Thermochimica Acta, 156 (1989) 117–128
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

LINEAR SYSTEM THEORY OF A HEAT CONDUCTION CALORIMETER. PART 2. THE INVERSE FILTER METHOD IN THERMOKINETICS

SATOHIRO TANAKA

National Chemical Laboratory for Industry, Tsukuba, Ibaraki 305 (Japan)

(Received 18 April 1989)

ABSTRACT

The inverse filter method for obtaining unknown input variable $x(t)$ from known output signal $y(t)$ assuming an ordinary differential equation of the nth order of $y(t)$ and mth order of $x(t)$, is discussed ($n > m$). The differential equation leads to the transfer function of a rational form in the Laplace transform parameter, and a more straightforward inverse filter method based on the reciprocal of the rational form of the transfer function is presented. The inverse filterings are derived for special cases of $n = 1$, 2 and 3, and are examined with the aid of two- and three-body models of a calorimeter.

INTRODUCTION

Recently, the inverse filter method has been developed during thermokinetic studies on the thermal process using a heat conduction calorimeter [1–5]. The method assumes a calorimeter system as described by the following differential equation

$$\frac{d^n y}{dt^n} + a_1 \frac{d^{n-1} y}{dt^{n-1}} + \cdots + a_{n-1} \frac{dy}{dt} + a_n y$$
$$= b_0 \frac{d^m x}{dt^m} + b_1 \frac{d^{m-1} x}{dt^{m-1}} + \cdots + b_{m-1} \frac{dx}{dt} + b_m x \quad b_0 \neq 0 \tag{1}$$

where t = time; $x = x(t)$ = input variable = thermogenesis = rate of internal energy or enthalpy change caused by the reaction or transition under investigation, or applied electric power on the calorimeter; $y = y(t)$ = output variable = temperature change observed in the calorimeter experiment; and $a_1, \cdots, a_n$, and $b_0, b_1, \cdots, b_m$ are time-invariant constants.

Assuming zero initial conditions

$$\left.\begin{array}{l} x(t) = x^{(1)}(t) = \cdots = x^{(m)}(t) = 0 \\ y(t) = y^{(1)}(t) = \cdots = y^{(n)}(t) = 0 \end{array}\right\} \text{for } t < 0 \tag{2}$$

0040-6031/89/$03.50

and taking the Laplace transform on both sides of eqn. (1), we have

$$(s^n + a_1 s^{n-1} + \cdots + a_{n-1}s + a_n)\bar{y}(s)$$
$$= (b_0 s^m + b_1 s^{m-1} + \cdots + b_{m-1}s + b_m)\bar{x}(s) \tag{3}$$

where s is the parameter in the Laplace transform, and $\bar{x}(s)$ and $\bar{y}(s)$ are the Laplace transforms of $x(t)$ and $y(t)$ respectively [6]. Then, the transfer function $G_{mn}(s)$ of the calorimeter system can be expressed as a rational function in s

$$G_{mn}(s) = \frac{\bar{y}(s)}{\bar{x}(s)} = \frac{b_0 s^m + b_1 s^{m-1} + \cdots + b_{m-1}s + b_m}{s^n + a_1 s^{n-1} + \cdots + a_{n-1}s + a_n} = \frac{P_m(s)}{Q_n(s)} \tag{4}$$

where

$$P_m(s) = b_0 s^m + b_1 s^{m-1} + \cdots + b_{m-1}s + b_m \tag{5}$$

$$Q_n(s) = s^n + a_1 s^{n-1} + \cdots + a_{n-1}s + a_n \tag{6}$$

From examination of the step response, the output response for step input variable $u(t)$

$$\begin{aligned} u(t) &= 0 \quad \text{for} \quad t < 0 \\ u(t) &= 1 \quad \text{for} \quad t > 0 \end{aligned} \tag{7}$$

we can get

$$n > m \tag{8}$$

and can show that the zeros of $Q_n(s)$, called the poles of $G_{mn}(s)$, are all real and negative [6].

The main purpose of the inverse filter method is to obtain the unknown input variable $x(t)$ from the known output response data $y(t)$ observed in a calorimeter experiment, assuming the rational form of the transfer function $G_{mn}(s)$ in s.

