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# UNEXPECTED PROBLEMS IN THE CALIBRATION OF HEAT-FLUX DIFFERENTIAL SCANNING CALORIMETERS

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## Abstract:

It is a well-known problem that the values of the calibration constant of Heat-flux-DSC equipment obtained by means of heat of fusion are different from those by well-known heat capacities. Varying container geometry in several runs of determination of the heat of fusion of indium, we were able to show that there is no influence of the disturbation of steady-state conditions of heat-flux on the calculated value of the enthalpy of fusion. An error of about 20 % in the calculated values of this enthalpy may result, if not correctly closed containers are used, as is shown in this work. To get more information about these errors and disadvantages and their sources, a numerical calculation of 2-dimensional heat flux in a commercial DSC-equipment during melting of indium was carried out. Results of the model calculation are shown and discussed in this work.

## Aims:

The calibration of all heat-flux differential calorimeters must be varified from time to time. This is usually done by means of the heat of fusion of indium. It allows the caloric sensitivity to be determined as it is generally described in the operating instructions. The temperature dependence of the sensitivity can furthermore be determined by measuring the heat capacity of a suitable calibration substance. Practical experience has shown that with this procedure different values are obtained for equal temperatures. Fig. 1 shows, for two instruments, the caloric sensitivities measured by means of the heat of fusion of indium and the specific heat capacity of alumina, as a function of the heating rate.

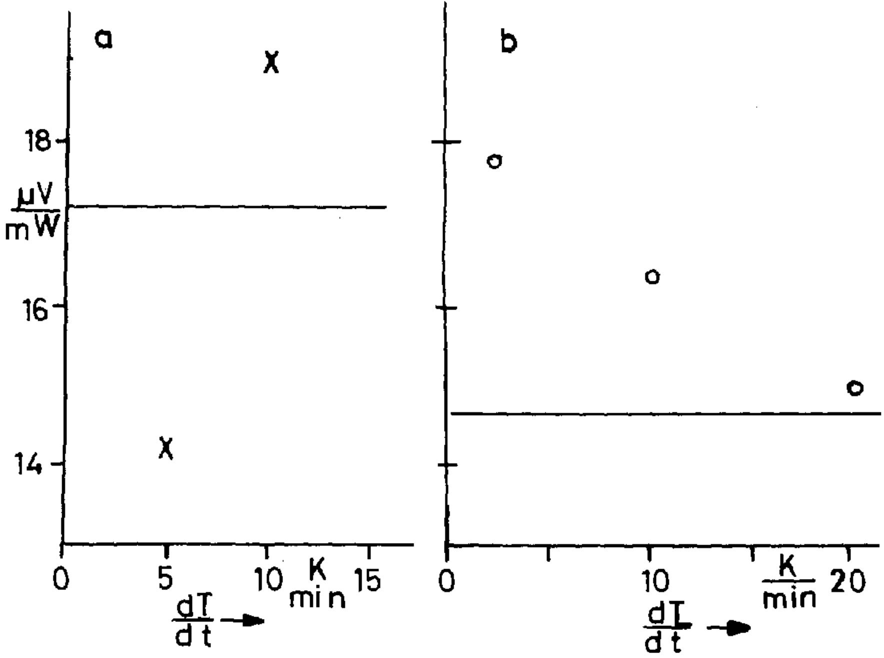

Fig. 1: Caloric sensitivity as a function of the heating rate.
a Heraeus TA 500, b Mettler TA 2000
x,o Alumina calibration; ——Indium mean value

In order to explain the different results obtained for a certain instrument it is conceivable that

a) due to the short-time heat absorption during fusion the temperature field is changed in such a way that there is no longer a linear correlation between the temperature difference $\Delta T$ (quantity to be measured) and the heat flux towards the sample;

b) the linear range of the heat-flux differential scanning calorimeter has been exceeded (dependence of the sensitivity on the heat flux due to the reaction);

c) the reproducibility of the base line is too poor.

## Experimental:

A theoretical study /1/ has confirmed that errors may be caused by the disturbance of the steady state. In order to check this statement experimentally, the test series described in the following were carried out.

