)$, provided R_{3S} and R_{23S} are known.

4. Transfer function

The EHA enables us to work out the transfer function of the calorimeter in two different experimental situations: (a) when the transient of the signal generated by the programmer is still in progress and consequently $t_P(L)$ is given by (6). This is the case when the calorimeter switches from the isothermal to the running state (or vice versa) and (b) when the reference signal has reached its steady state. In this case the action of the programmer is simply to produce a delay of the amount $2\zeta u_P/\omega$ in its input, as expressed in the time domain by Eq. (7). If, for simplicity's sake, we do not consider the term q, the reference signal in the complex domain turns out to be

$$t_P(L) = \frac{u_P}{L^2}\,e^{-(2\zeta u_P/\omega)L} \quad (20)$$

A signal coming from a pan should affect only the operations of the average temperature amplifier and the differential temperature amplifier but not the programmer. Consequently, in our view, the impulse response to use in the deconvolution of a signal coming from a pan should be that relating to (b).

Let us first consider this second case. If we inspect the explicit expression of coefficients P_{D3}, P_{D2}, P_{D1}, P_{D0}, we realize that in order to have a response from the calorimeter it is necessary to have a difference in the thermal capacities or the conductances of the two coupled holders. In EHA, whatever happens in a pan can be seen by the calorimeter only as a change in capacity C_{2S} or conductance $1/R_{2S}$ of the upper part of the sample-holder (where, in view of positions (13), both the pan and the sample are embodied). We should therefore investigate how Eq. (14) is affected when $1/R_{2S}$ or C_{2S} changes by a constant amount η.

Let us suppose that there is an increase in the conductance between the upper part of the sample-holder and its environment by a constant amount η. If we make the substitution

$$\frac{1}{R_{2S}} + \eta \rightarrow \frac{1}{R_{2S}} \quad (21)$$

Eq. (5) concerning the sample-holder are transformed as follows:

$$\alpha_1 + \eta R_{12S}C_{1S} \rightarrow \alpha_1, \qquad \alpha_0 + \eta + \eta\frac{R_{12S}}{R_{1S}} \rightarrow \alpha_0 \quad (22)$$

In the second substitution the third addend can be dropped, if we take into account that the fractional term has a very small value compared to the second. Carrying out substitutions (22) in (A.6) and (A.9) and taking into account Eq. (20), Eq. (14) can be written as

$$\mathrm{d}(L) = \frac{\Delta_\mathrm{d} + \eta N_2(L)}{\Delta + \eta D_4(L)} \frac{u_\mathrm{P}}{L^2} \mathrm{e}^{-(2\zeta u_\mathrm{P}/\omega)L} \tag{23}$$

where, for brevity's sake, we indicated the numerator and the denominator of Eq. (A.10) with Δ_d and Δ respectively, and with $N_2(L)$ and $D_4(L)$ the two polynomials of the second and fourth degree, which turn up in the numerator and in the denominator of Eq. (A.10) as a result of substitutions (21). When $\eta = 0$ we get the baseline. When $\eta \neq 0$ we get a response that is not linear as input η also appears in the denominator. If η is small we can expand Eq. (23) by a power series, and if we retain only the first-order term, we get

$$d(L) = \left[\frac{\Delta_\mathrm{d}}{\Delta}\frac{u_\mathrm{P}}{L^2} + \left(\frac{N_2(L)}{\Delta} - \frac{\Delta_\mathrm{d} D_4(L)}{\Delta^2}\right)\eta \frac{u_\mathrm{P}}{L^2}\right] \mathrm{e}^{-(2\zeta u_\mathrm{P}/\omega)L} \tag{24}$$

The first addend represents the baseline, while the second addend represents the response to the ramp input $\eta u_\mathrm{P}/L^2$ of strength ηu_P. The second fraction inside the round bracket can generally be neglected as the coefficients of the polynomial Δ_d are very small, since they are linear combinations of the differences $C_\mathrm{S} - C_\mathrm{R}$ and $1/R_\mathrm{S} - 1/R_\mathrm{R}$. Using this approximation, the transfer function for a change in conductance $1/R_{2\mathrm{S}}$ can be written as

$$\begin{aligned}\delta(L) &= \frac{N_2(L)}{\Delta} \\ &= \frac{N_2 L^2 + N_1 L + N_0}{A_5 L^5 + A_4 L^4 + A_3 L^3 + A_2 L^2 + A_1 L + A_0} \\ &\quad \times \mathrm{e}^{-(2\zeta u_\mathrm{P}/\omega)L}\end{aligned} \tag{25}$$

where N_2, N_1, N_0 are the coefficients of the polynomial $N_2(L)$, which are given by the following expressions:

$$N_2 = H_\mathrm{P} K_\mathrm{P} R_{12\mathrm{S}} C_{1\mathrm{S}}, \qquad N_1 = H_\mathrm{P} K_\mathrm{P} + H_\mathrm{P} K_\mathrm{I} R_{12\mathrm{S}} C_{1\mathrm{S}}, \qquad N_0 = H_\mathrm{P} K_\mathrm{I} \tag{26}$$

Let us suppose that it is the thermal capacity $C_{2\mathrm{S}}$ that increases by a constant amount η. In this case the substitution to be made is

$$C_{2\mathrm{S}} + \eta \to C_{2\mathrm{S}} \tag{27}$$

and, operating as in the previous case, we get in place of substitutions (22):

$$\alpha_2 + R_{12\mathrm{S}} C_{1\mathrm{S}} \eta \to \alpha_2, \qquad \alpha_1 + \eta + \frac{R_{12\mathrm{S}}}{R_{1\mathrm{S}}}\eta \to \alpha_1 \tag{28}$$

and in place of Eq. (23), we have

$$d(L) = \frac{\Delta_\mathrm{d} + \eta L N_2(L)}{\Delta + \eta L D_4(L)} \frac{u_\mathrm{P}}{L^2} \mathrm{e}^{-(2\zeta u_\mathrm{P}/\omega)L} \tag{29}$$

