A double twin isothermal microcalorimeter

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Abstract

The design and properties of a double twin heat conduction microcalorimeter are described. In this instrument two twin microcalorimeters are placed close together, one on top of the other. The size of the instrument is the same as that of a commercial single twin microcalorimeter and each of the twin parts has similar properties as one normal twin microcalorimeter. The cross-talk between the calorimeters can be made low; we measured <0.1% of the signal generated in one calorimeter in the other calorimeter. This figure is, however, dependent on how well the two sides of the instrument are thermally balanced. The paper also contains a general discussion of the use of a reference in reducing the effect of temperature changes in the heat sink.

The advantage with a double calorimeter is that one may easily perform two related calorimetric experiments at the same time and in close proximity to each other, e.g. both sorption isotherms and sorption enthalpies may be measured simultaneously, or the heat production rate of a biological process may be monitored at the same time as the CO_2 production is measured. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Isothermal calorimetry is the measurement of heat and thermal power at constant temperature. This is a very general measurement technique as almost all processes (physical, chemical, biological) produce heat. Isothermal calorimetry is today used to study such diverse processes as microbiological growth, cement hydration and stability of pharmaceuticals and explosives [1–3].

Isothermal calorimeters are primarily used to study processes by the heat the processes themselves produce. There have, however, also been reported more advanced measurements where a second calorimeter has been used to assess a secondary parameter characterizing the same process. One example is the simultaneous monitoring of a biological process in one calorimeter and the on-line measurement of the same process' CO_2-production in a second calorimeter reported by Johansson and Wadsö [4]. The calorimetric CO_2 measurement was made by measuring the thermal power produced when the gas stream containing the CO_2 was bubbled through a NaOH-solution.

Another example is a number of sorption calorimeters in which water is vaporized in one calorimeter and absorbed by a sample in another calorimeter [5–9]. In these instruments one of the calorimeters measures the thermal power of sorption (the sorption enthalpy) and the other measures the thermal power of vaporization (from which one may calculate the mass change and/or vapor pressure of the sample). A

