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The influence of heat resistances and heat transfers on the uncertainty of heat-capacity measurements by means of differential scanning calorimetry (DSC)

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Abstract

The uncertainty of heat-capacity determinations by means of differential scanning calorimeters (DSCs) is essentially given by the heat-transfer conditions between heater, sample and surroundings. Changes in heat transfer become apparent as an offset between the initial and final isotherms. This offset is a quantitative measure of the systematic uncertainty of a heat-capacity determination and can, therefore, be applied to correct the measurement result. Offsets of approx. 5% yield systematic deviations of up to 1%. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: DSC; Calorimetry; Heat-capacity measurements; Heat transfer

1. Introduction

Differential scanning calorimetry (DSC) is a method for the determination of heat capacities widely applied in research and industry. A major question of all methodical examinations is that of the minimum measurement uncertainty achievable with these devices. It has turned out that, when power-compensated instruments and a stepwise temperature program are used, an uncertainty of 1% can be obtained in the temperature range from 250 to 700 K, which increases to 2% in the ranges from 150 to 250 K and from 700 to 800 K [1]. When a continuous temperature program is applied, an uncertainty of 2–3% is to be expected [2].

It is known that this uncertainty is essentially influenced by the heat-transfer conditions between furnace, sample and surroundings prevailing in the system [3–5]. Heat losses and changes in heat transfer become apparent as an offset between the initial and final isotherms of the three measurements (sample measurement, empty measurement, calibration sample measurement) necessary for the determination of heat capacities.

In the following it is shown that this offset is a quantitative measure of the systematic uncertainty of a heat-capacity measurement and that it can, therefore, be applied to correct the measurement result adequately, or as a criterion for rejecting the measurement.

Uncertainties due to contamination of the measuring system, weighing errors, calibration uncertainties, stability of the purge-gas flow, and deviations from room temperature, etc. are not considered in the following.

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2. Experimental

Experiments were performed with a power-compensated calorimeter (DSC-2C, Perkin-Elmer, Connecticut, USA) equipped with a personal computer instead of the original computer (TADS) for control, data acquisition and evaluation (DSC-Profi, IFA-GmbH, Ulm, Germany).

Argon (4N) was used as purge gas; the surrounding temperature was −30°C. The initial temperature of all measurements was 323 K, the final temperature 623 K, the heating rate 10 K/min, the isothermal phases lasted 10 min each. Standard aluminium crucibles from Polymer-Laboratories, Sussex, England, were used as crucibles. A sapphire single crystal 7 mm in diameter, 1 mm in height and 80 mg in mass supplied by Netzsch-Gerätebau, Selb, Germany, was used as the sample.

3. Calorimeter model

For the analytical and numerical analysis of the influences which heat transfer and other measuring conditions exert on the systematic uncertainty of heat-capacity measurements, an one-dimensional model of the calorimeter used was applied [3–5], see Fig. 1.

The model consists of a sample system (S) and a reference sample system (R) in temperature-constant surroundings (environment E) at temperature T_E. Sample system and reference sample system consist of sample supports (holder H), in which thermometer and heater are installed, at temperatures T_H (S≠R), and covers (C) at temperatures T_C (S≠R). Each sample support carries a crucible (pan P) with the sample (unknown U) in the sample crucible. Heat flows between the constructional parts are characterised by heat-transfer coefficients. These heat-transfer coefficients result from the properties of the gas (flow rate, kinematic viscosity, thermal diffusivity, thermal conductivity), the radiation properties of the surfaces involved and the gaps (distance d) between two constructional parts. The gap widths d are used here to describe the heat transfer. In detail, there are:

- d_{HP} distance between sample support and crucible (S≠R)
- d_{HC} distance between sample support and cover (S=R)
- d_{PU} distance between crucible and sample (S)

