2DTemperatureCalibration Dependent on Temperature and Heating Rate for DSC and STA Instruments

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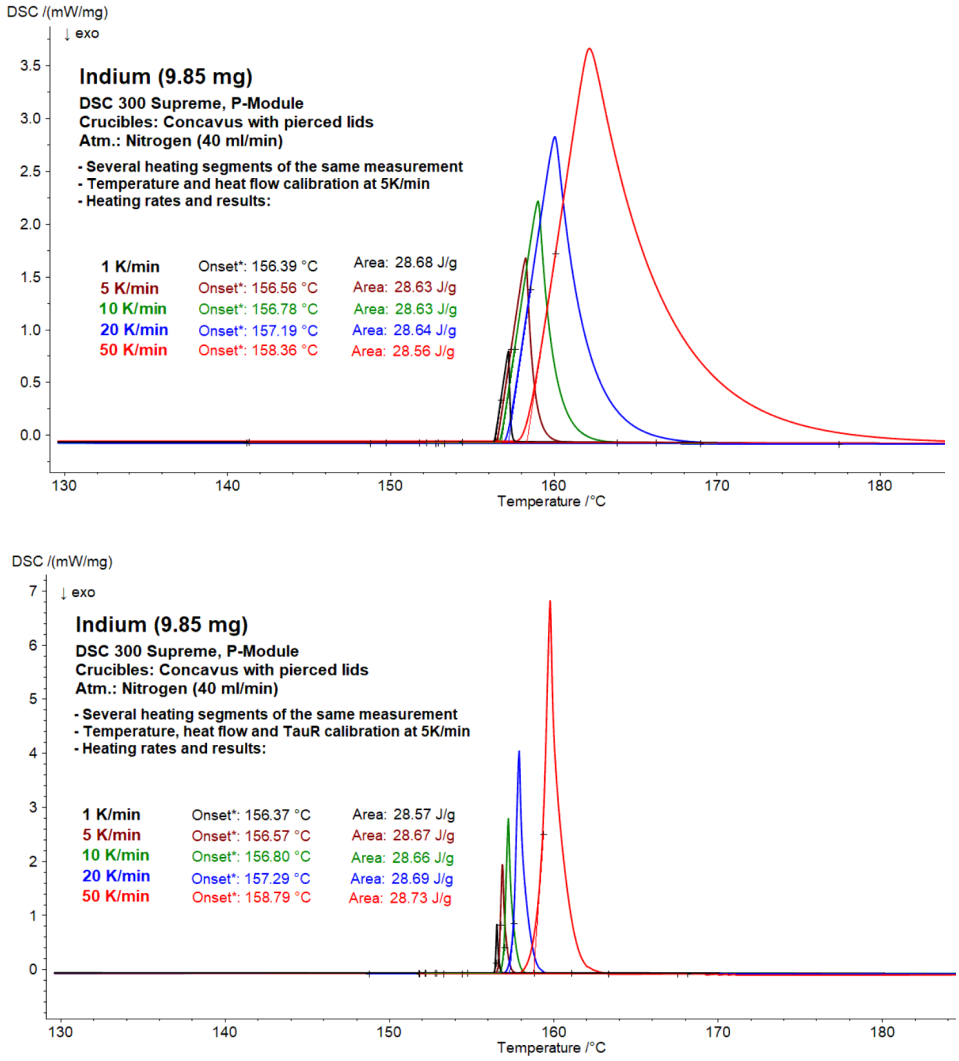
As of *Proteus*® version 9.5, the temperature calibration of DSC and STA instruments can be effectuated to be dependent not only on temperature, but simultaneously also on the heating rate. This so-called *2DTemperatureCalibration*, which is in accordance with international standards, is beneficial regarding the temperature accuracy in particular when various heating rates are applied for the same measurement.

Introduction

In general, the sample temperature of a DSC or STA instrument must be calibrated using the melting effect (or other crystal transformations) of sufficiently pure substances such as indium, aluminum or gold [1]. The measured temperature, T_{exp}, is corrected via $T_{corr} = T_{exp} + \Delta T_{corr}$ where the temperature correction, ΔT_{corr}, is determined



1 **a) und b):** DSC measurement on indium at various heating rates using a DSC 300 *Caliris® Supreme*. The temperature, heat flow and *Tau-R®* calibration (*3in1* calibration) were carried out at 5 K/min. For the upper diagram (a), the *Tau-R®* mode was disabled, while it was enabled for the lower diagram (b). The nominal vales of the melting temperature, T_m, and enthlapy, ΔH, *are* 156.6°C and 28.6 J/g.