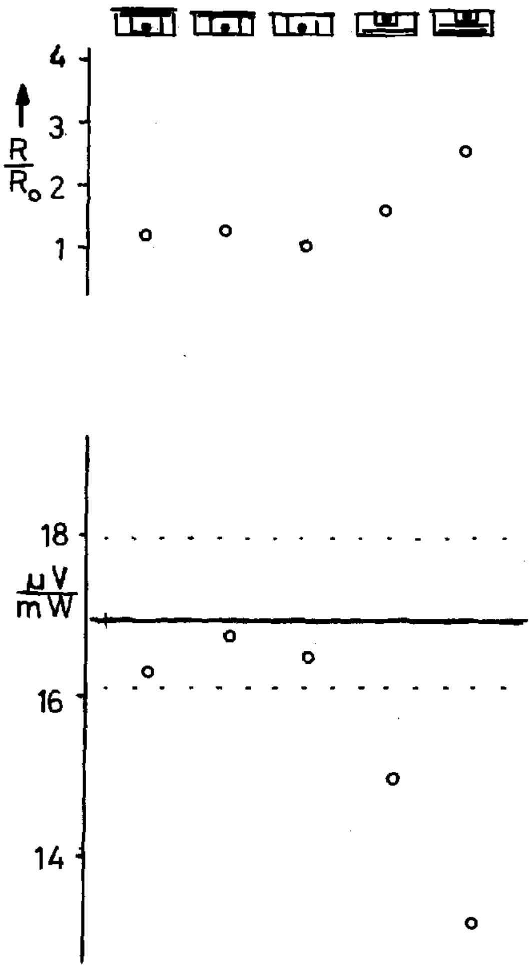

Fig. 2:

Container geometry (top
relative heat resistanc
$R/R_0$ (middle) and sensitivity (bottom) for
open containers.
$R_0$ is the heat resistan
without foils.
Heating rate:
o 2 K/min
— Indium mean value f
all runs
- - - range of ± 5 % scat

An indium sample (approx. 10 mg) was placed in a small aluminium pan which in turn was placed in a larger aluminium pan. In order to change the thermal resistance, no teflon foil, one foil or two foils respectively (thickness: approx. 0.75 mm) were placed between these two pans. This combination of pans was then inserted into a heat-flux calorimeter (Heraeus TA 500). Owing to the increa in thermal resistance due to the teflon foils, peak shape and widt were noticeable changed, so that with low thermal resistance the disturbance of the steady state was great whereas it was small in the case of high thermal resistance. The caloric sensitivities obtained by peak integration, the thermal resistance between sample and furnace as well as the pan geometry are represented in Fig. 2.

There is apparently a correlation between the thermal resistance and the sensitivity, as it had been staed in /1/.

Closer observations revealed, however, that obviously the abovementioned result is due to another effect: The lid of the large pan rested only loosely on the pan so that as a consequence, thermal coupling to the pan was poor. When two teflon foils were placed beneath the small pan, the lid even rested on the small pan and not on the brim of the large pan. Due to radiation and conduction by air the lid also exchanges heat between sample and surroundings (furnace). This portion of heat exchange cannot, however, be covered. The resulting error will be small when lid and pan have (almost) the same temperature; it will increase when a temperature difference exists between pan and lid.

As long as the lid rested on the large pan, the measurements yielded always the same sensitivity. However, if it rested on the small pan, the values obtained were smaller because the temperature of the small pan during fusion of the indium was lower than that of the large pan. The reason is that in this case part of the heat added in order to compensate the fusion effect will flow via the pan's lid towards the sample and a correspondingly smaller portion will follow the heat path covered by the **Δ** T sensors. It can thus be concluded from this observation that it is not permissible to transfer the calibration by means of hermeti container to that carried out with non-hermetic container (not to mention deformed containers).

