Summer Student Project Work: Test of a Sample Oven and Differential Scanning Calorimetry Measurements

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1 Calibration of a Differential Scanning Calorimetry Device (DSC)

1.1 Operating Principle of a DSC

Differential Scanning Calorimetry (DSC) is a method widely used in laboratories to study thermal effects of small samples. Measurements obtained by DSC allow determination of heat capacity, heat of transformation, transformation temperature and purity of samples.

The basic configuration of a disk type DSC is shown in figure 1. Two crucibles are placed on top of a plate inside of a temperature controlled oven. One of the crucibles, the reference, is typically empty. The other one is filled with the sample material. Temperature is measured via thermocouples mounted beneath the crucibles.

During a measurement run, the oven is heated or cooled with a constant rate. Figure 2 shows the time dependence of the temperatures in case of an empty sample crucible. The sample/reference temperature lags behind the oven temperature due to the heat capacity of the crucibles and the finite heat conductivity. A time constant *tau_lag* or τ describes the time the sample needs in order to heat up to the same temperature the oven has. Of course the sample will never reach the oven temperature since the oven is driven with a constant heating rate β. But τ is an estimate how many seconds ago the oven temperature was equal to the actual sample temperature. Therefore the product of τ and the heating rate β gives the

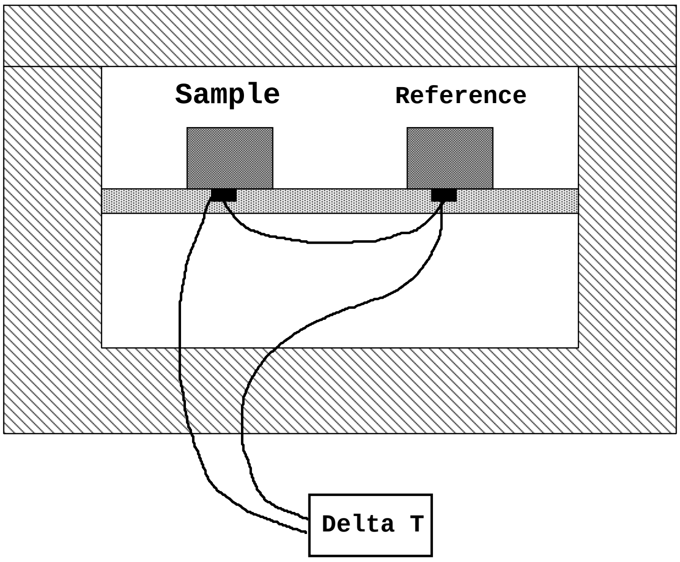

Figure 1: Basic configuration of a DSC.

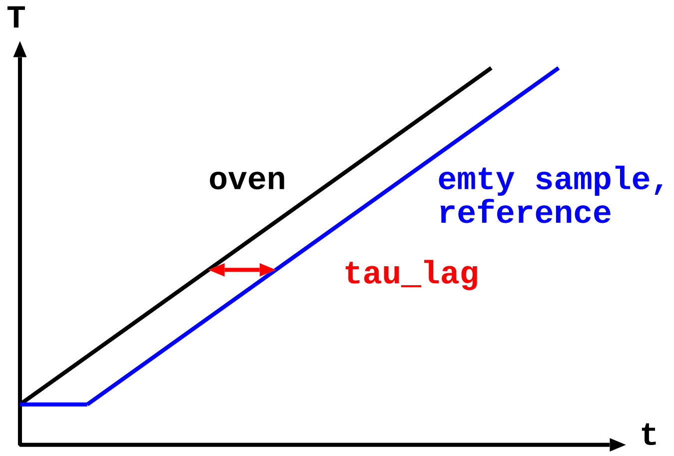

Figure 2: Temperature of an empty sample crucible.

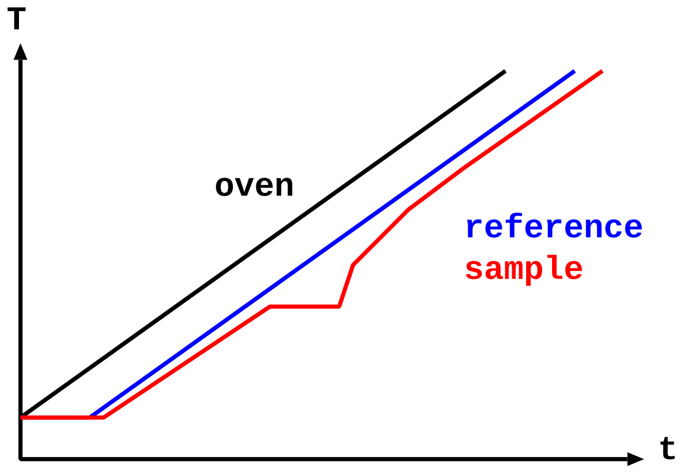

Figure 3: Non-empty sample showing a phase transition.

temperature difference between sample and oven. The sample temperature is then given by

$$T_{\text{sample}} = T_{\text{oven}} - \beta\tau. \tag{1}$$

In case of a non-empty sample crucible, the temperature of the sample will lag behind even further due to the enlarged heat capacity. This situation is shown in figure 3. The temperature difference between reference and sample in the absence of a phase transition is directly proportional to the heat capacity of the sample.

During a phase transition, the heat transferred to the sample is used to alter the phase of the sample material and can therefore not be used to heat up the sample any further. As a consequence temperature of the sample remains more or less constant while the reference is heated up further. This results in an increasing temperature difference between sample and reference, which is recorded by the DSC device.

Figure 3 shows the signal of a typical phase transition. The measured voltage signal is plotted versus the oven temperature. The line connecting the signal lines before and after the phase transition is called the *baseline*. Usually the lower edge of the signal can be fitted with a straight line. The crossing between this line and the base line is called T_onset or T_{onset}. This point defines the beginning of the phase transition. Note that T_onset is not the real transition temperature since it depends on the heating rate β and the time constant τ_{lag}. Equation 1 has to be used in order to eliminate these dependencies.

The area of the signal curve confined by the baseline is a measure for the heat used in the phase transition.

1.2 Determining of the Time Constant tau_lag

The value of τ_{lag} depends on the sample mass and the heating rate β. Since the heat capacity increases with the mass of the sample, τ_{lag} increases also. Same is true for the heating rate. The sample needs more time to heat up for larger heating rates.

