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COMMISSION ON THERMODYNAMICS\*

# STANDARDS, CALIBRATION, AND GUIDELINES IN MICROCALORIMETRY PART 2. CALIBRATION STANDARDS FOR DIFFERENTIAL SCANNING CALORIMETRY\*\*

(IUPAC Technical Report)

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# Standards, calibration, and guidelines in microcalorimetry

## Part 2. Calibration standards for differential scanning calorimetry

### (IUPAC Technical Report)

*Abstract:* Differential scanning calorimeters (DSCs) are widely used for temperature, heat capacity, and enthalpy measurements in the range from subambient to high temperatures. The present recommendations describe procedures and reference materials (RMs) for the calibration of DSCs. The recommendations focus on the calibration of the response of the instrument and on the estimation of the measurement uncertainty. The procedures for temperature, enthalpy, and heat-flow rate calibration are given in detail. Calibration on cooling has also been considered. Recommended RMs are listed, and the relevant properties of these materials are discussed.

*Keywords:* IUPAC Physical and Biophysical Chemistry Division; microcalorimetry; DSC; heat capacity; enthalpy measurements.

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## 1. INTRODUCTION

The aim of this report is to describe calibration procedures and to review reference materials (RMs) for temperature, heat capacity, and enthalpy measurements made by differential scanning calorimetry (DSC) in the temperature regions from subambient to high temperatures. The paper should be helpful to those who wish to participate in laboratory accreditation schemes—involvement with such schemes is now often essential before a work program can be agreed upon. Key components on the route to accreditation are well-defined operating procedures and their validation using certified reference materials (CRMs).

The calibration procedures are based on a series of publications developed by a working group of the German Society of Thermal Analysis (GEFTA) [1–4]. The publications were adopted in 2000 by the International Confederation for Thermal Analysis and Calorimetry (ICTAC) as recommendations to its members.

DSC is a relative technique. Because of its dynamic temperature characteristics, the measurements are not made in thermal equilibrium. Since current theories of DSC are inadequate for a complete description of the behavior of a particular sample in a given instrument, calorimeters must be operated in a relative, rather than absolute, mode. The relative data must be converted to absolute values by a calibration procedure requiring the employment of standards whose property values and their associated uncertainties are known and established following a metrological procedure.

DSCs are used widely as relatively simple and rapid instruments to determine, as thermometers, temperatures of phase transitions or reactions, or, as calorimeters, heat capacities or enthalpies of transition or reaction in the temperature range from about 100 to 1800 K.

The quality of the measurements is influenced by instrumental-, sample-, and operator-related parameters. These parameters include not only temperature and heating rate, but also sample mass and sample size, type of effect measured, magnitude of effect measured, crucible, thermal resistance between calorimeter, crucible and sample, reference sample, thermal resistance and emissivity (or emittance) of sample and crucible, purge gas, purge gas pressure, purge gas flow, position of sample in a crucible and crucible in a calorimeter, data acquisition, data treatment, etc. In spite of the large number of influencing parameters, it has been acknowledged that “true” thermodynamic data can be obtained with careful operation and after rigorous calibration [5,6].

With careful work and over a temperature range from about 200 to 800 K, modern DSCs have measurement uncertainties of 0.1 to 0.5 K in temperature, 0.5 to 1.0 % in enthalpy changes, and 1 to 2 % in heat capacity.

## 2. PRINCIPLES OF MEASUREMENT

A DSC signal is a differential temperature or power (vertical axis) as a function of time or temperature (horizontal axis).

The aim of any calibration procedure is thus both to define the temperature scale for a given set of experimental conditions and to fix the ordinate so that it refers to known heat-flow rates—either directly or, in combination with the abscissa, as an area that corresponds to a known enthalpy change (e.g., an enthalpy of fusion).

The quantities determined by DSC are:

- temperature (e.g., of transition or fusion)
- enthalpy (e.g., of transition or fusion)
- heat-flow rate (e.g., for determination of the heat capacity of a substance and its change with temperature or for studies of reaction kinetics).

It is thus necessary to calibrate the temperature, enthalpy, and heat-flow rate scales. Additionally, the influence of the above-mentioned parameters can be quantified, and their contribution to the uncer-

tainty of measurement can be assessed. Because heat-flow patterns within a DSC are asymmetric with respect to heating and cooling, procedures and materials for calibration in both directions are highly desirable.

By definition, calorimeters measure heat or heat-flow rates. The first law of thermodynamics gives the relation between heat and enthalpy change. Only under specific conditions (i.e., equilibrium conditions and constant pressure) are these two quantities identical. Nevertheless, with ordinary DSCs these requirements are fulfilled to a good approximation and, thus, enthalpy changes can be determined by DSC.

## 2.1 Temperature

In a DSC instrument, the temperature sensors are relatively remote from the sample. Thus, even if the sensor itself is reading correctly, the sample temperature may differ because of a thermal gradient between sensor and sample, in both temperature scanning and isothermal mode.

Under scanning conditions, the thermal gradient will change because of an additional “dynamic” thermal lag that is negative in heating and positive in cooling. The temperature scale is calibrated by comparing known temperatures of transition and/or fusion of RMs with the corresponding indicated temperature at zero heating rate. A correction curve is then plotted over a given range of temperatures. Depending on the range to be covered, and the shape of the calibration curve, at least three calibrants are needed—even if the curve is linear, a third point is needed to demonstrate this. Because temperature sensors are located within the instrument rather than in the sample, extrapolation to zero heating rate requires calibration at several heating rates.

## 2.2 Enthalpy changes

Fusion or a solid-to-solid phase transition appears as a peak on a DSC curve, and calibration relates the peak area obtained with an RM to the known enthalpy change to give an area-to-enthalpy conversion factor. Because of the complex heat-flow paths in DSC, it cannot be guaranteed that this factor is independent of temperature or scanning rate (or, indeed, of any of the experimental variables which must therefore be kept constant throughout a series of measurements). Thus, several enthalpy RMs are needed to span the whole temperature range covered by the DSC.

## 2.3 Heat-flow rate

The ordinate in a DSC experiment is related to the heat capacity of the sample, or, in the case of reactions taking place in the calorimeter, to its apparent heat capacity. An ideal calibrant should be thermodynamically inert over a wide temperature range. There is an almost universal use of  $\alpha$ -aluminum oxide (corundum or synthetic sapphire) as a calibrant for DSC heat capacity work. Its use appears to be justified because, with it, other well-characterized heat capacity data can be reproduced to  $\pm 1\%$  and, in exceptional cases, even better [7]. Alumina is less useful as a low-temperature calibrant because its heat capacity decreases rapidly with temperature so that the signal at 120 K, for example, is only 25 % of the value at 300 K. In addition, the sensitivity of the commonly used temperature sensors decreases with decreasing temperature.

For both enthalpy change and heat capacity measurements, electrical calibration is possible with only a few DSCs (e.g., Calvet-type instruments) either by means of an additional electrical heater which can be replaced with the sample crucible, or a built-in electrical heater close to the sample crucible, according to the procedures recommended by the manufacturers.

### 3. CALIBRATION AND DETERMINATION OF MEASUREMENT UNCERTAINTY

From a practical point of view, calibration should be regarded as a series of thoroughly defined procedures aimed at both increasing the accuracy of the instrumental response and decreasing the uncertainty contribution of the sample measurement to the total uncertainty.

The approach to calibration of a DSC apparatus can be regarded as consisting of *two main steps*:

- Calibration of the response of the instrument.
- Characterization of the measurement uncertainty (including sample contribution).

Therefore, RMs are needed for characterization of DSC instruments through the establishment of appropriate calibration factors and determination of their variation as a function of temperature.

*First calibration step:* There are in principle no restrictions with regard to the type of substance that can be used as RM. However, for temperature and enthalpy calibration, metals are obvious choices since high purity forms are readily available and show only a small heat capacity change during fusion, two strategic advantages for their adoption as DSC calibrants. Fusion of pure metals is thus recommended for calibration of DSC instruments in terms of the evaluation of their instrumental qualities. Metals can be used to cover a large temperature range but below ambient temperature, other RMs (e.g., organic or inorganic compounds) are needed. These should have solid-to-solid transitions and/or fusion characteristics as close as possible to those of metals. Unfortunately, non-metals are not generally available with purities comparable to those of metals. Their transition or fusion behavior is therefore less well defined.

*Second calibration step:* Further RMs are needed to approach the total uncertainty of a measurement made by DSC. For samples showing a less clear-cut transitional behavior than pure metals, additional calibration with RMs having properties similar to those to be measured will enable a better estimate of the total uncertainty. In this case, the use of such (additional, cf. Section 5, Tables 3 and 5) RMs is strongly recommended. This results partly because of the problems of getting samples of high enough purity and partly since the apparent enthalpy of fusion in these cases may depend on the sample characteristics to a larger degree than for pure metals.

In Section 5, specific RMs that can be used to characterize the instrument as well as those that can be used for assessment of total measurement uncertainty, including the sample contribution, are proposed. Further possible RMs are evaluated and compiled in two authoritative publications [8,9].

