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Sensitivity changes with injection rate in heat-conduction calorimeters

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Abstract

Injection rate is the most relevant perturbing effect detected in the ThermoMetric TAM 2277-204 injection calorimeter. In other studies about this subject, several phenomenological expressions can be found. In this work, the connection between sensitivity and heat capacity $C = \rho c_p v$ (ρ density, c_p specific heat and v volume) and injection rate will be proved by physical models, using experimental values of the sensitivity, obtained from Joule effects. Sensitivity decreases when the injection rates and/or the specific heat of the liquids increase. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The TAM 2277-204 by ThermoMetric is a continuous-injection heat conduction calorimeter used nowadays for the determination of molar excess enthalpies of liquid mixtures [1,2]. The principle of performance consists in the continuous-injection of two liquids in the reaction zone. It is supposed that when the equilibrium is reached, the mixture is homogeneous, the dissipation is constant and the heat of mixing is directly related to the calorimetric output. In these conditions, in the case of two pure liquids, the excess enthalpy is given by the following expression:

$$H^E(x_1) = \frac{1}{S}\frac{y}{\dot{n}_1 + \dot{n}_2}\ (\mathrm{J\,mol^{-1}}), \qquad (1)$$

with y being the calorimetric output (in mV), $\dot{n}_1$ and $\dot{n}_2$ the injection rates (in mol s^{-1}), S the sensitivity (in mV W^{-1}), and x_1 the molar fraction $x_1 = \dot{n}_1/(\dot{n}_1 + \dot{n}_2)$.

The calibration of this device fundamentally consists in the determination of the sensitivity. Monk and Wadsö [3] and Harsted and Thomsen [4] propose analytical expressions of the sensitivity as function of the injection rates. On the other hand, Tanaka et al. [5] also take into account, the heat capacities of the injected liquids.

An experimental study of the perturbations detected during the normal performing of injection calorimeters shows that the injection rate is the most relevant perturbation in the TAM 2277-204 calorimeter [6]. For instance, the sensitivity approximately diminishes 10% when injecting water at a rate of 30 cm^3 h^{-1}.

In this work a calorimetric system modellization has been made; it permits the determination of a

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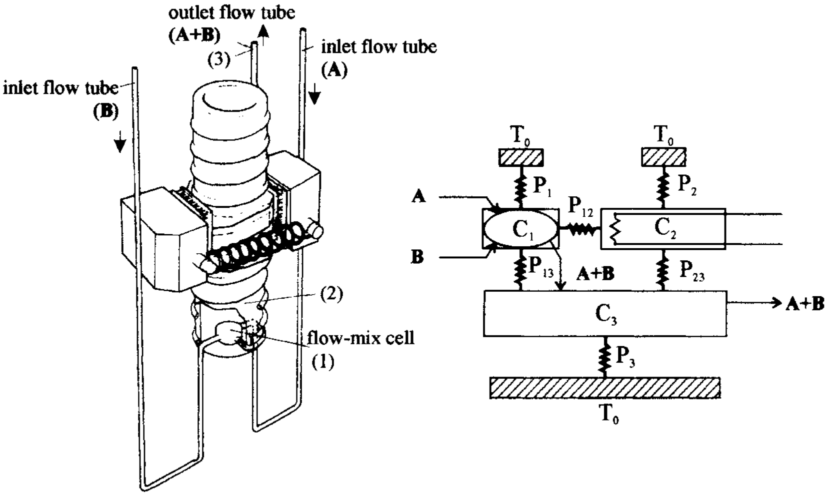

Fig. 1. Constructive detail of the TAM2277-204 calorimeter [7] and scheme of the model with physical image.

relation of the sensitivity with the rate and heat capacities of the injected liquids. Experimental thermograms corresponding to Joule effect dissipations have been used for the adjustment of the model (electric calibrations).