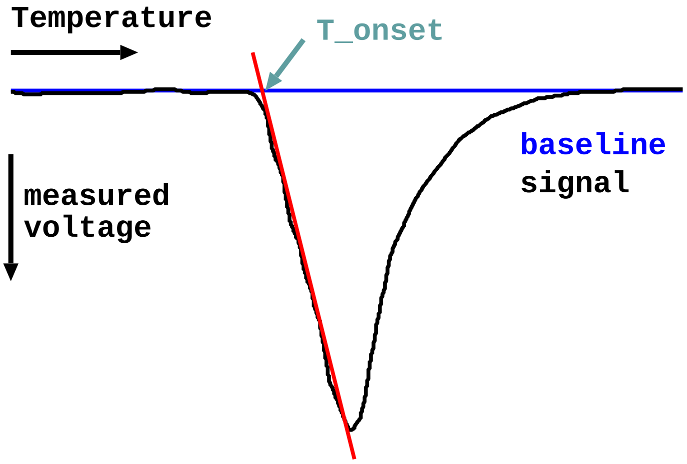

Figure 4: Recorded signal of a phase transition.

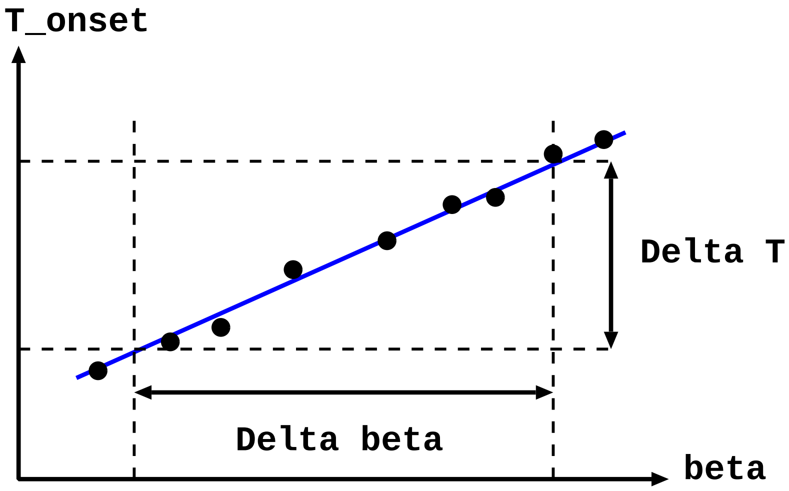

Figure 5: Basic configuration of a DSC.

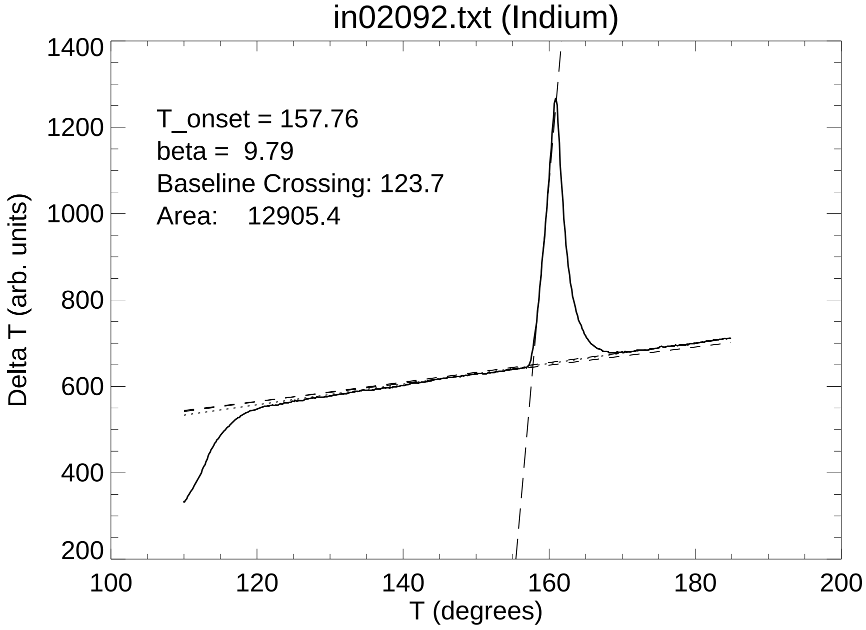

Figure 6: Measurement curve of an indium sample.

In order to determine the value of τ_{lag}, several measurement runs with a calibration substance, e.g. indium, have to be carried out with different heating rates. The onset temperature T_{onset} has to be determined for each of those runs. Since τ_{lag} is in first order linear dependant on the heating rate β, a linear regression as shown in figure 5 describes the β-dependence reasonably well. τ_{lag} is then simply given by the slope of the regression line.

The real temperature of the phase transition can now be found by extrapolating the T_{onset} values for $\beta = 0$. This is equivalent to a DSC measurement run with the heating rate β approaching zero and thereby vanishing τ_{lag}. In a real experiment the sample temperature would follow the oven temperature immediately. This corresponds to the case of an ideal DSC.

1.3 Measurement of Calibration Substances

1.3.1 Determination of T_onset and the Heating Rate

Figure 6 shows the result of a typical measurement run. A small IDL program was written to fit the baseline and the forward edge of the peak. The baseline was fitted within an interval ranging from $T_{\text{pt}} - 10$ til $T_{\text{pt}} - 5$ °C. The subscript *pt* denotes the estimated temperature of the phase transition.

Fitting of the forward edge of the peak needs to be done more carefully regarding the true shape of the curve. Just selecting a temperature interval does not work. Therefore an interval defined relative the maximum of the peak and the baseline was chosen. Starting at low temperatures, the temperature of the first occurrence

