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ELECTRIC AND CHEMICAL CALIBRATION IN FLOW CALORIMETRY

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Abstract: The TAM 2277-204 injection calorimeter by Thermometric is used nowadays for the determination of enthalpies of liquid mixtures. A good calibration of the device permits to obtain accurate thermal measures and advance in the knowledge of the energetic processes that are developed in the calorimeter. We identify the system with transfer functions of two poles; the parameters of the TF are determined through a non-linear least-square fit based on Marquardt´s method. Within the identification process we observe that the first time-constant and the sensitivity depend on rc_pf *(r is the density,* c_p *is the heat capacity and f is the flow rate of the injected liquid). We also observe differences between the sensitivity obtained from the electrical calibration and the sensitivity obtained from chemical calibration for the same values of* rc_pf*; these differences are produced by the fact that the mixture and the electrical dissipation do not occur in the same place. To suppose that the poles of the TF only depend on* rc_pf *and not on the dissipation place permits to accomplish a complete identification and to evaluate the dissipated power in the mixture as function of the time.*

Keywords: Thermal measurement, conduction calorimetry, flow calorimetry, liquid mixtures, modelling, signal processing.

1 INTRODUCTION

In this work, the calibration of a TAM 2277-204 conduction calorimeter by Thermometric [1] is made. This calorimeter is used to measure the energy produced when mixing two liquids, this energy is related to the thermodynamic properties of the mixture. For instance, for the case of pure liquids and homogeneous mixture, the excess enthalpy (in Jmol^{-1}) for a molar fraction x_1 can be calculated using the following expression:

$$H^E(x_1) = \frac{W}{\dot{n}_1 + \dot{n}_2} \tag{1}$$

W is the dissipated power, $\dot{n}_1$ and $\dot{n}_2$ are the flow rates of each liquid in mole/s, $x_1 = \dot{n}_1/(\dot{n}_1 + \dot{n}_2)$

Two independent pumps inject the liquids toward the cell and the mixture coil (see figure 1). The detector system, based on thermocouples, provides the experimental output. When the mixture is already homogeneous the energetic dissipation is constant; in this situation the dissipated power is W(t)=y(t)/K, K is the sensitivity in mVW^{-1} and y(t) the output in permanent state in mV.

The users of these instruments base the calibration just on the calculation of the sensitivity and propose empirical expressions of the sensitivity as a function of the volumetric heat capacity and also of the flow rate of the injected liquids [2]. The effect of the injection rate is the most relevant disturbance detected in these calorimeters [3]. A model, with physical image, that adequately represents the performance of the instrument and which provides an expression of the sensitivity as function of ρc_pf (ρ is the density, c_p is the heat capacity and f is the flow rate of the injected liquid) has already been proposed in a previous study [4]. However, that model was obtained starting form electrical calibrations and did not sufficiently represent the results of the chemical calibrations due to the fact that the mixture does not occur in the same place where the calibration resistance is located.

In this work we incorporate the results provided by the chemical calibrations, this is: dissipations produced when mixing two liquids that are used as "standard". The objectives are to study the static and dynamic performance of the device, to relate both calibration results (electric and chemical calibration) and to show that they are complementary. For this, first we make a short description of the experimental equipment and of the measures accomplished for the calibration. After this we expose the model and the identification method of the parameters of the model. Finally we make an analysis of the results.

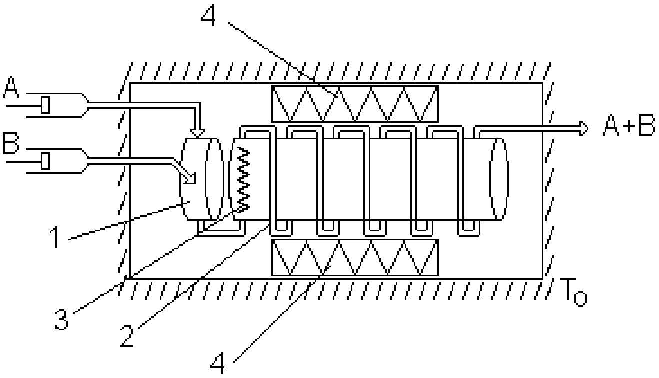

Figure 1. Scheme of the TAM2277-204 injection calorimeter by Thermometric. 1: mixture cell; 2: mixture coil; 3: calibration resistance; 4: thermocouple detector system; T_0: thermostat temperature.