2. Model

The calorimetric device [7] is decomposed in three domains that represent the different parts of the calorimeter (Fig. 1). Each domain, with heat capacity C_i and temperature T_i, is connected to the next domains by thermal couplings P_i and P_{ij}. The injection of the liquids takes place in the first domain, wherein the dissipation due to the mixing (W_1) occurs. We suppose that the output pipe of the mixing passes through domain 3, surrounding bodies 1 and 2. Joule effect dissipation (W_2) takes place in the second element and the output of the model $y(t)$ is proportional to the temperature difference between the third element and the thermostat: $y(t) = k(T_3 - T_0)$, in this case we take $k = 1\ \mathrm{V\ K^{-1}}$. This method called "localized-constants model" has acceptably been used in modellization of other conduction calorimeters [8,9]. The energy balance applied to each model element can be expressed as follows:

$$\begin{aligned} W_1 &= C_1\frac{\mathrm{d}T_1}{\mathrm{d}t} + P_{12}(T_1-T_2) + P_{13}(T_1-T_3) \\ &\quad + P_1(T_1-T_0) + g_1(T_1-T_0),\ W_2 \\ &= C_2\frac{\mathrm{d}T_2}{\mathrm{d}t} + P_{12}(T_2-T_1) + P_{23}(T_2-T_3) \\ &\quad + P_2(T_2-T_0),\ 0 = C_3\frac{\mathrm{d}T_3}{\mathrm{d}t} + P_{13}(T_3-T_1) \\ &\quad + P_{23}(T_3-T_2) + P_3(T_3-T_0) + g_{13}(T_3-T_1). \end{aligned} \tag{2}$$

Terms $g_1(T_1 - T_0)$ and $g_{13}(T_3 - T_1)$ are the calorific powers due to the injection when changing the temperature of the liquid from T_0 to T_1 (from the thermostat to the first element) and from T_1 to T_3 (from the first to the third element).

3. Identification

The parameters of this model with physical image have been evaluated using the AIRRT identification technique [10]. The mean quadratic error of adjustment between the experimental curves and the calculated ones is 0.0015 mV. Experimental curves corresponding to Joule effect dissipations have been used; during these measurements water or ethanol is injected at different rates. All measurements have

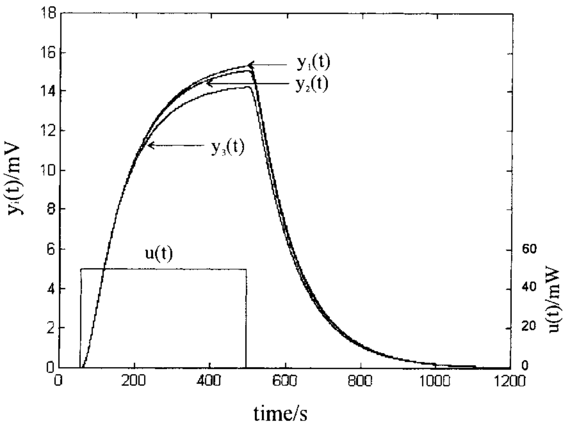

Fig. 2. Calorimetric curves corresponding to Joule effect dissipations when injecting water at distinct rates: 6.53 cm^3 h^{-1} ($y_1(t)$), 13.61 cm^3 h^{-1} ($y_2(t)$) and 27.22 cm^3 h^{-1} ($y_3(t)$).

been accomplished for a thermostat temperature of 25°C and a sampling period of $\Delta t = 0.55$ s. Fig. 2 shows the results for the case of injecting water.

Parameters C_i, P_{ij} and P_i are obtained from curves when there is no injection and taking $g_1 = 0$ and $g_{13} = 0$. Maintaining C_i, P_{ij} and P_i constant, g_1 and g_{13} are determined for each injection rate. Table 1 shows the values obtained for C_2, C_3, P_1, P_2, P_3, P_{12}, P_{13}, and P_{23}, which do not depend on the type of liquid nor on the injection rate. Table 2 shows the values for C_1, g_1 and g_{13} in the cases of injecting water or ethanol. Parameters g_1 and g_{13} are functions of the density (ρ in g cm^{-3}), of the specific heat (c_p in J g^{-1} K^{-1}) and of the injection rate ($\dot{v}$ in cm^3 h^{-1}):

$$g_1 = (\alpha_1 \dot{v} + \alpha_2 \dot{v}^2)\rho c_p, \qquad g_{13} = \beta \rho c_p \dot{v}, \qquad (3)$$

where $\beta = 0.9278 \times 10^{-3}$ and the values of α_1 and α_2 are shown in Table 3. Fig. 3 shows the adjustment of parameter $g_1/(\rho c_p)$ as function of the injection rate; a slight difference between the values obtained in case of injecting water and in case of injecting ethanol is revealed. This difference appears because the proposed model does not consider other physical properties of the liquids, for instance, thermal conductivity (this property could be incorporated in the thermal couplings P_i and P_{ik}).

