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A NEW CALORIMETER FOR TEMPERATURES ABOVE 1400 K *

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ABSTRACT

A new high temperature calorimeter, based on modifications and improvements to the commercial integrated heat flux Setaram design is described. In this unit thermal effects are measured differentially along the vertical axis of the calorimeter. Performance was tested at 1473 K through the measurement of the enthalpies of formation of intermetallic compounds, using high temperature mixing calorimetry.

INTRODUCTION

The publication some 30 years ago by Calvet and Prat [1] of the important monograph "Microcalorimetrie" has had a profound influence on the development of heat flux calorimetry as carrried out both near room temperature and at elevated temperatures. Since about 1960 one of the present authors has been associated with the design an construction of a number of high temperature calorimeters based on the Calvet twin integrated heat flux principle. The first of these units had a calorimeter thermostating block constructed from pure aluminum [2]; hence it was limited to temperatures below about 500 °C. Later units of related design were constructed using more refractory materials, e.g. pure nickel, silver [3], inconel [4], silicon carbide, and recrystallized alumina [5]. The alumina calorimeter is maintained in a large cylindrical furnace with top and bottom heaters, the heating elements constructed from Pt 40%Rh wire. This calorimeter has been in nearly continuous operation near and above 1300 K for a number of years. In principle this apparatus should be capable of satisfactory performance even above 1400 K. However, we found that above this temperature the operation of the calorimeter often gave rise to base-line instabilities which had a serious impact on experimental precision. Also, expensive and time-consuming interruptions for maintenance were neces-

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* Dedicated to Prof. Edgar F. Westrum, Jr., on the occasion of his 70th birthday and in honour of his contribution to calorimetry and thermal analysis.

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sary. For these reasons, operation of the equipment above 1400 K is impractical.

At the present time it is possible to purchase, at very considerable cost, a differential high temperature integrated heat flux calorimeter which allows calorimetric measurements at temperatures up to about 1800 K. This calorimeter is produced by Setaram in France, and has been available commercially for many years. In this unit the thermal effects are measured differentially along the axis of the cylindrical calorimeter, rather than radially as in the Calvet-type apparatus. The 'working' junctions of the differential thermopile surround the crucible in which the reaction takes place, while the 'reference' junctions are maintained in a constant temperature environment some distance removed from the crucible. Unfortunately, most investigators who have used this equipment have complained about difficulties associated with precise calibration, and the number of scientific publications which have resulted from its use is quite small. The reasons for this are now fairly well understood: the construction of the differential thermopile in the Setaram calorimeter does not satisfactorily integrate the heat flux over the surface of the crucible in which the reaction is carried out. The calibration factor of the calorimeter therefore depends critically on the amount of material contained in the crucible. Investigators active in this area have recognized this, and have made modifications to the Setaram design. However, both in the commercial Setaram unit and in the modified versions known to us, there is still poor thermal coupling between the crucible in which the reaction takes place, and the thermopile.

During the past year we have experimented with a new high temperature calorimeter which represents a modification of units described by French groups [6,7], which in turn are improved versions of the Setaram design.

DESCRIPTION OF THE CALORIMETER

Overall design

The principal features of the new calorimeter assembly are shown in Fig. 1. The apparatus is heated by a furnace which consists of a 50 mm I.D. × 65 mm O.D. alumina tube, 1 m long (H in Fig. 1), which has a 65 cm long heating element, wound with a smaller pitch towards both ends. The heating coil is made from five Pt40%Rh wires of 0.5 mm diameter, purchased from Engelhard, consolidated into a single resistance element. The furnace core is centrally located in a larger alumina tube (furnace shell) of about 200 mm I.D. (A). The space between the core and the furnace shell is filled with hollow alumina insulating beads (J). The space between the furnace shell and the surrounding water jacket (P) is filled with refractory brick insulation (R). The bottom ends of the furnace core and the furnace shell tube are also

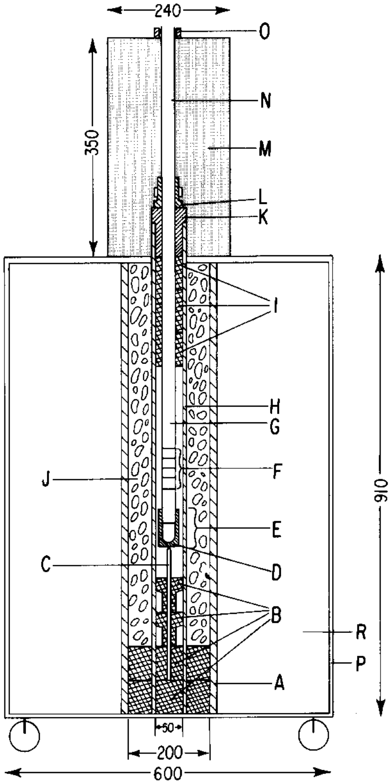


Fig. 1. General view of high temperature calorimeter: A, alumina tube (furnace shell); B,I, insulation (firebrick); C, alumina supporting tube; D, alumina tube (cemented onto calorimeter); E, 'reference section' (one thermocouple level); F, calorimeter section or 'working section' (five thermocouple levels shown); G, calorimeter tube; H, alumina furnace core; J, alumina beads; K, lavite support; L, lavite sleeve with stainless steel clamp; M, ceramic wool insulation; N, alumina extension tube; O, bakelite clamp; P, water cooled jacket; R, refractory insulation.

