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Determination of the Enthalpy of Fusion of Indium by Direct Comparison with Joule Heats

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Summary

A simple calibration device for a commercial heat flux calorimeter is presented allowing enthalpies of fusion to be determined very precisely. The heats of fusion are referred to Joule heats which can be measured with high accuracy.

The basic principle of the device is that during measurements and calibration the experimental arrangement should be as similar as possible. It is of utmost importance that the heat to be measured is conveyed to the calorimeter always at the same point.

The device has been tested by measuring the heat of fusion of indium. The measurement results are in excellent agreement with Grønvold's results /3/ who used an adiabatic calorimeter with pulse heating.

Introduction

The calibration of a calorimeter requires that a known heat is released in its interior. Calibration is carried out by using Joule heats, well-known heat capacities, heat fluxes of radioactive samples and, above all, enthalpies of fu-

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sion or transformation of various substances /1/. In particular the last cal bration method is very frequently used. Apart from the specific enthalpy of fusion or transformation, only one weighing is involved which can easily be carried out with high precision.

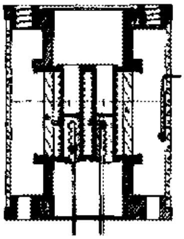
Unexpected problems arise, however, from the values of the specific enthalpi For the frequently used enthalpy of fusion of indium, the enthalpy values gi in the literature scatter by several percent.

The absolute determination of the specific enthalpy of fusion requires a con siderable amount of work. Reliable values can be expected here above all fro adiabatic calorimetry. Here the enthalpies of fusion are compared with Joule heats which can be measured very precisely.

It will be shown in the following that quite exact determinations of the enthalpies can be realized also with relatively simple means. The enthalpy of fusion of indium was directly compared with electrically produced heats usin a small supplementary device for a commercial heat-flux calorimeter, made in the workshop of the Institut für Werkstoffe.

Description of the calorimeter

A type MCB differential heat-flux calorimeter of Thermanalyse, Grenoble, is used (Fig. 1). In the cylindrical furnace which is heated linearly with tim during the measurement, two tubes have been mounted between the upper and lo flange. In the middle, these tubes are subdivided into the sample vessel pro (upper part) and an auxiliary vessel (lower part). A thermopile, i.e. 70 dif ferential thermocouples connected in series, is located between the two tube



1. Sample and reference vessel, resp.
2. Electrically heated furnace
3. Thermopile (70 differential thermocouples)
4. Radiation shield
5. Auxiliary vessels with built-in calibration resistors
6. Platinum resistance thermometer for furnace control
7. Upper flange
8. Lower flange

Fig. 1: Cross sectional view of the MCB calorimeter.

Sample and reference are placed into the vessels. The auxiliary vessels each accomodate an electric resistor for the calibration and a thermocouple for the measurement of the vessel temperature.

The dimensions of the vessels which are comparably large (9 mm in diameter, 25 mm in height) are a characteristic feature; they are advantageous for measurements on samples of low energy density. The measurement signal, i.e. thermovoltage, is proportional to the heat flux released by the sample:

$$\dot{Q} = k \cdot U_{\text{thermopile}}.$$

The calibration factor k is temperature-dependent.

Calibration

The calibration factor k can be determined most easily by means of the incorporated resistors. A current generator with timer has therefore been provided in the controlunit by the manufacturer. It is disadvantageous that with this calibration procedure, the heat is not released at the same point as during the measurement.

Part of the heat released in the tube is transferred to the upper vessel fixture, another part to the lower fixture, part of it even flows radially into the surroundings due to heat conduction in the filling gas and heat radiatio Depending on the position of the heat source in the tube, the heat flux is d tributed to these heat paths in different amounts. Thus the sensitivity chan when the location of heat production is changed. This effect was investigate previously by using two other calibration procedures /2/:

1. Calibration with special devices
   (electrical resistors were built into small copper blocks);
2. Calibration with enthalpies of fusion.

Both methods release the heat used for calibration at the sample site. It turned out that these calibrations differed by more than 1 % from those carr out with the incorporated resistors.

