DETERMINATION OF THE HEAT OF FUSION OF BISMUTH WITH A HEAT-FLUX DSC

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SUMMARY

   With a cylinder-type DSC the heat of fusion of bismuth (purity 99.995% and
99.9999%) was determined. The applied method of the quasi-direct comparison of
the heat of fusion with heat generated electrically allows measurements to be
performed with a small uncertainty because the calibration is not carried out
here by the customary indirect calorimetric methods using calibration substan-
ces but with exactly known electric energy in close vicinity to the thermal
effect investigated.

INTRODUCTION

   For the calibration of heat-flux DSCs (differential scanning calorimeters
(DSC)), pure metals are generally used whose heats of fusion must be exactly
known.

   Endeavours are therefore made to recheck the respective "best value" of the
heat of fusion of the metal if this value has been averaged from measurements
with great uncertainties and if improved methods of measurement promise
reasonable results. In contrast to the metals indium and tin frequently
measured, the situation is unsatisfactory for bismuth (T_{fus} = 271.3 °C). The
measurement results obtained since 1952 show a continuous decrease of the
measured heats of fusion from 57.04 J/g (1952) to 53.26 J/g (1975; last
measurement result published; Table 2). During this period of time, five
publications were edited with values which lie between the above-mentioned
values.

   In order to be able to state an actual "best value", it appeared necessary
to carry out additional thorough measurements. For this purpose, the method of
the quasi-direct comparison of the heat of fusion with electrical energy was
applied /1/. The material used was bismuth (supplier: PREUSSAG AG) with a
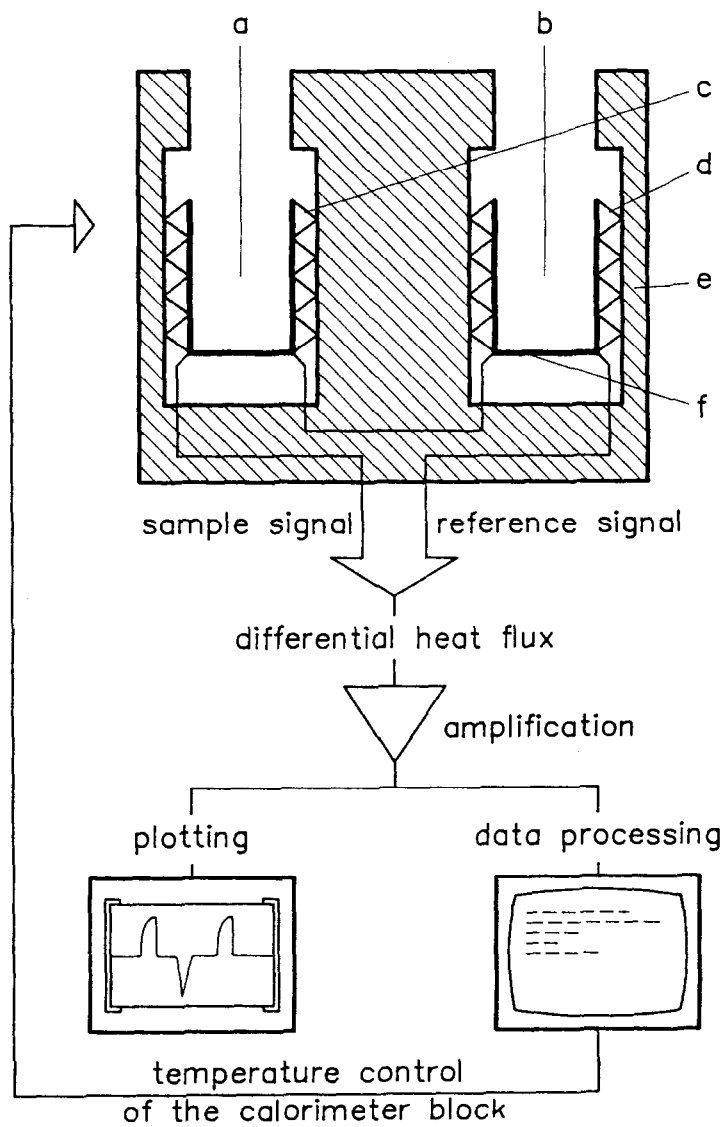purity of 99.995% and 99.9999%.

