CALORIMETRIC EQUIPMENT WITH TIME-EVOLUTION PARAMETERS MEASUREMENTS AND MODELLING IN FLOW AND MASS-VARYING CALORIMETRY

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Abstract

The injection calorimeters are used to evaluate thermodynamic properties of the mixtures and solutions. The H_i^E partial molar excess enthalpies or the $L_{\varphi,\,i}$ relative apparent molar enthalpies against mole fraction are available from an appropriate signal processing of the calorimetric curves. An evolution of the thermal properties of the calorimetric vessel are associated with the injection process. Description of calorimetric equipments by means of a localized – constants model (RC analogy) allows us to systematize and to extent these systems into time dependent situations. Experimental measurements based on Joule effects and associated mathematical analysis permits to determine the absolute limits of the dynamic behaviour of these equipments from several standard and easily experimental parameters (sensitivity, noise level, τ_1 the first time constant, sampling period). Models and experimental study provide an estimation of the corrections in order to compensate the evolution of the physical characteristics of the device.

Keywords: conduction calorimetry, flow calorimetry, liquid mixtures, low concentration, modelling, signal processing, time dependent systems

Introduction

The flow and mass-varying heat-flux or conduction calorimeters provided with an advanced and automatized system for calibrating and signal processing of the calorimetric curves [1] make it possible to obtain thermodynamic magnitudes of the mixture. For example, and according to the type of mixture, we can obtain the excess molar enthalpies [2] or the relative apparent partial molar enthalpies [3] against mole fraction.

In this paper we describe the experimental conditions, the appropriate mathematical formalism and the possibilities offered by these calorimeters, operating in variable conditions. The permanent interaction of an advanced mode-

lization, continued experimental study, and in each case behaviour simulation permits:

a) the use of the equipment up to the limits of its theoretical possibilities from previous analysis made by means of Joule effects;

b) appropriate assessment of the various corrections necessary to compensate for the developments in time of the physical characteristics of the apparatus associated with volume changes and the calorific capacity of the calorimetric cell;

c) the differences between the energy dissipations, either localized or distributed, relating to the various types of the experimental measurements and also the influence of the small temperature differences between the injected liquid and/or the thermostat and/or the outside environment.
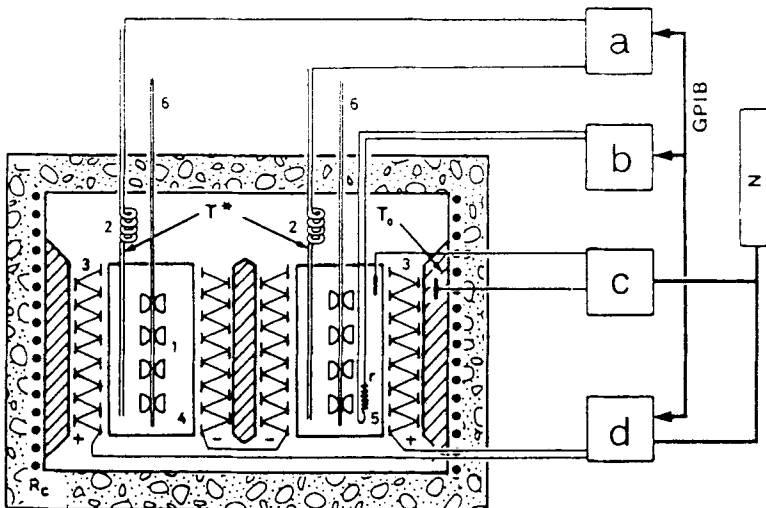

Fig. 1 Conduction calorimeter Tian-Calvet type; a) injection system; b) calibration by Joule effects; c) temperature control; d) PC-computer: automatized measurement and data storage; T_0 thermostat temperature; T^* room temperature; z) external network for the signal processing and further data analysis

Experimental set-up and representative model

Figure 1 shows a diagram of the calorimetric system continuous injection (flow and mass-varying) based on the heat-flux-conduction-calorimeter Tian-Calvet type (maximal volume of the calorimetric cell near 70 cm^3). The noise effect in the full working state is near 1 μV. The sensitivity is $\approx$ 50 $mV \cdot W^{-1}$. The effect of the injection causes an increase in the level inside the laboratory cell and an increase of its heat capacity.