2 EXPERIMENTAL MEASURES

The calorimetric output of TAM 2277-204 calorimeter is directly digitized by a Hewlett Packard HP3457A multimeter (10 nV of resolution). The electrical calibration is made by the dissipation of a known power in a resistance of 50 Ω located inside the calorimeter, the resistance is connected to a source HP6284A controlled by a HP59501B. The system is controlled through the bus GPIB by a PC computer and the readings are stored for the subsequent analysis, the sampling interval used is $\Delta t = 1.0989$ s.

Dissipations with variable power and different pulses (see figure 2) are programmed for the electrical calibration. The same pure liquid is injected through both pumps during the electrical dissipation. The accomplished measures are made for different flow rates: from 0 to 60 cm^3h^{-1}, and the used liquids are cyclohexane and benzene.

The standard mixture cyclohexane(A)+benzene(B) has been used for the chemical calibration. The reference data proceed of Stokes et al. [5]. All measures have been made for $f_A=f_B$, this means, for a fixed molar fraction $x_A = 0.541$. The excess enthalpy is $H^E_{ref}= 796.2045$ $Jmol^{-1}$ for the given molar fraction and for a thermostat temperature $T_0=298.15$ K. Figure 3 shows the experimental output corresponding to a mixture with $f_A=f_B=5.44$ cm^3h^{-1}, the injection is accomplished from t =109.89 s to t =1208.80 s. Observe that the mixture is endothermic, this means that the dissipated power (mW) and the output (mV) have opposed signs in comparison to the power and output corresponding to the dissipation by Joule effect.

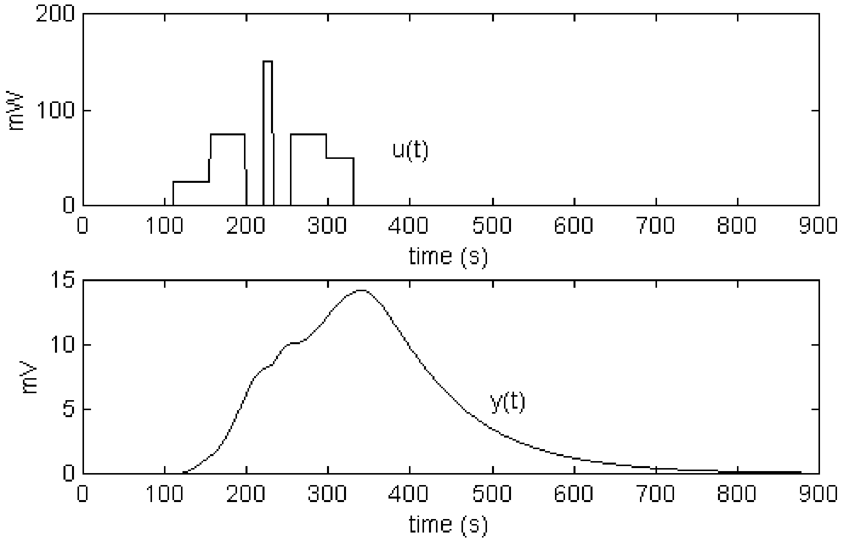

Figure 2. u(t): Dissipated power in the calibration resistance; y(t): Experimental output. In this case, benzene for both pumps is injected with $f_A=f_B=21.78$ cm^3h^{-1}.

