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A simple calorimetric method to avoid artifacts in a controversial field: the ice calorimeter

Jacques Dufour, Xavier Dufour, Denis Murat, Jacques Foos
CNAM - Laboratoire des sciences nucléaires - CC304A - 75141 Paris Cedex 03

Introduction

The idea of the ice calorimeter is rather old. Antoine Lavoisier (1743-1794) developed in 1783 a calorimetric method based on the measurement of the mass of the ice that melts when heated. Robert Bunsen (1811-1899) improved this method in 1870 and designed a calorimeter based on the measurement of the volume rather than the mass of ice melted. Nowadays this method is still used [1] because it is simple, accurate, sensitive and most of all rather insensible to interference, which is a key point in order to have convincing experiment in a controversial field. Moreover, an ice calorimeter is adiabatic and isotherm (0°C) thus suppressing the problem of heat transfer in wires and tubing connecting the experiment to the outside of the calorimeter. It is an integrating calorimeter that measures enthalpy.

Principle of the measurement

At 0°C, 1 gram of ice occupies 1.0908 cm^3, 1 gram of water 1.0001 cm^3. Thus, when 1 gram of ice melts, its volume shrinks by $\Delta V = 0.0907\ \text{cm}^3$. The measured reduction in volume of a mixture of melting ice and water thus indicates the number of grams of ice which have melted, and thus the amount of energy deposited in the calorimeter. To measure the volume of melted ice, an automatic sensing unit has been designed that weights a reserve of the indicator liquid, mercury (see below, description of the calorimeter).

$\left(d_{Hg}\right)_{0°C} = 13.595\ \text{g/cm}^3$ being the mercury density at 0°C

$\Delta H_w = 6.01\ \text{kJ} \cdot \text{mol}^{-1} = 333.7\ \text{J} \cdot \text{g}^{-1}$ being the latent enthalpy of fusion of ice

The total energy deposited in the calorimeter is:

$$H = \left(\Delta H_w \cdot \frac{m}{\left(d_{Hg}\right)_{0°C} \cdot \Delta V} \right) \cdot \chi$$

where m is the weight of mercury which is transferred from the reserve tank during the experiment and χ a correction factor due to the buoyant force on the capillary tube (see Figure 1). χ was measured to be 0.998.

Thus for m = 1 gram, the constant of the calorimeter is $H_0 = 270.085\ J / g_{Hg}$

Description of the calorimeter

A cylindrical insulated container, 40 cm diameter and 75 cm high, is filled with a mixture of ice and water (melting ice). The ice is generated through an ice machine from very pure water (distilled and then passed through resins) so that the temperature of the melting ice is very close to 0°C.

The calorimeter itself is placed inside the container and is completely surrounded by the melting ice. All tubes and electrical wires connecting the reactor inside the calorimeter are immersed in the melting ice (for a length of about 1 m), thus avoiding exchanges of heat with the outside. The calorimeter is made from Pyrex (or alternatively stainless steel). Its total volume is some 3000 cm^3, which is filled with ultra pure water. Figure 2 shows a detailed description of the calorimeter: the well inside the calorimeter (36 mm diameter, 340 mm high) contains the experiment where energy is released. It is filled with a mixture of water and ethanol. This well is surrounded by an ice layer, formed prior to the experiment by inserting a tube in the well, where water mixed with ethanol flows at a temperature of around -15°C. At the bottom of the calorimeter, a 5 kg reserve of pure mercury is placed. The mercury is hydraulically connected to an Erlenmeyer through a Pyrex (or alternatively stainless steel) capillary tube. The Erlenmeyer is placed on a scale where its weight can be recorded. The mercury in the Erlenmeyer is covered by a layer of water for safety reasons. No mercury can thus be detected on top of the water layer, and it has been shown that the rate of evaporation of this water is sufficiently low not to have any influence on the measurements. In first approximation, the whole measuring system is thus isotherm and adiabatic. Checking the constancy of the temperatures of the melting ice during an experiment is of prime importance. This is done by four temperature sensors (Pt 100) one in the middle of the container, a second one at the bottom of the container, a third one at 5 cm of the bottom and the last one at 10 cm. These sensors where not calibrated (what is important is that their indication remains constant during an experiment). An increase of the bottom temperature indicates the formation of a water layer transferring heat from the outside to the calorimeter. The measurements are then no longer valid. The calorimeter is placed in a temperature regulated room and the outer container is surrounded by a temperature regulated water jacket.