## 4. CALIBRATION PROCEDURES

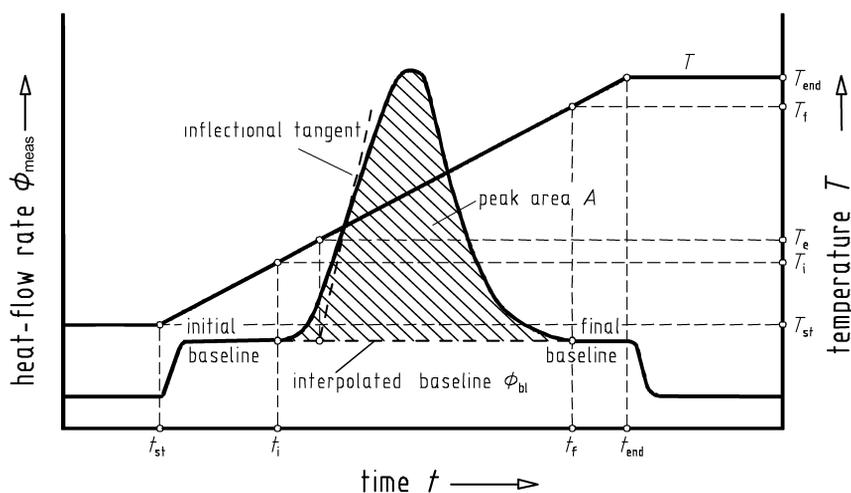
### 4.1 Definitions

The primary outputs of a DSC instrument referred to in Section 2 are represented by voltages as a function of time. These are usually transformed to temperature  $T$  in K or °C and heat-flow rate  $\Phi$  in W or  $\text{J s}^{-1}$  [10].

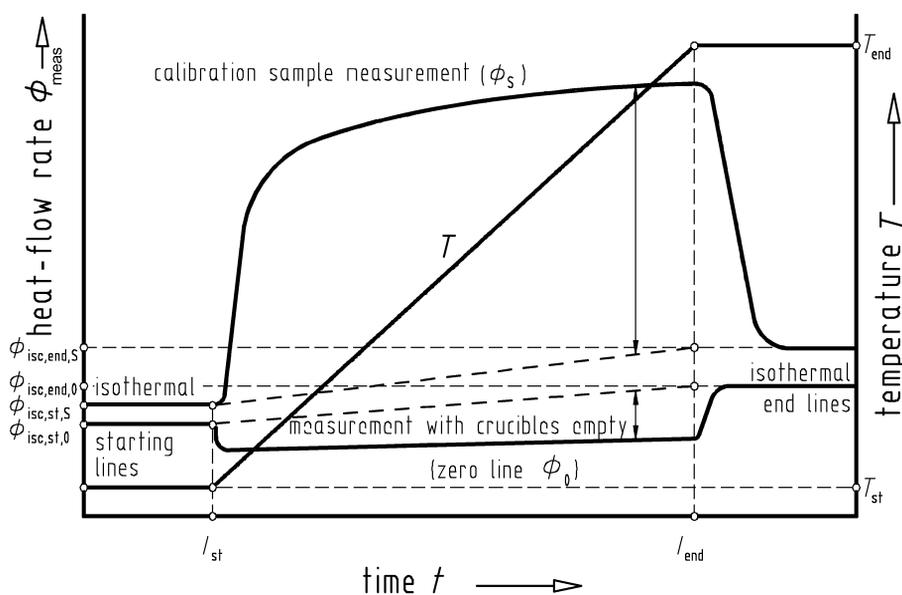
The quantities and terms used in the proposed calibration procedures are defined in the following (see Fig. 1, where  $\Delta C_p \approx 0$  is assumed, and Fig. 2. Figure 1 also shows other quantities, such as  $T_i$  and  $T_f$ , that have been used to characterize a DSC curve):

- *temperature calibration:* establishment of the relationship between the temperature  $T_{\text{meas}}$  indicated by the instrument and the true temperature  $T_{\text{tr}}$ :  $T_{\text{tr}} = T_{\text{meas}} + \Delta T_{\text{corr}}(T_{\text{meas}})$ ;
- *enthalpy calibration:* establishment of the relationship between the enthalpy change  $\Delta H_{\text{meas}}$  (peak area  $A$ ) measured by the instrument and the true enthalpy change  $\Delta_{\text{trs}}H$  absorbed or released by the sample as a result of a transition at the transition temperature  $T_{\text{trs}}$ :  $\Delta_{\text{trs}}H = K_{\text{H}}(T_{\text{tr}}) \Delta H_{\text{meas}}$ ;
- *heat-flow rate calibration:* establishment of the relationship between the heat-flow rate  $\Phi_{\text{meas}}$  indicated by the instrument and the heat-flow rate  $\Phi_{\text{tr}}$  absorbed or released by the sample due to its heat capacity (at constant pressure)  $C_p$ :  $\Phi_{\text{tr}} = K_{\Phi}(T) \Phi_{\text{meas}}$ , where  $\Phi_{\text{tr}}$  is equal to  $C_p \beta$ ;

- *heating rate*  $\beta$ : change of the temperature with time (generally linear);
- *peak*: section of a measured curve comprising: (i) ascending slope, maximum, and descending slope, or (ii) descending slope, minimum, and ascending slope within a specific time or temperature interval, due to a reaction or transition in the sample;
- *interpolated baseline*  $\Phi_{bl}$ : here defined as a horizontal straight line between initial and final peak temperatures (according to the assumption  $\Delta C_p \approx 0$ )
- *starting temperature*  $T_{st}$ : temperature at time  $t_{st}$  when the temperature program starts
- *ending temperature*  $T_{end}$ : temperature at time  $t_{end}$  when the temperature program ends
- *initial peak temperature*  $T_i$ : temperature of the first deviation of the curve of measured values from the interpolated baseline (at time  $t_i$ )
- *final peak temperature*  $T_f$ : temperature where the curve of measured values  $\Phi_m$  reaches the final baseline (at time  $t_f$ )
- *extrapolated peak onset temperature*  $T_e$ : temperature where the inflectional tangent through the ascending peak slope intersects the interpolated baseline. This represents the temperature of fusion or transition.
- *calibration sample measurement*  $\Phi_S$ : here defined as the measured curve between  $T_{st}$  and  $T_{end}$  with the sample (reference crucible empty)
- *starting isothermal baseline*  $\Phi_{iso,st,S}$ : here defined as a straight line representing the measured heat-flow rate until the starting of the dynamic phase of the temperature program at  $T_{st}$  (at time  $t < t_{st}$ ) with the sample (reference crucible empty)
- *final isothermal baseline*  $\Phi_{iso,end,S}$ : here defined as a straight line representing the measured heat-flow rate after finishing the dynamic phase of the temperature program at  $T_{end}$  (at time  $t \geq t_{end}$ ) with the sample (reference crucible empty)
- *zero line*  $\Phi_0$ : here defined as the measured curve between  $T_{st}$  and  $T_{end}$  without the sample (both crucibles empty)
- *starting isothermal baseline*  $\Phi_{iso,st,0}$ : here defined as a straight line representing the measured heat-flow rate until the starting of the dynamic phase of the temperature program at  $T_{st}$  (at time  $t < t_{st}$ ) without the sample (both crucibles empty)
- *final isothermal baseline*  $\Phi_{iso,end,0}$ : here defined as a straight line representing the measured heat-flow rate after finishing the dynamic phase of the temperature program at  $T_{end}$  (at time  $t \geq t_{end}$ ) without sample (both crucibles empty)



**Fig. 1** Definition of terms for describing measured curves with the peak representing a transition or reaction in the sample (subscript meas denotes measured quantities) in a plot of heat-flow rate and temperature against time.



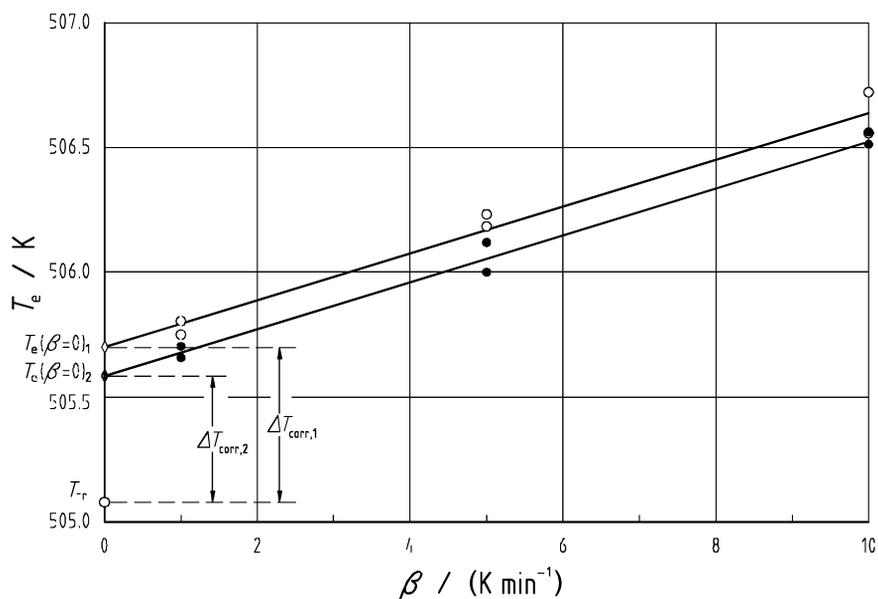
**Fig. 2** Definition and terms describing measured curves for determining the heat capacity of the sample (subscript meas denotes measured quantities) in a plot of heat-flow rate and temperature against time.

