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A simple adiabatic low-temperature calorimeter based on a helium refrigerator system[1]

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Abstract

The construction of an adiabatic calorimeter for the 15–300 K range is described. It is fully automated and set up in a helium refrigerator system. The operation of the calorimeter was tested by measuring the specific heat capacity of a pure copper sample. The results show good agreement with the standard literature values. The specific heat capacity of a magnesium hydride sample was also determined. For MgH_2, the standard molar entropy of $S^0(298.15)=30.64\ \mathrm{J\ mol^{-1}\ K^{-1}}$ was calculated from the obtained data. © 1998 Elsevier Science B.V.

Keywords: Adiabatic calorimeter; Low temperature; Magnesium hydride

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1. Introduction

Reliable data remain a crucial basis for thermodynamical calculations, so that classical methods to obtain these data have not lost their importance. One of these methods is adiabatic low-temperature calorimetry for entropy determination. Nearly all calorimeters based on this principle operate with cryostats using refrigerants like liquid helium or liquid nitrogen, thus complicating the handling of the calorimeter. In this work, an adiabatic calorimeter operating with the classical step method is described, which is set up in a refrigerator system and, therefore, does not require liquid gases as refrigerants. Its operating range is from 15–300 K. The principal design of the calorimeter and the use of the controlling program are quite simple. The mounting of the samples is usually done within a few minutes and the measurement itself is fully automated. The function of the calorimeter was tested by measuring the heat capacities of copper sample and magnesium hydride.

2. The calorimeter

The fundamental design of the calorimeter is shown in Fig. 1. On a simple frame formed by a steel capillary tube, the sample holder is suspended by four very thin nylon threads. This sample holder, a small gold-plated copper disc (∅ 13 mm) is the actual calorimeter. It contains the sample heater and a platinum resistance thermometer of type Pt-100 (Lake Shore Cryotronics, model PT-111). Any compact and mechanically treatable sample can be screwed on the bolt containing the thermometer. For powder

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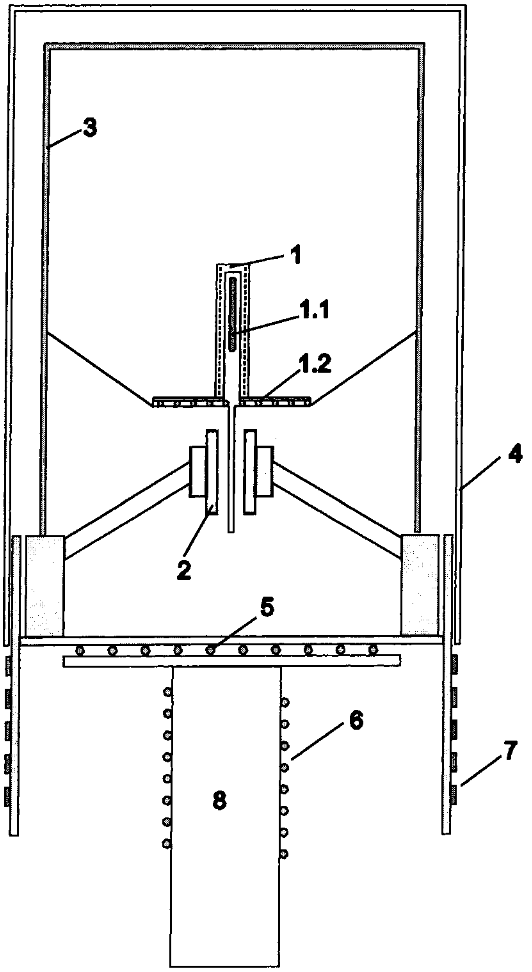

Fig. 1. Cross section of the calorimeter: (1) – sample holder, (1.1) – resistance thermometer, (1.2) – sample heater; (2) – thermal switch; (3) – capillary tube; (4) – thermal shield; (5,6) – auxiliary heater; (7) – shield heater; and (8) – second stage of the refrigerator.

samples, either a container is necessary, or the sample is pressed in a way such that it can be mounted onto the bolt. Some Apiezon grease may be necessary to make proper thermal contact. The sample heater, a bifilare, helically winded constantan wire with a resistance of 113.6 Ω is mounted on the bottom side of the sample holder. Also, on the bottom side, there is a thin copper strip enabling the contact with the mechanical heat switch.

