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AN ISOTHERMAL LABYRINTH FLOW CALORIMETER WITH THERMISTORS

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ABSTRACT

An isothermal labyrinth flow calorimeter was constructed using thermistors and low-cost materials. Electrical calibrations data, time constant and other characteristics are presented. For testing the system, the molar heat capacity of copper and aluminum were determined by drop calorimetry; both showed a difference of $<1\%$ from the literature values.

INTRODUCTION

The labyrinth flow calorimeter was developed by Swietoslawsky and his school, based on Junker's calorimeter [1–3]. The main feature of this apparatus is the heat exchange by the calorimetric vessel (or lab-cell) with fluid circulating around it, flowing in a "labyrinth" to maximize this exchange. If the temperature difference (ΔT) between the fluid-in and the fluid-out to the labyrinth, the flow ($f =$ mass/time), and the fluid specific heat (c) are known, it is possible to calculate the heat (q) exchanged by the fluid from the equation

$$q = fc\int \Delta T\,\mathrm{d}t \qquad (1)$$

In this equation, t is the measurement time, and f and c are considered constants in this time. For the same interval of time, the value, accuracy and precision of q should be dependent on ΔT measurements and its integration.

The calorimeters developed by Swietoslawsky and his school used mercury-in-glass thermometers or thermocouples. In our model, we have used thermistors, which are more sensitive than any other temperature sensor and present a smaller heat capacity [4].

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DESCRIPTION OF CALORIMETER

The calorimeter is shown schematically in Fig. 1. The lab-cell (1) is in glass with a maximum capacity of 5 cm^3. The labyrinth is made of aluminum and epoxy (2, 3 and 4), inside which flows the heat-exchange fluid or thermal fluid. The all-glass thermistors (5 and 6) have a nominal resistance of 2.2 kΩ at 298 K and the thermal coefficient is 0.04 K^{-1}. The thermo-hydraulic homogenizer (7) is put into the metallic jacket (see below). The thermal fluid tubing (8) is connected to the holes of the cover (9). The metallic jacket (12) is made of brass and copper and is chrome-plated. The cover is connected to the jacket by screws (10) and sealed with a rubber O-ring (11). The lab-cell is joined by the glass tube (13).

The thermo-hydraulic homogenizer (in aluminum and epoxy) is a can with fins inside, where the thermal fluid heat exchanges and mixes, thereby homogenizing its temperature before entering the labyrinth.

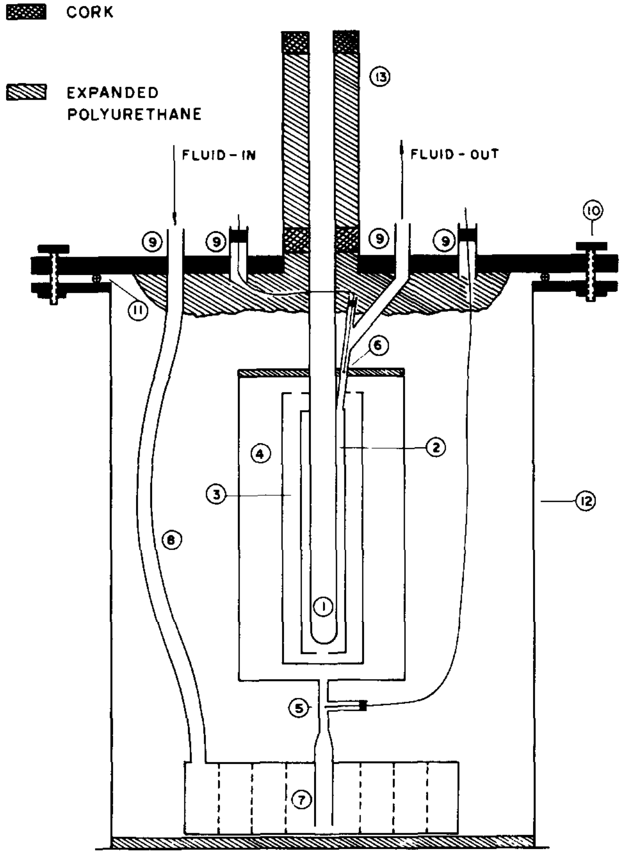

Fig. 1. Scheme of calorimeter (see text for description).

