Thermochimica Acta, 94 (1985) 387–392
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

A SIMPLE MODEL FOR CALORIMETERS WITH TEMPERATURE PROGRAMMING

E. CESARI

Departament de Termología, Facultat de Física, Universitat de Barcelona, Diagonal 645, Barcelona (Spain)

J. FONT and J. MUNTASELL

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

(Received 24 April 1985)

ABSTRACT

We present a theoretical study of an RC-model constituted only by one heat capacity and one coupling with the thermostat. It is assumed that the thermostat temperature varies as a function of time, and the heat capacity variation is due to its dependence either on temperature or on the mass exchange with the exterior.

The results are parallel to the corresponding RC-models where the thermostat temperature is constant. The variations of sensibility are shown, as well as a criterion for the applicability of inverse filtering as a deconvolution technique in calorimeters with temperature programming.

INTRODUCTION

The deconvolution of experimental thermograms by means of numerical algorithms, in order to get the thermogenesis of a process, is well known as an application to invariant calorimeters under isothermal conditions [1,2]. Nowadays, inverse filtering is one of the most advantageous techniques because of its easy numerical application and its extension to non-invariant systems [3,4].

In this study we analyse the response of calorimeter devices with temperature programming, bearing in mind its evolution when the sample heat capacity varies (non-invariant systems) [5,6]. The purpose is to obtain suitable sensibility expressions and to justify the appropriate use of inverse filtering in these devices.

0040-6031/85/$03.30

MODEL

With the most simple RC-model (one capacity coupled to the thermostat) under isothermal conditions, the classical Tian equation is obtained. We have generalized this equation when the temperature of the thermostat varies at constant heating rate ($T_0 = T_1 + \beta t$, with β = constant). If the heat capacity is not constant ($C = C(t)$) we impute two reasons for this variation: (a) specific heat varies noticeably with temperature, or (b) a mass exchange exists with the surroundings.

In Fig. 1 we show the scheme of the analysed model.

We present the three studied cases below.

(1) Heat capacity constant

This case describes processes in which the mass and the specific heat do not vary with time or temperature.

When a power release takes place, the balance equation is

$$w(t) = C\frac{dT}{dt} + P(T - T_0) = C\frac{dT}{dt} + P(T - \beta t) \quad (T_1 = 0) \tag{1}$$

If $w(t)$ equals zero, eqn. (1) yields

$$T = \beta t - \frac{C}{P}\beta\left[1 - \exp\left(-\frac{P}{C}t\right)\right] \tag{2}$$

As is well known one should note that the temperature, T, in eqn. (2) when $t \gg C/P$, that is, when the baseline is established, shows a constant delay with regard to the thermostat temperature (βt).

Sensibility

(a) Defined as the quotient between the total area under the thermogram and the total energy released.

We assume that the thermal effect takes place when T in eqn. (2) is reduced to (baseline established)

$$T_M = \beta t - \frac{C}{P}\beta \tag{3}$$

Subtracting T_M from T (solution of eqn. 1), the response $\Delta T(t)$ from the experimental device is obtained

$$\Delta T(t) = T(t) - T_M(t) = T - \beta t + \frac{C}{P}\beta \tag{4}$$

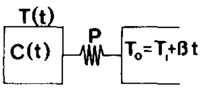

Fig. 1. Scheme of the analysed model.

By integration of eqn. (1) between $t = 0$ and $t = t_f$ (initial and final instants from the thermal effect) and taking account of eqn. (4), we obtain for the sensibility, S

$$S = \frac{\int_0^{t_f} \Delta T(t)\, dt}{\int_0^{t_f} w(t)\, dt} = \frac{1}{P} \tag{5}$$

(b) Defined as the asymptotic value of the ΔT signal when the power released inside cell is constant and equals 1 W.

Equation (1) may be rewritten as

$$w(t) = P\left[T + \frac{C}{P}\frac{dT}{dt} - \beta t\right] \tag{6}$$

in which, by substitution of T from eqn. (4)

$$w(t) = P\left[\Delta T + \frac{C}{P}\frac{d(\Delta T)}{dt}\right] \tag{7}$$

If $w(t)$ is constant (Heaviside-like dissipation) the expression of the constant power release at stationary state ($\Delta T =$ constant) is obtained from eqn. (7)

$$w = P\Delta T \tag{8}$$

Therefore, the sensibility becomes $1/P$.

Equation (7) verifies the correct utilization of inverse filtering with $S = 1/P$ and with the time constant $\tau = C/P$. The results are the same as in the classical case under isothermal conditions ($T_0 =$ constant). One should note that if C and P are constants and T_0 varies linearly with time (constant heating rate), inverse filtering may be used.

We point out that these results are not particular for one-body RC-models but common for any linear chain of capacities and couplings when a heat effect takes place in the first body and we detect in the last one (the nearest to the thermostat).

(2) Heat capacity not constant (specific heat varies with temperature)

This case describes processes where the sample specific heat varies with T, without mass exchange. We assume that $C(t) = \dot{C}t + C_0$ where $\dot{C}$ and C_0 are constant.

When a power release takes place the balance equation is

$$w(t) = C(t)\frac{dT}{dt} + P(T - \beta t) \tag{9}$$

If $w(t) = 0$, eqn. (9) yields

$$T = \frac{\beta C_0}{P + \dot{C}}\left(\frac{C(t)}{C_0}\right)^{(-P/\dot{C})} + \frac{P\beta}{P + \dot{C}}t - \frac{C_0\beta}{P + \dot{C}} \tag{10}$$

From eqn. (10), when the baseline is established, we can see that the sample heating rate is only equal to β when $\dot{C} = 0$. That is, if $\dot{C}$ is constant, the temperature difference between sample and thermostat evolves linearly with time.

