

# Introduction to Characterization of heat storage and heat release (calorimetry)

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## Overview

1. Introduction to Calorimetry
  - Calorimetry: basics
  - Calorimetric methods: general aspects
  - Calorimetric methods: examples
2. Specifics of phase change materials (PCM)
  - PCM: specific effects and data presentation
  - PCM: specific effects and measurement guidelines
3. Specifics of sorption materials
  - ...

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## Calorimetry: basics

**Heat Q** is one of two forms of energy in transit:  $dU = dQ - dW$

$dQ$  depends on the process, including boundary conditions!

**Calorimetry: measurement of quantities of heat  $\Delta Q$  (Calor = lat. heat) transferred to or from a sample,**

between an **initial state** and a **final state**,

composition 1  $\rightarrow$  2 (heat of combustion, heat of solution),

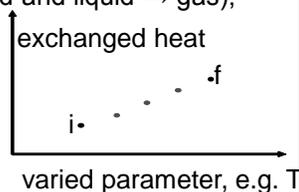
phase 1  $\rightarrow$  2 (heat of phase change solid  $\rightarrow$  liquid and liquid  $\rightarrow$  gas),

temperature 1  $\rightarrow$  2 (specific heat capacity, ...),

pressure 1  $\rightarrow$  2 (compression heat) ...

at given **boundary conditions**

constant  $c, T, p, V \dots$



A **calorimeter** is an instrument for calorimetric measurements.

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**The heat exchanged is determined by the initial and final state, and the process path between (including boundary conditions)**

For comparison with other samples, materials, or with thermodynamic calculations, it is advantageous if the transfer of heat follows well defined states. Such states are thermodynamic equilibrium states (throughout the whole sample).

### thermodynamic equilibrium

physical equilibrium

chemical equilibrium

temperature equilibrium

phase equilibrium

composition equilibrium

Thermodynamic equilibrium is however not always wanted, e.g. for the heat of combustion, glass transition, subcooling ...

problems e.g. HDPE (FUTURESTOCK), Erythritol ...

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### Requirements: calorimeter and calorimetric measurement

Measurement of quantities of heat  $\Delta Q$  transferred to or from a sample

- at given boundary conditions
- between initial state and final state

Requirements - general:

- measurement of  $\Delta Q$  with sufficient accuracy
- range of boundary conditions, e.g. p, T, ...

Requirements - additional:

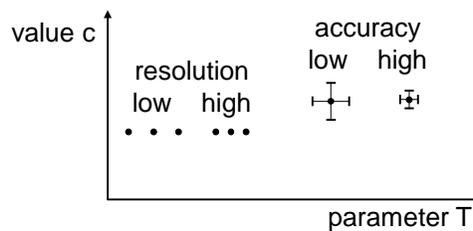
- if a material property is to be determined: representative sample
  - homogeneity,
  - subcooling ...  $\rightarrow$  necessary sample geometry (shape, size)

### Resolution and accuracy

For  $\Delta Q$  and any parameter defining initial, final, or intermediate states being kept constant (e.g. p) or varied in a range (e.g. T)

data point accuracy = measure for the precision of a value

data point density / resolution = density of data points in a parameter range



## experimental methods are combinations of

- measurement principle
- measurement setup
- measurement and evaluation procedure

selected from a  
tool box

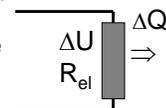
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### Options to measure the quantity of the heat exchanged

1. supply of work and conversion to heat at / in the sample  
electrical heating  $\Delta Q = W_{el} = (\Delta U)^2 / R_{el} \cdot \Delta t$  (only heating)



radiative heating, magnetic cooling ... are hard to make quantitative

2. heat exchange with a reference amount of heat

$$\Delta Q = C_r \cdot \Delta T_r \text{ (sensible heat) or}$$

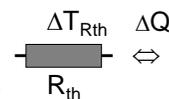
$$\Delta Q = L_r \text{ (latent heat)}$$



3. heat exchange via a thermal resistance

$$\Delta Q = \Delta T_{Rth} / R_{th} \cdot \Delta t$$

Attention: upon change of the temperature in the resistance  
the resistance itself becomes an additional heat source / sink



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### Options to measure the temperature and its change

Temperature measurement is standard; high accuracy methods are available. Common are RTDs, thermocouples, ...

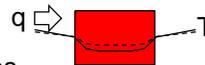
### Options to assure that the sample is in T equilibrium

The accuracy of a property as a function of temperature relies on the fact that the sample has a single temperature. When heat flows into or out of the sample a temperature gradient in the sample is inevitable. Then, the temperature attributed to the measured property as well as the property itself is affected.

To avoid or limit this problem

- determine  $\Delta Q$  (property) between isothermal states
- Or use small rate of temperature change, heat flux, sample size

To check if the result is affected, modify the parameters



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### Options to improve the density of data points (= resolution)

initial  $\leftrightarrow$  final state: single interval  $\rightarrow$  steps  $\rightarrow$  continuous (scanning)

### Options to check / improve the accuracy of the data points

check repeatability (any material)  $\rightarrow$  check accuracy (standard)  $\rightarrow$  calibration (standard)

**Calibration** is the determination of the functional relationship between values measured on standard materials and their literature ("correct") values, and the use of that relationship for evaluation.

Calibration is used for a **correction of measured values**, e.g. aged thermocouples, in the extreme the **determination of a relationship completely**, e.g. thermal resistance for heat flow.

Amounts of heat: materials with well known heat capacity or latent heat

Temperature: materials with characteristic temperature, often melting

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## General method: “Absolute and relative methods”

An **absolute method** determines the effect of the sample as an absolute value.

A **relative method**, in contrast, determines the effect of the sample relative to the effect of a reference. Relative methods are often also called **comparative methods**, and by a calibration can be used to finally determine absolute values.

**Comparative measurements** can be done

- in series, in a **single setup**
  - in parallel, in two identical setups, called **twin setup**
- comparison of sample and reference by their absolute values
- correction of unwanted effects from the measured value (e.g. heat exchange with the environment, heat capacity of crucible ...)

