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DESIGN AND CHARACTERISTICS OF A DIFFERENTIAL CALORIMETER FOR HIGH-TEMPERATURE MEASUREMENTS

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SUMMARY

A high-temperature differential calorimeter developed from the Setaram "HT 1500 Calorimeter" has been built for isothermal measurements in inorganic systems at temperatures between 600 and 1750 K. Details of the mechanical design, the auxiliary equipment and the performance (mode of operation) of the calorimeter are given. Enthalpic effects ranging from about 5 to 200 J have been measured with a reproducibility and accuracy of approximately ±2,5%. During calorimetric measurements conducted over a period of several months at high temperatures, the new differential calorimeter proved reliable and safe to operate.

INTRODUCTION

During the last decade, the Setaram HT 1500 Calorimeter has been used frequently for enthalpy measurements at high temperatures, see e.g. Gaune-Escard and Bros (ref. 1), Arpshofen et al. (ref. 2), Pool et al. (ref. 3), Hatem et al. (ref.4), Naumann and Petzold (ref. 5), Klein and Müller (ref. 6). The design of this apparatus and its mode of operation have been described in detail, and its features have been investigated and discussed thoroughly by Gaune-Escard and Bros (ref. 1), Arpshofen et al. (ref. 2), Pool et al. (ref. 3). The special advantages of this apparatus are: It can operate continuously at relatively high temperatures (1750 K), and allows minimum heat effects of approximately ±2 J to be measured with a reproducibility of about 2,5 %. Because its temperature can be changed rapidly, it can be operated not only isothermally, but also in a scanning mode. In case of damage, the calorimetric detector can be repaired easily, or may be replaced at relatively low cost.

However, the apparatus has one particular deficiency. Since the alumina sample crucible (in which the sample reacts during a calorimetric measurement) is coronally surrounded by eight temperature sensors only positioned at half height, the calibration factor (sensitivity) of the calorimeter depends on the height to which the crucible is filled and hence on the sample mass in the crucible (refs. 2-5). Calorimetric measurements performed in this laboratory confirmed this "filling effect". However, it has

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also been found that the calibration factor is constant with respect to the filling height, if the sample crucible is lined with a platinum crucible (ref. 6), which apparently provides rapid heat conduction along the wall of the sample crucible and, in addition, good thermal contact with the sample. Even so, efforts have been made to eliminate the dependence of the calibration factor on the filling height by arranging, around the sample crucible, temperature sensors in two planes (ref. 7).

In the present study, a high-temperature differential calorimeter developed from the Setaram HT 1500 Calorimeter is described: The mechanical design of the calorimetric detector is explained in detail and the features of the calorimeter are investigated by several different measurements. On the basis of the results thus obtained, improvements to the calorimeter with respect to the original apparatus are discussed.

DESIGN OF THE CALORIMETRIC DETECTOR

The essential details of the design of the calorimetric detector are schematically shown in the dimetric representation in figure 1 and in the sectional view illustrated in figure 2. The detector is composed of the following main parts:

- two crucibles, arranged one above the other,
- two "grooved tubes", one of which surrounds the upper crucible, while the other encloses the lower one; into the wall of each tube 52 grooves equidistantly cut from the outer surface, run parallel to the longitudinal axis.
- two "end plates", one of which is located in the bottom end of the upper grooved tube, while the other is inserted into the top end of the lower grooved tube,
- a thermopile, composed of (28 + 28) Pt-30mass-%Rh/Pt-6mass-%Rh couples interconnected in series,
- one "protecting jacket" tightly enclosing the grooved tubes,
- one "supporting tube" suspended from three two-bore tubes.

All the ceramic parts are made from α-alumina (purity: 99.7 mass-% Al_2O_3).

