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IDENTIFICATION AND DECONVOLUTION IN TIME-VARYING CALORIMETRIC SYSTEMS BY AN OPTIMAL TRACKING APPROACH

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ABSTRACT

Excess partial molar enthalpies of binary liquid mixtures can be accurately measured at very low concentrations by means of continuous-injection heat conduction calorimetry. This method causes evolution of the thermal properties of the calorimeter as a function of time. In this paper it is shown that identification and deconvolution of the thermal signal are equivalent problems when dealing with time-varying systems. A signal treatment analysis is proposed based upon optimal tracking, and different numerical examples, where the actual calorimeter is replaced by a discrete RC model, are presented.

INTRODUCTION

In recent years, continuous-injection heat conduction calorimetry has been extensively used for the determination of excess partial molar enthalpies in binary liquid mixtures. The most outstanding advantage of this technique is that the whole range of concentrations can be scanned in a single run. Numerical treatment of the thermograms, i.e., identification and deconvolution to eliminate the thermal inertia of the calorimeter, leads to highly accurate values for the excess molar partial enthalpies at concentrations as low as $x \leqslant 0.001$. Phenomena like phase separation and micellation can also be studied with this experimental technique [1,2].

In all the preceding cases there is a flow of liquid solute from outside, at the temperature of the thermal bath, into the calorimetric vessel, at the

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temperature of the reaction. This flow modifies the thermal properties of the calorimeter in three ways: the heat capacity of the calorimetric vessel increases with time, there is an energy contribution devoted to warming up the liquid entering the vessel, and, finally, the thermal couplings between the vessel and the detectors may also change [3]. These modifications cannot a priori be neglected when numerically processing the thermograms, and there is, in fact, experimental evidence for them: changes in the steady-state temperature for a constant power dissipation, and evolution of the dynamic properties of the calorimetric response with the amount of mixture in the vessel.

From the same measurements, however, it is clear that the relative influence of the changes associated with the injection is only significant for noise-free experiments. In these experiments, deconvolution of the thermal response will have to be performed explicitly taking into account the time-varying character of the calorimetric dynamic properties during injection.

Methods proposed so far are generalizations of the corresponding time-invariant ones. Firstly, the multi-body method is easily extended to the time-varying situation by explicitly considering the time behaviour of the heat capacities and couplings in the model. Secondly, inverse filtering of the thermogram can handle time-varying calorimetric experiments by considering the sensibility and the time constants of the device as functions of time. The dependence can be obtained from static measurements with different contents of the vessel, as detailed in refs. 4–6.

In this paper we present a generalization of the optimal control method, described in ref. 7, to the time-varying experimental problem. The thermal behaviour of the calorimeter is expressed in terms of state variables, and identification and deconvolution are formulated as tracking problems in signal analysis. The generalized method is applied to several simple and realistic examples to test its performance. The examples are computed with the aid of an RC model consisting of three thermal capacities, which roughly represents an actual continuous-injection calorimeter.

METHODS FOR DECONVOLUTION AND IDENTIFICATION

Deconvolution and the optimal tracking problem

Let $u(t)$ be an unknown input signal which provides an output signal $y(t)$ as represented in Fig. 1. When the system behaves linearly, the restoration of u from the knowledge of y is referred to as deconvolution.

The basic idea of the method proposed is as follows: for the lack of knowledge about the input signal, u, a signal $\hat{u}$ which gives an output signal $\hat{y}$ near to y is considered as a good approximation of u. Two signals, u'' and

Fig. 1. Schematic diagram of the input–output calorimetric system.

$\hat{u}$, which provide the same output cannot be distinguished. Therefore, the deconvolution may be considered as the synthesis of a signal $\hat{u}$ which minimizes a function of the error $e(t)$ defined below. Different techniques have been proposed to solve this problem [7,8]. The situation is schematically represented in Fig. 2.

Obviously, a model of the system is required, but modelling, in fact, already comprises a deconvolution. In the time-invariant case some techniques are able to perform the identification without effective deconvolution [7]. Here, another use of the optimal control theory is proposed in order to identify a time-varying model.