The series expansion gives

$$d(L) = \left[\frac{\Delta_\mathrm{d}}{\Delta}\frac{u_\mathrm{P}}{L^2} + \left(\frac{N_2(L)}{\Delta} - \frac{\Delta_\mathrm{d} D_4(L)}{\Delta^2}\right)\eta \frac{u_\mathrm{P}}{L}\right] \mathrm{e}^{-(2\zeta u_\mathrm{P}/\omega)L} \tag{30}$$

As in the previous case, the first addend represents the baseline, while the second addend represents the response to the step function $\eta u_\mathrm{P}/L$ of strength ηu_P. Comparing the terms in round brackets in Eqs. (24) and (30) we see that they are identical. So also in this case the transfer function is still given by Eq. (25) which can be reasonably considered the transfer function of the calorimeter, at least in the first-order approximation.

The transfer function related to case (a) is simply that related to case (b) but using as transfer function of the programmer the one given by Eq. (6), i.e.

$$\begin{aligned}\delta(L) &= \frac{N_2(L)}{\Delta} \\ &= \frac{N_2 L^2 + N_1 L + N_0}{A_5 L^5 + A_4 L^4 + A_3 L^3 + A_2 L^2 + A_1 L + A_0} \\ &\quad \times \frac{\omega^2 u_\mathrm{P}}{L^2 + 2\zeta\omega L + \omega^2}\end{aligned} \tag{31}$$

5. Results and discussion

To test the theory, we used it: (a) to fit with Eq. (14) the unbalance that occurs when the calorimeter switches from the isothermal to the running state, in order to understand the characteristics of the measured curve; (b) to calculate the transfer function of the instrument by which we deconvolute the melting peak of indium samples and then we interpret the dependence of the melting temperature on the scanning rate [11]. This problem has already been addressed with different approaches [12,13].

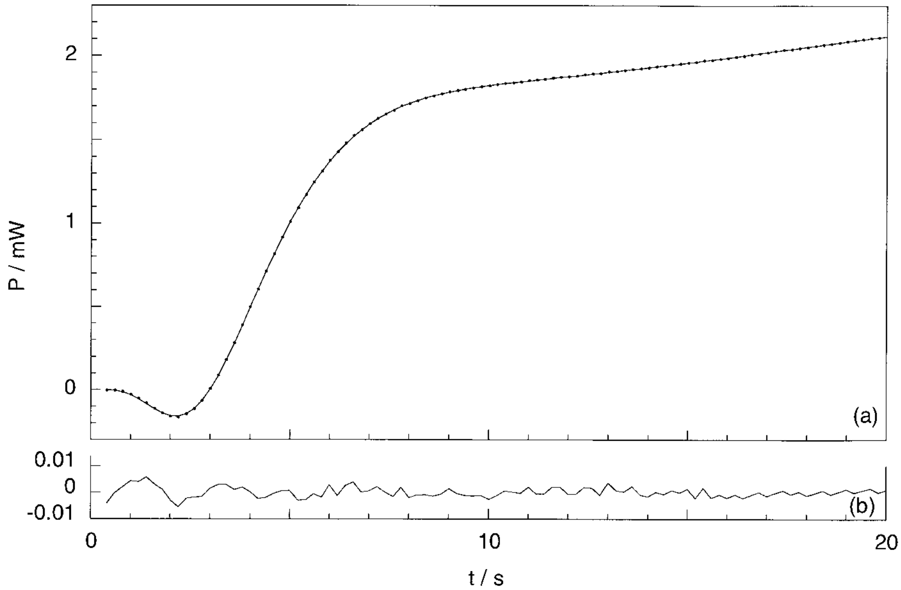

Fig. 2. Unbalance in a DSC curve on switching from isotherm to heating at 40 K min^{-1}. Pan plus indium sample of 2.937 mg in sample-holder, empty pan in reference-holder: (a) experimental points, recorded in 0.2 s steps, and fitting function (solid line) in accordance with Eq. (14); (b) difference between measured and fitting curves.

Measurements were carried out with a DSC-7 calorimeter operating in subambient mode (with Intracooler II accessory), with helium as purge gas. Aluminum pans were used in all experiments. The following settings were maintained throughout all experiments: ordinate filter factor $= 0$; lag compensation $= 0$; ΔT balance $= 56$; slope $= 51.1$. Temperature calibration was made at 5 K min^{-1} using Hg and In as standards. Ordinate calibration was performed using In as the standard. An empty pan, closely matched with the one enclosing the sample, was put in the reference-holder.

To describe the details of the procedure used we refer to an In sample of 2.937 mg heated at 40, 30, 20, 10, 5, 2 K min^{-1}. Figures reported refer to the scan at 40 K min^{-1}. Fig. 2 shows the fitting, by Eq. (14), of the start of a measured curve. The results are generally as good as this, particularly when samples are scanned at high rates as a consequence of the high signal-to-noise ratio. The fixed parameters are reported in Table 1, the ones obtained from the fitting are reported in Table 2.