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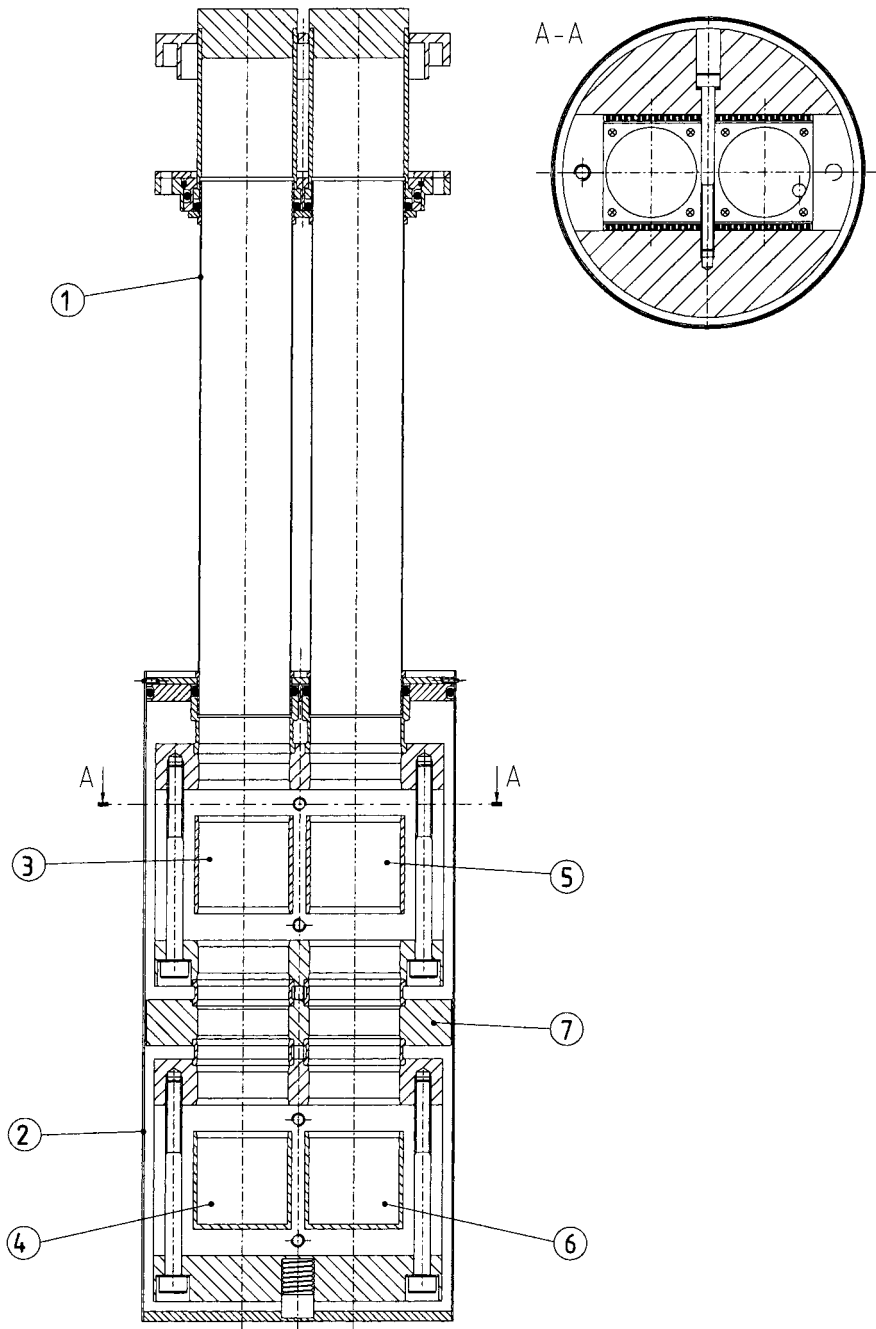E-mail address: lars.wadso@byggtek.lth.se (L. Wadsö).

Fig. 1. Cross sections of the double twin microcalorimeter. (1) Tubes through which the calorimeters are charged; (2) steel can; (3) top reference ampoule position; (4) bottom reference ampoule position; (5) top measuring ampoule position; (6) bottom measuring ampoule position; (7) heat flow breaker (cf. text).

microcalorimeter of the type presented in this paper measures, for example, 50 μW with better than 1% accuracy. If this thermal power is produced by the vaporization of water it corresponds to a mass change rate of 20±0.2 ng/s. This is clearly a sensitive way to measure the rate of mass change of a vaporizing liquid.

The examples given above have in common the simultaneous measurements in two heat conduction calorimeters. As it is advantageous to make such double measurements in two calorimeters placed as close to each others as possible we have designed one calorimetric unit with two microcalorimeters. Apart from the quadruple calorimeters designed by Calvet [5,6] and the prototypes of the present instrument [8,9] we know of no other double twin microcalorimeters.

2. Instrument

Fig. 1 shows a drawing of the instrument. The double microcalorimeter is composed of two differentially connected twin calorimeters; one placed above the other. It has been designed to fit into the 2277 TAM ampoule calorimetric unit of Thermometric AB (Järfälla, Sweden). The two calorimeters of the double twin calorimeter are therefore housed in the same type of steel can as one twin 2277-000 20 ml ampoule microcalorimeter. This has been made possible by the use of smaller heat sinks and a heat flow breaker between the two twin calorimeters so that they will not disturb each other.

The heat flow breaker has low thermal contact with the two calorimeters. At the same time it has more contact with the thermostated bath than the calorimeters so the major part of a heat leak from one calorimeter towards the other will flow out into the bath instead of disturbing the other calorimeter.

