Thermochimica Acta, 63 (1983) 341-350
Elsevier Science Publishers B.V., Amsterdam - Printed in The Netherlands

THERMOGENESIS: RESPONSE GIVEN BY CALORIMETERS WHOSE PHYSICAL PARAMETERS CHANGE IN TIME

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(Received 25 October 1982)

ABSTRACT

The response given by conduction calorimeters whose physical parameters change in time is analysed in terms of heat transport equations particularly through "localized time constants" or RC models including variable coefficients.

The results obtained in simple models exhibit several anomalies concerning the sensibility of the device: its value usually differs from that given by classical models and also from the temperature of the stationary state (corresponding to a constant power release inside the laboratory cell). These facts could question the standard calibration procedures in the case of phase transitions and liquid mixtures.

INTRODUCTION

Electronic systems and a great variety of numeric algorithms are nowadays common techniques to obtain a given thermogenesis. In other words, all of them allow a deconvolution of experimental thermograms to yield the instantaneous power released inside the laboratory cell. A systematic analysis of the dynamic response of very many calorimeters [1-3] and of the various deconvolutive techniques used [4-6] has contributed to optimize their efficiency and to obtain a fair account of their possibilities.

Their application to actual thermogenesis has produced quite remarkable results [7-9] concerning, mainly, temperature-induced solid-solid transformations (martensitic) and liquid mixtures. In the latter case, one component is injected into the solution; the thermogenesis is, then, directly related to the excess molar enthalpy which may be calculated down to very low concentrations (mole fraction $x_s \gtrsim 0.001$, the concentration range attained being of considerable theoretical interest). Nevertheless, in both cases, the mass of the substance contained in the cell and/or its specific heat change. Consequently, not only do we encounter the classical problems concerning the identification of the system but also the transfer function (TF) of the system is changing during the experiment.

These facts are analysed in this work in terms of heat transport equations particularly through what have been called "localized time constants" or RC models [10–12] but including variable physical parameters of the system.

MODEL

The liquid mixture is formed inside the laboratory cell by injecting the solute by means of an electromechanical pump. The fluid travels a long way inside the calorimetric vessel to ensure a proper thermalization (the temperature of the calorimetric block is controlled by a thermostat). It is obvious that there is a heat capacity change while the injection takes place due to the introduction of supplementary mass and to eventual changes in the properties of the fluids involved in the mixture as a consequence of the mixing process itself. Moreover, the fluid which is being introduced inside the cell is at the same temperature as the calorimetric block, whereas the liquid which is already inside the cell is at a somewhat higher temperature because of the energy released during the mixing. Consequently, the energetic balance inside the cell must include a new term associated with the heating of the fluid which is coming in.

On the other hand, concerning solid–solid transformations, the mass of the sample does not change during the process but there is a heat capacity change while the transformation is developing. It is assumed that the temperature of the thermostat is constant during the process. This is a very good approximation only for very slow temperature programs. What is more, the thermal couplings between the sample and the detector system are also modified because of changes in the surface relief of the sample during the transformation.

A general RC model is based on a discrete representation of the calorimeter and defined by a set of differential equations [10–12]

$$W_i(t) = C_i \frac{\mathrm{d}T_i}{\mathrm{d}t} + \sum_{k \neq i} P_{ik}(T_i - T_k) + P_i T_i \qquad i = 1, \ldots, N$$

where W_i, C_i, P_{ik} and P_i are the power released at the ith element (W), its heat capacity (J K^{-1}), the coupling between elements i and k (W K^{-1}) and the coupling with the thermostat (W K^{-1}) where the temperature of the thermostat has been taken as reference.

It is considered that the different parameters are functions of time: $C_i(t)$, $P_{ik}(t)$ and $P_i(t)$, and, in the case of liquid mixtures discussed above, a term accounting for the heating of the fluid which is entering the laboratory cell has to be added. This term is simply

$$W_\mathrm{h} = \frac{\mathrm{d}C_i(t)}{\mathrm{d}t} T_i \equiv \dot{C}_i(t) T_i$$

The system of equations in a general case now reads

$$W_i(t) = C_i(t)\frac{\mathrm{d}T_i}{\mathrm{d}t} + \sum_{k \neq i} P_{ik}(t)(T_i - T_k) + P_i(t)T_i + \dot{C}_i(t)T_i$$

In fact, only a small number of parameters will change during the process, namely, in both cases mentioned, the parameters related to the cell contents and the couplings between the sample and the rest of the calorimeter. We will sometimes consider a linear dependence of the parameters vs. time because this is approximately the case experimentally either in liquid mixtures, using steady injection, or in solid–solid transformations, when it is a first order phase transition and abrupt changes in heat capacity occur; a linear dependence of the heat capacity of the whole sample during the transformation is only an idealization of the process.