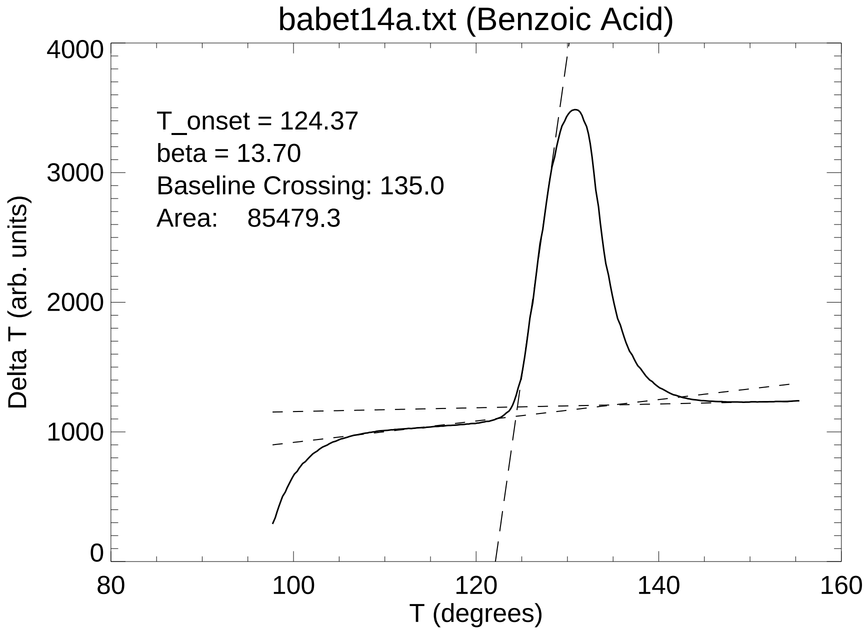

Figure 7: Example of a measurement run with intersecting baselines.

of a value larger than 1.2 times the value of the baseline is taken as the left border of the fit interval. The first occurrence of a value larger than 0.8 times the peak maximum defines the right border.

The onset temperature T_{onset} is finally obtained by computing the crossing between the baseline and the fitted peak edge. The other important parameter of the measurement run, the heating rate β, is given by the slope of the baseline.

1.3.2 Determination of the Heat of Transformation

The heat of transformation, Q, is proportional to the area of the curve confined by the baseline. However it is often difficult to get an accurate approximation for the baseline. Figure 7 shows an extreme example of such a problematic case. Relying on a single baseline would lead to an underestimation of the peak area and therefore result in too small values for the transformation heat.

To improve the peak area calculation, a second baseline is fitted to the signal above the transformation peak and the crossing of both baselines is computed. Integration of the peak area with respect to time starts at the upper end of the fit interval of the first baseline. When the crossing is reached, the second baseline is used as lower boundary.

1.3.3 Check of the Temperature Calibration of the DSC

Several different substances with well-defined transformation temperatures in the region of interest are used to check the temperature calibration of the DSC. Each substance is measured several times with different heating rates in order to accurately determine the time constant τ_{lag}. Usually data of the first run of each new sample has to be discarded since the substance has to be molten once in order to get in good thermal contact with the crucible. One exception to this rule are all measurements of benzophenone. No further phase transition could be observed after heating this substance above the transformation temperature followed by cooling to the start temperature. So a new sample was prepared for each measurement run.

Figure 8 shows the results of all calibration runs. The first four measurement series were obtained with the sample being filled in standard Mettler crucibles. The plots in the bottom of the panel show results of two indium samples placed in self-made aluminium foil crucibles.

The data points shown in the top row of the panel seem to be spread out much wider compared to the other other plots. This can be attributed to two facts: The measurements included in these two plots were taken on different days and the sample, as well as the reference crucible, were repositioned after each run. In contrast, all measurements belonging to one of the other four plots were taken in a row without touching the crucibles. One exception are the benzophenone samples as mentioned above.

Results Figure 9 shows the deviation of the measured transformation temperatures from literature values. The value obtained for benzophenone is not as significant as the other ones because of the problems encountered with this substance. Excluding benzophenone, no clear trend can be found. However, the temperature scale of the DSC seems to be offset by -1.2 K.

1.3.4 Heat Calibration

The computed peak area of all calibration runs except benzophenone samples are plotted in figure 10. The statistical spread indicates a precision of the heat measurements of approximately 5 percent.

The plot labeled with *Caffeine* shows a distinct feature: Two points measured at 10 Kelvin per minute are well separated from the other points. Together with a third measurement run which is not included in this plot, the two corresponding runs were done shortly after switching on the DSC device. Then the DSC oven was kept at 200 °C for about 40 Minutes before the rest of the measurements were taken. Since the DSC was at room temperature before the first run, it can be concluded that the DSC needs approximately one hour in order to stabilize itself at high temperatures.

Note that the heat in those plots is given in arbitrary units. It has to be normalized by the sample mass before any comparisons can be done.

Determination of the Unit of the Peak Area Figure 11 shows the values normalized by the sample mass divided by the transformation heat of the substance[1].

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[1] Indium: 3.128 kJ/mol, Benzoic Acid: 147.3 J/g