Table 1
Heat capacities and coupling coefficients of the model

C_1 (in Table 2)	$P_1 = 0.347$ W K^{-1}	$P_{12} = 2.083$ W K^{-1}
$C_2 = 85$ J K^{-1}	$P_2 = 0.382$ W K^{-1}	$P_{13} = 0.347$ W K^{-1}
$C_3 = 30$ J K^{-1}	$P_3 = 1.233$ W K^{-1}	$P_{23} = 0.382$ W K^{-1}

Table 2
Heat capacity of the first element (C_1) and parameters g_1 and g_{13} of the model, in the cases of injecting water or ethanol

$\dot{v}$ (cm^3 h^{-1})	C_1 (J K^{-1})	g_1 (W K^{-1})	g_{13} (W K^{-1})
Injecting water ($\rho c_p = 4.186$ J cm^{-3} K^{-1})			
0.0	40.716	0.0	0.0
6.53	40.716	0.02731	0.0254
13.61	40.716	0.08448	0.0529
27.22	40.716	0.24099	0.1057
Injecting ethanol ($\rho c_p = 1.9276$ J cm^{-3} K^{-1})			
0.0	28.847	0.0	0.0
6.53	28.847	0.00948	0.0117
13.61	28.847	0.02944	0.0243
27.22	28.847	0.09680	0.0487

Table 3
Coefficients of Eq. (3) that adjust parameter g_1

Injected liquid	α_1	α_2
Water	0.7776×10^{-3}	0.0492×10^{-3}
Ethanol	0.4027×10^{-3}	0.0530×10^{-3}
Water or ethanol	0.5902×10^{-3}	0.0511×10^{-3}

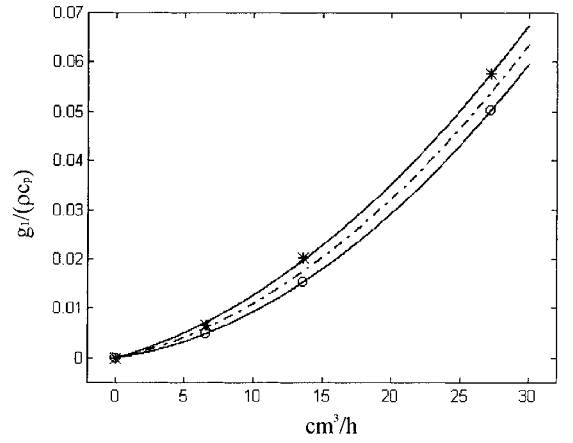

Fig. 3. Representation of parameter $g_1/(\rho c_p)$ as function of the injection rate and polynomial adjustment by Eq. (3), in case of injecting water (*), in case of injecting ethanol (o), mean adjustment for both cases (---).

The coefficients of the differential equation system (2) are calculated for each chosen injection rate. The system is invariant and the transfer function between

Table 4
Parameters of the transfer function (Eq. (4)) directly obtained from the model in the cases of injecting water or ethanol

$\dot{v}$ (cm^3 h^{-1})	τ_1 (s)	τ_2 (s)	τ_3 (s)	τ_1* (s)	S (mV W^{-1})
Injecting water					
0.0	109.8	14.9	11.1	8.7	313.0
6.53	109.0	14.8	10.9	8.4	313.3
13.61	107.6	14.6	10.6	8.1	307.4
27.22	96.1	14.3	10.4	7.4	288.3
Injecting ethanol					
0.0	102.4	14.9	8.5	6.2	313.0
6.53	101.9	14.8	8.4	6.1	313.9
13.61	100.7	14.8	8.4	6.0	312.6
27.22	96.6	14.6	8.2	5.7	303.9

the output $y(t)$ and the power W_2 (for $W_1 = 0$), has the following expression:

$$\frac{Y(s)}{W_2(s)} = S\frac{1+s\tau_1^*}{(1+s\tau_1)(1+s\tau_2)(1+s\tau_3)}. \tag{4}$$

Table 4 shows the values of the parameters of the transfer function that have directly been obtained from the model.

