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Thermochimica Acta 413 (2004) 117–125

thermochimica acta

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An analytical expression of the output of a power-compensated DSC in a wide temperature range

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Received 5 August 2003; received in revised form 8 October 2003; accepted 11 October 2003

Abstract

We present an upgrade of our previous theoretical model of a power-compensated twin calorimeter with particular reference to the DSC-7 manufactured by Perkin-Elmer. The aim of this generalization is to provide an analytical description of a measured heating curve in a fairly wide range of temperature. To reach this goal, we emulate the "ΔT balance" (ΔT_B) control and the "slope" (SL) control of the DSC-7, which are used to modify curvature and slope of a measured curve. The implementation of these two functions has simply required the introduction of three new parameters. In this way, we got a fairly good analytical description of the calorimeter response, when the holders are empty, whatever the setting of both controls. We present results in the temperature range from 248 to 423 K. One of the above mentioned parameters turns out to be linearly dependent exclusively on the ΔT_B; while the other two are linearly dependent both on the ΔT_B and SL. These results provide the means to get a calibration of the instrument with respect to the ΔT_B and SL settings.

Keywords: DSC; Theoretical output; Fitting

1. Introduction

In our previous paper [1], we described a mathematical model of a power-compensated differential scanning calorimeter (PCDSC) with particular reference to a DSC-7 manufactured by Perkin-Elmer, considered in its three fundamental elements: average temperature amplifier, differential temperature amplifier and programmer.

Fig. 1 shows a schematic representation of a holder in its surroundings. We considered the slab ABCD of the holder as made up of two parts, as indicated by the broken line in Fig. 1 and as a third part the pan (plus the sample to be studied). Then, we applied the energy conservation law to the various parts obtaining [1], in case of an empty holder:

$$P(t) = C_1\frac{dT_1(t)}{dt} + \frac{T_1(t)}{R_1} + \frac{T_1(t) - T_2(t)}{R_{12}}$$
$$\frac{T_1(t) - T_2(t)}{R_{12}} = C_2\frac{dT_2(t)}{dt} + \frac{T_2(t)}{R_2} \qquad (1)$$

where t is the time; $P(t)$ the power provided to the holder; C_1 and C_2 the heat capacities; $T_1(t)$, $T_2(t)$ the temperatures; R_{12} the coupling resistance between the two parts of the holder; and R_1, R_2 the coupling thermal resistances between the holder enclosure block (HEB, hatched in Fig. 1) and the two parts of the holder respectively. All quantities in system (1) are referred to the HEB temperature, but can also be referred to the initial isothermal temperature and we suppose so throughout this paper. From this system, a second order equation was worked out, whose Laplace transform is

$$p(L) = \left[R_{12}C_1C_2L^2 + \left(C_1 + C_2 + \frac{R_{12}C_1}{R_2} + \frac{R_{12}C_2}{R_1}\right)L + \left(\frac{1}{R_1} + \frac{1}{R_2} + \frac{R_{12}}{R_1R_2}\right)\right]t_2(L) \qquad (2)$$

where 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.

As it is well known, temperature control of the two coupled holders, in a DSC-7, is realized in two half-cycles: the average power half-cycle and the differential power half-cycle. These two operations are performed by the

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0040-6031/$ – see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2003.10.006

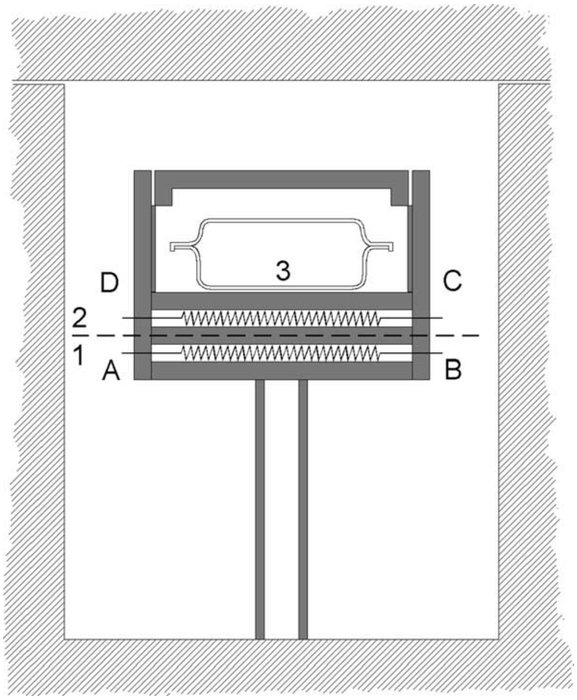

Fig. 1. Schematic representation of a holder in its surroundings. The broken line divides the slab ABCD into two parts, 1 and 2, where the heater and sensor respectively are embodied. Pan (plus its content) is the third part. (From: N. Zucca, G. Erriu, S. Onnis, D. Zedda, A. Longoni, Thermochim. Acta 366 (2001) 15–30.)

average temperature amplifier and by the differential temperature amplifier, respectively. During the power half-period $\tau/2$, the relevant control system operates so that the average temperature $T_A = (T_{2S} + T_{2R})/2$ increases linearly with time, tracking the signal $T_P(t)$ coming from the programmer (letters S and R in the subscripts refer to the sample and reference holders, respectively). During the differential half-cycle, 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.

The fundamental equations describing the operation of an empty calorimeter are therefore the energy conservation law, expressed by Eq. (2) and written for both holders, and equations for the temperature control for the two half-cycles. We postulated a PID (proportional, integral, differential) control for both the half-cycles and then we got [1] the final system, which we now report in its complex form

$$\begin{aligned}
&p(L) + \tfrac{1}{2}d(L) = [\alpha_2 L^2 + \alpha_1 L + \alpha_0]t_{2S}(L)\\
&p(L) - \tfrac{1}{2}d(L) = [\beta_2 L^2 + \beta_1 L + \beta_0]t_{2R}(L)\\
&p(L) = A_C[t_P(L) - t_A(L)]\\
&d(L) = -B_C[t_{2S}(L) - t_{2R}(L)]\\
&t_A(L) = \tfrac{1}{2}[t_{2S}(L) + t_{2R}(L)]\\
&t_D(L) = [t_{2S}(L) - t_{2R}(L)]
\end{aligned} \tag{3}$$

The explicit forms of α_2, α_1, α_0, β_2, β_1, β_0, A_C, and B_C are reported in Eq. (A.1).