#### 4.2 Procedures for temperature and enthalpy calibration

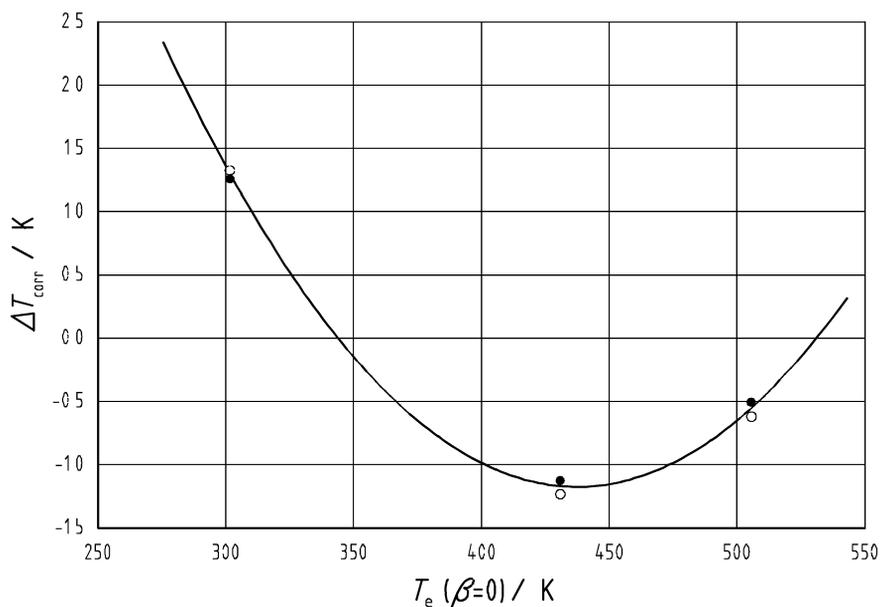
Because most of the recommended calibration materials for enthalpy calibration show a clearly defined first-order phase transition with a well-known transition temperature, temperature and enthalpy calibration can be performed simultaneously [3].

- From the available recommended calibration substances, at least three substances covering the temperature range of interest should be selected.
- At least two samples of each substance with masses corresponding to the mass range recommended for the respective calorimeter and varying by a factor of at least 3 are weighed into suitable crucibles after removing possible contaminants (e.g., oxide layers).
- Each sample is subjected to at least 2 measurements at a minimum of 3 heating rates corresponding to the usual heating rates of the calorimeter and varying by a factor of at least 10. The first measurement of each sample is not considered.
- For each peak, the extrapolated peak onset temperature  $T_e$  (for the temperature calibration) and the peak area  $A$  (for the enthalpy calibration) are determined (Fig. 1).
- For each calibration substance, the extrapolated peak onset temperatures are determined as a function of the heating rate and linearly extrapolated to the heating rate  $\beta = 0$  (Fig. 3).
- The temperature correction term ( $\Delta T_{corr}$ ) is obtained by subtracting the experimental onset temperature of transition  $T_e(\beta = 0)$  from the true transition temperature  $T_{trs}$ :  $\Delta T_{corr} = T_{trs} - T_e(\beta = 0)$ . The temperature correction terms are reported as a function of  $T_e(\beta = 0)$ , thus yielding the temperature calibration curve  $\Delta T_{corr}(T)$  (Fig. 4), provided the dependence on the sample mass is negligible.
- The ratio of the true enthalpy of transition  $\Delta_{trs}H$  and measured peak areas  $A$  yield the enthalpy calibration factors at  $T_{trs}$ :  $K_H(T_{trs}) = \Delta_{trs}H/A$
- The enthalpy calibration factors for each calibration substance are represented as a function of the transition temperature  $T_{trs}$  (Fig. 5). Provided the dependences on heating rate and sample mass are negligible (i.e., within the scatter of the individual experiments), the  $\Delta_{trs}H$  calibration factors

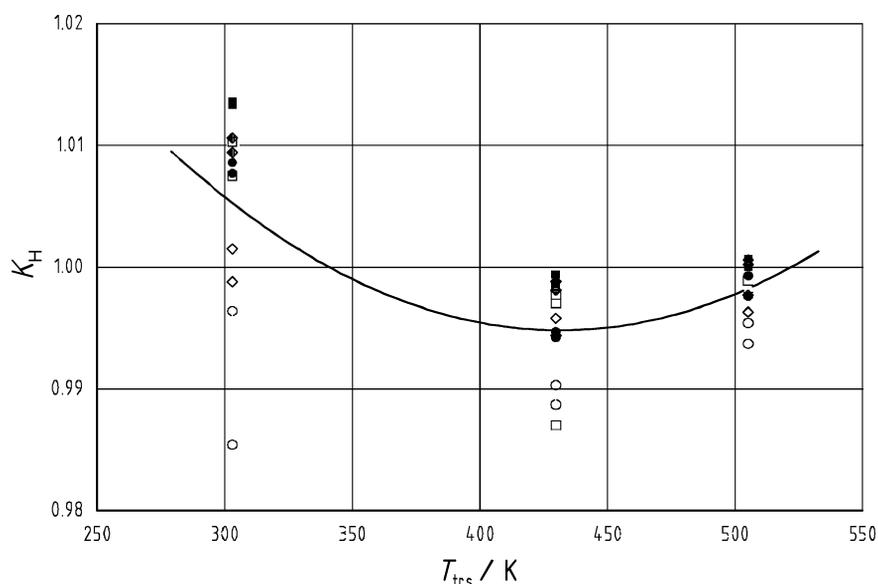
$K_H(T_{\text{trs}}, m, \beta)$  give the enthalpy calibration function  $K_H(T)$ . Otherwise, the dependences are to be quantified and taken into account during subsequent experiments on unknown samples. The choice of the degree of the fitting polynomial should be based on statistical evaluation of the significance of the chosen degree.



**Fig. 3** Plot of the extrapolated peak onset temperatures  $T_e$  against heating rate  $\beta$  for the fusion of tin. The curve is extrapolated to zero heating rate to determine the temperature correction term  $\Delta T_{\text{corr}}$ .  $\circ m = 3.240$  mg (1);  $\bullet m = 9.800$  mg (2).



**Fig. 4** Plot of the temperature correction term  $\Delta T_{\text{corr}}$  against the experimental peak onset temperatures at zero heating rate  $T_e(\beta = 0)$  determined with gallium, indium, tin.  $\circ m \approx 3$  mg,  $\bullet m \approx 10$  mg.



**Fig. 5** Enthalpy calibration factor plotted against transition temperature. Example with gallium, indium, tin. Open symbols:  $m \approx 3$  mg; solid symbols:  $m \approx 10$  mg. Circles:  $\beta = 1$  K min<sup>-1</sup>; diamonds:  $\beta = 5$  K min<sup>-1</sup>; squares:  $\beta = 10$  K min<sup>-1</sup>.

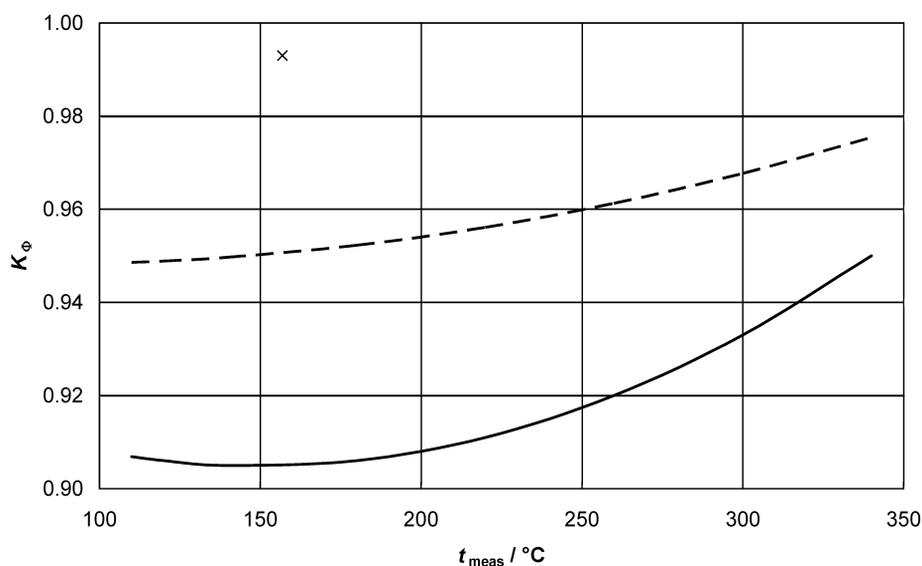
### 4.3 Procedures for heat-flow rate calibration

The DSC signal, whatever the type of instrument, is related to the energy requirement of the total “sample” (the actual sample plus container). Heat transfer problems complicate the relationship in a transition region but there is direct proportionality when there are only heat capacity contributions [3,10,11].