The development of the inverse filter method has three stages: the first stage consists of differential procedures [7–10]; the second stage involves both the differentials and integrals [11]; and the third is development of the method applicable to time-varying calorimetric systems, which are described by eqn. (1) with the time-variable coefficient $a_i(t)$ [12–17].

FIRST STAGE OF THE INVERSE FILTER METHOD

In early works on the inverse filter method, the following differential procedures were proposed. Dubes et al. suggested the following iterative differential procedures [7]

$$\left.\begin{aligned} y_1(t) &= y(t) + \tau_1 \frac{\mathrm{d}y(t)}{\mathrm{d}t} \\ y_2(t) &= y_1(t) + \tau_2 \frac{\mathrm{d}y_1(t)}{\mathrm{d}t} \\ &\cdots\cdots\cdots\cdots \\ y_n(t) &= y_{n-1}(t) + \tau_n \frac{\mathrm{d}y_{n-1}(t)}{\mathrm{d}t} \end{aligned}\right\} \tag{9}$$

where τ_1, τ_2, $\cdots$ are the first, second, $\cdots$ time constants of the calorimeter respectively. The above procedures are equivalent to the following procedures in the Laplace transform [2,7]

$$\left.\begin{aligned} \bar{y}_1(s) &= (\tau_1 s + 1)\bar{y}(s) \\ \bar{y}_2(s) &= (\tau_2 s + 1)\bar{y}_1(s) = (\tau_2 s + 1)(\tau_1 + 1)\bar{y}(s) \\ &\cdots\cdots\cdots\cdots \\ \bar{y}_n(s) &= (\tau_n + 1)\bar{y}_{n-1}(s) \end{aligned}\right\} \tag{10}$$

Procedures (9) and (10) give precisely the input variable $x(t)$ and transfer $\bar{x}(t)$ when the transfer function is not zero and is represented by

$$G_{0n}(s) = \frac{B_0}{(\tau_1 s + 1)(\tau_2 s + 1) \cdots (\tau_n s + 1)} \tag{11}$$

Tachoire et al. state that the method is the elimination of the poles of the transfer function because procedures (10) are the eliminations of the poles of $G_{0n}(s)$, $-1/\tau_1$, $-1/\tau_2$, $\cdots$ [3].

Let us examine the above procedures (9) on the linear system (1) which is represented by

$$y(t) = \int_0^t g(t - \xi)x(\xi)\,\mathrm{d}\xi \tag{12}$$

where $g(t)$ is the impulse response of the system [18]. Substituting (12) into eqn. (9)

$$y_1(t) = \int_0^t \left[g(t - \xi) + \tau_1 \frac{\partial g(t - \xi)}{\partial t} \right] x(\xi)\,\mathrm{d}\xi + \tau_1 g(0)x(t) \tag{13}$$

$$y_2(t) = \int_0^t \left[g(t - \xi) + (\tau_1 + \tau_2)\frac{\partial g(t - \xi)}{\partial t} + \tau_1\tau_2 \frac{\partial^2 g(t - \xi)}{\partial t^2} \right] x(\xi)\,\mathrm{d}\xi \tag{14}$$

$$+ \left[(\tau_1 + \tau_2)g(0) + \tau_1\tau_2 g^{(1)}(0) \right] x(t) + \tau_1\tau_2 g(0) x^{(1)}(t)$$

$$y_3(t) = \int_0^t \left[g(t-\xi) + A_1 \frac{\partial g(t-\xi)}{\partial t} + A_2 \frac{\partial^2 g(t-\xi)}{\partial t^2} + A_3 \frac{\partial^3 g(t-\xi)}{\partial t^3} \right] x(\xi)\, d\xi$$
$$+ \left[A_1 g(0) + A_2 g^{(1)}(0) + A_3 g^{(2)}(0) \right] x(t)$$
$$+ \left[A_2 g(0) + A_3 g^{(1)}(0) \right] x^{(1)}(t) + A_3 g(0) x^{(2)}(t)$$
$$\cdots\cdots\cdots \qquad (15)$$

where

$A_1 = \tau_1 + \tau_2 + \tau_3$

$A_2 = \tau_1\tau_2 + \tau_2\tau_3 + \tau_3\tau_1$

and

$A_3 = \tau_1\tau_2\tau_3$

When the impulse response $g(t)$ of the calorimeter system is given by [19]