$T_P(t)$, the reference signal for the average temperature amplifier, is generated by the programmer, whose input is the so called programmed temperature, $\theta(t) = u_P(t+q)$, where u_P is the scanning rate. In our previous paper, we approximated the programmer transfer function by a linear second order equation obtaining for $t_P(L)$

$$t_P(L) = \frac{\omega^2 u_P}{L^2 + 2\zeta\omega L + \omega^2}\left(\frac{1}{L^2} + \frac{q}{L}\right) \tag{4}$$

In system (3), $t_P(L)$ is the input and all the other quantities are the outputs. For the power difference $d(L)$, as spelt out in [1], we got

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

The explicit forms of the coefficients of the polynomials in the numerator and in the denominator are reported in Eq. (A.2).

Eq. (5) enabled us to get good results in fitting the unbalance that occurs when the calorimeter switches from the isothermal to the running state, and consequently to obtain an analytical expression of the transfer function of the instrument. We now want to generalize Eq. (5) to make it suitable to interpret the behavior of measured curves in temperature ranges as wide as those commonly used. To achieve this, we take a closer look at temperature measurement by electrical resistances, furthermore we incorporate into our model two characteristic functions of the DSC-7, namely the "ΔT balance" (ΔT_B) control and the "slope" (SL) control, which are used to optimize curvature and slope of the experimental curves in the temperature range in which one operates.

2. Temperature measurement

Electric resistivity dependence on temperature is largely exploited for temperature measurement. The dependence between these two quantities is usually expressed by a polynomial. In small temperature ranges, it is sufficient to use only its linear term, but this approximation is no longer adequate as the range increases. Fig. 2 shows the behavior of the resistivity (ρ) of a metal as a function of its temperature (T^*) and its approximation by a straight line in the range between T_1^* and T_2^*. As one can see, temperatures (T_l) worked out by this straight line are greater than the temperatures T^* obtained by the $\rho(T^*)$ function.

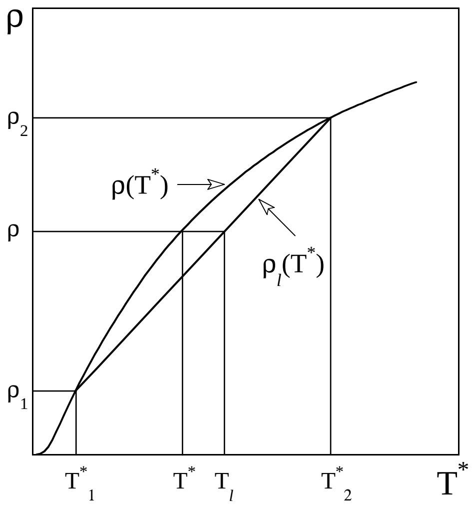

Fig. 2. Behavior of the resistivity, ρ, of a metal as a function of temperature, T^*, and its approximation by a straight line in the range between T_1^* and T_2^*. Temperatures T_l worked out by this straight line, between T_1^* and T_2^*, are greater than temperatures T^* obtained by the $\rho(T^*)$ function.

DSC-7, the instrument by which we will test our theoretical model, uses distributed platinum thermometers [2]. Platinum resistance thermometers calibrated under specified conventions play a major role, as they enter in the definition of a part of the international temperature scale ITS-90 [3]. As an approximation, we simply fit literature data on platinum resistivity as a function of temperature [4] by a third degree polynomial

$$\rho(T^*) = \rho_3 T^{*3} + \rho_2 T^{*2} + \rho_1 T^* + \rho_0 \tag{6}$$

In the range between 60 and 900 K, the coefficients are

$$\begin{aligned}&\rho_3 = -4.37 \times 10^{-10}\,\Omega\,\mathrm{m\,K^{-3}};\\ &\rho_2 = -5.23 \times 10^{-6}\,\Omega\,\mathrm{m\,K^{-2}};\\ &\rho_1 = 4.22 \times 10^{-2}\,\Omega\,\mathrm{m\,K^{-1}}; \quad \rho_0 = -1.42\,\Omega\,\mathrm{m}\end{aligned} \tag{7}$$

The full range of operation of a DSC-7 is between $T_1^* = 103\,\mathrm{K}$ and $T_2^* = 1003\,\mathrm{K}$ [2]. To make a calibration in this full range, we calculated $\rho(1003)$ using Eq. (6). To obtain the relation between the temperatures T^* and T_l, let us indicate by $G(T^*)$ the difference

$$G(T^*) = T_\mathrm{l} - T^* \tag{8}$$

From Fig. 2, we see that for every value of resistivity ρ we can write

$$\rho_3 T^{*3} + \rho_2 T^{*2} + \rho_1 T^* + \rho_0 = \rho_1^* T_\mathrm{l} + \rho_0^* \tag{9}$$

where the second term indicates the straight line through the two calibration points. From Eqs. (8) and (9), we obtain

$$G(T^*) = G_3 T^{*3} + G_2 T^{*2} + G_1 T^* + G_0 \tag{10}$$

whose coefficients are

$$\begin{aligned}&G_3 = -1.22 \times 10^{-8}\,\mathrm{K^{-2}}; \quad G_2 = -1.46 \times 10^{-4}\,\mathrm{K^{-1}};\\ &G_1 = 0.175; \quad G_0 = -16.44\,\mathrm{K}\end{aligned} \tag{11}$$

In the temperature range in which we operated (between 248 and 423 K), the correction polynomial $G(T^*)$ can be approximated by a 2nd degree polynomial, whose coefficients are

$$\begin{aligned}&G_2 = -1.59 \times 10^{-4}\,\mathrm{K^{-1}}; \quad G_1 = 0.18;\\ &G_0 = -17.04\,\mathrm{K}\end{aligned} \tag{12}$$

We can now apply these considerations to the temperatures of the two holders. As it has been said in the previous section, we refer all quantities to their values at the temperature T_I of the lower isotherm. For the temperature T^* we obviously get $(T^* - T_\mathrm{I})$, which in addition we shall consider to be the programmed temperature, namely $T^* – T_\mathrm{I} = \theta(t) = u_\mathrm{P}(t+q)$. The correction polynomial, in its 2nd degree approximation, referred to its isotherm value becomes

$$G^*(t) = G(T_\mathrm{I} + \theta) - G(T_\mathrm{I}) = G_2^*(u_\mathrm{P} t)^2 + G_1^* u_\mathrm{P} t + G_0^* \tag{13}$$

where we put

$$\begin{aligned}&G_2^* = G_2\\ &G_1^* = G_1 + 2G_2(T_\mathrm{I} + q u_\mathrm{P})\\ &G_0^* = q u_\mathrm{P}[G_1 + G_2(2T_\mathrm{I} + q u_\mathrm{P})]\end{aligned} \tag{14}$$

