THERMOGENESIS: IDENTIFICATION AND DECONVOLUTION IN MICROCALORIMETRIC SYSTEMS WITH CONTINUOUS INJECTION FOR THE STUDY OF LIQUID MIXTURES

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ABSTRACT

The results obtained by means of different identification methods, tested on the experimental thermograms of calorimeters with a continuous injection device, are compared. The experimental system is specially suited to investigating the thermodynamic properties of mixtures. Particular attention is devoted to defining the conditions that allow a satisfactory approach to the transfer function of the system at the beginning of the injection. The accuracy of such an approach determines that of the excess enthalpies measured at large dilutions.

INTRODUCTION

The application of system identification techniques has brought significant advances in the use of conduction microcalorimeters to study the power released as a function of time both in liquid mixtures and in thermoelastic transitions such as the martensitic transformations of Cu–Al–Zn alloys [1–3].

In the latter field, the abruptly discontinuous thermokinetics of the $\beta \rightarrow \beta'$ and $\beta \rightarrow \gamma'$ transformations has been clearly observed. In the former, excess enthalpies have been measured continuously from molar fractions close to 0.001, which is of great interest in studying the formation of micellary aggregates or interfaces between immiscible phases.

At very large dilutions, mixing is performed by continuous injection of one of the components into a calorimetric cell already containing a certain quantity of the other. The increase in the quantity of liquid inside the cell modifies the dynamic properties of the experimental device, and henceforth the transfer function of the system [4,5].

In this paper, several different numerical methods of empirical system identification [6–9] are used in order to show the evolution of the transfer function from an experimental point of view, laying aside any reference to mathematical models of heat transfer.

THE TRANSFER FUNCTION OF SLOWLY VARYING SYSTEMS

Firstly, different series of experiments were carried out to determine the evolution of poles and zeros in the transfer function of the calorimeter when the contents of the cell are increased stepwise (Fig. 1 and Table 1). After each increase the decay curve corresponding to the calorimetric output signal was recorded. Moreover, the calorimetric response to a pulse of heat generated at each step by a Joule effect experiment was also recorded. Separate identification of the system was performed from each decay curve and pulse response. An initial heat pulse, previous to the beginning of injection of the second component, was also generated in order to evaluate the accuracy with which the results calculated from the decay curves could be extrapolated back to zero concentration.

Table 2, which lists the results for a series of experiments, shows that there is very little difference between the time constants calculated by the different numerical methods used.
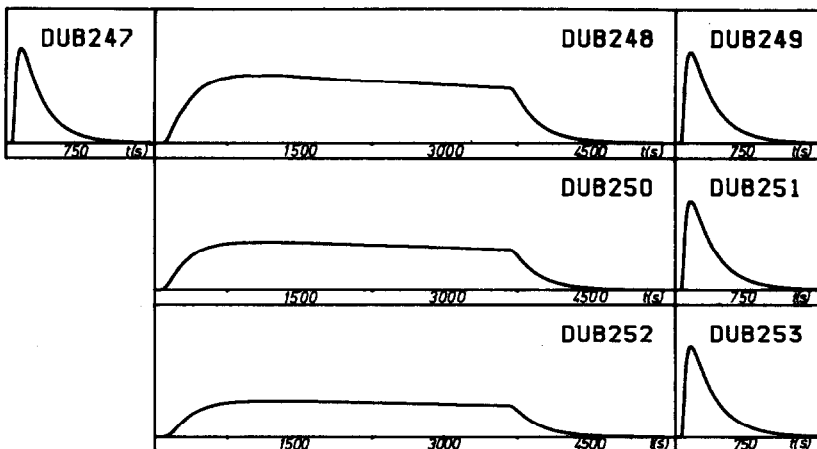

Fig. 1. The output signal for a series of measurements. DUB247-249-251-253 are heat pulses generated by the Joule effect. DUB248-250-252 are the responses to injections of benzene (see Table 1).