In a twin setup additionally

- reduction of the effect of a bad repeatability, e.g. of ambient conditions
- when recording the differential signal instead of each signal individually, called **differential setup** → comparison of two samples by their difference for higher sensitivity

## Calorimetric methods: examples

The following discussion of the different methods follows a logical path regarding the options to measure the quantity of heat exchanged

**tool box**

1. heat supply by electrical heating
  - adiabatic cal.: adiabatic, electrical heating or no heating (chem. r.)
  - diabatic cal.: as above, heat exchange with ambient by thermal resistance corrected via a calibration
2. heat exchange with a reference heat capacity
  - "maxibox": adiabatic (ideally), reference heat capacity is a flowing fluid, single temperature step or multiple steps
  - mixing cal.: adiabatic (ideally), reference heat capacity is a stationary fluid, single temperature step

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3. heat exchange via a known thermal resistance  
single setup

**tool box**

- HFM: single temperature step
  - 3-layer calorimeter: single temperature step
- twin setups
- T-history method: single temperature step
  - twin bath method: single temperature step or ramp
- twin setups with differential signal
- heat flux DSC: temperature change as ramp, multiple steps, modulated
  - power compensation DSC: as above plus el. heating to keep both temperatures equal.

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method	heat exchange	sensor setup	T program
adiabatic calorimeter	electrical heating	single	multiple steps
diabatic calorimeter	electrical heating (+ thermal resistance)	single	multiple steps
maxibox	reference heat capacity	single	single step
mixing calorimeter	reference heat capacity	single	single step
HFM	thermal resistance	single	single step, multiple steps
3-layer calorimeter	thermal resistance	single	single step
T-history	thermal resistance	twin	single step
twin bath method	thermal resistance	twin	single step, ramp
hf-DSC	thermal resistance	twin, differential	ramp, multiple steps, modulated
power compensated DSC	thermal resistance + electrical heating	twin, differential	ramp, multiple steps, modulated

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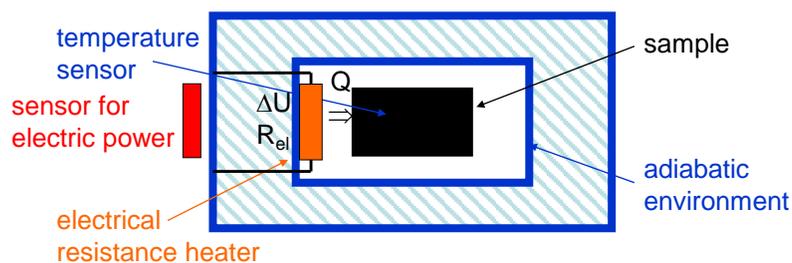
## Calorimetric method: adiabatic and diabatic calorimetry

### measurement principle

A sample is placed in an adiabatic vessel.

Heat transfer to the sample is by an electrical resistance heater, thus only heating possible (work is converted to heat).

Due to the adiabatic environment  $\Delta Q_s = W_{el}$  ( $\rightarrow$  absolute method)



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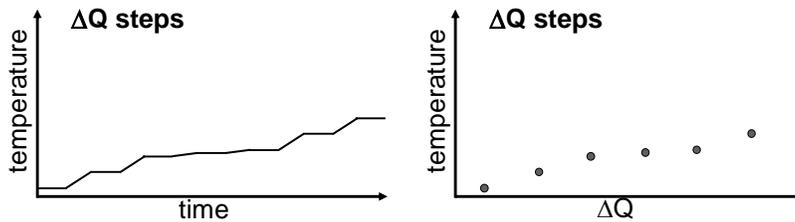
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### measurement and evaluation procedure

The heating is usually in small steps of  $\Delta Q$  (set action), then temperature equilibrium is waited for (or by a chemical reaction)

The temperature and temperature change of the sample (response) is recorded.



$\Delta Q$  as set action and  $\Delta T$  as response allows isothermal measurements in the case of latent heats with very high temperature resolution!

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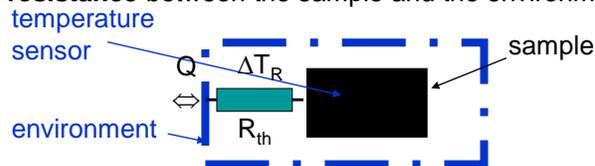
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### Calorimetric method: “Heat flow methods”

#### measurement principle

The sample is placed in an environment with a controlled temperature (set action).

The heating or cooling of the sample is by **heat exchange via a thermal resistance** between the sample and the environment



The heat flux (reaction)  $q_s = \Delta Q/\Delta t$  is  $q_s = \Delta T_R/R_{th}$ .  $R_{th}$  must be calibrated and must transport all the heat flow.

The heat transfer can be by conduction, convection, or radiation, or any combination, ....

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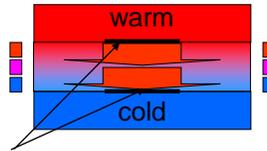
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## Calorimetric method: HFM (not standard)

### measurement principle

The HFM (heat flow meter) is actually for measurements of the thermal resistance / conductivity of a sample

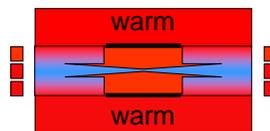


the thermal resistance is a commercial heat flux sensor (pre-calibrated)  
the "sample" is only an area fraction of the real sample (the rest makes the "adiabatic environment")

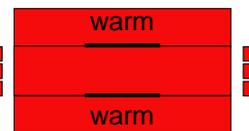
For calorimetry the external temperatures are equal and changed, e.g. in steps



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### Advantages of HFM:

- large samples (solids or containment necessary)
- standard equipment
- widely available
- not too expensive

### used at

- ASTM: T resolution by multiple steps (ASTM C1784-13)
- ZAE: single step; T resolution by: thermal resistance leads to slow temperature change as in T-history and 3-layer calorimetry (publication at EURO THERM seminar no99)

