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A DIRECT ISOPERIBOL ANEROID CALORIMETER

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ABSTRACT

An aneroid isoperibol calorimetric apparatus is described which is particularly suitable for measurement of the reaction heat among solids. Such an apparatus contains four calorimeters and allows to carry out differential measurements. Each calorimeter includes two small electric furnaces employed for heating the solid mixture until the reaction begins and for the successive electric calibrations, respectively. The temperature trend of each calorimeter is followed by 80 thermocouples in series. The instrument characteristics are briefly discussed. Examples of its employment in the alloy thermochemistry are given.

INTRODUCTION

Different calorimetric techniques are very useful in many cases for the measurement of the heats of reaction among solids[1]: for instance for alloys systems, the methods based on DTA, liquid metal solution or precipitation[2], etc. However, a single method is generally not suitable for all of the solid systems and, moreover, when possible, it may be convenient to have thermochemical data obtained from different methods in order to achieve a greater accuracy. For an exothermic reaction among solids, provided it may be completed, it can also be useful to have it take place inside the calorimeter itself and to measure the heat directly. When the reacting system is able to reach equilibrium even if the surrounding is at room temperature, an isoperibol calorimeter may be advantageous for its greater simplicity in construction and working, compared with a high temperature calorimeter.

In the literature different types of direct calorimeters are discussed and a simple model of a direct isoperibol calorimeter was previously described elsewhere[3] and used for a number of measurements on several systems of alloys (Pt–Sn[4], Y–Bi[5], Nd–Bi[6], La–Bi[7] and Mg–Ge[8]). The apparatus consists of a bomb containing a small tantalum furnace for preheating the solid mixture till the reaction begins. The bomb is submerged in an oil-bath the temperature of which, followed by 18 thermocouples in series, allows the evaluation of the reaction heat.

Referring now to Calvets[9] principles of constructing calorimeters we thought it useful to adopt the same ideas for this type of direct calorimetry. Therefore the calorimetric aneroid apparatus described below was built.

GENERAL DESCRIPTION OF THE INSTRUMENT

In Fig. 1 the structure of the apparatus is sketched. It consists of an aluminum block surrounded by an ultra-thermostat. In the block there are four holes each containing a calorimeter. Inside each calorimeter (as fully described hereinafter) are contained two electric furnaces used for starting the reaction and for the electric calibration, respectively. On the surface of each calorimeter are placed the hot junctions of 80 copper–constantan couples, connected in series; the cold junctions are