In a double twin calorimeter the properties of the instrument will be dependent on the measurement vessel used. Except for calibration coefficients and time constants the properties of the instrument will, therefore, be described with the inserted sorption vessel that is schematically shown in Fig. 2. The top part of the vessel is positioned in the top calorimeter and the bottom part is positioned in the bottom calorimeter. The top and bottom parts of the vessel are connected by a 9 mm diameter tube with a low thermal conductance as it is made of stainless steel with a
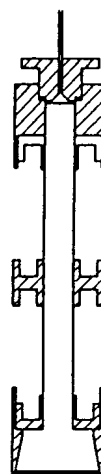

Fig. 2. A cross section of the sorption vessel used to test the double twin microcalorimeter. During a sorption measurement the bottom ampoule is charged with a sample and the top ampoule is charged with water.

thickness of 0.1 mm. A heat exchanger in contact with the heat flow breaker is placed on the middle of the tube. A similar vessel is placed in the reference (the top part of the present vessels were slightly different, cf. Fig. 3 below). Wadsö and Wadsö [9] describe the use of the vessel for measuring sorption isotherms and sorption enthalpies for vapor sorption on solid substances.

3. Thermal model

Fig. 3 shows the heat transfer model used to optimize the design of the calorimeter. Each circle is a heat capacity in the calorimeter and each line denotes a heat conductance between heat capacities. This type of model is realistic for a microcalorimeter that consists of different blocks of aluminum with very good internal thermal conductivity separated by air gaps and heat flow sensors with relatively low thermal conductivity. The heat capacities were calculated as the sum of the heat capacities of the parts, e.g. C_4 is the sum of the heat capacity of the top part of the sorption vessel, the ampoule holder, and half the thermocouple plate. The thermal conductances were estimated by connecting the relevant parts in series and parallel, e.g. k_{12} is the thermal conductances of two steel screws and two plastic distances, all in parallel. Data on the
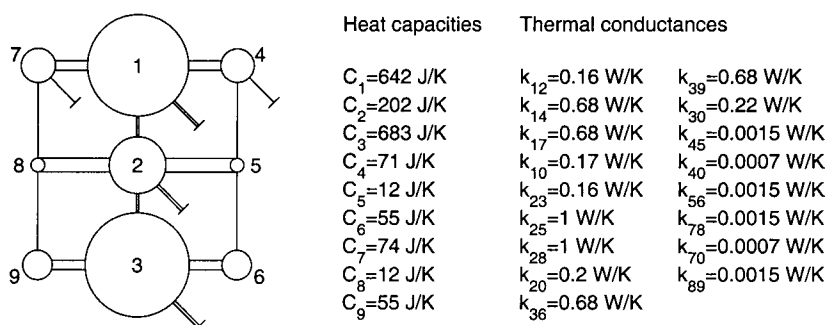
Fig. 3. A thermal model of the microcalorimeter with the sorption vessel. (1) Top heat sink; (2) heat flow breaker; (3) bottom heat sink; (4) top measurement ampoule; (5) measurement side heat exchanger; (6) bottom measurement ampoule; (7) top reference ampoule; (8) reference side heat exchanger; (9) bottom reference ampoule. The area of the circles are proportional to the heat capacities of the parts (the ampoule parts include the ampoule holders, but not any sample as this is comparatively small in this type of instrument). The width of the lines are proportional to the thermal conductance between the different parts. The lines angled down right are the thermal connections to the water thermostat. Parts 5–6 and 8–9 are embedded within the calorimeter and have no direct connections to the thermostat. The indices of the thermal conductances indicate which heat capacities the conductances connect; '0' is the surrounding thermostat.

thermocouple plates were from the manufacturer (Melcor, Trenton, NJ, USA). It should be noted that the heat capacities are easy to calculate rather accurately, but the thermal conductances are much more difficult to assess, and will therefore, have quite large uncertainties. However, the model presented is good enough to show the principles of the instrument and it gives results close to those found from measurements.