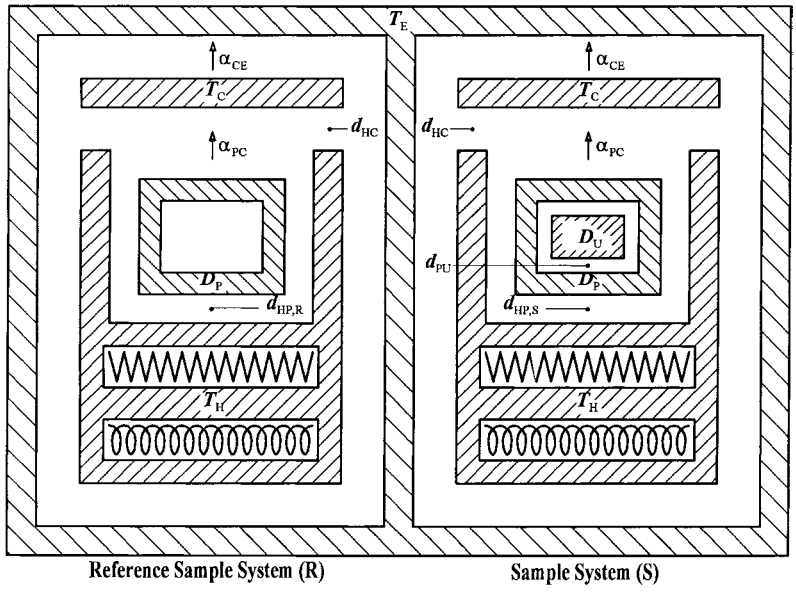


Fig. 1. Calorimeter model: α heat transfer coefficient; d distance; D thickness; T temperature; indices: H holder; P crucible (pan); U sample (unknown); C cover; E environment; R reference sample system; S sample system.

D_P thickness of the crucible material (S=R)
D_U thickness of the sample (S)
α_{PC} heat-transfer coefficient between crucible and cover (S=R)
α_{CE} heat-transfer coefficient between cover and surroundings (S=R)

The temperature program used for this model corresponds to the conventional temperature program for heat-capacity measurements:

$$T = T_{ini} \quad \text{for } t < t_{ini},$$
$$T = T_{ini} + \beta \cdot t \quad \text{for } t_{ini} \le t \le t_{fin},$$
$$T = T_{fin} \quad \text{for } t > t_{fin},$$

with t time, T temperature, β heating rate, index ini for initial, index fin for final.

Due to the thermal resistances between sample support and cover and the isothermal surroundings, the sample is heated at a rate lower than that of the sample support ($\beta_U<\beta_H$), and the heating rate of the cover is lower than that of the sample ($\beta_C<\beta_U<\beta_H$), and the sample's final temperature is lower than that of the sample support ($T_{C,fin}<T_{H,fin}$) (see Fig. 2(a)). During heating the heater produces a heat flow Φ part of which is stored in the sample system while the other part flows to the surroundings. In the isothermal state (at T_{fin}), the complete heat flow Φ produced in the heater is transferred to the surroundings.

Each sample in the sample crucible causes an asymmetry, which leads to a differential heat flow rate $\Delta\Phi$ ($\Delta\Phi=\Phi_S-\Phi_R$), unequal to zero, even with complete symmetry of all heat capacities and heat transfers.

The system of differential equations describing this model was solved analytically, whereas the heating rate of the cover β_C and the cover temperature T_C were determined numerically.

In the case of small heat-transfer resistances the calculations show that, due to asymmetric heat losses, the offset between isothermal initial line and isothermal final line, related to the dynamic signal, is a measure of the amount by which the measurement result is lower than the ideal value [5]. Because the stationary heat flow on the sample side is always smaller than that on the reference side, a negative offset results. Only when extreme device-specific parameters are chosen can the sign of the offset be reversed.