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from the deviations between the measured extrapoled onset temperatures T_{exp}^{cal} of the melting process of these substances and the nominal melting temperatures of the calibration substances T_{nom}^{cal} [2, 3]:

$$\Delta T_{corr} = T_{nom}^{cal} - T_{exp}^{cal} = f(T) \qquad (1)$$

The temperature correction, ΔT_{corr}, is a linear or quadratic function f which is usually created only with respect to temperature, T.

Due to the "thermal lag" of the DSC signal [4, 5], however, the measured onset temperatures depend significantly on the heating rate. This is illustrated in figures 1a and b, where a measurement on indium at heating rates between 1 K/min and 50 K/min is shown.

Before each heating segment, the sample was cooled down below the crystallization temperature at -20 K/min. Since the temperature calibration applied was carried out at 5 K/min, the onset temperature matches almost perfectly with the nominal value of 156.6°C at this heating rate. However, the onset temperature is about 2 K higher at 50 K/min compared to that at the heating rate of 1 K/min reflecting the "thermal lag".

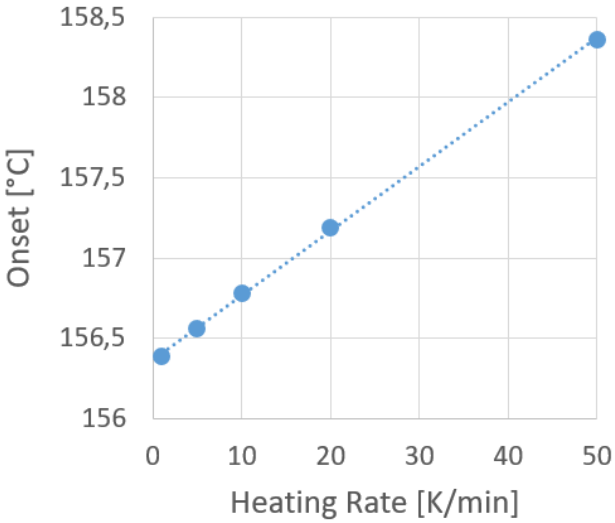
In contrast, the melting enthalpies determined do not significantly depend on the heating rate and match well with the nominal value of 28.6 J/g. This can be understood since, firstly, the DSC peaks are integrated over time and not over temperature. Secondly, the heat flow or "sensitivity" calibration of the DSC signal is temperature-dependent, so the shift of the melting peaks to higher temperatures at higher heating rates does not affect the resulting enthalpy very much.

2DTemperatureCalibration

The shift of the onset temperatures at the heating rate described above is depicted again in figure 2 for the data shown in figure 1a. A linear dependence between the onset temperature and the heating rate is observed, which can be expected from a theoretical point of view. It is also described in references [3] and [5]. Based on that linear dependence, a temperature calibration dependent on temperature, T, and heating rate, HR, is introduced which is in accordance with the standards [2, 5]:

$$\Delta T_{corr} = f(T, HR) =$$
$$= a_0 + a_1 \cdot T + a_2 \cdot T^2 + (b_0 + b_1 \cdot T + b_2 \cdot T^2) \cdot HR \qquad (2)$$

where T and HR are T_{exp}^{cal} and HR^{cal} when the calibration with its coefficients a_i and b_i is created. When the calibration is applied, T and HR are the current non-corrected values for the temperature, T_{exp}, and the current heating rate HR_{exp}. As can be seen from the formula (2), the temperature calibration/correction has a heating rate-independent part and a heating rate-dependent part, where both contributions can have a quadratic or linear (then a_2 and b_2 are equal to zero) dependence on the temperature. The slope $\Delta T_{corr}/\Delta HR$ is designated as "thermal lag" in reference [5].



2 Onset temperatures of the melting effect of indium as a function of the heating rate. The corresponding DSC measurement curves and evaluations can be seen in figure 1a.