Identification and optimal control

In order to illustrate our method, we use a one-dimensional system described by its state equation

$$\dot{x} = f(t)x(t) + u(t)$$

This can be considered to be equivalent to a first-order linear system with a varying time constant. $u(t)$ is the input signal, $x(t)$ the output signal and $f(t)$ a time-varying gain. The block diagram corresponding to the state equation is shown in Fig. 3.

The preceding equation may, however, be considered from another point of view. It can represent the state equation of a system with two different inputs, u and f, as represented in Fig. 4. Therefore, it is clear that $f(t)$ and $u(t)$ have an equivalent meaning and, henceforth, identification and deconvolution become the same thing. In particular, we may consider that $f(t)$ is an input signal and $u(t)$ is internal and known.

Suppose now that we want to identify this system. We look for a model described by

$$\dot{x}_{\mathrm{m}} = f_{\mathrm{m}}(t)x_{\mathrm{m}} + u(t)$$

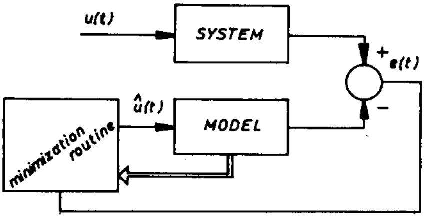

Fig. 2. Block diagram for the tracking problem.

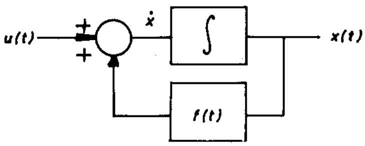

Fig. 3. Block diagram corresponding to a time-varying one-dimensional system described by the state equation $\dot{x}=f(t)x(t)+u(t)$.

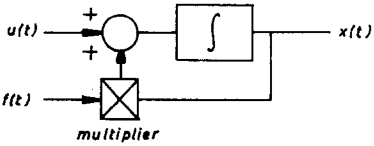

Fig. 4. Block diagram representing the state equation of a time-invariant system which has two different inputs: $u(t)$ and $f(t)$.

which must provide an output signal, x_m, as close as possible to the actual output, $x(t)$, for the same input, $u(t)$. We then face the tracking problem schematically represented in Fig. 5, namely, to find an optimal control, f_m^*, such that the corresponding output, x_m^*, minimizes a performance criterion

$$J(f_m)=\int_0^T h(e,\, u)\, \mathrm{d}t$$

This problem can be solved by using an iterative procedure [8].

An example

The method described above can be illustrated using simple examples.

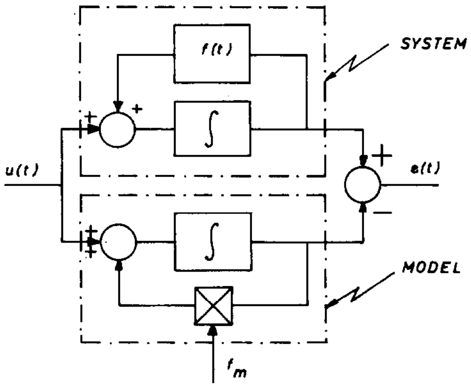

Fig. 5. Block diagram of the optimal control problem encountered in the identification of a time-varying linear system.