Fig. 1. Cylinder-type heat-flux DSC according to CALVET (model C 80 of SETARAM)
a sample cavity, b reference cavity, c, d thermopile, e heatable calorimeter block, f hollow cylinder

MEASURING ASSEMBLY - METHOD OF MEASUREMENT

The measurements were carried out with a cylinder-type heat-flux DSC accor-
ding to CALVET (manufacturer: SETARAM, model C 80). The calorimeter consists
of two hollow cylinders axially arranged in parallel with each other and
inserted into a heatable metal block, the calorimeter block (Fig. 1). Each
hollow cylinder is thermally coupled to the calorimeter block by means of a
thermopile. For the measurement of heats of fusion, electrically heatable
calibration probes of largely identical design are inserted in each of the two
hollow cylinders. One calibration probe contains the fusion sample and the
other an inert reference sample whose heat capacity complies with that of the
sample.

When the calorimeter block is heated at a constant heating rate (scanning
mode), the thermopiles will ensure a heat exchange between the hollow cylin-
ders - and thus the samples - and the calorimeter block.

The thermopiles are differentially connected so that there will be no dif-
ferential voltage if the samples have the same temperature. When the tempera-
ture of the calorimeter block is linearly increased, there will be different
heat fluxes through the thermopiles as soon as the sample substance melts.
With the time derivatives of ΔU disregarded, the ensuing differential thermo-
voltage ΔU is proportional to the instantaneous difference of the heat fluxes
$\Delta \Phi$ between the calorimeter block and the two hollow cylinders (or samples).

$$\Delta \Phi = K \cdot \Delta U$$

The enthalpy of fusion $\Delta_{fus} H$ is exactly proportional to the integral over
$\Delta \Phi (t)$:

$$\Delta_{fus} H = \int \Delta \Phi(t) dt = \int K \Delta U(t) dt,$$

i.e. proportional to the area of the fusion peak (cf. Fig. 3). The calibration
factor K must be determined by experiments.

For this purpose, two electrically heatable calibration probes were deve-
loped which are described in /1/. For the probes presented there, the arran-
gement of the filament winding turned out to be unsuitable as due to the
brittleness of the insulating varnish layer there are often short-circuits.

This is why in the case of the probes used here the heating wire is not wound on the sample carrier but on the newly designed container accommodating the sample carrier.

The new container which is 17 mm in diameter is made from aluminium. For the reception of the heating wire, the container according to Fig. 2 has a helically turned groove 0.15 mm in width and 0.2 mm in depth.
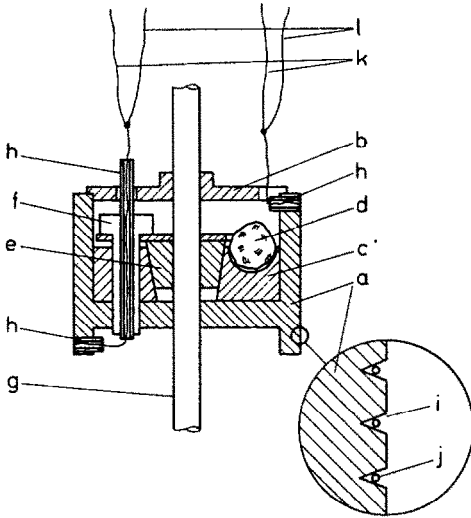

Fig. 2. Sample container of the calibration probe -
Detail: Grooves with inserted heating wire
a aluminium container, anodized, b cover, c sample support, d sample,
e wedges, f clamping screws, g stainless steel tubes, h glass capillaries,
i grooves, j heating wire, k, l current and potential lines

The pitch is 0.4 mm and designed so that flat trapezoidal webs are formed between the grooves. This design ensures good thermal contact between the calibration probes inserted without play into the cylinders of the calorimeter and the cylinder walls.

Before being wound with the heating wire, the aluminium container was anodized to form an insulation layer between the container and the heating wire. Each end of the groove is provided with a hole with cemented glass

capillaries through which the resistance wire is radially led towards the axis. The wire ends are soldered to platinum wires 0.1 mm in diameter (current supply and voltage measurement).

