

THERMOKINETICS BY HEAT-CONDUCTION CALORIMETRY

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ABSTRACT

A scheme is presented for the analysis of the signal given by a calorimetric system used to measure the thermodynamic properties of solutions and liquid mixtures. The standard method of inverse filtering is generalized to an experimental situation where the continuous addition of reactant results in a continuous increase in the mass of the vessel contents and, therefore, causes a small change in the transfer function of the calorimetric device. In the framework of thermodynamics of binary mixtures, the calorimetric signal, upon deconvolution, can be related to the excess partial molar enthalpies or to the apparent molar enthalpies of the reactants. The application of the technique to aqueous solutions of ionic and non-ionic amphiphiles is described.

I. INTRODUCTION

For many years, heat-conduction microcalorimeters have been used to measure the energy released in thermal processes taking place in mixtures of reactants or in phase transitions induced by a change in temperature [1]. In such systems, the detector is a fluxmeter and its response depends both on the dynamics of the phenomena studied and on the instrumental inertia. In the last fifteen years, analogue and numerical processing have permitted a marked reduction in the instrumental inertia while not affecting the quality of the signal.

The construction of calorimeters equipped with semiconducting detectors of high sensitivity has opened up new possibilities for research in calorimetry. Thus it has enabled development in the following areas:

(1) The thermokinetic study of phase transitions in shape-memory alloys like Cu/Al/Zn and Cu/Al/Ni. Often, such a study is coupled with the

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simultaneous measurement of other properties: acoustic emission (thermosonimetry), resistivity, optical observations or scanning electron microscopy [2].

(2) The thermodynamic study of complexes, molecular mixtures and solutions of ionic and non-ionic amphiphiles, using continuous addition of a reactant (particularly in the range of high dilutions) [3].

In all these applications the transfer function of the calorimetric systems is not completely invariable: during a phase change induced by a change in temperature, the dynamics and sensitivity of the device change as well; in the same sense, the continuous addition of reactant to the measurement cell results in a change in the heat capacity of the cell contents, and, therefore, a small modification in the dynamic response of the device [4].

In this brief report, we first review the conditions imposed on the thermograms by the heat-transfer equations. We also give a description of the methods used for signal processing of thermograms corresponding to processes involving continuous addition of a reactant. Then, we show the relationship between the results and the thermodynamic quantities studied and present two examples of the systems amphiphile (ionic and non-ionic)-water.

II. INSTRUMENTS AND MODELS

Figure 1 shows a calorimetric device used for the thermodynamic study of mixtures (Arion-Électronique calorimeter of the BCP type with a system for continuous injection of reactant) (see ref. 1 and related references). The reaction takes place in a cell surrounded, successively, by the thermal fluxmeter detector and by an isothermal calorimetric block. This element is differentially related to a twin reference in such a way that a possible drift of the experimental zero, caused by a corresponding drift of the room temperature, is minimized.

For an exactly differential system, the heat-transfer equations for the reference element can be replaced by new variables for the temperature, namely the differences between two symmetric points. The general equations (method of localized constants) describing the energy balance for an invariable system (without continuous addition of a reactant) take the form [5]:

$$W_i(t) = C_i \, dT_i/dt + \sum_{k \neq i} P_{ik} (T_i - T_k) + P_i T_i \quad i = 1, 2, \dots, N$$

The coupling coefficients P_{ik} are related to the thermal resistances R_{ik} by the following equations:

$$R_{ik} = R_{ki} = 1/P_{ik} \quad P_i = 1/R_i$$

$W_i(t)$ is the thermal power released at time t in the i th element. The

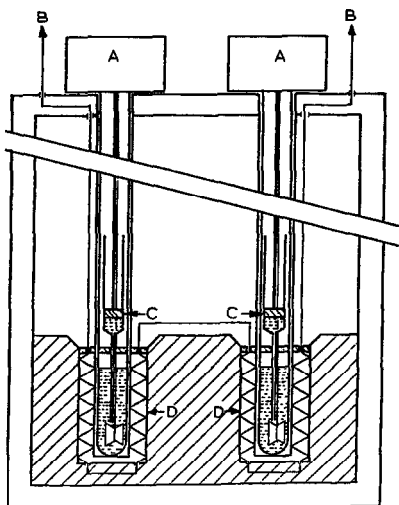


Fig. 1. A calorimetric device for measuring partial molar excess enthalpies and relative apparent molar enthalpies. (A) Stirrer and mixing system, (B) to the amplifier, (C) syringe, (D) laboratory cell, (E) reference cell.

temperature of the isothermal calorimetric block (thermostat) is taken to be zero.