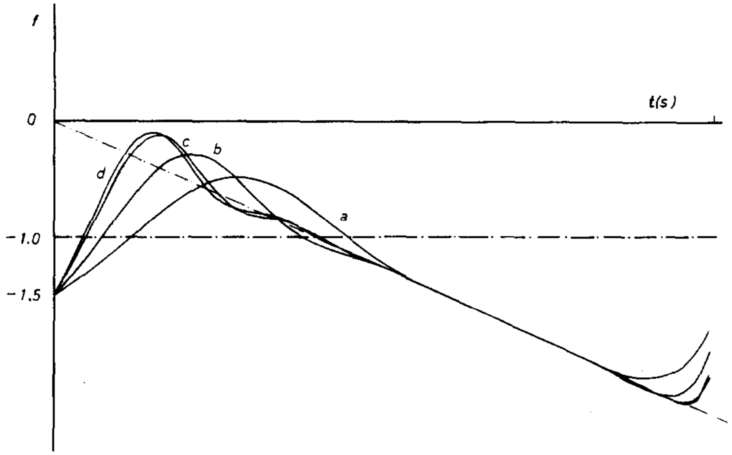

Fig. 6. Evolution of $f(t)$ with time for an initial guess at the origin given by $f(t=0) = -1.5$. Curves (a), (b), (c) and (d) correspond to the results of identification obtained after 20, 32, 132 and 173 iterations, respectively. The exact result in this case is $f(t) = -t$ represented by the line (·—·—·).

Figure 6 shows the results of identification for a system modelled by

$$\dot{x} = -tx + 1$$

for which, correspondingly, $f(t) = -t$. Although the imposed initial value $f(t=0) = -1.5$ is very different from the actual one, $f(t=0) = 0$, after 100–150 iterations the identification method gives the true behaviour of $f(t)$.

EXAMPLES CORRESPONDING TO BINARY LIQUID MIXTURES

A discrete model consisting of three heat capacities, equivalent to that in Fig. 1 of ref. 4, has been used to obtain simulated thermograms corresponding to well-known input thermal power functions. The model roughly simulates a continuous-injection heat conduction calorimeter in which, due to the mixing and stirring, the heat is supposed to be released into the bulk of the vessel, of global heat capacity $C_1(t)$. The variation of C_1 with time has been assumed to be linear, since it is due to the injection of liquid solute at a constant rate, and the parameters used to carry out the simulations are

$$C_1(t=0) = 40;\ C_2 = 20;\ C_3 = 20\ (\mathrm{J\ K^{-1}})$$

$$P_{12} = 0.35;\ P_{23} = 1.25;\ P_3 = 0.79;\ \dot{C}_1 = 9.60912 \times 10^{-4}\ (\mathrm{W\ K^{-1}})$$

The model at $t = 0$ is exactly the same as that proposed in ref. 4 and the variation of C_1 is 10% in 1 h. The time constants of the model at $t = 0$ (invariant system) have the values $\tau_1 = 225.3$ s, $\tau_2 = 31.8$ s and $\tau_3 = 6.5$ s.

The first simulation takes, as the heat power dissipation, that of an injection of cyclohexane into the vessel initially containing 16.18 cm^3 of benzene during a total of 3600 s. The power released (in the first element of the model) is given by

