

Sharp DSC Peaks and Flat Baselines: Which Calibrations, Corrections and How Many Temperature Sensors Are Required?

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Heat flow Differential Scanning Calorimetry (DSC) is defined as “a technique in which the heat flow difference into a substance and a reference material is measured as a function of temperature while the substance and reference material are subjected to a controlled temperature program” [1, 2]. The heat flow difference between sample and reference is determined via the temperature difference between sample and furnace and reference and furnace or between sample and reference [3]. These definitions reflect the fact that no DSC instrument can measure caloric effects like enthalpy changes in unit J/g, or the specific heat capacity in unit J/(g·K) of a sample directly. In order to obtain such values, calibrations and corrections have to be carried out and applied to the raw DSC data, which is the temperature difference signal between the sample and the reference side of the DSC sensor. The creation and application of calibrations and corrections, which must be compliant to the DSC standards, is nowadays accomplished by software.

Temperature Calibration

In general, the sample temperature sensor is to be calibrated using the melting effect (or other crystal transformations) of sufficiently pure substances such as indium, bismuth or gold [4]. The measured temperature T_{meas} is corrected via $T_{corr} = T_{meas} + \Delta T_{corr}$ where the temperature calibration ΔT_{corr} is determined from the deviations between the nominal melting temperatures of the calibration substances T_{nom}^{cal} and the measured extrapolated onset temperatures T_{meas}^{cal} of the melting process of these substances [5]:

$$\Delta T_{corr} = T_{nom}^{cal} - T_{meas}^{cal} = f(T, \dots) \quad (1)$$

The temperature calibration ΔT_{corr} is a linear or polynomial function f of the temperature T and of other parameters such as the heating rate or the purge gas [5, 6].

Baseline Correction

If just an empty reference crucible and an empty sample crucible with the same mass were measured in a DSC device with perfectly symmetrical sensor and surrounding furnace chamber, zero DSC signal would be expected. The so-called baseline as a function of temperature would be a flat line at a value of zero. In reality, a DSC device is not perfectly symmetric and the crucible masses may be slightly different, resulting in a temperature-dependent baseline other than zero. For many DSC applications, this is not disturbing, because the DSC signal originating from the sample is far higher than the baseline. For small sample signals, however, a baseline correction is recommended. For evaluation of the specific heat capacity of a sample from DSC signals (see below), baseline correction is obligatory [4, 7, 8].

Subtraction of the DSC signal measured with empty reference and sample crucibles is in most cases the ideal baseline correction for DSC measurements when always carried out with the same temperature program and the same sample crucible. A more flexible alternative is a DSC baseline correction applying the NETZSCH *BeFlat+* software solution. A baseline with two empty crucibles and at two different heating and cooling rates needs to be measured just once, leading to the *BeFlat+* baseline calibration according to:

$$DSC_{baseline} = Offset(T) + \beta \cdot [K_{sensor}(T) + c_p^{crucible} \cdot (m_{sample}^{crucible} - m_{reference}^{crucible}) \cdot Sens.(T)] \quad (2)$$