$$g(t) = c_1\, e^{-t/\tau_1} + c_2\, e^{-t/\tau_2} + c_3\, e^{-t/\tau_3} + \cdots$$
$$= \sum_{i=1}^{n} c_i\, e^{-t/\tau_i}, \quad \tau_1 > \tau_2 > \tau_3 > \cdots \qquad (16)$$

eqns. (12)–(15) become

$$y(t) = \sum_{i=1}^{n} c_i \int_0^t e^{-(t-\xi)/\tau_i} x(\xi)\, d\xi \qquad (17)$$

$$y_1(t) = \sum_{i=2}^{n} c_i \left(1 - \frac{\tau_1}{\tau_i}\right) \int_0^t e^{-(t-\xi)/\tau_i} x(\xi)\, d\xi + \tau_1 (c_1 + c_2 + \cdots) x(t) \qquad (18)$$

$$y_2(t) = \sum_{i=3}^{n} \left[1 - \frac{(\tau_1 + \tau_2)}{\tau_i} + \frac{\tau_1\tau_2}{\tau_i^2}\right] c_i \int_0^t e^{-(t-\epsilon)/\tau_i} x(\xi)\, d\xi$$
$$+ \left[(\tau_1 + \tau_2)(c_1 + c_2 + \cdots) - \tau_1\tau_2 \left(\frac{c_1}{\tau_1} + \frac{c_2}{\tau_2} + \cdots \right) \right] x(t)$$
$$+ \tau_1\tau_2 (c_1 + c_2 + \cdots) x^{(1)}(t) \qquad (19)$$

$$y_3(t) = \sum_{i=4}^{n} \left(1 - \frac{A_1}{\tau_i} + \frac{A_2}{\tau_i^2} - \frac{A_3}{\tau_i^3}\right) c_i \int_0^t e^{-(t-\epsilon)/\tau_i} x(\xi)\, d\xi$$
$$+ \left[A_1 (c_1 + c_2 + \cdots) - A_2 \left(\frac{c_1}{\tau_1} + \frac{c_2}{\tau_2} + \cdots \right) + A_3 \left(\frac{c_1}{\tau_1^2} + \frac{c_2}{\tau_2^2} \cdots \right) \right] x(t) + \left[A_2 (c_1 + c_2 + \cdots) - A_3 \left(\frac{c_1}{\tau_1} + \frac{c_2}{\tau_2} + \cdots \right) \right] x^{(1)}(t) + A_3 (c_1 + c_2 + \cdots) x^{(2)}(t)$$
$$\cdots\cdots\cdots \qquad (20)$$

The integrals on the right hand of eqns. (17)–(20) show that the contributions from the terms

$$e^{-(t-\xi)/\tau_i}$$

in $y_n(t)$ decrease in succession as n increases. Alternatively, $y_n(t)$ does not contain only the term $x(t)$ but also the extra terms

$$x^{(1)}(t),\ x^{(2)}(t), \cdots,\ x^{(n-1)}(t) \tag{21}$$

When

$$g(0) = g^{(1)}(0) = g^{(2)}(0) = \ \cdots \ = g^{(n-1)}(0) = 0 \tag{22}$$

$y_n(t)$ does not contain the terms in eqn. (21). However, any validity of the condition in eqn. (22) is not generally proved in real calorimeter systems.

The existence of the terms in eqn. (21) in $y_n(t)$ are shown in the experimental results of the application of the inverse filter method on the output response for the step input [8,11]. When the input variable $x(t)$ is a step input, $x^{(1)}$ gives an overshoot peak at the beginning of the addition of the step input. In fact, Fig. 8 in ref. 8 and Fig. 6 in ref. 11 show that an overshoot peak appears in the curve of $y_n(t)$ simultaneously with the addition of the step input [8,11].

In their experiments, they start the input of the thermogenesis with time delay d, a lapse of time $t = d$ from time zero $t = 0$. The resulting $y_d(t)$ from the inverse filtering of the input variable $x_d(t)$ with time delay d is represented by

$$y_d(t) = \int_0^t g(t-\xi)x_d(\xi)\ d\xi = \int_d^t g(t-\xi)x_d(\xi)\ d\xi \tag{21d}$$

where $x_d(t) = 0,\ t < d$.

