

## A MODEL FOR VARIABLE MASS CALORIMETRY SYSTEMS

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### ABSTRACT

In continuous injection calorimeter systems the mass of the contents of the calorimeter cell varies. This article describes a mathematical model for microcalorimeter systems employing this technique. By assuming the heat capacity of the variable element to depend linearly on time, an analytical expression for the transfer function of the system can be obtained. As an example, the unit pulse response calculated for a variable mass calorimeter by numerical methods is compared graphically with that predicted by the model when just two time constants are taken into account.

### INTRODUCTION

Recently, a number of deconvolution techniques have been developed for use in conduction calorimetry [1–6], mainly for their application to the study of liquid mixtures and solid–solid transitions [7,8]. In the case of liquid mixtures, particular interest is taken in systems in which a low concentration of one component is dissolved in another. To study these regions the minor component is slowly injected into the calorimeter cell, which contains a known quantity of the major component. This procedure causes the heat capacity of the contents of the calorimeter cell to vary, hence, the transfer function of the calorimeter system as a whole changes with time, and the mathematical models and deconvolution techniques hitherto developed are no longer applicable.

This article presents a method for obtaining an analytical expression for the transfer function of a calorimeter system when one of its parameters varies slowly with time. The computer-simulated unit pulse response of a typical system is then compared with that predicted by the model.

### THE MODEL

A “localized constants” (RC) model is adopted, in which the calorimeter is assumed to consist of  $n$  elements of heat capacities  $c_i(t)$  ( $i = 1, \dots, n$ ). The

heat balance in each element is given [9,10] by

$$p_i(t) = \frac{d}{dt} [c_i(t)J_i(t)] + \sum_{\substack{j=0 \\ j \neq i}}^n R_{ij}(J_i - J_j) \quad i = 1, \dots, n \quad (1)$$

where  $p_i(t)$  is the power dissipated in element  $i$ ,  $J_i$  is the temperature of element  $i$ , and  $R_{ij}$  is the thermal coupling between elements  $i$  and  $j$ .  $J_0$  is the temperature of the thermostat, which is used as a reference point, i.e.,  $J_0 = 0$ . The Laplace transform of eqn. (1) is

$$P_i(s) = sL[c_i(t)J_i(t)] + R_{i0}T_i(s) + \sum_{\substack{j=1 \\ j \neq i}}^n R_{ij}[T_i(s) - T_j(s)] \quad i = 1, \dots, n \quad (2)$$

where capital letters represent the Laplace transforms of the functions represented in eqn. (1) by the corresponding lower case letters, and  $T(s)$  is the Laplace transform of  $J(t)$ . Equation (2) may be put in the form

$$P_i(s) = sL[c_i(t)J_i(t)] + Q_i T_i(s) - \sum_{\substack{j=0 \\ j \neq i}}^n R_{ij} T_j(s) \quad i = 1, \dots, n \quad (3)$$

where

$$Q_i = \sum_{\substack{j=0 \\ j \neq i}}^n R_{ij} \quad i = 1, \dots, n \quad (4)$$

In the following it is assumed that the heat capacity of only one of the elements of the system ( $i = 1$ ) varies with time, and that this is the only element in which energy is dissipated. Equation (3) then becomes

$$P_1(s) = sL[c_1(t)J_1(t)] + Q_1 T_1(s) - \sum_{j=2}^n R_{1j} T_j \quad (5)$$

$$P_i(s) = [sC_i(s) + Q_i] T_i - \sum_{\substack{j=1 \\ j \neq i}}^n R_{ij} T_j \quad i = 2, \dots, n \quad (6)$$