It is interesting to match the particular features of a measured curve with the various terms of the theoretical curve. Eq. (14) turns out to be the sum of four fractional terms whose numerators are P_{D0}, $P_{D1}L$, $P_{D2}L^2$, $P_{D3}L^3$. We do not lose in generality if in this discussion we do not consider the terms containing q, taking into account that q is generally small and that these terms do not add any new particular aspect. The exponents of the variable L in the complex domain corresponds to derivatives in the time domain. Consequently, as shown in Fig. 3, the total response $D(t)$ in the time domain turns out to be the sum of the following responses: (1) the term with P_{D0}, which

Table 1
Parameters kept fixed in all fitting procedures

C_{1S} (J K^{-1})	C_{1R} (J K^{-1})	C_{2R} (J K^{-1})	R_{1S} (K W^{-1})	R_{1R} (K W^{-1})	R_{2R} (K W^{-1})	R_{12R} (K W^{-1})	K_D (W s K^{-1})	H_D (W s K^{-1})	H_I (W K^{-1} s^{-1})
0.25	0.25	0.25	130	130	320	2.3	0	0	0

Table 2
Fitting parameters related to the measured curve in Fig. 2, obtained by Eq. (14), together with the standard deviation σ and the correlation coefficient r. C_{25} and R_{25} worked out using the constraints expressed by Eq. (16)

C_{2S} ($\mathrm{J\,K^{-1}}$)	R_{2S} ($\mathrm{K\,W^{-1}}$)	K_P ($\mathrm{W\,K^{-1}}$)	K_I ($\mathrm{W\,K^{-1}\,s^{-1}}$)	H_P ($\mathrm{W\,K^{-1}}$)	ζ (–)	ω ($\mathrm{s^{-1}}$)	R_{12S} ($\mathrm{K\,W^{-1}}$)	q (s)	X_P (s)	σ (mW)	r (–)
0.2526	119.26	0.902	0.521	0.522	0.863	0.627	2.232	0	0	1.9×10^{-3}	0.999997

is the answer to the reference signal $T_P(t)$, which in turn is the solution of Eq. (6), (2) the term with P_{D1}, which is the answer to the first derivative $\mathrm{d}T_P/\mathrm{d}t$, (3) the term with P_{D2}, which is the answer to the second derivative $\mathrm{d}^2T_P/\mathrm{d}t^2$ and (4) the term with P_{D3}, which is the answer to the third derivative $\mathrm{d}^3T_P/\mathrm{d}t^3$. Now let us look at the expressions of the coefficients P_{D0}, P_{D1}, P_{D2}, P_{D3} in (A.9). The first term basically depends on the difference in conductance of the sample-holder and reference-holder and is responsible for the slope of the measured curve. The second term basically depends on the difference in capacity of sample-holder and reference-holder and is responsible for the intercept of the measured curve. The third and the fourth terms affect only the transient. They mainly depend on internal resistance and capacity of the two holders. The fourth term accounts for the negative spike in the experimental curve, since if $P_{D3} < 0$ then $\mathrm{d}^3T_P/\mathrm{d}t^3$ is subtracted. If we increase the thermal capacity of the sample-holder, all coefficients, except the first, increase and we observe a progressive disappearance of the negative minimum in the experimental curve.

In Section 4, we obtained two different expressions for the transfer function of the calorimeter. In our opinion, the function to be used to deconvolute a melting peak is the one obtained in accordance with point (b), as the reference signal $T_P(t)$ has already reached its steady state when the phase transition takes place. Fig. 4 shows the impulse response calculated by Eq. (25) using the parameters reported in Tables 1 and 2. As envisaged by this equation, the response has a delay of $2\zeta u_P/\omega$. Fig. 5 shows the deconvolution of the peak of fusion by the impulse response of the calorimeter shown in Fig. 4, normalized to 1, carried out using the Fourier transforms with no filtering. We often used both the numerical and the Fourier deconvolution technique, always obtaining the same results.

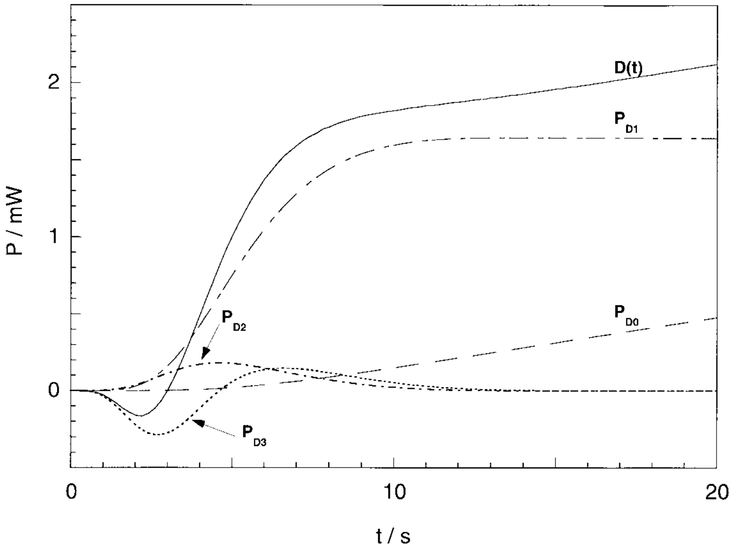

Fig. 3. Component curves (P_{D0}, P_{D1}, P_{D2}, P_{D3}) of the fitting function ($D(t)$) of Fig. 2, in accordance with Eq. (14).