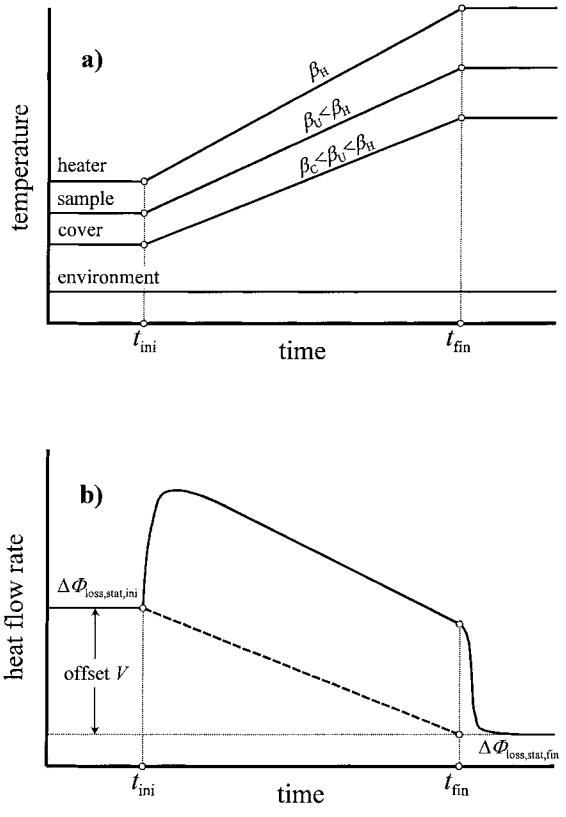


Fig. 2. Calculated DSC curve: (a) temperature program; (b) measured signal. t_{ini}: initial time of the temperature program; t_{fin}: final time of the temperature program; $\Delta\Phi=\Phi_s-\Phi_R$; $\Delta\Phi_{loss,stat,ini/fin}$: differential heat flow rate due to heat losses during isothermal periods.

4. Calculated DSC curves

For calculating DSC curves by means of the above-mentioned model, it was necessary to assign values to the geometrical and thermal parameters which are reasonable from the viewpoint of heat transfer and agree sufficiently well with reality.

The gap width between sample support and cover d_{HC} was estimated from experience. The coefficient of heat transfer between cover and surroundings, α_{CE}, as well as between crucible and cover resulted from the properties of the surrounding gases (gas flow rate, thermal diffusivity, thermal conductivity, kinematic viscosity) and the radiation properties of the surfaces involved.

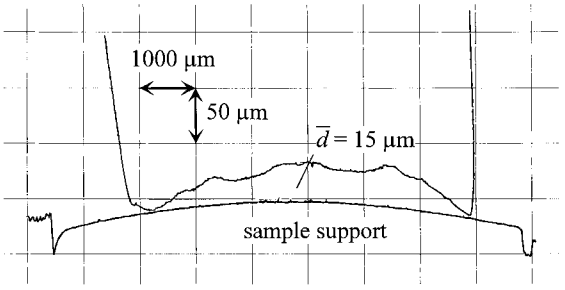


Fig. 3. Surface geometry of sample support and carefully flattened crucible.

The gap between sample support and crucible was determined experimentally by means of a roughness measuring instrument. For the measurements described here, a crucible carefully flattened by means of a stamp and a plane base (see Fig. 3) served as reference crucible. A similar crucible and a deliberately deformed crucible (see Fig. 4) were used as sample crucibles. With these two crucibles the extreme conditions for heat transfer were covered. The flattened crucibles represented the best possible thermal coupling between crucible and support, the deformed crucible the worst. The sample support's surface geometry was determined by the same experimental method.

The distances $\bar{d}$ stated are the integral mean values of the corresponding gap widths $d_{HP,S}$ and $d_{HP,R}$.

Fig. 2(b) shows a DSC curve calculated by means of the above-mentioned model. The following parameters were used: $d_{HC,R}=d_{HC,S}=10\,\mu m$; $\alpha_{CE}=30\,Wm^{-2}\,K^{-1}$; $\alpha_{PC}=19\,Wm^{-2}\,K^{-1}$; $d_{HP,R}=15\,\mu m$; $d_{HP,S}=174\,\mu m$; $d_{PU}=20\,\mu m$.

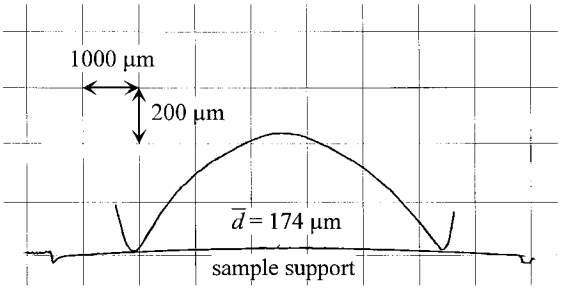


Fig. 4. Surface geometry of sample support and deliberately deformed crucible.

5. Experimental DSC curves

The slope and onset of the baseline of the calorimeter under investigation must be electronically adjusted, so that a measurement of the "true" zero line is impossible. Instead, the measurements must always be related to the same state. This state is obtained by adjusting the baseline horizontally, when one of several measurements furnishes a particularly low isothermal final line. During the measurements described here, the attempt was made to find the geometry which ensured optimum heat transfer. For this purpose, the position of the cover was repeatedly slightly changed.