The solution of eqn. (6) is

$$T_i(s) = \frac{D_i}{D} T_1 \quad i = 2, \dots, n \quad (7)$$

where  $D$  is the determinant

$$D = \begin{vmatrix} (sC_2 + Q_2) & -R_{23} & -R_{24} & \dots & -R_{2n} \\ -R_{23} & (sC_3 + Q_3) & -R_{34} & \dots & -R_{3n} \\ -R_{24} & -R_{34} & (sC_4 + Q_4) & \dots & -R_{4n} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ -R_{2n} & -R_{3n} & -R_{4n} & \dots & (sC_n + Q_n) \end{vmatrix} \quad (8)$$

and  $D_i$  is the same determinant except for the  $(i = 1)$ th column having been replaced by

$$\begin{vmatrix} R_{12} \\ R_{13} \\ R_{14} \\ \cdot \\ \cdot \\ \cdot \\ R_{1n} \end{vmatrix} \quad (9)$$

$D$  is a polynomial of degree  $n - 1$  in  $s$  and  $D_i$  a polynomial of degree  $n - 2$  in  $s$ .

Equations (5) and (7) together imply that

$$P_1(s) = sL[c_1(t)J_1(t)] + G_1(s)T_1(s) \quad (10)$$

where

$$G_1(s) = Q_1 - \frac{1}{D} \sum_{j=2}^n R_{1j}D_j \quad (11)$$

If the variation of  $c_1$  with time is assumed to be linear, then

$$c_1(t) = at + b \quad (12)$$

and eqn. (10) becomes

$$P_1(s) = [G_1(s) + sb]T_1 - sa \frac{d}{ds} T_1 \quad (13)$$

Assuming the sensors of the calorimeter to be located in the  $n$ th element, then the overall transfer function of the system is given by

$$H(s) = \frac{D_n}{D} T_1^* \quad (14)$$

where  $T_1^*$  is the solution of eqn. (13) when  $P_1(s) = 1$ , i.e., when the dissipation in element 1 is a Dirac unit delta function. Unfortunately, eqn. (14) generally has no exact solution (see Appendix A), and approximate methods must be used.

#### AN APPROXIMATE SOLUTION FOR $H(s)$

If the heat capacity  $c_1$  only changes slowly, i.e., if  $a$  in eqn. (12) is small, then Poincaré's method [11] may be used to obtain an approximate solution of eqn. (13). It is therefore assumed that the solution of the differential equation is of the form

$$T_1^* = T_{10} + aT_{11} + a^2T_{12} + a^3T_{13} + \dots \quad (15)$$

Equation (13) therefore becomes

$$(sb + G_1)(T_{10} + aT_{11} + a^2T_{12} + \dots) - 1 = as \frac{d}{ds} T_{10} + a^2s \frac{d}{ds} T_{11} + \dots \quad (16)$$

and the equation of equal powers of  $a$  yields

$$\begin{aligned} (sb + G_1)T_{10} - 1 &= 0 \\ (sb + G_1)T_{11} &= s \frac{d}{ds} T_{10} \\ (sb + G_1)T_{12} &= s \frac{d}{ds} T_{11} \end{aligned} \quad (17)$$

which, expressed as an explicit recursion, becomes

$$\begin{aligned} T_{10} &= \frac{1}{(sb + G_1)} \\ T_{11} &= \frac{s}{(sb + G_1)} \frac{d}{ds} T_{10} \\ T_{12} &= \frac{s}{(sb + G_1)} \frac{d}{ds} T_{11} \end{aligned} \quad (18)$$

Thus  $T_{1j}^*$  and, via eqn. (14),  $H(s)$  can be approximated to whatever order is desired.

It may be noted that  $T_{10}$  is the only term that appears in eqn. (15) if the heat capacities are all constant. The remaining  $T_{1j}$  have the same poles as  $T_{10}$ , but their multiplicities increase according to the sequence 1, 3, 5, etc.

#### A UNIT PULSE RESPONSE

In order to test the method set out above, the behaviour of a calorimeter consisting of two elements ( $n = 2$ ) under the three regimes shown in Table 1 is examined. The time-invariant regimes A and C correspond to regime B at times  $t = 0$  and  $t = 1000$  s, respectively. The unit pulse responses corresponding to A and C are readily calculated [1], but that of B must be obtained by numerical methods. All three unit pulse responses are shown in Fig. 1A, together with that predicted by the proposed model as described below.