The heat switch is a brass construction, pressing two jaws against the copper strip, thus making thermal contact between sample and environment. It can be opened and closed by means of a linkage and a rotary switch on the outside of the cryosystem.

The upper part of the inner adiabatic shield is formed by a removable cylinder-shaped hood of gold-plated copper, which is tucked to the lower part that carries the shield heating. In this way, the sample is easily accessible.

The shield heating is again a bifilar constantan wire, wrapped around the lower part of the heat shield and fixed there with some glue. An auxiliary heating is attached on the upper part of the second refrigerator stage. It is used only near ambient temperatures and above. The temperature of the shield is measured using a silicon diode, which was attached to lower part of the heat shield.

All the measuring and heating wires (60 μm copper and 80 μm constantan, respectively) are anchored to the lower part of the heat shield prior to reaching the calorimeter.

3. Instrumentation and controlling software

Fig. 2 shows the block diagram of the measuring system. A digital voltmeter with $7\frac{1}{2}$ digits is used to determine the resistance of the Pt-100 platinum resistance thermometer. The current of 100 μA is supplied by a 6 V battery and adjusted by a series of potentiometers and monitored as voltage drop over a standard resistor, using a Prema DV 5001 voltmeter.

A Siemens B 3050 calibrator is used as the power supply for the sample heater. The heating current and heating voltage are again measured with the DV 5001, which was extended with a 10-channel scanner for this purpose. A LakeShore 330 controller is used to maintain adiabatic conditions. The proportional and integral parameter of this PID controller were optimised, depending on the respective temperature; furthermore, differential parameter adjustment was not applied. The auxiliary shield heating, which is necessary at temperatures ca. 300 K, is still adjusted manually.

All the instruments and the controller are linked with a PC via an IEEE 4.88 interface. This computer runs the measuring software, developed with Borland C for DOS. The program controls the complete measurement, calculates c_p for each heating step and displays the respective temperatures of sample and