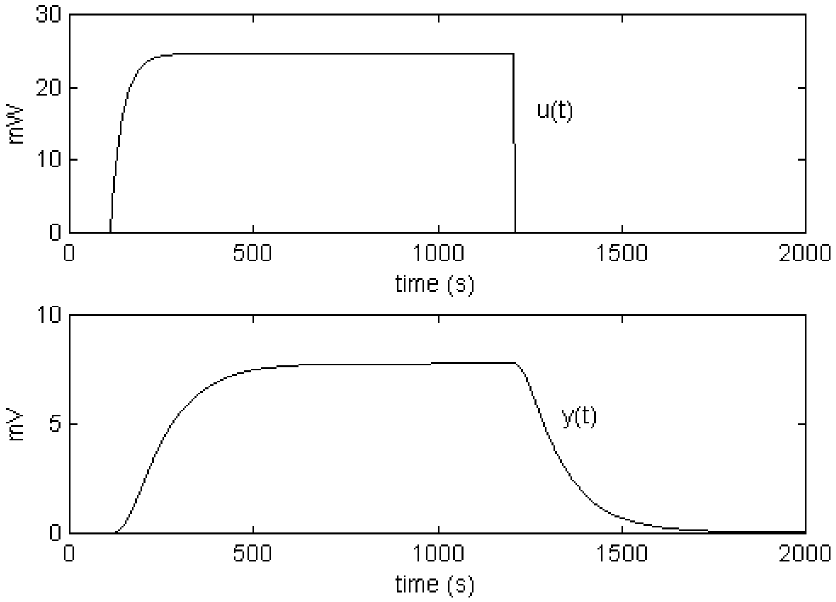

Figure 3. y(t): Experimental output corresponding to the injection of cyclohexane and benzene (f_A=f_B=5.44 cm^3h^{-1}); u(t): Calculated input for W_{ref}=24.620 mW.

3 MODEL AND IDENTIFICATION

In order to model the calorimeter, we consider a system of two inputs and one output. The inputs are the dissipated power in the calibration resistance and the dissipated power during the mixture of the liquids. The output is provided by the thermocouple detector system. An analysis of the curves obtained in the electrical calibration shows that the system can be identified using a TF of two poles.

$$FT(s) = \frac{Ke^{-\Delta s}}{(1+st_1)(1+st_2)} \qquad (2)$$

In the electrical calibration the input and the output are known, but in the chemical calibration the input power is not known and experimentally we observe that the output reaches the stationary state when the mixture is homogeneous, for this permanent state the input is:

$$W_{ref} = H^E_{ref}(\dot{n}_A + \dot{n}_B) \qquad (3)$$

As first approximation we suppose that the mixture power, $u_{mix}(t)$, follows an exponential function whose time-constant depends on the flow rates of the injected liquids:

$$u_{mix}(t) = W_{ref}(1 - e^{-t/t_{mix}}) \qquad (4)$$

To determine the parameters of the TF we use a nonlinear least-squares fit based on Marquardt´s method [6] making use of the routines facilitated by Numerical Recipes in Fortran [7]. We limit the possible variations of the sought parameters so that they do not change in more than a 40% of their value in each iteration. Calculated output, y_{cal}, is obtained as a numerical convolution between the input, u(t), and the impulsive output, h(t).

$$h(t) = \frac{K}{t_1 + t_2}\left[e^{-(t-\Delta)/t_1} - e^{-(t-\Delta)/t_2}\right] \qquad (5)$$

The derivatives of the outputs with respect to the sought parameters (K, τ_1, τ_2, Δ) are obtained making the numerical convolution between the input, u(t), and the analytical derivative of h(t) with respect to the corresponding parameter. The derivative of the output with respect to τ_{mix} is obtained through the numerical convolution between the analytical derivative of $u_{mix}(t)$ and the impulsive output.

