Lecture Series: Modern Methods in Heterogeneous Catalysis Research

Practical Aspects of Thermoanalytical Methods

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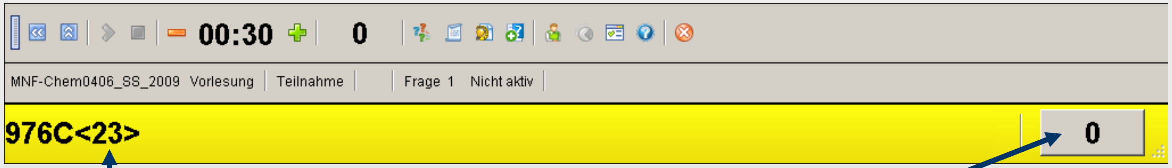
How to use the “RF-Clicker“?

1. **Switch on the clicker**
   press the on/off button
2. **Enter the numerical “code“**
   you are logged in, if the 2. diode flash slowly



00:30 0

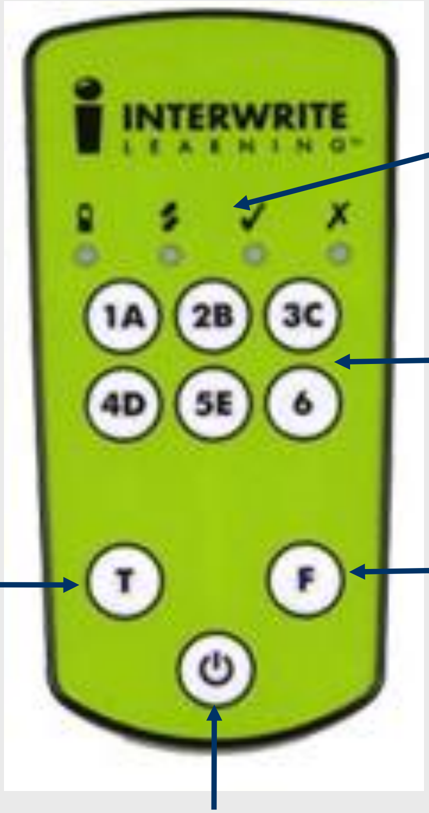
MNF-Chem0406_SS_2009 Vorlesung | Teilnahme | Frage 1 Nicht aktiv

976C<23> 0

code (e.g. 23)

Number of participants that have logged successfully into the system

3. **Enter your answer**
   press one of the multiple choice or T/F buttons
4. **After the lecture please switch off the clicker**
   press the on/off button for about two seconds .

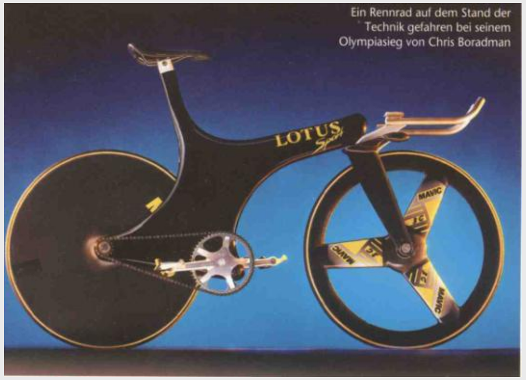


Question to become familar with the clicker?

What is the name of the legendary sword of King Arthur?

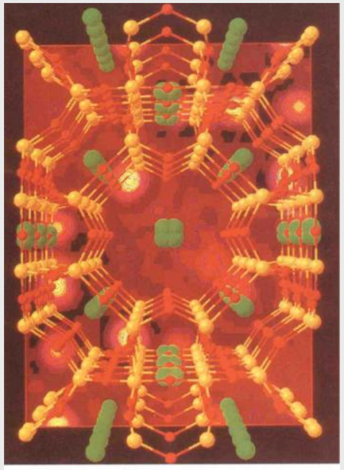
Button	Answer
1A	Example
2B	Express
3C	Excalibur
4D	Excess
5E	Eva
6	Egon

What are the key aspects of this lecture? Why they were selected?

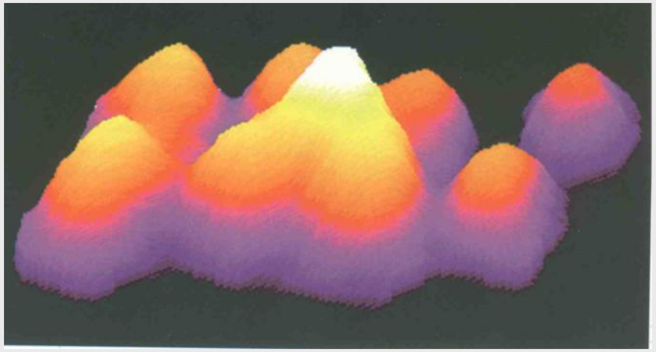


material testing

quality control



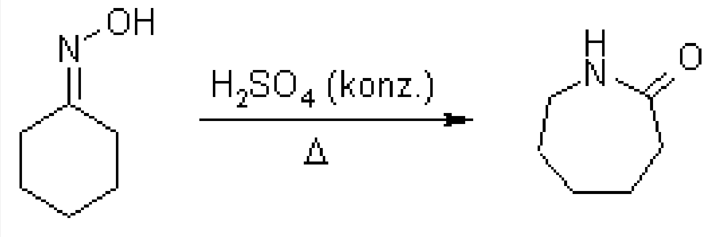
catalysis



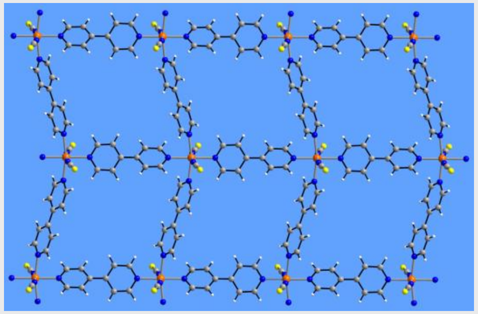
surface technologies

optimization of materials

analytic



synthesis of new compounds



$\xrightarrow{\Delta T}$ **?**

investigation on the reactivity of compounds

What are the key aspects of this lecture? Why they were selected?

Problem oriented selection of a method: Which questions are of importance for the selection of a specific method?

- ***What should be investigated?***
  Elemental analysis (qualitative/quantitative) / thermal properties / reactivity / structural information / ……
- ***State of matter of the sample?***

  solid / liquid / gaseous
- ***State of the sample?***
  amorphous / semi crystalline / crystalline (large single crystals or powder)
- ***Properties of the sample?***
  large or small particles / diamagnetic / paramagnetic / conducting / isolating
- ***On which area of the sample information is needed?***
  surface / bulk
- ***How precise or accurate the information should be?***
  qualitative composition / quantitative composition / crystal structures

What are the key aspects of this lecture? Why they were selected?

Which knowledge is needed for a problem oriented selection of a method?

- ❖ Which methods exists ?
- ❖ Theoretical basics (only what is needed)?
- ❖ Which information can be extracted by one specific method?
- ❖ On which area of a sample information is provided ?
- ❖ Are there specific requirements concerning the nature of the sample ?
- ❖ How precise and accurate is the information provided by one specific method?
- ❖ Which are the limitations of a specific method ?
- ❖ Are there any parameters that influence a measurement ?
- ❖ Which are possible pitfalls and errors that can occur?

Introduction into thermoanalysis

Thermoanalysis (TA)

Generic term for methods in which chemical or physical properties of a substance, a mixture of substances or a reaction mixture are measured as **function of temperature or time**, whereas the sample is subjected to a **controlled temperature program**.

DIN 51005

DIN = Deutsche Industrienorm (German Industry Standard)

Characteristics

- Extremely large area of applications starting from basic research up to quality control
- Indispensable component in chemical research, material development and material testing
- Versatile methods: practically any chemical or physical reaction can be investigated

Which methods belongs to thermonalytical methods?

Problem: There is no common characteristic feature of thermoanalytical methods. Because in most methods physical properties are measured as function of temperature or time, any other method should belong to thermoanalytical methods.

Solution: Only methods are considered which are defined by the ICTA or the DIN, for which commercial devices exist and which are in general accepted as thermoanalytical methods.

Methods

Thermo**g**ravimetry (**TG**)

Differential **T**hermo**a**nalysis (**DTA**)

Differential **S**canning **C**alorimetry (**DSC**)

Thermomicroscopy

Dilatometrie (DIL)

Thermo**m**echanical **A**nalysis (**TMA**)

Dynamic **M**echanical **A**nalysis (**DMA**)

Simultaneous and supplement methods

Simultaneous methods combine different thermoanalytical techniques

Advantegous

- Differences in the sample behaviour do not play any role
- Environmental parameters are identical (atmosphere, temperature program)
- Temperature is always comparable

Examples

- TG-DTA: thermogravimetry with differential thermoanalysis
- TOA-DSC: thermooptical analysis with differential scanning calorimetry
- TG-MS: thermogravimetry coupled to mass spectroscopy

Supplement methods are used to get further information about the sample behaviour

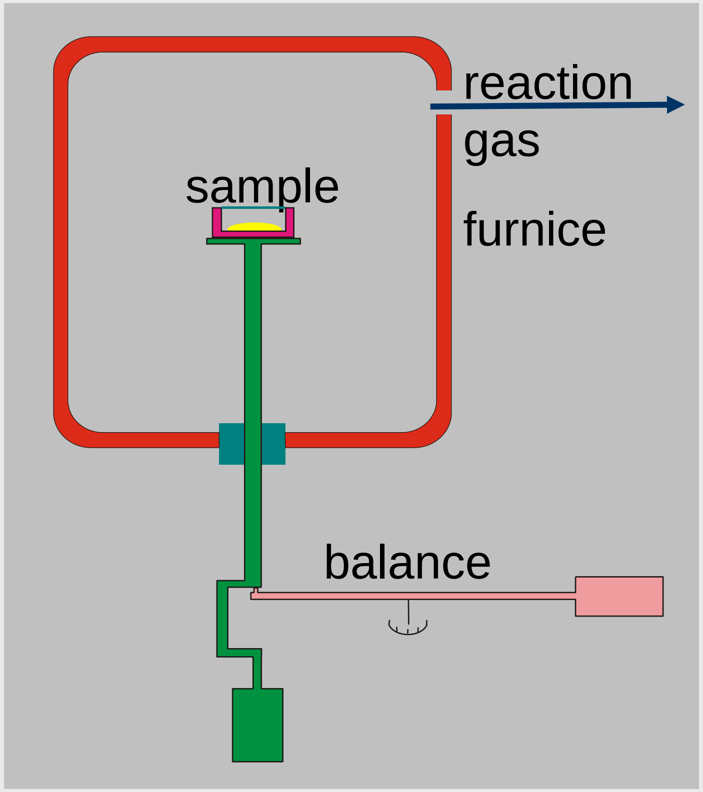
Examples

- Temperature and time resolved X-ray powder diffraction
- Thermomagnetometry (measurement of magnetic properties)
- Thermoconductometrie (measurement of conductivity)
- Thermophotometry (measurement of the optical properties)

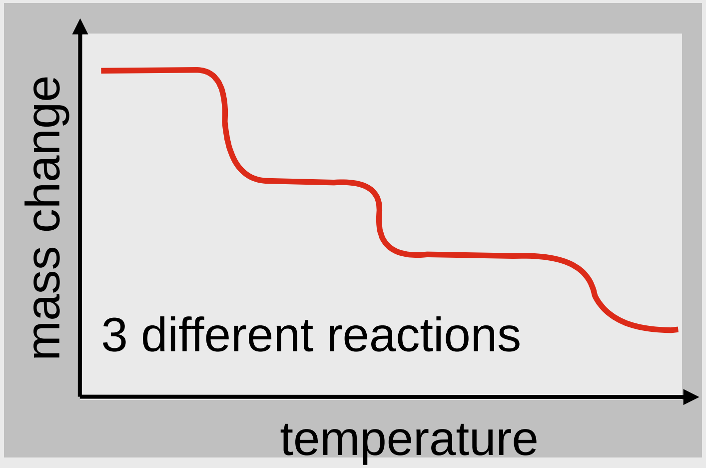
Examples for the application of therm. methods in catalysis

- Investigations on the properties of catalyst precursor compounds and on the preparation of catalysts
- Investigations on the thermal behaviour of catalysts e.g. in different atmospheres by e.g. pulse thermoanalysis
- Investigations on deactivation processes of the catalyst during exposure with reactive gases or gas mixtures
- Investigations on phase changes or sintering of catalysts in different atmospheres

Thermogravimetry



Thermogravimetry (TG) is a method which measure the mass change of a sample in a well defined atmosphere applying a controlled temperature-time program.



What is measured in thermogravimetry

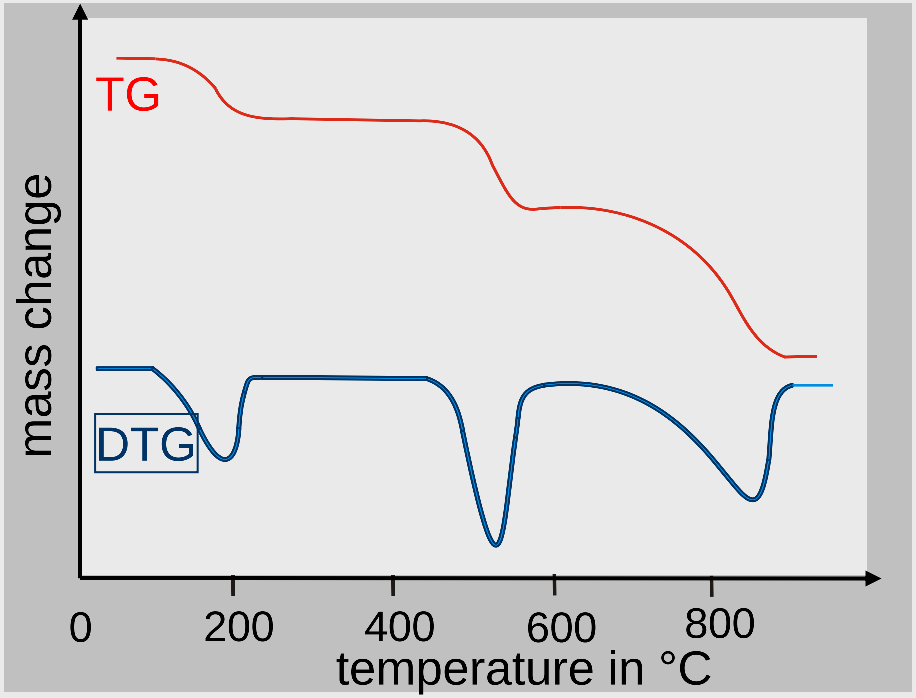
Measured variable:

$m = m(T)$ oder $\Delta m = m(T) - m_0$

m = sample mass

m_o = sample mass at the beginning

T = temperature



Differentiated thermogravimetric curve

1. derivative of the measured variable:

$d(\Delta m) / dt = d(m - m_0) / dt = dm / dt$

Each mass step is shown as a peak;

Can help if the different mass steps are poorly resolved.

Can help in analyzing the exact mass loss for poorly resolved TG curves.

Question

In a TG measurement a compound start to decompose at 400°C.

Is it correct in this case that this compound is

thermally stable up to this temperature?

Button	Answer
T	yes (true)
F	no (false)

Question

On which parameters the characteristic of a TG curve will <u>not</u> depend?