From Eq. (8), written for temperatures of the sample holder (T_2S) and of the reference holder (T_2R), we therefore get

$$\begin{aligned}&T_\mathrm{2S} = T_{l,\mathrm{2S}} - G^*(t)\\ &T_\mathrm{2R} = T_{l,\mathrm{2R}} - G^*(t)\end{aligned} \tag{15}$$

If we insert Eq. (15) into the power control equation (3rd equation in system (3)), we get

$$p(L) = A_\mathrm{C}\left[t_\mathrm{P}(L) - \left(\frac{t_\mathrm{l,2S}(L) + t_\mathrm{l,2R}(L)}{2} - g^*(L)\right)\right] \tag{16}$$

which can be obviously written

$$p(L) = A_\mathrm{C}\left[(t_\mathrm{P}(L) + g^*(L)) - \frac{t_\mathrm{l,2S}(L) + t_\mathrm{l,2R}(L)}{2}\right] \tag{17}$$

which means that the non-linear response of the sensors can be accounted for in the reference signal t_P rather than in the t_l temperatures. Consequently, if the average temperature of the two holders has to increase linearly as the programmed temperature $\theta(t)$, then the reference signal $T_\mathrm{P}(t)$ cannot be linear any longer, but has to increase as a 3rd degree polynomial (or as a 2nd degree polynomial if we use the approximation (12)). Taking this into account, we will consider, from now on, temperatures in system (3) as T_l temperatures and we drop the subscript “l” to make symbols easier to read.

For simplicity sake, we assume that the transfer function for the correction signal $G^*(t)$ is the same as that for the programmed temperature (Eq. (4)) and consequently we use for the reference signal the following expression

$$
\begin{aligned}
t_{\mathrm{P}}(L) &= \frac{\omega^2 u_{\mathrm{P}}}{L^2 + 2\zeta\omega L + \omega^2}\left(\frac{1}{L^2} + \frac{q}{L}\right)\\
&\quad + \frac{\omega^2 u_{\mathrm{P}}}{L^2 + 2\zeta\omega L + \omega^2}\left(\frac{2u_{\mathrm{P}}G_2^*}{L^3} + \frac{G_1^*}{L^2} + \frac{G_0^*}{L}\right)\\
&= \frac{S_2 L^2 + S_1 L + S_0}{(L^2 + 2\zeta\omega L + \omega^2)L^3} \qquad (18)
\end{aligned}
$$

where we put

$$
\begin{aligned}
S_2 &= (q + G_0^*)\omega^2 u_{\mathrm{P}}\\
S_1 &= (1 + G_1^*)\omega^2 u_{\mathrm{P}} \qquad (19)\\
S_0 &= 2G_2^*\omega^2 u_{\mathrm{P}}^2
\end{aligned}
$$

3. ΔT_{B} and SL controls

Small asymmetries in heat capacities of the holders, in their coupling thermal resistances with the environment and in electric resistances of the temperature sensors obviously affect the output of a differential calorimeter. All these causes of unbalance can be easily accounted for in our model by replacing, in system (3), the average temperature t_{A} and the temperature difference t_{D} with the weighted average temperature and the weighted temperature difference. Namely

$$
\begin{aligned}
t_{\mathrm{A}}(L) &= \tfrac{1}{2}[(1-\eta)t_{2\mathrm{S}}(L) + (1+\eta)t_{2\mathrm{R}}(L)],\\
t_{\mathrm{D}}(L) &= [(1-\eta)t_{2\mathrm{S}}(L) - (1+\eta)t_{2\mathrm{R}}(L)], \quad (-1 < \eta < 1)
\end{aligned} \qquad (20)
$$

When η=0, we obtain the original equations in system (3). In view of the 4th and 6th equations of this system, if η varies progressively from -1 to $+1$ the output $d(L)$ passes from a negative to a positive value, with a consequent variation both in its curvature and slope. As a mater of fact, when we operate on the knob of the ΔT_{B} control of a DSC-7 we just obtain the same kind of modifications. We can therefore consider Eq. (20) as the ΔT_{B} equations of our model.

To see how the output $d(L)$, given by Eq. (5), is affected by Eq. (20), we can solve these equations with respect to $t_{2\mathrm{S}}$ and $t_{2\mathrm{R}}$

$$
t_{2\mathrm{R}} = \frac{1}{1+\eta}\left(t_{\mathrm{A}} - \frac{t_{\mathrm{D}}}{2}\right); \quad t_{2\mathrm{R}} = \frac{1}{1+\eta}\left(t_{\mathrm{A}} + \frac{t_{\mathrm{D}}}{2}\right) \qquad (21)
$$

Substituting into the first two equations of system (3) we obtain

$$
\begin{aligned}
p(L) + \frac{d(L)}{2} &= [\alpha_2 L^2 + \alpha_1 L + \alpha_0]\frac{1}{1-\eta}\\
&\quad \times \left[t_{\mathrm{A}}(L) + \frac{t_{\mathrm{D}}(L)}{2}\right]\\
p(L) - \frac{d(L)}{2} &= [\beta_2 L^2 + \beta_1 L + \beta_0]\frac{1}{1+\eta}\\
&\quad \times \left[t_{\mathrm{A}}(L) - \frac{t_{\mathrm{D}}(L)}{2}\right]
\end{aligned} \qquad (22)
$$

If we make the following positions

$$
\begin{aligned}
\alpha_2 &\to \frac{\alpha_2}{1-\eta} \approx \alpha_2(1+\eta), \quad \beta_2 \to \frac{\beta_2}{1+\eta} \approx \beta_2(1-\eta)\\
\alpha_1 &\to \frac{\alpha_1}{1-\eta} \approx \alpha_1(1+\eta), \quad \beta_1 \to \frac{\beta_1}{1+\eta} \approx \beta_1(1-\eta)\\
\alpha_0 &\to \frac{\alpha_0}{1-\eta} \approx \alpha_0(1+\eta), \quad \beta_0 \to \frac{\beta_0}{1+\eta} \approx \beta_0(1-\eta)
\end{aligned} \qquad (23)
$$

system (3), modified by Eq. (20), turns out to be formally identical to its unmodified form. This means that the output $d(L)$ is still formally given by Eq. (5), which in view of positions (23) can be written