GENERALIZED TIAN EQUATION

The most simple case is a system consisting only of a capacity, C, and a coupling to the thermostat, P. If both parameters are constant, the classical Tian equation is obtained [13]. Several features of a general model with variable parameters are shown. The equation which now defines the model is

$$W(t) = C(t)\frac{\mathrm{d}T}{\mathrm{d}t} + P(t)T + \dot{C}(t)T$$

Relaxation of the system from an initial temperature, T_0

The equation

$$0 = C(t)\frac{\mathrm{d}T}{\mathrm{d}t} + P(t)T + \dot{C}(t)T$$

is considered. Integrating the equation, we obtain

$$T(t) = T_0 \exp\left\{ -\int_0^t \frac{P(t') + \dot{C}(t')}{C(t')}\,\mathrm{d}t' \right\}$$

Obviously, if $C(t) = C$, and $P(t) = P$, are both constant, the Tian equation is obtained again. If a linear relation is assumed, $C(t) = at + b$ and $P(t) = P$, giving

$$T(t) = T_0(at + b)^{-(P+a)/a}$$

This solution would correspond, for instance, to a Dirac dissipation at $t = 0$

and a steady injection of solute. The moment the injection ends, the response turns out to be Tian's exponential decay from then on.

Sensibility

The sensibility of the system is defined as

$$S = \int_0^\infty T(t)\,\mathrm{d}t$$

Let us now distinguish between two different cases: whether there is or is not mass injection. In the first case, the equation reads

$$C(t)\frac{\mathrm{d}T}{\mathrm{d}t} + PT + \dot{C}(t)T = \delta(t)$$

One should note that we have taken the coupling to the thermostat to be constant. Otherwise it is difficult even to precisely define the sensibility. In any case, this parameter is associated with the detector system which, obviously, does not change during the experiment. More complex models allow introduction of variable couplings, while keeping those related to the detector system constant (see next section).

The previous equation may be rewritten as

$$\frac{\mathrm{d}}{\mathrm{d}t}(C(t)T) + PT = \delta(t)$$

Integrating both sides of the equation from zero to infinity

$$[C(t)T]_0^\infty + P\int_0^\infty T(t)\mathrm{d}t = 1$$

So, finally

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

which is the same value given by Tian's model.

On the other hand, if injection is not taken into account

$$C(t)\frac{\mathrm{d}T}{\mathrm{d}t} + PT = \delta(t)$$

or, after integration,

$$\int_0^\infty C(t)\frac{\mathrm{d}T}{\mathrm{d}t}\mathrm{d}t + P\int_0^\infty T(t)\mathrm{d}t = 1$$

Integrating by parts

$$-\int_0^\infty T(t)\dot{C}(t)\mathrm{d}t + PS = 1$$

Finally

$$S = \frac{1 + \int_0^\infty T(t)\dot{C}(t)\mathrm{d}t}{P}$$

and the sensibility changes in a general case.

Response to a Heaviside-like dissipation

Consider the equation

$$C(t)\frac{\mathrm{d}T}{\mathrm{d}t} + P(t)T + \dot{C}(t)T = W$$

where W is the power released (constant) and the initial temperature is $T_i = 0$. Solution of the homogeneous equation

$$C(t)\frac{\mathrm{d}T}{\mathrm{d}t} + P(t)T + \dot{C}(t)T = 0$$

gives

$$T_1(t) = A \exp\left\{ -\int_0^t \frac{P(t') + \dot{C}(t')}{C(t')} \mathrm{d}t' \right\}$$

If $P(t)$ and $\dot{C}(t)$ become constant for t greater than a certain value of t_0, a particular solution of the inhomogeneous equation is

$$T_2(t) = \frac{W}{P(t) + \dot{C}(t)}$$

If $T(t = 0) = 0$, the final solution reads

$$T(t) = \frac{W}{P(t) + \dot{C}(t)} \left[1 - \exp\left\{ -\int_0^t \frac{P(t') + \dot{C}(t')}{C(t')} \mathrm{d}t' \right\} \right]$$

The asymptotic behaviour when $t \to \infty$ is easily found provided that the capacity and the coupling behave according to usual experimental conditions

$$T(t) \to \frac{W}{P(\infty) + \dot{C}(\infty)}$$

which reduces to the usual value only if $\dot{C}(t) = 0$; otherwise this limit differs from W/P which is the stationary state temperature corresponding to a model with constant parameters.