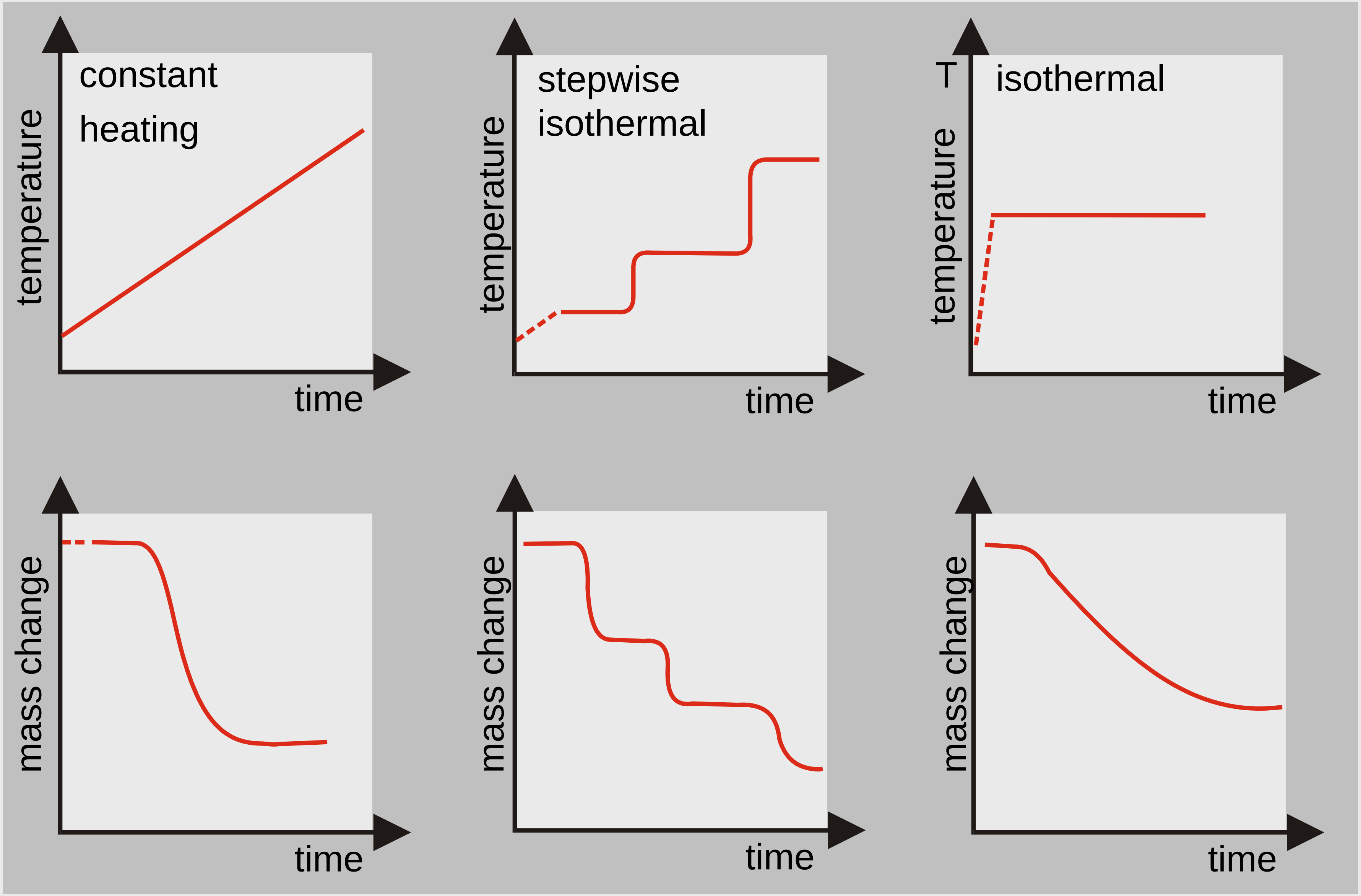
Button	Answer
1A	Heating rate
2B	Nature of the atmosphere
3C	Pressure in the atmosphere
4D	Amount of sample
5E	Shape of the cruicibles used in measurement
6	Kind of the thermobalance (instrument)

Parameters that influence the TG curve

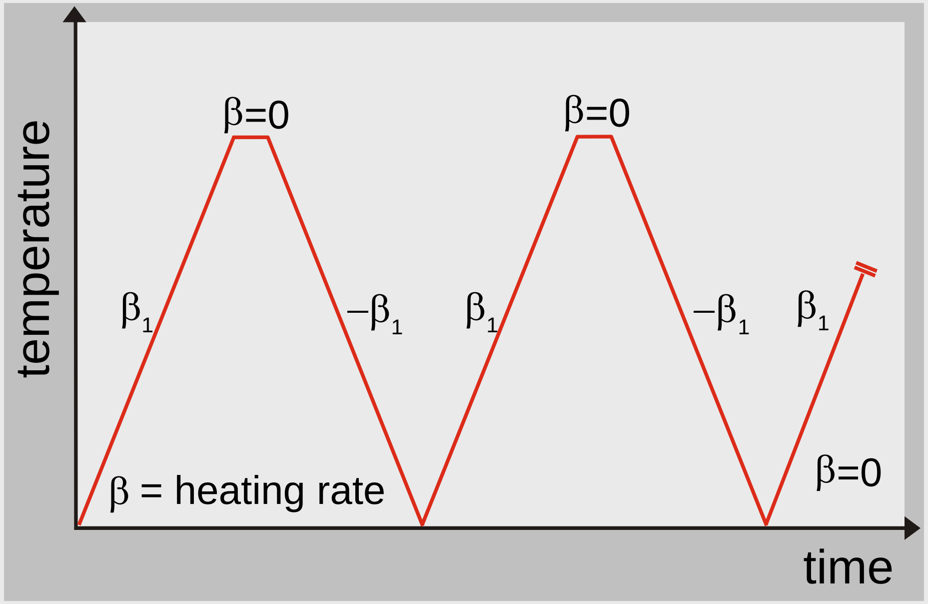
The measured variable and the course of the reaction depends on the following parameters:

- Temperature time program
- Properties of the sample
- Atmosphere in the thermobalance
- Heat conductance
- Effects of gas flow and bouyancy
- Temperature inhomogenities within the sample (influence of the heat conductance)
- Nature of the sample (e.g. large crystals or microcrystalline powder)
- Pressure
- Nature of the gas
- Reactions of the sample

Temperature time programs (common to all methods)



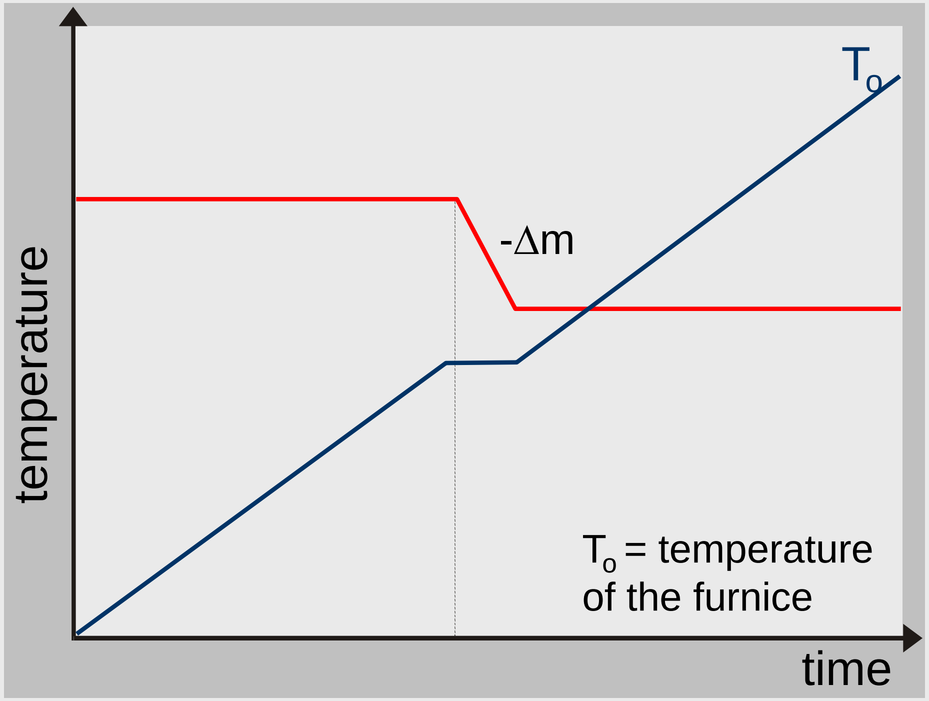
Temperature time programs (common to all methods)



In practically all modern thermoanalytic instrument any temperature time program can be used

Example

Continuous heating and cooling to determine the reversibility of a reaction.



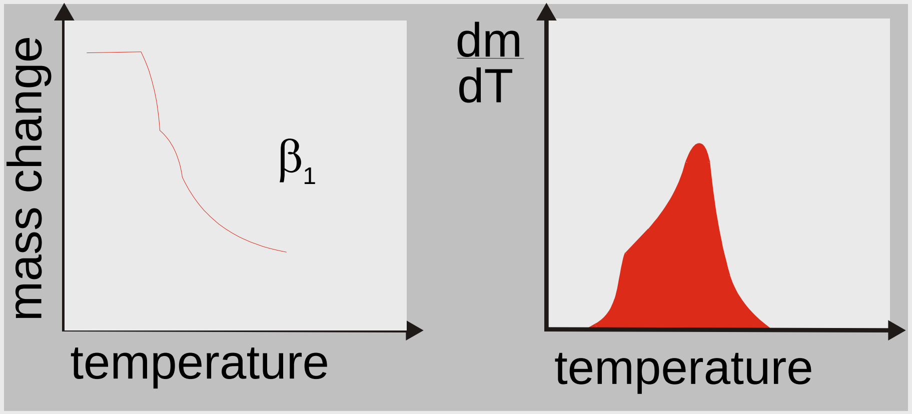
Reaction controlled TG experiment

-Δm as f(t) = constant.

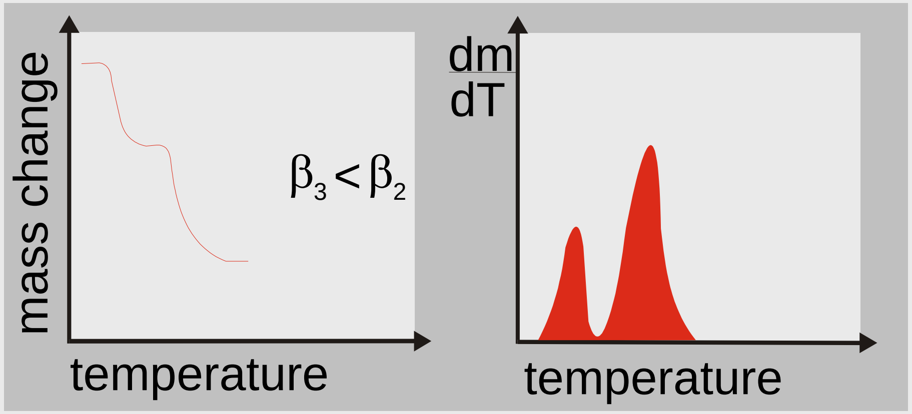
Device automatically detect change of the signal (e.g. Δm) and stop heating until the signal is constant.

Can increase resolution

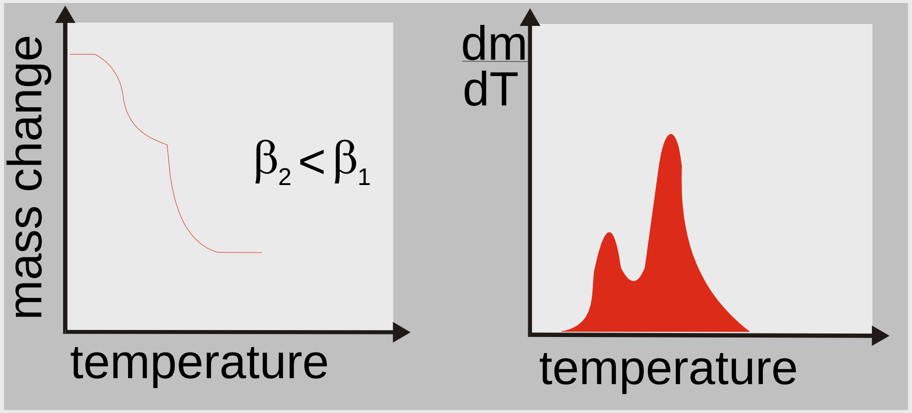
Influence of the heating rate *β* on the resolution of a reaction



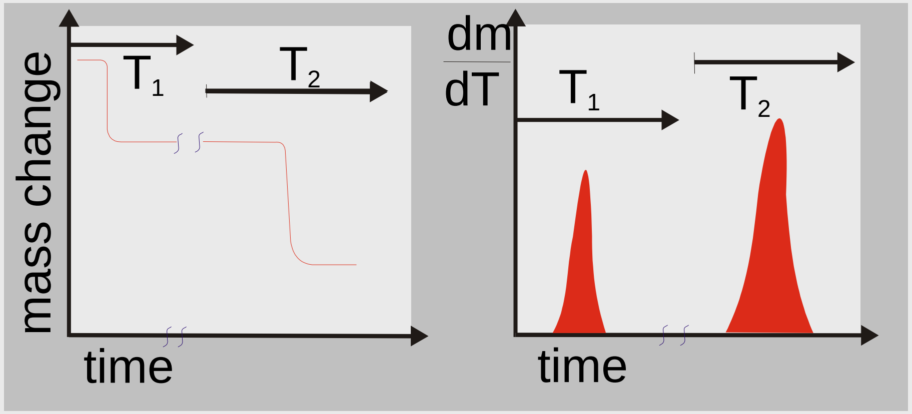
- ❖ fast heating rate
- ❖ low resolution
- ❖ only one peak is visible in DTG curve



- ❖ slow heating rate
- ❖ good resolution
- ❖ complete separation of the peaks



- ❖ mid heating rate
- ❖ better resolution
- ❖ two different unresolved peaks are visible



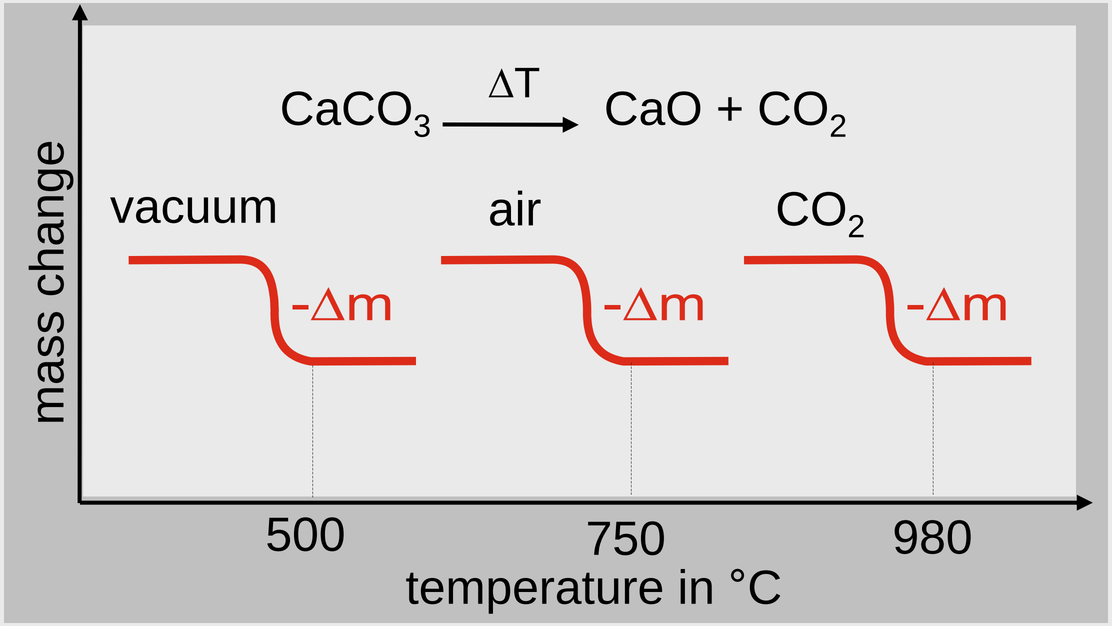
- ❖ quasi isothermal
- ❖ best resolution
- ❖ any separation of the peaks

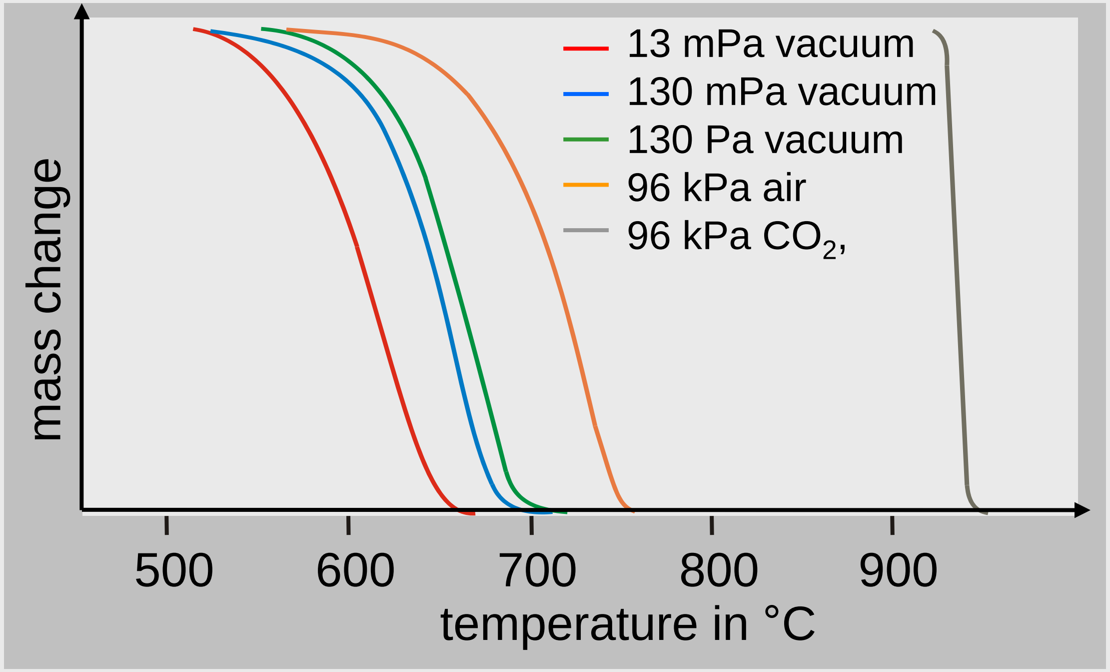
Question

What is expected for the decomposition temperatures if $CaCO_3$ is investigated by thermogravimetry in vacuum, in air under normal pressure and in pure CO_2?