The model has been solved for different cases with a forward difference program written in MATLAB 5 (MathWorks, Natick, MA, USA). Some results are given in the sections below. The methods used may be found in modern text-books on heat transfer, e.g. Hagen [10].

4. Results and discussion

4.1. Calibration coefficients

Calibrations of different types have been made both with the internal calibration heaters (situated in the ampoule holders) and with insertion heaters. The latter was problematic as the electrical leads to the bottom insertion heater had to pass through the top calorimeter. Therefore, the results presented here are mainly from calibrations of the empty calorimeter with the internal heaters.

The calibration coefficient is the factor the voltage output from a calorimeter has to multiplied with to

yield the thermal power. Theoretical calibration constants based on data from the manufacturer of the thermocouple plates (Melcor, Trenton, NJ, USA) are 6.0 W/V for both the top and the bottom calorimeters as they have the same type of thermocouple plates. Table 1 gives the measured calibration coefficients for the empty calorimeter. Similar values were obtained when the calorimeter was calibrated with the sorption vessel in place.

When measured calibration coefficients are higher than theoretically derived values this is usually thought to reflect that part of the heat flow does not pass through the heat flow sensors [11]. Part of the difference seen may, however, also be caused by inaccuracies in the data used for the heat flow sensors.

4.2. Time constants

The time constant is a measure of the time lag between the thermal power generated in a calorimeter and the signal registered from the calorimeter [12].

Table 1
Calculated and measured calibration coefficients and time constants, both for a empty calorimeter

	Calibration coefficient (W/V)		Time constant (s)	
	Top	Bottom	Top	Bottom
Calculated	6.0	6.0	45	49
Measured	6.9	7.3	45	47

Table 1 gives values of measured (empty calorimeters) and calculated time constants. The calculated time constants are found from heat capacities and thermal conductances, e.g. $\tau_{top} = C_4/k_{14}$ [12]. The values agrees well.

4.3. Cross-talk

One obvious problem of placing two calorimeters very close to each other is that a certain fraction of the heat produced in one calorimeter will flow to the other calorimeter and give a signal there. In our earlier designs [8,9] the cross-talk was nearly one percent and one main aim with the design of the present instrument was to lower this value.

The cross-talk is the ratio of what is measured in calorimeters 1 and 2, when the thermal power is only produced in calorimeter 1. Its numerical value depends to some extent on how it is defined. We have used the following definition of cross-talk: a 1200 s thermal power pulse is applied in calorimeter 1. The cross-talk is the maximal (peak) thermal power measured in calorimeter 2 divided by the maximal (peak) thermal power measured in calorimeter 1.

Table 2 gives measured values of the cross-talk. It is not known how accurate these values are as the signal measured in calorimeter 2 is very low. We have also made simulations of the cross-talk and found that it is extremely dependent on imbalances in heat capacities and heat conductances within the twin calorimeters; it is lowest when the reference side exactly matches the sample side (in the model given in Fig. 3 there is a perfect symmetry between the sample and reference sides in the bottom, but not in the top).

In a perfectly balanced calorimeter, the heat leaks from calorimeter 1 will influence the sample and reference sides of calorimeter 2 nearly equally, and

thus, give no net signal. This is because almost all the heat flow between the two calorimeters goes through k_{12} and k_{23} (as k_{45}, k_{56}, k_{78}, and k_{89} are much lower, cf. Fig. 3), and therefore, enters the other calorimeter symmetrically. If, however, calorimeter 2 is unbalanced it does not help that the heat enters symmetrically; it will still influence the sample and reference sides differently, and thus, give a net signal.