Since the output $s(t)$ from the thermocouples is proportional to the differences in temperature, we can write:

$$aW(t) + bW'(t) + \dots = A \frac{d^N s(t)}{dt^N} + B \frac{d^{N-1} s(t)}{dt^{N-1}} + \dots$$

If a continuous injection takes place, the corresponding change in the heat capacity of the vessel contents and, also, the difference in temperature between the compound being injected and the mixture in the vessel, have to be taken into account.

An extra term has to be included in the energy balance of the element representing the mixing process [6]:

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

The experimental response $s(t)$ is such that:

$$a'W(t) + b'W'(t) + \dots = A' \frac{d^N s(t)}{dt^N} + B' \frac{d^{N-1} s(t)}{dt^{N-1}} + \dots$$

The equations describing both situations (invariable and variable) have the same form, but the coefficients a' , b' , ..., A' , B' , ... are functions of time. The coefficients reflect the dependence of the variable parameters (heat capacity $C(t)$ and, eventually, variable coupling coefficients, etc.) on the derivatives.

If we choose a series of different levels (V_1 , V_2 , ...) in the vessel contents (heat capacities C_1 , C_2 , ...), the corresponding coefficients in the equation

for the invariable system are different from those in the equation for the variable system for the same levels.

III. IDENTIFICATION AND DECONVOLUTION OF THE INSTRUMENTAL RESPONSE

Modelling the time-invariant devices by means of N first-order differential equations or an equation of order N , shows that the response to a DIRAC pulse is a sum $h(t)$ of exponential terms [5]

$$h(t) = \sum_{i=1}^N a_i \exp(-\omega_i t)$$

with a series of time constants τ_i such that:

$$\tau_i = 1/\omega_i$$

The sum will have infinite terms when we describe the system by means of Fourier's general equation.

The Laplace transform of the previous expression for $h(t)$ gives the instrumental transfer function $H(p)$

$$H(p) = \sum_{i=1}^N a_i \tau_i (1 + \tau_i p)^{-1}$$

$$H(p) = S \left[\frac{\prod_1^M (1 + \tau_j^* p)}{\prod_1^N (1 + \tau_i p)} \right] \quad (M < N - 2)$$

where $S (= \sum_1^N a_i \tau_i)$ is the sensitivity (or the static gain) of the calorimetric device; $-\omega_i (= -1/\tau_i)$ represent the poles and $(-1/\tau_i^*)$ the zeros of the transfer function.

Knowledge of the poles and zeros of the transfer function completes the identification of the calorimetric system. The objective of the deconvolution is to obtain an approach to the thermogenesis from the experimental thermogram, which is a deformation of the thermogenesis due to the instrumental inertia.

Inverse filtering is adequate for both the identification of the calorimetric system and the deconvolution of its response.

Applying the relationship

$$s'(t) = s(t) + \tau ds(t)/dt$$

results in compensation of the pole $-\omega (= -1/\tau)$. If the value selected for τ coincides with that of the first time constant τ_1 , this constant disappears from the series $\{\tau_i\}$ [7].

While performing the identification, the sequence of values which accelerate the response of the device (e.g. from a decay of a Heaviside input) to a maximum are searched for; the values are taken as the poles of the transfer function.

By inverting the preceding equation, the main zeros of the transfer function can be obtained. The identification can be carried out iteratively if the conditions

$$\tau_i \geq 3\tau_{i+1}$$

$$\tau_j^* \geq 3\tau_{j+1}^*$$

are obeyed, as they usually are.