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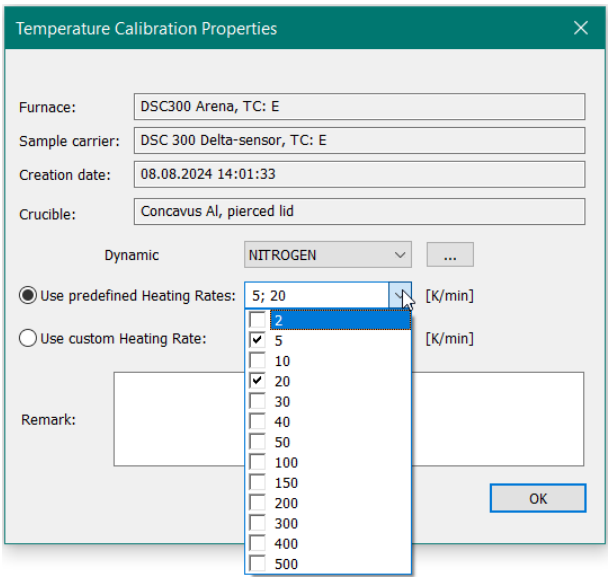
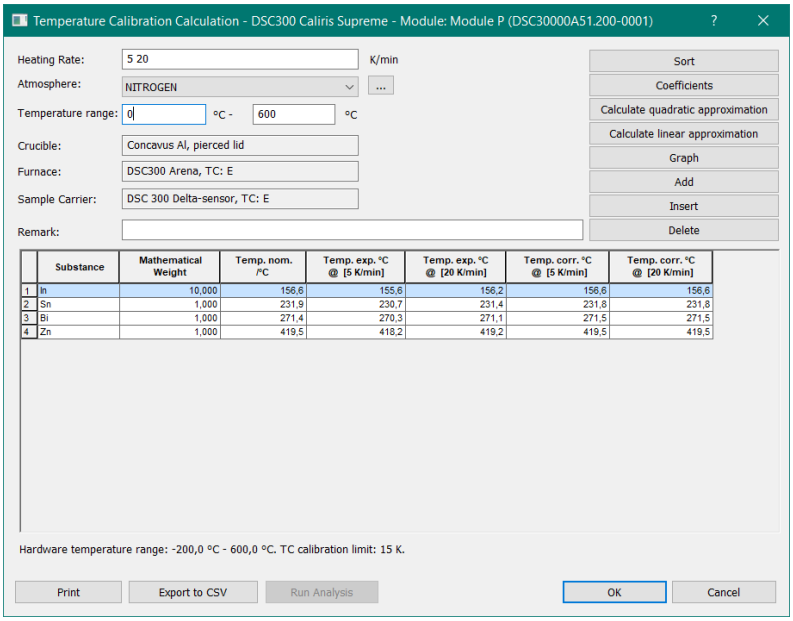
The creation and application of a *2DTemperature Calibration* according to formula (2) is possible in the *Proteus*® software as of version 9.5. The creation is done as follows: As the first step, one can select predefined heating rates with which the calibration measurements were carried out (see figure 3), where if only one heating rate is selected, this means that no dependence on the heating rate will be contained in the calibration. It is, of course, possible to select more than two heating rates if the corresponding calibration measurement data are available.

Possible heating rates of up to 500 K/min, visible in figure 3, are a specialty of the P-Module available for NETZSCH DSC 300 *Caliris*® instruments. For most experiments, the two heating rates 5 K/min and 20 K/min used also for the *2DTemperatureCalibration* of this example are sufficient, as shown below.

The second step is to enter the experimental onset data determined for the corresponding heating rates (see figure 4). This data may originate from several single temperature calibrations done with *AutoCalibration*.