The most outstanding features of the model are summarized in Table 1. In both the cases discussed, the limiting value of the temperature does not coincide with the sensibility of the model.

TABLE 1

Some features of the models

	Classical RC model	$C = C(t)$ without mass change	$C = C(t)$ with mass change
A [a]	$\frac{1}{P}$	$\frac{1+\int_0^{\infty} T\dot{C}(t)\mathrm{d}t}{P}$	$\frac{1}{P}$
B [b]	$\frac{1}{P}$	$\frac{1}{P}$	$\frac{1}{P(\infty)+\dot{C}(\infty)}$

[a] A is the sensibility of the model defined as the quotient between the total area under the thermogram and the total energy released (1J).

[b] B is the asymptotic value of the temperature when the power released inside the cell is constant and equals 1 W.

COMPLEX SYSTEMS

The system of differential equations which rules the behaviour of a multi-body system reads

$$C_i(t)\frac{\mathrm{d}T_i}{\mathrm{d}t} + \sum_{k \neq i} P_{ik}(t)(T_i - T_k) + \dot{C}_i(t)T_i + P_i(t)T_i = W_i(t) \qquad i = 1,\ldots,N$$

which is equivalent to a single linear equation of order N with variable coefficients that cannot be solved for an arbitrary choice of the parameters. Nevertheless, we have considered a two-body system which already shows the most relevant characteristics of the model. In fact, the previous section already showed several peculiar characteristics which will be derived again in this case. They may possibly be generalized to an arbitrary model.

Of interest here is a two-body model whose parameters are

$$C_1(t) = at + b \qquad P_1(t) = 0$$

whereas C_2, P_{12} and P_2 are constant. This choice roughly simulates the actual calorimeter during both injection and martensitic transformation.

Response to a Dirac pulse

Figure 1 shows the response, $T_2(t)$, of the system when $W_2(t) = \delta(t)$ obtained by numerically integrating the system of differential equations. We have used Euler's method with active repeated Richardson extrapolation [14]. The headings in the extrapolation scheme are $\Delta/1$, $\Delta/3$, $\Delta/7$, $\Delta/15$ and $\Delta/31$. The actual choice of the parameters has been

$$C_1 = \begin{cases} 10 + 0.01t & 0 \leqslant t \leqslant 1000 \\ 20 & t \geqslant 1000 \end{cases} \qquad C_2 = 10$$

$$P_{12} = 0.152055 \qquad P_2 = 0.076026$$

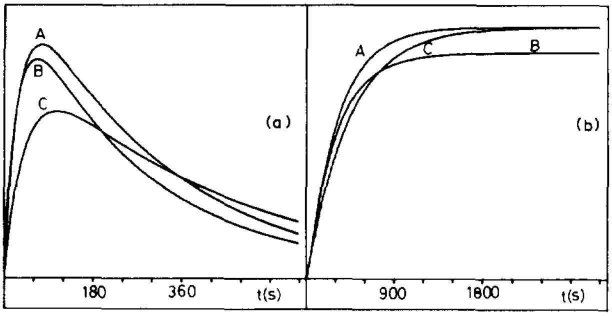

Fig. 1. (a) Response to a Dirac pulse corresponding to the models

(A) $C_1 = 10 \quad P_{12} = 0.152055$
$C_2 = 10 \quad P_2 = 0.076026$

(B)

$$C_1 = \begin{cases} 10 + 0.01t & 0 \leqslant t \leqslant 1000 \\ 20 & t \geqslant 1000 \end{cases} \qquad P_{12} = 0.152055$$

$$C_2 = 10 \qquad P_2 = 0.076026$$

(C) $C_1 = 20 \quad P_{12} = 0.152055$
$C_2 = 10 \quad P_2 = 0.076026$

(b) Response of same three models [(A), (B), (C)] to a constant power released, $W = 1$ W. The choice of the parameters is somewhat different here in order to show better the stationary state. C_1 in model B is now

$$C_1 = \begin{cases} 10 + 3.33333 \times 10^{-3} t & 0 \leqslant t \leqslant 3000 \\ 20 & t \geqslant 3000 \end{cases}$$