- The calibration substance should be selected according to the temperature range of interest. Two samples are weighed, and their masses are selected to bring the heat capacity of unknown samples approximately within the heat capacities of the calibration samples.
- The temperature program is subdivided into three intervals (Fig. 2): first isothermal interval, dynamic interval (heating rate 10 K min<sup>-1</sup> or other as recommended by the manufacturer), second isothermal interval. Each interval should last long enough to allow the establishment of quasi-steady-state conditions.
- Each calibration measurement is preceded or followed by a measurement with empty crucibles, and both measurements are carried out 3 times.
- In the quasi-steady-state range of the dynamic interval, the corresponding pairs of values of empty and sample measurement are evaluated according to the following equation (see Fig. 2).

$$K_{\Phi}(T) = \frac{C_p(T)\beta}{\left\{ \Phi_S - \left[ \Phi_{\text{iso,st,S}} + \frac{\Phi_{\text{iso,end,S}} - \Phi_{\text{iso,st,S}}}{t_{\text{end}} - t_{\text{st}}} (t - t_{\text{st}}) \right] \right\} - \left\{ \Phi_0 - \left[ \Phi_{\text{iso,st,0}} + \frac{\Phi_{\text{iso,end,0}} - \Phi_{\text{iso,st,0}}}{t_{\text{end}} - t_{\text{st}}} (t - t_{\text{st}}) \right] \right\}}$$

- For each sample, mean values of  $K_{\Phi}(T)$  are calculated and yield an average heat-flow rate calibration function  $K_{\Phi}(T)$ , provided the mass dependence is negligible (cf. Fig. 6).



**Fig. 6** Plot of heat-flow rate calibration factors against indicated temperature determined with sapphire to demonstrate sample mass dependence and difference between enthalpy and heat-flow rate calibration. Solid line:  $m = 7.79$  mg, dashed line:  $m = 129.6$  mg, star: enthalpy calibration factor determined with indium.

#### 4.4 Calibration in the cooling mode

Calibration in the cooling mode may give different results from those obtained in the heating mode since the temperature distribution in DSCs is asymmetrical with respect to heating and cooling. Heat transfer is a complicated function of the temperature difference, so that different local heat fluxes are formed during heating and cooling, leading to different heat and heat-flow rate calibration factors. These effects may, however, be small enough so that, to a first approximation, a calorimeter can be assumed to be symmetric with respect to heating and cooling. It is therefore necessary to verify and check this symmetry at regular intervals to assess correction values. An additional problem is the super-cooling that is essential before most phase changes will take place. This may require several degrees and, because it is influenced by subtle nucleation effects, it is not reproducible from one sample to another. *Whatever the behavior of a particular instrument, a prerequisite for calibration in the cooling mode is a correct and complete calibration of the DSC in the heating mode* [4].

##### 4.4.1 Temperature calibration

Because of super-cooling effects, the temperatures of phase transitions are not reproducible for the usual temperature calibration materials. It is therefore not possible to define by the classical procedures an independent temperature of calibration in the cooling mode using conventional RMs. What can be done is to check the symmetry of the temperature scale in cooling relative to that already found for the heating mode. Special calibration substances are not needed for this relative calibration. Pure substances whose transitions have only a small and well-defined super-cooling effect are sufficient [4]. There are sound theoretical reasons why super-cooling is minimized for higher-order transitions, and in this respect liquid-crystal transitions show promise as calibrants for work in cooling. Here, the relevant temperature is that of the transition peak, and, since this may depend on sample mass in addition to the heating/cooling rate, additional investigation is needed.

##### 4.4.2 Enthalpy calibration

Enthalpy calibration in the cooling mode is completely analogous to that in the heating mode. RMs should show (with the unavoidable super-cooling) only an insignificant or a known temperature de-

pendence of the phase transition enthalpy (e.g., cyclopentane, gallium, indium, tin, zinc, lithium sulfate, aluminum).

#### 4.4.3 Heat-flow rate calibration

Heat-flow rate calibration in the cooling mode is also completely analogous to that in the heating mode. The substances recommended for the heating mode can also be used for calibration in the cooling mode. Due to the sample cooling which takes place as a result of thermal conduction in its different ways, contact, convection and radiation, the thermal lag may be more pronounced in cooling relative to heating. It may, therefore, *appear* that heat capacities measured in cooling systematically differ from those measured in heating, although the experiments are in both cases performed according to the same procedures.

## 5. REFERENCE MATERIALS

### 5.1 Introduction

Accurate RMs for temperature and heat-flow rate are available. For enthalpy RMs, the situation is less clear. While the accuracy of the enthalpy of fusion determined by DSC often is claimed to be within 1 %, literature values used for calibration or for assessing the accuracy of the DSC measurements often vary to a comparable or even greater extent [12].

When using a DSC, the possibility of reaction or alloying processes between the sample and/or RM and the calorimeter must always be considered. Sample/crucible interactions are particularly important. Reference [2] discusses this problem and contains a table of compatible combinations of reference and crucible material.

*Temperature:* Temperature calibration is most often achieved through fusion of pure metals and in any case needs updated information on the 1990 international temperature scale (ITS-90) [1,2,13]. The main problem relates to the actual fusion temperature of the RM in use. The fusion behavior depends on the type and amount of impurities, even for very pure metals [14]. Only substances with very high purities melt with a macroscopic behavior that appears isothermal within the sensitivity of the best thermometry available.

*Heat-flow rate:* A DSC instrument should be calibrated with respect to both enthalpy and heat-flow rate since the calibration factors are not identical even at the same temperature [3]. Highly accurate heat-flow rate standards, such as synthetic sapphire and copper, are available. The uncertainty in the value of the RM, therefore, does not contribute significantly to the total uncertainty of a heat capacity determination by DSC.

*Enthalpy change:* For the enthalpy RMs, the situation is rather complicated. Since the calibration factor of a DSC instrument varies with temperature, it becomes necessary to calibrate its response in the ranges of interest. Thus, a large number of enthalpy (and temperature) standards are needed. The use of common commercial DSCs has been limited to temperatures below 1000 K. However, accurate enthalpy standards are available for low and moderate temperature use only. In view of the development of new high-temperature DSCs, enthalpy standards for high temperature use should also be considered. Our recommendations have, therefore, been extended to calibrants melting up to  $T = 1800$  K.

### 5.2 Recommended reference materials

#### 5.2.1 Temperature and enthalpy calibrants

In Table 1, the temperatures of fusion of metals selected as primary and some secondary reference points of ITS-90 are given in both K and °C. The enthalpies of fusion for the same metals (except Hg) obtained from the statistical treatment in ref. [15] are also reported in both  $\text{J g}^{-1}$  and  $\text{J mol}^{-1}$ . Recently reported experimental determinations are taken into account (footnote e). The uncertainties here are twice the standard deviation of the mean and can be regarded as GUM-compatible uncertainties (GUM: Guide to the Expression of Uncertainty in Measurement [16]).

**Table 1** Recommended values of temperatures and enthalpies of fusion of metals.

Element	Symbol	Molar mass/g mol <sup>-1</sup> <sup>a</sup>	$T_{\text{fus}}/\text{K}$	$T_{\text{fus}}/^{\circ}\text{C}$	$\Delta_{\text{fus}}h/\text{J g}^{-1}$ <sup>d</sup>	$\Delta_{\text{fus}}H_{\text{m}}/\text{J mol}^{-1}$ <sup>d</sup>
Mercury	Hg	200.59	234.315 6 <sup>b</sup>	-38.834 4		
Gallium	Ga	69.723	302.914 6 <sup>b</sup>	29.764 6	80.07 ± 0.13	5583 ± 9 <sup>e</sup>
Indium	In	114.818	429.748 5 <sup>b</sup>	156.598 5	28.62 ± 0.04	3287 ± 5 <sup>e</sup>
Tin	Sn	118.710	505.078 <sup>b</sup>	231.928	60.38 ± 0.15	7168 ± 18 <sup>e</sup>
Bismuth	Bi	208.980 38	544.552 ± 0.001 <sup>c</sup>	271.402	53.18 ± 0.12	11 114 ± 25 <sup>e</sup>
Cadmium	Cd	112.411	594.219 ± 0.001 <sup>c</sup>	321.069	55.25 ± 0.68	6211 ± 77
Lead	Pb	207.2	600.612 ± 0.001 <sup>c</sup>	327.462	23.08 ± 0.11	4782 ± 22
Zinc	Zn	65.39	692.677 <sup>b</sup>	419.527	108.09 ± 0.43	7068 ± 28
Antimony	Sb	121.760	903.778 ± 0.001 <sup>c</sup>	630.628	162.55 ± 4.91	19 792 ± 598
Aluminum	Al	26.981 538	933.473 <sup>b</sup>	660.323	399.87 ± 1.33	10 789 ± 36
Silver	Ag	107.868 2	1234.93 <sup>b</sup>	961.78	104.61 ± 2.09	11 284 ± 225
Gold	Au	196.966 55	1337.33 <sup>b</sup>	1064.18	64.58 ± 1.54	12 720 ± 304
Copper	Cu	63.546	1357.77 <sup>b</sup>	1084.62	203.44 ± 4.36	12 928 ± 277
Nickel	Ni	58.693 4	1728 ± 1 <sup>c</sup>	1455	290.36 ± 6.41	17 042 ± 376
Cobalt	Co	58.933 200	1768 ± 3 <sup>c</sup>	1495	272.44 ± 6.26	16 056 ± 369