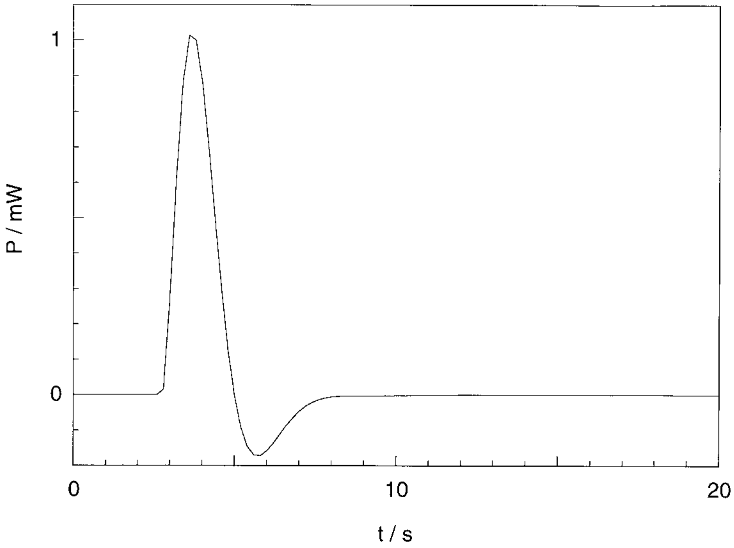

Fig. 4. Impulse response worked out by inserting the fitting parameters, reported in Tables 1 and 2, into Eq. (24).

Table 3 reports the values of the melting temperature as a function of the scanning rate, which is reported in column 1. Column 2 shows the value of the melting temperature worked out directly from the output of the calorimeter. Column 3 reports the value of the melting temperature obtained from the peaks deconvolted using the impulse response of the calorimeter worked out from the measured curve at 40 K min^{-1}. As one can see they are practically independent of the scanning rate. Column 4 reports results

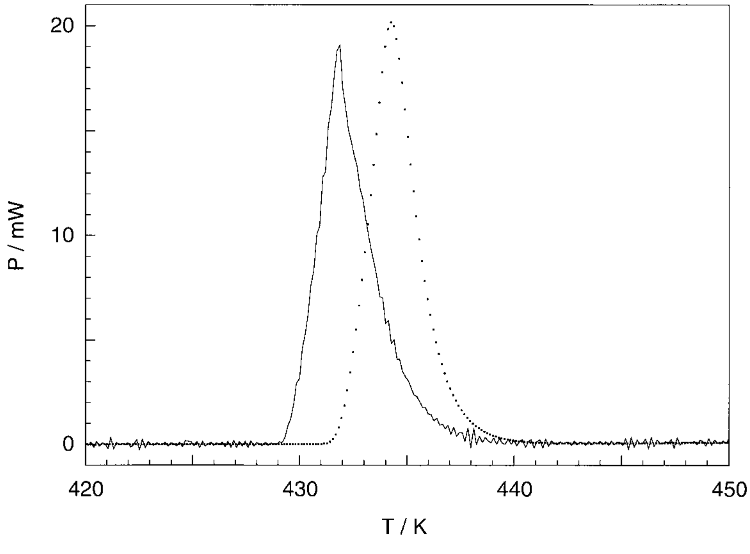

Fig. 5. Measured indium melting peak (dotted line), clipped from the curve whose initial unbalance is reported in Fig. 2. Deconvoluted peak (solid line), by the impulse response shown in Fig. 4.

Table 3
Melting temperatures of the indium sample as in Fig. 2, worked out at different scan rate

Heating rate u_P (K min^{-1})	From experimental peak T (K)	After deconvolution[a] T (K)	After deconvolution[b] T (K)
40	431.78	429.40	429.41
30	431.19	429.40	429.46
20	430.64	429.45	429.46
10	430.08	429.49	429.49
5	429.75	429.46	429.45
2	429.54	429.43	429.42

[a] Using impulse response of Fig. 4 at 40 K min^{-1}.

[b] Following the same procedure so as to arrive at column 3 but from the measured curve at 10 K min^{-1}.

Table 4
Fitting parameters related to the measured curve in Fig. 6, obtained by Eq. (14), together with the standard deviation σ and the correlation coefficient r. C_{25} and R_{25} worked out using the constraints expressed by Eq. (16)

C_{2S} (J K^{-1})	R_{2S} (K W^{-1})	K_P (W K^{-1})	K_I (W K^{-1} s^{-1})	H_P (W K^{-1})	ζ (–)	ω (s^{-1})	R_{12S} (K W^{-1})	q (s)	X_P (s)	σ (mW)	r (–)
0.2511	119.43	0.789	0.313	2.61	1.02	1.46	2.228	0.13	0	2.3×10^{-3}	0.999986

analogous to those in column 3 but obtained using the data worked out from the fitting of the experimental curve at 10 K min^{-1}.

Figs. 6–8 report the results relating to an In sample of 1.203 mg, but using the measured curves obtained after our calorimeter had been updated to enable it to perform measurements of dynamic differential scanning calorimetry (DDSC) as well. The relevant fitting parameters are reported in Tables 1 and 4. Table 5 reports the values of the melting temperature as a