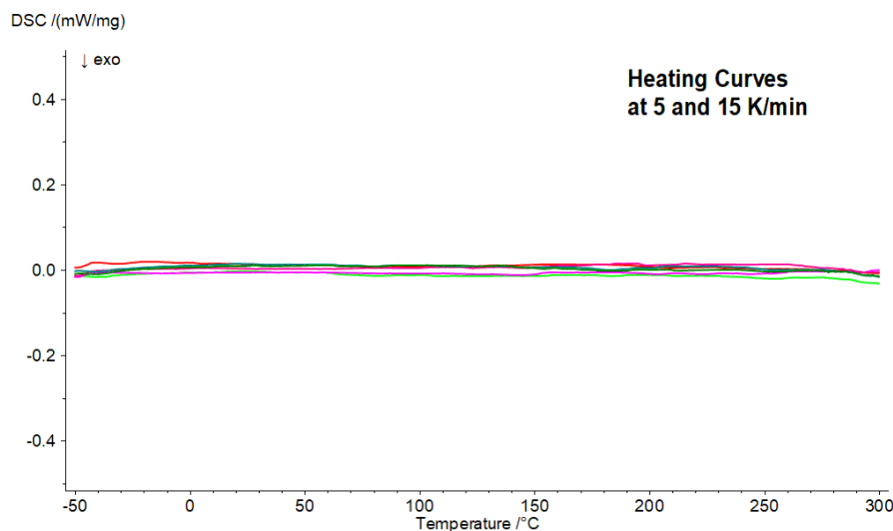
where β is the heating rate, $c_p^{crucible}$ is the specific heat capacity of the crucible material, $m_{sample}^{crucible}$ and $m_{reference}^{crucible}$ are the masses of the sample and reference crucibles and $Sens.(T)$ is the temperature-dependent calorimetric sensitivity of the DSC sensor as explained below.

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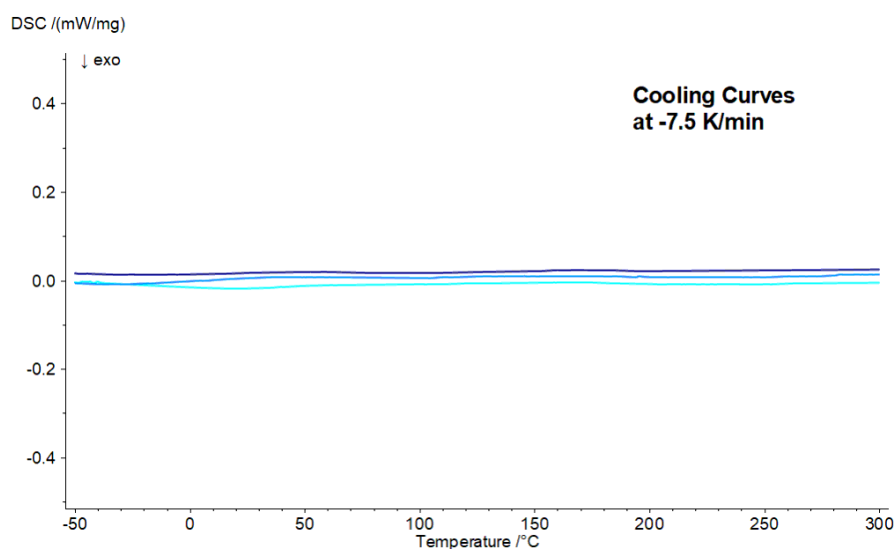
Since the calculated *BeFlat+* baseline takes the actual heating rate and the crucible masses into account, it can be applied to DSC measurements with various temperature programs (within the covered temperature range) and with different crucibles of the same type. The *BeFlat+* baseline of equation (2) has a heating-rate-independent part $Offset(T)$, which is due to any asymmetry of thermal resistances between sample and reference side and due to finite asymmetry of the temperature profile in the DSC furnace chamber. The heating-rate-dependent part is mainly due to any asymmetric heat capacity of the DSC sensor reflected by $K_{sensor}(T)$ and due to different masses of the sample and reference crucibles.

Figures 1 and 2 display typical DSC baselines that are *BeFlat+* corrected. These measurements are repeatability tests with two empty *Concavus*[®] crucibles with pierced lids, placed in a DSC 300 *Caliris*[®] equipped with H-Module and intracooler cooling. The heating rates of 5 and 15 K/min and cooling rate of -7.5 K/min that are used are different from those applied in the *BeFlat+* calibration (10, -5, 20, -10 K/min). Nevertheless, the *BeFlat+* corrected baselines are flat and they are within about $\pm 20 \mu W$ ¹⁾. This demonstrates the correctness of the model equation (2) for the heating-rate-dependent DSC baseline as well as very good repeatability.

¹⁾ At a heating rate of 10 K/min, the baseline repeatability of the DSC 300 *Caliris*[®] equipped with H-Module is $<10 \mu W$ in the temperature range between -50°C and 300°C.