filled with firebrick insulation, as shown (B) in Fig. 1. In the center of the furnace core there is an 8 mm diameter alumina centring tube (C), on which the calorimeter tube (G) rests. Further details of the construction of the calorimeter tube will be given below.

Cemented to the bottom of the calorimeter tube is a short section of alumina tubing, about 70 mm long and about 40 mm O.D. (D). This serves to increase the mass of the 'reference section' of the calorimeter. The calorimeter tube (G) is centered in the top of the furnace by three cylinders made from insulating firebrick (I), and by a cylindrical lavite plug (K). It is supported from the top by means of a lavite sleeve, using a stainless steel clamp (L). In order to optimize the temperature profile of the furnace, and obtain a central furnace section with a very low temperature gradient, a 350 mm insulated extension (M) has been added to the top of the furnace assembly, as illustrated in Fig. 1. Abutting the top of the calorimeter tube there is an alumina extension tube (N) of slightly larger diameter than the calorimeter tube proper. This extension tube is held in place by a cylindrical bakelite clamp (O).

The temperature of the calorimeter assembly is controlled by a Leeds and Northrup automatic temperature controller. In order to increase the sensitivity of the control system, the control signal is generated by two Pt–Pt13%Rh thermocouples connected in series and located in an alumina tube cemented onto the furnace core.

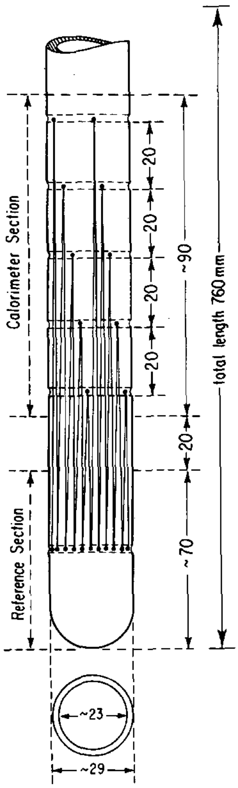
Details of thermopile assembly

The calorimeter tube and details of the construction of the thermopile are shown schematically in Fig. 2. The calorimeter consists of a tube of recrystallized alumina, about 29 mm O.D., 23 mm I.D., and 760 mm long, one end of which is closed. On the outside surface of this tube have been ground 40 shallow vertical grooves, to allow the placement of a 20 couple thermopile, shown schematically in Fig. 2 (only half the junctions are shown). Twenty thermocouple junctions are distributed over the 'working section' of the calorimeter, located at five different levels, about 20 mm apart. The other 20 junctions are placed at the same level near the closed end of the calorimeter tube, forming the 'reference section'. The couples were made from 0.5 mm diameter Pt–Pt13%Rh wire, purchased from Engelhard, and were cemented into the grooves with morganite cement.

This thermopile measures small temperature differences along the vertical axis of the calorimeter tube arising from the reactions which occur in the 'working section'. The 'reference section' is some distance (about 50–60 mm) removed from the 'working section'. To maintain a constant and uniform temperature in the 'reference section', the section is loaded with a small platinum crucible filled with some additional platinum scrap. The mass of the section has also been increased, as previously described. Two long platinum wires, cemented into two parallel grooves in the alumina tube, carry the differential e.m.f. to a constant temperature Dewar. Here junctions are made to copper wires connected to the amplifier. The output of the amplifier is fed in parallel circuits to the recorder, and through a voltage-to-frequency converter to an Apple IIe computer.

Measurement of heat effects

All calorimetric experiments are performed inside a special calorimeter 'liner' of 20 mm I.D. The lower part of this liner is constructed from Pt–20Rh tubing of about 0.5 mm wall thickness, total length about 80 cm, one end of which is closed. The upper end of the liner is connected to a thin-walled stainless steel tube, and has a standard ground joint. The lower