The study of the internal structure of a calorimeter reveals a high internal complexity. The construction of a model, although it is simplified and based solely on the Fourier conduction equation, requires a large number of domains in the three space dimensions (x, y, z). Also, the use of various insulators renders the allocation of values to each parameter, at most, approximate. It is practically impossible to use strictly realistic models, which, in the case in question, should include convection terms. This suggested the use of approximate semiquantitative methods based on models at localized constants (the R–C analogy used in electrical network systems) since the primary aim is satisfactorily to represent the most relevant features of the experimental systems.

The most relevant parts of the calorimeter (Fig. 2) are: 1) the agitating device located inside the laboratory cell; 2) the liquid mixture that gradually changes as it is injected; in this element there is dissipation of the heat produced by mixing process or by a Joule effect; 3) the calorimetric vessel; 4) the cell container that is fixed inside the calorimeter; 5) and 6) the welds of the detector thermocouples. For each relevant element there is a heat capacity C_i and thermal couplings P_{ik} with neighbouring elements and with the thermostat (at temperature T_o). Due to construction features of the particular experimental system described here, element 4 is mechanically (and thermally) linked to element 6 and thus an additional coupling P_{46} has been included.
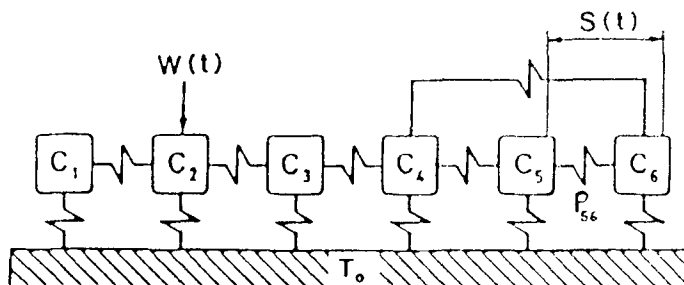

Fig. 2 Model by localized constants; C_i heat capacity; P_{ik} thermal couplings; $W(t)$ heat power; $s(t)$ output curve

In order to describe the effect of the continuous injection system a model is used at localized constants with variable coefficients (time-dependent). The energy balance of each relevant domain into which the experimental system is divided makes it possible to write [4]

$$W(t) = C_2 \frac{dT_2}{dt} + \sum_{k \neq 2}^{6} P_{2k}(T_2 - T_k) + P_2(T_2 - T_o) + \frac{dC_2}{dt}(T_2 - T^*) \qquad (1)$$

$$0 = C_i \frac{dT_i}{dt} + \sum_{k \neq i}^{6} P_{ik}(T_i - T_k) + P_i(T_i - T_o) ; \quad i = 1, 3, 4, 5, 6 \qquad (2)$$

The energy balance of element 2 includes the term $dC_2/dt(T_2 - T^*)$ relating to the energy necessary to compensate for the difference in temperature existing between the injected liquid and the contents of the laboratory cell. The system of differential equations has at least one variable coefficient. In this model, C_2 representing the mixture located in the cell is a function of time $(C_2 = C_2(t))$. The model structure presupposes that, inside each domain, the temperature as strictly uniform. For the liquid associated with domain 2 this means that agitation is sufficient in order to consider that all dissipation types are totally equivalent and that there is no temperature difference in the whole volume of the laboratory cell. Temperatures T_o and T^* have been located in the equations. The first one is the thermostat temperature. The second one is the temperature of the injected liquid which, coming for outside, could be different from T_o. Normally it is considered satisfactory to identify them $(T_o \equiv T^*)$.