On the other side, mathematical models of heat transfer of continuous mixing devices have clearly shown the difference between integral sensitivity (the ratio of the area under the calorimeter output trace to the energy dissipated) and instantaneous sensitivity (the ratio of the amplitude of the signal to the value of the constant power input in the steady state).

To evaluate the relative importance of this difference, a further series of experiments was carried out. With a constant and permanent energy input, a single liquid was continuously injected into the calorimetric cell, thus increasing the level of the cell contents (Fig. 2). The substance used, the injection rate and the power dissipated were changed between experiments. The results show that the change in the instantaneous sensitivity of the system is very small during the experiments. The relative change for a dissipation of 37.48 mW in a quantity of water increasing at an injection rate of 0.00126 g s^{-1} is only 1.2%. The magnitude of the corresponding correction is found to be proportional to the power input and to the mass rate and specific heat capacity of the liquid injected.

When the calorimeter is calibrated using a standard liquid, only the differences in specific heat capacity and injection rate need to be taken into account, and the correction factor is even smaller.

TABLE 1

Two series of experiments. The sampling period in all cases is 1.5 s. The injection driving turned at a constant rate of 1/4 rpm, resulting in injection rates of 5.8546 and 7.1179 μmol s^{-1} for cyclohexane and benzene, respectively

Name	Type	No. of points	Power (W)	Pulse duration (s)	Inject. duration (s)	Starting time (s)
Series I: initial contents 15 cm^3 of benzene						
DUB240	pulse	3000	0.311	25.7		60
DUB241	inject.	5000			3600	60
DUB242	pulse	3000	0.305	30.0		60
DUB243	inject.	5000			3600	60
DUB244	pulse	3000	0.304	30.0		60
DUB245	inject.	5000			3600	60
DUB246	pulse	3000	0.304	30.4		60
Series II: initial contents 15 cm^3 of cyclohexane						
DUB247	pulse	3000	0.305	30.9		60
DUB248	inject.	5000			3600	60
DUB249	pulse	3000	0.305	30.1		60
DUB250	inject.	5000			3600	60
DUB251	pulse	3000	0.305	30.0		60
DUB252	inject.	5000			3600	60
DUB253	pulse	3000	0.293	31.6		60

TABLE 2

Time constants (s) of the system obtained from the output of series II of Table 1 by means of different methods, namely: A, inverse filtering; B, modulating functions; C, Padé approach; D, simultaneous fit. E: Value of τ_1 extrapolated from the values given by method D applied to the decay curves

	τ_1	τ_2	τ_3	τ_1^*
DUB247 (heat pulse)				
A	226	41		19
B	226	40		23
C	229	40		–
D	227	36	2.5	3
E	229			
DUB248 (decay curve)				
A	235	47		–
B	237	45		–
C	242	41		–
D	239	45	2.1	4
DUB249 (heat pulse)				
A	236	39		17
B	236	39		25
C	239	37		–
D	237	36	2.6	3
DUB250 (decay curve)				
A	249	44		–
B	245	44		11
C	249	41		–
D	246	44	1.9	3
DUB251 (heat pulse)				
A	245	39		18
B	245	39		27
C	246	39		–
D	246	37	2.8	3
DUB252 (decay curve)				
A	260	40		–
B	245	80		32
C	–	–		–
D	257	42	1.1	4
DUB253 (heat pulse)				
A	253	38		15
B	253	38		–
C	256	38		–
D	254	37	2.8	3