Sensibility

(a) Defined as the quotient between the total area under the thermogram and the total energy released.

Supposing that the thermal effect takes place when the baseline is established, that is, when T in eqn. (10) is

$$T_M = \frac{P\beta}{P + \dot{C}} t - \frac{C_0\beta}{P + \dot{C}} \tag{11}$$

The ΔT(t) signal may be obtained by subtracting T_M from T (solution of eqn. 9)

$$\Delta T(t) = T(t) - T_M(t) = T - \frac{P\beta}{P + \dot{C}} t + \frac{C_0\beta}{P + \dot{C}} \tag{12}$$

By integration of eqn. (9) between $t = 0$ and $t = t_f$ and taking account of eqn. (12), we get

$$S = \frac{1}{P - \dot{C}} \tag{13}$$

(b) Defined as the asymptotic value of the ΔT signal when the power released inside cell is constant and equals 1 W.

Writing eqn. (9) in an equivalent expression

$$w(t) = P\left[T + \frac{C(t)}{P}\frac{\mathrm{d}T}{\mathrm{d}t} - \beta t\right] \tag{14}$$

and substituting T from eqn. (12), we obtain the inverse filtering algorithm

$$w(t) = P\left[\Delta T + \frac{C(t)}{P}\frac{\mathrm{d}(\Delta T)}{\mathrm{d}t}\right] \tag{15}$$

Therefore, we can apply inverse filtering, taking into account the evolution of the time constant ($\tau = C(t)/P$) with the heat capacity. If $w(t)$ corresponds to a Heaviside-like dissipation, we obtain, from eqn. (15), when the stationary state is reached

$$w = P\Delta T \tag{16}$$

Then the sensibility is

$$S = \frac{1}{P} \tag{17}$$

Equations (13) and (17) give different expressions of S, depending on its definition.

(3) Heat capacity not constant (mass exchange with the surroundings)

We assume that $C(t) = \dot{C}t + C_0$, where $\dot{C}$ and C_0 are constants, and that the mass exchange takes place between the exterior at temperature T_0 and the sample at temperature T. In this case the balance equation is

$$w(t) = C(t)\frac{\mathrm{d}T}{\mathrm{d}t} + P(T - \beta t) + \dot{C}(T - \beta t)$$
$$= C(t)\frac{\mathrm{d}T}{\mathrm{d}t} + (P + \dot{C})(T - \beta t)$$
$$= C(t)\frac{\mathrm{d}T}{\mathrm{d}t} + P'(T - \beta t) \quad (18)$$

Since $P + \dot{C} = P'$ is constant, eqn. (18) is identical to eqn. (9) if P is changed by P'. The results are, therefore, the same as in the above case by means of substitution of P by $P + \dot{C}$. In this form, the sensibility, defined as the quotient between the total area under the thermogram and the total energy released is

$$S = \frac{1}{P' - \dot{C}} = \frac{1}{P} \quad (19)$$

When a Heaviside-like dissipation takes place

$$S = \frac{1}{P'} = \frac{1}{P + \dot{C}} \quad (20)$$

The inverse filtering is possible with

$$\tau = \frac{C(t)}{P'} = \frac{C(t)}{P + \dot{C}} \quad (21)$$

and

$$S = \frac{1}{P + \dot{C}}$$

TABLE 1

Some features of the model

	S [a]	S [b]	τ [c]
C constant	$1/P$	$1/P$	C/P
$C = C(t)$ without mass exchange	$1/(P - \dot{C})$	$1/P$	$C(t)/P$
$C = C(t)$ with mass exchange	$1/P$	$1/(P + \dot{C})$	$C(t)/(P + \dot{C})$

[a] The sensibility defined as the quotient between the total area under the thermogram and the total energy released.

[b] The sensibility defined as the asymptotic ΔT value when the power released inside the cell is constant and equals 1 W.

[c] The time constant.

As well as in the above case, different expressions of S can be obtained, depending on its definition.

We have also analysed non-invariant multibody systems under non-isothermal conditions. Generally, we cannot obtain in these cases the expression of the inverse filtering algorithm.

The most outstanding features of the one-body RC-model with temperature programming are summarized in Table 1.

CONCLUSIONS

The one-body RC-model under isothermal conditions (T_0 = constant) is equivalent, in terms of sensibility, to the same model with temperature thermostat as a linear function of time. If the model is non-invariant, the sensibility defined either as the quotient between the total area under the thermogram and the total energy released or as the asymptotic ΔT value when the power released inside the cell is constant and equal to 1 W, is different.

We must use the second definition of S to deconvolute the experimental thermograms by means of the inverse filtering technique. We can conclude that the term $\dot{C}$ plays a different role when the heat capacity varies due to a change of specific heat or a mass exchange with the surroundings.

Though for the one-body RC-model an inverse filtering algorithm is reached, we have verified that the above algorithm cannot be obtained for non-invariant n-body systems.

REFERENCES

1 J. Navarro, V. Torra, E. Cesari, J.L. Macqueron, R. Prost, J.P. Dubes and H. Tachoire, Bull. Soc. Chim. Fr., I (1982) 49, 54; I (1983) 89.
2 Proc. of Journées d'étude sur la déconvolution, Société Chimique de France et Association Française de Calorimétrie et Analyse Thermique, Cadarache, 1982, 1983.
3 J. Ortin, A. Ramos, V. Torra and J. Viñals, Thermochim. Acta, 75 (1984) 173.
4 J. Ortin, A. Ramos and V. Torra, Thermochim. Acta, 84 (1985) 255.
5 E. Cesari, J. Viñals and V. Torra, Thermochim. Acta, 63 (1983) 341.
6 C. Rey, V. Pérez Villar and J.R. Rodríguez, Thermochim. Acta, 81 (1984) 87.