$$
\begin{aligned}
d(L) &= \frac{P_{D3}L^3 + P_{D2}L^2 + P_{D1}L + P_{D0}}{A_5L^5 + A_4L^4 + A_3L^3 + A_2L^2 + A_1L + A_0} t_{\mathrm{P}}(L)\\
&\quad + \eta\frac{D_{B3}L^3 + D_{B2}L^2 + D_{B1}L + D_{B0}}{A_5L^5 + A_4L^4 + A_3L^3 + A_2L^2 + A_1L + A_0} t_{\mathrm{P}}(L)\\
&\quad - \frac{P_{D3}q\omega^2 u_{\mathrm{P}}}{A_5L^5 + A_4L^4 + A_3L^3 + A_2L^2 + A_1L + A_0}
\end{aligned} \qquad (24)
$$

where we put

$$
\begin{aligned}
D_{B3} &= (\alpha_2 + \beta_2)K_{\mathrm{P}}H_{\mathrm{P}}\\
D_{B2} &= (\alpha_1 + \beta_1)K_{\mathrm{P}}H_{\mathrm{P}} + (\alpha_2 + \beta_2)K_{\mathrm{I}}H_{\mathrm{P}}\\
D_{B1} &= (\alpha_0 + \beta_0)K_{\mathrm{P}}H_{\mathrm{P}} + (\alpha_1 + \beta_1)K_{\mathrm{I}}H_{\mathrm{P}}\\
D_{B0} &= (\alpha_0 + \beta_0)K_{\mathrm{I}}H_{\mathrm{P}}
\end{aligned} \qquad (25)
$$

We leave unchanged the denominators of Eq. (24) as modifications induced by positions (23) are practically negligible as they contain terms in η^2 and terms which are linear combinations of the differences $(\alpha_2 - \beta_2)$, $(\alpha_1 - \beta_1)$, and $(\alpha_0 - \beta_0)$.

The parameter η modifies both curvature and slope of the output signal, but it could be useful, as in the case of the DSC-7, to modify separately its slope. This could be achieved by adding a “slope signal” either upstream, i.e. summed directly to the reference signal $T_{\mathrm{P}}(t)$ or downstream, i.e. summed directly to Eq. (24). In the first case, as results from Eq. (24), the slope signal would be affected by the transfer function of the calorimeter. This last function depends on the heat capacity of the two holders, and consequently the slope signal would be different whether the holders are empty or not. In the second case, the slope signal would be independent of the state of the holders. We opted for this last solution. We indicate by $f(L)$ the transfer function of a circuit devoted to generate the slope signal and suppose its input to be the reference signal $t_{\mathrm{P}}(L)$. With these hypotheses, the general form of the calorimeter output becomes

$$\begin{aligned} d(L) = {} & \frac{P_{D3}L^3 + P_{D2}L^2 + P_{D1}L + P_{D0}}{A_5L^5 + A_4L^4 + A_3L^3 + A_2L^2 + A_1L + A_0} t_{\mathrm{P}}(L) \\ & + \eta \frac{D_{B3}L^3 + D_{B2}L^2 + D_{B1}L + D_{B0}}{A_5L^5 + A_4L^4 + A_3L^3 + A_2L^2 + A_1L + A_0} t_{\mathrm{P}}(L) \\ & - \frac{P_{D3}q\omega^2 u_{\mathrm{P}}}{A_5L^5 + A_4L^4 + A_3L^3 + A_2L^2 + A_1L + A_0} \\ & + f(L)t_{\mathrm{P}}(L) \end{aligned} \tag{26}$$

We shall try to work out a simple analytical expression for *f*(*L*) from the analysis of the measured curves. The difference of two measured curves differing exclusively in their slope signal, in view of Eq. (26), should be described by the following equation

$$\Delta d(L) = [f_2(L) - f_1(L)]t_{\mathrm{P}}(L) \tag{27}$$

If $[f_2(L) - f_1(L)]$ is a constant then Eq. (27) turns out to be a polynomial whose coefficients are proportional to those of the reference signal $t_{\mathrm{P}}(L)$. But in this way the fittings are not very good. One gets much better results if Eq. (27) incorporates both the signal $t_{\mathrm{P}}(L)$ and its integral. This means that the numerator of *f*(*L*) should be $H_0/L + H_1$, where H_0 and H_1 will be better specified in the following section. To account for the initial transient of the above mentioned curve differences, we supposed *f*(*L*) to be a second order function and, to reduce the number of parameters, we supposed in addition its roots to be equal. As a consequence, we used for *f*(*L*) the following expression

$$f(L) = \frac{H_0 + H_1L}{(L+\mu)^2 L} \tag{28}$$

where μ is the root. Eq. (27) can therefore be written

$$\Delta d(L) = \frac{\Delta H_0 + \Delta H_1 L}{(L+\mu)^2 L} t_{\mathrm{P}}(L) \tag{29}$$

where ΔH_0 and ΔH_1 stand for the differences of the homonymous parameters related to two curves differing exclusively in the SL values.

In conclusion, taking into account Eqs. (26) and (28) the final expression for the theoretical output of the calorimeter becomes

$$\begin{aligned} d(L) = {} & \frac{P_{D3}L^3 + P_{D2}L^2 + P_{D1}L + P_{D0}}{A_5L^5 + A_4L^4 + A_3L^3 + A_2L^2 + A_1L + A_0} t_{\mathrm{P}}(L) \\ & + \eta \frac{D_{B3}L^3 + D_{B2}L^2 + D_{B1}L + D_{B0}}{A_5L^5 + A_4L^4 + A_3L^3 + A_2L^2 + A_1L + A_0} t_{\mathrm{P}}(L) \\ & - \frac{P_{D3}q\omega^2 u_{\mathrm{P}}}{A_5L^5 + A_4L^4 + A_3L^3 + A_2L^2 + A_1L + A_0} \\ & + \frac{H_0 + H_1L}{(L+\mu)^2 L} t_{\mathrm{P}}(L) \end{aligned} \tag{30}$$

4. Results and discussion

To verify the final expression of the output, given by Eq. (30), we used a DSC-7 calorimeter. We carried out several heating runs with empty holders, using three settings of ΔT_{B}, namely 45, 57 and 65. For each of these values we used the following settings of SL: 15, 25, 35, 45, 55, 65, and 75. All experiments were repeated three times. All measurements were carried out with the calorimeter operating in subambient mode (with Intracooler II accessory), with helium as a purge gas. The following settings were maintained throughout all experiments: ordinate filter factor = 0; lag compensation = 0; heating rate = $20\,\mathrm{K\,min^{-1}}$. Temperature calibration was repeated at each ΔT_{B}, using Hg and In as standards. Ordinate calibration was performed using In as the standard. Laboratory temperature was controlled at $295.0 \pm 0.3\,\mathrm{K}$ throughout all experiments.