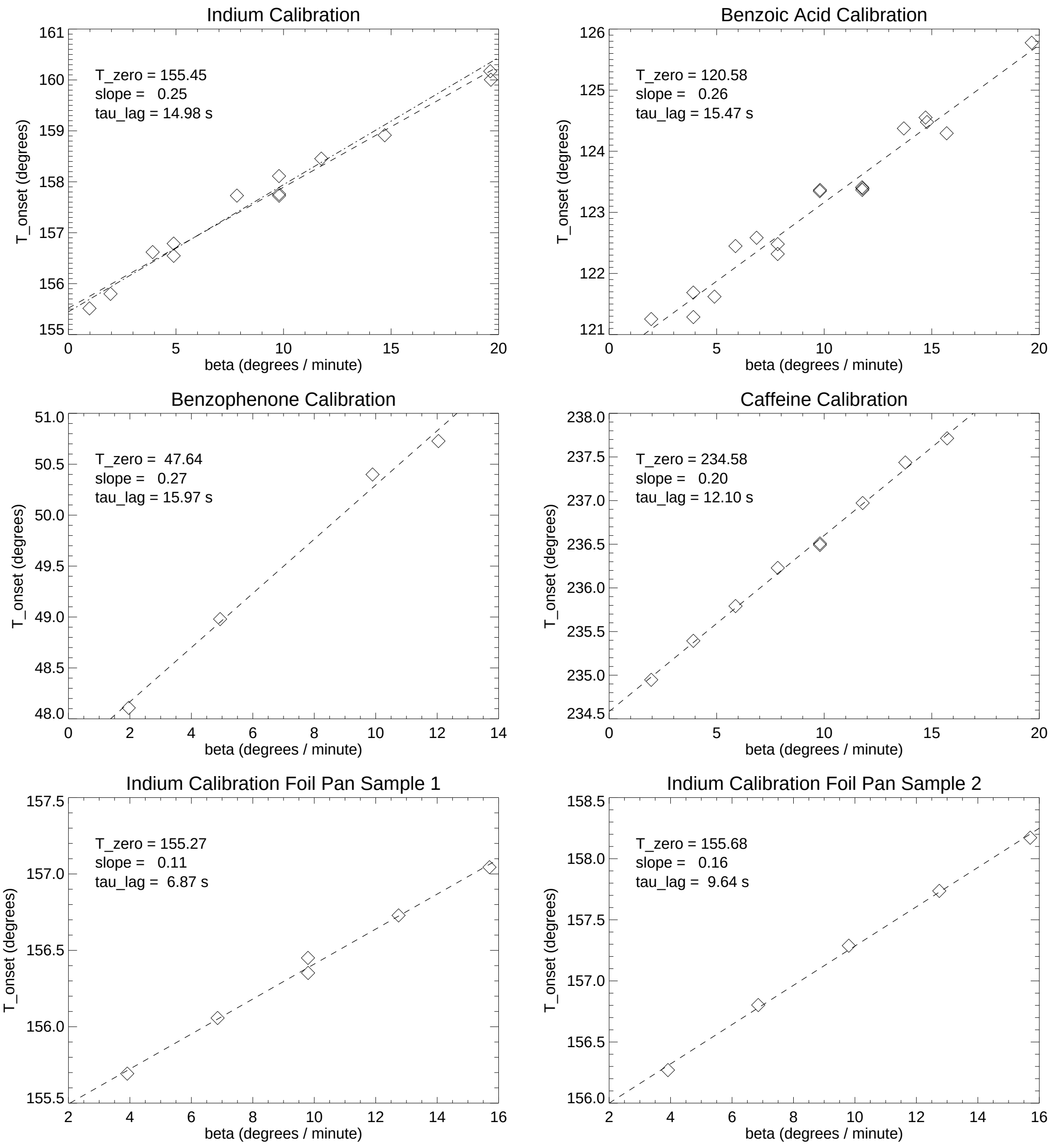


Figure 8: Measurement of calibration substances with different heating rates. The transformation point T_zero is obtained by extrapolating the linear regression for zero heating. The time constant tau_lag is given by the slope of the regression line.

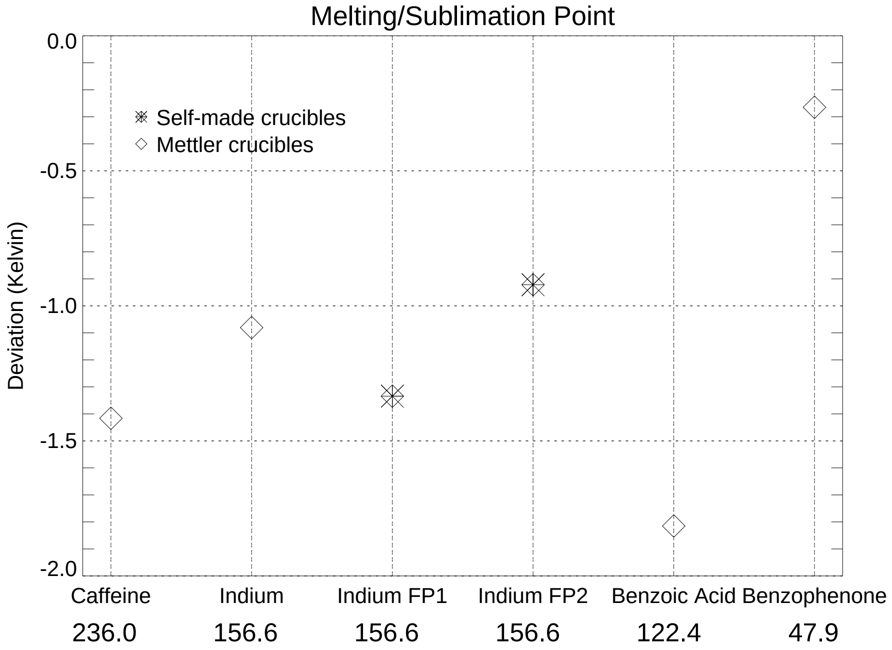


Figure 9: Deviation of the transformation temperatures are plotted for different calibration samples. The literature values are written below the sample names.

The mean value of all measurements of samples inside standard Mettler crucibles is 7.8×10^4 integrated device units/Joule.

Values obtained with samples inside self-made aluminium foil crucibles are somewhat smaller and less reliable. This can be attributed to the lower heat resistance of the crucible due to the thin foil. In addition, the heat resistance changes from sample to sample because of small changes in the geometry of the crucible. Since the crucibles consist of thin aluminium foil it is impossible to construct perfectly flat pans. However, the contact area between the crucible and the contact pads of the thermocouples is an important parameter which influences the accuracy of the temperature measurements.

Measurements values shown in the bottom left of figure 11 are far-off relative all the other plotted values. It could not be found out whether there was an error introduced when the sample was weighted. Another explanation for low values would be bad contact between the sample and the thermocouples. Further measurement runs with new samples are needed to answer the question, though.

1.4 Measurement of PTB

Figure 12 shows the result of a measurement run with a standard Mettler crucible filled to maximum with PTB. The phase transition around 50 °C is hardly detectable and clearly not usable for calibration purposes.