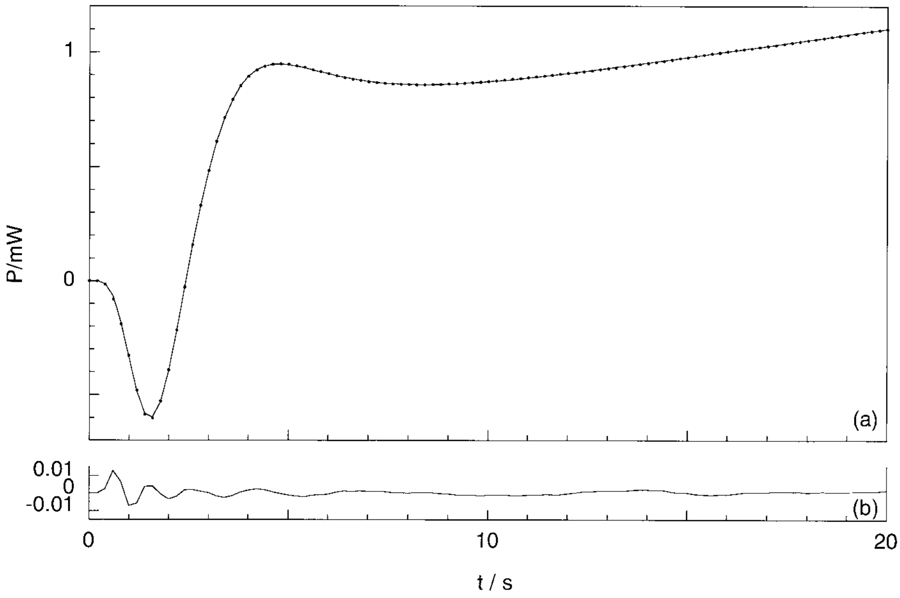

Fig. 6. Unbalance in a DSC curve on switching from isotherm to heating at 40 K min^{-1}. Pan plus indium sample of 1.203 mg in sample-holder, wide pan in reference-holder: (a) experimental points, recorded in 0.2 s steps, and fitting function (solid line) in accordance with Eq. (14); (b) difference between measured and fitting curves.

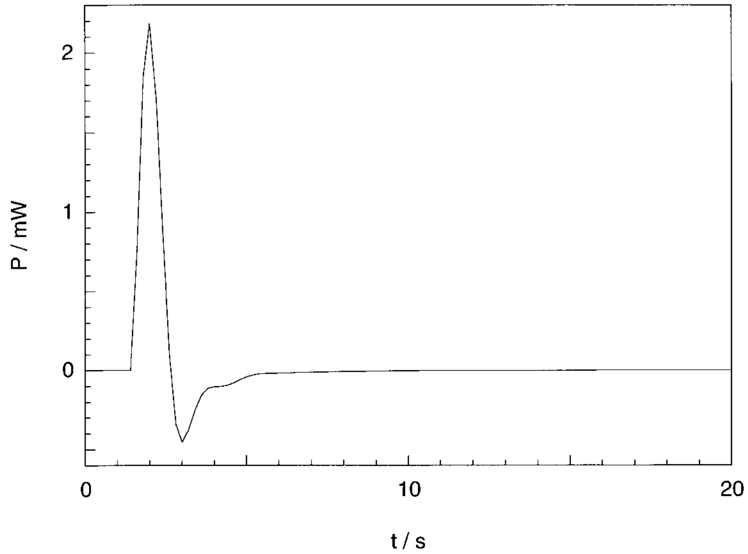

Fig. 7. Impulse response worked out by inserting the fitting parameters, reported in Tables 1 and 4, into Eq. (24).

function of the scanning rate. As can be seen by comparing Figs. 2 and 6, the starting parts of the two scans are quite different, but the method works quite well in both cases.

At first glance the result of our deconvolution may appear incomplete. However, the transfer function used for deconvolution is that of the instrument and consequently the result is the signal coming from the sample still convoluted with the impulse response of the sample [5].

We must also point out that the values of the fitting parameters shown in Tables 2 and 4 are to be

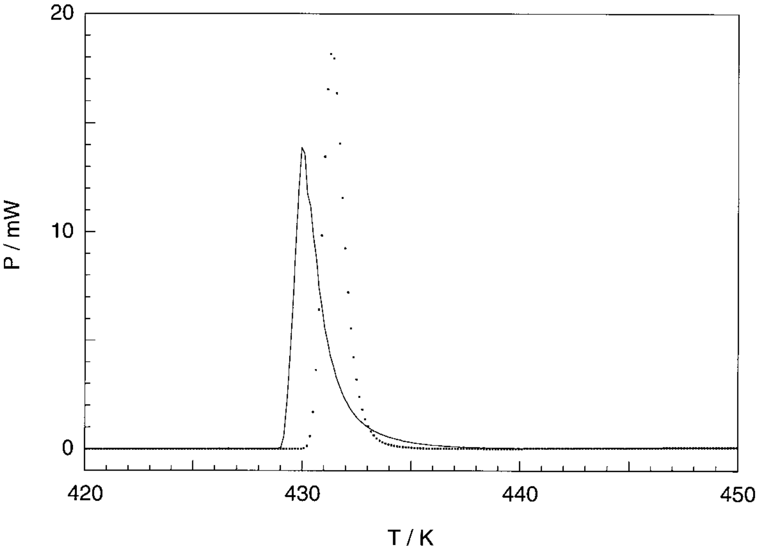

Fig. 8. Measured indium melting peak (dotted line), clipped from the curve whose initial unbalance is reported in Fig. 6. Deconvoluted peak (solid line), by the impulse response shown in Fig. 7.

Table 5
Melting temperatures of the indium sample as in Fig. 6, worked out at different scan rate

Heating rate u_P (K min^{-1})	From experimental peak T (K)	After deconvolution[a] T (K)	After deconvolution[b] T (K)
40	430.85	429.60	429.60
30	430.54	429.60	429.60
20	430.22	429.61	429.61
10	429.91	429.61	429.62
5	429.75	429.60	429.60
2	429.63	429.58	429.58

[a] Using impulse response of Fig. 7 at 40 K min^{-1}.