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## Calorimetric method: 3-layer calorimeter

### measurement principle

The 3-layer calorimeter is quite similar to the HFM



however

- geometry different
- the thermal resistance is a layer of insulation around the sample; it has to be calibrated!
- single T-step; still T resolution due to slow T change because of the thermal resistance while the sample is practically isothermal (as in T-history and HFM)

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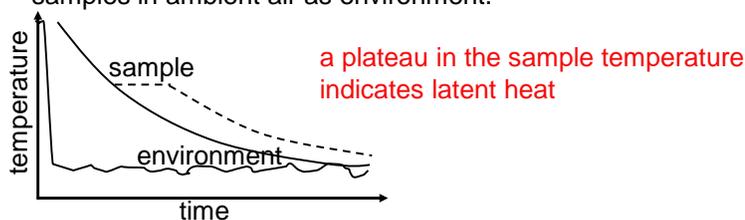
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## Calorimetric method: T-history method

### measurement principle

The development of this method started with cool down experiments of samples in ambient air as environment.



To be able to compare different samples, several setups were used in parallel → relative method

Bad repeatability in uncontrolled ambient temperature  $T_a$

The next step was to use a climatic chamber to improve repeatability and to freely select the start/end temperature (heating/cooling)

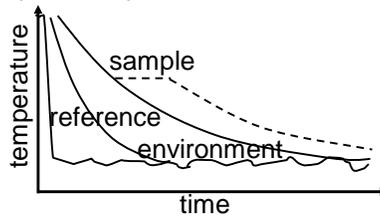
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First step towards a calorimetric method (→ quantitative measurement) was by the use of a reference material, not just for comparison, but to gain information on the heat flow → heat flow method measurements in parallel in a twin setup → comparative method

$q = \Delta Q/\Delta t$  is  $q = \Delta T_{R_{th}}/R_{th}$ ,  
with  $\Delta T_{R_{th}} = T_{s/r} - T_a$  and  $R_{th} = \alpha$   
(free convection)



Sample and reference have the

same geometry, surface area → a calibration of  $R_{th}$  is possible

From the known heat storage capacity of the reference material and the recorded temperatures the thermal resistance  $R_{th}$  is calculated; it is then used to determine the heat flux of the sample.

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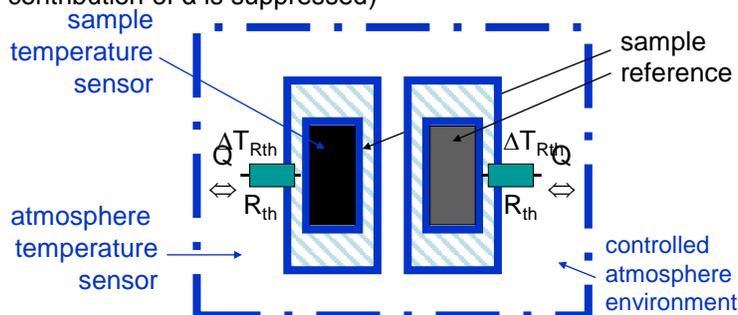
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The T-history method is like a 3-layer calorimeter, but as twin setup.

### measurement setup

The full step towards a calorimetric method (→ quantitative measurement) was done when the **use of an insulation** was introduced to make  $R_{th}$  a more reproducible constant in time (the contribution of  $\alpha$  is suppressed)



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## Calorimetric method: Differential Scanning Calorimetry

A **differential setup is a twin setup where** the differential signal is recorded instead of both signals separately. Advantages are

- high sensitivity to small differences between sample and reference
- elimination of unwanted effects in the signal from the sample; for this the same effect is incorporated in the reference, e.g. the heat capacity of the crucible

“**Scanning**” refers to the quasi-continuous recording of the heat flux.

**Differential Scanning Calorimetry (DSC)** A thermo-analytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature. Both the sample and reference are maintained at nearly the same temperature throughout the experiment.

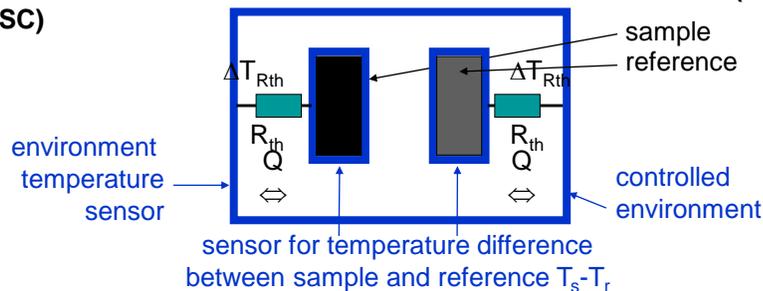
**Basic types of DSC: heat flux DSC and power compensated DSC**

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## Calorimetric method: heat flux DSC (hf-DSC)

**Heat flux DSC (hf-DSC)** A technique in which the temperature of the sample unit, formed by a sample and reference material, is varied in a specified program, and the temperature difference between the sample and the reference material is measured as a function of temperature. The temperature change is commonly at a constant rate or modulated. In the latter case it is called **modulated DSC (m-DSC)**



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### measurement principle

Heat flows between the ambient and the sample, as well the reference:

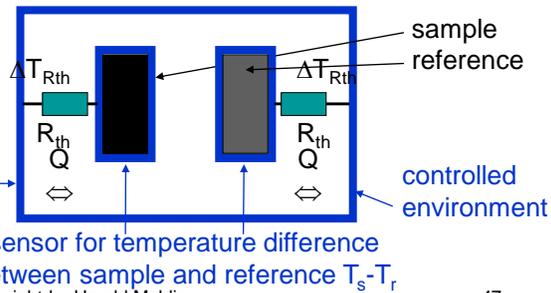
$$q_s = dQ_s/dt = (T_s - T_a)/R_{th} = C_s \cdot dT_s/dt$$

$$q_r = dQ_r/dt = (T_r - T_a)/R_{th} = C_r \cdot dT_r/dt$$

assuming the same  $dT/dt = \beta$ , follows  $T_s - T_r = R_{th} \cdot (C_s - C_r) \cdot \beta$  = net heat flux  $dQ/dt$