4. Sensitivity

Electric sensitivity (for $W_1 = 0$) can also be obtained as the value of the permanent output to a Heaviside input ($W_2(t) = 1$, for $t \geq 0$):

$$S = \lim_{t\to\infty} = y(t) = k(T_3 - T_0).$$

In the permanent state $\mathrm{d}T_1/\mathrm{d}t = \mathrm{d}T_2/\mathrm{d}t = \mathrm{d}T_3/\mathrm{d}t = 0$ and the differential equation system (2) has this form:

$$\begin{aligned} 0 &= P_{12}(T_1-T_2) + P_{13}(T_1-T_3) + P_1(T_1-T_0) \\ &\quad + g_1(T_1-T_0), \\ 1 &= P_{12}(T_2-T_1) + P_{23}(T_2-T_3) + P_2(T_2-T_0), \\ 0 &= P_{13}(T_3-T_1) + P_{23}(T_3-T_2) \\ &\quad + P_3(T_3-T_0) + g_{13}(T_3-T_1). \end{aligned} \tag{5}$$

By rearranging the preceding expressions and substituting the model parameters, we obtain an expression of the sensitivity as function of ρc_p and $\dot{v}$:

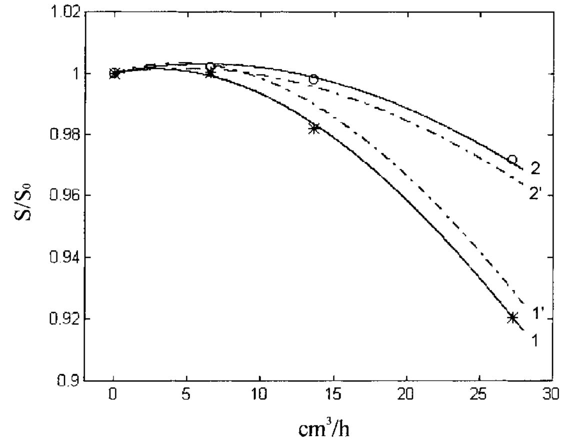

Fig. 4. Relative evolution of the sensitivity as function of the injection rate. Experimental values for the case of injecting water (*) or ethanol (o) and adjustment made with the model (curves 1 and 2). Curves 1′ and 2′ correspond to the adjustment provided by the model (Eq. (6)). S_0 is the sensitivity value when there is no injection ($S_0 = 313$ mV W^{-1}).

In order to determine this expression we have used the same values of α_1 and α_2 for both liquids (see last file in Table 3). Fig. 4 shows the sensitivity as function of the injection rate in the case of injecting water or ethanol. There is a difference of sensitivity between considering the values of α_1 and α_2 obtained for each liquid and considering the same values of α_1 and α_2.

$$S = \frac{1.78 + 2.16\times10^{-3}\rho c_p\dot{v} + 1.95\times10^{-5}\rho c_p\dot{v}^2}{5.7 + 4.87\times10^{-3}\rho c_p\dot{v} + (2.78\times10^{-4} + 1.56\times10^{-6}\rho c_p)\rho c_p\dot{v}^2 + 1.35\times10^{-7}(\rho c_p)^2\dot{v}^3}. \tag{6}$$

This difference is less than 1% for the case of water and less than 0.5% for the ethanol.

5. Conclusions

Variation of the sensitivity with injection rate is a very important phenomenon in this type of calorimeters. For injection rates less than $10\,\text{cm}^3\,\text{h}^{-1}$, the sensitivity has a variation less than 1%. It has to be taken in account that the dissipated energy is proportional to the injection rate, and if the liquids on study present a weak heat of mixing, it is necessary to inject to a higher rate, in that case a correction of the sensitivity must be made using expression (6).

A model with a physical image that dynamically and statically adjusts the performing of the calorimeter has been determined; it clearly shows the dependence of the sensitivity on the injection rate and on the heat capacity of the injected liquids: $C=\rho c_p v$ (ρ density, c_p specific heat and v volume). The model has been obtained from electric calibrations and it provides an adjustment of sensitivity with an error less than 1%.

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