Improved enthalpy determination

The calibration method mentioned, too, does not allow the enthalpy values to be measured more exactly than to within ±1 to 2 %, the essential reason for this being that the arrangement differs during the calibration and the measurement proper:

- For the calibration with electrically heated calibration resistors, leadwires are necessary. The systematic error caused by them has, of course, been corrected computationally. As, however, the assumptions required for the calculation are not known with sufficient accuracy, an error remains in spite of the correction.

- The heat transfer conditions between sample and calorimeter also change fortuitously from one measurement to the other. Basically, the resulting error - as it is of statistical nature - can be ascertained by adequately frequent repetitions.

These error influences can be avoided or decisively reduced by further developing the calibration devices. For this purpose, an electrically heatable device was designed which additionally offers sufficient space to take up a fusion sample. With the arrangement fixed, an electrical calibration can be carried out and the heat of fusion be measured, so that all leaks and all heat transfer conditions are maintained.

Design of the improved calibration devices

The devices consist of a copper cylinder (8 mm in diameter, 15 mm in height) with a drilled-in sample container (6 mm in diameter, 9 ,, in height) (Fig.2).

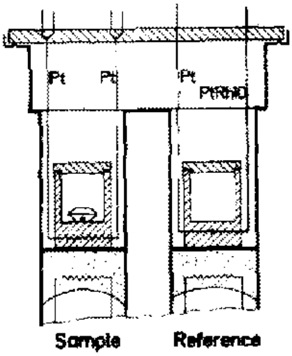


Fig. 2: Basic drawing of the calibration device including indium sample, installed in the calorimeter.

A lid ensures that the head transfer by radiation remains constant independent of the filling of the sample container. A calibration resistor (Pt 100) has been fitted in the bottom of the device whose lead-in wires (platinum, 0,15 mm in diameter) are led out via a transverse yoke. Up to this yoke a two-wire circuit has been used, beyond the yoke a four-wire circuit. The reference device equals the sample device, except that instead of the calibration resistor a Pt-PtRh thermocouple has been installed which will be used in future for temperature calibration. The lead-in wires are long enough so that the devices can be securely arranged on the bottom of the calorimeter vessel.

The transverse yoke fixes the lead-in wires mechanically (Fig. 3). The devic can be removed from the calorimeter together with the transverse yoke and ar thus easy to handle. At the same time the yoke ensures the "heat setting" o the wires, i.e. the temperature difference along the lead-in wires remains fined.

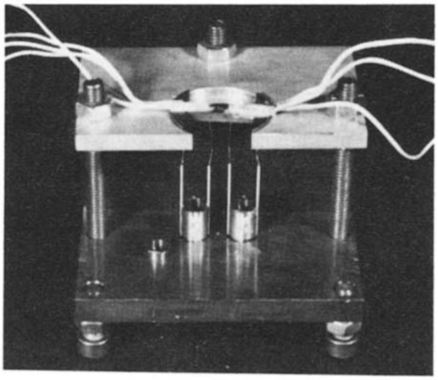


Fig. 3: Calibration device with lids and transverse yoke in mounting fixture.

The indium is introduced into the calibration device in a commercial aluminium pan. The calibration devices are so designed that the indium sample is located as close as possible to the calibration resistor. In spite of this, a distance, though small, between the two heat sources cannot be avoided. F the calibration it is not absolutely necessary that indium sample and resis are at the same site. It is, however, indispensable that the heats to be co pared are conveyed to the calorimeter at the same point. With the present a rangement, independent of the heat source, the heats are first exchanged wi the small copper block which has good conduction properties; only then are they transferred to the calorimeter via a comparably high thermal contact r sistance. The largest heat portion flows via the thin gas layer between calibration device and vessel bottom to the calorimeter. All other heat transfer mechanisms contribute only little to this heat transfer. Due to this special heat flux established between heat source and calorimeter, the heat to be measured is fed into the calorimeter always at the same point. The abovementioned error resulting from site-dependent sensitivity is thus avoided.

Carrying-out of experiments and results

Threee calibration experiments were made with 45.111 mg indium at a heating rate of 0.1 K/min. Electrical calibration was carried out at about 5 K before and after the fusion peak. The data for the electrical calibration was so chosen that - apart from the sign - it was as similar as possible to the measured fusion peaks (Fig. 4).