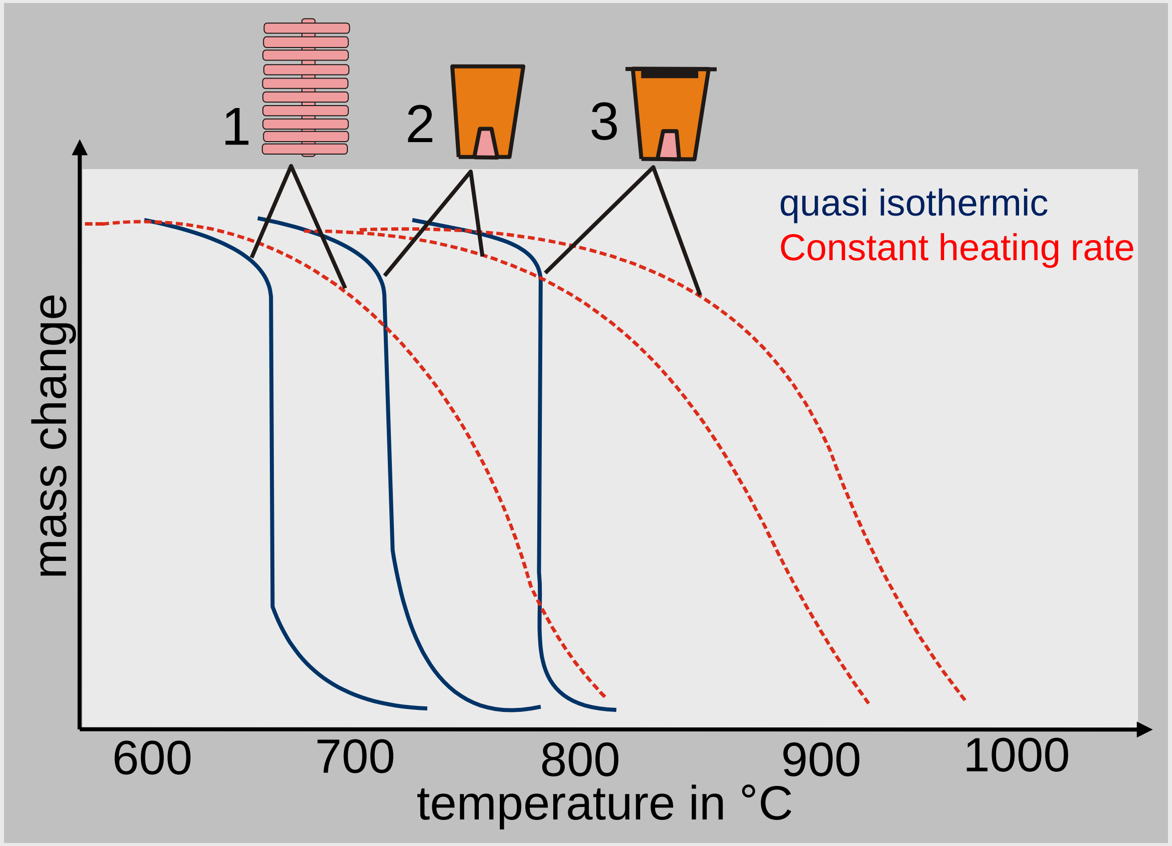
Button	**Answer**
1A	There is no influence on the TG curve
2B	vacuum < air < CO_2
3C	vacuum > air > CO_2
4D	vacuum < CO_2< air
5E	vacuum > CO_2 > air
6	CO_2 > vacuum > air

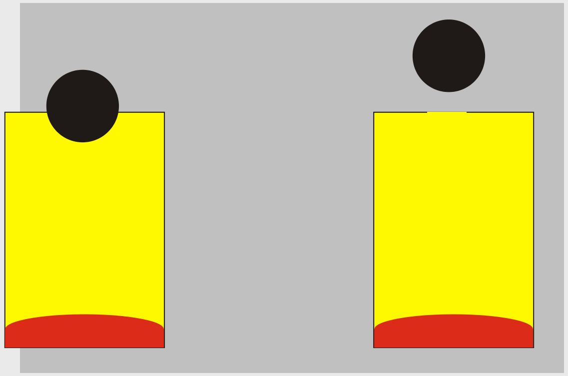
Influence of the pressure and nature of the atmosphere





Influence of the cruicibles





Cruicibles for a self produced atmosphere

1: open cruicible with large surface area

2: open cruicible

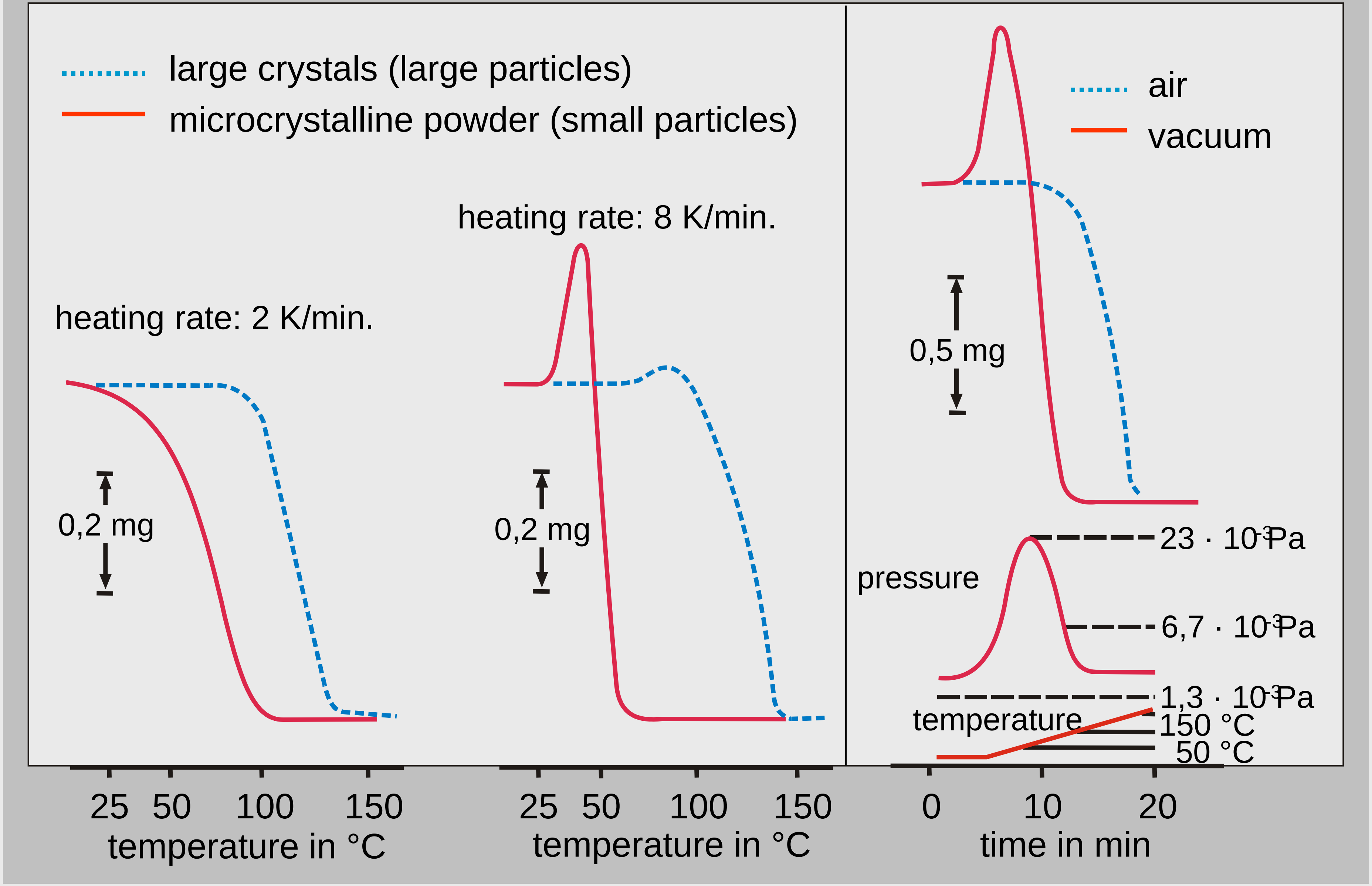
3: cruicible with a small hole

Question

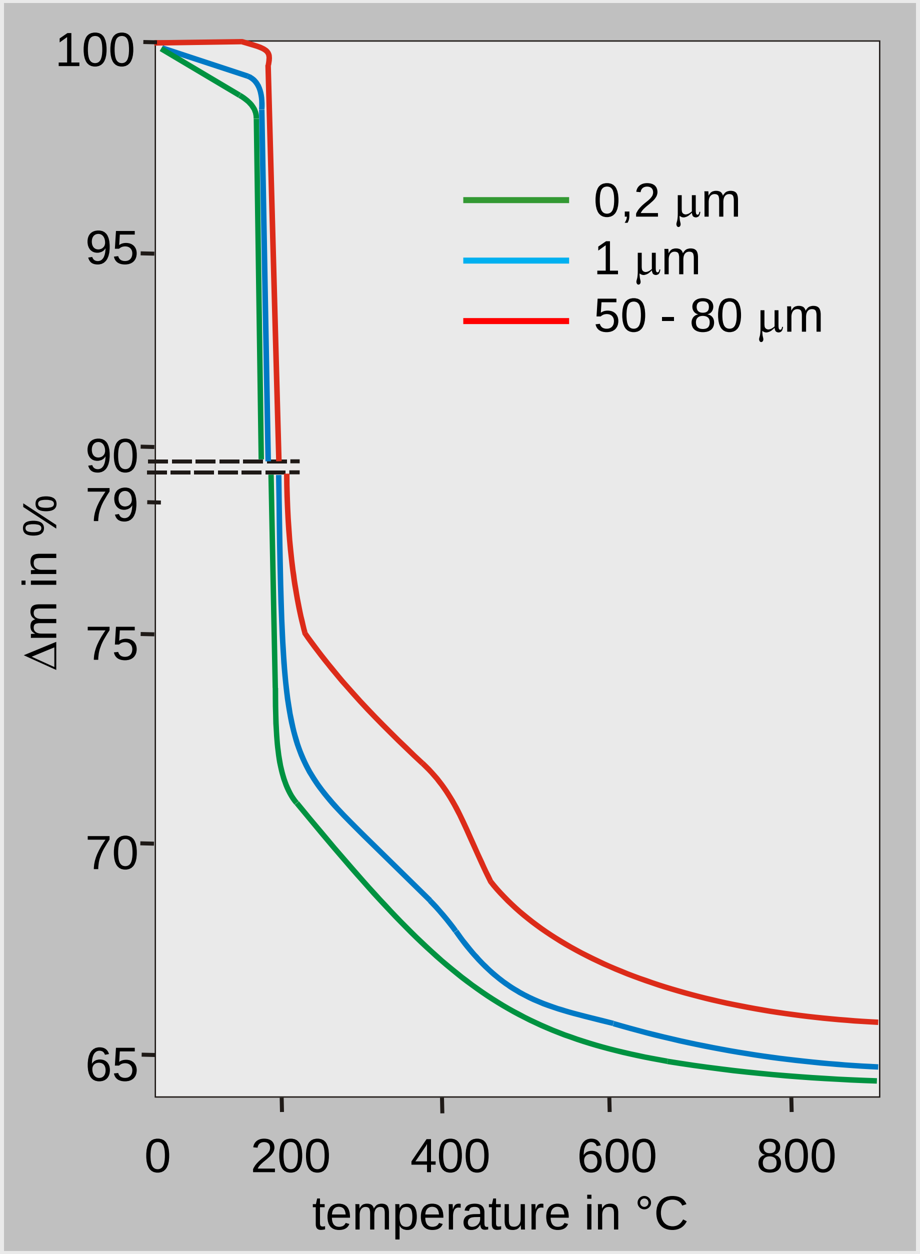
What is expected for the decomposition temperatures if a first measurement is performed with larger, a second with smaller particles?

Button	Answer
1A	This will have no influence on the decomposition temperatures
2B	The decomposition temperature increases
3C	The decomposition temperature decreases

Influence of the nature of the sample: $CaC_2O_4 \cdot H_2O$



Influence of the particle size on the decomposition of $Al(OH)_3$



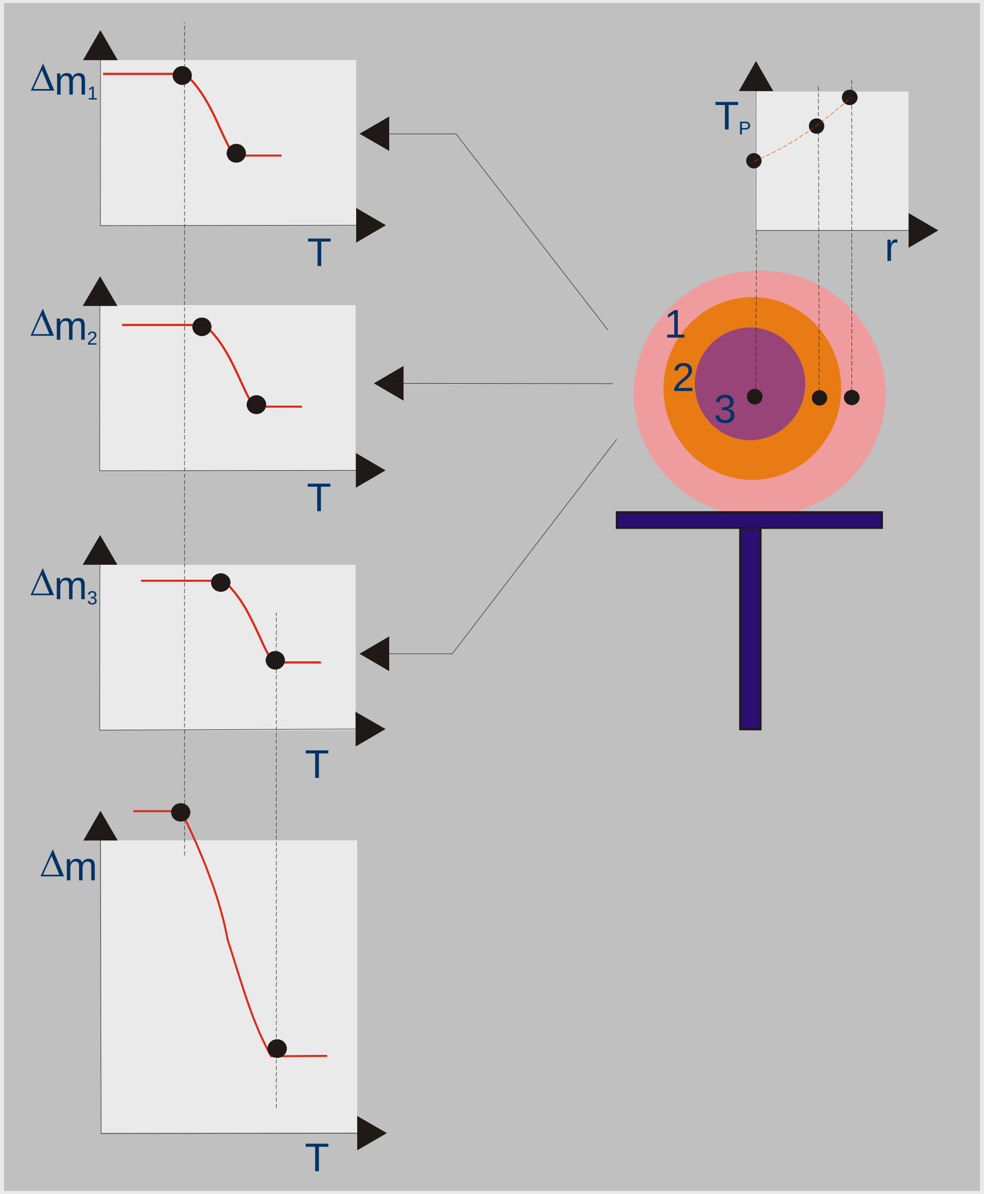
Small particles:

- Fast diffusion in the particles and from their midpoint to their surface
- Faster decomposition

Large particles:

- Slow diffusion in the particles and from their midpoint to their surface
- Slower decomposition

Time lag of the reaction in the particles of the sample



T	temperature
T_P	temperature of the sample area
r	position in the sample
1,2,3	sample areas
$\Delta m_{1,2,3}$	mass change in the sample areas
Δm	complete mass change

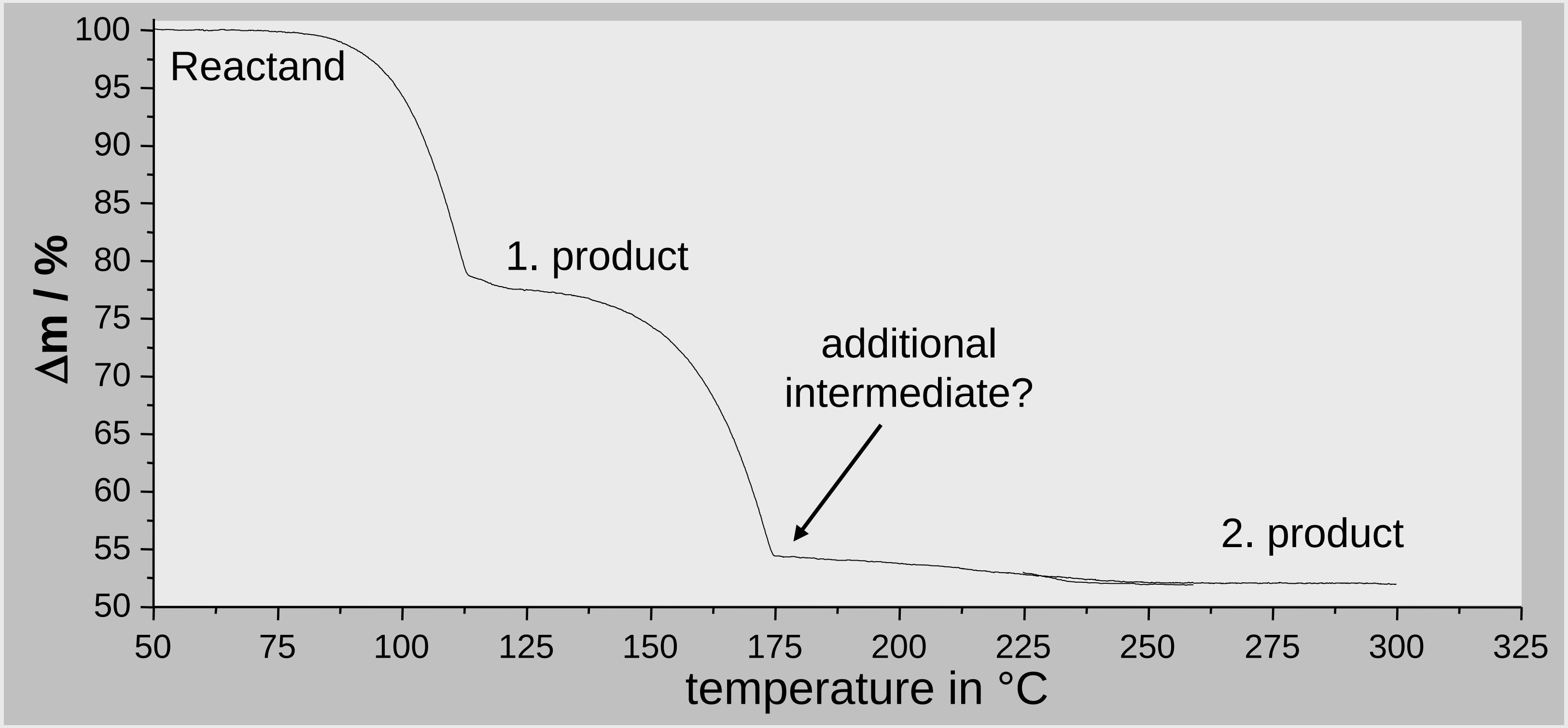
$$\Delta m = \Delta m_1 + \Delta m_2 + \Delta m_3$$

Question

Is it correct that each TG step correspond to the formation of a new compound with distinct stoichiometry ?

Button	**Answer**
T	yes (true)
F	no (false)

Does each TG step correspond to the formation of a compound?



No !

It might be that that the reaction is very fast in the beginning but slow down with increased reaction time

Several steps might be involved and in the end, a reaction might proceed via diffusion which can be the rate-determining step.

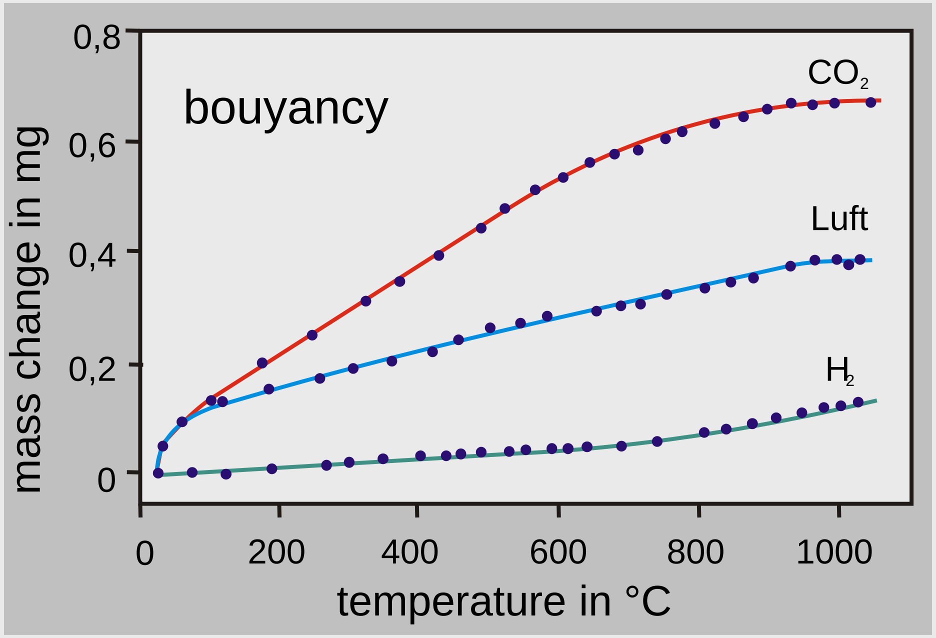
Effects of bouyancy and gas flow

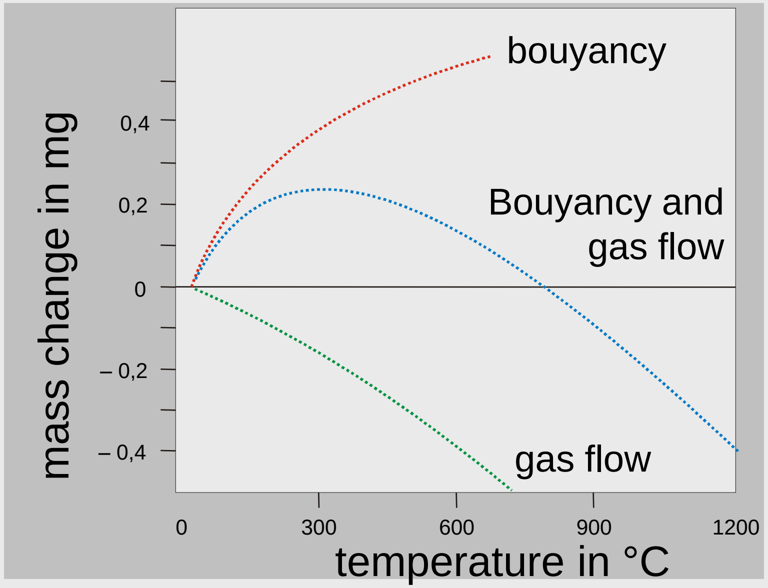
Sentence of Archimedes

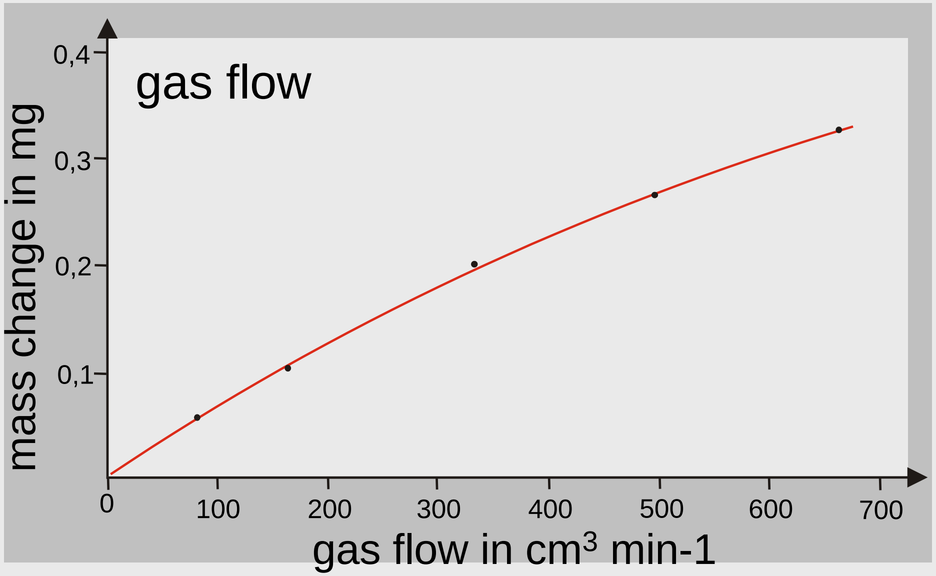
An object which is immersed in a fluid is buoyant up by force equal to the weight of fluid discovered by the object.

Solution

Substracting the TG curve of a similar measurement without sample from that with the sample.







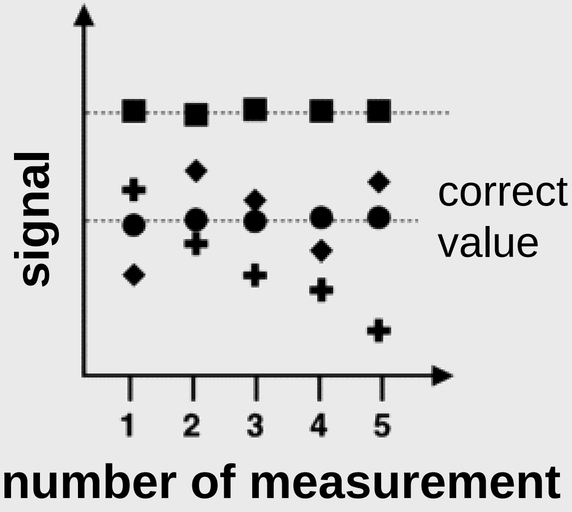
Question

In which case the TG curve is only minor influenced if there is no correction fow bouyancy and gas flow

Button	Antwort
1A	large sample weight
2B	small sample weight
3C	small sample weight and large mass loss
4D	large mass loss
5E	large sample weight and small mass loss
6	large sample weight and large mass loss

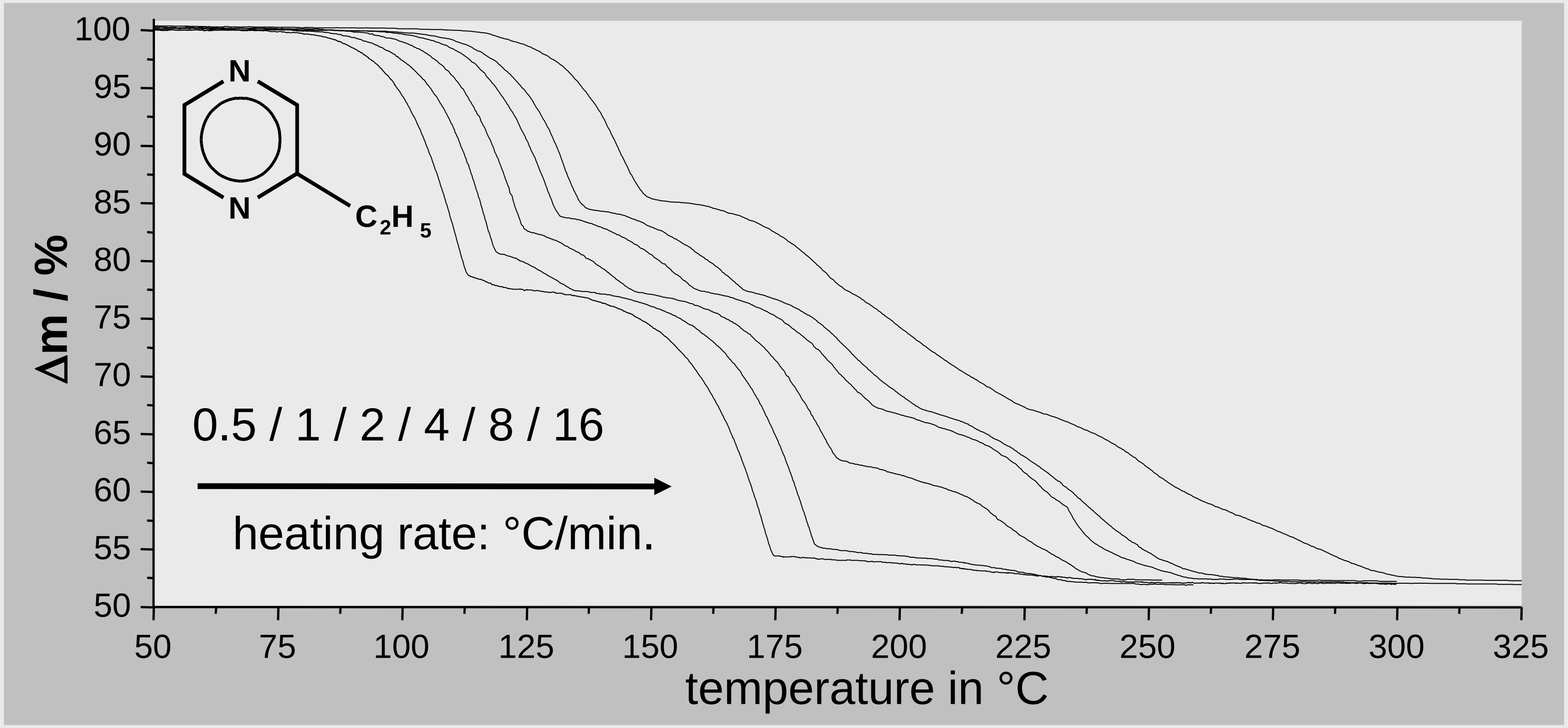
Question

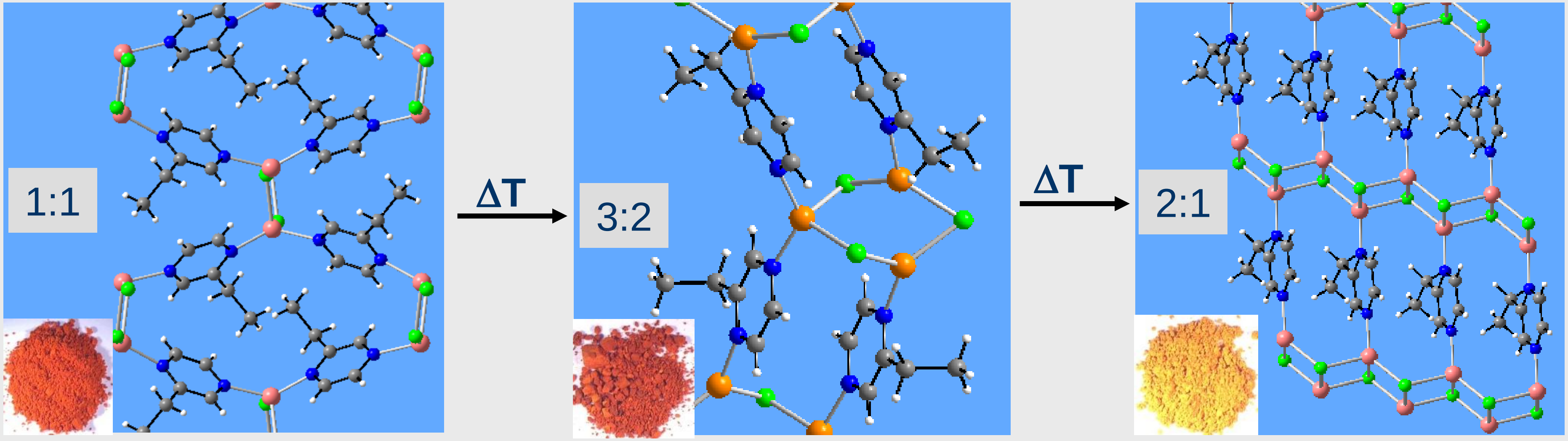
Which of the values shown in the figure are measured with high precission but with low accuracy?