[b] Following the same procedure so a to arrive at column 3 but from the measured curve at 10 K min^{-1}.

considered only as apparent values. This is the consequence not only of EHA and all other simplifications but also of certain controls at the operator's disposal. Measured curves can be modified drastically by adjustment of ΔT balance or slope controls, as shown in Figs. 9 and 10, respectively. They can still be fitted with Eq. (14) but of course with different parameter values.

Lastly we add that all programs and subroutines used to perform these calculations were written by us.

6. Conclusion

We have presented a linear model of DPSC with special reference to the DSC-7 manufactured by Perkin-Elmer. The aim is to account for the general features of the instrument, taking into account the inevitable asymmetries between the two coupled holders. We obtained the theoretical output of the instrument from the working transfer functions of each of the three fundamental elements of the

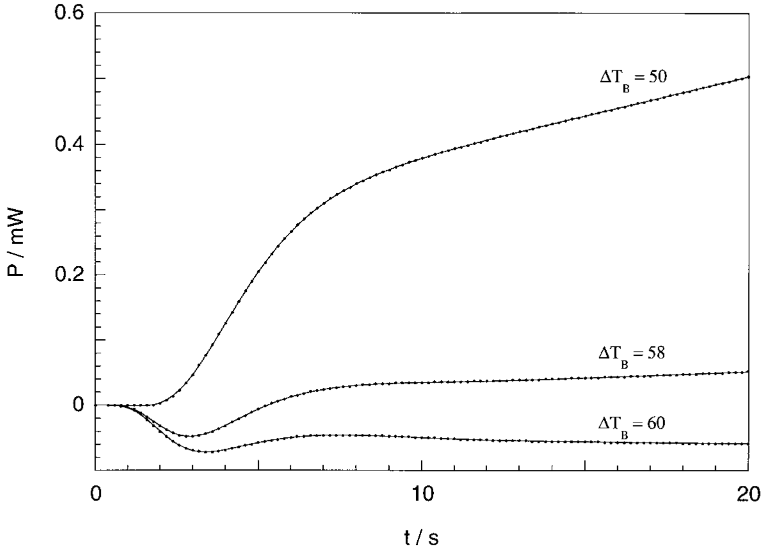

Fig. 9. Modifications induced by adjustment of ΔT balance (ΔT_B) control on measured curves when the calorimeter is switched from isotherm to heating. Sample-holder and reference-holder empty; heating rate, 5 K min^{-1}; slope control setting, 45. Experimental points, recorded in 0.2 s steps, and fitting functions (solid lines) in accordance with Eq. (14).

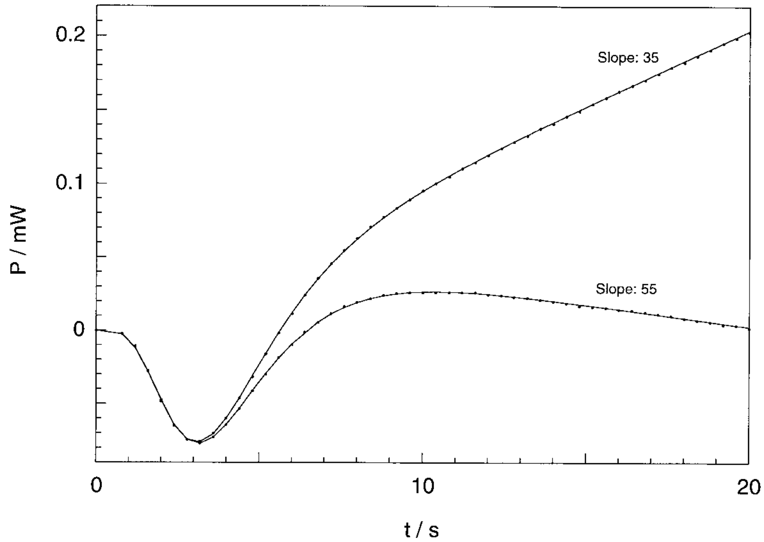

Fig. 10. Modifications induced by adjustment of slope control on measured curves when the calorimeter is switched from isotherm to heating. Sample-holder and reference-holder empty; heating rate, 5 K min^{-1}; ΔT_B control setting, 56. Experimental points, recorded in 0.4 s steps, and fitting functions (solid lines) in accordance with Eq. (14).

calorimeter, namely: the average temperature amplifier, the difference temperature amplifier and the programmer.

A model's efficiency increases as the number of parameters needed to achieve its goals decreases. For this purpose we introduced the empty holder approximation (EHA) which allows us to treat all experimental situations in the same framework. Moreover, we have seen that a maximum of eight parameters (instead of 20 envisaged in the general model) are needed to adequately fit the unbalance which occurs when the calorimeter switches from isothermal to running state.

The EHA allows calculation of the transfer function of the calorimeter in two different experimental situations: (a) when the calorimeter switches from isothermal to running state (or vice versa); (b) when the reference signal generated by the programmer has reached its steady state. The impulse responses obtained in situation (a) have shapes similar to the ones worked out by differentiation of the initial unbalance, when the thermal capacity in the sample-holder is somewhat greater than that of the reference-holder. The dependence of the melting temperature on the scan rate can be eliminated by deconvolution of the melting peaks using the impulse response relating either to situation (a) or situation (b) but the results of the deconvolution are very different. When something happens in a pan (e.g. a phase transition), the reference signal has already reached its steady state and, in our view, the impulse response to be used should be that of situation (b).

Our model was successful in interpreting qualitatively and quantitatively the situations in which it has been used up to now. It explains various features of a measured curve, associating them with certain parameters. All this makes us hope that it can be used profitably in further applications.