The coincidence between the modelized response based on a model with a single laboratory cell and the experimental response is satisfactory. Furthermore, having excellent thermostats and using digital voltmeters with 5 or 6 figures and resolution of 10 or 100 nV, current experimental conditions are more higher than those that imposed the use of differential systems. The use of an advanced simulation with "non-differential" physical image suggests the possibility of eliminating the reference cell and simplifying the construction of the experimental devices.

From the thermal curves to the thermogenesis

The study of the representative model suggests maintaining the form of the system of equations of the invariant systems. For this, the definition of the auxiliary quantity $W^*(t)$ is

$$W^*(t) = W(t) - \frac{dC_2}{dt} (T_2 - T^*) \qquad (3)$$

In this way in the instant t_i, the variable system has in the laboratory cell the heat capacity $C_2(t = t_i)$. We can construct an "identical" invariant system which has a heat capacity C_2 equal to that of the variable system in an instant t_i:

$$C_{2 \text{ (invariant)}} \equiv C_2(t = t_i)_{\text{(variable)}} \qquad (4)$$

Similarly, we can construct a series of invariant systems which correspond with each instant t_i. If injection is stopped in a given instant, the experimental system (and the model) are converted into the corresponding invariable system.

Firstly, it is necessary to make an identification based on physical images (5) from a series of returns relating different liquid levels. This makes it possible to obtain all the system parameters and the mathematical form of $C_2 = C_2(t)$. Then it is necessary to estimate the difference between $W(t)$ and $W^*(t)$ produced by the injection.

In an initial phase, the system is identified from poles and the zeros of the transference function for each quantity and kind of liquid situated in the laboratory cell and in an invariant situation. Then, from an initial estimate, with the aid of iterative routines derived from the Marquardt algorithm, the series of values is obtained for the coefficients P_{ik}, the heat capacities C_i and the evolution of $C_2 = C_2(t)$. The calculated values are "equivalent" but not equal to the experimental ones. Figure 3 B shows the dependence of the first time constant τ_1 (approximately proportional to C_2) on the heat capacity of the cell contents.
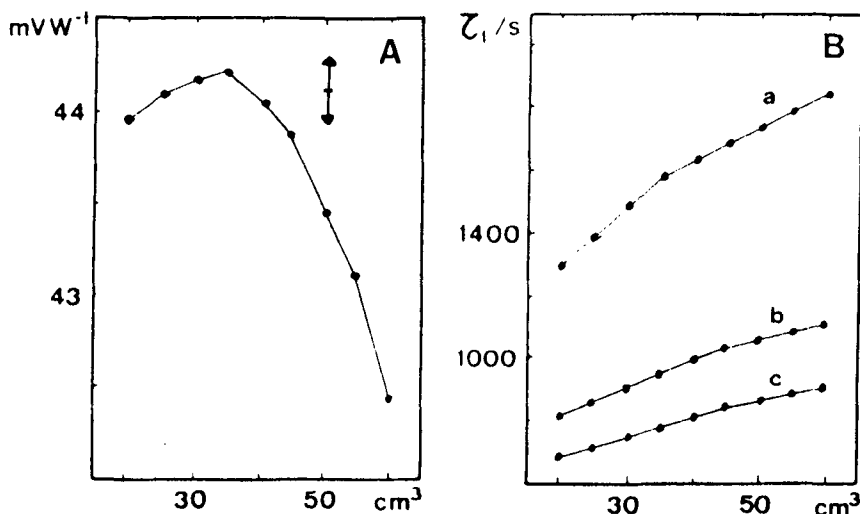

Fig. 3 Experimental results associated to the Joule effects; A) sensitivity against volume of the liquid in the cell contents, arrow indicates the $\pm 0.5\%$; B) first time constant τ_1 against volume for water (a), ethanol (b) and benzene (c)

When there is a satisfactory identification of the variable system $W^*(t)$ can be obtained by means of deconvolution techniques. It is useful to invert the model equations by means of the classical techniques of resolution of the differential equations (see, for instance, Runge-Kutta algorithms). Then, high frequency filtering is easy by means of the Fast Fourier Transform (the "noise" is heavily amplified by the deconvolution procedure).