3 Temperature calibration properties dialogue in the *Proteus*® software.



4 Temperature calibration table dialogue in the *Proteus*® software.

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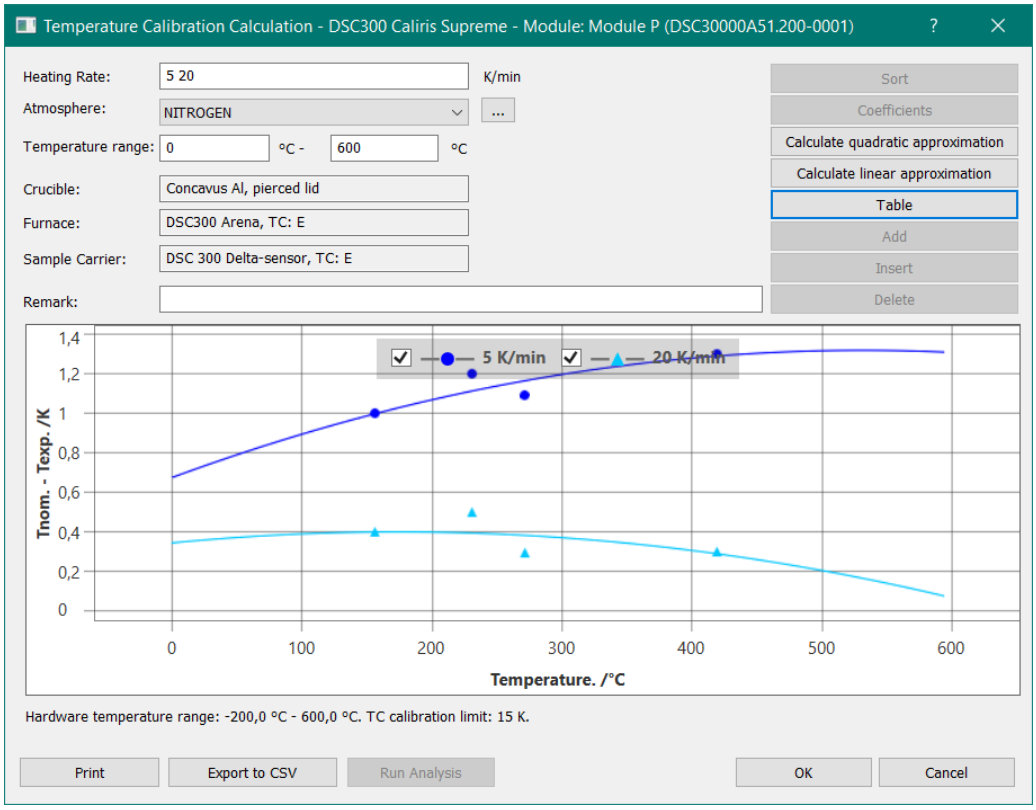
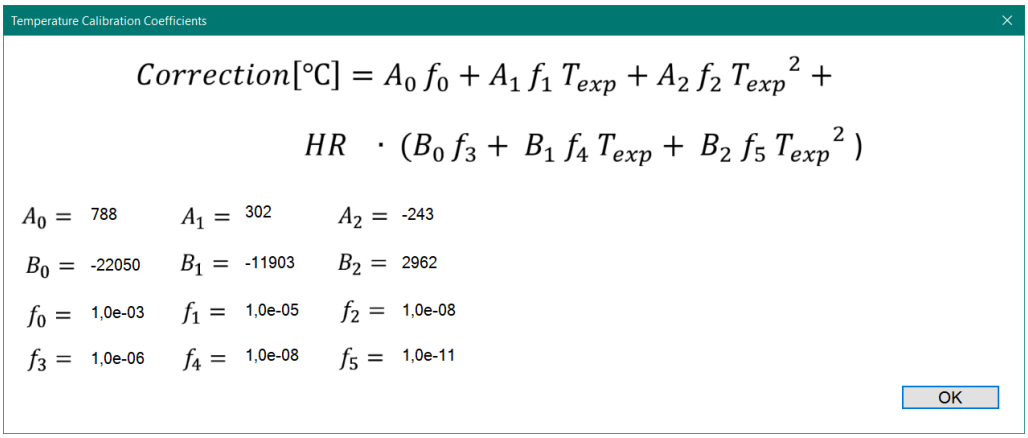
After calculating a quadratic or linear approximation, the calculated, corrected onset temperatures are visible in the table. A graphical presentation of the temperature correction $\Delta T_{corr} = T_{nom}^{cal} - T_{exp}^{cal}$ is shown in figure 5 for both heating rates:

The calibration coefficients $a_i = A_i \cdot f_i$ and $b_i = B_i \cdot f_i$ are also accessible (see figure 6).