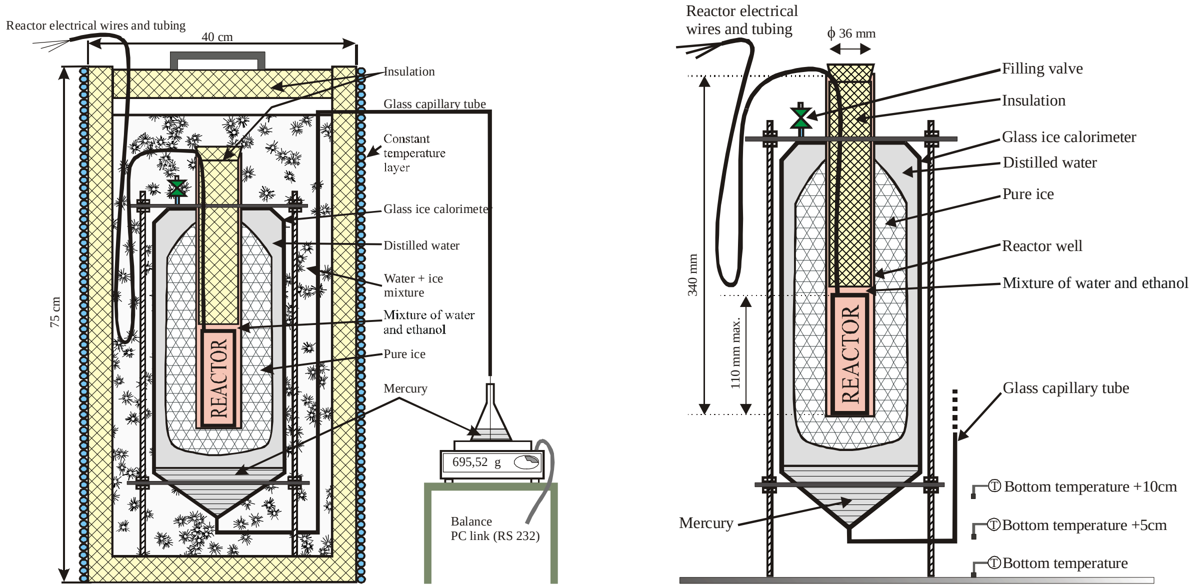


Figure 1. The calorimeter setup.

The detailed conditioning procedure of the calorimeter is not given here. An important step is the complete degassing of the ultra pure water filling the calorimeter.

Description of an experiment

The cylindrical container is first replenished with fresh ice and water. The reactor is placed in the well, after the ice layer has been formed and the calorimeter is left until the weight of the mercury reaches the base line (nearly horizontal straight line). The baseline value “before the experiment” is recorded for 3000 seconds. The reaction to be studied is then initiated: heating, electrolysis, electrical discharge or hydrogen admission.

Figure 2 shows a typical example of mass as a function of time. Due to the energy released, part of the ice layer melts and the mercury reenters the calorimeter, thus showing a decrease of the recorded weight. The experiment phase is recorded for 6000 seconds (for a typical energy input of 8000 J), after which the calorimeter reaches the "after experiment" baseline, which is then recorded for 3000 seconds. The total mass m of the mercury transferred is then measured (as shown in Fig. 2) and the energy released calculated from the calibration curve of the calorimeter (see below). The mass of the mercury is recorded every 30 seconds during the 2 base lines. This mass, together with the electrical energy injected (intensity and voltage) and H_2 / D_2 flow rate (for gas admission) are recorded every second during the experiment phase.