The upper crucible (inside diameter 13 mm, height 40 mm), which accomodates the sample during a calorimetric run, together with the surrounding grooved tube and end plate represents the "working cell", while the lower crucible, together with the corresponding grooved tube and end plate constitutes the "reference cell" of the differential calorimeter. The thermopile, which extends from the grooved tube and end plate of the working cell on the one hand to the grooved tube and end plate of the reference cell on the other, monitors the temperature difference between the calorimetric cells. In order to position the thermojunctions of the thermopile, holes are

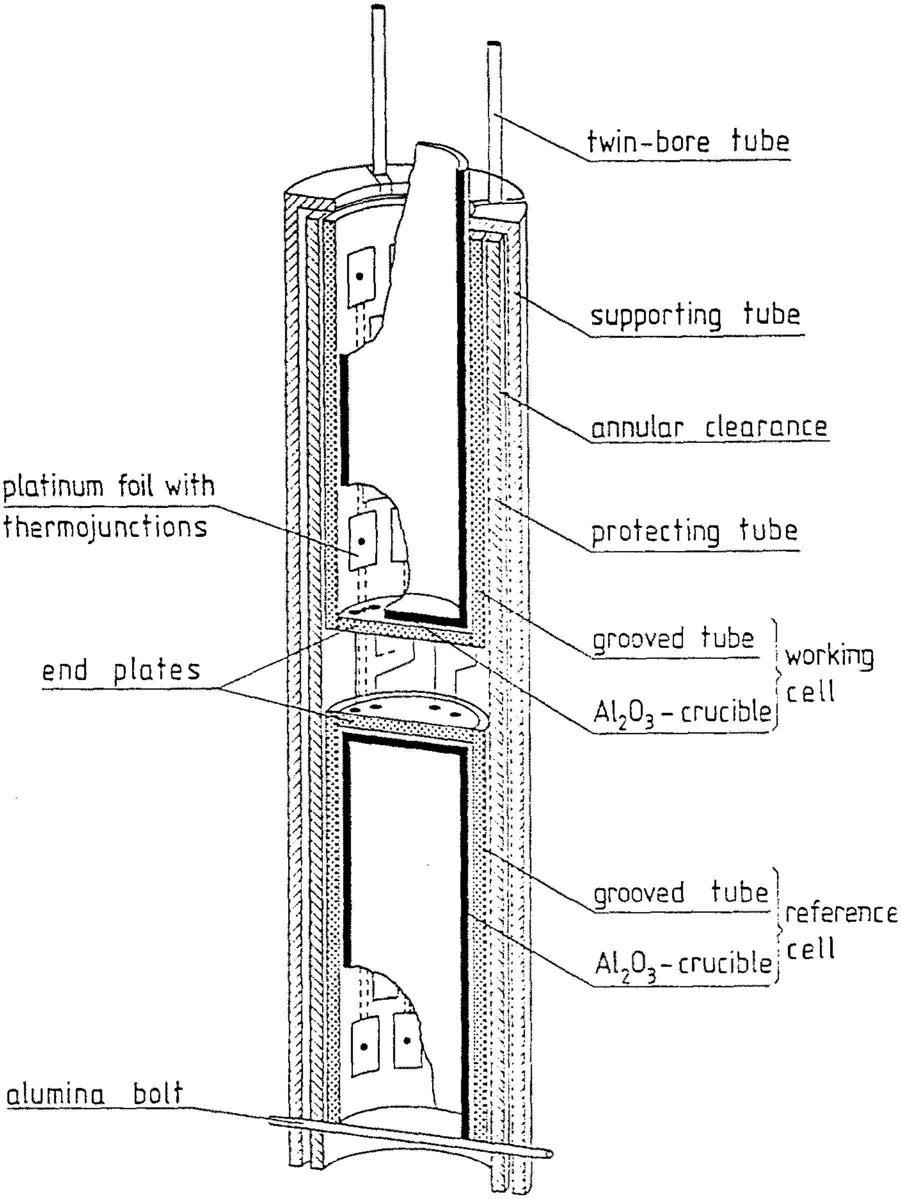

Fig. 1. Dimetric representation of the calorimetric detector (schematic).