5 Temperature calibration graph dialogue in the *Proteus*® software.



6 Temperature calibration coefficients dialogue in the *Proteus*® software.

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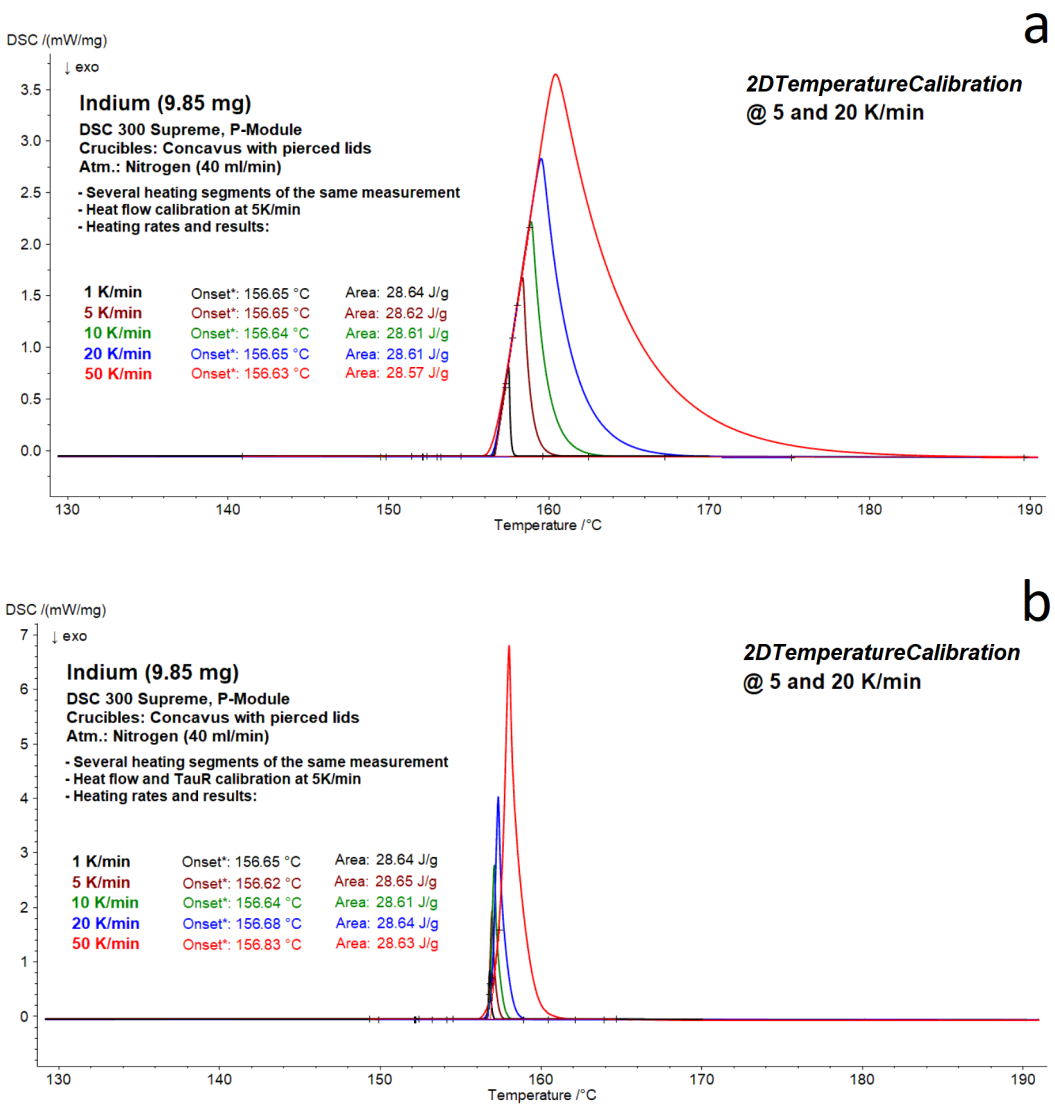
Experimental Results

The indium sample, used for the data displayed in figure 1, was again measured with the DSC 300 *Caliris® Supreme* using the *2DTemperatureCalibration* shown above, which was carried out at 5 K/min and 20 K/min. The results are depicted in figure 7. It is visible that the calibration of the temperature is almost perfect for all heating rates in the range 1…50 K/min. It should again be pointed out that the curves shown in figures 1 and 7 are different heating segments of one measurement, respectively. The excellent agreement of the onset and enthalpy data with the nominal values also indicates very good repeatability, since the indium sample was removed from the DSC instrument after the measurement shown in figure 1 and measured several days later, resulting in the data displayed in figure 7.