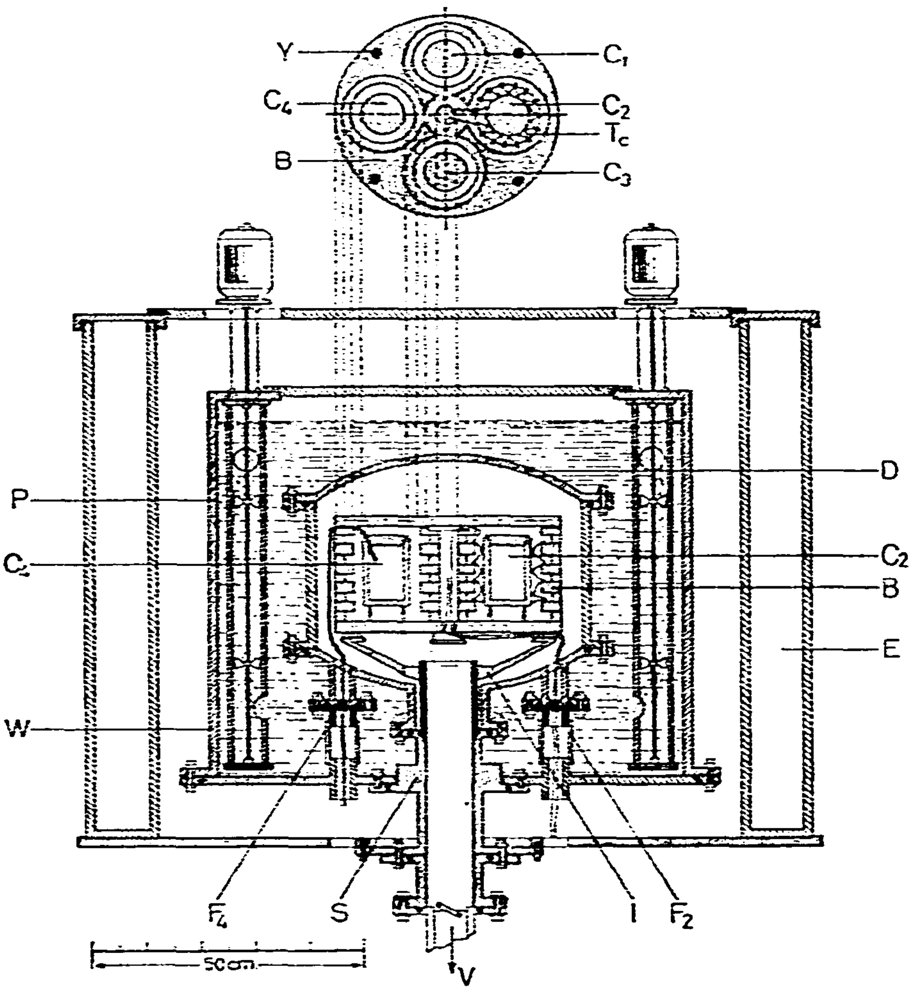

Fig. 1. General scheme of the calorimetric apparatus. In the lower part of the figure the vertical section of the whole instrument is shown. in the upper part the horizontal section of the thermostatic block B (built by overplaced aluminum discs rigidly connected by the bolts Y) and of the calorimeters (C_1, C_2, C_3 and C_4). For one calorimeter (C_2) the scheme is given of the connections of the 80 thermocouples (T_c). Moreover are shown: E = external insulating enclosure; W = thermostat with the propellers (P) for the water stirring; S = support of the thermostat and of the internal container connected through V to the vacuum pump and to the argon bottle; I = block supporting brackets; F_2, F_4 = sintered glass leadthroughs for the electric wires, thermopiles, etc.

intentionally placed on the internal surface of the block hole. The block is contained inside a vessel (which can be evacuated and filled with inert gas) immerged in the thermostat water.

The block itself was built by overplacing a series (12) of disks opportunely holed and rigidly connected all together by four screw studs. Such a building device allowed a quick and easy assembling of the thermopiles. This structure gives also a maximum value in the horizontal direction for the thermal conductivity improving the thermal symmetry of the four calorimeters. Actually four calorimeters were foreseen both to increase the number of measurements obtainable at the same time and, above all, to allow differential measurements.

THERMOSTAT

The water temperature is controlled by a mercury switch operating a small heater whose power is regulated so as to have "on" and "off" times as equal and