The differential setup, giving the net heat flux, is used to eliminate the effect of the crucible, → the reference crucible is always empty

environment temperature sensor



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### Calibration of the heat flux

$$T_s - T_r = R_{th} \cdot (C_s - C_r) \cdot \beta$$

Measured thermocouple voltage  $\Delta U = a \cdot (T_s - T_r) + b$  net heat flux

- the thermocouple sensitivity (a) and offset (b) are not known,
- the thermal resistance  $R_{th}$  is unknown,
- the twin setup is used to eliminate the effect of the crucible from the signal, to get the net heat flux, but there is still a small difference in the crucibles!

$$\Delta U = a \cdot (T_s - T_r) + b$$

$$= a \cdot R_{th} \cdot (C_s - C_r) \cdot \beta + b$$

$$= a \cdot R_{th} \cdot dQ/dt + b$$

$$= a \cdot R_{th} \cdot \beta \cdot (C_{sa/r} + C_{sac} - C_{rc}) + b$$

$$= a \cdot R_{th} \cdot \beta \cdot (C_{sa/r}) + a \cdot R_{th} \cdot \beta \cdot (C_{sac} - C_{rc}) + b$$

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$$\Delta U = a \cdot R_{th} \cdot \beta \cdot (C_{sa/r}) + a \cdot R_{th} \cdot \beta \cdot (C_{sac} - C_{rc}) + b$$

$$= A \cdot dQ_{net}/dt + B$$

Because of the unknown difference in empty  $C_{sac}$  and  $C_{rc}$  ( $=f(\beta)$ ) and unknown thermocouple offset  $b$  ( $\neq f(\beta)$ )

→ measurement with both crucibles empty, the **base-line (B)**

Because of the unknown  $R_{th}$  and the thermocouple sensitivity ( $a$ )

→ measurement with a standard in the sample crucible, the **standard-line ( $A \cdot dQ_{net}/dt + B$ )**

standards:

- heat capacity  $c$ ; calibration for small signals, in a  $T$  range
- enthalpy  $\Delta h$ ; calibration for medium to large signals, at  $T$  points

This has to be done for the used  $\beta$ , covering all  $T$  for the measurement

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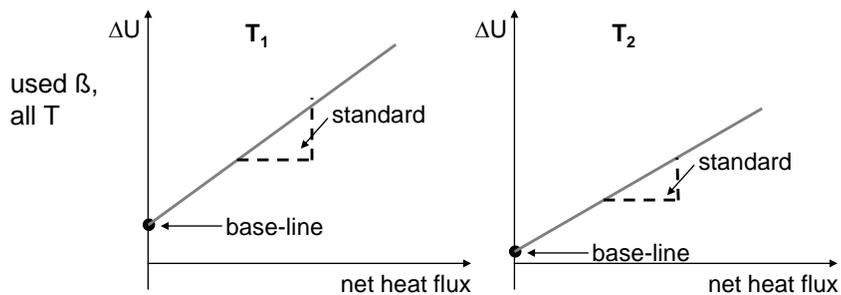
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$$\Delta U = a \cdot R_{th} \cdot \beta \cdot (C_{sa/r}) + a \cdot R_{th} \cdot \beta \cdot (C_{sac} - C_{rc}) + b$$

$$= A \cdot dQ_{net}/dt + B$$

**base-line (B)**

**standard-line ( $A \cdot dQ_{net}/dt + B$ )**

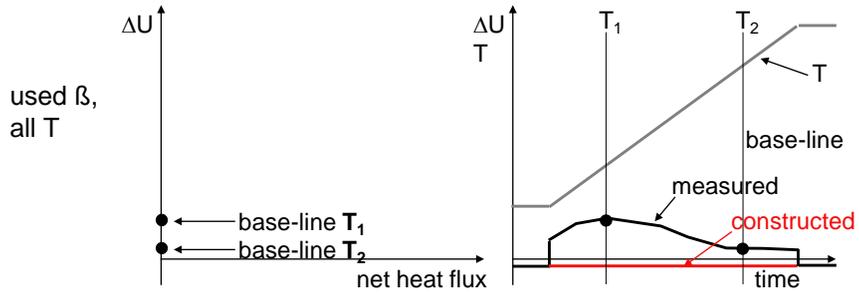


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→ measurement with both crucibles empty, the **base-line** takes into account the difference in empty  $C_{\text{sac}}$  and  $C_{\text{rc}}$  and unknown thermocouple offset (b)



construction: interpolation between zero heating rate (ASTM); only thermocouple offset (independent of  $\beta$ ) eliminated!

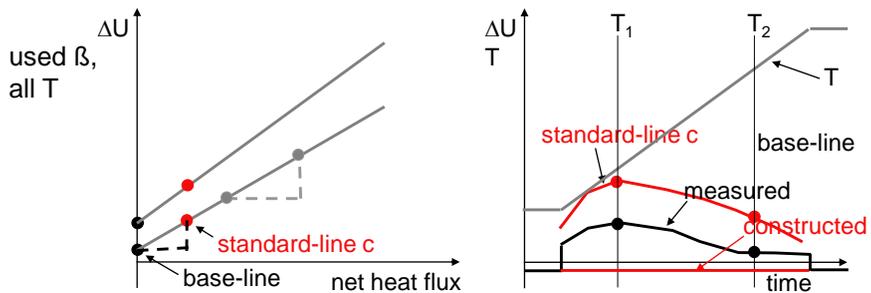
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→ measurement with a standard in the sample crucible, the **standard-line**

**heat capacity  $c$** ; calibration for small signals, in a  $T$  range  
enthalpy  $\Delta h$ ; calibration for medium to large signals, at  $T$  points