7 **a und b:** DSC measurement on indium at varous heating rates using a DSC 300 *Caliris® Supreme*. The heat flow and *Tau-R®* calibrations (*3in1* calibration) were carried out at 5 K/min. The *2DTemperatureCalibration* applied was done at 5 K/min and 20 K/min. For the upper diagram (a), the *Tau-R®* mode was disabled, while it was enabled for the lower diagram (b). The nominal values of the melting temperature, T_m, and enthalpy, ΔH , are 156.6°C and 28.6 J/g.

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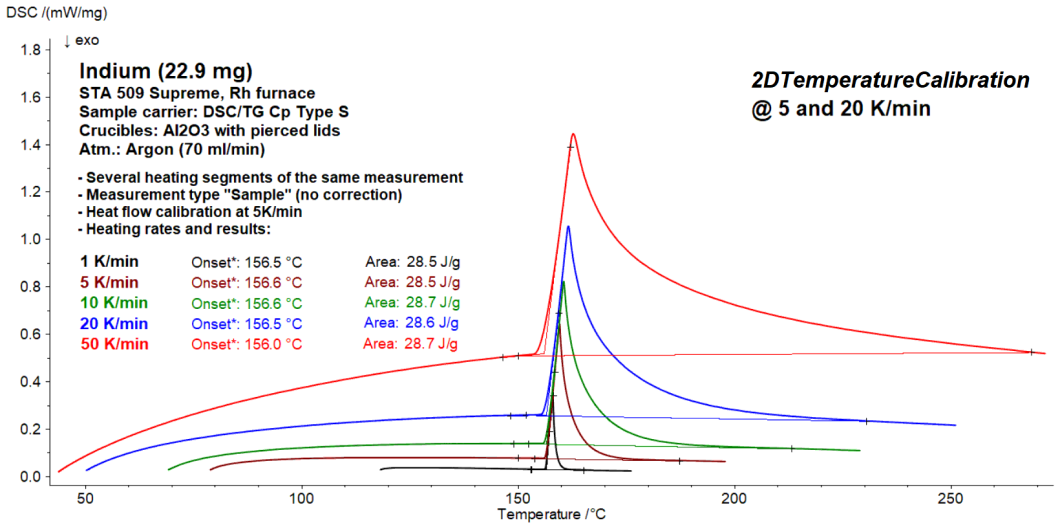
The tin, bismuth and zinc standards, also used for the calibrations, were re-measured applying the *2DTemperatureCalibration* carried out at 5 K/min and 20 K/min, too. These measurements also revealed a very good agreement of the onsets/melting temperatures and enthalpies with the nominal values for all heating rates in the range 1…50 K/min. All results obtained for indium, tin, bismuth and zinc using the DSC 300 *Caliris® Supreme* are summarized in table 1. It should be noted that the results depend slightly on the position of the evaluation cursors used. This effect is, however, negligible. While the melting temperatures, T_m, are almost perfect for indium and zinc, there are slight systematic deviations from the nominal values for tin and bismuth of about 0.2 K. This is due to the fact that the calibration data for tin and bismuth deviate slightly from the quadratic fit of the temperature dependence (see figure 5).

Figure 8 shows experimental results for indium at heating rates in the range 1…50 K/min for which an STA 509 *Jupiter® Supreme* was used. The *2DTemperatureCalibration* applied is based on measurements on the calibration standards indium, aluminum and gold at the heating rates of 5 K/min and 20 K/min, respectively. Further experimental details can be seen in figure 8.

Table 1 Melting temperatures, T_m, and enthalpies, ΔH, of indium, tin, bismuth and zinc determined with measurements with a DSC 300 *Caliris® Supreme* applying heat flow and *Tau-R®* calibrations (from *3in1* calibration) carried out at 5 K/min as well as a *2DTemperatureCalibration* done at 5 K/min and 20 K/min. The values in brackets refer to evaluations where the *Tau-R®* mode was enabled. *Concavus®* crucibles with pierced lids (both made of aluminum) and nitrogen as purge gas (flow rate: 40 ml/min) were used. Further experimental details can be seen in figure 7.