If only the first two terms of eqn. (15) are taken into account, then the transfer function of the two-element system, as calculated by the model (eqn. 14), is

$$H(s) = \frac{R_{12}}{bc_2} \frac{1}{(s - p_1)(s - p_2)} - a \frac{R_{12}}{b^2c_2} \frac{s(s^2 + 2fs - r_0 + fr_1)}{(s - p_1)^3(s - p_2)^3} \quad (19)$$

TABLE 1

The three models examined

Model	$c_1$	$c_2$	$R_1 = R_2$	$R_{12} = R_{21}$
A	10	12	0.07	0.14
B	$10 + 0.01t$	12	0.07	0.14
C	20	12	0.07	0.14

where  $a$  and  $b$  are the coefficients appearing in eqn. (12),  $p_1$  and  $p_2$  are the poles of the solutions of

$$s^2 + r_1s + r_0 = 0 \quad (20)$$

and the other coefficients are given by

$$f = \frac{1}{c_2} (R_{20} + R_{12}) \quad (21)$$

$$r_0 = \frac{1}{bc_2} (R_{10}R_{20} + R_{12}(R_{10} + R_{20})) \quad (22)$$

$$r_1 = \frac{R_{10}}{b} + \frac{R_{20}}{c_2} + R_{12} \left( \frac{1}{b} + \frac{1}{c_2} \right) \quad (23)$$

The Laplace transform of eqn. (19) gives the desired unit pulse response

$$h(t) = \frac{R_{12}t}{bc_2} \frac{1}{p_1 - p_2} (e^{p_1t} - e^{p_2t}) - a \frac{R_{12}}{b^2c_2} \left( \sum_{i=1}^2 \sum_{j=0}^2 A_{ij} \frac{t^j}{j!} e^{p_i t} \right) \quad (24)$$

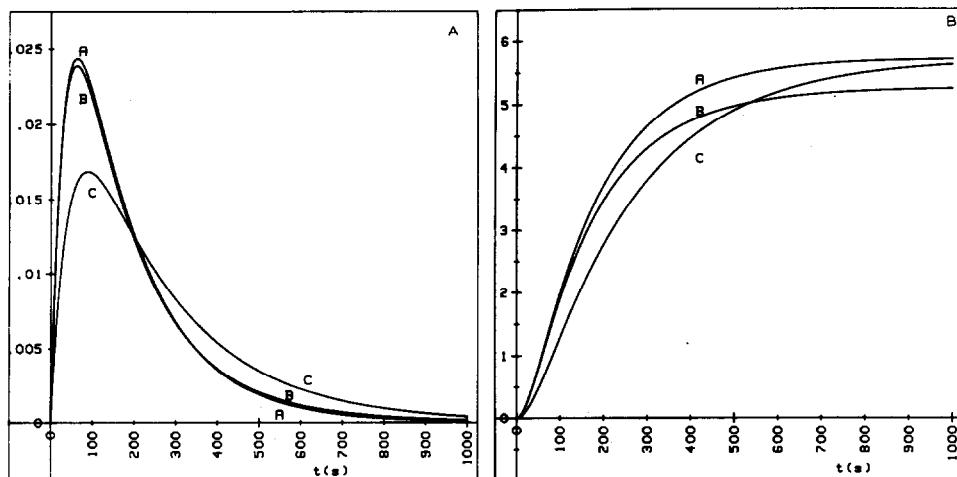


Fig. 1. (A) The unit pulse responses corresponding to models A, B and C of Table 1. B is obtained using numerical methods. (B) The unit step function responses corresponding to models A, B and C of Table 1.

where the  $A_{ij}$  are given by

$$A_{ij} = \lim_{s \rightarrow p_i} \frac{1}{(2-j)!} \frac{d^{2-j}}{ds^{2-j}} \left[ (s-p_i)^3 \frac{s(s^2 + 2fs - r_0 + fr_1)}{(s-p_1)^3(s-p_2)^3} \right] \quad (25)$$

The  $A_{ij}$  are calculated explicitly in Appendix B. The agreement between eqn. (24) and the numerically calculated unit pulse response is excellent. Figure 2 shows a detail of the most critical region of  $h(t)$  in Fig. 1A together with the response predicted by eqn. (24).