In table 1, we expose the results of the identification obtained from the electrical calibrations when injecting cyclohexane or benzene. The first time-constant and the sensitivity change with the injection rate. As a rule, it can be said that the greater $\rho c_p f$ the smaller the sensitivity (though there is a maximum of the sensitivity due to the relative situation of the resistance and mixture coil with respect to the detector system). The volumetric heat capacities of the used liquids are: $(\rho c_p)_{cyclohexane}$= 1.39 Jcm^{3}K^{-1};$(\rho c_p)_{benzene}$= 1.53 Jcm^{3}K^{-1}. In figure 4, the module of the experimental TF and the module of the TF corresponding to the calculated model are represented as functions of the frequency .

Flow-rate in each pump		Cyclohexane injection Δ=6.8 s σ_d <0.024 mV σ_m<0.163 mV			Benzene injection Δ=6.1 s σ_d <0.021 mV σ_m<0.144 mV		
f_A (cm^{3}h^{-1})	f_b (cm^{3}h^{-1})	τ_1 (s)	τ_2 (s)	K (mVW^{-1})	τ_1 (s)	τ_2 (s)	K (mVW^{-1})
0.00	0.00	99.6	23.9	312.42	99.9	24.2	311.87
2.72	2.72	99.6	23.9	313.55	99.9	24.1	313.04
5.44	5.44	99.4	23.8	314.06	99.6	24.1	313.47
8.17	8.17	98.9	23.8	313.75	99.1	24.1	313.08
10.89	10.89	98.2	23.9	312.97	98.3	24.1	312.16
13.61	13.61	97.3	23.9	311.66	97.4	24.1	310.85
16.33	16.33	96.4	24.0	309.37	96.4	24.1	309.10
19.06	19.06	95.4	23.8	307.76	95.4	24.1	307.12
21.78	21.78	94.3	23.9	305.76	94.0	24.4	304.74
24.50	24.50	93.2	24.0	303.77	93.0	24.2	302.27
27.22	27.22	92.0	24.0	301.27	91.8	24.2	299.72
29.95	29.95	90.9	24.0	298.73	90.6	24.2	297.17

Table 1. Parameters of the TF´s obtained from the electrical calibrations injecting cyclohexane or benzene for both pumps. Error parameters σ_d and σ_m (equation 7).

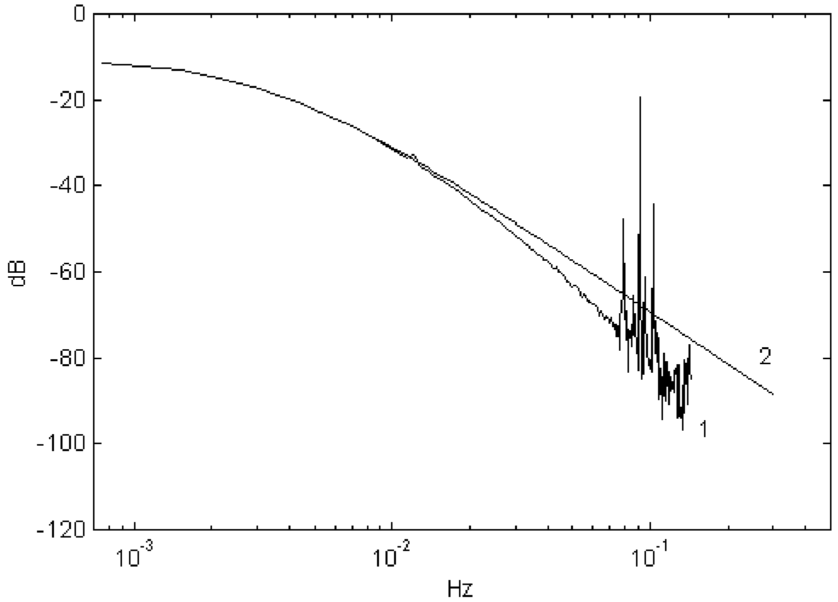

Figure 4. Module of the experimental TF (1) and module of the TF of the calculated model (2) versus frequency.

