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Instrumentation

HIGH-PRECISION ADIABATIC CALORIMETRY AND THE SPECIFIC HEAT OF CYCLOPENTANE AT LOW TEMPERATURE

R. Jakobi, E. Gmelin and K. Ripka

MAX-PLANCK-INSTITUT FÜR FESTKÖRPERFORSCHUNG, D-7000 STUTTGART 80,
HEISENBERGSTRASSE 1, FRG

We describe a fully automated adiabatic calorimeter designed for high-precision covering the temperature range 15 to 300 K. Initial measurements were performed on synthetic sapphire (20 g). The statistical error of the apparatus estimated from the scattering of the C_p data of sapphire is about 0.1% and the average absolute error of specific heat between 100 and 300 K was 0.7% compared to values given in the literature. The heat capacity and the three phase transitions of cyclopentane (C_5H_{10}) which is recommended as a standard for the temperature calibration of scanning calorimeters have also been measured. The transition temperatures were determined to be (literature values in parentheses): 122.23 K (122.39 K) 138.35 K (138.07 K) and 178.59 K (179.69 K), with an experimental error of ± 40 mK.

Keywords: cyclopentane, high-precision adiabatic calorimetry, specific heat

Introduction

Knowledge of thermodynamic quantities such as enthalpy, entropy and free energy is important for material science and the chemical industry. These functions can be derived from the specific heat and its temperature dependence. Measurement of heat capacity is now a standard procedure. However, most measurements are carried out using commercially available scanning calorimeters, which are convenient to operate and provide the facility for rapid investigation of samples in the mg range. However, these instruments are limited to temperatures above 100 K and their precision is rarely less than 2%. Often it is essential to obtain more comprehensive and accurate thermodynamic data. This can only be provided by adiabatic calorimetry which is the oldest, but still most precise,

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Akadémiai Kiadó, Budapest

method for determining specific heat. An accuracy of 0.1% is possible, but this requires special equipment and involves much effort in setting up and testing the apparatus. At present only a few groups of investigators are involved in high-precision adiabatic calorimetry [1, 2]. We have started to build a calorimeter that should be able to fulfill the requirements for high-precision measurements. Initial results show that a statistical error of less than 0.1% can be achieved with our equipment; the absolute accuracy, however, is in the range 0.5–0.8% and still requires improvement.

A priority in our work was the re-investigation of the specific heat and phase transitions of cyclopentane. This compound has recently been recommended as a standard material for temperature calibration of scanning calorimeters below room temperature [3]. Precise determinations of its thermodynamic properties were last reported between 1943 and 1947 [4–6].

Description of the calorimeter

The equipment is based on the Nernst 'step heating' method. The main concepts of previous adiabatic calorimeters – mechanical set-up, cryostat and measuring method – were adopted [7, 8]. Only the new features of the equipment are therefore described here.

The sample holder consists of a small cylinder made of gold-plated copper with a volume of about 5 cm^3, similar to that described by White *et al.* [9]. A constantan wire with a resistance of ≈ 1000 Ω is wound non-inductively around the cylinder and serves as electrical heater. The thermometer, a 100 Ω platinum resistor (Rosemount, type MF118C), is mounted at the bottom on the outer surface of the sample holder. Helium gas is used to improve the heat exchange between sample and holder, and the container has to be hermetically sealed. This is accomplished by an O-ring type indium wire between the cylinder and lid. The latter is fixed by six screws made of stainless steel.

The temperature is measured with an AC resistance bridge (Automatic System Laboratories, ASL, model F17) which has a resolution of 0.1 mΩ corresponding to approximately 0.25 mK between 50 and 300 K. The uncertainty of the absolute temperature measurement is ±40 mK according to the specification of the calibrated platinum resistor [10].

The sample holder is surrounded by two thermal shields. Both are equipped with a platinum thermometer and an electrical heater. The inner shield is controlled by a combination of resistance bridge (ASL, model F26) and a temperature controller (ASL, model 300). The temperature resolution is about 1 mK. The shield is programmed to follow continuously the sample temperature.

The outer shield is regulated by a second temperature controller (Scientific Instrument, model 9650) with a resolution of 10 mK. The temperature is always kept 1.0 K below that of the inner shield.

Measurement of the heater power is by a digital multimeter (Keithley, DMM 199). Heating current and voltage are determined with an accuracy of less than 0.01% using the three-wire method. Heating time is measured by the clock of a computer with a resolution of 10 ms. The whole system is fully automated using the IEEE-488 facility of all instruments. The program is written in HP-BASIC and runs on a HP 9000/340 computer under UNIX.