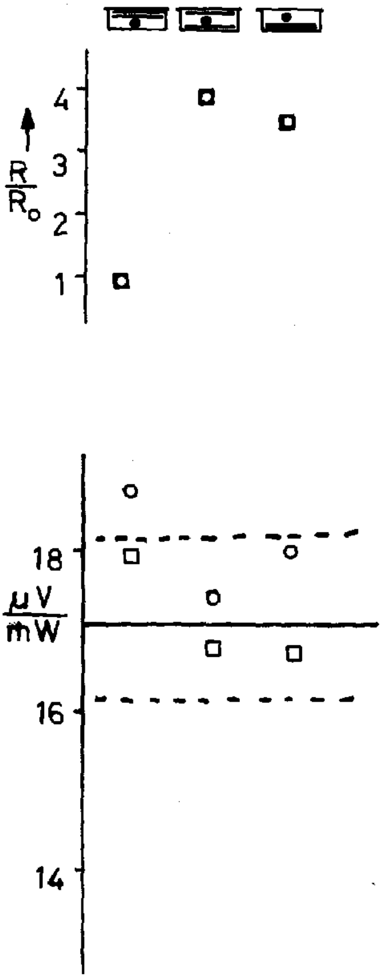

Fig. 3:

Container geometry (top), relative heat resistance R/R (middle) and sensitivity (bottom) for hermetic containers. $R_0$ is the heat resistance without foils.

Heating rate:

o 20 K/min

□ 10 K/min

—— Indium mean value for all runs

--- range of ± 5 % scatter

The source of error was eliminated in the next step by placing the samples - without the small pan - directly on the foils in the large pan and by sealing pan and lid together. Fig. 3 shows that a connection between peak shape (influenced by heat resistance and heating rate) and caloric sensisitivity can no longer be established.

The same samples were investigated at heating rates of 2 K/min to 20 K/min with the following instruments: Heraeus TA 500 DCS-Cell; Mettler TA 2000; DuPont 990 Thermal Analyzer and Perkin Elmer DSC 4-C. A sensitivities' dependence on heating rate and/or heat resistance could not be established on any of the instruments used. Theoretical reasons can be furnished /2/ according to which the same results would have to be obtained if the calibration was carried with heats of fusion or by using a substance of well-known specific heat capacity. This is not, however, always the case (cf. Fig. 1).

## Theory:

An attempt was therefore made to find possible reasons for the different results obtained according to the two calibration methods by carrying out model calculations.

Fourier's differential equations for heat conduction and temperature distribution are:

$$\frac{\partial q}{\partial t} = -k\vec{A} \text{ grad } T \qquad \text{and} \qquad \frac{\partial T}{\partial t} = \frac{k}{\varrho \cdot c_p} \text{ div grad } T$$

($m = k/(\varrho \cdot c_p)$) being the thermal diffusivity, k the thermal conductivity, $\varrho$ the density, $c_p$ the specific heat capacity, $\vec{A}$ the area, div grad corresponding to the Laplace operator.

For the phase transformation in a real measuring system these differential equations can no longer be solved in closed form. It is therefore common practice to pass from differential quotie to difference quotients /3/ and to solve the new equation system in an iterative way. Rules of calculation for this procedure hav e.g. been given in /4/.

The calculation is based on the following assumptions:

- The circular disc with the temperature sensors is made of a homogeneous material;
- the disc rests on two supports (2 mm · 3 mm) whose temperature is always identical to that of the furnace;
- both containers (sample and reference) have an infinitely high thermal conductivity and can thus be described by a uniform temperature;
- sample and container are connected by an (experimentally determined) heat resistance;

- container and pan are connected by a heat-conducting layer without heat capacity. The thermal conductivity was estimated from experimental values.

For further evaluation, the quantities to be measured - temperature difference between pan supports, measured sample temperature, i.e. temperature of the disc beneath the sample, and furnace temperature - were obtained as results.

The heat flux towards the sample (not towards the pan with the sample!) was calculated and given in addition.

The fusion of 10 mg indium ($\Delta H_f$ = 0.2833 J; $c_p$ = 0.0028 J/K) was taken as the data for phase transformation.

The computational results of this simple model have been compiled in Figs. 4a-d. Figs. 4a and 4b represent the DSC curve in the usual way, i.e. temperature and temperature difference as a function of time. Fig. 4c shows the heat flux towards the sample, Fig. 4d the heat flux towards the sample referred to the respective temperature difference (reciprocal sensitivity).