Using electrical calibrations, the experimental system is modelled by TF's in which τ_1 and K vary with $\rho c_p f$. Supposing that the main difference between the electrical and chemical dissipation is the place of dissipation, we consider that the TF's corresponding to both dissipations should contain the same time-constants. Because of this, we assign as time-constants of the chemical measures the arithmetic mean of the time-constants obtained in the electrical calibration for each liquid and each injection rate:

$$\left|t_i(f_A+f_B)\right|_{mix} = 0.5\left|[t_i(f)]_A + [t_i(f)]_B\right|_{electric} \tag{6}$$

Under this supposition we obtain the rest of the parameters of the TF's (K and Δ) and the time-constant of the mixture τ_{mix}. Table 2 shows the results of the chemical calibration. In tables 1 and 2 the maximum errors of the adjustment, the Standard deviation (σ_d) and the Maximum deviation (σ_m) are exposed:

$$s_d = \sqrt{\sum_{i=1}^{N}\left((y_i)_{\exp} - (y_i)_{cal}\right)^2 / N-1} \qquad (7)$$

$$s_m = max\left|(y_i)_{\exp} - (y_i)_{cal}\right|$$

f_A (cm^3h^{-1})	f_B (cm^3h^{-1})	W_{ref} (mW)	Δ (s)	τ_1 (s)	τ_2 (s)	τ_{mix} (s)	K (mVW^{-1})	σ_d (mV)	σ_m (mV)
2.72	2.72	12.310	12.2	99.75	24.0	61.5	311.95	0.027	0.054
5.44	5.44	24.620	12.4	99.50	24.0	32.3	315.82	0.028	0.069
8.17	8.17	36.931	11.6	99.00	24.0	22.1	318.51	0.033	0.076
10.89	10.89	49.241	11.5	98.25	24.0	18.1	318.10	0.033	0.086
13.61	13.61	61.551	12.0	97.35	24.0	16.4	316.05	0.037	0.070
16.33	16.33	73.861	10.4	96.40	24.0	12.4	311.64	0.043	0.102
19.06	19.06	86.172	9.9	95.40	24.0	10.6	306.52	0.047	0.096
21.78	21.78	98.482	12.0	94.15	24.0	7.1	300.97	0.095	0.245
24.50	24.50	110.792	10.7	93.10	24.0	5.9	299.88	0.045	0.133
27.22	27.22	123.102	9.7	91.90	24.0	5.2	297.89	0.047	0.105
29.95	29.95	135.412	10.6	90.75	24.0	3.0	296.78	0.055	0.156

Table 2. Parameters of the TF's obtained in the chemical calibration using the standard mixture cyclohexane(A)+benzene(B), $H^E_{ref}(x_A)=796.2045$ $Jmol^{-1}$, $x_A=0.541$. Error parameters σ_d and σ_m (equation 7).

4 CONCLUSIONS

The obtained model of two poles is very simple. It does not provide a physical image of the calorimeter but facilitates a very useful and necessary information to determine a more complete and representative model of the instrument. The most relevant aspects of the calibration study accomplished in this work are the following:

1) The effect of the injection affects to the static and dynamic output of the calorimeter causing variation of the first time-constant and the sensitivity with $\rho c_p f$ of the injected liquids (ρ is the density, c_p it is the heat capacity and f the injection flow).
2) The effect of the dissipation place causes the sensitivity obtained in the electrical calibration and in the chemical one to be different for the same or similar values of $\rho c_p f$ of the injected liquids.
3) The mixture is not instantaneous but progressive, so that the dissipated power increases in an exponential way and its time-constant diminishes with the injection rate.
4) The effect of the thermal conductivity of the used liquids is made manifest in the different sensitivities obtained in the electrical calibration for the cyclohexane and the benzene when the injection rate is zero.

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