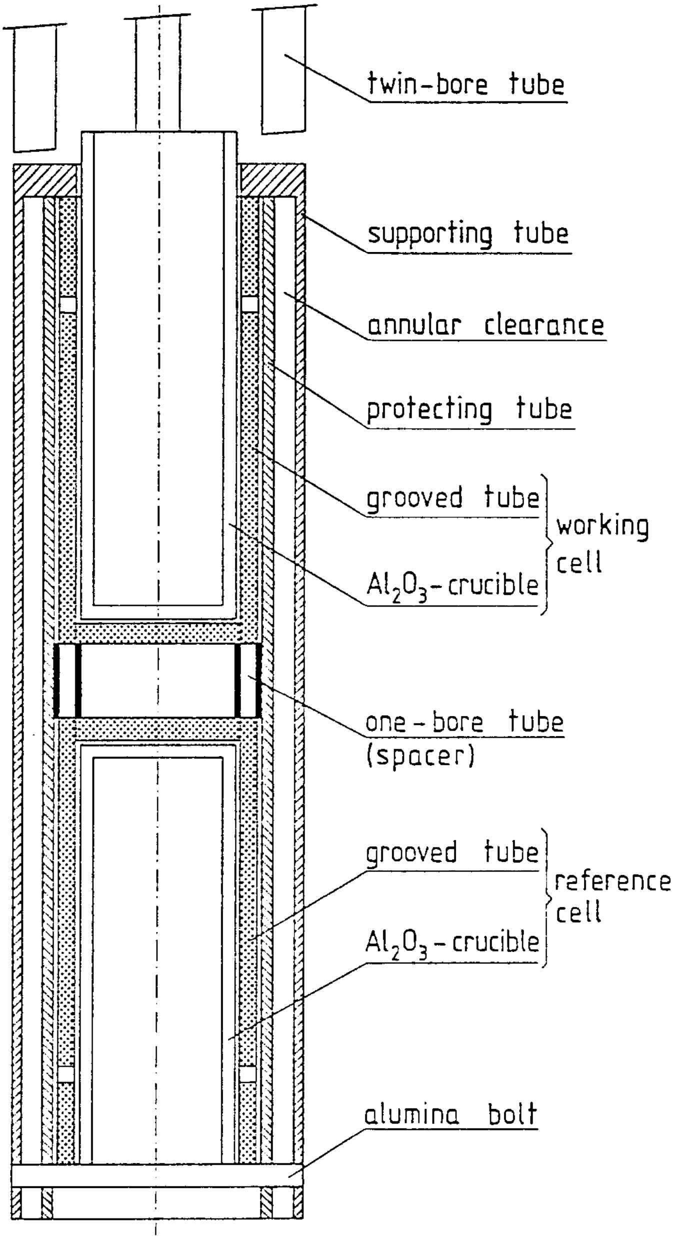

Fig. 2. Diagram showing the sectional view of the calorimetric detector (schematic).

distributed regularly in the grooved tubes and end plates: In the wall of each tube, 24 holes are arranged in 4 planes situated equidistant from each other and vertical to the longitudinal axis of the tube; in each end plate, 4 pairs of holes are located on a circle; thus, for each hole of the working cell a mirror-inverted counterpart exists in the reference cell. Each pair of corresponding holes is interconnected by two "neighbouring leads" (Pt-Rh6 + Pt-Rh30) of the thermopile. Along the walls of the grooved tubes, these leads run through the grooves, while, within the gap between the end plates, the leads are electrically insulated from each other by single-bore alumina tubes. On the walls of the grooved tubes, the thermojunctions formed by two neighbouring leads are passed through the holes, and, at the inside of the grooved tubes, each junction is welded to a piece of platinum foil (thickness $\approx 25\mu m$) fitting closely into the very narrow gap ($\approx 0,05$ mm) between the inner surface of the grooved tube and the outer surface of the crucible. The complete set of platinum foil pieces fixes the thermojunctions of the thermopile and ensures an excellent thermal contact between the thermopile and the crucibles. The thermopile leads which bridge the gap between the end plates run separately through holes from the outside to the inside surface of the end plates, where neighbouring leads are welded together to form thermojunctions making direct contact with the bottom of the crucibles. Here, the density of thermojunctions is sufficiently high to ensure a high "thermal effectiveness" without use of platinum foil.