<sup>a</sup>See ref. [17].<sup>b</sup>See ref. [13].<sup>c</sup>See ref. [18]. Uncertainties are here the standard deviations resulting from calculating a consensus value taking into account within-group and between-group variables.<sup>d</sup>See ref. [15].<sup>e</sup>Obtained by including the recent values from PTB and NIST [19–21] into the statistical analysis of ref. [15].

In Table 2, temperatures and enthalpies of fusion for a number of (metallic) CRMs available from the German Physikalisch-Technische Bundesanstalt (PTB), the U.K. Laboratory of the Government Chemist (LGC) [22], and the U.S. National Institute of Standards and Technology (NIST) [23] are reported.

**Table 2** CRMs (metals) for temperatures and enthalpies of fusion<sup>a</sup>.

Element	$T_{\text{fus}}/\text{K}$ <sup>b</sup>	$T_{\text{fus}}/^{\circ}\text{C}$ <sup>b</sup>	$\Delta_{\text{fus}}h/\text{J g}^{-1}$	$\Delta_{\text{fus}}H_{\text{m}}/\text{J mol}^{-1}$
Mercury*	234.31 ± 0.03	-38.84	11.469 ± 0.008	2301 ± 2
Gallium@	302.930 ± 0.010	29.780	80.14 ± 0.17	5587 ± 13
Indium*	429.7485 ± 0.000 34	156.5985	28.51 ± 0.19	3273 ± 22
Indium#	429.76 ± 0.02	156.61	28.71 ± 0.08	3296 ± 9
Indium@	429.748 ± 0.004	156.598	28.64 ± 0.06	3288 ± 7
Tin#	505.07 ± 0.02	231.92	60.54 ± 0.09	7187 ± 11
Tin*	505.06 ± 0.01	231.91	60.22 ± 0.19	7147 ± 22
Tin@	505.078 ± 0.004	231.928	60.24 ± 0.16	7151 ± 19
Bismuth@	544.550 ± 0.010	271.400	53.14 ± 0.12	11 106 ± 25
Lead#	600.62 ± 0.02	327.47	23.00 ± 0.05	4766 ± 10
Zinc#	692.68 ± 0.02	419.53	108.6 ± 0.5	7101 ± 33
Aluminum#	933.48 ± 0.05	660.33	401.3 ± 1.6	10 827 ± 43

\*NIST (U.S. National Institute of Standards and Technology) sample.

#LGC (U.K. Laboratory of the Government Chemist) sample.

@PTB (German Physikalisch-Technische Bundesanstalt) sample.

<sup>a</sup>When comparing the values and their uncertainties, take into account the different methods used for the determination of the uncertainty and refer to the certificates.<sup>b</sup>Where necessary, IPTS-68 temperatures have been corrected to ITS-90.

Measurements, traceable to national standards, have been made on the batch of material from which the CRM is formed, and relevant uncertainty limits are given. Measurements are of the highest current metrological quality. Many of these values were determined by adiabatic calorimetry and the associated platinum resistance thermometry [24]. Other techniques included a method of mixtures and phase change calorimeter [25], power-compensation DSC, and a Calvet calorimeter using an electrical compensation principle.

For temperatures of fusion, the agreement with ITS-90 fixed points (see Table 1) is excellent, between 0 (for In from NIST and Sn from PTB) and 0.0004 % and 0.003 % (except Hg 0.01 % (25 mK)).

The position is less satisfactory for enthalpies of fusion. The uncertainties in Table 2 are estimates based on the features of the apparatus, the procedures employed, and the substances used, and are quite similar to those given for the statistical treatment in Table 1. However, enthalpies of fusion agree with the tabulated “best” values of Table 1 only within 0.2 to 0.5 %. These differences must be expected to be of instrumental origin and not related to differences in the samples. Thus, the example emphasizes the importance of the statistical treatment of the literature data and recommendation of its results that we have adopted, even though users should be advised to consistently use certified values if CRMs with the desired properties exist.

In Table 3, temperatures and enthalpies of fusion of a group of organic CRMs fusion from about 320 to 560 K are reported. Their use is especially intended for the assessment of the sample contribution to the total uncertainty of the measurements (i.e., the second step of the calibration procedure indicated in Section 3).

**Table 3** CRMs (organic substances) for temperatures and enthalpies of fusion.

Substance	$T_{\text{fus}}/\text{K}$	$T_{\text{fus}}/^{\circ}\text{C}$	$\Delta_{\text{fus}}h/\text{J g}^{-1}$	$\Delta_{\text{fus}}H_{\text{m}}/\text{kJ mol}^{-1}$
Phenyl salicylate [phenyl 2-hydroxybenzoate]	314.94	41.79	$89.5 \pm 0.4$	$19.18 \pm 0.08$
4-nitrotoluene	324.76	51.61		
Biphenyl	342.08	68.93	$120.6 \pm 0.8$	$18.60 \pm 0.10$
Naphthalene	353.38	80.23	$147.6 \pm 0.6$	$18.92 \pm 0.08$
Benzil [1,2-diphenylethane-1,2-dione]	368.00	94.85	$110.6 \pm 0.5$	$23.26 \pm 0.10$
Acetanilide [N-phenylacetamide]	387.49	114.34	$161.2 \pm 0.6$	$21.79 \pm 0.08$
Benzoic acid	395.50	122.35	$147.2 \pm 0.3$	$17.98 \pm 0.04$
Diphenylacetic acid	420.34	147.19	$146.8 \pm 0.6$	$31.16 \pm 0.13$
Anisic acid [4-methoxybenzoic acid]	456.43	183.28		
Chloroanthraquinone [2-chloro-9,10-anthraquinone]	482.98	209.83		
Carbazole	518.95	245.80		
9,10-Anthraquinone	557.67	284.52		

All samples are from LGC (U.K. Laboratory of the Government Chemist) [22]. Where no  $\Delta_{\text{fus}}h$  is shown, the sample is from a set for use in calibrating fusion point apparatus.  $T_{\text{fus}}$  was determined using a “static” method with equilibration between temperature increments of 5–10 mK. Temperature uncertainties are  $\pm 0.02$  K where  $\Delta_{\text{fus}}h$  is shown, and  $\pm 0.05$  K for the fusion point materials. When comparing the values and their uncertainties, take into account the method used for the determination of the uncertainty and refer to the certificates.

### 5.2.2 Specific heat capacity (heat-flow rate) calibrants

The use of  $\alpha$ -alumina for this kind of calibration is recommended. The material is available from NIST (SRM 720), and many independent measurements suggest that the heat capacity of  $\alpha$ -alumina is known

to within 0.1 %. Tables 4a and 4b contain polynomials that accurately represent the molar heat capacity at constant pressure of both  $\alpha$ -alumina in three distinct ranges of temperature and oxygen-free high-conductivity copper in only one extended range of temperature.

**Table 4a** Substances for heat-flow rate calibration.

Substance	$M/\text{g mol}^{-1}$	$T$ interval/K	Molar heat capacities at constant pressure $C_{p,m} = f(T)$ as polynomial functions
$\alpha\text{-Al}_2\text{O}_3^{\text{a}}$	101.961 3	70–150 150–900 900–2250	$\frac{C_{p,m}}{\text{J K}^{-1} \text{mol}^{-1}} = a_1 + a_2 \left(\frac{T}{\text{K}}\right) + \frac{a_3}{(T/\text{K})^2} + \sum_{n=4}^8 a_n \left(\frac{T}{\text{K}}\right)^{n-1}$
Cu <sup>b</sup>	63.546	14–320	$C_{p,m}/\text{J K}^{-1} \text{mol}^{-1} = \sum_{n=0}^{16} a_n (T/\text{K})^n$

<sup>a</sup>See ref. [27].

<sup>b</sup>See ref. [28].