Acknowledgements

Financial support by the Italian Ministry of University and of Scientific and Technological Research (MURST) is acknowledged.

Appendix A.

We express t_{2S} and t_{2R} in the first four equations in terms of t_A and t_D and substitute p and d in the first two equations using the third and the fourth equations. If we put

$$A_C = K_P + \frac{K_I}{L} + K_D L, \qquad B_C = H_P + \frac{H_I}{L} + H_D L,$$
$$A_S = \alpha_2 L^2 + \alpha_1 L + \alpha_0 + A_C,$$
$$B_S = \tfrac{1}{2}[\alpha_2 L^2 + \alpha_1 L + \alpha_0 + B_C],$$
$$A_R = \beta_2 L^2 + \beta_1 L + \beta_0 + A_C,$$
$$B_R = \tfrac{1}{2}[\beta_2 L^2 + \beta_1 L + \beta_0 + B_C] \tag{A.1}$$

system (8) can be written in the following matrix form:

$$\left|\begin{matrix} 0 & 0 & A_S & B_S & 0 & 0 \\ 0 & 0 & A_R & -B_R & 0 & 0 \\ 0 & 1 & A_C & 0 & 0 & 0 \\ 1 & 0 & 0 & B_C & 0 & 0 \\ 0 & 0 & -1 & -\frac{1}{2} & 1 & 0 \\ 0 & 0 & -1 & \frac{1}{2} & 0 & 1 \end{matrix}\right| \left|\begin{matrix} d \\ p \\ t_A \\ t_D \\ t_{2S} \\ t_{2R} \end{matrix}\right| = \left|\begin{matrix} A_C t_P \\ A_C t_P \\ A_C t_P \\ 0 \\ 0 \\ 0 \end{matrix}\right| \tag{A.2}$$

The relevant determinants of this system are easily calculated and for the transfer functions of the various outputs we get the following expressions:

$$t_D(L) = \frac{\Delta_{t_D}}{\Delta} t_P(L) = \frac{(A_R - A_S)A_C}{A_S B_R + A_R B_S} t_P(L),$$
$$t_A(L) = \frac{\Delta_{t_A}}{\Delta} t_P(L) = \frac{(B_S + B_R)A_C}{A_S B_R + A_R B_S} t_P(L),$$
$$p(L) = \frac{\Delta_p}{\Delta} t_P(L) = \frac{(A_S B_R + A_R B_S)A_C - (B_S + B_R)A_C^2}{A_S B_R + A_R B_S} t_P(L),$$
$$d(L) = \frac{\Delta_d}{\Delta} t_P(L) = \frac{(A_S - A_R)B_C A_C}{A_S B_R + A_R B_S} t_P(L),$$
$$t_{2S}(L) = \frac{\Delta_{t_{2S}}}{\Delta} t_P(L) = \frac{[B_S + B_R + \frac{1}{2}(A_R - A_S)]A_C}{A_S B_R + A_R B_S} t_P(L),$$
$$t_{2R}(L) = \frac{\Delta_{t_{2R}}}{\Delta} t_P(L) = \frac{[B_S + B_R - \frac{1}{2}(A_R - A_S)]A_C}{A_S B_R + A_R B_S} t_P(L) \tag{A.3}$$

Taking into account positions (A.1), the determinants in Eq. (A.3) can be written in polynomial form. Calculations are time-consuming but elementary.

We report the explicit form of the determinants Δ, Δ_d and $\Delta_{t_{2S}}$ to have $d(L)$ and $t_{2S}(L)$ in rational algebraic form. The following positions are constantly used in the process of fitting:

$$K_D = H_D = H_I = 0 \tag{A.4}$$

For Δ, we have

$$\Delta = A_5 L^4 + A_4 L^3 + A_3 L^2 + A_2 L^1 + A_1 L^0 + A_0 L^{-1} \tag{A.5}$$

where we put

$$A_5 = \alpha_2\beta_2, \qquad A_4 = (\alpha_2\beta_1 + \alpha_1\beta_2),$$
$$A_3 = (\alpha_2\beta_0 + \alpha_1\beta_1 + \alpha_0\beta_0) + \tfrac{1}{2}(K_P + H_P)(\alpha_2 + \beta_2),$$
$$A_2 = (\alpha_1\beta_0 + \alpha_0\beta_1) + \tfrac{1}{2}(K_P + H_P)(\alpha_1 + \beta_1) + \tfrac{1}{2}K_I(\alpha_2 + \beta_2),$$
$$A_1 = (\alpha_0\beta_0 + K_P H_P) + \tfrac{1}{2}(K_P + H_P)(\alpha_0 + \beta_0) + \tfrac{1}{2}K_I(\alpha_1 + \beta_1), \qquad A_0 = H_P K_I + \tfrac{1}{2}K_I(\alpha_0 + \beta_0) \tag{A.6}$$

The explicit form of the terms α and β are: (Eq. (5) of the text)

$$\alpha_2 = R_{12S} C_{1S} C_{2S},$$
$$\alpha_1 = C_{1S} + C_{2S} + R_{12S}\left(\frac{C_{1S}}{R_{2S}} + \frac{C_{2S}}{R_{1S}}\right),$$
$$\alpha_0 = \frac{1}{R_{1S}} + \frac{1}{R_{2S}} + \frac{R_{12S}}{R_{1S}R_{2S}}, \qquad \beta_2 = R_{12R} C_{1R} C_{2R},$$
$$\beta_1 = C_{1R} + C_{2R} + R_{12R}\left(\frac{C_{1R}}{R_{2R}} + \frac{C_{2R}}{R_{1R}}\right),$$
$$\beta_0 = \frac{1}{R_{1R}} + \frac{1}{R_{2R}} + \frac{R_{12R}}{R_{1R}R_{2R}} \tag{A.7}$$