To obtain the poles and zeros, we use simple numerical algorithms [7] (index I such that $t = I \Delta t$):

$$s_1(I) = s(I) + \tau_1 [s(I + K) - s(I - K)] / (2K \Delta t) \quad (\text{pole})$$

$$s^*(I) = [\tau^* / (\tau^* + \Delta t)] s^*(I - 1) + [\Delta t / (\tau^* + \Delta t)] s(I) \quad (\text{zero})$$

Once the values for the poles and zeros are known, the preceding equations also apply to obtain an approach to the thermogenesis.

Some other identification techniques have been proposed and analysed: the method of Padé approximations to describe the Laplace numerical transform of the impulse response, the method of modulating functions, methods taking advantage of the Fast Fourier Transform and correlation algorithms [8].

The deconvolution process has been studied and carried out by means of different calculation schemes: harmonic analysis (using the FFT), tracking methods by optimum control, Z-transforms etc. [9].

Study of a calorimetric system with a continuous injection device

The signal output from such systems shows that there is a small change in their dynamic properties with the level of the contents in the cell. Figure 2 shows an example of the change in the first time constant τ_1 with the volume of liquid in the vessel; the time constant has been obtained from the decays to the experimental zero of step-like inputs made without the

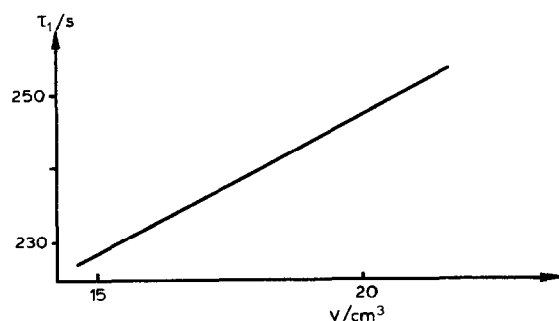


Fig. 2. Arion-Électronique calorimeter of the BCP type: example of the change in the first time constant τ_1 with the volume (cyclohexane) contained in the cell.

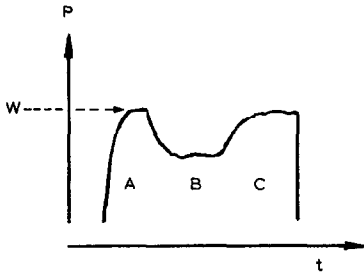


Fig. 3. The amplitude of the instrumental response corresponding to a Joule effect releasing a constant power W . Zone B: injection of reactant (cyclohexane) into the vessel, already partially filled with the same reactant. Zones A and C: without any injection.

injection of reactant (invariable system) [4]. The dynamic response of the instrument is then well described by two or three poles (signal-to-noise ratio between 100 and 1000). On the other hand, the sensitivity of the calorimeter does not depend on the volume of liquid in the vessel.

On the contrary, by studying the effect of a continuous addition of a reactant to itself at the same time as a constant power W is being released in the vessel (Joule effect in a steady state), it is found that the height of the instrumental response changes slightly with the level in the vessel (see Fig. 3): the change in $s(t)$ depends on the liquid added and on the injection rate [4].

To describe this situation, we choose a model for which the heat-balance equations are:

$$W_1 = C_1(t) dT_1/dt + \sum P_{1k}(T_1 - T_k) + P_1 T_1 + \dot{C}_1 T_1$$

$$0 = C_i (dT_i/dt) + \sum P_{ik}(T_i - T_k) + P_i T_i \quad i = 2, \dots, N$$

These equations can be rewritten in the form of a global differential equation:

$$W^* = W - \dot{C}T = [A(t) d^N s(t)/dt^N + B(t) d^{N-1} s(t)/dt^{N-1} + \dots] S$$

where S is the sensitivity and the coefficients $A(t)$, $B(t)$, ..., have, at times t_1, t_2, \dots , exactly the same values as those of the invariant coefficients, related to corresponding volumes of the vessel content, V_1, V_2, \dots