To asses a practical value of the cross-talk we have made Monto–Carlo simulations with normally distributed heat capacities and thermal conductances (5 and 10% standard deviations for heat capacities and thermal conductances, respectively). The result is given in Table 2. Note that the numerical start model (before the normally distributed errors are added) is perfectly symmetrical except for the two top ampoules (C_4 and C_7). Therefore, the bottom-to-top cross-talk is higher than the top-to-bottom cross-talk. Comparison with the measured cross-talks indicates that the actual imbalance in our top calorimeter is not as large as in the simulation model.

The measured cross-talks are insignificantly low so the two calorimeters of the double calorimeter do not in practice disturb each other. It should, however, be noted that it is important to make all parts and paths of the reference side closely similar to those of the sample side, e.g. one should have the same type of vessel in the reference side as in the measurement side.

4.4. Linearity

A calorimeter is linear when the calibration coefficient does not depend on the level of thermal power. The double twin microcalorimeter has been calibrated with thermal powers between 25 and 1300 µW and the calibration coefficients were are almost constant; the coefficients of variation (standard deviations divided by the mean) were 0.4 and 0.1% for top and bottom calorimeters.

4.5. Periodic disturbances

Fig. 4 gives the result of simulations with periodic temperature disturbances in the surrounding thermostated bath. The amplitude of the disturbance has been kept constant at 0.1 mK (stated stability of Thermometric 2277 thermostat [13]), but the period of the disturbance (i.e. the inverse of the frequency) has been

Table 2
Results from measurements and Monte–Carlo simulations of the cross-talk in the double twin calorimeter with the sorption vessel (cf. discussion in text)[a]

	Top-to-bottom (%)	Bottom-to-top (%)
Measured	0.04	0.06
Simulated	±0.01	−0.26±0.02

[a] For the measurements the actual values are given; for the simulations the range in which approximately 90% of the result was found is given.
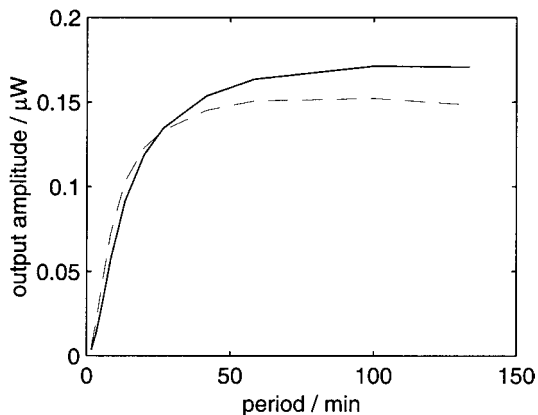
Fig. 4. Results from simulations of the double twin microcalorimeter with periodic temperature variations in the thermostated bath and a 5% difference between the heat capacities in the sample and reference cells.