In order to obtain $W(t)$ from $W^*(t)$ is necessary to have an experimental estimate of the term $dC_2/dt(T_2-T^*)$. For this, an analysis is made of the effects the injection produces in steady states (Fig. 4). The correction may reach 2%. If

$T_o \neq T^*$, it is necessary to evaluate the effects of both terms in which the action of $dC_2/dt(T_2-T^*)$ is broken down. In fact, there remains

$$\frac{dC_2}{dt}(T_2-T^*) = \frac{dC_2}{dt}(T_2 - T_o) + \frac{dC_2}{dt}(T_2-T^*) \qquad (5)$$

The differences found between the results of the models and those obtained from the corresponding measurements help us towards a better understanding of the features of the experimental equipment. Sensitivity has slight dependence on the level of liquid in the cell (see Fig. 3 A). This presupposes an actual dependence of the couplings to the thermostat on the level of liquid. They could be simulated by breaking down the laboratory cell into 2 or 3 elements situated "vertically". Slight systematic differences are also found between the Joule sensitivities and those obtained by means of reference mixtures. They are associated with the differences between the two types of dissipation (localized in the resistance of the Joule effect or distributed inside the mixture).
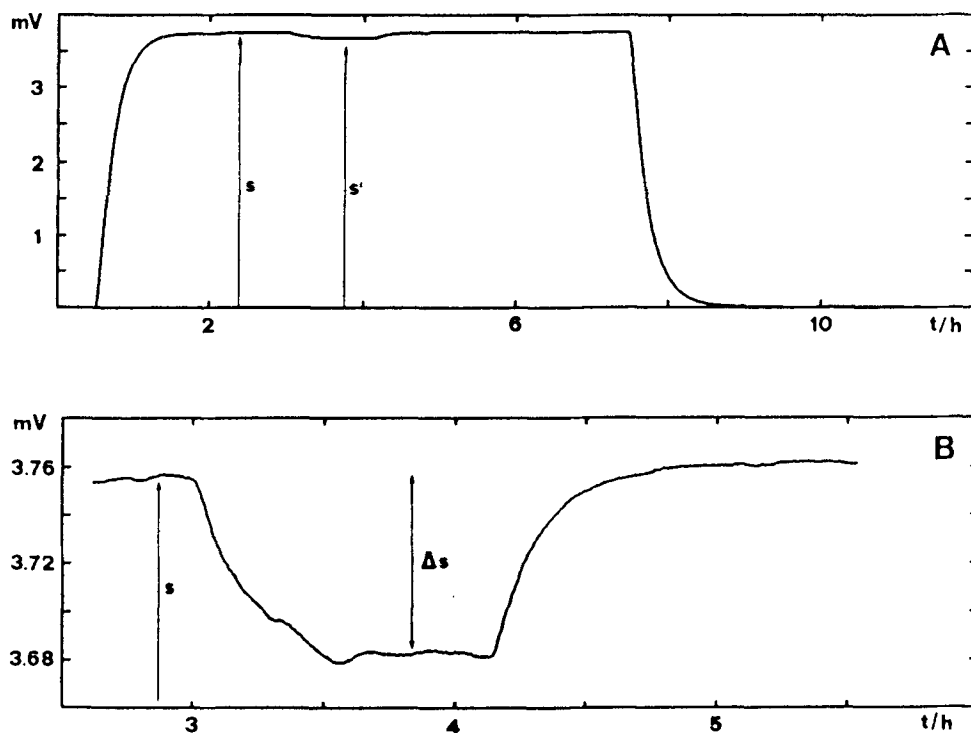

Fig. 4 Experimental curve; A) constant Joule heat power (87.8 mW) having a partial process of the cyclohexane injection 2.44 $\mu l \cdot s^{-1}$ over cyclohexane; B) magnification of the central zone

Both effects are produced by the macroscopic evolution of C_2 internal structure. A much more intense agitation could ease it by increasing C_2 "internal uniformity". It is necessary to reach a compromise so that there is no indefinite increase in the disturbances introduced by agitation (mechanical vibrations, electrical noise and "random" dissipative actions caused by changes of the viscosity with the concentration).