Expanding the determinant Δ_d, we have

$$\Delta_d = [P_{D3}L^2 + P_{D2}L^1 + P_{D1}L^0 + P_{D0}L^{-1}] \tag{A.8}$$

whose coefficients are

$$P_{D3} = (\alpha_2 - \beta_2)K_P H_P,$$
$$P_{D2} = (\alpha_1 - \beta_1)K_P H_P + (\alpha_2 - \beta_2)K_I H_P,$$
$$P_{D1} = (\alpha_0 - \beta_0)K_P H_P + (\alpha_1 - \beta_1)K_I H_P,$$
$$P_{D0} = (\alpha_0 - \beta_0)K_I H_P \tag{A.9}$$

Therefore $d(L)$ can be written in the following rational algebraic form:

$$d(L) = \frac{P_{D3}L^3 + P_{D2}L^2 + P_{D1}L + P_{D0}}{A_5 L^5 + A_4 L^4 + A_3 L^3 + A_2 L^2 + A_1 L + A_0} t_P(L) \tag{A.10}$$

We now work out the explicit form for $t_{2\mathrm{S}}(L)$. For $\Delta_{t_{2\mathrm{S}}}$, we get

$$\Delta_{T_{2\mathrm{S}}} = T^*_{\mathrm{S}3}L^2 + T^*_{\mathrm{S}2}L^1 + T^*_{\mathrm{S}1}L^0 + T^*_{\mathrm{S}0}L^{-1} \tag{A.11}$$

whose coefficients are

$$T^*_{\mathrm{S}3} = \beta_2 K_\mathrm{P}, \qquad T^*_{\mathrm{S}2} = \beta_1 K_\mathrm{P} + \beta_2 K_\mathrm{I},$$
$$T^*_{\mathrm{S}1} = \beta_0 K_\mathrm{P} + \beta_1 K_\mathrm{I} + K_\mathrm{P} H_\mathrm{P}, \qquad T^*_{\mathrm{S}0} = \beta_0 K_\mathrm{I} + K_\mathrm{I} H_\mathrm{P} \tag{A.12}$$

and for $t_{2\mathrm{S}}(L)$, we have

$$t_{2\mathrm{S}}(L) = \frac{T^*_{\mathrm{S}3}L^3 + T^*_{\mathrm{S}2}L^2 + T^*_{\mathrm{S}1}L + T^*_{\mathrm{S}0}}{A_5L^5 + A_4L^4 + A_3L^3 + A_2L^2 + A_1L + A_0} t_\mathrm{P}(L) \tag{A.13}$$

For an easier reference we report the formulae used for the fitting of the starting unbalance (Eq. (14) of the text):

$$d(L) = \frac{P_{\mathrm{D}3}L^3 + P_{\mathrm{D}2}L^2 + P_{\mathrm{D}1}L + P_{\mathrm{D}0}}{A_5L^5 + A_4L^4 + A_3L^3 + A_2L^2 + A_1L + A_0} \times \frac{\omega^2 u_\mathrm{P}}{L^2 + 2\zeta\omega L + \omega^2}\left(\frac{1}{L^2} + \frac{q}{L}\right) - \frac{P_{\mathrm{D}3} q \omega^2 u_\mathrm{P}}{A_5L^5 + A_4L^4 + A_3L^3 + A_2L^2 A_1L + A_0} \tag{A.14}$$

The values of the parameters kept constant are

$$K_\mathrm{D} = H_\mathrm{D} = H_\mathrm{I} = 0,$$
$$C_{1\mathrm{S}} = C_{1\mathrm{R}} = C_{2\mathrm{R}} = 0.25\,\mathrm{J\,K^{-1}},$$
$$R_{1\mathrm{S}} = R_{1\mathrm{R}} = 130\,\mathrm{K\,W^{-1}}, \qquad R_{2\mathrm{R}} = 320\,\mathrm{K\,W^{-1}},$$
$$R_{12\mathrm{R}} = 2.3\,\mathrm{K\,W^{-1}} \tag{A.15}$$

while $R_{2\mathrm{S}}$ and $C_{2\mathrm{S}}$ are obtained from Eq. (16) of the text, i.e.

$$Z_1 A_0 = P_{\mathrm{D}0} u_\mathrm{P},$$
$$Z_1(A_1\omega + 2\zeta A_0) + Z_2 A_0 \omega = (P_{\mathrm{D}0} q + P_{\mathrm{D}1})\omega u_\mathrm{P} \tag{A.16}$$

The transfer function of the calorimeter is given by Eq. (25) of the text, i.e:

$$\delta(L) = \frac{N_2(L)}{\Delta} = \frac{N_2L^2 + N_1L + N_0}{A_5L^5 + A_4L^4 + A_3L^3 + A_2L^2 + A_1L + A_0} \times \mathrm{e}^{-(2\zeta u_\mathrm{P}/\omega)L} \tag{A.17}$$

where N_2, N_1, N_0 are given by the following expressions:

$$N_2 = H_\mathrm{P} K_\mathrm{P} R_{12\mathrm{S}} C_{1\mathrm{S}}, \qquad N_1 = H_\mathrm{P} K_\mathrm{P} + H_\mathrm{P} K_\mathrm{I} R_{12\mathrm{S}} C_{1\mathrm{S}},$$
$$N_0 = H_\mathrm{P} K_\mathrm{I} \tag{A.18}$$

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