This figure also presents the two classical RC limiting models: ($C_1 = 10$, $C_2 = 10$, P_{12}, P_2) and ($C_1 = 20$, $C_2 = 10$, P_{12}, P_2), whose response can be calculated analytically.

Sensibility

In this case the sensibility is defined as

$$S = \int_0^{\infty} T_2(t) \mathrm{d}t$$

In this case, the system of equations is

$$C_1(t)\frac{\mathrm{d}T_1}{\mathrm{d}t} + P_{12}(t)(T_1 - T_2) + \dot{C}_1(t)T_1 = \delta(t)$$

$$C_2(t)\frac{\mathrm{d}T_2}{\mathrm{d}t} + P_{12}(t)(T_2 - T_1) + \dot{C}_2(t)T_2 + P_2T_2 = 0$$

Assuming that $T_2(0) = T_2(\infty) = 0$, integration of the second equation yields

$$\int_0^{\infty} P_{12}(t)(T_2 - T_1)\mathrm{d}t + P_2 S = 0$$

Whereas integrating the first equation yields

$$\int_0^{\infty} P_{12}(t)(T_1 - T_2)\mathrm{d}t = 1$$

Finally

$$S = \frac{1}{P_2}$$

which is the same result given by the model involving constant parameters. If the terms proportional to $\dot{C}_1(t)$ and $\dot{C}_2(t)$ were not included (remember that this is the case when the mass of the sample does not change), the sensibility would again depend on $\dot{C}_1(t)$ and $\dot{C}_2(t)$.

Response to a Heaviside-like dissipation

Figure 1(b) also shows the response of the model to a Heaviside input ($W = 1$ W) together with the response of the two limiting constant models mentioned previously. Notice how, again, the temperature $T_2(t)$ tends to a lower value than the two limiting models.

It is clear that an arbitrary model including variable parameters will never reach a stationary state, $\dot{T}_1(t) = 0$, $\dot{T}_2(t) = 0$, but there exist several choices of the parameters that lead to this state and that bear some resemblance to the actual experimental conditions. For instance, the model so far discussed and solved numerically [$C_1(t) = at + b$, all other parameters being constant] does present a stationary state

$$T_2 = \frac{W}{P_2 + a(P_{12} + P_2)/P_{12}}$$

If $\dot{C}_1(t) = 0$, then $T_2 = W/P_2$ which is the value given by the two conventional models, but if $\dot{C}_1(t) > 0$, then $T_2 < W/P_2$ as shown in the figure. It is now clear that the incoming mass into the laboratory cell is responsible for the decrease in the temperature of the stationary state even though the sensibility of the device remains unaffected. What is more, a stationary state is only obtained when steady injection is used, i.e. $\dot{C}_1(t)$ is constant.

On the other hand, if there is no mass change the stabilization temperature will be W/P_2 whereas the sensibility will be altered.

CONCLUSION

The changes in sensibility and stationary state presented here in simple models presumably occur in more general cases although its relevance could be different (probably less). This is why the previous analysis should be carried out either on more complex models, and consequently closer to an actual calorimeter, or directly on experimental measurements. Some tentative conclusions are made.

1. It seems feasible to obtain numerically the response given by simple RC models even if the physical parameters such as heat capacities or couplings between elements change in time. Consequently, the experimental response given by the systems used to study the molar excess enthalpy in liquid mixtures or the power released during a martensitic transformation may be simulated during or after the processes have taken place.
2. Both the cases analysed show that the sensibility (total area under the thermogram vs. total energy released) does not coincide with the temperature reached in the stationary state. Standard calibrations either based on Joule dissipations or by means of standard mixtures may produce not altogether true values of the sensibility.

ACKNOWLEDGEMENT

One of us (J.V.) acknowledges a fellowship from the Ministerio de Educación y Ciencia within the Plan Nacional de Formación del Personal Investigador.

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