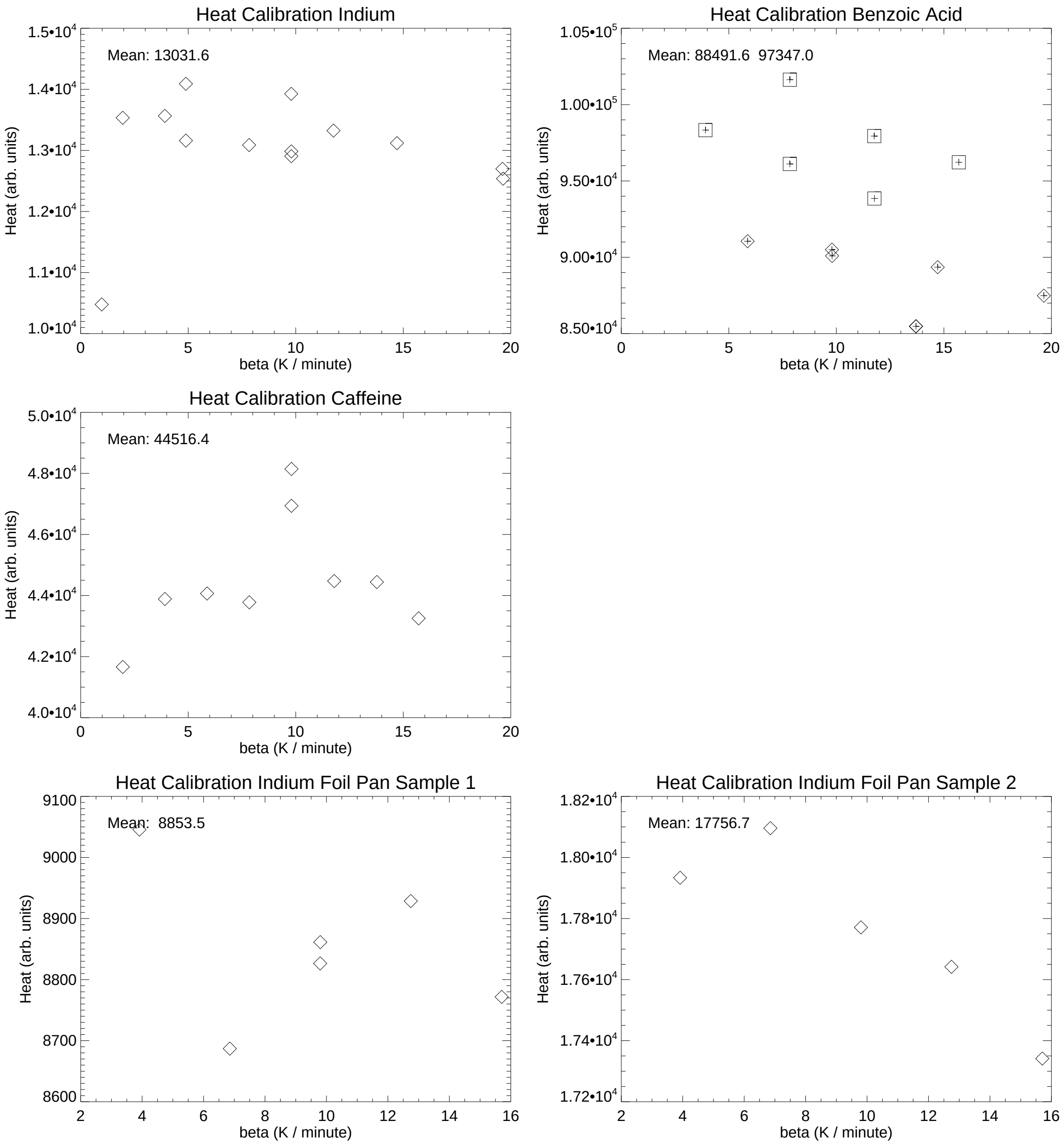


Figure 10: Computed peak area for different calibration runs. The plot labeled with *Benzoic Acid* consists of two separate runs with different sample masses indicated by the two symbols.

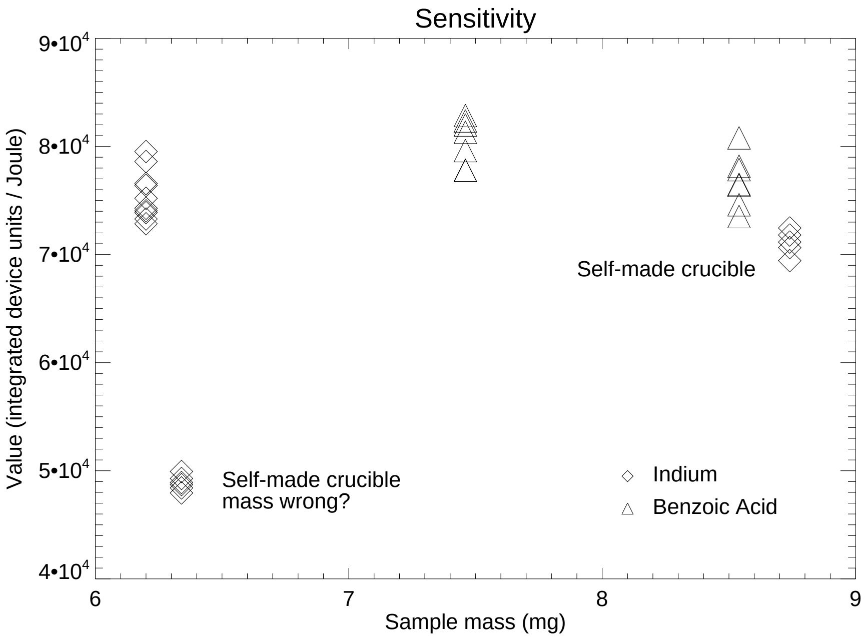


Figure 11: Normalized transformation heat computed for indium and benzoic acid samples.

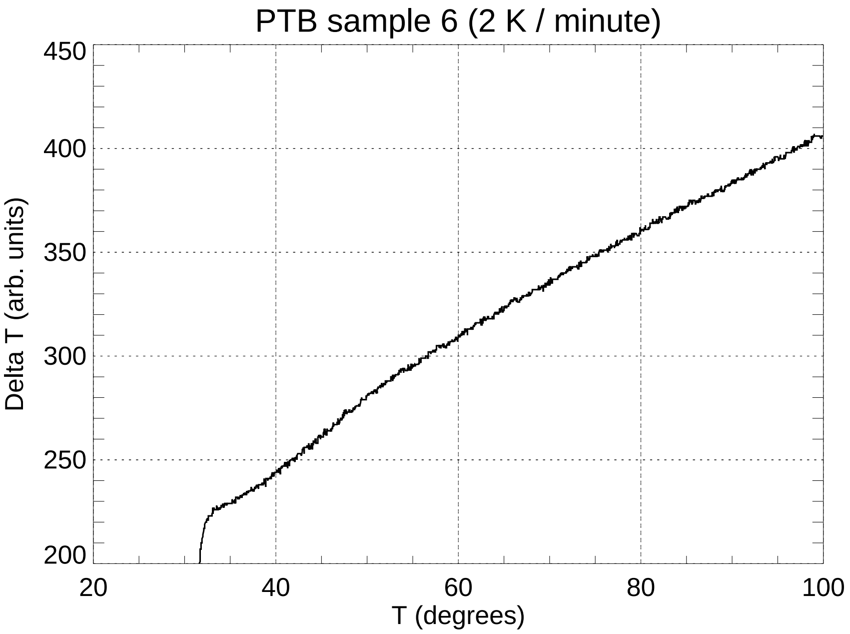


Figure 12: Measurement run of a PTB sample. The phase transition around 50 °C is hardly visible.