Fig. 5 shows four measurements using the flattened and the deformed crucible as the sample crucible and with empty and with filled crucible. There is an offset of −5% between the initial and final baselines of the measurements with the deformed crucible, and the difference $\Delta\Phi_{\text{sample measurement}}-\Delta\Phi_{\text{empty measurement}}$ is about 2% smaller than with the measurements with the flattened crucible. The order of magnitude of these values is in good accordance with those obtained using the model. By this, it has been proved that the model used for simulating the calorimeter describes the existing heat-transfer conditions sufficiently precise, and that the values of the parameters for the heat transfer and the geometry of the calorimeter under investigation agree well with reality.

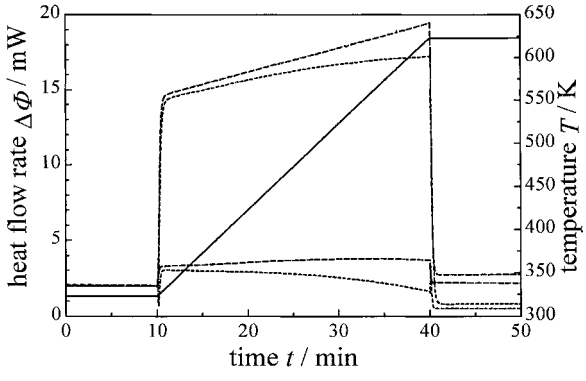
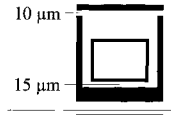
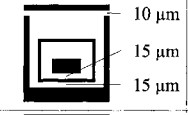
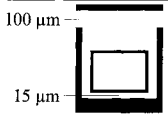
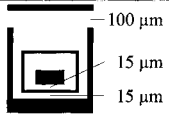
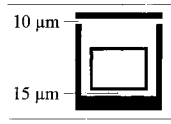
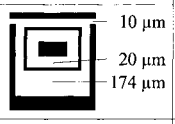
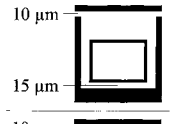
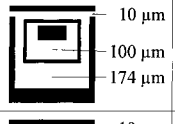
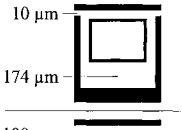
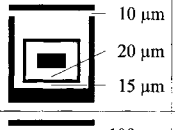
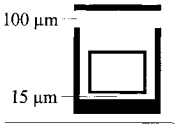
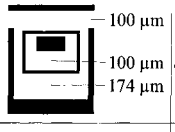


Fig. 5. Experimental determination of the offset using crucibles of different planeness. - - - carefully flattened crucible, · · · deliberately deformed crucible.

Table 1
Influence of heat transfers between sample support, crucible and sample, here expressed by the gap width, on the offset of a DSC measurement and the resulting deviation of the calculated heat capacity.

Reference system	Sample system	Offset in %	Deviation in %
		-0.4	0.1
		-1.9	0.6
		-5.1	1.0
		-33.1	3.4
		-3.4	-0.1
		-174.1	15.4

6. Conclusions and recommendations

Table 1 shows a summary of the results of the model calculations, which were obtained by varying the corresponding parameters. Accordingly, an offset of −5%, as can indeed be observed experimentally, leads to a deviation of 1% of the DSC signal and the heat capacity determined by the conventional method.

From the model calculations and the experiments it follows that the heat resistances within a differential scanning calorimeter adversely affect the accuracy of the measurements. If the measurements are carefully performed and all heat resistances optimised, a correlation exists between offset and measurement deviation so that either the experimental assembly can be optimised until the offset disappears, or the measurement result can be corrected mathematically.

The geometric and thermal values used for the simulation of the calorimeter under investigation are not only valid for this specific instrument but representative for this type of instrument. Thus, the data given in Table 1 may serve as a source for the determination of the correction factor for any heat-capacity determination.

Generally, as all of the system's heat resistances lead to a decrease of the DSC signal compared with the ideal value, during repeated measurements it is the measured curve with the smallest offset and the largest signal, which is the most accurate one.

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