As a first step of our elaboration, we used Eq. (29) for fitting the curve differences of two heating measured curves differing exclusively in SL setting. ΔH_0 and ΔH_1 are the coefficients of a linear combination of the two functions $h_0(L) = t_{\mathrm{P}}(L)/(L+\mu)^2L$ and $h_1(L) = t_{\mathrm{P}}(L)/(L+\mu)^2$ which are non linear in the parameter μ and in the parameters ζ, ω, appearing in the expression of t_{P} in Eq. (18). Consequently, the error function χ 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 [5]. We took for the parameters ω and ζ the values $\omega = 1.46\,\mathrm{s^{-1}}$ and $\zeta = 1.02$, obtained in our previous work [1], and we optimized the parameter μ by the Marquardt algorithm [5]. At every optimization cycle the two functions $h_0(L)$ and $h_1(L)$ were worked out and then the coefficients ΔH_0 and ΔH_1 were calculated by a linear fitting on the whole measured curve. Following this, using these values of ΔH_0 and ΔH_1, the parameter μ was optimized using only the transient part of the measured curve, where the variation of μ has a prominent effect. The parameters ΔH_0 and ΔH_1 turned out to be proportional to the slope difference ΔSL of the two measured curves, precisely their mean values and standard deviations are: $\Delta H_0 = (-0.0131 \pm 0.0004) \times 10^{-7}\,\Delta\mathrm{SL}$ and $\Delta H_1 = (0.076 \pm 0.001) \times 10^{-4}\,\Delta\mathrm{SL}$. The units of ΔH_0 and ΔH_1 are $\mathrm{W\,K^{-1}\,s^{-3}}$ and $\mathrm{W\,K^{-1}\,s^{-2}}$, respectively. The mean value of μ and its standard deviation, obtained from all pairs of measured curves differing exclusively in SL setting, is $\mu = 1.02 \pm 0.01\,\mathrm{s^{-1}}$. Fig. 3a shows some curve differences and their fittings. Fig. 3b is the zoom in their transient zone.

The elaboration of each measured curve, using Eq. (30), was carried out using an analogous procedure. The parameters H_0, H_1 and η were calculated by linear fitting on the whole measured curve and the parameters K_{P}, K_{I}, H_{P}, $R_{12\mathrm{S}}$ and q were optimized in the transient zone by the Marquardt algorithm. ζ, ω and μ were kept constant in these elaborations, using the values obtained from the fitting of the above mentioned curve differences. Heat capacities $C_{2\mathrm{S}}$ and $C_{2\mathrm{R}}$,

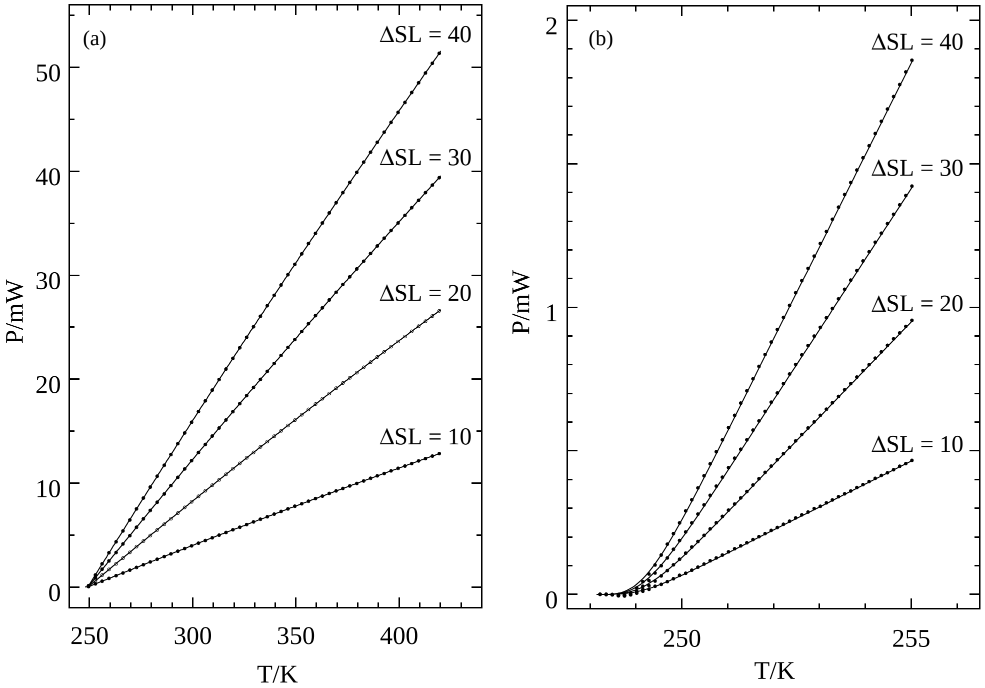

Fig. 3. Typical curves obtained by subtracting two measured curves differing exclusively in the SL values (ΔSL = 10, 20, 30, and 40). Sample and reference holders are empty; heating rate, 20 K min^{-1}; ΔT_B setting, 57. (a) Difference between experimental points, recorded in 0.2 s steps (actually shown, 1 every 50) over the entire scanning range, and fitting function (—) in accordance with Eq. (29). Standard deviation (σ) and correlation coefficient (*R*) of the fittings: ΔSL = 40, $\sigma = 7.02 \times 10^{-3}$ mW, $R = 0.9999999$; ΔSL = 30, $\sigma = 7.41 \times 10^{-3}$ mW, $R = 0.9999998$; ΔSL = 20, $\sigma = 7.49 \times 10^{-3}$ mW, $R = 0.9999995$; and ΔSL = 10, $\sigma = 7.28 \times 10^{-3}$ mW, $R = 0.9999998$; (b) Zoom on the initial transient (points actually shown, 1 every 2).

as well as R_{2S} and R_{2R}, the thermal coupling resistances with the HEB, have been put equal to each other, namely $C_{2S} = C_{2R} = 0.25\,\mathrm{J\,K^{-1}}$ and $R_{2S} = R_{2R} = 120\,\mathrm{K\,W^{-1}}$. This means that possible small differences between these quantities will be accounted for in the other fitting parameters (especially in the ΔT_B and SL parameters). The values of all the other parameters in Eq. (30), which have been left constant in all fitting procedures, are reported in Appendix A (Eq. (A.3)). The values of the parameters K_P, K_I, H_P, R_{12S}, q and their standard deviations, obtained from these elaborations, are reported in Table 1.