In this way, an identification performed on the decays to zero corresponding to different levels of contents gives the value of the poles and, therefore, the coefficients $A(V_i)$, $B(V_i)$, ... Transforming from a volume scale to a time scale gives the value of the coefficients $A(t)$, $B(t)$, ... from which $W^*(t)$ can be obtained:

$$W(t) = W^*(t) + \dot{C}_1 T_1$$

Making the simplifying assumption that the amplitude $s(t)$ of the thermo-

gram is proportional to the temperature T_1 , it is possible to write [6]:

$$W(t) = \{ A(t) \frac{d^N s(t)}{dt^N} + \dots + s(t) + [(\rho c \dot{V})_m / (\rho c \dot{V})_j] (\Delta s/s)_j s(t) \} S$$

where $(\Delta s/s)_j$ represents the relative variation in the output signal due to a continuous addition of reactant when a constant and permanent power is released, by means of the Joule effect, in the cell. In the products $(\rho c \dot{V})_j$ and $(\rho c \dot{V})_m$, the densities ρ , the heat capacities c and the volumes added per unit time \dot{V} are related to a measurement in which the power is released by the Joule effect and to a measurement carried out with the mixture under study, respectively.

IV. APPLICATION TO THE THERMODYNAMIC DESCRIPTION OF SOLUTIONS AND MIXTURES

The study of liquids requires the knowledge of the thermodynamic properties of each component i in the mixtures or in the solutions.

Industrial engineers, chemists and biochemists may need the partial excess, H_i^E , the partial relative L_i and the relative apparent molar enthalpies ϕL_i of molecular mixtures or ionic and non-ionic amphiphile solutions, particularly in the range of high dilutions. These quantities are interesting both practically—for the petrol industry, for example—and theoretically to check models representing changes in the system properties.

Thanks to the deconvolution of the instrumental response, heat-conduction calorimetry with injection of a reactant is able to measure, directly and continuously, the above thermodynamic properties [3].

Measurement of the partial molar excess enthalpies: mixture of components 1 and 2

If the calorimetric cell initially contains a certain quantity of component 1 or a mixture of the two components 1 and 2, and the liquid injected is the pure substance 1, it is possible to show that the relationship between the power P absorbed upon mixing and the molar rate of injection d_1 of the substance $d1$ represents the partial molar excess enthalpy H_1^E of this component in the mixture:

$$P/d_1 = H_1^E$$

If component 2 is added at a constant rate d_2 , the function P/d_2 gives the partial molar excess enthalpy H_2^E for substance 2.

The high sensitivity, characteristic of heat-conduction calorimeters designed after the Tian and Calvet devices, allows measurements at very low rates of injection. Deconvolution of the thermograms obtained from these mixtures gives accurate values for the searched quantities since the molar fraction of the injected component in the mixture may be as low as a few thousandth parts, or even less.

Measurement of the relative apparent molar enthalpies: system of two components 1 and 2

If the solute 2 is in the solid phase when it is pure, it cannot play the role of the injected substance. In order to give a meaning to the calorimetric data obtained when an aqueous solution of such a component is slowly and continuously added to a given quantity of pure solvent 1 previously placed in the cell, the relative apparent molar enthalpy ϕL_2 of the solute is introduced.

Suppose that d_2 represents the molar rate of addition of the solute, P the power absorbed by the dilution process at time t , ϕL_2 and $\phi L'_2$ the relative apparent molar enthalpies of the solute in the solvent and in the liquid injected. Then, the ratio \bar{P}/d_2 gives the difference $\phi L_2 - \phi L'_2$ (\bar{P} is the mean power absorbed during the time interval between the beginning of the dilution and time t). At infinite dilution, i.e., at the beginning of the process, the ratio $\{P/d_2\}^\infty$ measured is

$$\{P/d_2\}^\infty = (\phi L_2)^\infty - \phi L'_2 = -\phi L'_2$$

because, by definition of the function ϕL_2 , $(\phi L_2)^\infty$ is zero.

In this way, at a certain stage of the dilution in which the molality of solute 2 in the calorimetric cell is m , we get:

$$\phi L_2(m) = (\bar{P}/d_2)_m - (P/d_2)^\infty$$

Again, in this case, processing of the instrumental response gives, directly and continuously, the change in the function ϕL_2 ; knowledge of this quantity, as of the quantities H_i^E , is essential for several thermodynamic considerations.

Examples of results [10]

(1) System 2-butoxyethanol (2)–water (1) at 25°C

The plots given in Figs. 4 and 5 were obtained by continuous addition of non-ionic amphiphiles to water. Figure 4 shows the function $P/d_2 = f(x)$, where x is the molar fraction of the amphiphile and d_2 its molar rate of addition.