**Table 4b** Polynomial coefficients for molar heat capacity at constant pressure of calibrants in Table 4a.

Substance	$\alpha\text{-Al}_2\text{O}_3$			Cu	
	$T$ -range/K	70–150	150–900	900–2250	14–320
$a_0$					–0.820 955 046 298 9
$a_1$		–0.216 580 E+02	–0.687 717 E+02	0.144 480 E+03	0.187 708 011 440 3
$a_2$		0.509 380 E+00	0.715 500 E+00	–0.238 535 E–01	–0.157 208 857 071 6 E–01
$a_3$		0.110 644 E+05	0.145 685 E+06	–0.820 895 E+07	0.583 248 486 276 1 E–03
$a_4$		–0.149 302 E–03	–0.596 292 E–05	0.296 245 E–07	–0.145 229 653 312 9 E–05
$a_5$		0.286 388 E–05	0.169 120 E–07	–0.252 435 E–10	–0.345 777 346 109 3 E–06
$a_6$		–0.227 457 E–07	–0.221 044 E–10	0.949 225 E–14	0.102 953 768 453 4 E–07
$a_7$		0.853 876 E–10	0.144 189 E–13	–0.170 262 E–17	–0.162 054 724 020 3 E–09
$a_8$		–0.125 607 E–12	–0.378 847 E–17	0.115 882 E–21	0.167 783 599 172 2 E–11
$a_9$					–0.122 571 053 043 9 E–13
$a_{10}$					0.649 706 032 594 5 E–16
$a_{11}$					–0.251 678 989 511 1 E–18
$a_{12}$					0.706 452 308 526 4 E–21
$a_{13}$					–0.140 013 135 764 8 E–23
$a_{14}$					0.185 872 855 709 4 E–26
$a_{15}$					–0.148 350 597 021 5 E–29
$a_{16}$					0.538 262 983 381 4 E–33
Uncertainty/%	0.17–0.08	0.08	900–2200 K: 0.08–1.0 %	30–300 K: 0.1 %	

High-quality (99.999 %) synthetic sapphire is readily available and relatively cheap to produce in the form of discs that fit snugly into a variety of DSC pans. Of course, such fabricated discs are not certified, but it has been shown that the heat capacity of  $\alpha$ -alumina is little affected when impurities at low levels are deliberately added to improve processability or particular properties [26]. Within the level of uncertainty required for calibration of DSCs, the use of such noncertified substances is thus justified. Copper is useful at subambient temperatures where the heat capacity of  $\alpha$ -alumina changes rather rapidly with temperature.

A discussion about the given uncertainties is given in Addendum 2.

Three calibrants for the assessment of the contribution of the sample to the total uncertainty of heat-flow rate measurements have been selected to cover different types of samples: benzoic acid, for

organic compounds; polystyrene, for polymers; and molybdenum, for metals. Their polynomials and related uncertainties are reported in Tables 5a and 5b. Although benzoic acid is the recommended calibrant for subambient temperatures [29], it should never be used much above 350 K because of potential problems that can originate from its rapid increase in vapor pressure. The heat capacity of polymers depends on crystallinity and molar mass. The polystyrene example shown in Tables 5a and 5b is atactic and therefore of zero crystallinity. In any case, the data for this material refer only to temperatures below the glass transition where amorphous and crystalline heat capacities are very similar [30]. The number average molar mass of the polymer is  $1.8 \times 10^5 \text{ g mol}^{-1}$ , which is well into the range where the effects of chain ends become insignificant [31].

**Table 5a** RMs for the assessment of the sample contribution to the heat-flow rate measurement uncertainty.

Substance	$M/\text{g mol}^{-1}$	$T$ interval/K	Molar heat capacity at saturation pressure $C_{\text{sat,m}} = f(T)$ , and molar heat capacity at constant pressure $C_{p,m} = f(T)$ , resp., as polynomial functions
Benzoic acid <sup>a</sup>	122.12	115–350	$\frac{C_{\text{sat,m}}}{\text{J K}^{-1} \text{ mol}^{-1}} = a_1 + a_2 \left(\frac{T}{\text{K}}\right) + \frac{a_3}{(T/\text{K})^2} + \sum_{n=4}^8 a_n \left(\frac{T}{\text{K}}\right)^{n-1}$
Polystyrene <sup>b</sup>	104.152 <sup>d</sup>	115–350	$\frac{C_{p,m}}{\text{J K}^{-1} \text{ mol}^{-1}} = a_1 + a_2 \left(\frac{T}{\text{K}}\right) + \frac{a_3}{(T/\text{K})^2} + \sum_{n=4}^8 a_n \left(\frac{T}{\text{K}}\right)^{n-1}$
Molybdenum <sup>c</sup>	95.94	273.15–2400	

<sup>a</sup>See ref. [33].

<sup>b</sup>See ref. [34]. Although the polynomial given is valid for the CRM of NIST SRM 705 it is almost certainly valid for any high molar mass, atactic polystyrene glass (see accompanying discussion).

<sup>c</sup>See ref. [35].

<sup>d</sup>Per repeating unit.

**Table 5b** Polynomial coefficients for molar heat capacity of calibrants in Table 5a. Benzoic acid: at saturation pressure, polystyrene and molybdenum: at constant pressure.

Substance	Benzoic acid	Polystyrene	Molybdenum
$T$ -range/K	115–350	115–350	273.15–2400
$a_1$	0.218 935 E+02	0.208 629 E+02	0.219 505 E+02
$a_2$	0.448 006 E+00	0.280 756 E+00	0.109 225 E–01
$a_3$	0.265 695 E+04	–0.188 767 E+05	–0.822 220 E+05
$a_4$	–0.664 849 E–05	0.835 464 E–07	–0.204 280 E–07
$a_5$	0.459 704 E–07	0.546 353 E–08	0.284 220 E–10
$a_6$	–0.102 623 E–09	0.131 819 E–10	–0.164 837 E–13
$a_7$	0.472 856 E–13	–0.130 307 E–12	0.456 849 E–17
$a_8$	0.612 844 E–16	0.182 460 E–15	–0.495 026 E–21
Uncertainty/%	1.0	0.4	237.15–1000 K: 0.4 % 1000–2000 K: 0.8 %

## 6. ADDENDUM 1: UNCERTAINTY OF ENTHALPY OF FUSION VALUES (FROM REF. [15])

Several pure metals are available as certified enthalpy RMs. However, most of the enthalpy of fusion results for metals reported in the literature have also been made on high-purity samples. Hence, the spread in the experimental enthalpy of fusion values  $\Delta_{\text{fus}}h$  is due primarily to differences in experimental techniques and procedures rather than to differences between samples. It is thus possible to de-

give a set of recommended  $\Delta_{\text{fus}}h$  values to be employed for quantitative DSC. The recommended values given in Section 5 are in accordance with the  $\Delta_{\text{fus}}h$  values for most of the certified metals within twice the given standard deviation, or within twice the assessed uncertainty.

In order to obtain recommended values of  $\Delta_{\text{fus}}h$  for metals on the basis of literature data, the uncertainty of each individual determination had to be estimated. In all experimental studies, nonrandom, systematic errors are expected to occur to some extent. Errors of this type are normally not treated in the statistical analysis. They may result from inadequate measuring techniques, faulty calibration of the equipment, or bias on the part of the observer. The uncertainties due to such systematic errors must be estimated from an analysis of the experimental conditions and techniques. Different experimental techniques will result in different uncertainties and different systematic errors. Although random errors will vary according to a probability density function for a certain instrument as operated, the systematic errors will not. Still, in the present case it may reasonably be assumed that the systematic errors arising in the various techniques, under varying operating conditions, are randomly distributed about the mean. Enthalpies determined by drop techniques may be expected to be slightly low due to quenching effects, whereas values determined by adiabatic calorimetry may be slightly high due to heat losses especially at high temperatures. Hence, there is no reason to assume a biased distribution, taking the different principles of measurements into account.

If the systematic errors are randomly distributed about the mean, the weighted mean,  $\mu'$ , of a series of determinations with nonuniform uncertainties is:

$$\mu' = \frac{\sum_i N_i \left( \frac{x_i}{\sigma_i^2} \right)}{\sum_i N_i \left( \frac{1}{\sigma_i^2} \right)}$$

where  $N_i$ ,  $x_i$ , and  $\sigma_i$  represent the number of determinations, the reported value, and the uncertainty assigned to the  $i^{\text{th}}$  series of experiments. The uncertainty of the mean can be evaluated if all errors are random and, hence, due to fluctuations in observations which are distributed according to a probability density function. For nonuniform uncertainties of the individual determinations, the general formula for the uncertainty of the mean is given by

$$\sigma_{\mu}^2 = \frac{1}{\sum_i N_i \left( \frac{1}{\sigma_i^2} \right)}$$

The most difficult task in the evaluation of the  $\Delta_{\text{fus}}h$  of metals is obviously the assignment of uncertainties to each individual determination reported in the literature. In the following, a summary of the adopted procedure for this key point is reported. The uncertainty will depend on a large number of parameters related to sample quality, instrumentation, operating procedures, and data reduction. The sample quality is probably not the main reason for the large spread in literature values. Operating procedures and data reduction are not normally discussed at length in scientific papers and in general cannot be assessed. Hence, two factors can be singled out as parameters for evaluation of the quality of the result: the instrumental technique used and the scientist who uses it. In the evaluation of uncertainties, weight to the instrumental technique used was given. Furthermore, since most of the scientists who have determined enthalpies of fusion have done so on more than one metal, it often is possible to evaluate the consistency of a certain researcher's work. The "scientist factor" was given considerable weight in the present evaluation. An independent evaluation of the "scientist factor" is also possible when performance tests of the calorimeter are reported.