EXPERIMENTAL

The calorimeter is connected to a computer to control automatically the temperature/time program. During all measurements the heating rate is 0.1 K/min. The subsequent data evaluation is carried out through an integration program, the integration limits being defined by a method described in /1/.

For the quasi-direct comparison of the heat of fusion with electrically generated heat, about 4 K before and about 4 K after the fusion peak maximum one exothermic "calibration peak" is produced by supplying a known electrical energy to the filament winding of the calorimeter probe containing the sample (Fig. 3).
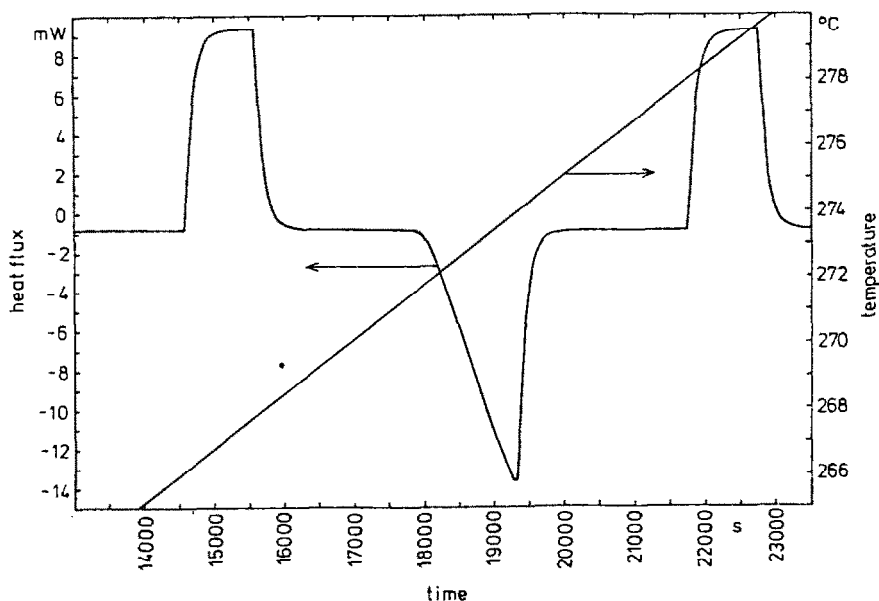

Fig. 3. Fusion peak of bismuth (middle) and two electrically generated calibration peaks (right and left). Heating power 10 mW, time of heating 1000 s.

During all experiments the heating power is 10 mW. With 1000 seconds the heating duration is selected so that the area of the calibration peak cor-

responds more or less to that of the fusion peak. The current for the pro-
duction of the calibration peak was supplied by a supply unit belonging to the
calorimeter.

The quotient of the known electric energy (in mWs) and the mean value of
the two peak integrals of the electrical calibration $\int \Delta U(t)dt$ (in mVs) yields
the calibration factor K (in mWs/mVs). The multiplication of the calibration
factor by the integral over the fusion peak (in mVs) yields the fusion
enthalpy.

RESULTS AND DISCUSSION

The experimental results are given in Table 1. For the fusion enthalpy of bis-
muth, at an estimated total uncertainty of 0.21 J/g (i.e. 0.4%),

$$\Delta_{fus}H = 52.93 \ J/g$$

resulted for the sample of higher purity (99.9999%).

The total uncertainty is obtained by addition of the uncertainties of the
calibration peaks (0.25%), of the systematic error of the area determination
(0.05%), of the heat losses during calibration and measurement (0.05%) and of
the uncertainty of the weighing (0.01%) (cf. /1/).

The mean value of the fusion enthalpy of the sample of lower purity
(99.995%) shows a distinct systematic deviation of 0.5% from the mean value of
the sample of higher purity. According to /1/, the same effect was observed
for indium and tin.