#### A UNIT STEP FUNCTION RESPONSE

If the input to the two-element calorimeter system described above is  $p_1(t) = 1$  ( $t > 0$ ), so that  $P_1(s) = 1/s$ , then the following expression for the output may be derived by applying a first-order approximation to eqn. (13)

$$Y(s) = \frac{R_{12}}{bc_2} \frac{1}{s(s^2 + r_1s + r_0)} - a \frac{R_{12}}{b^2c_2} \frac{2s^3 + (r_1 + 3f)s^2 + 2fr_1s + fr_0}{s(s^2 + r_1s + r_0)^3} \quad (26)$$

or in the time domain

$$y(t) = \frac{R_{12}}{bc_2} (B_1 e^{p_1 t} + B_2 e^{p_2 t} + B_0) - a \frac{R_{12}}{b^2c_2} \left( \sum_{i=1}^2 \sum_{j=0}^2 C_{ij} \frac{t^j}{j!} e^{p_i t} + D \right) \quad (27)$$

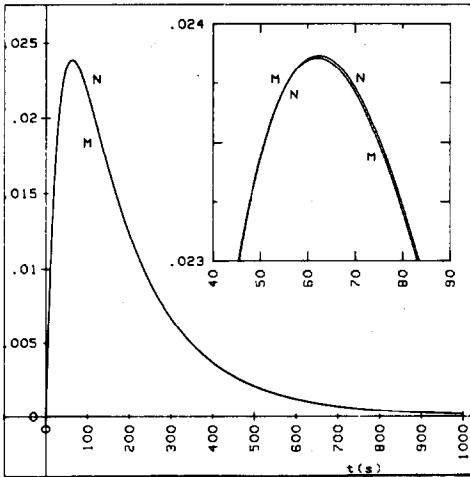


Fig. 2. Detail of the most critical region of  $h(t)$  in Fig. 1A together with the response predicted by eqn. (24).

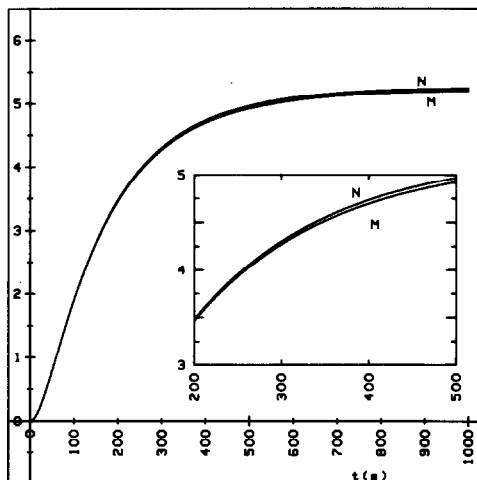


Fig. 3. Detail of the most critical region of the unit step function response of model B with the response predicted by eqn. (27).

The constants  $B_1$ ,  $B_2$ ,  $D$  and  $C_{ij}$  are obtained in a similar manner to those of the unit pulse response, and are shown explicitly in Appendix B. It is noteworthy that the model predicts that the calorimeter response as  $t \rightarrow \infty$  is less than that of the time-invariant system. According to eqn. (27)

$$y(\infty) = \frac{R_{12}}{bc_2 p_1 p_2} \left( 1 - a \frac{fr_0}{bp_1^2 p_2^2} \right) \quad (28)$$

and since  $f$ ,  $r_0$  and  $b$  are all positive, the absolute value of the response diminishes as the value of  $a$  increases.

The unit step responses calculated numerically for the three regimes of Table 1 are shown in Fig. 1B. Figure 3 details the steady-state responses of the three regimes together with that predicted by eqn. (27).

## CONCLUSION

The unit pulse response predicted by eqn. (24) for calorimeters in which the heat capacity of the contents of the cell varies is in excellent agreement with the numerically calculated behaviour of the system, and the response to a unit step function predicted by eqn. (27) is likewise satisfactory. The localized constants model used to derive eqns. (24) and (27) therefore promises to prove an important methodological advance in the characterization of calorimeters with time parameters.