In this case, the filtered output variables $y_{d,n}(t)$ contain the extra terms

$$x_d^{(1)}(t),\ x_d^{(2)}(t), \cdots,\ x_d^{(n-1)}(t) \tag{21d}$$

instead of terms (21) as shown in the following

$$y_{d,1}(t) = \int_d^t \left[g(t-\xi) + \tau_1 \frac{\partial g(t-\xi)}{\partial t} \right] x_d(\xi)\ d\xi + \tau_1 g(0) x_d(t) \tag{13d}$$

$$y_{d,2}(t) = \int_d^t \left[g(t-\xi) + (\tau_1 + \tau_2) \frac{\partial g(t-\xi)}{\partial t} + \tau_1\tau_2 \frac{\partial^2 g(t-\xi)}{\partial t^2} \right] x_d(\xi)\ d\xi$$
$$+ \left[(\tau_1 + \tau_2) g(0) + \tau_1\tau_2 g^{(1)}(0) \right] x_d(t) + \tau_1\tau_2 g(0) x_d^{(1)}(t) \tag{14d}$$

$$y_{d,3}(t) = \int_d^t \Big[g(t-\xi) + A_1 \frac{\partial g(t-\xi)}{\partial t} + A_2 \frac{\partial^2 g(t-\xi)}{\partial t^2}$$
$$+ A_3 \frac{\partial^3 g(t-\xi)}{\partial t^3} \Big] x_d(\xi)\, d\xi$$
$$+ \left[A_1 g(0) + A_2 g^{(1)}(0) + A_3 g^{(2)}(0) \right] x_d(t)$$
$$+ \left[A_2 g(0) + A_3 g^{(1)}(0) \right] x_d^{(1)}(t) + A_3 g(0) x_d^{(2)}(t) \quad (15d)$$

SECOND STAGE OF THE INVERSE FILTER METHOD AND ALTERNATIVE METHOD

Cesari et al. have presented the inverse filter method which eliminates both the poles and zeros of the transfer function of the calorimeter system [11]. However, their method is complicated because it eliminates the poles and zeros separately, and is plagued by the amplification of noise through repeated differential operations in the elimination of the poles.

Alternatively, the following method is a more straightforward way of obtaining the unknown input variable $x(t)$ from the known output signal $y(t)$. From eqns. (4) and (8)

$$x(t) = \mathrm{L}^{-1}[\bar{y}(s)/G(s)]$$
$$= \mathrm{L}^{-1}\left[\bar{y}(s) \frac{s^n + a_1 s^{n-1} + \cdots + a_n}{b_0 s^m + b_1 s^{m-1} + \cdots + b_m} \right] \quad n > m \quad (23)$$

where L^{-1} is the operator of the inverse Laplace transform. The right hand of eqn. (23) can be calculated for some special cases and is shown as follows.

Case 1.0: n = 1, m = 0

$$\frac{1}{G_{01}(s)} = \frac{s + a_1}{b_0} = \frac{1}{b_0} s + \frac{a_1}{b_0} \quad (24)$$

$$x(t) = \frac{1}{b_0} \frac{dy(t)}{dt} + \frac{a_1}{b_0} y(t) \quad (25)$$

Equation (25) has the same form as the Tian equation, the most simple for the heat conduction calorimeter [20].

Case 2.0: n = 2, m = 0

$$\frac{1}{G_{02}(s)} = \frac{s^2 + a_1 s + a_2}{b_0} = \frac{1}{b_0} s^2 + \frac{a_1}{b_0} s + \frac{a_2}{b_0} \quad (26)$$

$$x(t) = \frac{1}{b_0}\frac{d^2y(t)}{dt^2} + \frac{a_1}{b_0}\frac{dy(t)}{dt} + \frac{a_2}{b_0}y(t) \tag{27}$$

Equation (27) based on transfer function (26), represents the two-step filtering in the early studies of the method [6].