1 *BeFlat+* corrected DSC baselines (measured as "Sample" with mass $m = 1$ mg) as a function of temperature. Shown are three heating curves, measured at 5 K/min (green) and three heating curves, measured at 15 K/min (red, pink).



2 *BeFlat+* corrected DSC baselines (measured as "Sample" with mass $m = 1$ mg) as a function of temperature. Shown are three cooling curves, measured at -7.5 K/min (blue, cyan).

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Heat Flow (“Sensitivity”) Calibration

The raw signal of a heat-flow DSC is usually the differential thermocouple voltage between the sample and the reference side of the DSC sensor in unit [μV], which is proportional to the temperature difference and thus to the heat flow between the two sides. The heat flow has the unit [mW]. The temperature-dependent proportionality factor between the raw signal and the heat flow is the calorimetric sensitivity $Sens.(T)$ with unit [μV/mW]. It is basically the reciprocal of the heat flow calibration coefficient [4, 5, 9].

To determine sensitivity, there are two alternative ways [4, 9]. The first is based on the time integral of the melting effect (or other crystal transformation) of calibration standards. The sensitivity at the melting temperature can be calculated as the integral of the measured integral A of the melting effect in unit [μV·s/mg] divided by the nominal enthalpy of fusion H in unit [J/g] = [mW·s/mg]:

$$Sens. = \frac{A}{H} \quad (3)$$

The temperature-dependent sensitivity $Sens.(T)$ is derived from the best-fit curve through the individual sensitivity values for all calibration standards [4]. An obvious advantage of this method is that the DSC measurements of the calibration standards can be used for both sensitivity and temperature calibration. A second advantage is the high accuracy of each sensitivity value, since melting effects generate high DSC signals.

The second way to determine the temperature-dependent sensitivity is based on measuring a standard reference material with known specific heat capacity such as sapphire [4, 5]:

$$Sens.(T) = \frac{DSC_{st}^*(T)}{c_p^{st}(T) \cdot \beta} \quad (4)$$

where $DSC_{st}^*(T)$ is the baseline corrected DSC signal of the standard reference material in [μV/mg], c_p^{st} is its specific heat capacity in [J/(g·K)] and β is the heating rate in [K/s].

Methods according to equations (3) and (4) can also be combined [9]: The temperature-dependent sensitivity determined with the specific heat method is multiplied by a factor so that the sensitivity at the melting temperature of, for example, indium matches with the value determined by the enthalpy method for indium in this example.

The sensitivity calibration using a specific heat capacity standard according to equation (4) has two advantages: Firstly, a continuous temperature-dependent sensitivity curve can be created in a relatively short time. Secondly, the DSC measurement of the specific heat capacity standard can also serve for the evaluation of the specific heat capacity c_p^s of a different sample [4, 7, 8]:

$$c_p^s(T) = c_p^{st}(T) \cdot \frac{DSC_s^*(T)}{DSC_{st}^*(T)} \quad (5)$$

where $DSC_s^*(T)$ and $DSC_{st}^*(T)$ are the baseline corrected DSC signals of the sample and the standard reference material in unit [μV/mg], respectively.

Tau-R® Mode

At this point, the DSC instrument is temperature calibrated and the measured DSC_m shall refer to the heat flow calibrated signal. One further aspect regarding the shape of DSC peaks has to be discussed: Since there is a thermal resistance between the sample and the temperature sensors on the sample and reference sides, and since the crucibles and the DSC sensor have heat capacities, a “thermal lag” exists leading to a “smeared representation” of the heat flow from or into the sample [10]. For most applications, the measured signal DSC_m is completely sufficient, but for overlapping caloric effects when the requirements in resolution are higher, a correction of the thermal lag may be useful. For a DSC instrument, which operates linearly, the relation between DSC_m and the “desmeared” heat flow DSC is the convolution product

$$DSC_m = \int DSC(t') \cdot a(t-t') dt' \quad (6)$$

where a is the apparatus function and t is the time. The desired value DSC is calculated by deconvolution leading to a significantly shorter tailing of the heat flow curve, for example, after a melting peak, where melting of the sample has already finished (see figure 3).