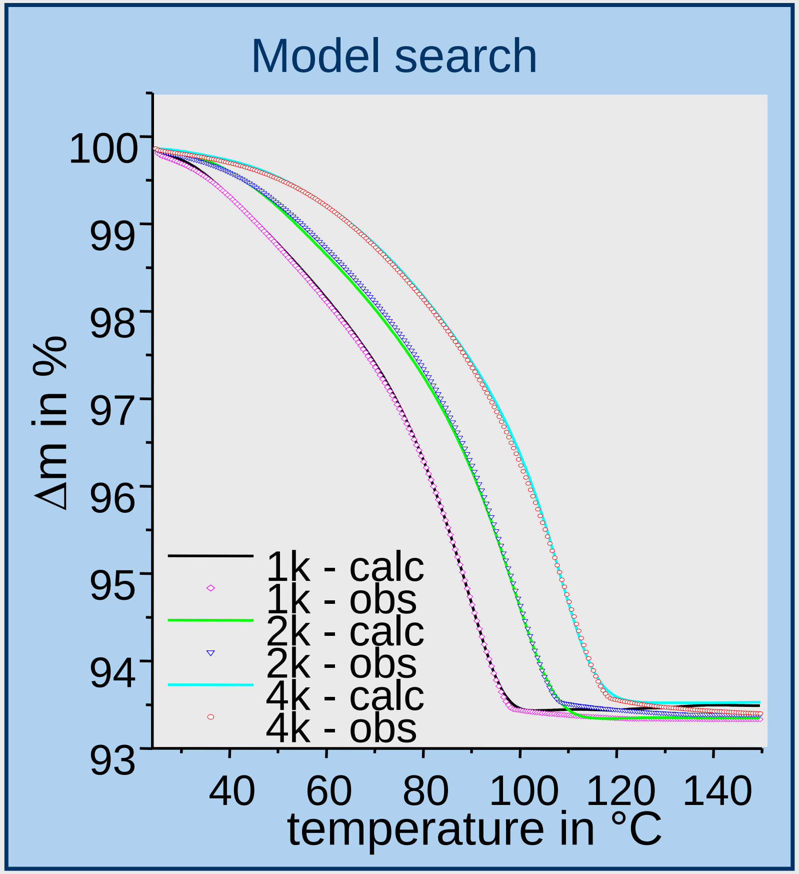
Taste	Antwort
1A	squares
2B	circles
3C	cross
4D	rhombi
5E	None of the values

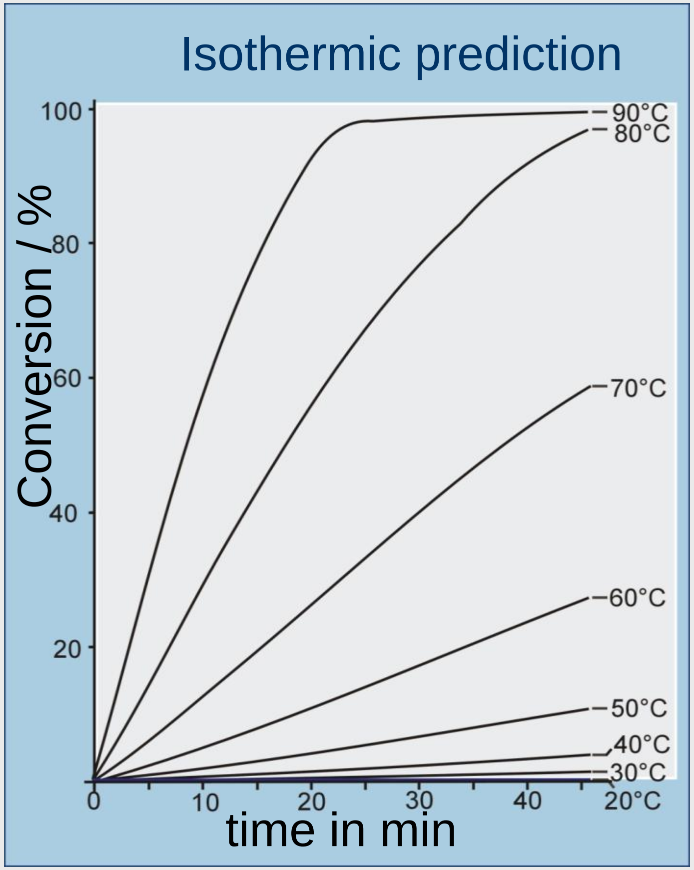
Influence of the heating rate on product formation





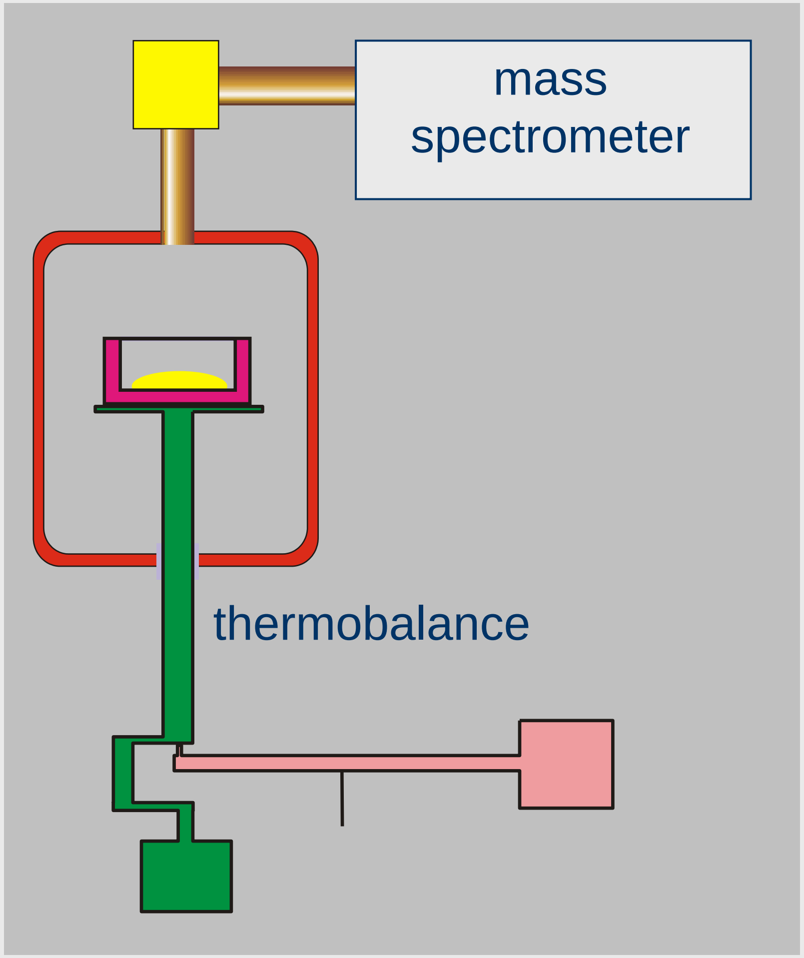
Investigations on the kinetics of a reaction (thermokinetic)

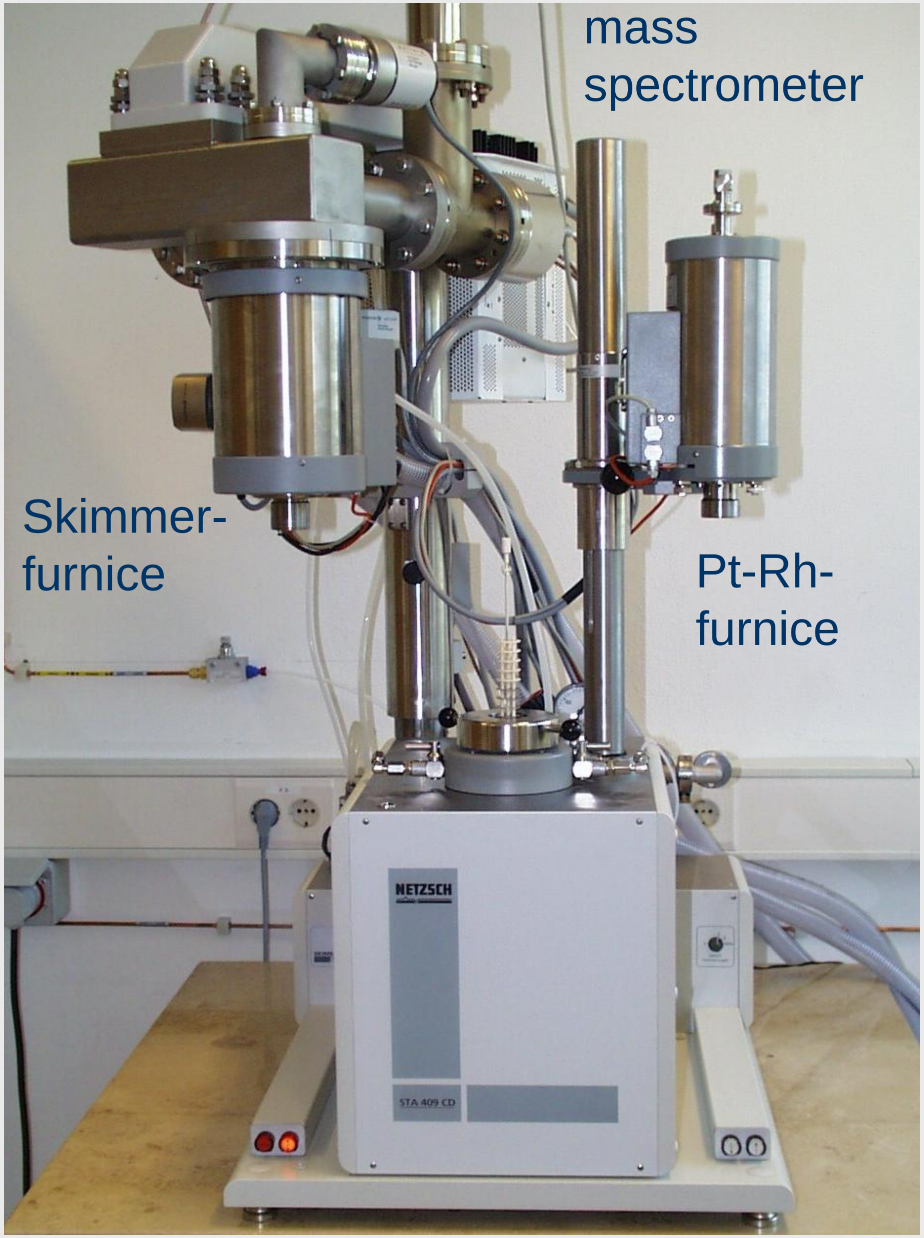

Model search


Isothermic prediction

- Formal kinetic; the e.g. TG curve is fitted to some special rate laws (e.g. 1. order, 2. order, Avrami equation, 1D or 2D diffusion, …) and the best fit is used.
- The result can be used e.g. for the prediction on the conversion rate of a compound.
- Only on the basis of these results no conclusions on the mechanism can be drawn.

Thermogravimetry coupled to mass spectroscopy





Advantegous

Information on the compounds emitted during a measurement are provided

Coupling of the mass spectrometer

Capillary coupling

mode of operation

- transfer of the gas via a heated capillary

disadvantages

- products can condense within the capillary
- order in which the products reach the MS can change

advantegous

- precise quantitative measurements are possible

Skimmer coupling

mode of operation

- transfer of the gas via a Skimmer that always have the sample temperature

advantegous

- No temperature gradient from the sample to the mass spectrometer
- detection of low volatile compounds

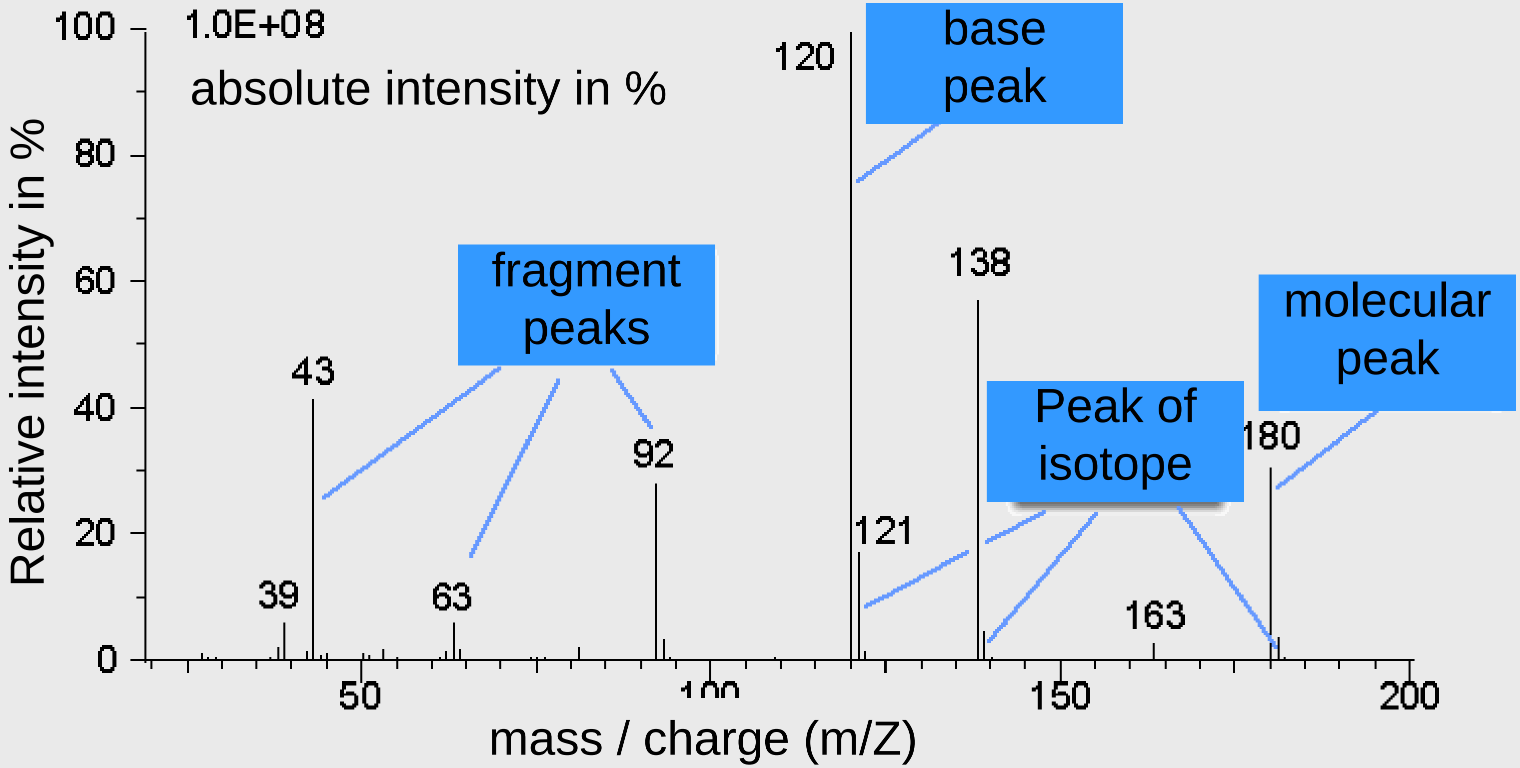
disadvantegous

- quantitative measurements are very often difficult to perform

Basics on mass spectroscopy

Basic principle

- gaseous products are ionized, the resulting cations are separated as function of their mass and charge (m/Z) and detected.
- In most cases for TG-MS quadrupol mass spectrometers are used
- Dependent on the energy of the electron beam used for ionization, different charged ions are generated (+1, **+2**, +3)