A set of recommended  $\Delta_{\text{fus}}h$  values and associated uncertainties of the mean were obtained, which are reported in Table 1. Even though the most difficult aspect of a study like this is the assignment of individual uncertainties to all experimental determinations, it should be noted that small changes in the uncertainties of the individual determinations will not affect the resulting values significantly. The statistical analysis would be less questionable if a larger number of determinations with realistic uncertainties were available. The lack of high-quality data is evident for metals fusion at  $T \geq 1000$  K.

## 7. ADDENDUM 2: UNCERTAINTY OF HEAT CAPACITY VALUES

One of the most difficult questions when giving reference values for any physical quantity is how to assign a reasonable uncertainty to this value. The notion of uncertainty of measurement is nowadays rather clearly defined as the “*parameter, associated with the result of a measurement, that characterizes the dispersion of the values that could reasonably be attributed to the measurand*” [16]. It is customary to give an uncertainty which covers a 95 % confidence interval. However, it is hardly possible to recalculate this quantity from data published in former times, mainly because of lack of information. Nevertheless, the authors of this paper made the attempt to convert the values taken from the literature to uncertainties according to ref. [16]. For each substance, a deviation plot (Figs. A1 to A4) is given to show the effect of the fitting procedure. The data and procedures applied are described in the following.

All regressions were performed with the LINEST function of Microsoft® Excel 2002. The standard error of the estimates  $\sigma_{\text{fit}}$  was calculated by

$$\sigma_{\text{fit}} = \sqrt{\frac{1}{n-k} \sum_{i=1}^n (y_i - \hat{y}_i)^2}$$

with  $n$  number of experimental values  
 $k$  number of coefficients in the fit  
 $y$  experimental value  
 $\hat{y}$  fitted value

The uncertainties of the fitted values for the given number of digits in the respective temperature range are expressed as relative standard deviations  $\sigma_{\text{red}}$  and were calculated by

$$\sigma_{\text{red}} = \sqrt{\frac{1}{n} \sum_{i=1}^n \left( \frac{y_i - \hat{y}_i}{y_i} \times 100 \right)^2}$$

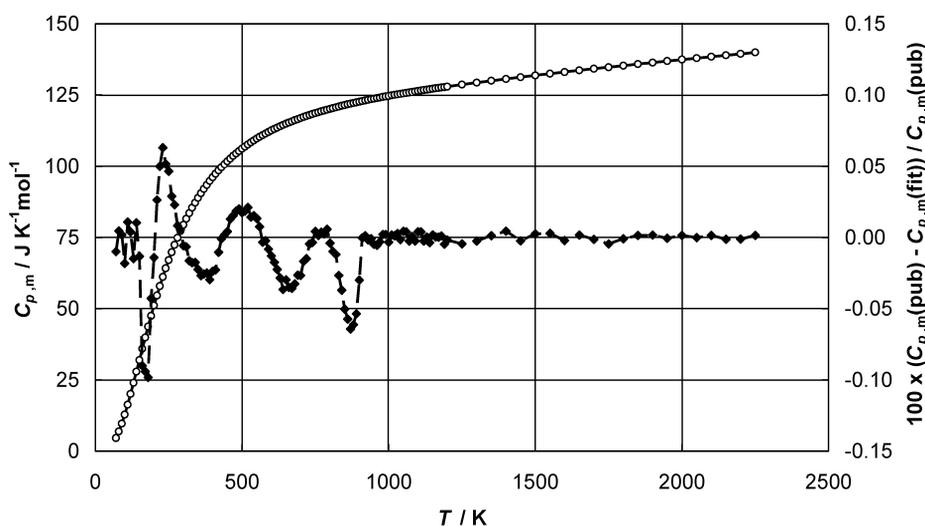
Combination of errors to render the total measurement uncertainty  $u$  was done by means of the error propagation law of Gauss. For conversion to a confidence interval of 95 %, this value was multiplied by a coverage factor  $k = 2$ . Irrespective of the number of measured or calculated data points which entered the uncertainty calculations, a standard (Gauss) distribution of errors was always assumed. Errors introduced by not taking Student's t-distribution into account when only few data points were available are negligible in our context.

*$\alpha$ -Alumina (70–150 K)*: Fit is based on 11 values between 60 and 160 K from Table 2 of ref. [27].  $\sigma_{\text{fit}} = 0.0032 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $\sigma_{\text{red}} = 0.010 \%$ . Statement of the author of ref. [27], page 1444, second paragraph: “The s.r.v. (square-root-of-variance) assigned to the heat-capacity results of Andrews et al. and of Inaba was 0.3 percent for all temperatures above 80 K. ... The s.r.v. assigned to the heat-capacity results from Chang was 0.1 percent for all temperatures above 100 K, 0.3 percent for 75 K < T < 100 K, 0.5 percent for 40 K < T < 75 K ...”. The following statement on accuracy can be found in ref. [33], fourth paragraph: “... the heat-capacity values have an accuracy ranging from  $\pm 0.1$  percent at 70 K to

$\pm 0.3$  percent at 1200 K ...". It is therefore assumed that all accuracy data given in refs. [32] and [27] refer to a confidence interval of 95 %. The resulting total uncertainty is  $u(k = 2) = 0.17$  % at 70 K.

*$\alpha$ -Alumina (150–900 K)*: Fit is based on 78 values between 140 and 910 K from Table 2 of ref. [27].  $\sigma_{\text{fit}} = 0.0024 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $\sigma_{\text{red}} = 0.032$  %. Statement of the author of ref. [27], page 1446, first paragraph: "In the region from 150 to 900 K the accuracy of the heat capacity is on the order of 0.05 percent...". Assuming a confidence interval of 95 % for this value, the resulting total uncertainty is  $u(k = 2) = 0.08$  % between 150 and 900 K.

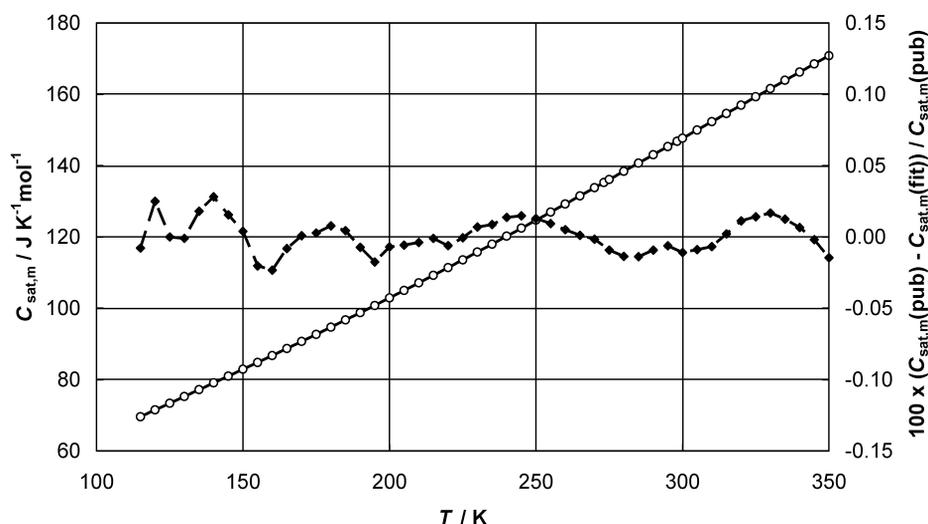
*$\alpha$ -Alumina (900–2200 K)*: Fit is based on 53 values between 890 and 2250 K from Table 2 of ref. [27].  $\sigma_{\text{fit}} = 0.0036 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $\sigma_{\text{red}} = 0.003$  %. Statement of the author of ref. [27], page 1446, first paragraph, fifth sentence: "...For temperatures of 900 to 2200 K, the relative enthalpy and heat capacity become less accurate, the inaccuracy reaching approximately 0.3 and 1.0 percent at 2200 K for relative enthalpy and heat capacity, respectively". Assuming a confidence interval of 95 % for this value, the resulting total uncertainty is  $u(k = 2) = 1.0$  % at 2200 K.



**Fig. A1** Molar heat capacity  $C_{p,m}$  of  $\alpha$ -alumina (open circles: published values; continuous line: fitted values) and relative deviation  $(C_{p,m}(\text{pub}) - C_{p,m}(\text{fit})) / C_{p,m}(\text{pub})$  (closed diamonds, broken line) between published values and values calculated by the fit as a function of temperature  $T$ .