HR [K/min]	T_m [°C] Indium	ΔH [J/g] Indium	T_m [°C] Tin	ΔH [J/g] Tinn	T_m [°C] Bismuth	ΔH [J/g] Bismuth	T_m [°C] Zinc	ΔH [J/g] Zinc
1	156.65 (156.65)	28.64 (28.64)	231.83 (231.83)	60.89 (60.73)	271.42 (271.42)	52.88 (52.77)	419.43 (419.48)	107.5 (107.6)
5	156.65 (156.62)	28.62 (28.65)	231.79 (231.83)	60.89 (60.98)	271.44 (271.43)	52.74 (52.74)	419.46 (419.47)	107.3 (107.3)
10	156.64 (156.64)	28.61 (28.61)	231.74 (231,83)	60.86 (60.09)	271.48 (271.44)	52.76 (52.72)	419.46 (419.45)	107.3 (107.4)
20	156.65 (156.68)	28.61 (28.64)	231.68 (231.80)	60.83 (60.04)	271.56 (271.47)	52.74 (52.86)	419.50 (419.40)	107.4 (107.5)
50	156.63 (156.83)	28.57 (28.63)	231.46 (231.74)	60.65 (60.02)	271.60 (271.52)	52.76 (53.08)	-	-
Nominal values	156.6	28.6	231.9	60.5	271.4	53.1	419.5	107.5



8 DSC measurement on indium at various heating rates using an STA 509 *Jupiter® Supreme*. The heat flow calibration was carried out at 5 K/min. The *2DTemperatureCalibration* applied was done at 5 K/min and 20 K/min. The nominal values of the melting temperature, T_m, and enthalpy, ΔH, are 156.6°C and 28.6 J/g.

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Tabelle 2 Melting temperatures, T_m, and enthalpies, ΔH, of indium, aluminum and gold determined with measurements with an STA 509 *Jupiter®* *Supreme* applying a heat flow calibration carried out at 5 K/min as well as a *2DTemperatureCalibration* done at 5 K/min and 20 K/min. Alumina crucibles with pierced lids and argon as purge gas (flow rate: 70 ml/min) were used. Further experimental details can be seen in figure 8.

HR [K/min]	T_m [°C] Indium	ΔH [J/g] Indium	T_m [°C] Aluminum	ΔH [J/g] Aluminum	T_m [°C] Gold	ΔH [J/g] Gold
1	156.5	28.5	660.2	407	1064.1	64.9
5	156.6	28.5	660.3	402	1064.2	64.9
10	156.6	28.7	660.5	401	1064.3	64.9
20	156.5	28.6	660.4	397	1064.3	64.1
50	156.0	28.7	659.7	395	1064.2	62.8
Nominal Values	156.6	28.6	660.3	397	1064.2	63.7

The onset temperatures for indium depicted in figure 8 match with the nominal value of 156.6°C within 0.1 K for all heating rates in the range 1…20 K/min. This is a very good result compared to the measurement without temperature calibration (data not shown), where the onset temperature at 20 K/min was 1.4 K higher compared to that at 5 K/min. At 50 K/min, a deviation of 0.6 K from the nominal value occurred with *2DTemperatureCalibration* applied (see figure 8). This is due to the finite linearity of the heating rate dependence of the onset temperatures, in particular for STA instruments and the fact that the heating rate of 50 K/min was not included in the data for the creation of the *2DTemperatureCalibration*. Furthermore, figure 8 shows that the agreement of the enthalpy data with the nominal value for indium is again excellent for all heating rates in the range 1…50 K/min. It should, however, be noted that the enthalpies determined depend significantly on the position of the evaluation cursors at 20 K/min and 50 K/min mainly because no correction measurement was subtracted, since the enthalpy determination is not the main focus of this work.

The results obtained for aluminum and gold are summarized in table 2 together with the results for indium. All onset temperatures match with the nominal values within about 0.1 K except for aluminum at 50 K/min, where the deviation is 0.7 K. The reason is the same as discussed above for indium. All enthalpy values obtained for aluminum and gold agree with the nominal values within about 2%. It should be noted that a linear DSC baseline was applied for the determination of the area of all melting peaks (also for the results shown in table 1) except for aluminum where sigmoidal baselines were used. The reason was a significant drop in the DSC baseline during the melting effect.

Summary and Further Discussion

In this work, the new *2DTemperatureCalibration* for DSC and STA instruments was introduced which is available as of *Proteus®* version 9.5 and which is in accordance with international standards [2, 5]. It is beneficial regarding the temperature accuracy, in particular when various heating rates are applied in the same measurement, since the *2DTemperatureCalibration* is not only temperature-dependent but at the same time also dependent on the heating rate.