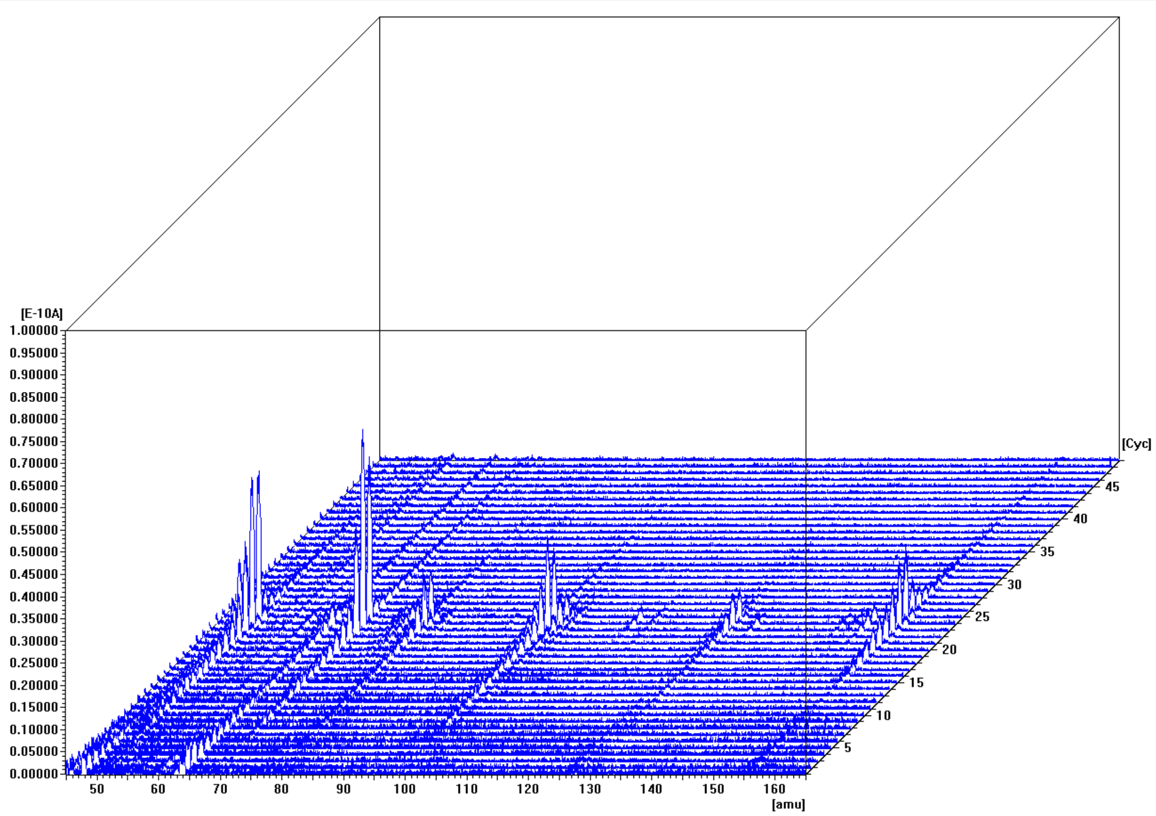
Scan modes

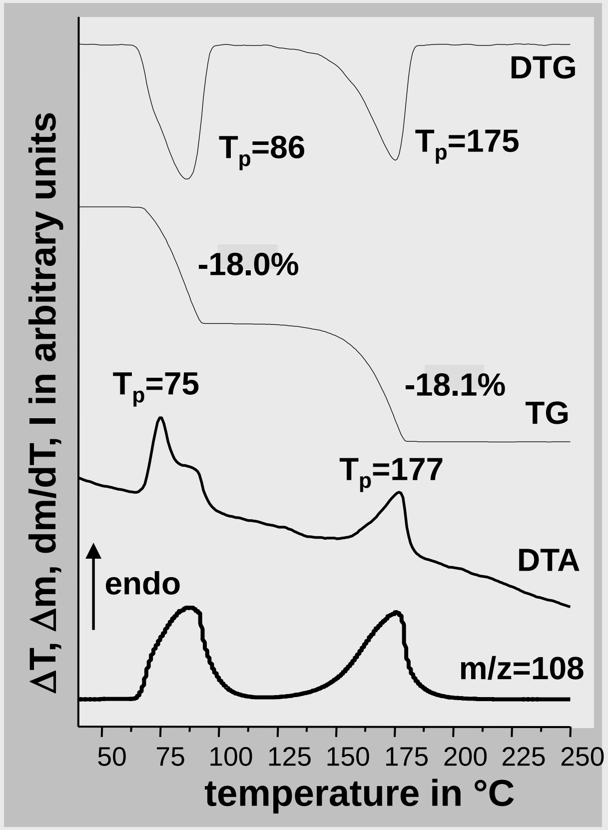
Analog scan

All masses were detected as function of time or temperature up to a given value

Trend scan

mid scan; **m**ulitple **i**on **d**etection; The intensity of selected signals were measured as function of time or temperature

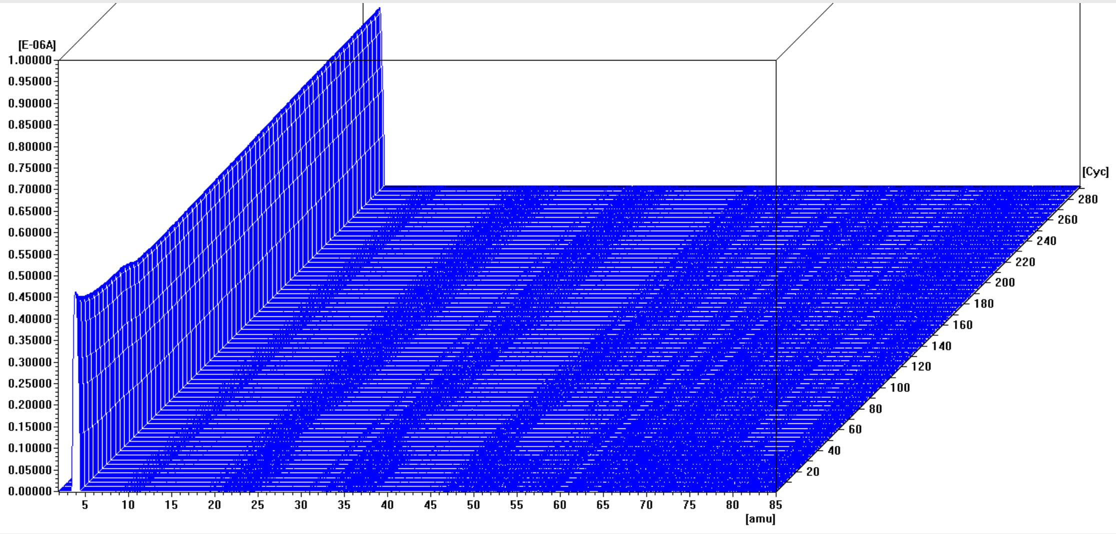




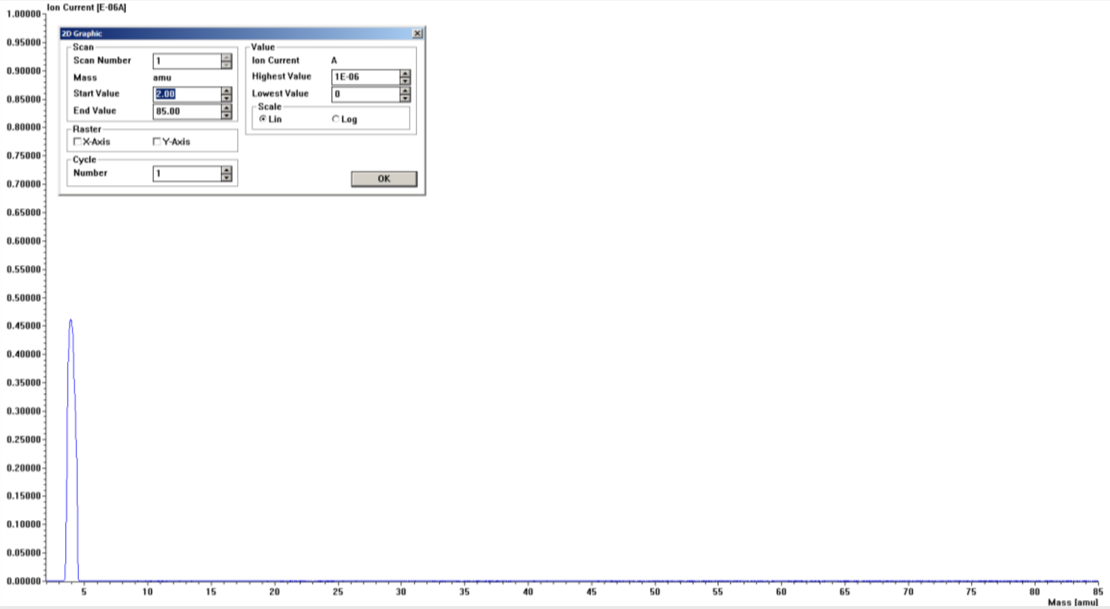
Problems with interpretation

- fragmentation and multiple ionization
- presence of natural isotops
- random overlap of the signals
- contaminations in the carrier gas
- wrong selection of the carrier gas

Influence of the carrier gas



The concentration of the carrier gas is much higher than those of the species which should be detected



Scan
Scan Number 1
Mass amu
Start Value 2.00
End Value 85.00

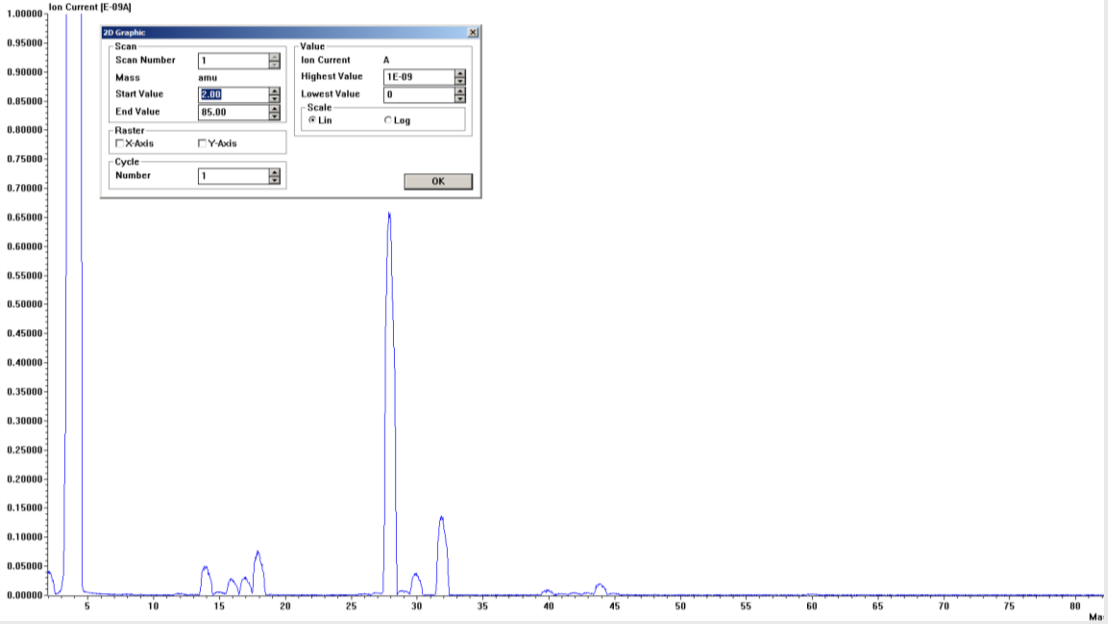
Raster
☐ X-Axis ☐ Y-Axis

Cycle
Number 1

Value
Ion Current A
Highest Value 1E-06
Lowest Value 0

Scale
● Lin ○ Log

Contaminations in the carrier gas



2D Graphic

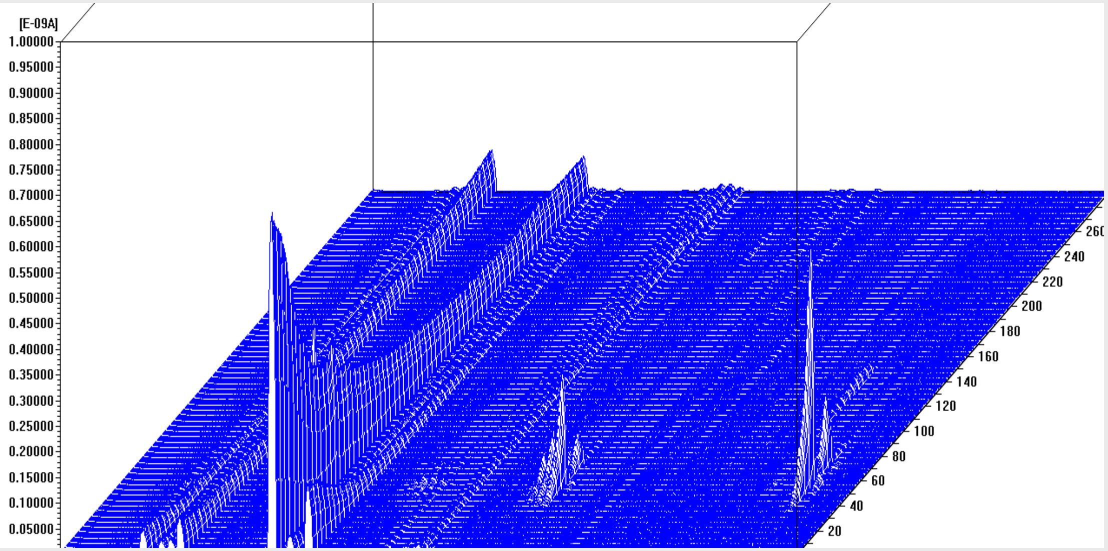
Scan
Scan Number: 1
Mass: amu
Start Value: 2.00
End Value: 85.00

Value
Ion Current: A
Highest Value: 1E-09
Lowest Value: 0
Scale: ● Lin ○ Log

Raster
☐ X-Axis ☐ Y-Axis

Cycle
Number: 1

OK



The carrier gas is always contaminated with different amount of other gases, which makes the interpretation much more difficult

Examples:

m/Z = 14: N_2; Z = 2

m/Z = 16: O_2; Z = 2

m/Z = 17: water; OH

m/Z = 18: water

m/Z = 28: N_2

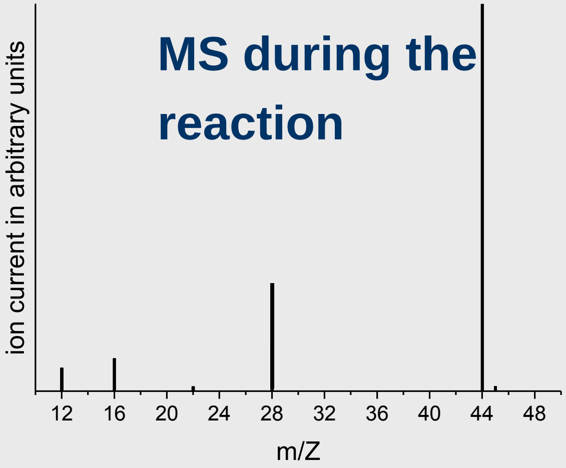
m/Z = 32 O_2,CO (CO from CO_2)

m/Z = 40: Ar

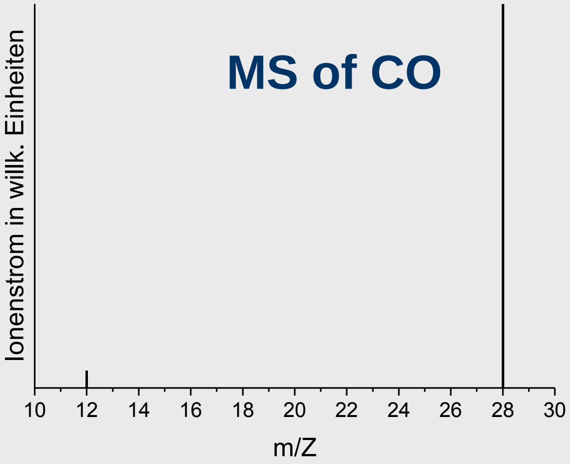
m/Z = 44: CO_2

Question

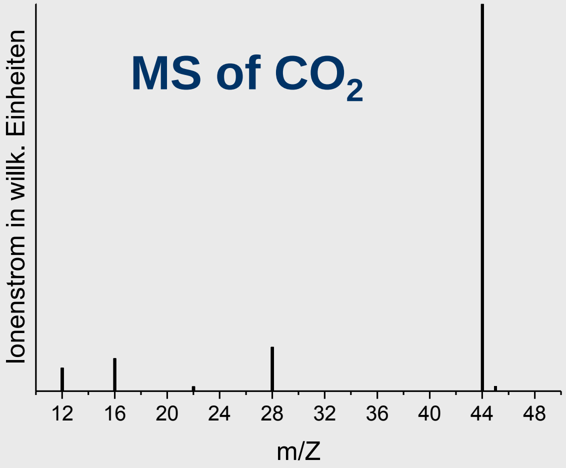
In a hypothetical reaction CO, CO_2 or a mixture of both gases is emitted and the MS measured in this reaction is shown below. What is emitted in this reaction?