From $W(t)$ it is necessary to establish thermodynamic relations in order to obtain, in each case, the magnitudes concerned: the H_i^E partial molar excess enthalpies or the $L_{\varphi, i}$ relative apparent molar enthalpies against mole fraction [1, 6]. To make ease the manipulation of $W(t)$ a fit using Pade approach can be used [1].

For each instrument it is possible to have an estimate of the theoretical dynamic limits in which the termodynamic magnitudes are correctly obtained [1, 7]. If we have interested in the low concentrations and have a calorimeter that responds, at an initial approximation, as a single exponential term (first time constant τ_1) and that has a sensitivity S, a pulse signal of duration Δt and heat power W_o, a calorimetric curve with surface area A τ_1 will occur. We can write

$$W_o\Delta t = \left(\frac{1}{S}\right) A\cdot\tau_1 \qquad (6)$$

In order to "detect" this calorimetric curve it will be necessary for A to be clearly higher than noise b of the curve. Thus, the thermogram overcomes from the noise. The following should be fulfilled:

$$W_o\Delta t > \left(\frac{1}{S}\right) b\cdot\tau_1 \qquad (7)$$

When we wish to determine the H_i^E at the first time interval Δt a small amount of liquid Δn_1 (the Δn_1 equals the n_1 value after the interval) is injected on the second component (n_2). In these conditions $n_1 < < n_2$ and energy dissipation W_o will be associated with the partial molar excess enthalpy at infinite dilution $(H_1^E)^\infty$. There remains;

$$x_1^{min} > \frac{b\tau_1}{Sn_2(H_1^E)^\infty} \qquad (8)$$

For example, by studying the partial molar excess enthalpy H_2^E of the cyclohexane in the benzene (1) – cyclohexane (2) mixture, a minimum value of x_2 is obtained from the experimental results of $x_2^{min} \approx 6\cdot10^{-4}$. The theoretical limit is the same case and for the same calorimeter [1] is $x_2^{min} > 1\cdot10^{-5}$. The theoretical value is situated approximately at an order of magnitude below the experimental value. The difference between the two results is associated with the real features of the experimental thermoanalytical curves. In fact, the pulse response has

more than one exponential and its maximum is smaller (or much smaller) than the value of parameter A.

Conclusions

Systematic study of the behaviour of the instruments and their analysis with the aid of models with physical image makes it possible to establish a reliability control of an experimental system and the results it produces. It also provides useful information for the construction, adjustment and computerization of new equipment and possibly for constructing more effective calorimetric systems without reference cell.

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References

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Zusammenfassung — Einspritzkalorimeter werden zur Schätzung der thermodynamischen Eigenschaften von Gemischen und Lösungen verwendet. Die partiellen molaren Überschußenthalpien H_i^E oder die relativen scheinbaren molaren Enthalpien $L_{\varphi, i}$ gegenüber dem Molenbruch können über eine entsprechende Signalverarbeitung der kalorimetrischen Kurven ermittelt werden. Die Veränderlichkeit der thermischen Eigenschaften des Kalorimetergefäßes werden mit dem Einspritzprozeß in Verbindung gebracht. Die Beschreibung der Kalorimeterausrüstung mit Hilfe eines lokalisierten Konstantenmodelles (RC-Analogie) gestattet die Systematisierung und Ausweitung dieser Systeme für zeitabhängige Situationen. Auf dem Joule'schen Effekt basierende experimentelle Messungen und die entsprechenden mathematischen Auswertungen erlauben die Bestimmung der absoluten Grenzen des dynamischen Verhaltens dieser Geräte anhand einiger Standard- und leichter experimenteller Parameter (Empfindlichkeit, Rauschpegel, die erste Zeitkonstante τ_1, Art der Probennahme). Modelle und die experimentelle Untersuchung bieten eine Abschätzung der Korrekturen zum Ausgleich der Veränderlichkeit der physischen Eigenschaften des Gerätes.