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## APPENDIX A

The solution of eqn. (13) is

$$T_1^*(s) = e^{-L} \int M(s) e^{Ls} ds \quad (\text{A1})$$

where

$$M(s) = \frac{P_1(s)}{sa} \quad (\text{A2})$$

$$L(s) = - \int \frac{sb + G_1(s)}{sa} ds \quad (\text{A3})$$

Taking eqn. (11) into account,  $L(s)$  may be put in the form

$$L(s) = - \frac{Q_1}{a} \ln s + N(s) \quad (\text{A4})$$

where

$$N(s) = - \int \frac{sb - \frac{1}{D} \sum_{j=2}^n R_{1j} D_j}{sa} ds \quad (\text{A5})$$



The solution is thus

$$T_1^* = s^{Q_1/a} e^{-N(s)} \int e^{N(s)} M(s) s^{-Q_1/a} ds \quad (\text{A6})$$

This is not integrable unless  $-Q_1/a$  is a whole number, which there is no reason to suppose is the case.

#### APPENDIX B

The parameters  $A_{ij}$  of eqn. (24) are given by

$$A_{i0} = -\frac{1}{2} \frac{2K_{i1}p_i^* + (2K_{i1}p_j + 3K_{i2})p_i + K_{i2}p_j + 4K_{i3}}{(p_i - p_j)^5} \quad i = 1, 2 \quad j = 1, 2 \quad j \neq i \quad (\text{B1})$$

$$A_{i1} = -\frac{2K_{i1}p_i^2 + K_{i2}p_i + K_{i3}}{(p_1 - p_2)^4} \quad i = 1, 2 \quad (\text{B2})$$

$$A_{i2} = (-1)^i \frac{p_i(p_i^2 + 2fp_i - r_0 + fr_1)}{(p_2 - p_1)^3} \quad i = 1, 2 \quad (\text{B3})$$

where

$$K_{i1} = 2f + 3p_j \quad i = 1, 2$$

$$K_{i2} = 2(fr_1 - r_0 + 2fp_j) \quad j = 1, 2 \quad (\text{B4})$$

$$K_{i3} = p_j(fr_1 - r_0) \quad j \neq i$$

Similarly, the coefficients that appear in eqn. (27) are given by

$$B_i = \frac{1}{p_i(p_i - p_j)} \quad i = 1, 2 \quad j = 1, 2 \quad j \neq i \quad (\text{B5})$$

$$B_0 = \frac{1}{p_1 p_2} \quad (\text{B6})$$

$$C_{i0} = \frac{p_i^5 + (3k_{i3} + 4p_j)p_i^4 + (4k_{i2} + k_{i3}p_j)p_i^3 + 5k_{i1}p_i^2 + (6k_{i0} - k_{i1}p_j)p_i - 2p_jk_{i0}}{2p_i^3(p_i - p_j)^5}$$

$$i = 1, 2 \quad j = 1, 2 \quad j \neq 1 \quad (\text{B7})$$

$$C_{i1} = (-1)^i \frac{2p_i^4 + k_{i3}p_i^3 + k_{i2}p_i^2 + k_{i1}p_i + k_{i0}}{p_i^2(p_j - p_i)^4} \quad (\text{B8})$$

$$C_{i2} = \frac{2p_i^3 + (r_1 + 3f)p_i^2 + 2fr_1p_i + fr_0}{p_i(p_i - p_j)^3} \quad (\text{B9})$$

$$E = \frac{fr_0}{p_1^3 p_2^3} \quad (\text{B10})$$

where

$$\begin{aligned} k_{i0} &= -fr_0 p_j & k_{11} &= k_{12} = 4fr_0 & k_{i2} &= 6fr_1 + p_j(r_1 + 3f) \\ k_{i3} &= 2(r_1 + 3f + 2p_j) & i &= 1,2 & j &= 1,2 \quad j \neq i \end{aligned} \quad (\text{B11})$$