The assembly composed of the working and measuring cells is enclosed by the protecting jacket, which aligns the grooved tubes and locks the thermocouple leads in position. The jacket is in turn surrounded radially by the supporting tube so that the radial clearance between the jacket and the tube has a constant width of 1 mm. The supporting tube is suspended from three twin-bore alumina tubes and adjusted in a zone of constant temperature, see below. Samples are introduced into the calorimeter through an alumina tube ("charging tube"), the lower end of which encloses tightly the top end of the working crucible. The temperature of the calorimeter is measured by a Pt-30mass-%Rh/Pt-6mass-%Rh thermocouple, the hot junction of which is located at the bottom of the working crucible. The end leads of the thermopile and the legs of the thermocouple reading the calorimeter temperature run through the bores of the twin-bore alumina tubes to a plug socket from where the measured values are fed into a data processing system, see below.

AUXILIARY EQUIPMENT

The calorimeter is suspended in an alumina tube which in turn is surrounded by a graphite tube, and this tube system is mounted in a water-cooled vacuum jacket. The graphite tube acts as heating element which, due to its special profile, enables a sufficiently large zone of constant temperature to be established around the calorimeter. The electric power fed into the heating element is taken through an electronic AC voltage stabilizer (Philips PE 1605) from the public mains. The stabilizer maintains the voltage constant to within 0.1%, while the electric power is regulated by thyristors.

Before initiating an experiment, the vacuum jacket accomodating the calorimeter chamber and the heating element is evacuated by a rotary pump (0,1 Pa), and, during a measurement, it is flushed with argon gas (purity: 99.9998 vol.-%). Flow controllers keep the flow rates of the flushing gas and of the water used for cooling the vacuum jacket at fixed values of 3 cm^3 s^{-1} and 25 cm^3 s^{-1}, respectively; these had been proved to be optimum values in test runs.

MODE OF OPERATION OF THE CALORIMETER

Prior to the commencement of a measurement, steady state conditions are established in the calorimeter. Under these conditions, the thermoelectric voltage, U, of the thermopile shows a constant basic value, U_0. When an enthalpic effect occurs in the calorimeter, the temperature of the working cell is changed with respect to the temperature of the reference cell, and U accordingly changes with respect to U_0. During a measurement, U is determined as a function of time, t, amplified, digitized, and then stored in a Hewlett-Packard 86 B computer. After the calorimeter has returned to the initial value of U_0, the computer calculates the integral

$$I = \alpha \int (U-U_0)dt$$

over the measurement period; here α denotes the amplification factor and I is proportional to the enthalpy change of the sample. The proportionality constant is derived by calibration, see below. The voltage of the thermocouple used for the measurement of the calorimeter temperature is measured using an electronically compensating reference unit, linearised and digitally displayed to $\pm$0,1 K.

CALIBRATION

The calorimeter is calibrated by the drop method: Spheres of platinum or α-alumina (sapphire) at room temperature are dropped into the calorimeter operating at the measurement temperature. The masses of the spheres are chosen so as to produce heat effects which are as similar in magnitude as possible to the heat effect of the corresponding reaction run. The calibration factor, f, is calculated from the relation,

$$f = \frac{\Delta H}{I} \quad (1)$$

The enthalpy change, ΔH, which the calibration sample experiences in the calorimeter, may be calculated from the mass, the initial temperature (= room temperature), and the final temperature (= calorimeter temperature) of the sample using enthalpy data tabulated in the literature (refs. 8,9) for platinum or α-alumina, respectively while the value of the integral I, corresponding to ΔH, is provided by the computer in arbitrary units . Thus in the following, f will also be given in arbitrary units (a.u.).