Fig. 4 shows the results of the fittings by Eq. (30) of a few measured heating curves carried out at constant SL and with different ΔT_B settings. Fig. 4a refers to the entire scan range and Fig 4b is the zoom in the transient zone.

Fig. 5 shows the analogous results for heating curves carried out at the same ΔT_B and at different SL settings. The fittings are generally as good as these.

Fig. 6 show the parameters H_0 and H_1 against SL. Slopes and intercepts of these straight lines are reported in Table 2. As one can see, the H_0 and H_1 slopes are practically independent of the ΔT_B setting. Their mean values and standard deviations are $(0.0129 \pm 0.0002) \times 10^{-7}\,\mathrm{W\,K^{-1}\,s^{-3}}$ and $(-0.0753 \pm 0.0005) \times 10^{-4}\,\mathrm{W\,K^{-1}\,s^{-2}}$, respectively, which are in agreement with the values obtained fitting by Eq. (29) the above mentioned curve differences. The H_0-intercept, q_{H_0}, and H_1-intercept, q_{H_1}, turn out to be linear functions of ΔT_B. Their mean values and standard deviations, obtained from Table 2, are

$$q_{H_0} = [(-0.1836 \pm 0.0003)\,\Delta T_B + 9.67 \pm 0.02] \times 10^{-7},$$
$$q_{H_1} = [(-0.019 \pm 0.003)\,\Delta T_B + 5.0 \pm 0.2] \times 10^{-4} \qquad (31)$$

where the units of q_{H_0} and q_{H_1} are $\mathrm{W\,K^{-1}\,s^{-3}}$ and $\mathrm{W\,K^{-1}\,s^{-2}}$ respectively. Taking these results into account, the explicit forms of H_0 and H_1 are

$$H_0 = (-0.1836\,\Delta T_B + 9.67 + 0.0129\mathrm{SL}) \times 10^{-7},$$
$$H_1 = (-0.0188\,\Delta T_B + 4.96 + 0.0753\mathrm{SL}) \times 10^{-4} \qquad (32)$$

where the units of H_0 and H_1 are $\mathrm{W\,K^{-1}\,s^{-3}}$ and $\mathrm{W\,K^{-1}\,s^{-2}}$, respectively.

Table 1
Mean value of the parameters obtained in the fitting, by Eq. (30), of all the measured curves, grouped according to their ΔT_B value (first column)

ΔT_B	K_P (W K^{-1})	K_I (W K^{-1} s^{-1})	H_P (W K^{-1})	R_{12S} (W K^{-1})	q (s)
45	0.65 ± 0.02	0.033 ± 0.003	2.60 ± 0.09	2.220 ± 0.001	0.058 ± 0.006
57	0.75 ± 0.03	0.043 ± 0.004	2.47 ± 0.13	2.222 ± 0.003	0.067 ± 0.005
65	0.86 ± 0.04	0.053 ± 0.007	2.53 ± 0.07	2.231 ± 0.003	0.077 ± 0.004

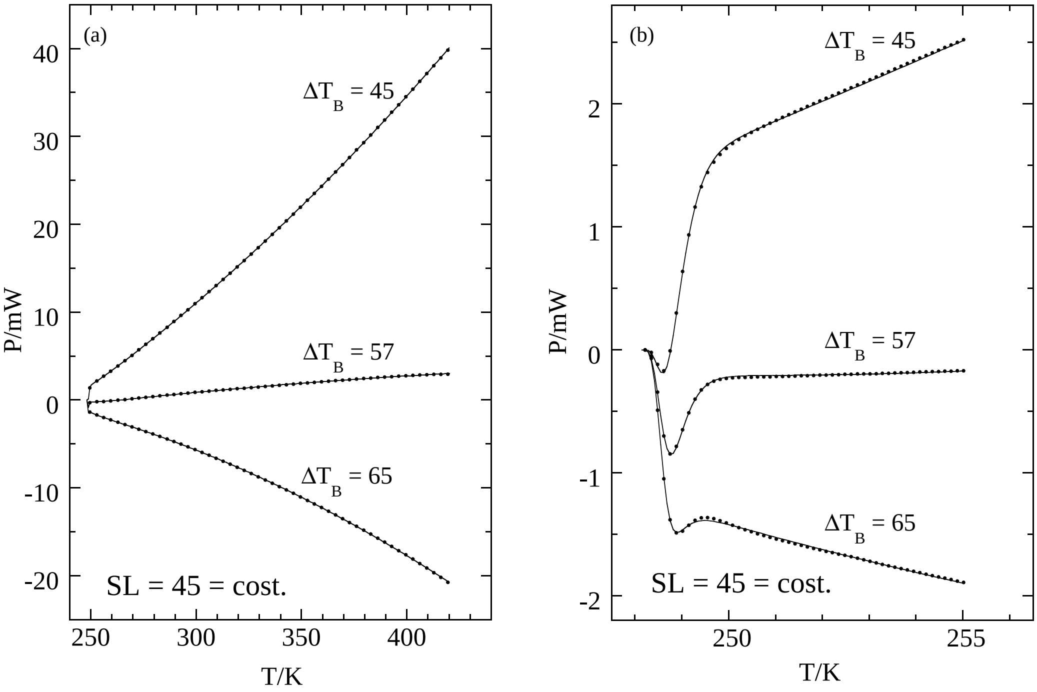

Fig. 4. Fittings of measured heating curves at constant SL and different ΔT_B. Sample and reference holders are empty; heating rate, 20 K min^{-1}. (a) Experimental points, recorded in 0.2 s steps (actually shown, 1 every 50) over the entire scanning range, and fitting function (—) in accordance with Eq. (30). Standard deviation (σ) and correlation coefficient (R) of the fittings: $\Delta T_B = 45$, $\sigma = 1.91 \times 10^{-2}$ mW, $R = 0.999998$; $\Delta T_B = 57$, $\sigma = 1.99 \times 10^{-2}$ mW, $R = 0.9998$; $\Delta T_B = 65$; and $\sigma = 2.31 \times 10^{-2}$ mW, $R = 0.999992$. (b) Zoom on the initial transient (points actually shown, 1 every 2).