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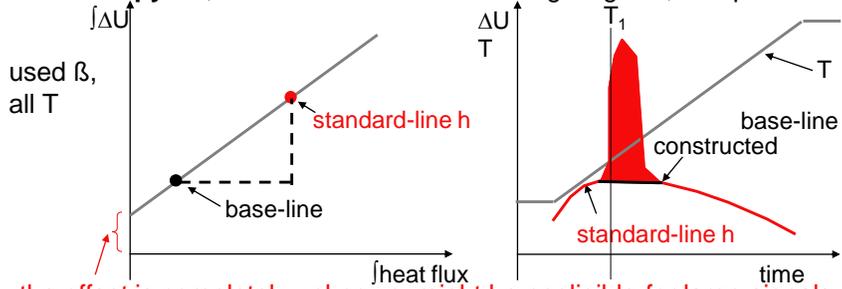
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→ measurement with a standard in the sample crucible, the **standard-line**

heat capacity  $c$ ; calibration for small signals, in a  $T$  range

**enthalpy  $\Delta h$** ; calibration for medium to large signals, at  $T$  points



used  $\beta$ , all  $T$

the offset is completely unknown; might be negligible for large signals, but not for the sensible heat in PCM!

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### real measurements

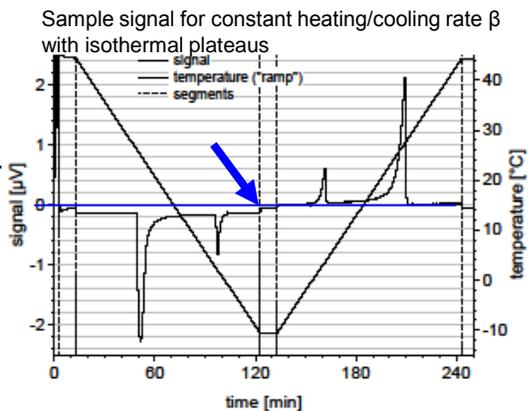
Base-line: signal from zero sample

Ideally,  $\Delta U$  is zero

when  $C_{sc}=C_{rc}$  or when  $\beta=0$

However,  $\Delta U \neq 0$  when  $\beta=0$  indicates asymmetries in temperature measurement.

A measured base-line includes both effects with their temperature dependence!

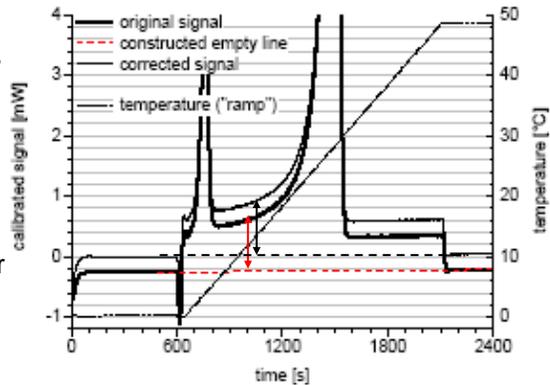


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Optionally, the base line can be constructed assuming a linear baseline as a function of temperature (ASTM E 1269) between the signal at heating rate zero (not the baseline of the peak!).

A constructed base-line includes only asymmetries in T, and not an exact temperature dependence!

Advantage:  
less experimental effort, especially an auto sampler does not have the sample crucible in an empty state



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**Standard measurement and evaluation procedure using a heat capacity standard** → small signal, wide T-range

Experimental effort: 3 measurements

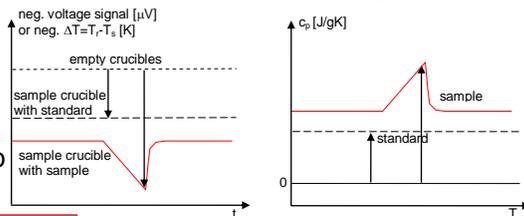
- base-line: both crucibles empty → signal with zero sample mass
- standard-line: standard in the sample crucible →  $R_{th}$
- sample-line: sample in the sample crucible → sample signal

$$\Delta U_{bl} = a \cdot R_{th} \cdot (C_{sac} - C_{rc}) \cdot \beta + b$$

$$\Delta U_{stl} = a \cdot R_{th} \cdot (C_{sac} + C_{st} - C_{rc}) \cdot \beta + b$$

$$\Delta U_{sal} = a \cdot R_{th} \cdot (C_{sac} + C_{sa} - C_{rc}) \cdot \beta + b$$

$$\boxed{(\Delta U_{sal} - \Delta U_{bl}) / (\Delta U_{stl} - \Delta U_{bl}) = C_{sa} / C_{st}}$$



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**Standard measurement and evaluation procedure using enthalpy standards** → large signal, small T-range

several standards with known enthalpy (often melting), are placed in the sample crucible;

the standards are measured individually; to compare with literature data, the peak baseline is constructed (the zero signal is the peak baseline, the signal is the peak area; this also eliminates b)

$$\int \Delta T \cdot dt$$

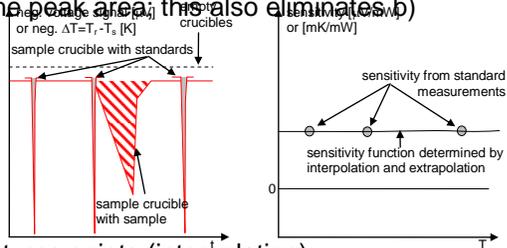
$$= a \cdot R_{th} \cdot \int (C_s - C_r) \cdot \beta \cdot dt$$

$$= a \cdot R_{th} \cdot \Delta H \quad \text{or}$$

$$\int \Delta U \cdot dt = a \cdot R_{th} \cdot \Delta H$$

it calibrates for

larger signal at temperatures points (interpolation)



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Experimental effort: only sample measurement necessary, calibration rarely