If the DSC instrument can be described by one time constant τ , the apparatus function a is $e^{-t/\tau}$ and DSC can be calculated [10] from

$$DSC = DSC_m + \tau \cdot \frac{d}{dt} DSC_m \quad (7)$$

It should be noted that the time constant τ , which is significantly temperature-dependent, depends on several further quantities: the specific heat capacities of the DSC

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sensor and the crucibles, the thermal resistances between sample and reference side of the DSC sensor, the thermal resistance between the crucibles and the DSC sensor, and the heat exchange to the surrounding gas [11].

The fact that the temperature is not measured directly at the sample but at the reference side of the DSC sensor has further impact on the shape of measured DSC peaks: From the beginning of, for example, a melting peak to its maximum (where the melting process is complete), a linear increase of the temperature-scaled DSC curve is observed (see figure 3). But during the melting process, the temperature of the sample is constant, so the DSC curve should increase vertically. This can be obtained by recalculating the temperature from T_r measured at the reference side to

$$T_s = T_r - R \cdot DSC \quad (8)$$

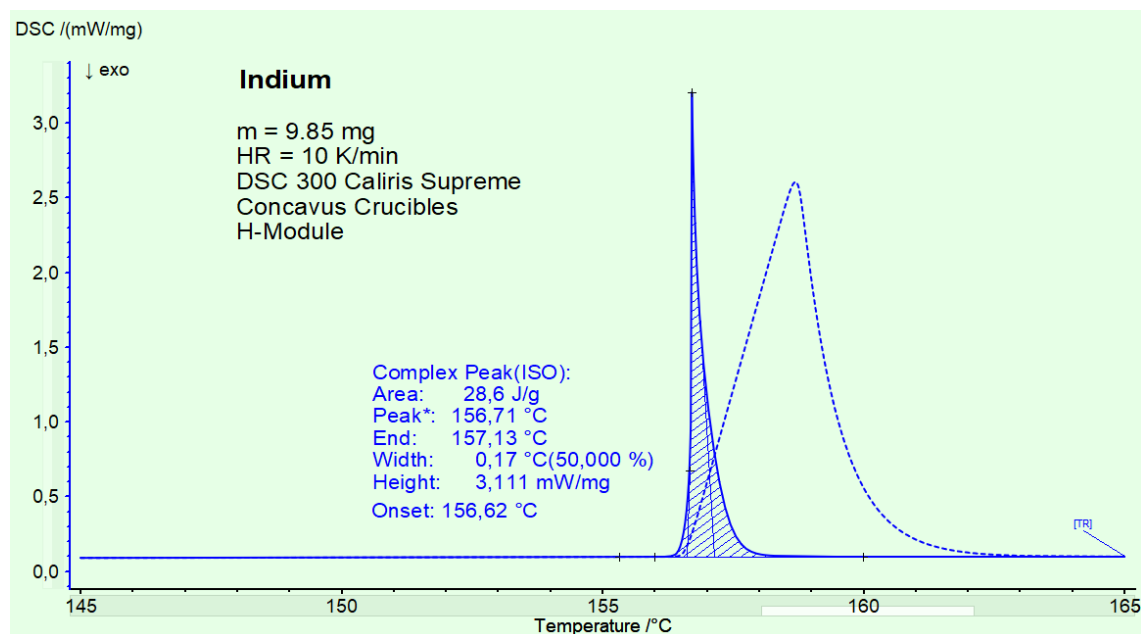
the sample temperature T_s via where R , which is the thermal resistance between sample and temperature sensor at the reference side, is the inverse slope of DSC before the peak maximum [10].