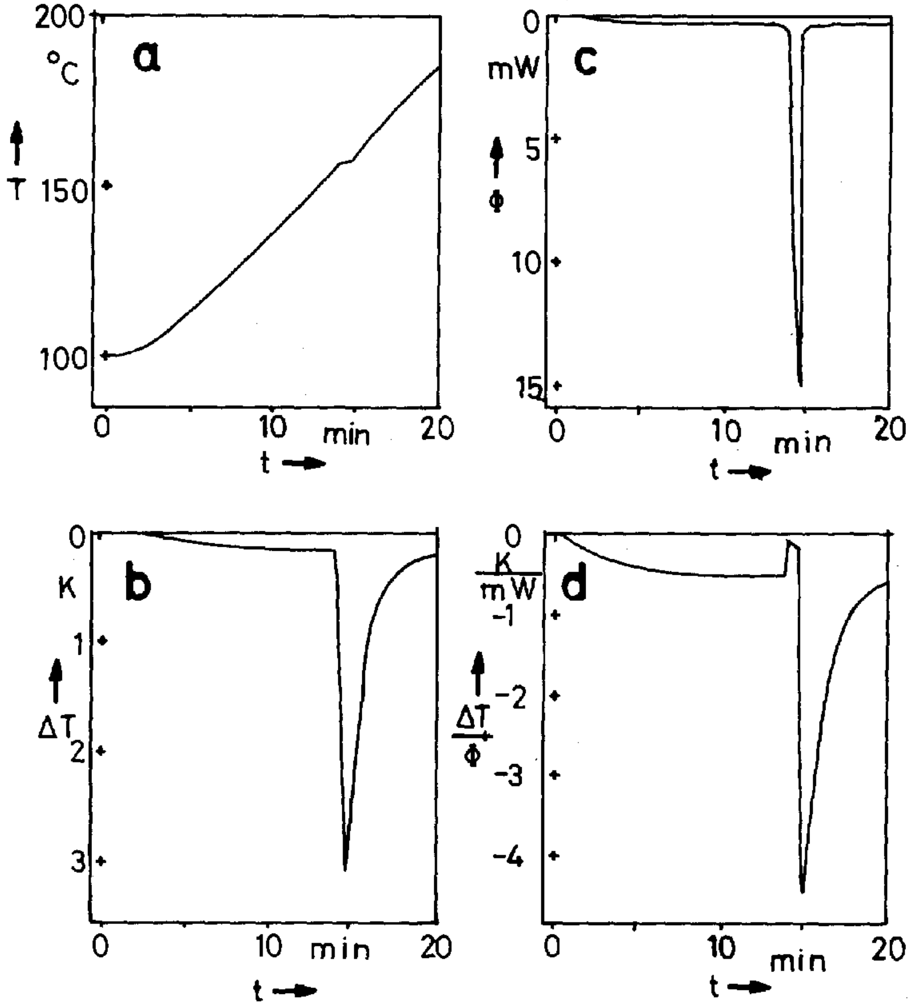

Fig. 4: Results of model calculation (for explanations, see text)

A comparison of Figs. 4b and 4c shows that for kinetic investigations considerable corrections of the DSC signal must be made in order to obtain the actual heat flux towards the sample as a function of time or even of temperature. This applies to power-compensated instruments, too!

Fig. 4d shows a crucial point which becomes obvious when calibrating by means of heat capacities: Only after approx. 10 min is the process of reaching a steady state terminated to such an extent that the "true" sensitivity, which can e.g. be determined by calibration using heats of fusion, is obtained with sufficient accuracy. Figs. 4a and 4b purport steady-state conditions already after 3 to 5 min. In this case the resulting error is of the order of magnitude of 10 - 15 % of the final value. If heat capacity and/or modes of heat transfer are temperature-dependent, this process will even take a longer time or a "steady state" will never be reached. The "apparent" sensitivity may then be a function of the mass of the sample, of the heat capacity and of the heating rate. This seems to be the main reason for the above-described discrepancies between the calibration using heats of fusion and that via heat capacities.

## Conclusions:

In order to substantiate this assumption, additional numerical simulations are being made which do not only take into account the conduction of heat in the disc and its temperature dependence, but also:

- the temperature dependence of heat capacity of the sample and the containers,
- the conduction of heat through the gas inside the calorimeter
- the heat radiation towards the containter,
- the conduction of heat through the connecting wires of the sensors.

It should thus be possible to calculate the sensitivity of a heat-flux differential scanning calorimeter and its dependence on various parameters in order to allow specific experimental controls to be made afterwards.

## Literature

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