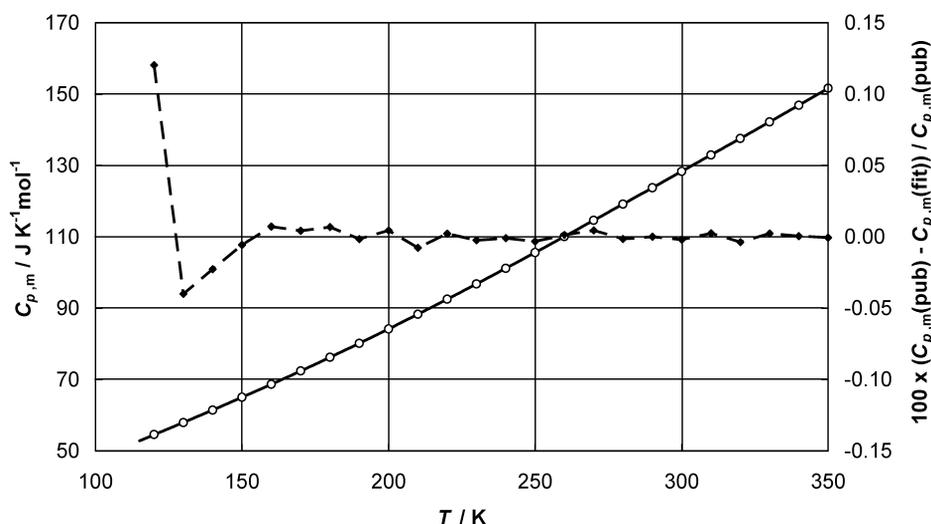
*Copper (30–300 K)*: The polynomial coefficients are directly taken from ref. [28]. This fit is based on 307 values between 14 and 320 K from ref. [36]. The standard error of the estimate is unknown. It is assumed that the conversion from IPTS-68 to ITS-90 did not introduce additional errors. Statement of the authors of ref. [36]: Introduction, last sentences: "The results ... are, therefore, proposed as representing a copper standard sample to  $\pm 0.1$  % in the temperature range 30–300 K". Assuming a confidence interval of 95 % for this value, the resulting total uncertainty is  $u(k = 2) = 0.1$  %.

*Benzoic acid (115–350 K)*: Fit is based on 57 values between 90 and 350 K from Table 1 of ref. [33].  $\sigma_{\text{fit}} = 0.0015 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $\sigma_{\text{red}} = 0.011$  %. Statement of the authors of ref. [33]: Chapter 3.2, first paragraph: "Considering the precision and the various known sources of errors a probable error (footnote 4) of  $\pm 0.2$  percent is assigned to the heat-capacity values from 60° to 395° K". Footnote 4: "For these experiments a true probable error cannot be computed statistically. The values given are estimates reached by examining contributions to the inaccuracy from all known sources. The authors estimate that there is a fifty-fifty chance that the error is no larger than that indicated". Multiplying the value 0.2 % by 5.2 converts the confidence interval of 50 to 95 %. The resulting total uncertainty is  $u(k = 2) = 1.0$  %.



**Fig. A2** Molar heat capacity  $C_{\text{sat,m}}$  of benzoic acid at saturation pressure (open circles: published values; continuous line: fitted values) and relative deviation  $(C_{\text{sat,m}}(\text{pub}) - C_{\text{sat,m}}(\text{fit})) / C_{\text{sat,m}}(\text{pub})$  (closed diamonds, broken line) between published values and values calculated by the fit as a function of temperature  $T$ .

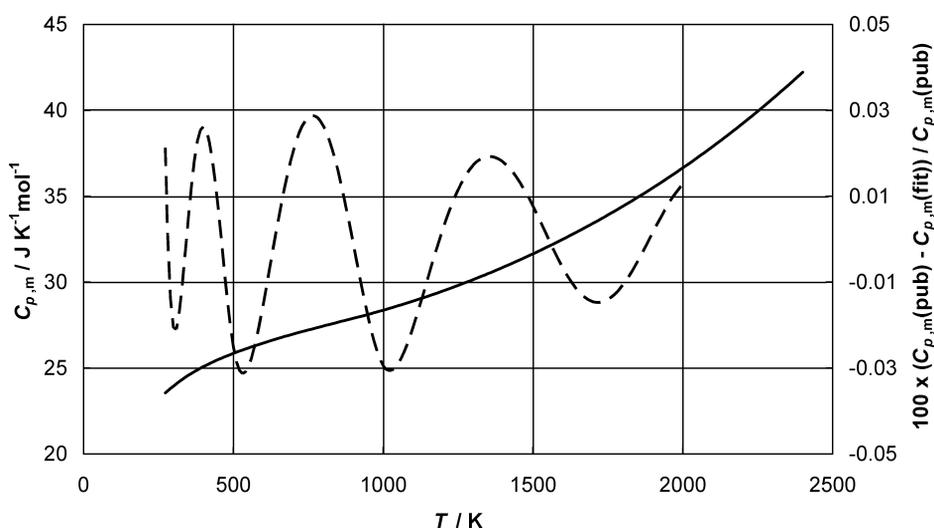
*Polystyrene (115–350 K)*: Fit is based on 28 values between 100 and 350 K from Table III of ref. [34].  $\sigma_{\text{fit}} = 0.0019 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $\sigma_{\text{red}} = 0.026 \%$ . Statements of the authors of ref. [34]: Introduction: “The present paper provides more precise heat capacity data.... It presents data precise to 0.1 % in the temperature range 10 to 360°K. for a sample having a narrow molecular weight distribution”. Page 858, second paragraph: “The root-mean-square percentage deviation of the individual values from the smoothed function is 0.09 % at temperatures above 100°K.”, page 859, first paragraph: “Comparisons of results for Calorimetry Conference Standard Sapphire Sample have indicated an instrumental accuracy comparable to its precision. Estimated inaccuracy for the present sample may be doubled due to its impurity content”, page 860, third paragraph: “...at temperatures between about 100 and 360°K., the heat capacity of polystyrene obtained in this investigation is believed to represent within 0.5 % the heat capacities for the atactic and isotactic isomers, or atactic samples of widely differing molecular weight distributions”. Because the authors compare a precision with an accuracy, we assume a confidence interval of 68 % for the value of 0.2 %. The resulting total uncertainty is  $u(k = 2) = 0.4 \%$ .



**Fig. A3** Molar heat capacity  $C_{p,m}$  of polystyrene (open circles: published values, continuous line: fitted values) and relative deviation  $(C_{p,m}(\text{pub}) - C_{p,m}(\text{fit})) / C_{p,m}(\text{pub})$  (closed diamonds, broken line) between published values and values calculated by the fit as a function of temperature  $T$ .

*Molybdenum (273.15–1000 K):* Fit is based on 214 values between 273.15 and 2400 K calculated from the spline representation of the data of ref. [35].  $\sigma_{\text{fit}} = 0.0048 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $\sigma_{\text{red}} = 0.016 \%$  for 74 values between 273.15 and 1000 K. Statement of the authors of ref. [35]: Chapter 6.2, second paragraph: “Figure 1 indicates that two enthalpy measurements at 323.15 and 373.15 K deviate considerably from all the others in the series (up to three times the standard deviation of residues). A re-calculation of the standard deviation of the ice-calorimeter data, neglecting these two measurements, yields 0.06 percent for this index of the imprecision of the measurements. Adding this index, taken at a 99-percent confidence level, to the estimated maximum systematic error (0.11 percent at 1200 K) yields 0.3 percent as an estimate of the overall inaccuracy of the enthalpy data. The inaccuracy on the heat-capacity values obtained by differentiating equation (2) is believed not to exceed 0.5 percent up to 1000 K”. Multiplying the value 0.5 % by 0.76 converts the confidence interval from 99 to 95 %. The resulting total uncertainty is  $u(k = 2) = 0.4 \%$ .

*Molybdenum (1000–2000 K):* Fit is based on 214 values between 273.15 and 2400 K calculated from the spline representation of the data of ref. [35].  $\sigma_{\text{fit}} = 0.0048 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $\sigma_{\text{red}} = 0.007 \%$  for 101 values between 1000 and 2000 K. Statement of the authors of ref. [35]: Page 38, first paragraph: “Addition of the observed standard deviation of residues for the enthalpy data (from equation (3), taken at a 99-percent confidence level) to the maximum estimated inaccuracy in enthalpy due to temperature error (0.15 percent at 2000 K) and the estimated inaccuracy due to sample impurity (0.05 percent) yields an estimate of the overall inaccuracy in the enthalpy measurements of 0.6 percent. The inaccuracy in the heat-capacity values derived from equation (3) by differentiation is believed to be about 1 percent”. Multiplying the value 1 % by 0.76 converts the confidence interval from 99 to 95 %. The resulting total uncertainty is  $u(k = 2) = 0.8 \%$ .



**Fig. A4** Molar heat capacity  $C_{p,m}$  of molybdenum (continuous line) and relative deviation  $(C_{p,m}(\text{pub}) - C_{p,m}(\text{fit})) / C_{p,m}(\text{pub})$  (broken line) between published values and values calculated by the fit as a function of temperature  $T$ .

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