DECONVOLUTION OF THE THERMOGRAMS

Figure 3A shows the differences between the deconvoluted thermograms corresponding to the beginning of the mixing process obtained by using the transfer function calculated with different identification methods.
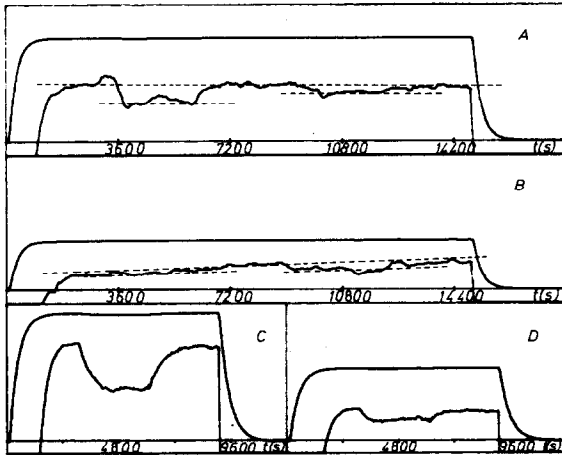
Fig. 2. Influence of the power input and the rate of injection. (A) cyclohexane injected into cyclohexane with a constant power input W(A) generated by the Joule effect during 1500 s. In the first half of the experiment the rate of injection is twice that used during the second half. (B) cyclohexane injected into cyclohexane. The power input W(B) = W(A)/2. The rates of injection are inverted with regard to A. (C, D) water injected into water. The rate of injection is the same in (C) and (D). W(C) = 2W(D).
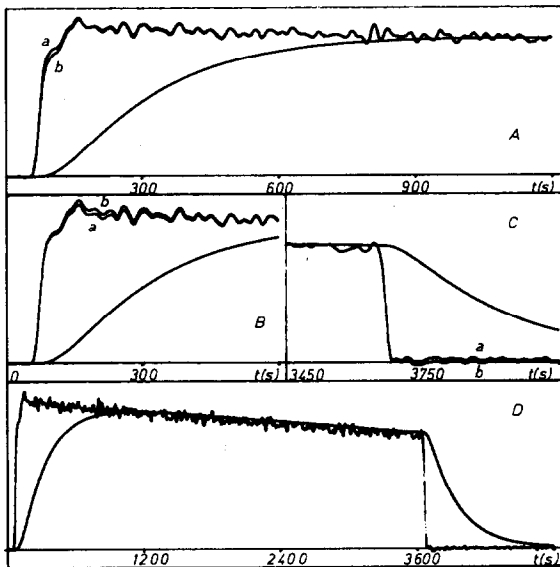

Fig. 3. Deconvolution by means of inverse filtering of the measurement DUB250. (A) The time constants have been obtained from the previous decay (DUB248) by inverse filtering (a) and by Padé approaching (b). The two thermogeneses (a and b) cover all the other deconvolutions which may be obtained from the different identifications. (B, C) Deconvolution of the initial (B) and final (C) part of the measurement with the time constants obtained by inverse filtering (a) of the previous decay (DUB248) and (b) of the own decay (DUB250). (D) Time-varying inverse filtering with a linear evolution of the time constants.

Figure 3B and C shows the deconvoluted thermograms obtained using stationary inverse filters corresponding to the initial and final states of the system, respectively.

Figure 3D shows the results obtained using a time-varying inverse filter calculated on the assumption that the time constants of the system vary linearly between their initial and final values.

CONCLUSIONS

When the signal-to-noise ratio of the experimental thermograms is high enough (greater, say, than 80 dB), the different identification methods tested produce very similar results and the transfer function parameters obtained may be assumed to be true parameters of the system. Deconvolved thermograms may therefore be obtained by inverting heat transfer equations approximated using the transfer function corresponding to the initial and final states of the device.

When the signal-to-noise ratio of the thermograms is less than 60 dB, not all the different identification techniques produce such similar results. Consequently, a straightforward election of the parameters for the design of a heat transfer calorimetric model is difficult. The instantaneous sensitivity of the device is nevertheless practically unchanged and the results of deconvolution are fairly similar whatever the method of identification used.

The calorimetric system can be satisfactorily characterized by analysing the decay curves following consecutive interruptions in the injections of the second component. The transfer function when injection begins can be obtained by extrapolation. If the system has been calibrated using a standard liquid the differences in the specific heat capacities of the liquids must be taken into account for an adequate correction of the sensitivity.

The use of a time-varying inverse filter for the deconvolution of the calorimeter output has proved effective, allowing excess enthalpies to be measured from molar fractions of the injected component as low as 0.001.

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