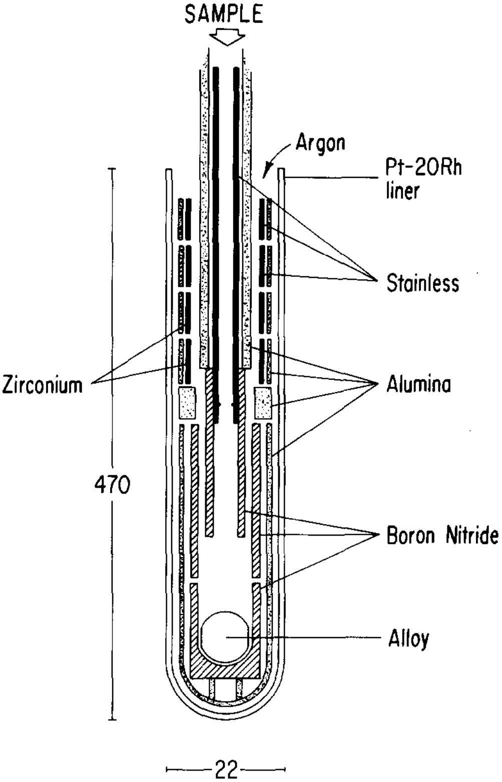


Fig. 2. Schematic view of calorimeter section ('working section') and 'reference section' of the new calorimeter.

Fig. 3. Schematic diagram of the calorimetric cell assembly, showing part of the Pt–20Rh liner, the boron nitride crucible, the boron nitride protective cylinder and stirrer, and the alumina protective crucible and protective cylinders, as well as parts of the final gettering system for the argon gas.

end of the liner contains the BN crucible assembly in which experiments are carried out. Details of this arrangement are shown in Fig. 3. The actual location of the liner is adjusted so as to maximize the e.m.f. generated by the calorimeter thermopile.

Calibration of the calorimeter is achieved by dropping weighed pieces of 3 mm diameter pure copper wire from room temperature into the BN crucible (see Fig. 3). The calibration is based on the heat content of copper at the operating temperatures of the calorimeter, taken from Hultgren et al. [8], and is generally reproducible within ±1%.

Examples of application

We first used the new single unit differential calorimeter to determine the enthalpies of formation of PtMe [9] and IrMe [10] at 1473 ± 2 K (Me = Ti, Zr, Hf). The three Pt compounds had recently been studied by Gachon and Hertz [11], who used direct reaction calorimetry. In our calorimeter we measured heat effects which ranged from 80 J to 200 J. For example, in our investigation of the intermetallic compound PtHf, the following two reactions were carried out in the calorimeter

$$0.05\ \mathrm{PtHf}(\mathrm{s}, 298) + 0.26\ \mathrm{Pt}(\mathrm{s}, 298) + 0.64\ \mathrm{Ge}(\mathrm{s}, 298) = \mathrm{Me}_{0.05}\mathrm{Pt}_{0.31}\mathrm{Ge}_{0.64}(\mathrm{l}, 1473) \quad (1)$$

and

$$0.05\ \mathrm{Hf}(\mathrm{s}, 298) + 0.31\ \mathrm{Pt}(2, 298) + 0.64\ \mathrm{Ge}(\mathrm{s}, 298) = \mathrm{Me}_{0.05}\mathrm{Pt}_{0.31}\mathrm{Ge}_{0.64}(\mathrm{l}, 1473) \quad (2)$$

On the basis of six measurements for each of these reactions we derived the following enthalpy changes, with reference to one mole of PtHf

$$\Delta H_{\mathrm{m}}(1) = 624.3 \pm 11.0\ \mathrm{kJ\ mol}^{-1}$$

$$\Delta H_{\mathrm{m}}(2) = 397.0 \pm 7.3\ \mathrm{kJ\ mol}^{-1}.$$

Combining eqns. (1) and (2), we obtain

$$\Delta H_{\mathrm{f}}^{\ominus}(\mathrm{PtHf}) = \Delta H_{\mathrm{m}}(2) - \Delta H_{\mathrm{m}}(1) = -227.3 \pm 13.2\ \mathrm{kJ\ mol}^{-1}.$$

Note that the mean values of $\Delta H_{\mathrm{m}}(1)$ and $\Delta H_{\mathrm{m}}(2)$ are associated with errors (standard deviations) of about 1.8%. The corresponding uncertainty in $\Delta H_{\mathrm{f}}^{\ominus}(\mathrm{PtHf})$ obtained from $(\delta_1^2 + \delta_2^2)^{1/2}$ was 5.8%. In comparison, the corresponding value for this compound quoted by Gachon et al. [11] was -226 kJ mol^{-1}. However, these authors were uncertain about the probable error in this value, which was quoted as “indicative” rather than definitive.

Concluding remarks

Among the significant differences between this calorimeter and calorimeters described previously are the following.

(i) The tubular graphite furnace used in the Setaram calorimeter, which is cycled between room temperature and elevated temperatures, has been replaced by a furnace with a Pt40%Rh heating element. This maintains the calorimeter continuously at a high temperature.

(ii) Integration of the heat flux over a major fraction of the surface area of the ‘working section’ has been achieved.

(iii) The thermal coupling between crucible and thermopile has been improved.

(iv) The diameter of the calorimeter has been increased as compared to previously known units. This allows the construction of a simple manipulation device for mixing and stirring, even if it also increases the time constant of the calorimeter.

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