Table 2 gives the results of measurements of the heat of fusion of bismuth.
(The values obtained before 1975 have been taken from Grønvold /2/. If the
values according to Table 2 were chronologically entered in Fig. 4, a drop to-
wards smaller measurement values is to be observed for recent measurements. To
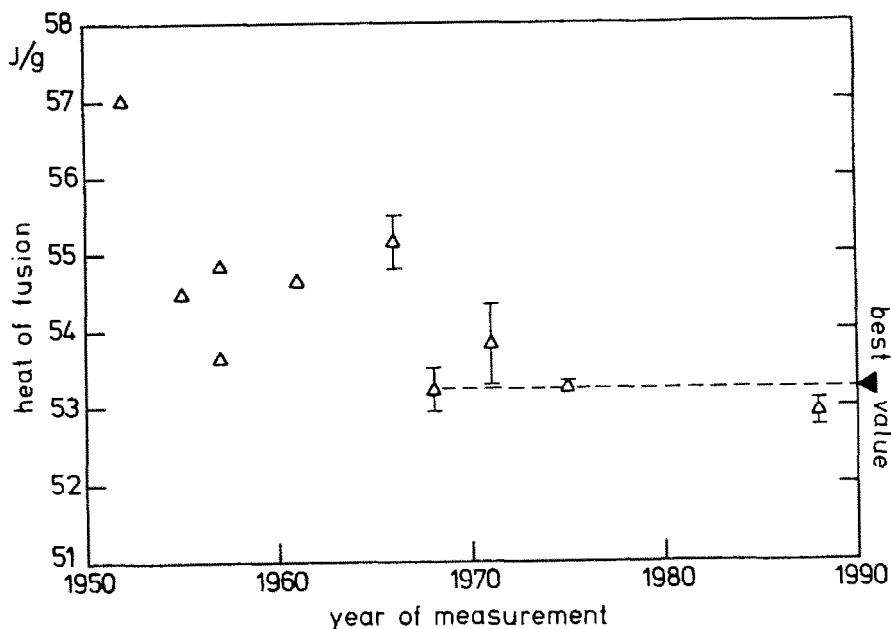calculate a mean value covering all values is therefore not convenient.

Fig. 4. Heat of fusion of bismuth measured since 1952; from 1966, the ranges of uncertainty are specified (best value: ◄).

The great difference between the results obtained by Chiotti /3/ and Grønvold /2/ who both used an adiabatic calorimeter for their measurements is striking. As Chiotti, however, states a value for tin which, with 58.03 J/g, lies far below the best value of 60.46 J/g recommended in /1/, a systematic error of /3/ can be presumed. Chiotti's measurement value is therefore not allowed for in the best value estimate.

Castanet /4/ and Malaspina /5/ carried out their measurements using a cylinder-type heat-flux DSC according to CALVET, a separate heating device which did not accommodate the samples being used for calibration.

If the estimate is only based on the measurements whose ranges of uncertainty overlap and if a subjective weighting complying with the reliability of the method is performed (Castanet once, Malaspina once, Grønvold three times, this publication twice) an actual "best value" for the heat of fusion of bismuth can be proposed of

$\Delta_{fus}H = 53.25 \pm 0.6$ J/g ($\pm 1.1\%$)

TABLE 1:

Heat of fusion of bismuth (σ standard deviation)

Purity in %	99.995	99.9999
Mass of sample in mg	188.311	196.049
Heat of fusion in J/g	52.68	52.94
	52.59	52.86
	52.74	52.96
	52.63	52.99
	52.61	52.95
	52.68	52.92
	52.64	52.90
Mean value	52.65	52.93,
2 σ	0.10	0.08$_5$

TABLE 2:

Heat of fusion of bismuth (values from literature)

Author	Year	$\Delta_{fus}H$ in J/g	Ref.
1 Nagasaki, Fujida	1952	57.04	acc. to /2/
2 Oelsen	1955	54.46	acc. to /2/
3 Oelsen	1957	52.64	acc. to /2/
4 Oelsen	1957	54.84	acc. to /2/
5 Schürmann, Träger	1961	54.65	acc. to /2/
6 Chiotti	1966	55.19 ± 0.36	/3/
7 Castanet	1968	53.27 ± 0.3	/4/
8 Malaspina	1971	53.85 ± 0.54	/5/
9 Grønvold	1975	53.26 ± 0.05	/2/
10 this paper	1989	52.93 ± 0.21	

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