Experiments at heating rates in the range 1…50 K/min applied in different segments of the same measurement, respectively, were carried out on various calibration standards using DSC 300 *Caliris®* and STA 509 *Jupiter®* *Supreme* instruments. They revealed an agreement of the melting temperatures determined with the nominal values within about 0.1 … 0.2 K for most cases. This demonstrates the benefit of the *2DTemperatureCalibration* since the melting temperatures determined at 5 K/min would differ by several degrees from the values determined at 50 K/min if a conventional temperature calibration were applied that disregards the heating rate-dependence.

The melting enthalpies of the calibration standards determined at heating rates in the range 1…50 K/min agreed with the nominal values within about 1% in the case of the DSC 300 and within about 2% in the case of the STA 509. This shows that *one* accurate heat flow calibration done at a rather low heating rate (in the case of this work, at 5 K/min) also yields correct results at lower and higher heating rates.

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The experimental results of this work certainly do not cover all relevant facets of the topic "Temperature calibration of DSC and STA instruments". Some aspects should be discussed in the following:

- It is evident that accurate temperature and heat flow calibrations should be created individually for each STA sample carrier/furnace combination or DSC module used. After a sample carrier/module was mounted again into an instrument, existing calibrations should at least be validated.

- Heat flow calibrations do strongly depend on the crucible type and the type of purge gas. Individual heat flow calibrations should therefore be done for the crucible and gas types that are used. Temperature calibration also depends on the crucible and gas types used, for which reason individual temperature calibrations are also recommended for highly accurate temperature results.

- The sample masses can also have an impact on the onset temperatures determined, where this effect is smaller than 0.1 K for indium with masses between about 1 mg and 20 mg when heating rates of up to 50 K/min and "low temperature" DSC instruments are considered.

- Repeatability and reproducibility of the measurements is furthermore important. In this work, the same samples were applied for the creation as for the validation of the calibrations, i.e., the samples were removed from the instruments after the calibration measurements and inserted again for the validation measurements. So, the results described above include repeatability. If different calibration samples of the same type were applied for the validation measurements, the reproducibility could be checked. This was not done in this work, but as known by experience, the calibration materials used for this work reveal a reproducibility of the onsets of about ± 0.1 K, where indium usually exhibits smaller and bismuth significantly higher deviations of up to ± 1 K.

- The accuracy of the results, which means the deviation from the nominal values, depends also on the choice of the calibration standards and the resulting quality of the fit of the model to the data. In the case of a temperature calibration, the model is described by equation 2, which contains six parameters. This means that six temperature calibration points originating from three calibration standards measured with two heating rates would be perfectly described by the model, and no loss of accuracy is expected *at the temperatures and heating rates of the calibration*. In exactly this way, the *2DTemperatureCalibration* of the STA 509 described above was done, which led to excellent results. In the case of the DSC 300, it was shown that the temperature-dependence of the onsets of more than three calibration standards cannot be fitted perfectly with a second order polynomial (see figure 5), resulting in reduced accuracy *at the temperatures of the calibration*. For an accurate thermometry, it is, of course, recommended to use enough calibration standards to cover the entire temperature range of interest. Regarding heating rates, optimum results can be expected when only two heating rates are used for temperature calibration and validation since in this case, the fit with respect to the heating rate is perfect (see equation 2). The measurements carried out on indium and aluminum with the STA 509 at 50 K/min (see table 2) were regarding the heating rate not covered by the *2DTemperatureCalibration* done at 5 K/min and 20 K/min, which led to bigger deviations from the nominal values of 0.6 K and 0.7 K. The accuracy at 50 K/min could be improved by including data at 50 K/min in the calibration, which would end up in a tradeoff, since accuracy would be slightly worse at lower heating rates then. Finally, it should be noted that the temperature accuracy specified officially for the instruments/configurations used in this work is ± 0.1 K for indium in the case of the DSC 300 *Caliris*® and ± 0.7 K for indium in the case of the STA 509 *Jupiter*®, when the instruments are calibrated in the entire temperature range.

Literature

[1] DIN 51007:2019-04: Thermische Analyse (TA) – Differenz-Thermoanalyse (DTA) und Dynamische Differenzkalorimetrie (DSC) – Allgemeine Grundlagen.
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