Case 2.1: n = 2, m = 1

$$\frac{1}{G_{12}(s)} = \frac{s^2 + a_1 s + a_2}{b_0 s + b_1}$$

$$= \frac{1}{b_0}s + \frac{1}{b_0}\left(a_1 - \frac{b_1}{b_0}\right) + \frac{1}{b_0}\left[a_2 - \frac{b_1}{b_0}\left(a_1 - \frac{b_1}{b_0}\right)\right]\frac{1}{s + (b_1/b_0)} \tag{28}$$

$$x(t) = \frac{1}{b_0}\frac{dy(t)}{dt} + \frac{1}{b_0}\left(a_1 - \frac{b_1}{b_0}\right)y(t) + \frac{1}{b_0}\left[a_2 - \frac{b_1}{b_0}\left(a_1 - \frac{b_1}{b_0}\right)\right]$$

$$\times \int_0^t y(\xi)\, e^{-\frac{b_1}{b_0}(t-\xi)}\, d\xi \tag{29}$$

Equation (29) based on transfer function (28) is identical with the inverse filtering presented by Cesari et al. in the second stage of the studies of the method [11]. They state that inverse filtering is the elimination of two poles and one zero of the transfer function.

Case 3.0: n = 3, m = 0

$$\frac{1}{G_{03}(s)} = \frac{s^3 + a_1 s^2 + a_2 s + a_3}{b_0}$$

$$= \frac{1}{b_0}s^3 + \frac{a_1}{b_0}s^2 + \frac{a_2}{b_0}s + \frac{a_3}{b_0} \tag{30}$$

$$x(t) = \frac{1}{b_0}\frac{d^3y(t)}{dt^3} + \frac{a_1}{b_0}\frac{d^2y(t)}{dt^2} + \frac{a_2}{b_0}\frac{dy(t)}{dt} + \frac{a_3}{b_0}y(t) \tag{31}$$

Equation (31) is identical with the third-order correction presented by Point et al. [8], and was used in the thermokinetic study of the hydration of cement by Yung et al. [21].

Case 3.1: n = 3, m = 1

$$\frac{1}{G_{13}(s)} = \frac{s^3 + a_1 s^2 + a_2 s + a_3}{b_0 s + b_1}$$

$$= \frac{1}{b_0} s^2 + \frac{1}{b_0}\left(a_1 - \frac{b_1}{b_0}\right)s + C + \frac{D}{s + (b_1/b_0)} \tag{32}$$

$$x(t) = \frac{1}{b_0}\frac{\mathrm{d}^2 y(t)}{\mathrm{d}t^2} + \frac{1}{b_0}\left(a_1 - \frac{b_1}{b_0}\right)\frac{\mathrm{d}y(t)}{\mathrm{d}t} + Cy(t)$$

$$+ D\int_0^t y(\xi)\exp\left[-\frac{b_1}{b_0}(t-\xi)\right]\mathrm{d}\xi \tag{33}$$

$$C = \frac{1}{b_0}\left[a_2 - \frac{b_1}{b_0}\left(a_1 - \frac{b_1}{b_0}\right)\right] \tag{34}$$

$$D = \frac{1}{b_0}\left\{a_3 - \frac{b_1}{b_0}\left[a_2 - \frac{b_1}{b_0}\left(a_1 - \frac{b_1}{b_0}\right)\right]\right\} \tag{35}$$

Case 3.2.a. n = 3, m = 2, $b_1^2 - 4b_0 b_2 > 0$

When equation

$$b_0 s^2 + b_1 s + b_2 = 0 \tag{36}$$

has two real roots $-\alpha$ and $-\beta$, we have

$$\frac{1}{G_{23}(s)} = \frac{s^3 + a_1 s^2 + a_2 s + a_3}{b_0 s^2 + b_1 s + b_2}$$

$$= \frac{s^3 + a_1 s^2 + a_2 s + a_3}{b_0 (s+\alpha)(s+\beta)}$$

$$= \frac{1}{b_0} s + \frac{1}{b_0}\left(a_1 - \frac{b_1}{b_0}\right) + \frac{C}{s+\alpha} + \frac{D}{s+\beta} \tag{37}$$

$$x(t) = \frac{1}{b_0}\frac{\mathrm{d}y(t)}{\mathrm{d}t} + \frac{1}{b_0}\left(a_1 - \frac{b_1}{b_0}\right)y(t)$$

$$+ \int_0^t y(\xi)\left[C\mathrm{e}^{-\alpha(t-\xi)} + D\mathrm{e}^{-\beta(t-\xi)}\right]\mathrm{d}\xi \tag{38}$$