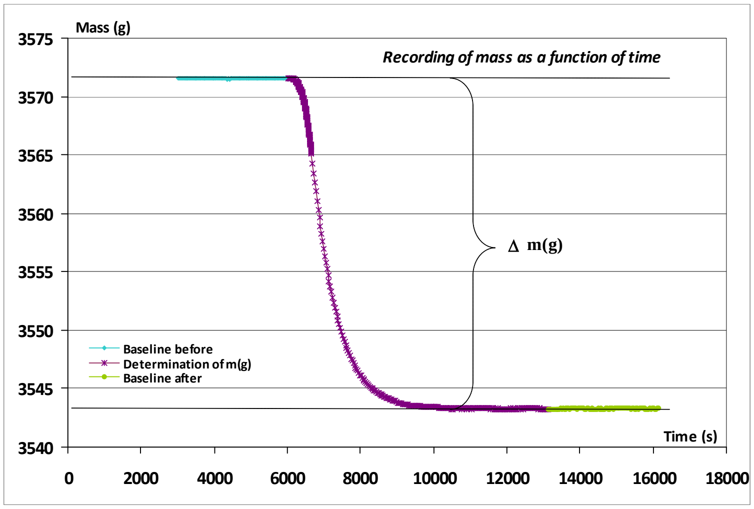
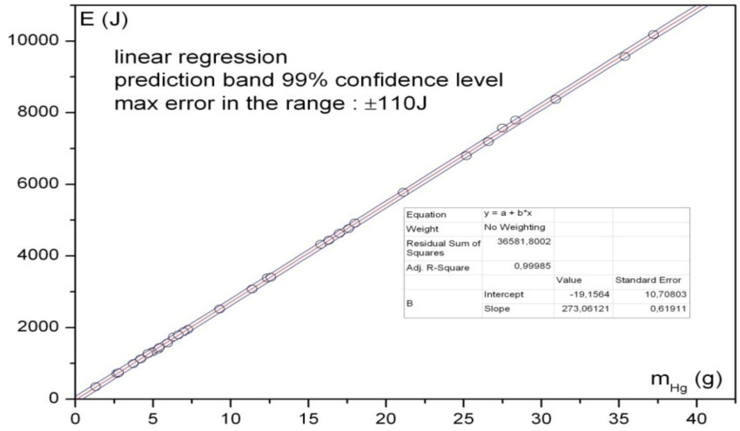


Figure 2. Typical example of mass as a function of time.

Calibration of the calorimeter

The calorimeter has been calibrated using resistors heated by direct current (DC), placed in various positions in the well and in reactors fitting the well. The results of these calibrations are shown on the following graph 2, where the amount of energy entering the calorimeter as electrical energy is plotted against the weight of mercury transferred. 32 measurements were performed, for P_{in} varying from 350 to 10000 J.



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	36581,8002		
Adj. R-Square	0,99985		
		Value	Standard Error
B	Intercept	-19,1564	10,70803
	Slope	273,06121	0,61911

Figure 3. Calibration with direct current resistors.

The linear regression prediction band at 99% confidence level has been calculated (Fig. 3) and shows that, at this level of confidence, the maximum error is in the range ±110 J.

In this regression, the constant of the calorimeter has been calculated to be 273.06 J/g_{Hg}, in good agreement with the value of 270.085 J/g_{Hg} calculated from published values of the thermodynamic properties of pure water and mercury.

Based on the fact that the direct current electrical energy input, is measured with a precision of 0.5%, it can be seen that at the level of 10000 J, the precision of the calorimeter is ±1.5%.

The duration of an experiment is limited by the melting of the ice in the cylindrical container that surrounds the calorimeter. As a result of this melting, a layer of pure water forms at the bottom of the cylindrical container and the temperature of this layer starts increasing (the maximum density of water occurs at 4°C). For an experiment to be valid, this layer must not reach the level of the mercury capillary. The upper limit of the energy that can thus be measured is 15000 J.

An example of application of the ice calorimeter: unexplained heat effects during palladium gas loading with hydrogen isotopes

Scope of the experiment

It has been reported [2] and [3], that unexplained heat effects occur when gas loading palladium with hydrogen isotopes. The palladium used is in a very dispersed form and deposited either on carbon black [2] or on Zr oxide [3]. These effects are characterized by the evolution of the temperature taken at one representative point of the palladium under loading. A comparison is made of this evolution for both isotopes. In [3], the effect shows up, only in the case of deuterium, as a long delay for the representative temperature to go back to base line, The ice calorimeter has shown this effect with such a sensitivity, that only 1 g of unsupported palladium black, activated at 450°C for 4 h under 3 Pa, gave a response.