At present, we apply the following parameters which have still not been optimized. The heating time for one step is 500 s. Using a temperature increase of approximately $\Delta T = 1$ K, we obtain a heating rate of ≈ 2 deg·min^{-1}. Recording of the drift starts 100–250 s after the end of the heating time. The delay is necessary to allow thermal relaxation between sample, holder and thermometer. The drift is measured over a 400 s acquiring time, and temperature values every 10 s. We achieve a drift of less than 5 μK/s with an error of about 0.3 μK/s.

Experimental

The specific heat of synthetic sapphire (α–Al_2O_3) was measured in order to check the accuracy of the calorimeter. The sample, weighing 19.5798 g, was cut from a single crystal. The measurement started at 77.3 K (boiling point of N_2) because the specific heat of sapphire rapidly decreases on cooling. Below 77 K the contribution of the sample to the total heat capacity is less than 25%; at 300 K the corresponding value is $\approx$ 70%. The second sample – cyclopentane – was purchased from MERCK ('cyclopentane for spectroscopy', purity 99.9%) and measured without any further purification or drying. The sample mass was 3.6734 g. In this case the sample contributed between 41 and 55% to the total heat capacity. Transition temperatures and enthalpies of cyclopentane were determined by continuous heating, starting at a temperature T_{st} about 1 K below the phase transition and ending at a temperature T_{end} about 1 K above. At a first-order transition (in phase equilibrium) the temperature remains constant. The enthalpy of the transition is given by the total heat input reduced by the energy that is necessary to heat up the sample:

$$\left(\int_{T_{st}}^{T_{end}} C_p(T)\,dT\right)$$

Results

The temperature-dependence of the heat capacity $C(T)$ of the empty sample holder is shown in Fig. 1. In order to check the statistical error of the measurement, a polynomial was fitted to the $C(T)$ curve (full curve in Fig. 1). The mean deviation of the measured points from the polynomial is less than 0.03%. This is in agreement with the results of an error propagation which was performed for the statistical error of heating voltage, current, time and the temperature.

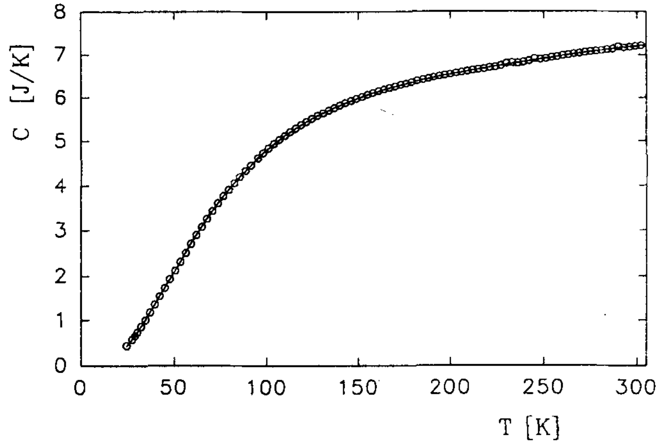

Fig. 1 Heat capacity of the sample holder as a function of temperature. The solid line represents a polynomial fit to the experimental data

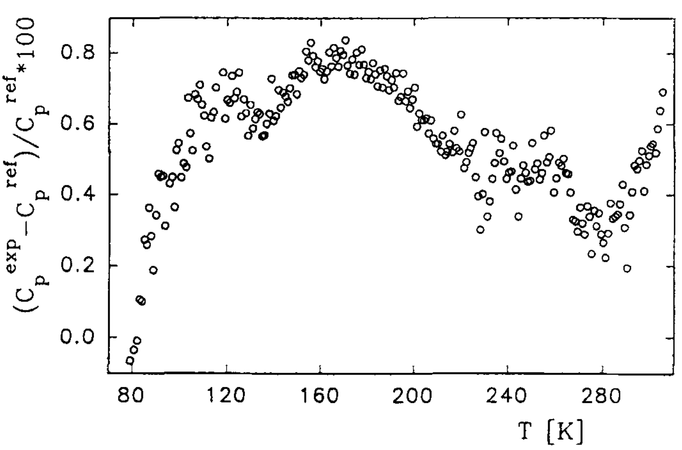

Fig. 2 Percentage deviation of the specific heat of synthetic sapphire as a function of temperature. Specific heat data recommended by NBS [11] are taken as reference