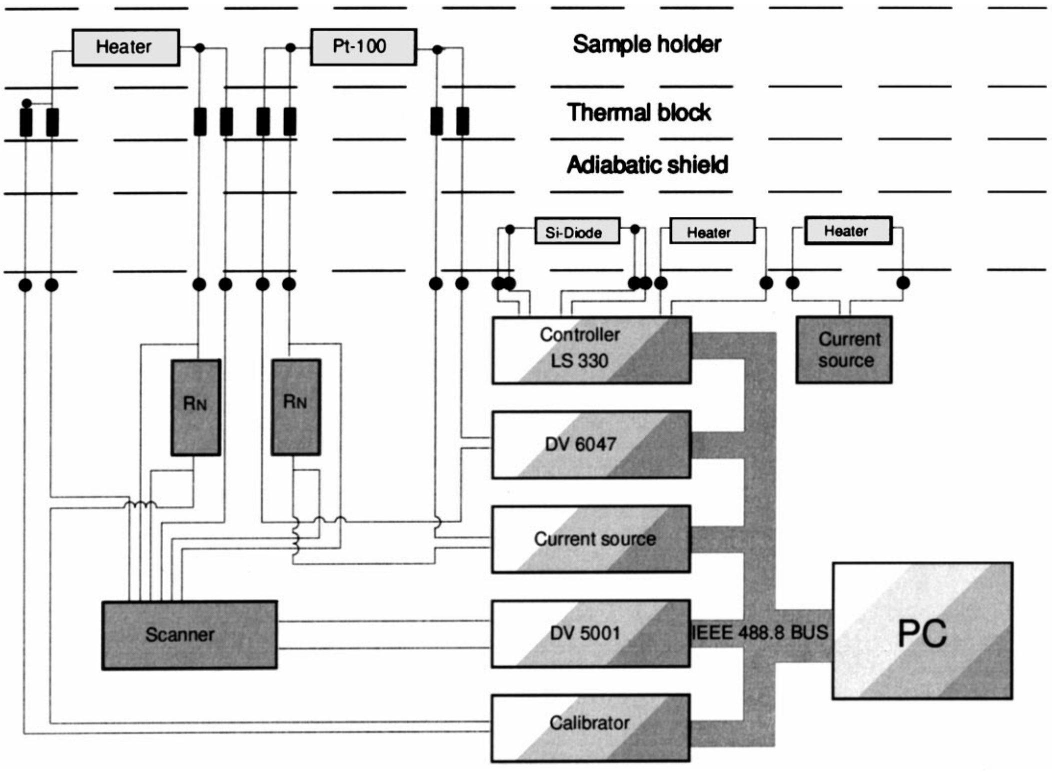

Fig. 2. Block diagram of the measuring system.

shield as functions of the time, and c_p/T as a function of the temperature. Several controlling features were included in the software, so the heater current is continuously adjusted to the respective heat capacity in order to attain the desired temperature step. Further, the length of the heating and equilibrium periods are adjusted according to the overheating of the sample. These features allow for autonomous measurements over more than 20 h without intervention.

4. Heat capacity of the empty calorimeter and of a standard copper sample

Measurements with a high density of points were carried out with the empty system in order to calibrate the calorimeter. Fig. 3 shows the deviation of the data from a fitted polynomial. The sudden increase after 200 K is probably caused by a partial loss of the shield controlling precision. To test the calorimeter, measurements on the heat capacity of a compact copper sample with a mass of 9.63 g and a purity of 99.999% were performed.

The standard deviation of our data from a fitted polynomial of 17th degree were 0.84% over the whole range of measurement and 0.54% above 25 K. Fig. 4 shows the deviations from this polynomial, Fig. 5 the deviations from the data of Martin [1], respectively. Only a few points at temperatures below 18 K and above 290 K deviate more than 1.5% from this reference curve.

5. Heat capacity and standard entropy of MgH_2

The specific heat capacity of a magnesium hydride sample (supplied by Th. Goldschmidt AG, Essen) was determined from 17–300 K. The aim of this measurement was not only to collect data for a reliable standard entropy calculation, but also to find out whether the calorimeter works satisfactorily for substances with rather poor thermal conductivities. A

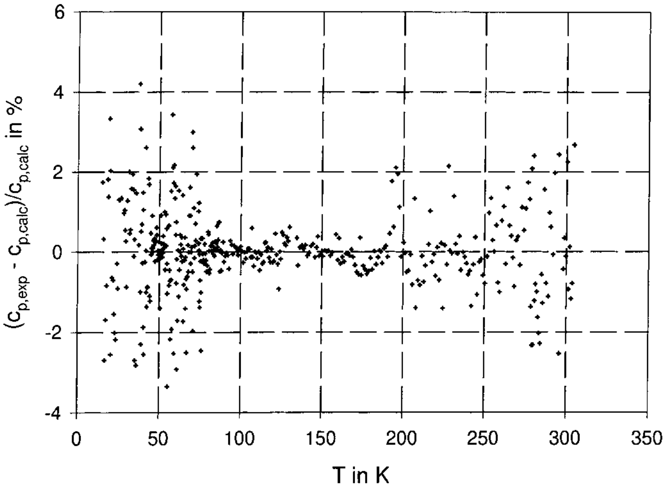

Fig. 3. Empty calorimeter – deviations of heat capacity of the measuring system from fitted curves.