- $\int \Delta T \cdot dt = a \cdot R_{th} \cdot \int (C_s - C_r) \cdot \beta \cdot dt = a \cdot R_{th} \cdot \Delta H$  or  $\int \Delta U \cdot dt = a \cdot R_{th} \cdot \Delta H$
- baseline: constructed (the zero signal is the peak baseline, the signal is the peak area)
- calibration points: standards with known melting enthalpies →  $R_{th}$
- sample: measured the same way → only „peak area“, no T resolution

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A measurement and evaluation procedure combines the measurement of the sample with some way of calibration and some way of base line determination. These can be combined in different ways.

application	sample-line	base-line		calibration	
	meas.	meas.	constr.	heat capacity st.	enthalpy st.
heat capacity	x	x		x	
"	x		x	x	
peak integral	x		x		x
melting effect in total	x	x			x
"	x		x		x

The last option is optimized for PCM with respect to effort and accuracy; constructed base-line (from  $\beta=0$  signal) in small temperature range (melting range) is expected to introduce small error compared to peak integral.

### Calibration of the temperature

...

## Conclusions

### Important things to consider

Representative sample size: homogeneity, subcooling

Sample preparation

Correct measurement of the temperature by the sensor  $\Rightarrow$  check repeatability (any material), check accuracy (standard), calibration (standard)

Correct measurement of heat flow  $\Rightarrow$  check repeatability (any material), check accuracy (standard), calibration (standard)

Thermodynamic equilibrium in the sample

- sample is isothermal
- sample is in reaction equilibrium

## Overview

### 1. Introduction to Calorimetry

- Calorimetry: basics
- Calorimetric methods: general aspects
- Calorimetric methods: examples

### 2. Specifics of phase change materials (PCM)

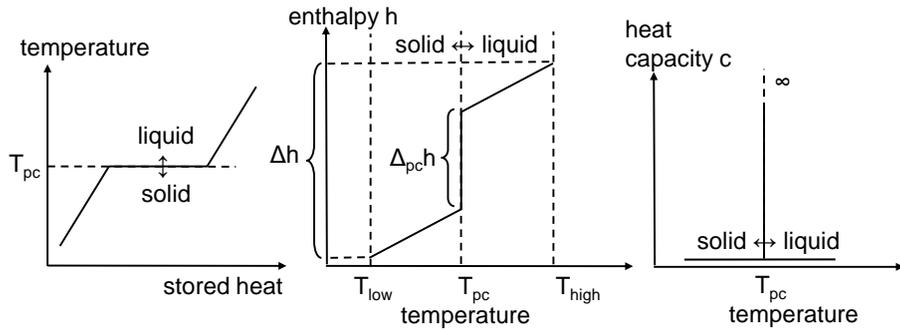
- PCM: specific effects and data presentation
- PCM: specific effects and measurement guidelines

### 3. Specifics of sorption materials

- ...

## PCM: specific effects and data presentation

### Ideal phase change: melting temperature, no hysteresis



#### data presentation:

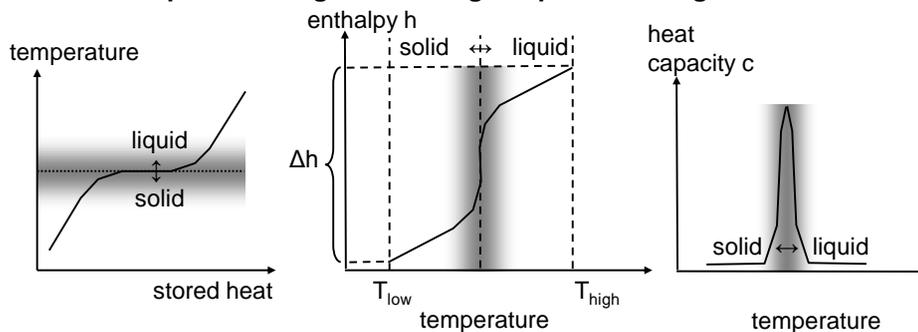
- $h(T)$  curve (optional)
- tabulation of  $T_{pc}$  and  $\Delta_{pch}$  (less space necessary)

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### Non-ideal phase change: 1. melting temperature range



- What is the melting temperature?
- What is the temperature range for  $\Delta_{pch}$ ? →  $\Delta h(T_{high}, T_{low})$ ?
- Is it with / without sensible heat?

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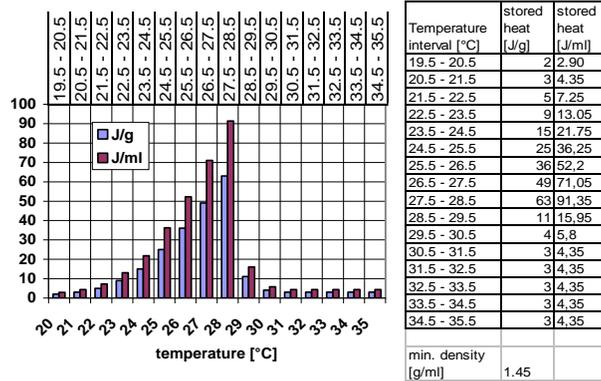
data presentation:

- h(T) curve (or c curve)

- tabulation of the stored heat in temperature intervals

in both options:

- no melting temperature
- no temperature range for integration
- all heat considered

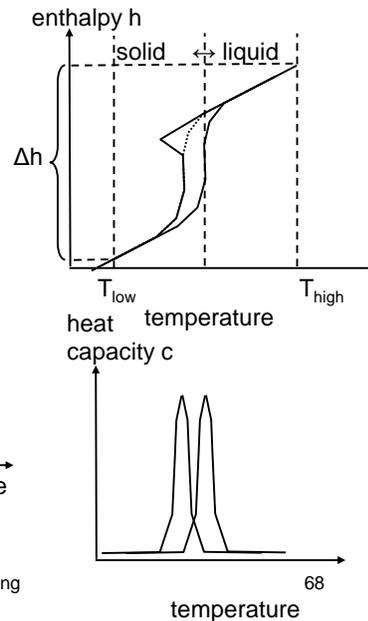
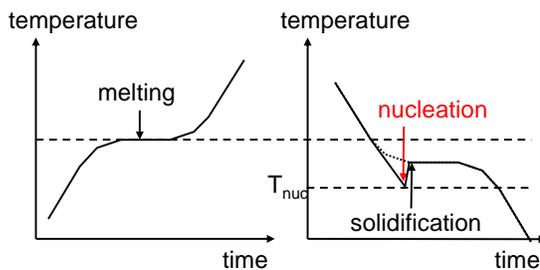