BEHAVIOUR OF THE CALORIMETER DURING OPERATION

The suitability of the differential calorimeter for measurements at high temperatures has been tested using the method of drop calorimetry. In the following, exemplary results characterizing the main features of the calorimeter are presented.

In a first series of measurements, the alumina sample crucible was lined with a platinum crucible, and platinum spheres with masses between 50 and 1000 mg were dropped at random from room-temperature into the working cell operating at a fixed higher temperature. From the data thus obtained, the calibration factor was calculated according to equation (1) as a function of the sample mass. Typical results for a calorimeter temperature of 1475 K are presented in figure 3. The data were determined in two runs, between which the calorimeter was cooled to room temperature and the crucible emptied. According to the information shown in figure 3 the calibration factor is constant and independent of the magnitude of the heat effects (ranging from about 9 to 175 J) produced in the working cell. The deviation of the individual values from the mean value is less than ± 2 %.

The results in figure 3 indicate that, at a given temperature, the calibration factor of the calorimeter is constant, i.e. independent of the filling height of the working cell, when the latter is lined with a (closely fitting) platinum crucible. In further measurements, investigations of the constancy of the calibration factor, when the calorimeter is used without a platinum lining in the working cell were made.

Thus, starting with an empty working cell (without any metallic lining), samples of pure tin, weighing between about 20 and 300 mg, were successively dropped from room temperature into the calorimeter maintained at a constant temperature, and for each drop the calibration factor was calculated with the use of the enthalpy data for tin tabulated by Barin et al. (ref.9). Exemplary results measured at 1150 and 1550 K are presented in figure 4, where the filling height of the working cell was calculated from the sample mass in the cell and the density of liquid tin. From the results it may be concluded that, at a given temperature, the calibration factor (sensitivity) of the calorimeter may be regarded as constant within the limits of uncertainty of

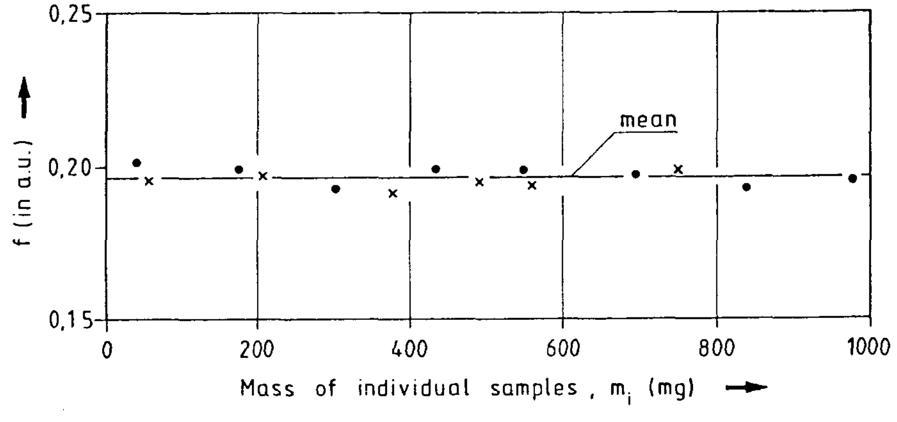

Fig. 3. Calibration factor f determined at 1475 K as a function of the masses m_i of the individual platinum samples; x measured on the first day, • measured on the second day.