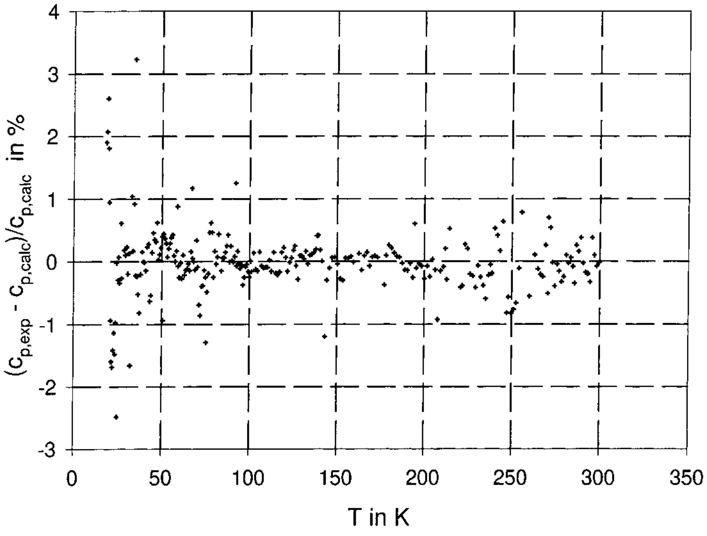

Fig. 4. Copper sample – deviations from fitted polynomial.

sample of 2.663 g was pressed to a pellet and mounted onto the sample holder. Some Apiezon grease was employed to improve thermal contact. The time of the heating periods varied from 60 to 240 s, the equilibrium periods were to a great extend dependent on the internal thermal relaxation of the sample, but usually did not exceed 500 s. In Fig. 6, the specific heat capacity of the sample is shown as a function of temperature, together with four values obtained by precision measurements from 293 to 353 K, performed in a Micro DSC II (Setaram) [2]. These data are in good accordance with the results of our measurement.

In order to obtain the molar heat capacity of magnesium hydride from the specific heat capacity of the sample, one must observe that the reaction of magnesium with hydrogen is very rarely complete [3]. This is due to the remarkably low diffusion rate of hydrogen

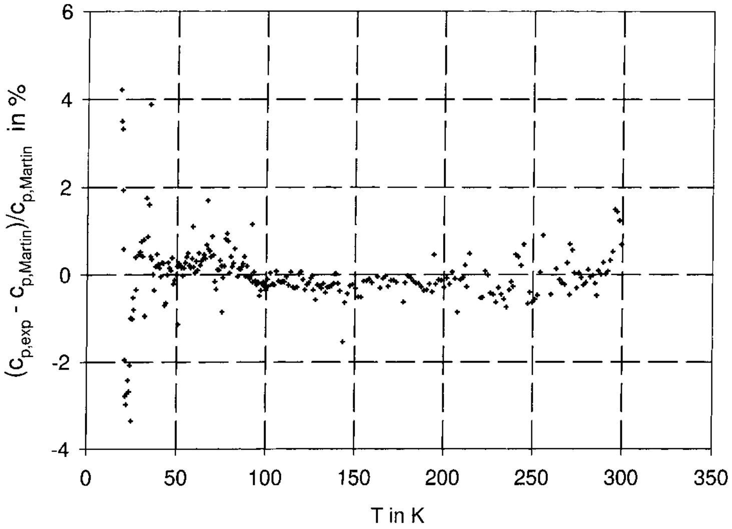

Fig. 5. Copper sample – deviations from the reference function of Martin [4].