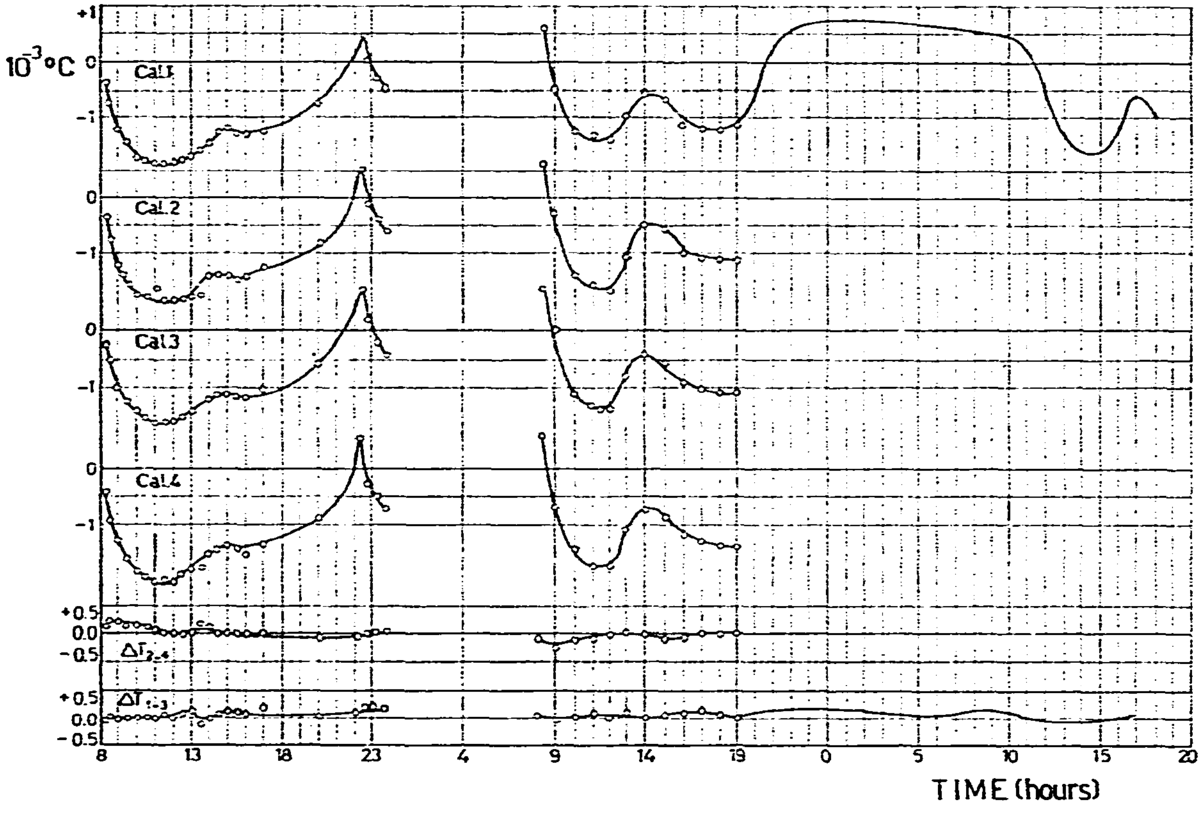

Fig. 2. Thermal drift of the calorimeters. Temperature differences between the four calorimeters and the reference block are plotted, for two successive days, against local time. In the lower part of the figure differential temperatures are given between opposite calorimeters. Some data were obtained using a hand balanced potentiometer and others (right-hand side of the figure) from a recording microvoltmeter.

short as possible (about 1–2 min). With a "1/500 °C" Beckman thermometer temperature variations cannot be observed within 1 h. During longer time intervals (24–48 h), fluctuations within ±0.004 °C were observed for the water temperature.

Figure 2 shows the trend of the temperature differences among the four calorimeters and the aluminum reference block. These differences, expressed in thousandths of °C, include both the real temperature variations and the possible effects connected

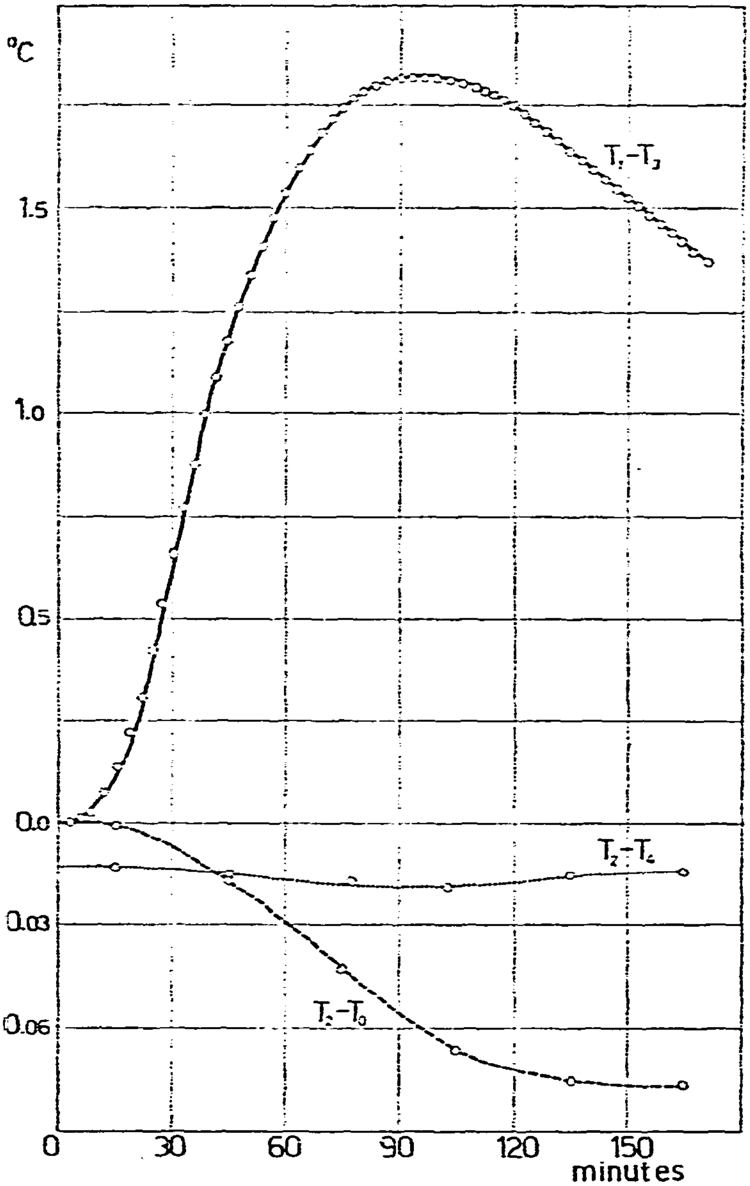

Fig. 3. Temperature difference between calorimeter 2 (or 4) and reference block (T_2–T_0) and differential temperature of calorimeters 2 and 4 (T_2–T_4) during the heating of the block produced by the working of calorimeter 1 (as indicated by the T_1–T_3 curve).