MS during the reaction



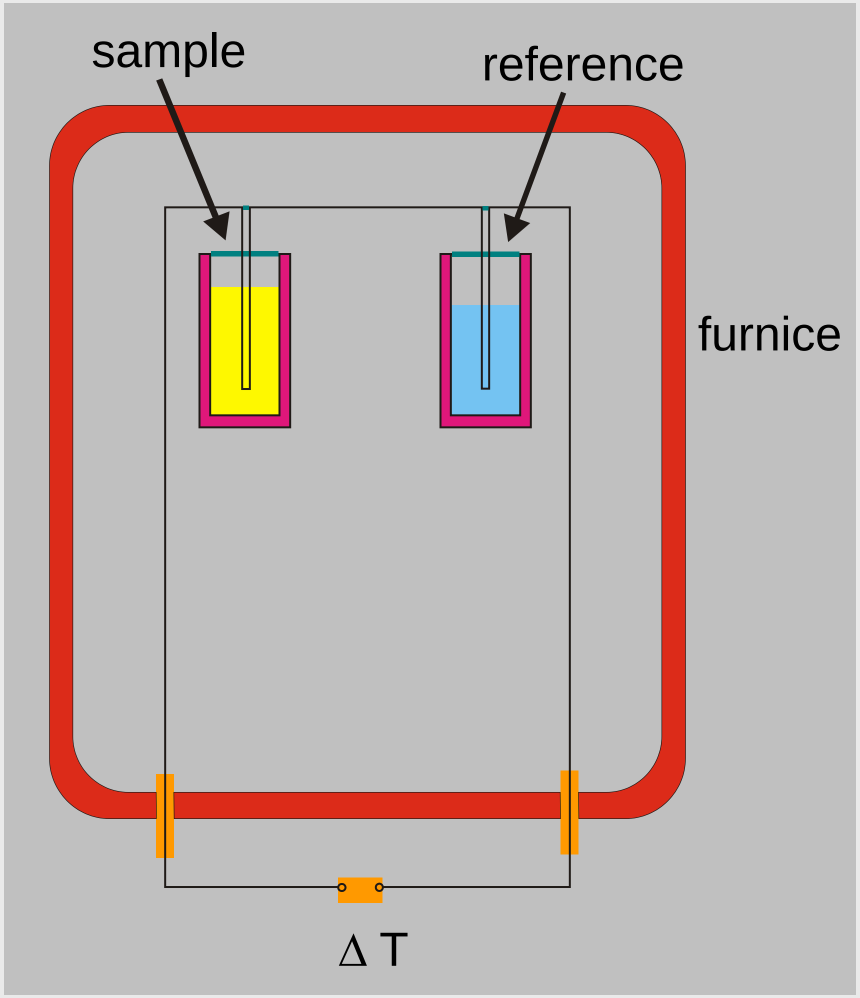
MS of CO



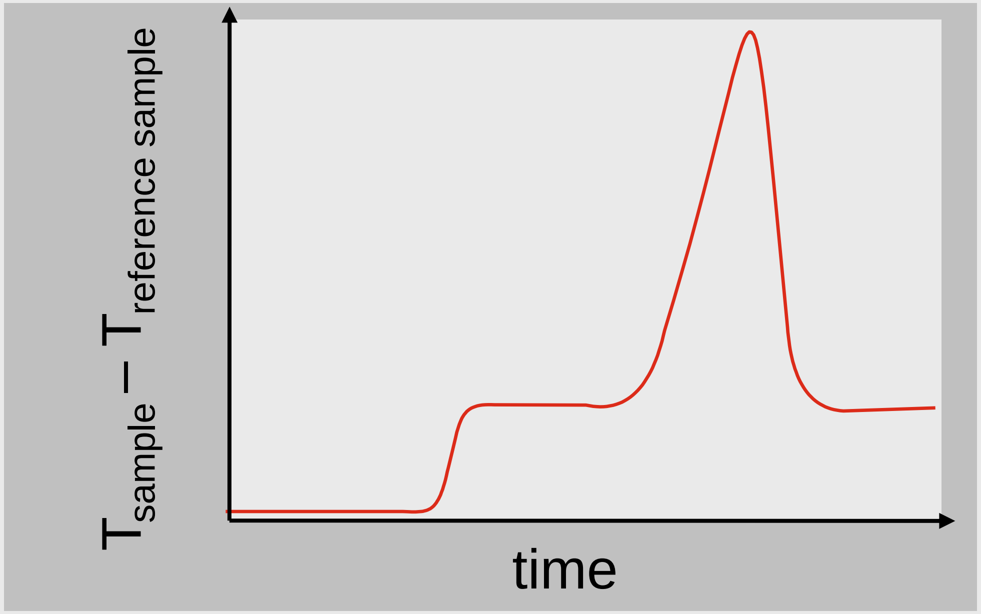
MS of CO_2

Button	Answer
1A	Only CO
2B	Only CO_2
3C	A mixture of both gases
4D	Cannot be answered based on only this spectrum

Differential thermoanalyses (DTA)



Differential Thermoanalysis (DTA) is a method in which the temperature difference between a sample and a reference sample is measured during a controlled temperature-time program.



Result:
Temperature and direction of a thermal event (endo or exo)

Question

A sample is heated with a constant heating rate.

What will happen if the sample start to melt?

Button	Answer
1A	The temperature of the sample still increases but with slower rate
2B	The temperature of the sample remain constant until melting is finished
3C	The temperature of the sample increases with the same rate
4D	The temperature of the sample decreases

Idealised temperature time curves during melting

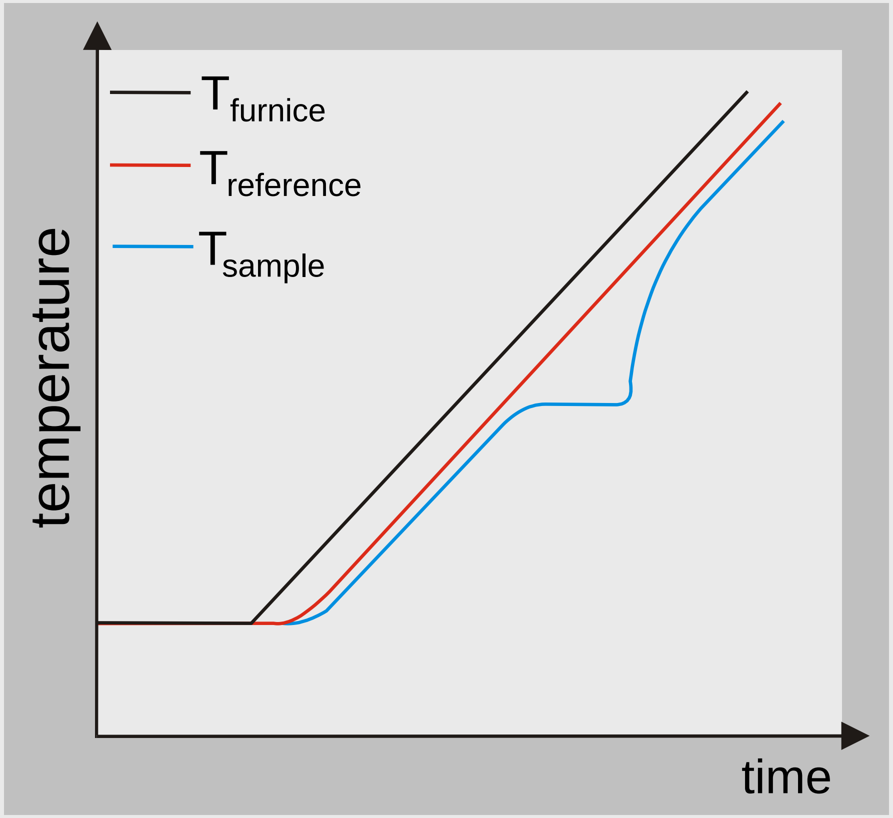
Measure of ΔT as function of time.

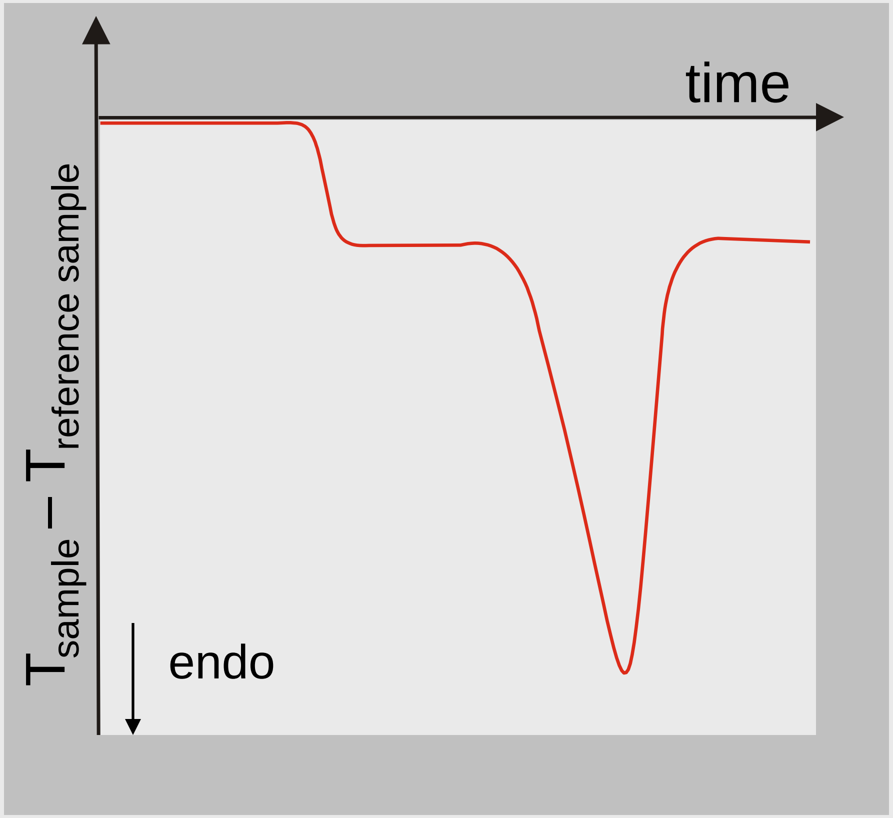
Requirement: linear interrelation between time and reference temperature.

ICTA: endothermic goes down and exothermic goes up

DIN 51005: endothermic goes up and exothermic goes down

In figures (publications) the direction (endo or exo) should always be given!





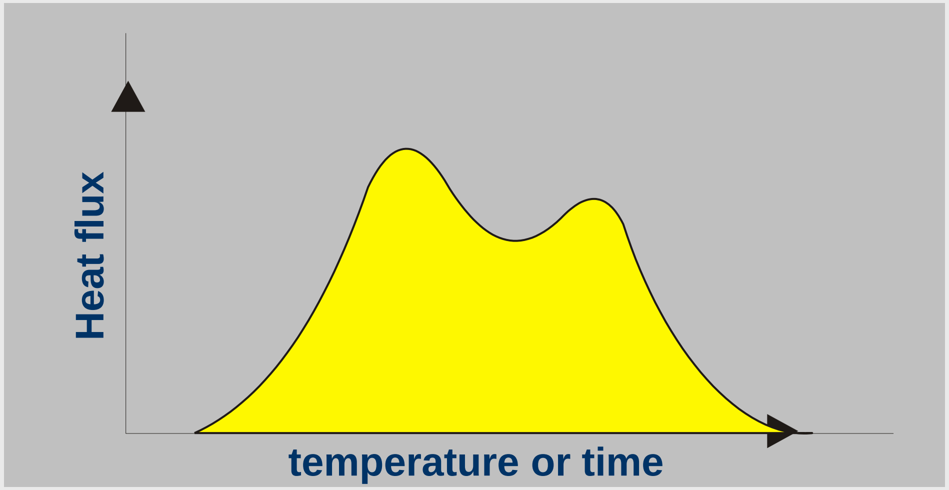
Question

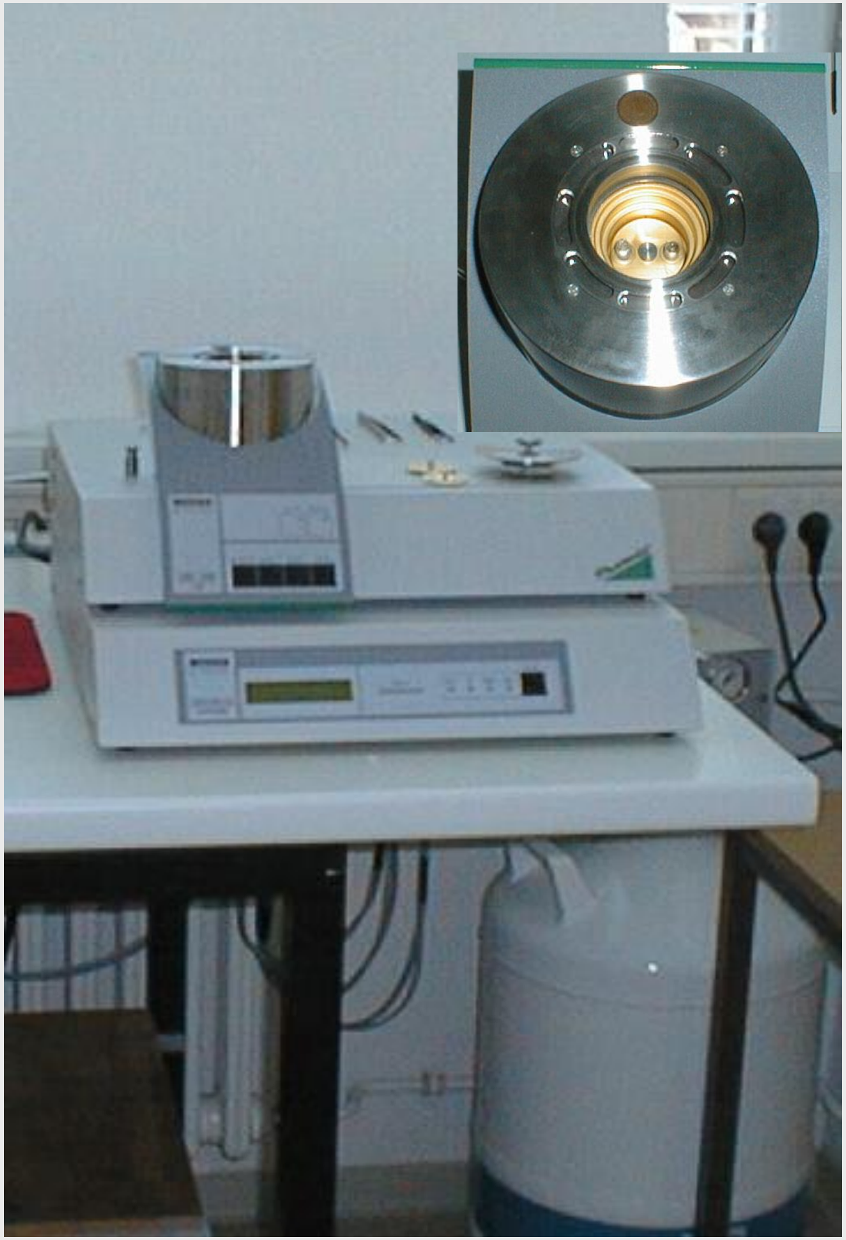
At which position of a DTA peak a thermal event is finished?