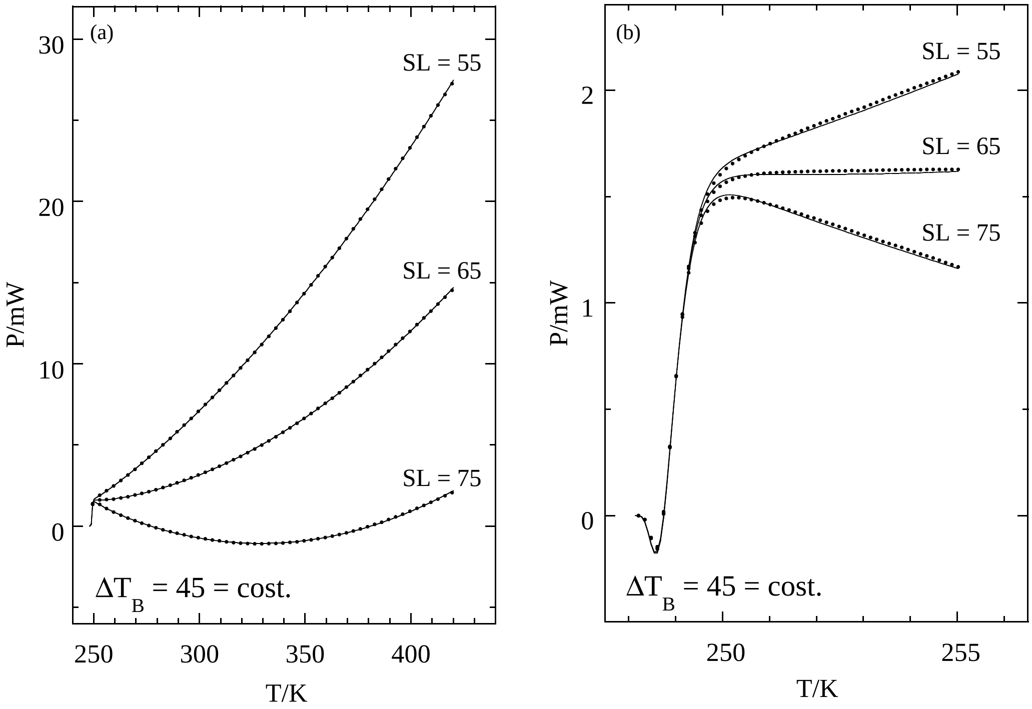

Fig. 5. Fittings of measured heating curves at constant ΔT_B and different SL. Sample and reference holders are empty; heating rate, 20 K min^{-1}. (a) Experimental points, recorded in 0.2 s steps (actually shown, 1 every 50) over the entire scanning range, and fitting function (—) in accordance with Eq. (30). Standard deviation (σ) and correlation coefficient (R) of the fittings: SL = 75, $\sigma = 1.87 \times 10^{-2}$ mW, $R = 0.9998$; SL = 65, $\sigma = 1.92 \times 10^{-2}$ mW, $R = 0.99999$; and SL = 55, $\sigma = 1.86 \times 10^{-2}$ mW, $R = 0.999997$. (b) Zoom on the initial transient (points actually shown, 1 every 2).

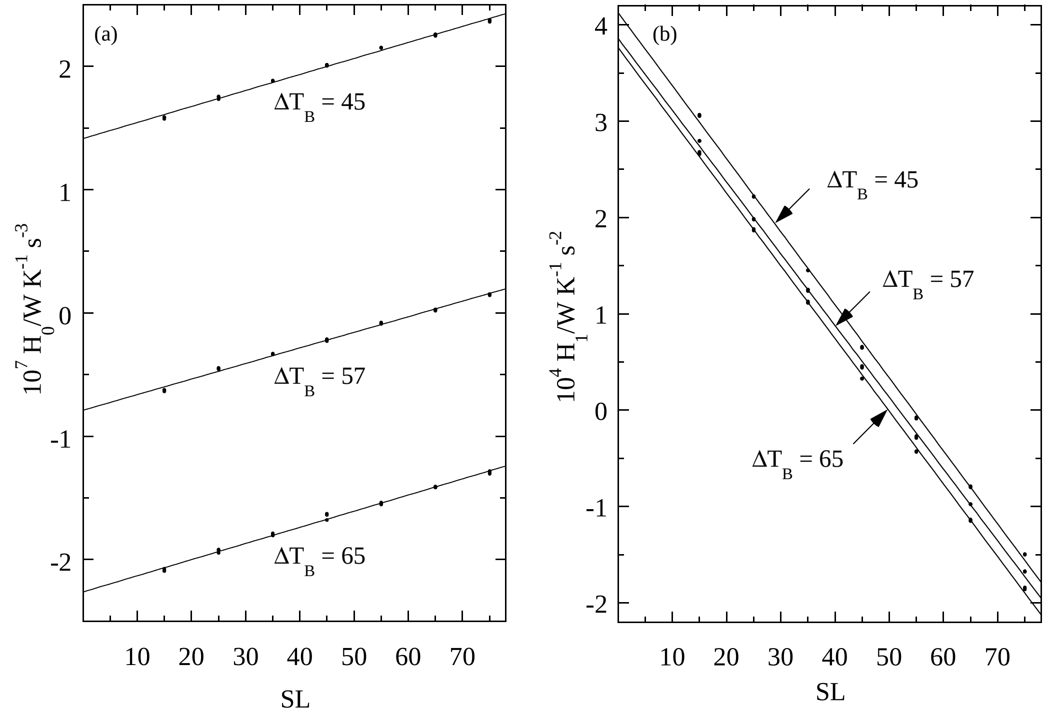

Fig. 6. Linear behavior of H_0 and H_1 as a function of SL. All experiments have been repeated three times, but the corresponding points are practically indistinguishable. Their slopes are practically independent of the ΔT_B setting, while their intercepts turn out to be linearly dependent on the ΔT_B setting. Their values, together with the standard deviation are reported in Table 2. (a) Standard deviation (σ) and correlation coefficient (R) of the linear fitting of H_0: $\Delta T_B = 45$, $\sigma = 0.007 \times 10^{-7}\,\mathrm{W\,K^{-1}\,s^{-3}}$, $R = 0.998$; $\Delta T_B = 57$, $\sigma = 0.006 \times 10^{-7}\,\mathrm{W\,K^{-1}\,s^{-3}}$, $R = 0.998$; $\Delta T_B = 65$; and $\sigma = 0.006 \times 10^{-7}\,\mathrm{W\,K^{-1}\,s^{-3}}$, $R = 0.998$. (b) σ and R of the linear fitting of H_1: $\Delta T_B = 45$, $\sigma = 0.05 \times 10^{-4}\,\mathrm{W\,K^{-1}\,s^{-2}}$, $R = 0.9996$; $\Delta T_B = 57$, $\sigma = 0.03 \times 10^{-4}\,\mathrm{W\,K^{-1}\,s^{-2}}$, $R = 0.9996$; and $\Delta T_B = 65$, $\sigma = 0.02 \times 10^{-4}\,\mathrm{W\,K^{-1}\,s^{-2}}$, $R = 0.9998$.