As the partial molar excess enthalpy H_2^E is equal and opposite in sign to the relative partial molar enthalpy (L_2^*) of pure component 2, and as

$$H_2^E = L_2 - L_2^*$$

it is easy to deduce, from the above plot, that of the function L_2 (relative partial molar enthalpy of the amphiphile 2) which is given in Fig. 5, where m represents the molality of the amphiphile in the aqueous solution.

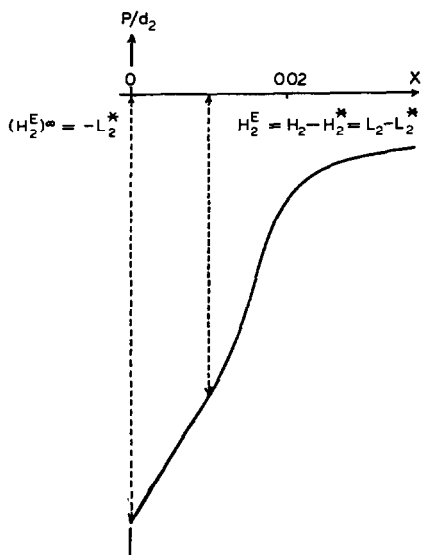


Fig. 4. Addition of 2-butoxyethanol to pure water. Plot of the function $P/d_2 = f(x)$, where x is the molar fraction of the amphiphile in the solution.

(2) System sodium dodecyl sulphate (2)–water (1) at 25°C

Figure 6 represents the function $\bar{P}/d_2 = f(c)$, where d_2 is the molar rate of addition of the surfactant and c its concentration in the solution placed in the calorimetric cell. The interpretation of this plot in terms of the relative apparent molar enthalpy ϕL_2 of the solute has been given before.

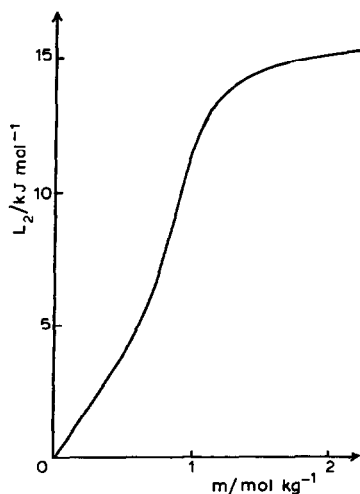


Fig. 5. System 2-butoxyethanol–water at 25°C. Plot of the function $L_2 = f(m)$, where m is the molality of the amphiphile in the solution.

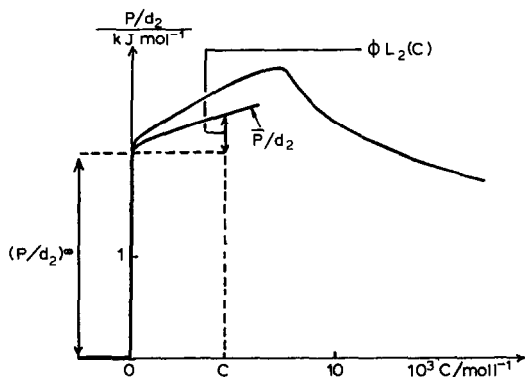


Fig. 6. Addition of a 0.4 M solution of sodium dodecyl sulphate to pure water at 25°C. Plot of the function $\bar{P}/d_2 = f(c)$, where c is the concentration of the surfactant in the solution.

V. CONCLUSION

Inverse filtering, and other methods for the deconvolution of the instrumental response (thermogram), give an accurate estimation of the instantaneous thermal power released during a certain process, either a phase transformation induced by a change in the temperature or a reaction caused by addition of a reactant. In this progress report, we have focussed attention on processes concerning continuous addition of a reactant.

The results of deconvolution are free from systematic errors if the identification of the experimental device is correctly performed. We have described, by means of modelling the devices (localized constants model) an approach to the identification and deconvolution of systems which are slightly non-invariant. The thermodynamic interpretation of the deconvolution results shows, clearly, the importance of developments in the study of solutions and mixtures, particularly in the range of high dilutions.

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