varied. The main function of the references in the calorimeters is to decrease outside disturbances. If we have a reference side with the same thermal properties as the measurement side, outside disturbances will influence the sample and reference sides in the same way, and the disturbances in the sample and reference signals will cancel out as the signals from the two parts of the twin calorimeters are differentially connected. We do, however, never have exactly matched references and the result seen in Fig. 4 is the result from simulations when there is a 5% imbalance between sample and reference ampoules (both top and bottom). This imbalance is probably quite typical for what is normally achieved by matching the heat capacities in a microcalorimeter. It is seen that for both the top and the bottom calorimeters the curve has a very flat maximum, so that periodic disturbances with a period
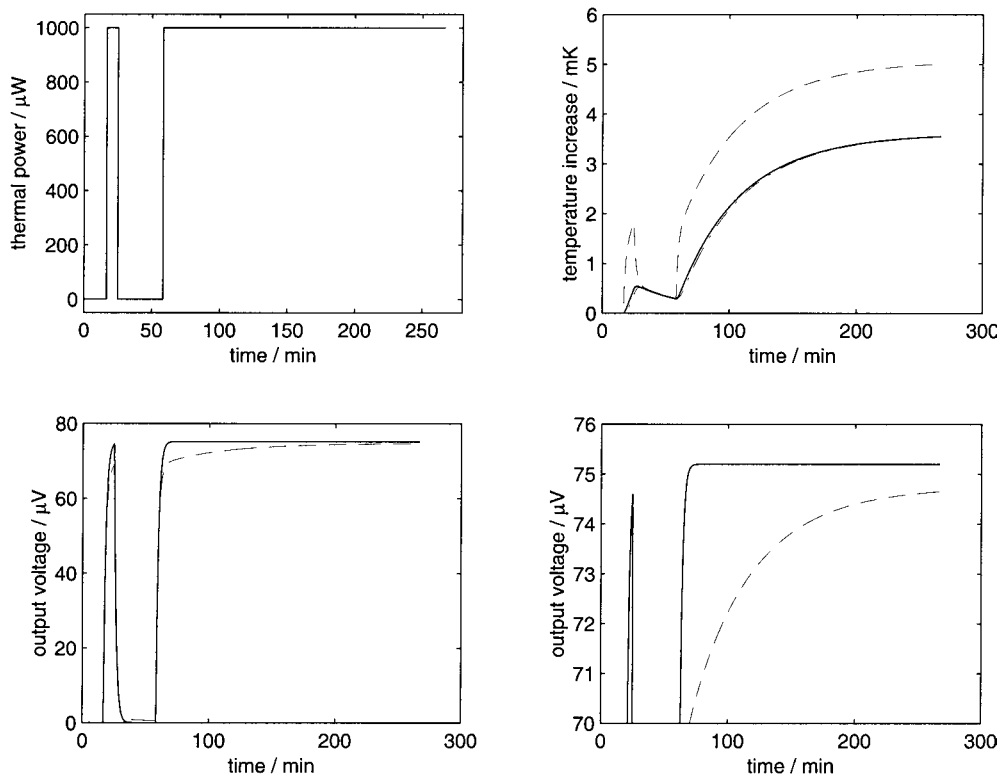

Fig. 5. Result from a simulation of a thermally balanced top part of the double microcalorimeter. (a) The thermal power program; (b) the temperature increases in the heat sink (solid line), the sample (dashed) and the reference (dash-dotted); (c) the voltage output from the calorimeter with (solid) and without (dashed) a reference; (d) part of the curve shown in Fig. 5c enlarged to show the time dependent output.

above 20 min will give about the same output thermal power amplitude of approximately 0.15 μW, which is lower than the stated detection limit of 0.2 μW of the Thermometric 2277-000 instrument on which we have based our design [13].

4.6. Temperature changes in the heat sink

Fig. 5 shows the result of a simulation of a measurement in the top part of the calorimeter. The thermal power program shown in Fig. 5a gives the temperature changes in the calorimeter shown in Fig. 5b. It is seen that the heat sink temperature increases during the measurement. However, note the small temperature increases that result from the application of the quite high thermal power of 1 mW for several hours [14].

In the simulation example shown in Fig. 5 there are no outside disturbances, but it clearly illustrates a second not so well known function of the reference. As heat is produced in the sample the heat sink temperature will rise (Fig. 5b). Because of this the output signal from the sample heat flow sensor (if no reference is used) will be slightly lower than it would have been if the temperature of the heat sink had been constant. The dashed line in Fig. 5c–d show the result of not having a reference. Fig. 5b shows that the temperature of the reference is slightly lower that that of the heat sink. If the sample and the reference have the same thermal properties the output signal from the reference side is exactly what we need to add to that of the sample side to get the output we would have had from the sample side if the heat sink would have had a constant temperature. This is the second important function of a reference and if we do not use a reference we will have an output signal that will not come to a steady state even after very long times with a steady state thermal power input.

5. Conclusions

The double twin microcalorimeter works essentially like two separate microcalorimeters, but with the advantage of having the two calorimeters in one unit. The cross-talk was insignificantly low in our calorimeter, but may present a problem in less well balanced designs.

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