$$W(t) = h_1^{\mathrm{E}} \dot{n}_1 \qquad 0 < t \leqslant 3600 \text{ s}$$

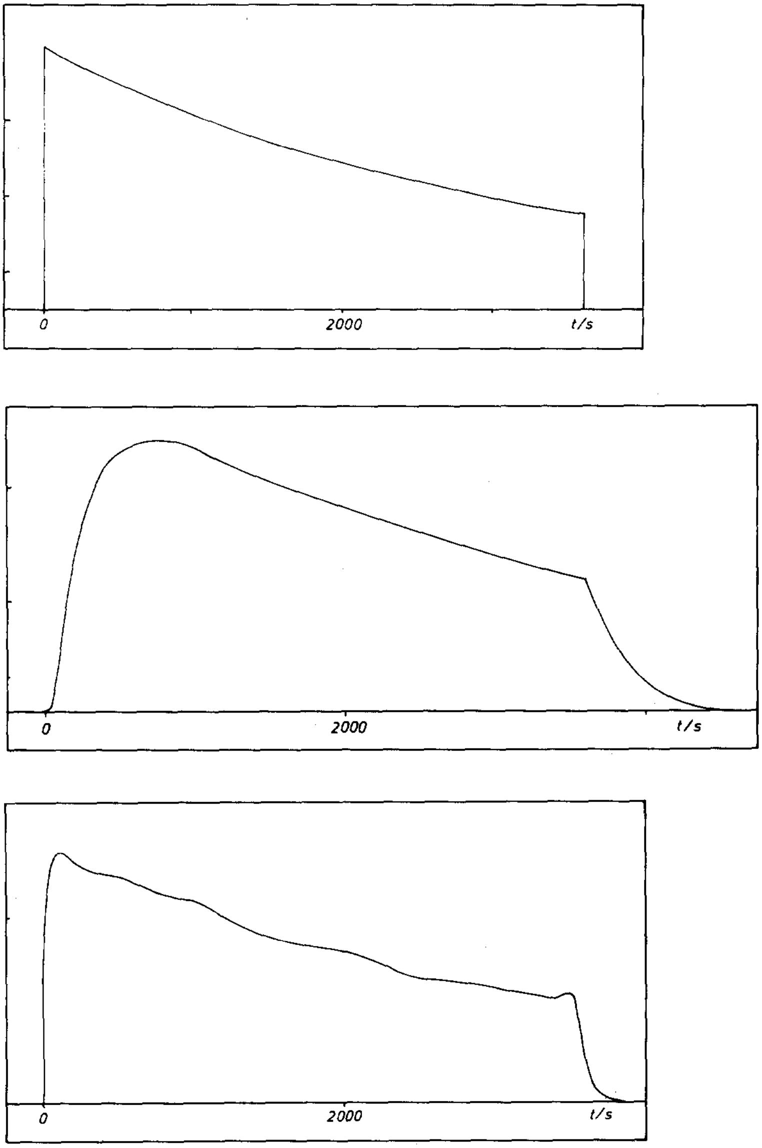

Fig. 7. (A) Heat power dissipation simulating an injection of cyclohexane into 16.18 cm^3 of benzene at a constant rate. (B) The corresponding calculated thermogram. (C) Deconvolution result achieved by means of an optimal tracking approach after 120 iterations, using 430 points of the thermogram sampled every 10 s.