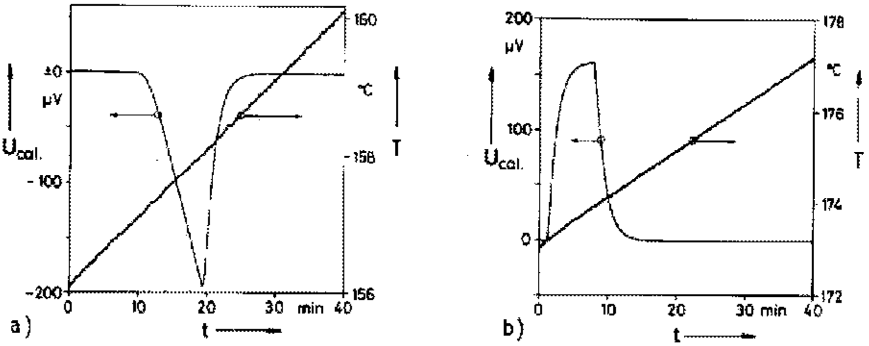


Fig. 4: Example of fusion peak (a) and electrical calibration peak (b). Electrical calibration with current 7 mA and heating time 7 min.

The remaining differences in the shape of the peak as well as the different sign should be of no special significance as the calorimeter shows excellent linearity as regards the heat fluxes /2/. With the current kept constant, the voltage was continuously recorded at the calibration resistor in order to allow an exact determination ot the integral Joule heat to be made, for the el tric resistance does not remain constant due to the temperature variations d ring measurement.

Via a digital voltmeter, the caloric measurement signal was directly recorde by a computer. Possible errors due to graphical registration and planimetry can thus be eliminated. Within the area of the peaks the base line was linea interpolated. The calibration factors were each time determined for the temp ature of the peak area center. Only the calibrations carried out during one were used to evaluate the appropriate fusion peak. As the sensitivity, i.e. reciprocal calibration factor, shows excellent linearity in the temperature terval under consideration, the value at the enclosed fusion peak was determined by linear interpolation from the electrically determined sensitivities before and after the fusion peak.

The uncertainties of current and voltage sum up to about 0.1 to 0.2 %, the t measurement showing a maximum uncertainty of 0.02 %. The correction for the lead-in wires to the calibration resistor amounts to 0.24 %. Even if the err in fixing this factor amounted to 20 %, this would affect the final measurement result by only 0.05 %. Thus the overall uncertainty of the determinatio of the electrical heat amounts to about 0.2 to 0.3 %.

After correction, the following values resulted for the specific enthalpy of fusion of Indium:

$$\Delta H_f^{In} = 3298,\ 3280 \text{ and } 3290 \text{ J/mol.}$$

Average value and standard deviation result from this as:

$$\Delta H_f^{In} = 3289 \pm 9 \text{ J/mol} \quad (\hat{=} \pm 0.3 \, \%)$$
$$= 28.65 \text{ J/g.}$$

The values of the enthalpy of fusion of indium given in the literature (cf. Table) lie between 3260 and 3360 J/mol. Measurements carried out recently yielded results close to 3300 J/mol. Grønvold's /3/ measurements are considered to be very reliable. The measurement results of the present work are in good agreement with his value, although the experimental outlay of the method described is considerably lower.

Table: Values of the enthalpy of fusion on indium given in the literature. Most of the data was taken from Grønvold's paper /3/.

Author	Year	ΔH_f^{In} in J/mol
ROTH et al.	1933	3272 ± 13
OELSEN et al.	1955	3270 ± 17
OELSEN	1955	3180
DAVID	1964	3268
PREDEL	1964	3370
TARWATER	1965	3810
ALPAUT et al.	1965	3340
BROS	1966	3314
GWINUP	1967	3452 ± 25
MECHOVSKII et al.	1969	3364 ± 100
REZNITSKII et al.	1970	3350 ± 345
MALASPINA et al.	1971	3318 ± 59
FLYNN	1974	3130
WIDMANN	1974	3290
MARTI	1974	3238 ± 39
RICHARDSON et al.	1975	3350 ± 30
GRØNVOLD	1978	3283 ± 7
MARTI /4/	1982	3332 ± 17
BREUER et al. /5/	1982	3280 ± 20
THIS WORK	1983	3289 ± 9

Literature

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