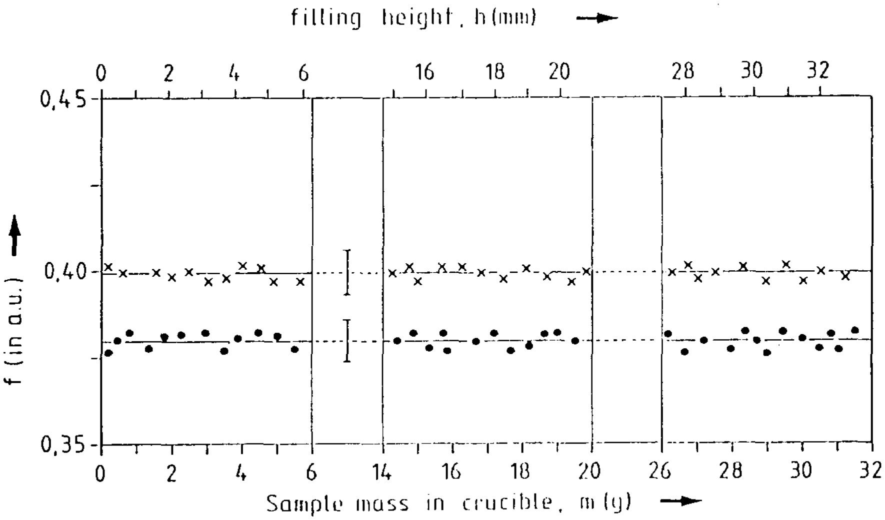

Fig. 4. Calibration factor f as a function of total sample mass m (filling height h) in the working cell for tin additions from room temperature to 1150 K (x) and 1550 K (•); error bars indicate maximum deviation.

measurement. The scatter of the data points around the corresponding mean value is less than ± 2.5 %.

In order to obtain information on the accuracy of the calorimetric data, the enthalpy of platinum was determined as a function of temperature, α-alumina (sapphire) being used for calibration. The platinum samples had the form of a sphere, while the calibration samples had the form of a cylinder (height ≈ 4 mm, diameter ≈ 3 mm). In Table 1 the results are compared with data from the literature. The deviations of the measured values from the tabulated data are, on the average, less than ± 1.5 %.

TABLE 1

Thermal enthalpy H (referred to 298 K) of platinum as a function of temperature T. Comparison of values (H'), measured in this study with data (H"), tabulated in the literature (ref. 8) and deviation $\delta = 100\ (H' - H'')/H''$.

T/(K)	$H'/(\mathrm{kJ\ mol^{-1}})$		$H''/(\mathrm{kJ\ mol^{-1}})$	(%)
679	10,36 ± 1,3*)	(5)+)	10,27	+ 0,2
885	15,78 ± 2,9	(6)	16,07	- 2,2
1077	21,98 ± 1,2	(5)	21,74	+ 0,9
1294	28,39 ± 0,8	(4)	28,41	- 1,2
1467	33,94 ± 2,5	(6)	33,90	+ 0,1
1671	39,73 ± 2,8	(7)	40,57	- 2,0

*) standard deviation
+) number of individual measurements

FEATURES AND PERFORMANCE OF THE CALORIMETER

In a series of test experiments carried out under widely differing conditions, the calorimeter described above has been found to be a reliable and safe apparatus. It can be used to measure enthalpic effects ranging in magnitude from approximately 2 J to 200 J at temperatures between about 600 and 1800 K with a reproducibility and accuracy of approximately ±2,0 to ±3,5 %. In comparison with its original, the calorimeter has several advantages:

a) Over the whole outer surface of the calorimetric cells, temperature sensors are distributed regulary with an optimal density. Consequently, the calibration factor (sensitivity) is independent of the filling height of the sample crucible (even in the absence of a platinum liner in this crucible).

b) The thermal coupling between the calorimetric cells and the thermopile is considerably closer. As a result,and because of the higher density of temperature sensors, the sensitivity of the thermopile was found to be increased by about 20 %. The sensitivity, which is a function of temperature, was determined to be 2 V/mW at 1450 K.

c) The position of the thermojunctions is better defined and remains virtually unaltered on changing the sample crucible. Thus, the calibration factor (sensitivity) is highly reproducible in succeeding runs.

d) The working volume (5 cm^3) of the sample crucible is larger by a factor of three (for the given inside diameter of the heating element of the Setaram high-temperature furnace).

With its larger sample crucible volume and increased sensitivity of the measurement system, the new differential calorimeter is particulary suitable for measurement of partial enthalpies of solution in oxide melts. The possibilities of carrying out such measurements are currently being investigated in this laboratory.

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