Description of the experimental set-up

A schematic of the experiment is shown in Figure 4. A cylindrical reactor, fitting the well of the calorimeter is connected through flexible tubing, to a manifold. This manifold connects a bottle of hydrogen (deuterium) to a vacuum pump. A metering valve allows controlled injection of the isotope of hydrogen from the bottle. A flow-meter (Brooks 5860 E) measures the flow of hydrogen entering the reactor and a Pt 100 the temperature of the reactor. The pressures in the manifold (and the reactor) are measured. A heater (regulated up to 500°C) is placed close to the calorimeter.

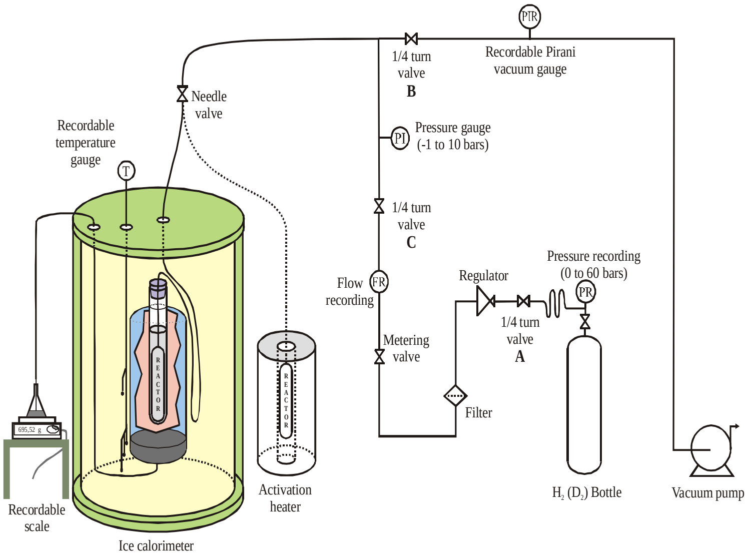


Figure 4. Schematic of experiment.

Description of an experiment

1 g of palladium black (Alpha Aesar 00659 Lot 0109400, purity 99,9%) is placed in a Pyrex tube in the reactor. The reactor is closed and placed in the heater where the palladium black is activated (450°C, 3 Pa for 4 hours). After cooling, the reactor is placed in the calorimeter without opening it. It is maintained under vacuum. After the base line registration, hydrogen (deuterium) is admitted in the reactor. The calorimeter then reaches the "after experiment" base line and the mass m is measured.

Results of the experiments

The main result is illustrated in Fig. 5. It can be seen that, for deuterium, the mass m of mercury reabsorbed by the calorimeter does not stabilize and goes on decreasing well after the usual base line should have been reached, although the temperatures of the melting ice in the container (bottom, bottom + 5 cm and bottom + 10 cm) have remained perfectly stable. This unexplained decrease is observed well after the end of the deuterium loading and corresponds to an extra power of some 2 mW (which could be heat after death [4]).

This result is not observed when hydrogen is used instead of deuterium.

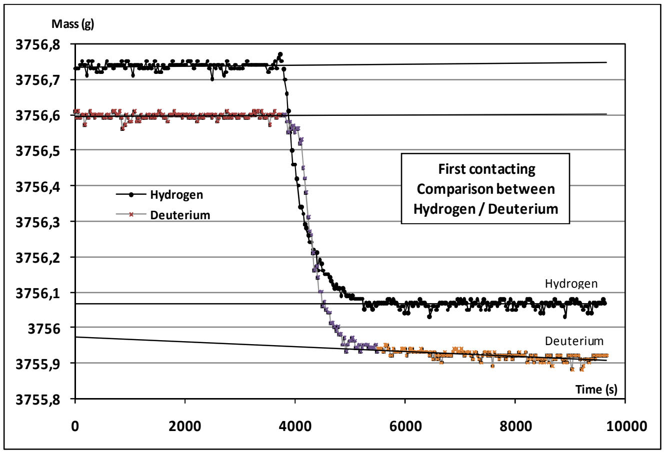


Figure 5. Main result of the experiment.

Conclusion

Ice calorimetry is a first principle method. It measures enthalpy with high absolute precision and sensitivity. This calorimeter is specially adapted to gas loading experiments.

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