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Non-ideal phase change: 2. hysteresis melting and solidification at different T including subcooling



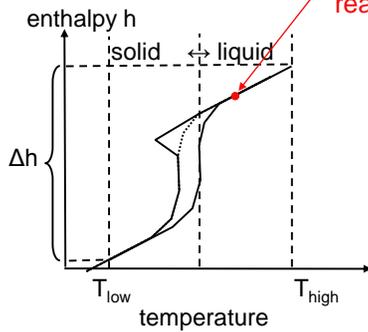
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**data presentation:**

- **h(T) curves for heating and for cooling, including the effect of subcooling**



use normalization point in the liquid phase  
reason: thermodynamic equilibrium is faster attained in the liquid such that measured data are more reliable and therefore more useful for a normalization point!

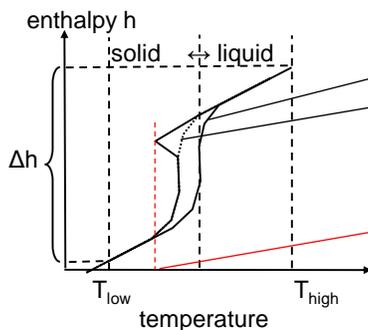
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- **tabulation of the stored heat in temperature intervals for the case of heating and for the case of cooling**

**+ nucleation temperature  $T_{nuc}$**



Temperature interval [°C]	stored heat [J/g]	stored heat [J/ml]
19.5 - 20.5	2	2.90
20.5 - 21.5	3	4.35
21.5 - 22.5	5	7.25
22.5 - 23.5	9	13.05
23.5 - 24.5	15	21.75
24.5 - 25.5	25	36.25
25.5 - 26.5	36	52.2
26.5 - 27.5	49	71.05
27.5 - 28.5	63	91.35
28.5 - 29.5	11	15.95
29.5 - 30.5	4	5.8
30.5 - 31.5	3	4.35
31.5 - 32.5	3	4.35
32.5 - 33.5	3	4.35
33.5 - 34.5	3	4.35

analogous

$T_{nuc} = \dots$

RAL prefers tabulated values as everybody understands them

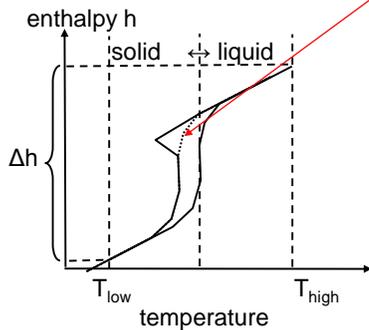
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use  $T_{\text{nucl}}$  and not degree of subcooling

reason: the degree of subcooling needs a reference temperature, which in the case of a melting and solidification temperature range is not well defined.



use  $h(T)$  during subcooling attributed to a case without subcooling for tabulation  
reason: 1) subcooling depends on the sample size, material data should not!  
For example water can subcool to  $-40^{\circ}\text{C}$ , but the full enthalpy change is always attributed to  $0^{\circ}\text{C}$ !  
2) using these data, any case with an estimated subcooling can be calculated!  
3) in real storages the heat release as  $f(T)$  does not show the subcooling observed in a calorimetric measurement

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## used by RAL

**Standard for data presentation  $\Rightarrow$  Accurate, simple, and precise!**

**The stored heat** ( $\Rightarrow$  no problems with choosing a baseline)  
**as a function of temperature** ( $\Rightarrow$  no problems with choosing a melting temperature or temperature range)  
**has to be declared for the case of heating and for cooling**  
( $\Rightarrow$  no problems with hysteresis).  
**Further on, the nucleation temperature must be given**

**The stored heat has to be tabulated in given temperature intervals** ( $\Rightarrow$  no problem with a step change in the enthalpy).

**This has to be done with respect to mass in  $\text{J/g}$  and volume in  $\text{J/ml}$**  (the volume specific values have to be calculated from the mass specific values by multiplication with the smallest density in the temperature range of application)

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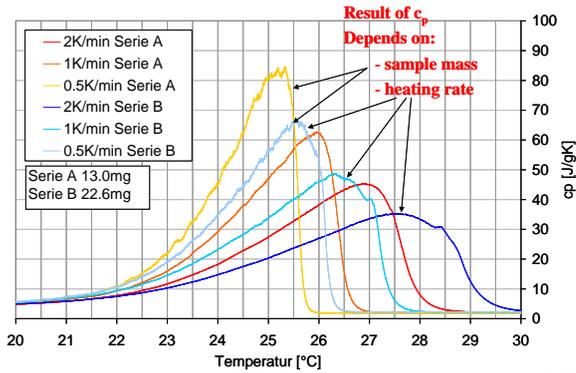
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## PCM: specific effects and measurement guidelines

Accuracy requirement:  $h=h(T)$  to  $\pm 10\%$  in  $h$  and  $T$  to  $\pm 0.5^\circ\text{C}$

Measurement with hf-DSC in dynamic mode



observed problem:

- results depend on
- sample mass
- heating rate

Accuracy of  $\pm 0.5^\circ\text{C}$   
is by far not  
achieved!

Which data are "correct"?