with

$$\dot{n}_1 = 7.11787 \times 10^{-6} \text{ mol s}^{-1}$$

and

$$h_1^{\mathrm{E}} = x_2^2\left(A_0 + A_1x_1 + A_2x_1^2 + A_3x_1^3\right)$$

where x_1 stands for the molar fraction of cyclohexane in the mixture, x_2 for

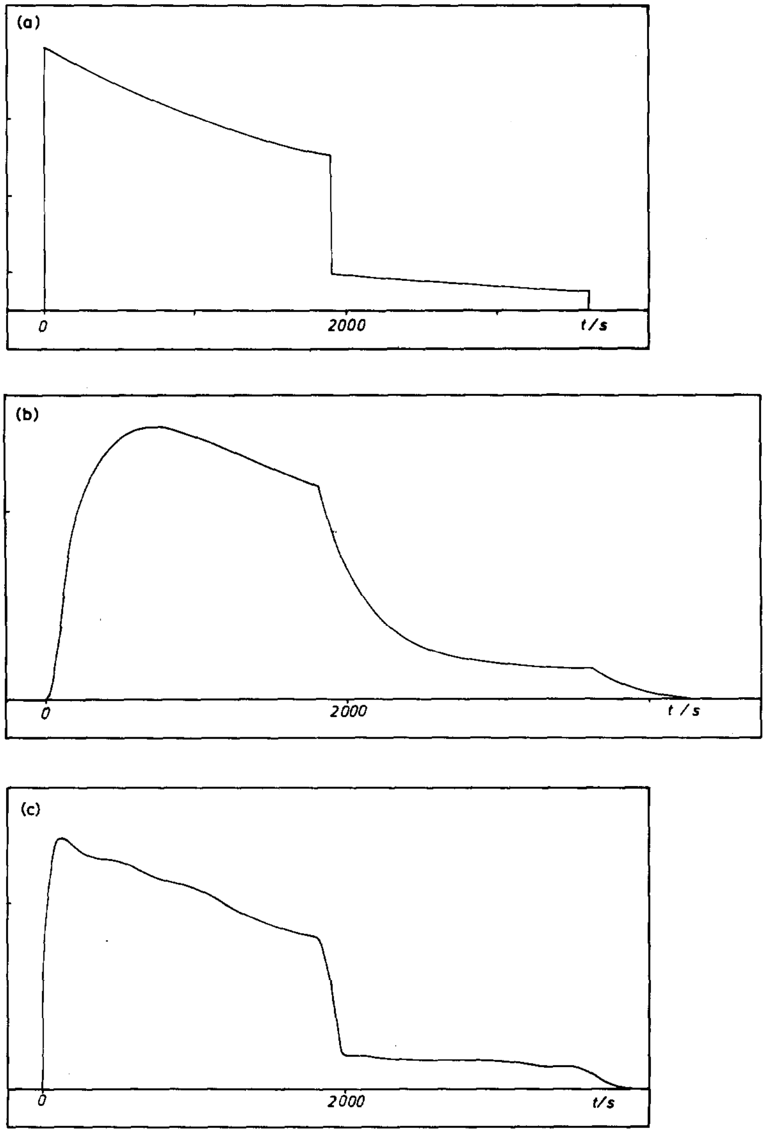

Fig. 8. (A) Heat power dissipation simulating a phase separation process for $t > 1800$ s. (B) The corresponding calculated thermogram. (C) Deconvolution result by means of an optimal tracking approach after 120 iterations, using 430 points of the thermogram sampled every 10 s.

that of benzene and the coefficients A_i have the following values

$A_0 = 3518.1$; $A_1 = -2082.2$; $A_2 = 2866.8$; $A_3 = -1253.6$

The resulting dissipation is shown in Fig. 7A together with the output thermogram obtained from the model (Fig. 7B) and the restoration of the input power (or thermogenesis) obtained by means of the optimal tracking approach (Fig. 7C).

The same kind of power dissipation has been simulated in Fig. 8A, with its magnitude being abruptly reduced by a factor of four at $t = 1800$ s, i.e.

$$W(t) = h_1^{\mathrm{E}}\dot{n}_1/4 \qquad \text{if } 1800 < t \leqslant 3600 \text{ s}$$

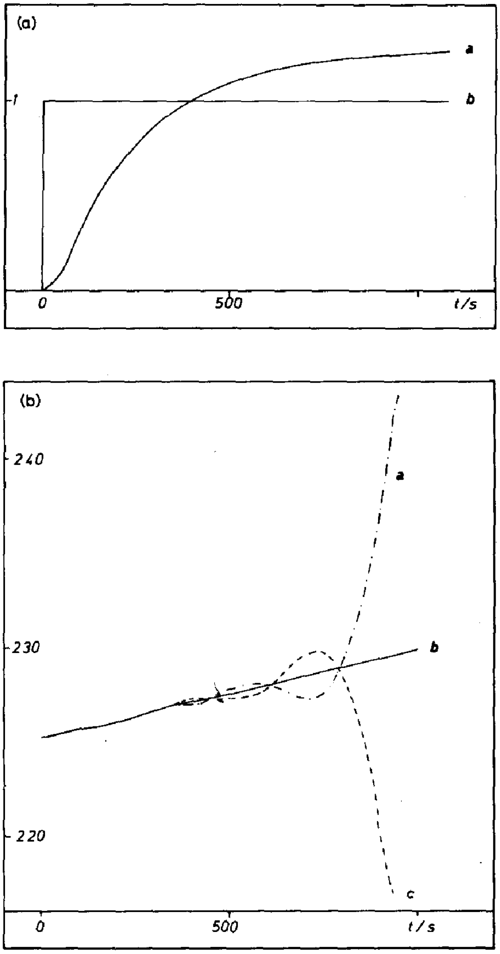

Fig. 9. Identification by the optimal control method. (A) A Heaviside-like input power (curve b) is simulated to be released in the vessel, giving rise to the thermogram shown as curve (a). (B) Evolution of τ_1 with time after 60 iterations using 100 points sampled each 10 s. Results for three different preliminary choices of $\tau_1(t)$ ($t = 1000$ s) are shown: (a) 245 s; (b) 230 s, which is the value given by the model; and (c) 215 s.

This is done in order to simulate a process of phase separation, sometimes encountered in liquid mixtures, and to test the stability of the deconvolution method against discontinuities in the input function. The corresponding thermogram is shown in Fig. 8B, while the result of applying the optimal tracking approach is presented in Fig. 8C.