with spurious e.m.f.'s in the thermocouples circuit, apart from the errors characteristic of the measurement instrument employed. The same figure shows the differential measurements effected between calorimeters symmetrically opposed. The thermal symmetry of the whole system is further on evidenced by Fig. 3.

All the data given above show that the temperature measurements are significant within 0.001 °C.

INTERNAL STRUCTURE OF THE CALORIMETERS

It is possible to introduce inside each calorimeter a sample consisting of a mixture of the solid substances which have to react. Such a mixture is heated inside the calorimeter itself until the reaction starts.

The calorimeter structure corresponds to the following distinctive features:

(a) Possibility of using rather large quantities of substance (up to about 12 cm^3 of compacted powders).

(b) Maximum utilization, for the sample heating, of the heat produced by the furnace.

(c) Availability of two furnaces: one for the electric calibration and one for starting the reaction; these separate functions are necessary to avoid further heating of the sample during the calibration, as it might change the sample.

The construction details of the calorimeter can be seen in Fig. 4. As it may be noticed the sample is placed into a thin iron (or molybdenum) container consisting of a double cylinder surrounding the heating resistance; a small inert metallic block of identical shape is placed around the other (calibration) heater contained in the same calorimeter. The two heaters are symmetrically and rigidly fixed to a central plate thermally connected to the external part of the calorimeter through a suitable thermal resistance. The latter (see Fig. 4) consists of a series of concentric inox steel cylinders connected one to the other by welding alternatively along the edges at the top and at the bottom. The purpose of this structure is to guarantee a fixed and reproducible way (identical for the two furnaces) for the thermal flow from the heart of the calorimeter to its surface. Moreover it allows (opportunely adjusting number, thickness and length of the cylinders) regulation of the flow intensity and therefore of the behavior of the calorimeter. As a matter of fact, with too low a thermal flow the time necessary for the reading and calibration would be too long. On the other hand, with too high a thermal flow, the calorimeter would work as an oscillograph and the temperature/time response would be different during reaction or calibration runs. The external part of the calorimeter, connected in series with the "thermal guide" described above, consists of a thick aluminum cylinder (low thermal resistance), in which there are small thermal gradients as a consequence of which there is an equal distribution of the temperature on the external surface where the thermopile junctions are placed. According to what was suggested by Calvet the couples are welded to thin metallic small plates arranged in such a way as to cover at least the whole lateral surface.

The furnaces contained in each calorimeter are made by two Kanthal coils:

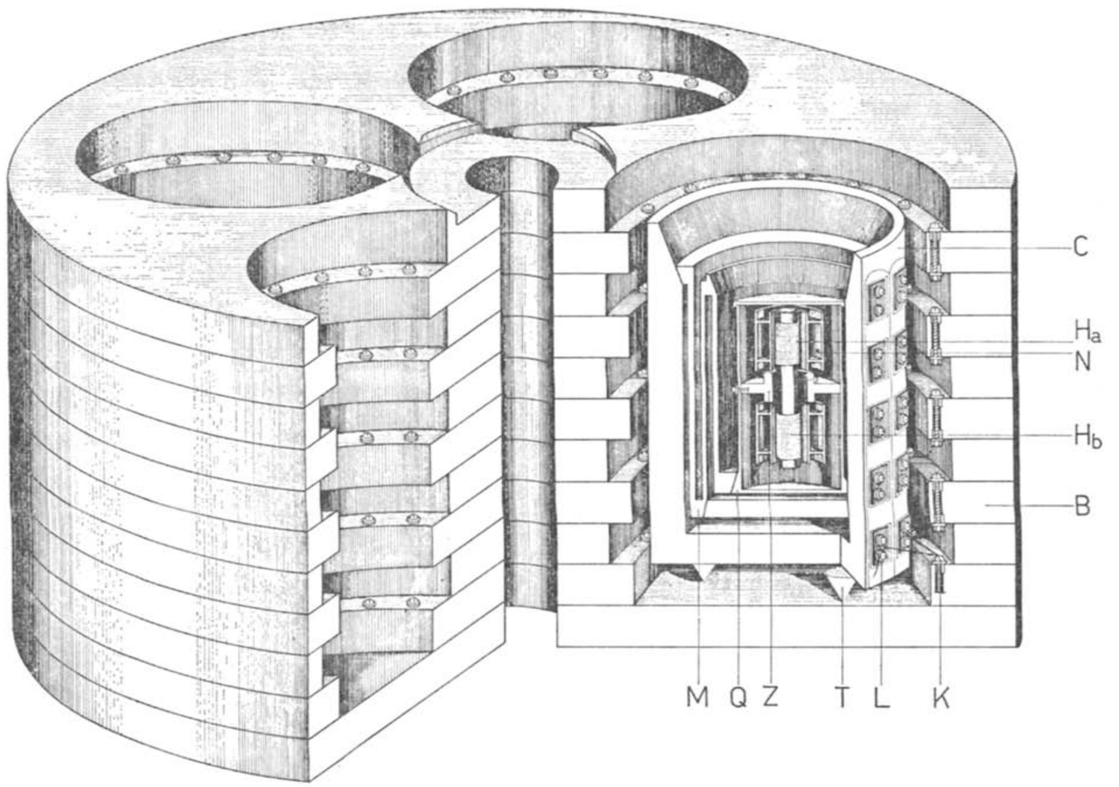

Fig. 4. View of the thermostatic reference block and of one calorimeter. B = overplaced aluminum discs; C = calorimeter external surface; H_a and H_b = heaters used for starting the reaction and for calibration symmetrically fastened to Z; N = container of the sample; Q = container of the heaters (and of the sample) connected through the cylindrical thermal conductor M to piece C; T = insulating pedestal; L = laminae to which thermopiles hot junctions are soldered; K = cold junctions.

each of which is able to dissipate a power of about 100 W and its temperature can exceed 1000 °C. The electric energy input (120 V, stabilized a.c.) is measured through a standard watt–hour meter (precision in the best loading conditions: 0.1%; sensibility: ±2 W sec). On the external surface of the container with the reacting mixture a thermocouple (not shown in the figure) is placed; it allows to follow the temperature trend and to observe the rapid increase in temperature at the time when the reaction is complete and the electric heating must be interrupted.

CALORIMETER WORKING

Figure 5 shows, for a typical experience, the temperature trend of the sample (on the external surface of its container) and the calorimeter response: this is given by the e.m.f. of the 80 couples pile differentially connected to that of the opposite calorimeter, which is used as reference (in the figure, these data are also reported after having converted them into °C).

We can see in the figure that, after about 90 min, during which the sample temperature has regained its initial value, the calorimeter response reaches its maximum. The calorimeter temperature then decreases and reaches quickly enough an exponential trend (half time about 83 min). One night is therefore enough to have the same calorimeter ready for a successive measurement.