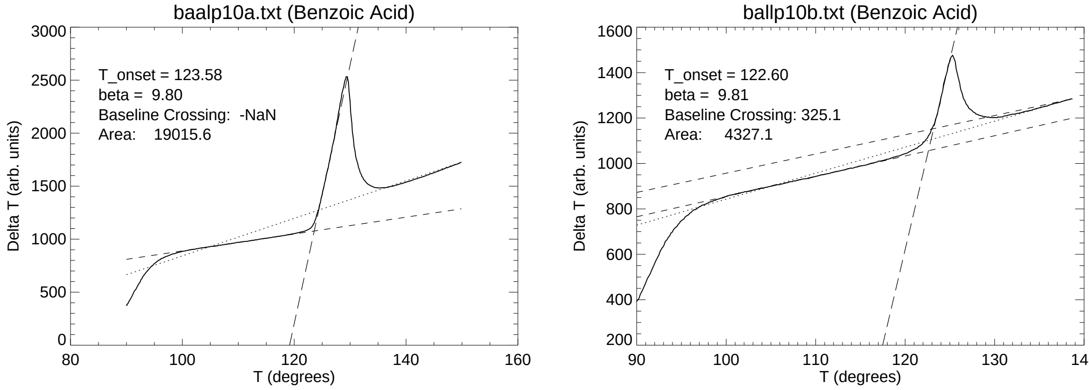


Figure 13: Measurements run of a benzoic acid sample. The second run of the same sample (right) was immediately done after the first run (left). The large difference in peak area between the two runs suggests a high loss of sample material due to evaporation/sublimation.

1.5 Measurement of Benzoic Acid Enclosed in a Self-Made Crucible

Measurement runs of evaporating/sublimating substances placed in self-made crucibles were unsuccessful. These crucibles consist of two small pans made of aluminium foil. One of the two pans serves as lid for the other pan. Since the interconnection of the two pans is a simple fold around the circumference, the self-made crucibles are not gas-tight and sample material is therefore lost during the measurement run.

Figure 13 shows an example of two consecutive runs of the same benzoic acid sample. The offset of the second baseline relative to the first one already indicates evaporation/sublimation of sample material during the first run (left figure). The peak area measured during the second run (right figure) is much smaller. More than 70 percent of the sample material is lost.

The standard Mettler crucible is cold-welded after filling it with the sample material. This weld makes the crucible gas-tight. Trying to cold-weld the self-made pans was rather unsuccessful, though. Since the aluminium foil pans have no really flat surface at the circumference, the resulting weld is very fragile and ruptures after the slightest hit with tweezers. It is not strong enough to withstand any overpressure also. In contrast, the Mettler crucibles are rated for up to 1 bar overpressure which is usually sufficient to confine any evaporating material.

2 Testing sample ovens

2.1 Capillary oven

2.1.1 Setup

The capillary oven is made of a massive cooper block with an embedded heating element. Cold air can be vented through a cooling pipe in order to cool the block. Heating and cooling is controlled by a microprocessor device named *Jumo* which is connected to a standard PC. Temperature profiles can be programmed via defining setpoints and heating rates for given time intervals. Afterwards these programs are transferred to the *Jumo* device for execution.

The sample capillary is placed in a central hole within the copper block. A sketch of such capillary can be seen in figure 16.

A thermocouple, which gives feedback for the temperature control loop, is mounted in direct vicinity of this hole inside the copper block. Measurements belonging to this sensor are denoted with the subscript ”heater” in the following section. The capillary was filled with water in order to simulate the heat capacity of ordinary sample substances such as lipids, and temperature of the water is measured with a 0.5 mm thermocouple placed inside the capillary. All measurements originating from this thermocouple are denoted with ”sample” in the following plots.

All sensor data can be directly recorded on the PC connected to the *Jumo* deivce. To be able to to so, the sensors have to be selected for data recording. A line plot visualization of the date is available unter the menu item ”Startup” listed in the control software.

2.1.2 Measurements

Figure 14 shows the temperature deviations of setpoint and heating element with respect to the sample for a typical temperature ramp of 1 Kelvin per minute. Histograms of the differences $T_{\text{heater}} - T_{\text{sample}}$ and $T_{\text{sample}} - T_{\text{setpoint}}$ are shown in the bottom row of the panel. Gaussians fitted to these histograms are overlaid as dashed line and it is rather interesting that the temperature deviations are almost perfectly gaussian distributed. It can therefore be conclude that the temperature control loop is well functioning with an overall precision of approximately 0.21 K. The temperature of the sample itself can be controlled to approximately 0.32 K accuracy.

Results of the same experiment carried out with heating/cooling rates of 5 Kelvin per minute are shown in figure 15. Precision of the temperature control is reduced to 0.34 K due to the increased slope of the temperature ramp. The control loop seems to be working better in zeroing out the residuals at high heating/cooling rates, though. Since the bias is only 0.03 K the accuracy is about the same as in the 1 Kelvin slope experiment.

The large deviation between sample temperature and setpoint near the end of the cooling cycle shown in figure 15 is caused by the decreasing cooling power. Using air at room temperature as cooling gas, the cooling power drastically reduces when the