where

$$C = \frac{1}{b_0(\alpha-\beta)}\left\{-a_3 + \frac{b_2}{b_0}\left(a_1 - \frac{b_1}{b_0}\right) + \alpha\left[a_2 - \frac{b_2}{b_0} - \frac{b_1}{b_0}\left(a_1 - \frac{b_1}{b_0}\right)\right]\right\} \tag{39}$$

$$D = \frac{1}{b_0(\alpha-\beta)}\left\{-a_3 - \frac{b_2}{b_0}\left(a_1 - \frac{b_1}{b_0}\right) - \beta\left[a_2 - \frac{b_2}{b_0} - \frac{b_1}{b_0}\left(a_1 - \frac{b_1}{b_0}\right)\right]\right\} \tag{40}$$

Case 3.2.b: $n = 3$, $m = 2$, $b_1^2 - 4b_0b_2 = 0$

When eqn. (36) has two identical real roots $-\alpha$, we have

$$\frac{1}{G_{23}(s)} = \frac{1}{b_0}s + \frac{1}{b_0}\left(a_1 - \frac{b_1}{b_0}\right) + \frac{C}{s+\alpha} + \frac{D}{(s+\alpha)^2} \tag{41}$$

$$x(t) = \frac{1}{b_0}\frac{\mathrm{d}y(t)}{\mathrm{d}t} + \frac{1}{b_0}\left(a_1 - \frac{b_1}{b_0}\right)y(t) + \int_0^t y(\xi)[C + D(t-\xi)]\,\mathrm{e}^{-\alpha(t-\xi)}\,\mathrm{d}\xi \tag{42}$$

where

$$C = \frac{1}{b_0}\left[a_2 - \frac{b_2}{b_0} - \frac{b_1}{b_0}\left(a_1 - \frac{b_1}{b_0}\right)\right] \tag{43}$$

$$D = \frac{1}{b_0}\left\{a_3 - \frac{b_2}{b_0}\left(a_1 - \frac{b_1}{b_0}\right) - \frac{b_1}{2b_0}\left[a_2 - \frac{b_2}{b_0} - \frac{b_1}{b_0}\left(a_1 - \frac{b_1}{b_0}\right)\right]\right\} \tag{44}$$

Case 3.2.c: $n = 3$, $m = 2$, $b_1^2 - 4b_0b_2 < 0$

When eqn. (36) has two imaginary conjugated roots $-\alpha + \mathrm{j}\beta$ and $-\alpha - \mathrm{j}\beta$, we have

$$\begin{aligned}\frac{1}{G_{23}(s)} &= \frac{s^3 + a_1s^2 + a_2s + a_3}{b_0s^2 + b_1s + b_2} \\ &= \frac{s^3 + a_1s^2 + a_2s + a_3}{b_0\left[(s+\alpha)^2 + \beta^2\right]} \\ &= \frac{1}{b_0}s + \frac{1}{b_0}\left(a_1 - \frac{b_1}{b_0}\right) + \frac{C(s+\alpha)}{(s+\alpha)^2 + \beta^2} + \frac{D}{(s+\alpha)^2 + \beta^2}\end{aligned} \tag{45}$$

$$\begin{aligned}x(t) &= \frac{1}{b_0}\frac{\mathrm{d}y(t)}{\mathrm{d}t} + \frac{1}{b_0}\left(a_1 - \frac{b_1}{b_0}\right)y(t) \\ &\quad + \int_0^t y(\xi)\left[C\cos\beta(t-\xi) + \frac{D}{\beta}\sin\beta(t-\xi)\right]\exp\left[-\frac{b_1}{2b_0}(t-\xi)\right]\mathrm{d}\xi\end{aligned} \tag{46}$$

where

$$C = \frac{1}{b_0}\left[a_2 - \frac{b_2}{b_0} - \frac{b_1}{b_0}\left(a_1 - \frac{b_1}{b_0}\right)\right] \tag{47}$$

$$D = \frac{1}{b_0}\left\{a_3 - \frac{b_2}{b_0}\left(a_1 - \frac{b_1}{b_0}\right) - \frac{b_1}{2b_0}\left[a_2 - \frac{b_2}{b_0} - \frac{b_1}{b_0}\left(a_1 - \frac{b_1}{b_0}\right)\right]\right\} \tag{48}$$