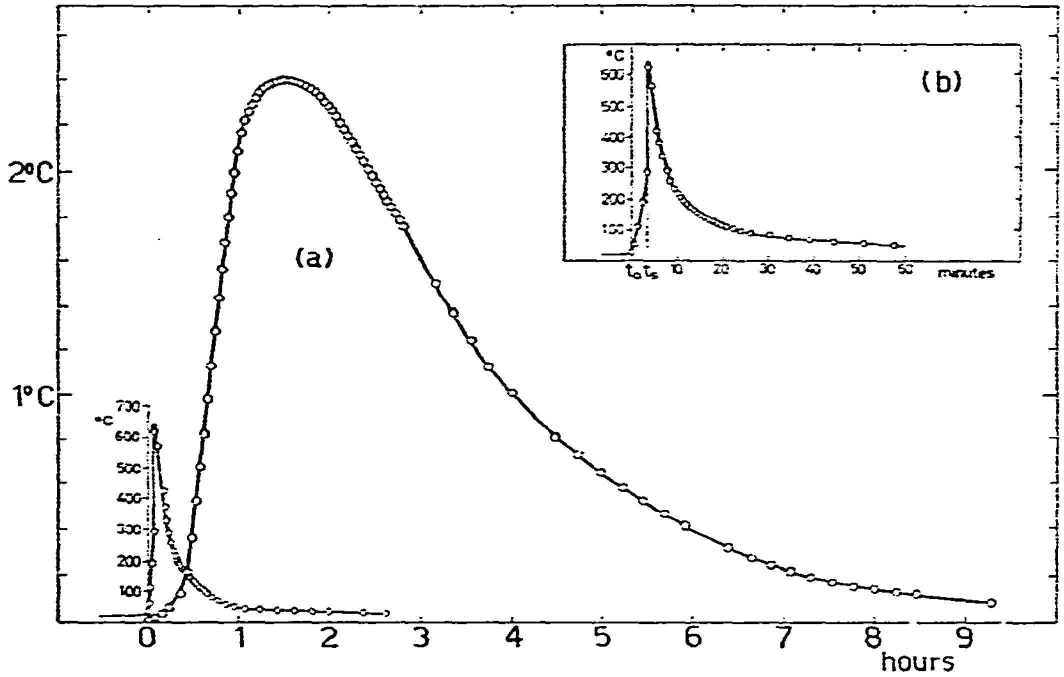

Fig. 5. (a) Temperature trend (°C) of the calorimeter surface in a typical experience. The sample temperature (hundreds of degrees) is shown, on the left, with the same scale of times. (b) The sample temperature (as measured on its external surface) is shown with an enlarged time scale; t_0 = heating start, t_s = reaction start and electric heating stop.

The areas enclosed under the temperature/time curves are computed as follows:

$$\sum_{i=0}^{n} T_i + \int_{n}^{\infty} ae^{-bt}\,dt$$

where T_i = readings at 1-min intervals, a and b are obtained by the least squares method. The areas are independent, within 0.1%, from the value of n for which the summation is interrupted, if $n \geq 250$. Typical values of the correlation coefficient obtained for interpolations effected between $n = 250$ and 700 were 0.9996 to 0.99999.

While studying the performance of the calorimeter, heatings were effected utilizing energies included between 1000 and 10000 cal: the corresponding $T_i - T_{0\ \mathrm{max.}}$ observed were included between 0.5 and 5°C, respectively. In other experiments the same quantity of energy (7–8000 cal) was dissipated at different times, viz. between 300 and 600 sec. In all the above runs the relation between area and energy appeared to be constant within 0.5%. This value, however, seems to be connected with the measurement technique so far used rather than with the performance of the calorimeter as such. Actually an error of this size is surely partially due to the uncertainty of the time at which the single potentiometric measurements are taken.

The same behavior was also observed in runs effected by using either one or the other of the furnaces contained in the same calorimeter.

UTILIZATION OF THE CALORIMETER

This calorimeter was built to measure heat of reactions involving solid particularly metallic) substances. It was considered useful to effect a thermochemical calibration by using alloys whose formation heats were already known. In typical cases (such as bismuthides, etc.), for which the reaction temperature is low and therefore the preheating energy is small, the heat of reaction was a remarkable portion of the total energy input to the calorimeter and the total error resulted to be about 2–3%.

Preliminary measurements were carried out particularly on alloys of the following systems:

Mg–Bi: For the composition 60.78 at. % Mg was obtained $\Delta H_{\text{form}}^{300\text{K}} = -7.9_8$ kcal/g-at., from which we compute, for the Mg_3Bi_2 composition, $\Delta H_{\text{form}} = -8.1$ kcal/g-at. (in the literature[10] it was reported -8.1 ± 0.6).

Y–Bi: For the composition 43.8 at. % Bi was obtained $\Delta H_{\text{form}}^{300\text{K}} = -21.1$ kcal/g-at.: the corresponding value computed for the YBi composition is $\Delta H_{\text{form}} = -22.2$ kcal/g-at. (the previously[5] known value is -22.0).

Nd–Bi: For the composition 52.8 at. % Bi was obtained $\Delta H_{\text{form}}^{300\text{K}} = -25.4$ kcal/g-at.: the corresponding value computed for the NdBi composition is $\Delta H_{\text{form}} = -26.6$ kcal/g-at. (the value previously reported in the literature[6] is -26.6).

Al–Au: For the composition 35.1 at. % Au was obtained $\Delta H_{\text{form}}^{300\text{K}} = -9.8$ kcal/g-at., corresponding to -10.0 for Al_2Au (the value previously reported in the literature[11, 12] is -10.1)

As usual in calorimetric measurement by means of a direct technique, the various samples were examined after the measurement by using chemical analysis, metallographic and X-ray examinations in order to check their state. Generally the preparation of the samples (filing of the metals, mixing, weighing, etc.) and their examination after the reaction were carried out in argon atmosphere.

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