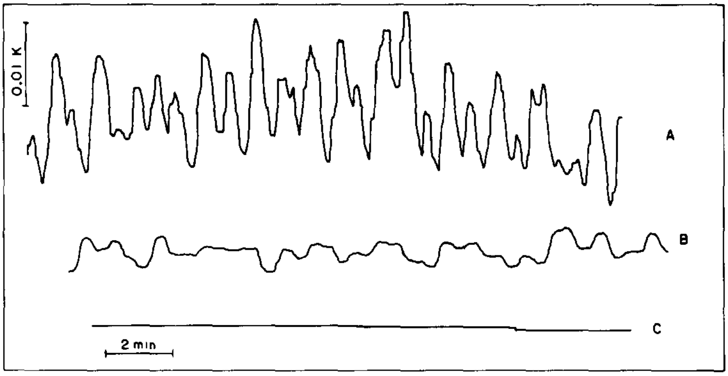

Fig. 2. Effect of thermo-hydraulic homogenizer on fluid temperature (see text for description).

This assembly (lab-cell, labyrinth and homogenizer) is put into the metallic jacket, which is immersed in a thermostated water bath (~ 80 dm^3). It is controlled by an on–off system, with thermal oscillation of ~ 0.015 K (Fig. 2, line A).

The thermal fluid (generally water) circulates by gravity. It is put in a constant-level reservoir above the thermostated bath and the flow is controlled by the height of this reservoir and by capillaries in the exit of the fluid line. It is possible to use a large range of flow (55–220 mg s^{-1}), with a good stability (fluctuations $< 0.3\%$ over a working day). The fluid, before entering the homogenizer, goes through a PVC coil (length = 10 m; internal diameter = 8 mm) immersed in the thermostated bath.

The thermistors are mounted in two arms of a Wheatstone bridge, leaving the other two wire potentiometers for rapid balance. A mercury cell is used as energy supply and the output is connected to a high-input impedance potentiometric recorder (Metrohm E-478 or ECB).

Since the calorimetric precision is a function of the temperature of the thermal fluid entering the labyrinth, it must be as stable as possible. This is attained with the thermo-hydraulic homogenizer. At the input, the temperature presents thermal fluctuations of ~ 0.005 K (Fig. 2, line B) while at the output, there are no detectable oscillations (Fig. 2, line C). The little break in line C (Fig. 2) is an external electrical perturbation (switching on the air conditioner system).

OPERATION AND CALIBRATION OF THE CALORIMETER

The heat involved in a process (exo or endothermic) running in the lab-cell was calculated by eqn. (1) put into the form:

$$q = k \int \Delta T \, \mathrm{d}t = kA \qquad (2)$$

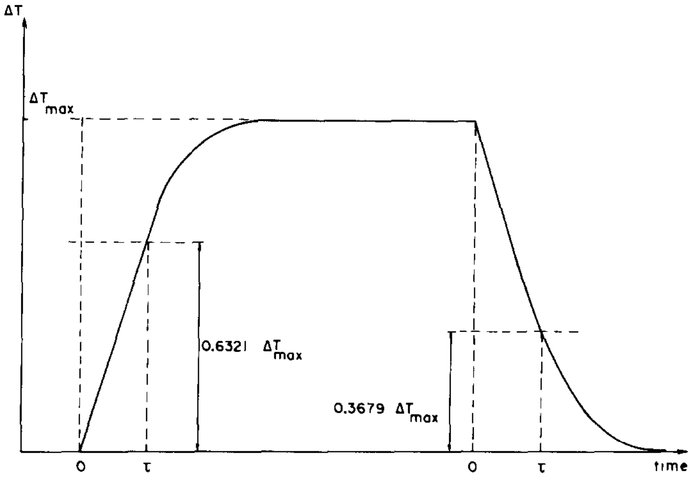

Fig. 3. Time-constant determination.

where $k = fc$ is a calibration coefficient and A is the area under the recorded curve of ΔT versus time (Fig. 3). In a work journey, k presented only a small variation. The value of A was determined by planimeter (graphical integration) or by electronic integration on the printer (CG-100).