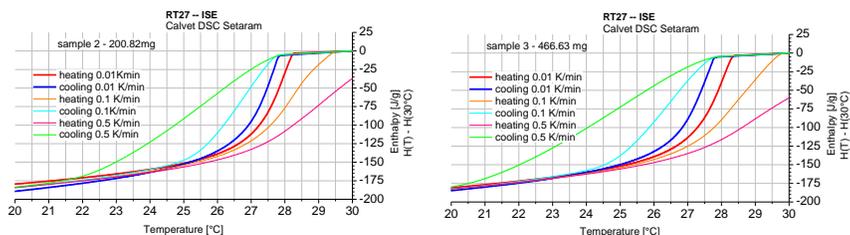
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## Intercomparison test: different hf-DSC and methods tested on a paraffin with little subcooling

1. Constant heating rate with variation



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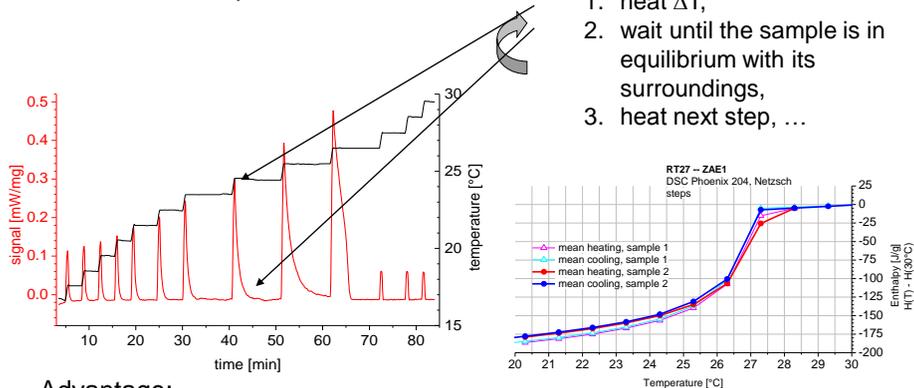
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## 2. Isothermal steps method

procedure:

1. heat  $\Delta T$ ,
2. wait until the sample is in equilibrium with its surroundings,
3. heat next step, ...



Advantage:

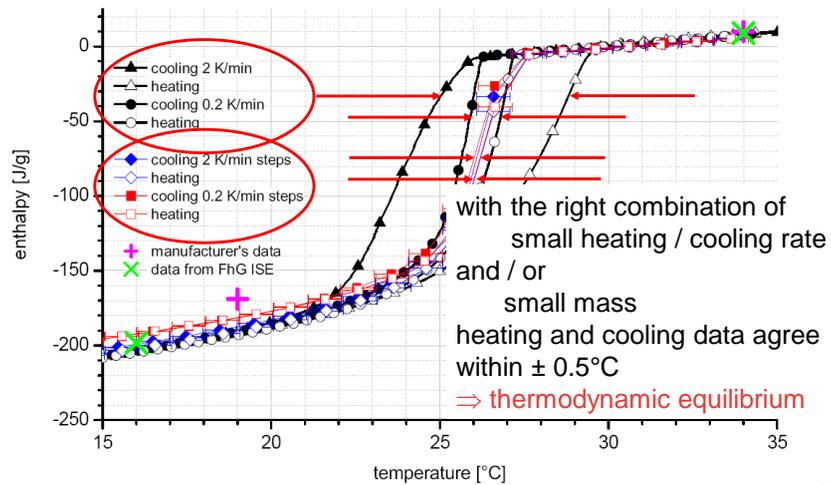
the non-isothermal state of the sample is confined to the step size  $\Delta T$

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The data agree very well!



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**General conflict:**

Thermodynamic equilibrium in the sample:

sample is isothermal  $\Rightarrow$  the heating / cooling rate should be small  
or the sample size should be small

sample is in reaction equilibrium (problem with subcooling)  $\Rightarrow$  the  
heating / cooling rate should be small

but at the same time

Representative sample size:

Homogeneity of the sample  $\Rightarrow$  the sample size should be large

Subcooling  $\Rightarrow$  the sample size should be typical for the application

Therefore, a selection of the appropriate measurement technique and  
parameters is important

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## used by RAL

RAL prefers general guidelines

as they must be applicable for different methods, systems ...

**The stored heat can be determined using one of the following methods:**

- hf-DSC dynamic mode with constant heating or cooling rate,
- hf-DSC quasi stationary measurement with stepwise heating
- m-DSC,
- T-History-method,
- CALVET-calorimeter,
- Multylayer-calorimeter-method

**Guidelines specifically regarding**

- **Number of samples and measurements**
- **Method to ensure the thermal equilibrium within the sample with sufficient accuracy**

**have to be followed.**

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### Number of samples and measurements

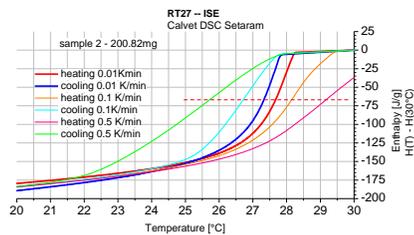
- at least three samples
- at least 3 cycles measured

### Method to ensure the thermal equilibrium within the sample with sufficient accuracy

- dynamic measurement = constant heating / cooling rate, e.g. DSC

vary the rate, be taking halves, until at the inflection of the  $h(T)$  curve

- a) the temperature changes by  $\leq 0.2^\circ\text{C}$  for the heating curves as well as for the cooling curves or
- b) the temperature of the heating or cooling curve deviate by  $< 0.5^\circ\text{C}$



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Trick: check measurement at low heating rate (high T resolution, low sensitivity) with a repetition at high heating rate for  $\Delta_{pc,h}$

- single step, as in T-history  
**vary the final temperature,**  
until at the inflection of the  $h(T)$  curve
  - a) the temperature changes by  $\leq 0.2^\circ\text{C}$  for the heating curves as well as for the cooling curves or
  - b) the temperature of the heating and cooling curve deviate by  $< 0.5^\circ\text{C}$

- isothermal steps, as in DSC  
**check that the heat flux goes to zero before the temperature is changed**

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