The combination of deconvolution of the heat flow and recalculation of the sample temperature lead to much better resolution of overlapping caloric effects and

significantly sharper DSC peaks, as is shown in figure 3. Both corrections applied to the DSC signal are the so-called *Tau-R*® Mode in NETZSCH terminology.

Required for the *Tau-R*® Mode are the temperature-dependent time constant(s) and the temperature-dependent thermal resistance, which are both also evaluated by the NETZSCH *Proteus*® software from the same DSC melting peaks used for temperature and heat flow calibration described above. This process can therefore be called a *3in1* calibration.

Figure 3 shows an exemplary DSC measurement of the melting of indium with active *Tau-R*® Mode in comparison with the same measurement without *Tau-R*® Mode. The difference is tremendous! It should be emphasized that numeric optimization of the *Tau-R*® Mode, which is available beginning with *Proteus*® 9.1, leads to even sharper DSC peaks for DSC modules with one time constant (H and P Modules): The so-called indium response ratio, which is the peak value divided by the temperature width at half maximum, is typically >100 mW/K thanks to the optimized *Tau-R*® Mode. For the measurements shown in figure 3, where a DSC 300 *Caliris*® instrument equipped with H module and *Concavus*® crucibles was used, the indium response ratio even has a value of 180.



3 DSC signal during melting of indium (sample mass: 9.85 mg) measured with a DSC 300 *Caliris*® Supreme equipped with H module at a heating rate of 10 K/min. The solid line represents the measurement with active *Tau-R*® Mode; the dashed line reflects exactly the same measurement, but without *Tau-R*® Mode.

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Remarks About Tzero®

It is well known that the Tzero® technology²⁾ has a third thermocouple, which is located in the center of the DSC sensor measuring T_0 . But is it of any advantage? The so-called Tzero® heat flow equation [12] is

$$q = -\frac{\Delta T}{R_r} + \Delta T_0 \cdot \left(\frac{1}{R_s} - \frac{1}{R_r}\right) + (C_r - C_s) \cdot \frac{dT_s}{dt} - C_r \cdot \frac{d\Delta T}{dt} \quad (9)$$

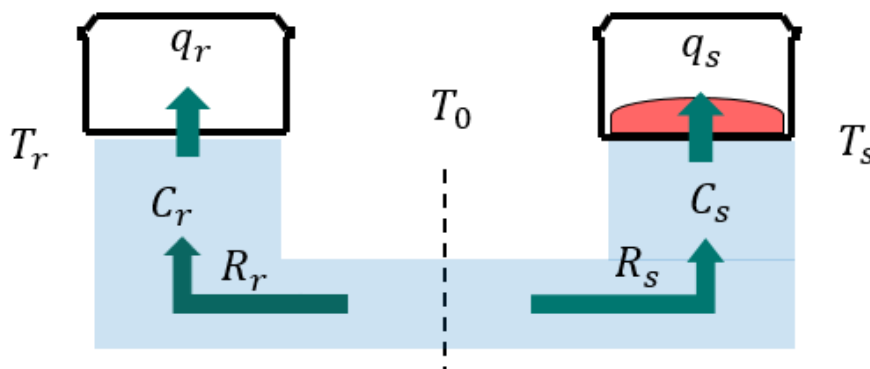
where $q = q_s - q_r$ is the net DSC heat flow from or into the sample, $\Delta T = T_s - T_r$ and $\Delta T_0 = T_0 - T_s$. The characters R and C refer to thermal resistances and heat capacities where the indices s and r stand for sample and reference side as illustrated in figure 4. The four terms of this equation can be viewed as: raw DSC signal (1st), thermal resistance imbalance (2nd), heat capacity imbalance (3rd), heating rate imbalance (4th). The Tzero® model has, however, the

drawback that it oversimplifies a real DSC instrument: The exchange with the surrounding gas and with the furnace is not taken into account.