Results for sapphire are given in Fig. 2. Here, the percent error of the measured specific heat $(100\cdot(C_p^{exp}-C_p^{ref})/C_p^{ref})$ is shown. The reference values are taken from [11]. A systematic error resulting in a positive deviation of almost all point is apparent. The average error between 100 and 300 K is about 0.7% but below 100 K this decreases. The reason for this systematic error is not yet known. As the deviation is not constant, but varies with temperature, it is likely that there is more than one source for the systematic error. One reason could be the thermometer calibration. The table provided by the manufacturer indicates only three calibration points, between which the values are calculated by a polynomial interpolation. Here, the accuracy may be less than 40 mK. Another error may result from the slow response of the shield regulation. At the start of the heating interval, it takes some ten seconds for the temperature of the shield to follow properly the sample temperature, and this can cause an additional heat exchange between sample and environment. However, the present data show, that the calorimeter enables collection of data with less than 0.2 % scattering. Figure 3 shows results of the cyclopentane measurement compared with literature data [4]. At temperatures remote from the phase transitions the deviation of our data is less than ± 1.5 %. For the phase transition at 122.4 K and for the melting point at 179.7 K, in particular, the increase of $C_p(T)$ starts some degrees Kelvin *before* the transition point. We interprete this as an indication of impurities in the sample, which lower the melting temperature. The measured transition temperatures and enthalpies are listed in Table 1 and compared to the values given in [4]. In contrast to the two other transitions, for the second phase transition a positive temperature deviation is shown compared to the reference value. Thus, the temperature interval between the first and the second transition is increased while the difference between the second transition temperature and the melting point is decreased in comparison to reference data. The same trend has been found by highly accurate DSC measurements of cyclopentane [12]. For the transition enthalpies we also find large differences between our data and values in [4]. These deviations strongly exceed the

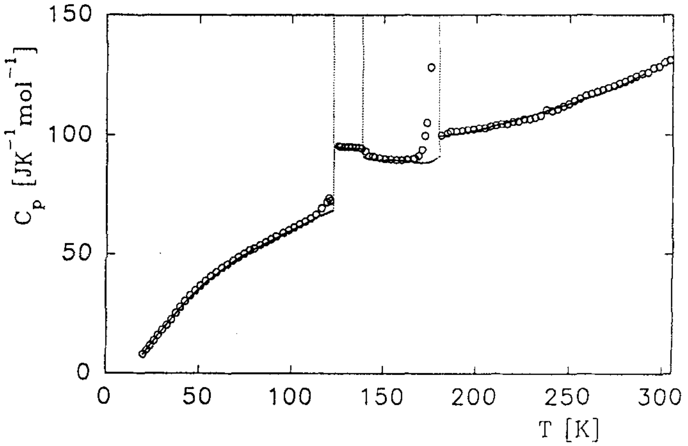

Fig. 3 Specific heat of cyclopentane as a function of temperature. Circles: present data. Solid line: values from [4]. Dotted lines indicate the phase transitions

Table 1 Transition temperatures and enthalpies of cyclopentane. Literuature values are indicated in parentheses. The experimental error of the temperature is ±40 mK, that of the entalpy about 1%

Transition type	Temperature/K	Enthalpy/J·mol^{-1}
Solid-solid 1	122.23 (122.39)	4760 (4880)
Solid-solid 2	138.35 (138.07)	329 (347)
Solid-liquid	178.59 (179.69)	5578 (603)

systematic errors detected by the reference measurement of the sapphire sample. Presumably, cyclopentane is very sensitive to impurities (including air and moisture) and, therefore, purification of the commercially available compound is required, before measurement.

Note added in proof: Very recently, we reduced the absolute error of measuring a sapphire sample to 0.35% by improving the thermal insulation of both heat-shields using 1–3 layers of superinsulation.

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Zusammenfassung — Es wird ein vollautomatisches adiabatisches Kalorimeter für eine hochpräzise Abdeckung des Temperaturbereiches 15 bis 300 K beschrieben. Erste Messungen wurden an einem synthetischen Saphir (20 g) durchgeführt. Der anhand der Streuung der C_p-Daten ermittelte statistische Fehler des Gerätes beträgt 0.1 % und der mittlere absolute Fehler der spezifischen Wärme zwischen 100 und 300 K betrug verglichen mit den Literaturangaben 0.7 %. Weiterhin wurden auch die Wärmekapazität und die drei Phasenumwandlungen von Cyclopentan (C_5H_{10}) untersucht, die als Standard für die Temperaturkalibrierung von Scanning-Kalorimetern empfohlen wird. Folgende Werte wurden für die Umwandlungspunkte festgestellt (Literaturangaben in Klammern): 122.23 K (122.39 K), 138.35 K (138.07 K) und 178.59 K (179.69 K) mit einem experimentellen Fehler von ±40 mK.