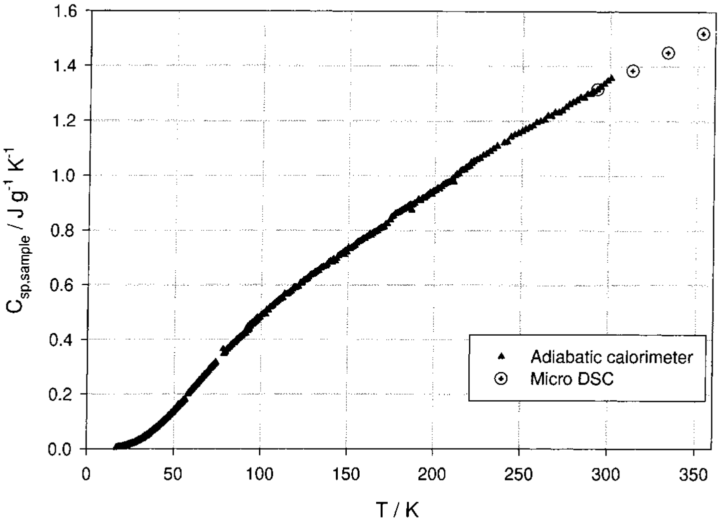

Fig. 6. Specific heat of the MgH_2 sample (prior to corrections).

in the hydride, which causes the reaction to halt if around a respective grain a closed MgH_2 layer of a certain thickness is formed, often surrounding a nucleus of unhydrogenated magnesium [4].

The hydride content in our sample was determined by means of thermogravimetry and found to be 82 wt%. A function for the specific heat capacity of magnesium was calculated by fitting a polynomial to the low-temperature data given in the literature [5]. The molar heat capacity of MgH_2 is then:

$$C_{\mathrm{p,MgH_2}}(T) = \frac{c_{\mathrm{sp,S}}(T) - (1 - w_{\mathrm{MgH_2}})c_{\mathrm{sp,Mg}}(T)}{w_{\mathrm{MgH_2}}} \times M_{\mathrm{MgH_2}},$$

where C_p is the molar heat capacity at constant pressure, c_{sp} the specific heat capacity, w the weight

Table 1
Smoothed values for the molar heat capacity of magnesium hydride

T/K	C_p/J K^{-1} mol^{-1}	T/K	C_p/J K^{-1} mol^{-1}
17.0	0.164	140.0	17.27
18.0	0.180	150.0	18.53
19.0	0.197	160.0	19.79
20.0	0.214	170.0	21.08
21.0	0.234	180.0	22.38
22.0	0.256	190.0	23.71
23.0	0.282	200.0	25.06
24.0	0.314	210.0	26.41
25.0	0.353	220.0	27.75
30.0	0.656	230.0	29.05
40.0	1.671	240.0	30.31
50.0	3.080	250.0	31.52
60.0	4.826	260.0	32.68
70.0	6.665	270.0	33.79
80.0	8.436	280.0	34.87
70.0	6.634	290.0	35.92
80.0	8.413	300.0	36.97
90.0	10.12	310.0	38.04
100.0	11.73	320.0	39.12
110.0	13.24	330.0	40.22
120.0	14.65	340.0	41.32
130.0	15.98	350.0	42.39

fraction and M the molar weight. Smoothed values of $C_{p,\mathrm{MgH_2}}$ at rounded temperatures are given in Table 1. Integration of $C_p/T(T)$ results in a molar standard entropy of MgH_2 of $S^0_{\mathrm{MgH_2}} = 30.64\ \mathrm{J\ K^{-1}\ mol^{-1}}$.

6. Conclusions

The constructed calorimeter is a suitable instrument to determine heat capacity data required for standard entropy determination of solids. In comparison to similar calorimeters, the effort for its maintenance is relatively low, as no liquid helium is applied and the system runs autonomously over a wide temperature range. The tests with the copper sample as well as the comparison of our MgH_2 data with those obtained by a different method show that precision and accuracy lie within an acceptable range. Further improvements should be made concerning the adiabatic shield control above 200 K.

The standard entropy of MgH_2 was determined with $S^0(298.15)=30.64\ \mathrm{J\ K^{-1}\ mol^{-1}}$. This is slightly less than the reference value of $31.09\ \mathrm{J\ K^{-1}\ mol^{-1}}$ [6]. Thermodynamical calculations based on the determined standard entropy result in a hydrogen equilibrium pressure which is in good agreement with actually observed pressures [7].

According to our information, there exists no comparable complete set of heat capacity data in the covered temperature range from 15 to 300 K yet.

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