The identification method based on optimal control, described before, has been tested in two different cases. Firstly, it has been applied on the thermal response corresponding to Heaviside-like input which reproduces typical Joule-effect calibration experiments. Both curves are shown in Fig. 9A, while Fig. 9B presents the variation of $\tau_1(t)$ with time after 60 iterations of the

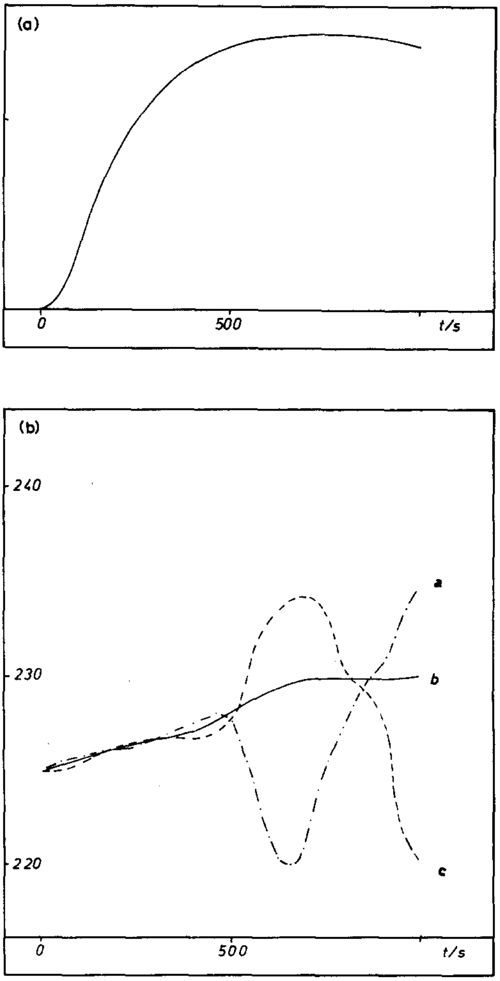

Fig. 10. Identification by the optimal control method. (A) The thermogram (initial part of Fig. 7B). (B) Evolution of τ_1 with time after 400 iterations using 100 points sampled each 10 s. Three different results are shown corresponding to the following preliminary choices for the value of $\tau_1(t)$ ($t = 1000$ s): (a) 235 s; (b) 230 s, actual value; and (c) 235 s.

method for three different initial guesses. The other two parameters, τ_2 and τ_3, are assumed to be constant and have the values given in the model at $t = 0$. A total of 100 points, sampled each 10 s, have been used. The figure shows that, independently of the initial choice of τ_1, the actual linear dependence of $\tau_1(t)$ appears at times $t < 500$ s which in turn can be extrapolated to the whole time domain.

Secondly, the identification method has been tested on the injection measurement described above (Figs. 7A and B). As before, 100 points, sampled each 10 s, have been used to carry out the calculations. Figure 10A shows the corresponding part of the thermogram. Again τ_2 and τ_3 were taken as constants, while for τ_1 three different initial values were tested. Figure 10B presents the corresponding behaviour of $\tau_1(t)$ after 400 iterations. For $t < 500$ s the three curves converge to the actual behaviour of $\tau_1(t)$ in the model. If the injection experiment was considered to be performed with a standard binary mixture, the figure shows that the optimal control method is able to identify the true variation of the calorimetric parameters during injection.

CONCLUSIONS

The optimal control method for signal treatment can be satisfactorily applied to identification and deconvolution problems in time-varying microcalorimetry.

The algorithms have been tested on different kinds of thermograms which have been numerically simulated with a non-stationary heat-transfer model. The model is like a continuous-injection heat conduction calorimeter.

The results presented show that a good convergence to the actual time-varying parameters of the model is achieved in spite of the uncertainty with which these parameters are known a priori. On the other hand, the resulting time-varying description of the system may be properly used to carry out a deconvolution yielding the actual thermal power dissipated in the system with satisfactory accuracy.

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