LINEAR MODEL OF CALORIMETER WITH LUMPED CONSTANTS AND TRANSFER FUNCTION

The linear model with lumped constants produces an ordinary differential equation between the input variable $x(t)$ and the output signal $y(t)$ which leads to the transfer function of rational function in the Laplace transform parameter s. The model gives an insight into the transfer function of a real calorimeter in terms of the structure of the model. Zielenkiewicz and coworkers have carried out extensive studies on the models of a calorimeter with lumped constants and have given the transfer function for the various models [22–32]. Their results serve to interpret the behaviour of the transfer function.

Tachoire et al. and Cesari et al. have studied the influences of the positions of the source of the thermogenesis on the transfer function of a calorimeter [3,11]. They state that when the source is near the temperature detector, the transfer function is zero and elimination of both the zero and the poles gives a good reconstruction of the input variable. Their statements are in agreement with the results of the two- and three-models of a calorimeter as shown in the following.

The two-body model gives the transfer function of which the denominator $Q_n(s)$ is second-order in s ($n = 2$ in eqns. (1), (4) and (6)) [22,24,28]. The order m of numerator $P_m(s)$ is determined by the mutual positions of the thermometer and source of the thermogenesis. When the locations of the thermometer and source are at the same body, the model gives $m = 1$ and one zero of the transfer function (see $H_{11}(s)$ and $H_{22}(s)$ in Ref. 28).

The three-body model gives similiar results [23,25]. The model shows that the denominator of the transfer function is the third order in s ($n = 3$ in eqns. (1), (4) and (6)), and the order of the numerator is determined by the mutual positions of the thermometer and source of the thermogenesis. When the thermometer and source are located at the same body, the transfer function has two zeros (see $H_{11}(s)$ and $H_{32}(s)$ in ref. 23). When they are located at the two bodies adjacent to each other, the transfer function has one zero (see $H_{21}(s)$ and $H_{22}(s)$ in ref. 23). When they are located at two separate bodies, the transfer function does not have a zero (see $H_{31}(s)$ and $H_{12}(s)$ in ref. 23).

The three-body model provides an insight into the roots of eqn. (36). For example, numerator $P_2(s)$ of transfer function $H_{32}(s)$ in ref. 23 is

$$P_2(s) = \frac{K}{T_1T_2T_3}\left[T_1T_2s^2 + (T_1 + T_2)s + 1 - K_2 + K_1K_2\right] \tag{49}$$

where T_1, T_2, T_3, K, K_1 and K_2 are constants represented by the heat capacities of the bodies and the heat transfer constants between the bodies, and have the following properties

$$T_1,\ T_2,\ T_3 > 0 \tag{50}$$

$$1 > K,\ K_1,\ K_2 > 0 \tag{51}$$

The discriminator of eqn. $P_2(s) = 0$ is

$$\left(\frac{K}{T_1T_2T_3}\right)^2\left[(T_1 + T_2)^2 - 4T_1T_2(1 - K_2 + K_1K_2)\right]$$
$$= \left(\frac{k}{T_1T_2T_3}\right)^2\left[(T_1 - T_2)^2 + 4T_1T_2K_2(1 - K_1)\right] > 0 \quad (52)$$

The coefficients of eqn. (49) are all positive. Thus, eqn. (49) has two real and negative roots. With the similar examination of the transfer function $H_{11}(s)$ in ref. 23, we can arrive at the following conclusions. When the source of the thermogenesis is located in the neighbourhood of the thermometer and the behaviour of the calorimeter is approximated by the transfer function $G_{23}(s)$, the zeros of $G_{23}(s)$ are both real and negative, and inverse filtering in case 3.2.a (eqn. (38)) is valid for the calorimeter.

ACKNOWLEDGEMENTS

The author would like to thank Prof. S. Sugimoto of Osaka University and Dr. I. Takeda of this Institute for very helpful discussions and advice.