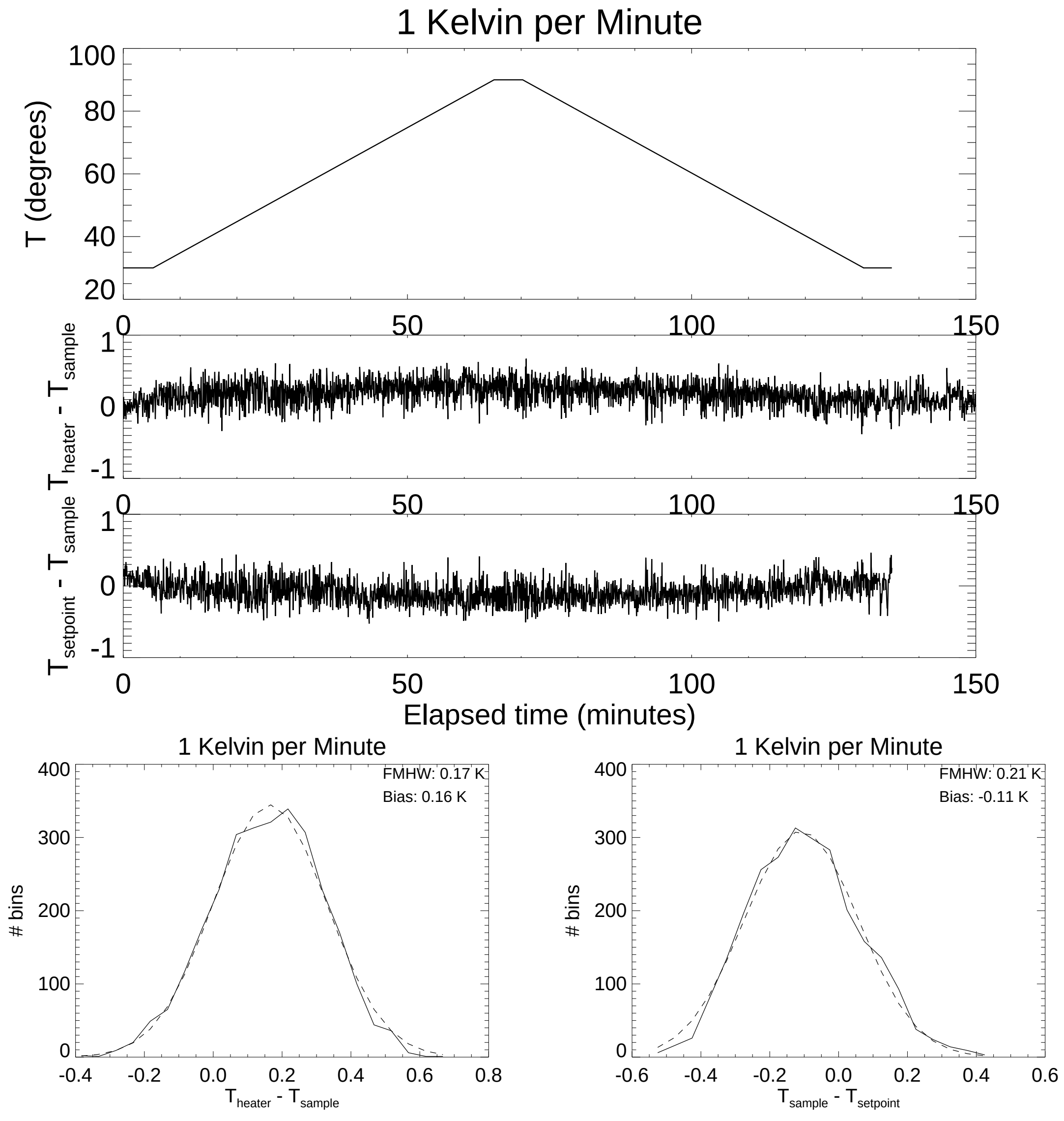


Figure 14: Capillary oven heated/cooled with 1 Kelvin per minute. The topmost figure shows the ramp of the setpoint of the oven. Temperature deviations are plotted in the figures below. Histograms of the temperature deviation measured between sample and heating element (left), as well as sample and setpoint (right), are shown in the bottom row of the panel.

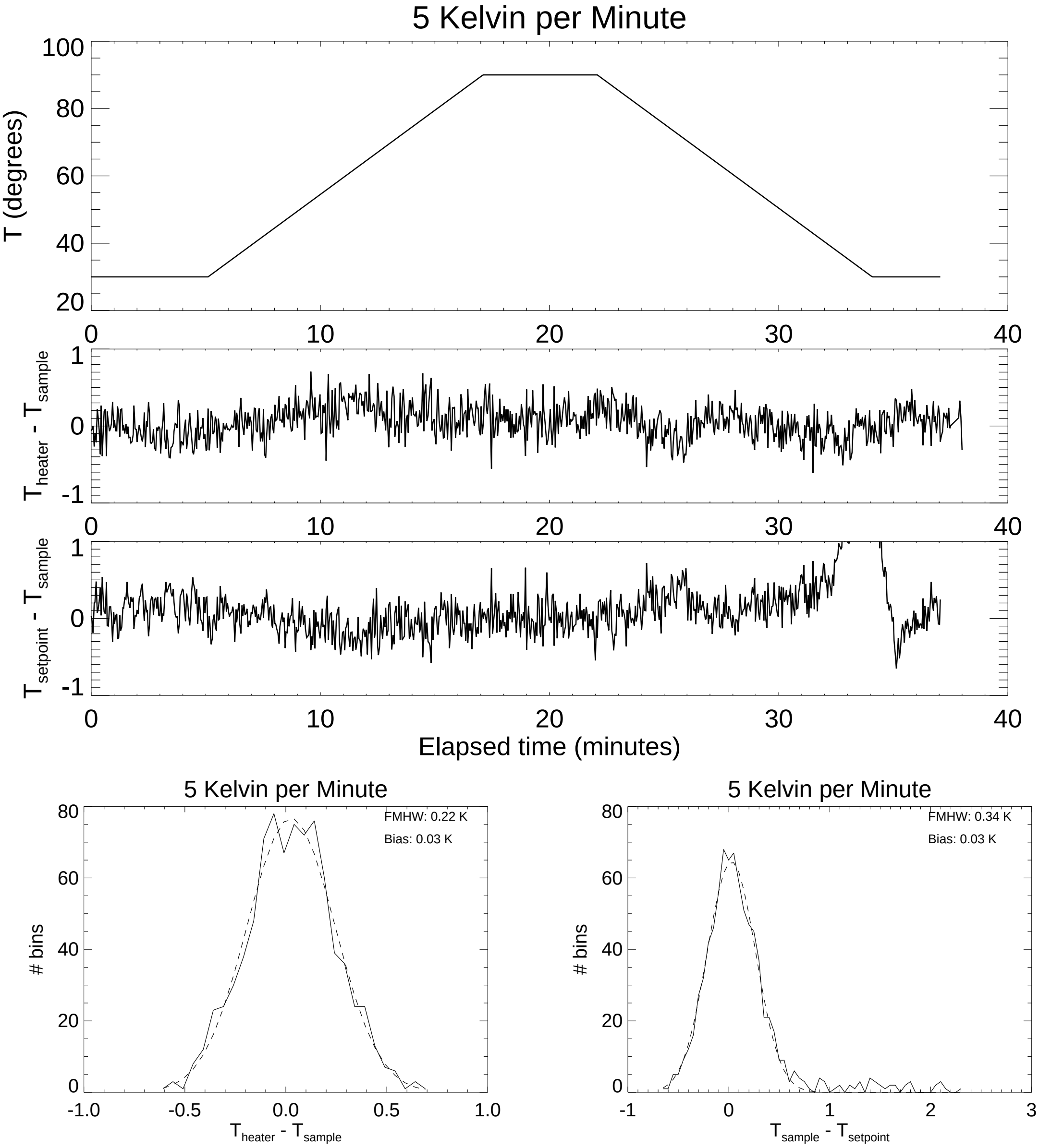


Figure 15: Capillary oven heated/cooled with 5 Kelvin per minute. The topmost figure shows the ramp of the setpoint of the oven. Temperature deviations are plotted in the figures below. Histograms of the temperature deviation measured between sample and heating element (left), as well as sample and setpoint (right), are shown in the bottom row of the panel.

setpoint approaches room temperature and, as a consequence, the sample simply can not be cooled down fast enough.