The electrical calibrations were performed by using a manganine wire resistor [resistance = (28.79 ± 0.01) Ω] in the lab-cell. A typical set of these calibrations, is shown in Table 1. Several values of electrical power (uncertainty < 0.1%) were applied to the resistor; the area was recorded and k was calculated by linear regression. The standard deviation is a measurement of the precision (reproducibility) of the system. A linear relationship between k and f, and the independence of k with the calorific capacity of the lab-cell were observed.

TABLE 1

Electrical calibration [a]

q (J)	A (cm^2)	q (J)	A (cm^2)
4.185	10.20	25.109	60.42
8.362	19.92	29.287	69.84
12.534	30.54	33.436	81.00
16.704	40.68	37.627	88.98
20.900	49.20	41.803	102.18

$k = (0.4156 \pm 0.0019)$ J cm^{-2}
$r = 0.99957$

[a] q = Dissipated heat in resistor; A = area under recorded curve; $k = q/A$ = calibration coefficient (mean ± standard deviation); r = correlation coefficient.

TIME-CONSTANT DETERMINATION

The time constant or relaxation time (τ) [5,6], defined by $\tau = C/K$, where C is the calorific capacity of the lab-cell and K is the global heat-exchange coefficient between the lab-cell and the thermal fluid, can be used to determine if the calorimeter is adequate to be used for a slow process. The method described by Stauffer and Jeanneret [6] (see Fig. 3), where τ is the time when $\Delta T = 0.6321\ \Delta T_{\max}$ (ΔT is the recorded pen deflection and $T_{\max}$ is this maximum) in the rise portion of the curve and $\Delta T = 0.3679\ \Delta T_{\max}$ in the fall portion, was used in the electrical calibration process. For comparison, τ is 141 s and 600 s for LKB-10700 and Tian-Calvet calorimeters, respectively.

An advantage of the labyrinth flow calorimeter is the possibility of a quick change of τ by a variation of f, as Table 2 shows where τ ranges from 250 s to 500 s, values which can be extended.

DETERMINATION OF HEAT CAPACITY

To test the accuracy of the system and to develop the technique for use in our laboratory, the molar heat capacities of copper and aluminum were determined by drop calorimetry. A jacketed copper tube (an "oven") was put over the tube (13) (see Fig. 1) through which thermostated water was circulated. The metallic sample was attached by a cotton thread and, after the necessary time for thermostatization, was dropped into the lab-cell. This process is done with a platinum thermometer (Heraus; 100.0 Ω at 273.15 K) to measure the oven's temperature and to check the time necessary for thermostatization. The molar heat capacity at constant pressure (C_{p_m}) was calculated by the equation:

$$C_{p_m} = AQM\ \Delta T'/A'm \tag{3}$$

where A = area under recorded temperature–time curve in a dropping process; A' = area under recorded temperature time curve in a dropping process for electrical calibration; Q = heat due to the Joule effect in the resistor; M = molar mass of metal, m = sample mass; $\Delta T'$ = temperature difference between the oven and the lab-cell.

In all runs (three for both samples) $\Delta T' = 5.40$ K, aluminum sample mass = (1.93135 ± 0.00001) g, and copper sample mass = (5.06270 ± 0.00001) g. Both samples were surface treated (chemical washing and polishing) and

TABLE 2

Time constant (τ) change with flow (f)

f (mg s^{-1})	75.8	91.1	109.2	127.5	150.3	175.6	213.6
τ (s)	495	480	420	308	285	263	255

the purity was > 99.9%, by chemical analysis. The results were: C_{p_m} (Al(s), 295.5 K) = (24.36 ± 0.35) J K^{-1} mol^{-1}, and C_{p_m} (Cu(s), 295.5 K) = (24.27 ± 0.13) J K^{-1} mol. The uncertainties are twice the median deviation. For comparison, the values calculated from [7] and [8], respectively, are: C_{p_m} (Al(s), 295.5 K) = 24.32 J K^{-1} mol^{-1} and C_{p_m} (Cu(s), 295.5 K) = 24.39 J K^{-1} mol^{-1}. The differences are within experimental error (< 1%), from these results the system can be considered very accurate.

CONCLUSION

With the utilization of thermistors, the isothermal labyrinth flow calorimeter shows good performance, as compared with other isothermal calorimeters. It also has the advantage of a simple, low-cost construction.

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