REFERENCES

1 S. Tanaka, in M. Taniguchi (Ed.), Progress in Calorimetry and Thermal Analysis, Kagakugijitsu-sha, Tokyo, 1983, p. 37.
2 W. Zielenkiewicz, J. Therm. Anal., 29 (1984) 179.
3 H. Tachoire, J.L. Macqueron and V. Torra, in M.A.V Ribeiro da Silva (Ed.), Thermochemistry and its Applications to Chemical and Biological Systems, D. Reidel, Dordrecht, 1984, p. 77.
4 H. Tachoire and V. Torra, Thermochim. Acta, 110 (1987) 171.
5 W. Zielenkiewicz, J. Therm. Anal., 33 (1988) 7.
6 S. Tanaka, Thermochim. Acta, 141 (1989) 181.
7 J.P. Dubes, M. Barres and H. Tachoire, Thermochim. Acta, 19 (1977) 101.
8 R. Point, J.L. Petit and P.C. Gravelle, J. Therm. Anal., 17 (1979) 383.
9 J.P. Dubes, M. Barres, E. Boitard and H. Tachoire, Thermochim. Acta, 39 (1980) 63.
10 J.P. Dubes and H. Tachoire, Thermochim. Acta, 51 (1981) 239.
11 E. Cesari, V. Torra, J.L. Macqueron, R. Prost, J.P. Dubes and H. Tachoire, Thermochim. Acta, 53 (1982) 1.
12 J. Ortin, A. Ramos, V. Torra and J. Vinals, Thermochim. Acta, 75 (1984) 173.
13 C. Rey, J.R. Rodriguez, V. Perez-Villar, J. Ortin, V. Torra, J.P. Dubes, R. Kechavarz and H. Tachoire, Thermochim. Acta, 81 (1984) 97.
14 J. Ortin, A. Ramos and V. Torra, Thermochim. Acta, 84 (1985) 255.
15 C. Rey, V. Perez-Villar, J.R. Rodriguez and V. Torra, Thermochim. Acta, 89 (1985) 307.
16 J. Ortin, C. Rey and V. Torra, Thermochim. Acta, 96 (1985) 37.
17 F. Marco, M. Rodriguez de Revera, J. Ortin, T. Serra and V. Torra, Thermochim. Acta, 126 (1988) 171.

18 B.C. Kuo, Automatic Control Systems, Prentice–Hall, Englewood Cliffs, 4th edn., 1982, p. 71.
19 E. Calvet, in H.A. Skinner (Ed.), Experimental Thermochemistry, Vol. 2, Interscience, London, 1962, Chap. 17, p. 391.
20 E. Calvet and H. Prat, Recent Progress in Microcalorimetry, translated by H.A. Skinner, Pergamon, Oxford, 1963, p. 31.
21 W.X. Yung, H.Y. Kang and W.C. Ning, Thermochim. Acta, 123 (1988) 177.
22 E. Margas, A. Tabaka and W. Zielenkiewicz, Bull. Acad. Polon. Sci., Ser. Sci. Chim., 20 (1972) 323 (in English).
23 E. Margas, A. Tabaka and W. Zielenkiewicz, Bull. Acad. Polon. Sci., Ser. Sci. Chim., 20 (1972) 329 (in English).
24 W. Zielenkiewicz and E. Margas, Bull. Acad. Polon. Sci., Ser. Sci. Chim., 21 (1973) 247 (in English).
25 W. Zielenkiewicz and E. Margas, Bull. Acad. Polon. Sci., Ser. Sci. Chim., 21 (1973) 251 (in English).
26 W. Zielenkiewicz, J. Therm. Anal., 14 (1978) 79.
27 E. Margas and W. Zielenkiewicz, Bull. Acad. Polon. Sci., Ser. Sci. Chim., 26 (1978) 503 (in English).
28 E. Margas and W. Zielenkiewicz, Bull. Acad. Polon. Sci., Ser. Sci. Chim., 28 (1980) 89 (in English).
29 E. Cesari, J. Hatt, E. Margas, J. Navarro, V. Torra, E. Utzig and W. Zielenkiewicz, Bull. Acad. Polon. Sci., Ser. Sci. Chim., 28 (1980) 297 (in English).
30 J. Hatt, E. Margas and W. Zielenkiewicz, Thermochim. Acta, 64 (1983) 305.
31 W. Zielenkiewicz, E. Margas and J. Hatt, Thermochim. Acta, 88 (1985) 387.
32 W. Zielenkiewicz and E. Margas, J. Therm. Anal., 32 (1987) 173.