2.1.3 Estimation of the Time constant of a heated capillary

The energy needed to heat up the inner volume of a water filled glass capillary hast to pass through the capillary walls. Since the heat conductivity is finite, a constant energy flux produces a temperature gradient within the walls, that is the temperature at the inner surface and at the outer surface of the capillary differ. An estimation of this temperature difference and the corresponding relaxation time is subject to the following calculations.

Heat conduction through a homogeneous medium is described by the equation

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = \lambda A \nabla T. \tag{2}$$

A is the area subject to transport of heat.

Since the wall thickness s is very small compared to the radius, equation 2 simplifies to

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = \lambda \frac{A}{s} \left(T_o - T_i\right). \tag{3}$$

T_o is the temperature at the outer surface and T_i the temperature at the inner surface of the capillary.

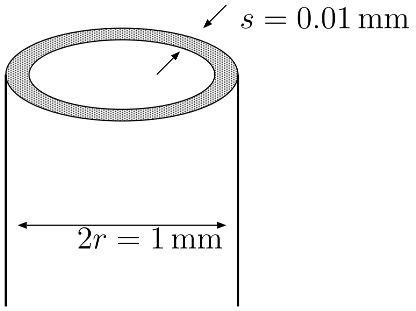
Now we assume that all energy transported through the capillary walls is used to heat the water inside the capillary. Heat conduction inside the water is assumed to be infinite, that is the temperature within the water is assumed to be homogeneous.

With definition of the specific heat

$$C = \frac{\mathrm{d}Q}{\mathrm{d}T} \tag{4}$$

follows for the energy change of the water

$$\mathrm{d}Q = CV\,\mathrm{d}T_i. \tag{5}$$



Specific heat of water	$C = 4.2\,\frac{\mathrm{J}}{\mathrm{g\,K}}$
Heat conductivity of glass	$\lambda = 0.76\,\frac{\mathrm{W}}{\mathrm{m\,K}}$
Heat conductivity of air	$\lambda_{\mathrm{air}} = 0.026\,\frac{\mathrm{W}}{\mathrm{m\,K}}$

Figure 16: Dimensions of the capillary.

Solving equation 5 for dQ yields

$$\mathrm{d}Q = \lambda \frac{A}{s} \left(T_o - T_i\right) \mathrm{d}t. \tag{6}$$

Since the energy is conserved, equation 5 and 6 have to yield equal results for dQ:

$$CV \, \mathrm{d}T_i = \lambda \frac{A}{s} \left(T_o - T_i\right) \mathrm{d}t \tag{7}$$

To solve this differential equation, the substitution $T_o - T_i = \Delta T$ is used. This yields the replacement $\mathrm{d}T_i = -\mathrm{d}\Delta T$:

$$-CV \, \mathrm{d}\Delta T = \lambda \frac{A}{s} \Delta T \, \mathrm{d}t \tag{8}$$

Now, the variables can be separated

$$\frac{\mathrm{d}\Delta T}{\Delta T} = -\frac{\lambda}{CV} \frac{A}{s} \, \mathrm{d}t \tag{9}$$

and integrated. In the last step the ratio surface to volume ratio of a cylinder $A/V = 2/r$ was used.

Solving for ΔT leads to the final result

$$\Delta T = \mathrm{const} \cdot \exp\left(-2 \frac{\lambda}{Crs} t\right) = \mathrm{const} \cdot e^{-\gamma t} \tag{10}$$

Putting in the numbers yields

$$\gamma = \frac{2 \cdot 7.6 \times 10^{-4} \, \frac{\mathrm{W}}{\mathrm{mm\,K}}}{0.5\,\mathrm{mm} \cdot 4.2 \times 10^{-3} \, \frac{\mathrm{J}}{\mathrm{mm^3\,K}} \cdot 0.01\,\mathrm{mm}} \, \frac{1}{\mathrm{s}} \approx 72 \, \frac{1}{\mathrm{s}}. \tag{11}$$

The time constant of this system, defined as $\tau = 1/\gamma$, is accordingly $\tau \approx 14\,\mathrm{ms}$. That is, the temperature difference between the inner and the outer surface has dropped to the part $1/e$ in approximately 14 milliseconds after switching on the heating at the outer surface. This calculation assumed an ideal heat transfer from the heating element (holder) to the surface of the capillary. The heat conductivity of air is about 1/30 of the heat conductivity if glass. A small gap between the holder and the capillary can easily decrease total heat conductivity by this factor. The time constant moves into the order of seconds then. This is in good agreement with the small temperature deviations seen in the experiments described in section 2.1.2.

2.1.4 Vacuum Oven

As the name already suggests, the vacuum sample oven is operated under vacuum. This is necessary in order to reach temperatures up to 400 °C. Apart from the vacuum, the operating principle is the same as for the capillary oven. Usually the samples are wrapped in very thin aluminium foil and are clamped on the copper block for thermal contact.

First tests of the sample oven with a PT-100 temperature sensor mounted on top of the aluminium foil were unsuccessful due to the large heat capacity of the sensor. Differences in temperature up to 40 K were observed between the PT-100 sensor and the sensor of the heating element. The tiny connection points between the rather huge sensor and the aluminium foil could not support the heat transport in order to heat the sensor sufficiently.

In later experiments the PT-100 sensor was replaced by a tiny 0.15 mm thermocouple placed directly inside the aluminium foil sandwich in close proximity of the sample. Temperature differences of less than 5 K for heating rates of up to 10 K per minute were observed then.