Table 2
Mean value and standard deviation of the parameters of the straight lines of H_0 and H_1 in Fig. 6, for each value of ΔT_B

ΔT_B	Slope of H_0 ($\times 10^{-7}\,\mathrm{W\,K^{-1}\,s^{-3}}$)	Intercept of H_0 ($\times 10^{-7}\,\mathrm{W\,K^{-1}\,s^{-3}}$)	Slope of H_1 ($\times 10^{-4}\,\mathrm{W\,K^{-1}\,s^{-2}}$)	Intercept of H_1 ($\times 10^{-4}\,\mathrm{W\,K^{-1}\,s^{-2}}$)	η ($\times 10^{-3}$)
45	0.0130 ± 0.0002	+1.41 ± 0.01	−0.0758 ± 0.0005	4.13 ± 0.02	+4.00 ± 0.02
57	0.0126 ± 0.0002	−0.79 ± 0.01	−0.0745 ± 0.0005	3.86 ± 0.02	−0.78 ± 0.04
65	0.0131 ± 0.0002	−2.26 ± 0.01	−0.0755 ± 0.0004	3.76 ± 0.02	−3.93 ± 0.03

The last column reports mean value and standard deviation of the parameter η of Eq. (30).

The last column of Table 2 reports the mean values and standard deviations of the parameter η for each family of curves with the same ΔT_B. The small values of the standard deviation suggest that η is independent of the slope while it turns out to be linearly dependent on the ΔT_B values. From Table 2 we get

$$\eta = (-0.397\,\Delta T_B + 21.84) \times 10^{-3} \tag{33}$$

The standard deviations of the slope and intercept are 0.001 and 0.07, respectively.

Eqs. (32) and (33) express the parameters H_0, H_1 and η as functions of the ΔT_B and SL values. These equations can therefore be considered as calibration equations of the instrument, with respect to ΔT_B and SL values.

5. Conclusion

We have presented an upgrade of our model of a PCDSC, with a particular reference to a DSC-7 manufactured by Perkin-Elmer. The aim of this generalization is to provide an analytical description of a measured heating curve in a fairly wide range of temperature. To reach this goal, we have implemented in our model two fundamental functions, namely the ΔT_B control and the SL control. The ΔT_B control is used to modify the curvature of a measured curve in the temperature range in which one operates. The use of the ΔT_B control also modifies the slope of a measured curve, and so the use of the SL control allows a user a further adjustment of the slope. The implementation of these two functions has simply required the introduction of three new parameters. In this way we got a fairly good analytical description of the calorimeter response, when the holders are empty, whatever the settings of both controls. We have presented results in the temperature range from 248 to 423 K. One of the above mentioned parameters turns out to be linearly dependent exclusively on ΔT_B; while the other two are linearly dependent both on the ΔT_B and SL. These results provide the means to get a calibration of the PCDSC with respect to the ΔT_B and SL settings.

The analytical description of the unbalance that occurs when a PCDSC switches from the isothermal to the scanning state, presented in our previous paper, allowed us to evaluate the impulse response of the instrument. The analytical description of the whole measured curve could allow us, as a natural development of this work, an accurate evaluation of the heat capacity of a sample.

Acknowledgements

Financial support by the Ministero dell'Istruzione, dell'Università e della Ricerca (MIUR) is acknowledged.

Appendix A

The explicit form of the functions in system (3) is

$$\begin{aligned}
\alpha_2 &= R_{12S}C_{1S}C_{2S}\\
\alpha_1 &= C_{1S}+C_{2S}+R_{12S}\left(\frac{C_{1S}}{R_{2S}}+\frac{C_{2S}}{R_{1S}}\right)\\
\alpha_0 &= \frac{1}{R_{1S}}+\frac{1}{R_{2S}}+\frac{R_{12S}}{R_{1S}R_{2S}}\\
\beta_2 &= R_{12R}C_{1R}C_{2R}\\
\beta_1 &= C_{1R}+C_{2R}+R_{12R}\left(\frac{C_{1R}}{R_{2R}}+\frac{C_{2R}}{R_{1R}}\right) \qquad \text{(A.1)}\\
\beta_0 &= \frac{1}{R_{1R}}+\frac{1}{R_{2R}}+\frac{R_{12R}}{R_{1R}R_{2R}}\\
A_C &= K_P+\frac{K_I}{L}+K_DL\\
B_C &= H_P+\frac{H_I}{L}+H_DL
\end{aligned}$$

The explicit form of the coefficients in Eq. (5) is

$$\begin{aligned}
P_{D3} &= (\alpha_2-\beta_2)K_PH_P\\
P_{D2} &= (\alpha_1-\beta_1)K_PH_P+(\alpha_2-\beta_2)K_IH_P\\
P_{D1} &= (\alpha_0-\beta_0)K_PH_P+(\alpha_1-\beta_1)K_IH_P\\
P_{D0} &= (\alpha_0-\beta_0)K_IH_P\\
A_5 &= \alpha_2\beta_2\\
A_4 &= (\alpha_2\beta_1+\alpha_1\beta_2)\\
A_3 &= (\alpha_2\beta_0+\alpha_1\beta_1+\alpha_0\beta_0) \qquad \text{(A.2)}\\
&\quad +\tfrac{1}{2}(K_P+H_P)(\alpha_2+\beta_2)\\
A_2 &= (\alpha_1\beta_0+\alpha_0\beta_1)+\tfrac{1}{2}(K_P+H_P)(\alpha_1+\beta_1)\\
&\quad +\tfrac{1}{2}K_I(\alpha_2+\beta_2)\\
A_1 &= (\alpha_0\beta_0+K_PH_P)+\tfrac{1}{2}(K_P+H_P)(\alpha_0+\beta_0)\\
&\quad +\tfrac{1}{2}K_I(\alpha_1+\beta_1)\\
A_0 &= H_PK_I+\tfrac{1}{2}K_I(\alpha_0+\beta_0)
\end{aligned}$$

The values of the parameters kept constant in all fittings are

$$\begin{aligned}
K_D &= H_D = H_I = 0\\
C_{1S} &= C_{1R} = C_{2R} = 0.25\,\mathrm{J\,K^{-1}}\\
R_{1S} &= R_{1R} = 120\,\mathrm{K\,W^{-1}} \qquad \text{(A.3)}\\
R_{2R} &= 280\,\mathrm{K\,W^{-1}}\\
R_{12R} &= 2.3\,\mathrm{K\,W^{-1}}
\end{aligned}$$

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