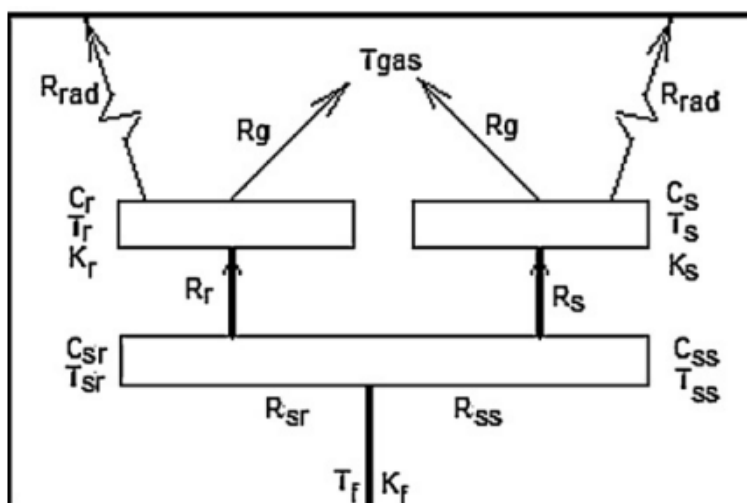
This oversimplification is apparently the reason why the four parameters R_r , R_s , C_r and C_s of the Tzero® equation derived from the so-called Tzero® calibration (two measurements) are not nearly enough: DSCs featuring this technique additionally require the so-called "cell constant" calibration for correct enthalpies, the thermal resistance calibration, and optionally the DirectCp calibration. Different crucible masses can be considered by the T4P calibration ("advanced Tzero®").

How can the Tzero® technology be compared with the solutions by NETZSCH? First of all, the NETZSCH model [11] shown in figure 5 takes the surrounding furnace and the gas into account.

²⁾ developed by TAI Instruments



4 Illustration of the Tzero® model [12] of a DSC instrument.



5 Illustration of the NETZSCH model of a DSC instrument [11].

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Terms 2 and 3 of the Tzero® equation 9 are similar to the more general *BeFlat+* baseline solution (see equation 2) except that in case of Tzero®, the crucible mass difference has to be taken into consideration using the separate T4P calibration. The 4th term of equation 9 can be viewed as a thermal lag correction similar to equation 7, which is, however, only valid for a DSC system with one time constant.

All in all, comparison of the two DSC solutions suggests that the third thermocouple used for Tzero® is not of any advantage. A similar number of calibrations and corrections is necessary in both cases.

Summary

In general, DSC instruments require calibrations and corrections for temperature, baseline, sensitivity and – in order to enhance the resolution – for thermal lag. NETZSCH offers complete and clear solutions, which are all compliant to the DSC standards. The NETZSCH *Proteus*® software creates temperature, sensitivity and *Tau-R*® calibrations as a *3in1* calibration from measurements of the metal melting standards – even self-acting when using an ASC (Automatic Sample Changer). The corrections are applied automatically afterwards. An automatic baseline correction can be done with *BeFlat+*, a flexible and efficient approach. Furthermore, determination of the specific heat capacity c_p is also easy and compliant to the norms. All that is required is a measurement of a c_p standard material; this measurement can be used again and again for evaluating c_p of different samples – thanks to the high reproducibility and long-term stability of DSC instruments by NETZSCH. And last but not least, all corrections and calibrations of DSCs by NETZSCH can be reversed individually on demand even back to the raw μ V-signal, allowing for full traceability.

The Author

Dr. Alexander Schindler has worked in the fields of experimental physics, thermal analysis and thermophysical properties for over 25 years. At NETZSCH, he has been employed in the Applications Laboratory as well as in the Hardware and Software Development. He is a known expert in thermal characterization methods and their applications.

Acknowledgement

Thanks to Mr. Liang Xu for sharing his knowledge and for helpful discussion.

References

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- [2] In general, the field of DSC is divided into heat flow DSC and power compensation DSC [1]. Since this article is focused on the more common heat flow DSC, the abbreviation DSC is used for simplicity for heat flow DSC. As a further remark, in most of the DSC measurements no reference sample is used, but just an empty reference crucible.
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