Button	Antwort
1A	At the beginning of the peak
2B	At the peak maximum
3C	At the end of the peak

Differential scanning calorimetry (DSC)

Differential Scanning Calorimetry (DSC; Dynamische Differenz-Kalorimetrie, DDK) is a method which monitors the differences in heat-flux between a sample and a reference sample during a controlled temperature-time program

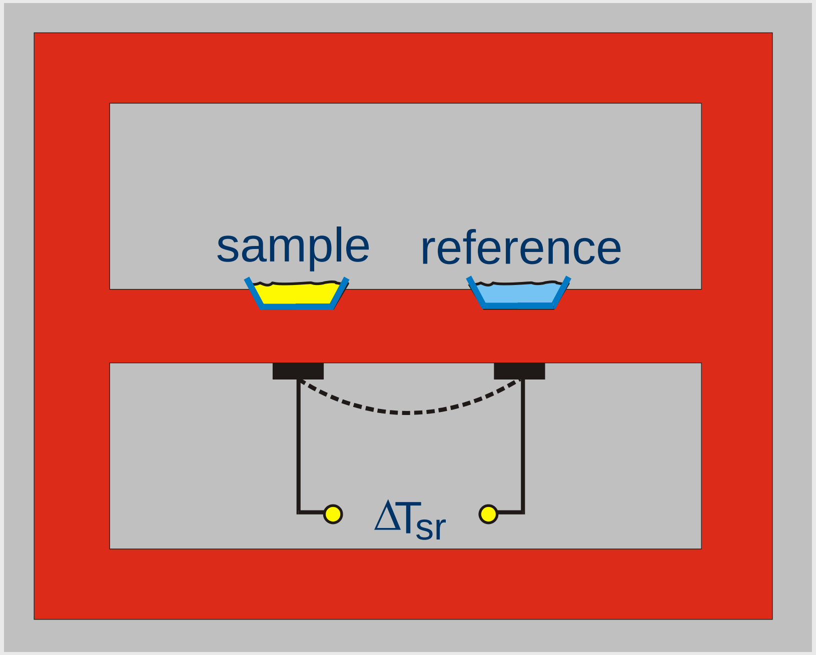




Advantegous over DTA

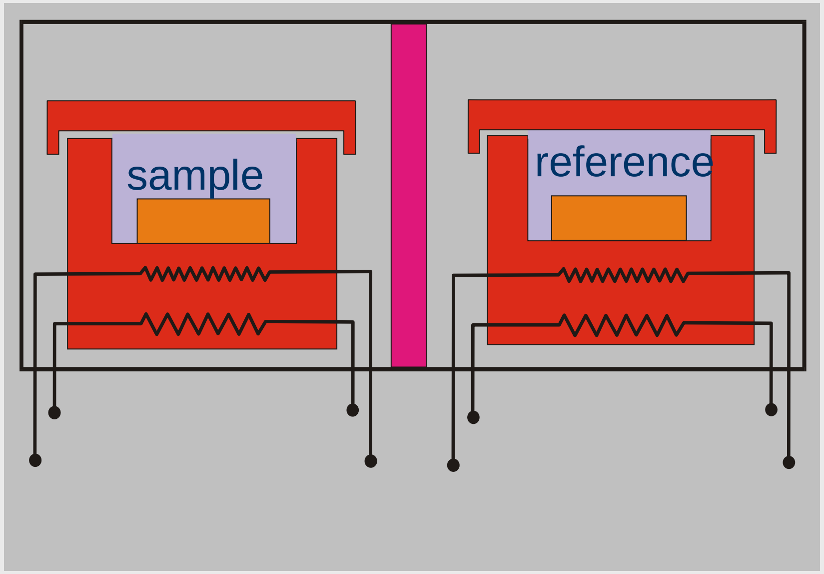
- ❖ Increased sensitivity
- ❖ Determination of the heat flow volume (instrument can be calibrated)
- ❖ Determination of the heat capacity

Measured variable in differential scannning calorimetry



Heat flux DSC

- ❖ Same principle like DTA
- ❖ ΔT is measured
- ❖ ΔT is proportional to the heat flux



Power compensating DSC

- ❖ Compensation of the reaction heat in order that ΔT is always zero
- ❖ Directed measurement of the electrical power

The reference sample (reference)

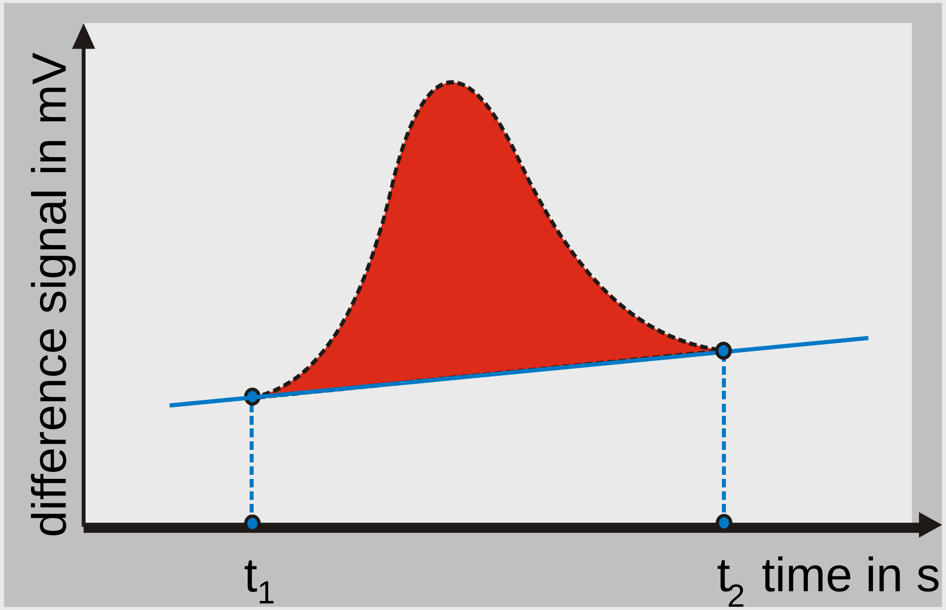
In DTA and DSC reference samples are used in order to ensure that always the same amount of heat is transfered to the sample and reference sample

Standards for a reference sample:

- Behaviour as function of temperature must be known
- No reaction of the reference sample in the temperature range which is investigated
- If possible comparable heat capacity of reference and sample

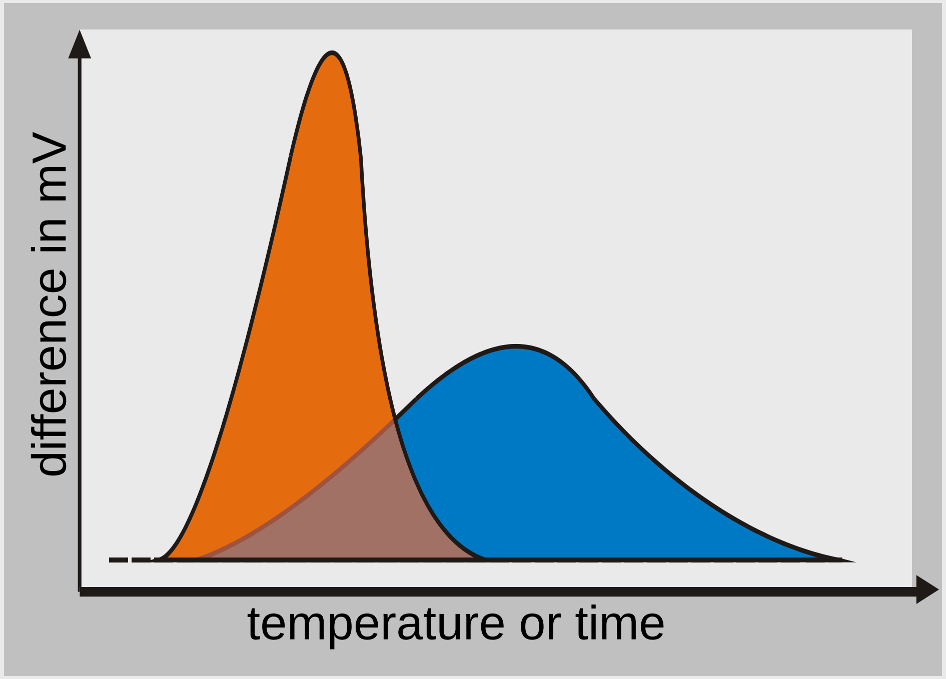
In the case of small sample mass and not to high demand for accuracy measurement can be performed only with an empty cruicible

Measured curve



Area between measured curve and baseline is proportional to the heat flow

Instrument must be calibrated for temperature and heat quantity using reference materials



Requirements for calibration (transition from DTA into DSC)

Peak area should not depend on external parameters like e.g. heating rate

Characteristic temperatures

T_i = Temperature of the start of a reaction (first deviation from baseline)

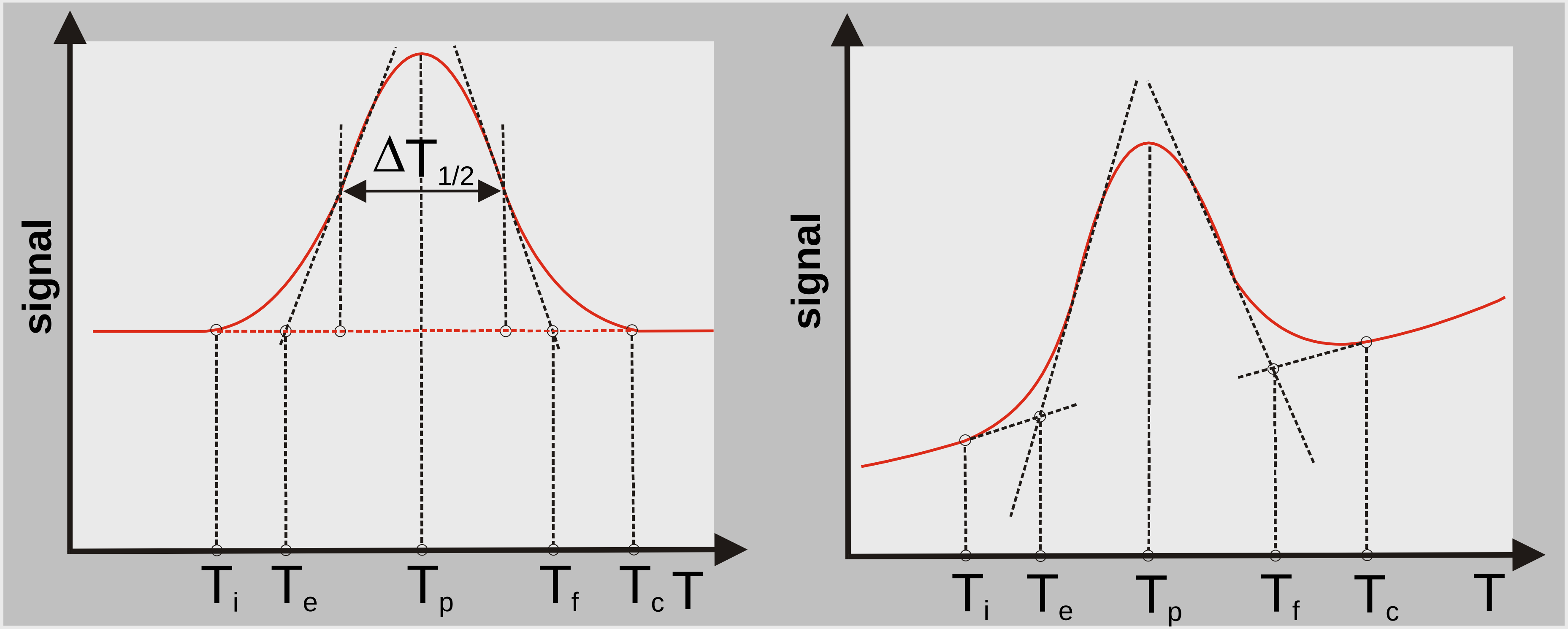
T_e = extrapolated onset temperature (intersection of the baseline with the tangen of the peak

T_p = peak temperature

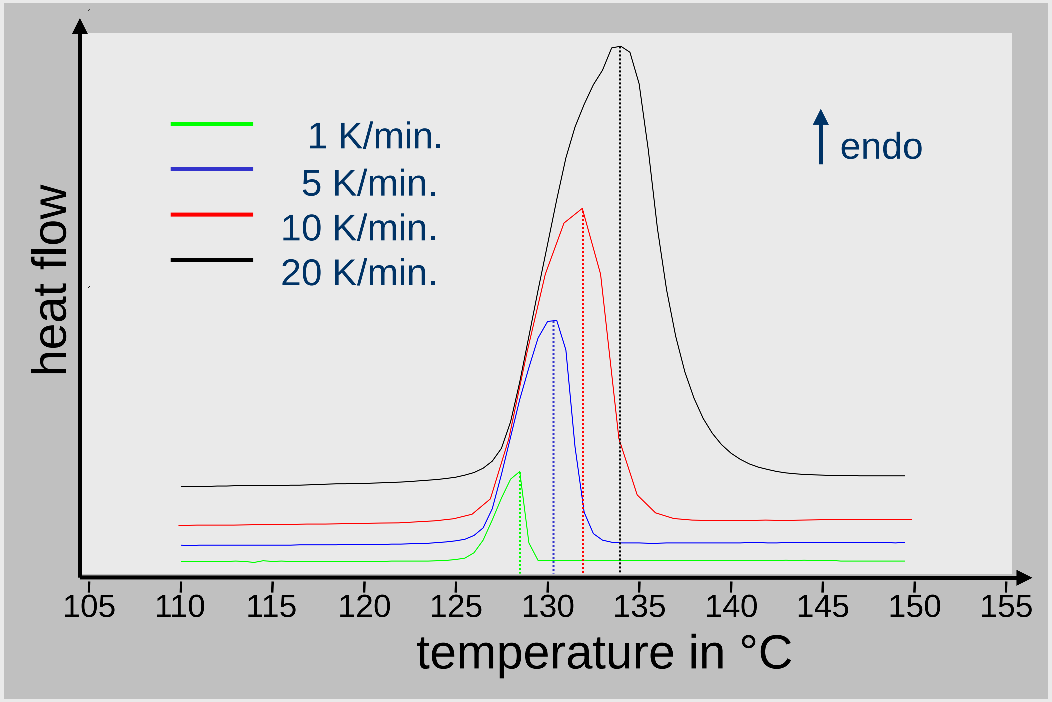
T_f = extrapolated end temperature

T_c = temperature at the end of a reaction

$\Delta T_{1/2}$ = half-with



Melting point of di-tert.butyl-biphenyl at different heating rates



Please note: extrapolated onset temperature does not depend on heating rate and should always be given if possible

If always the same heating rate is used, peak temperatures can also be used

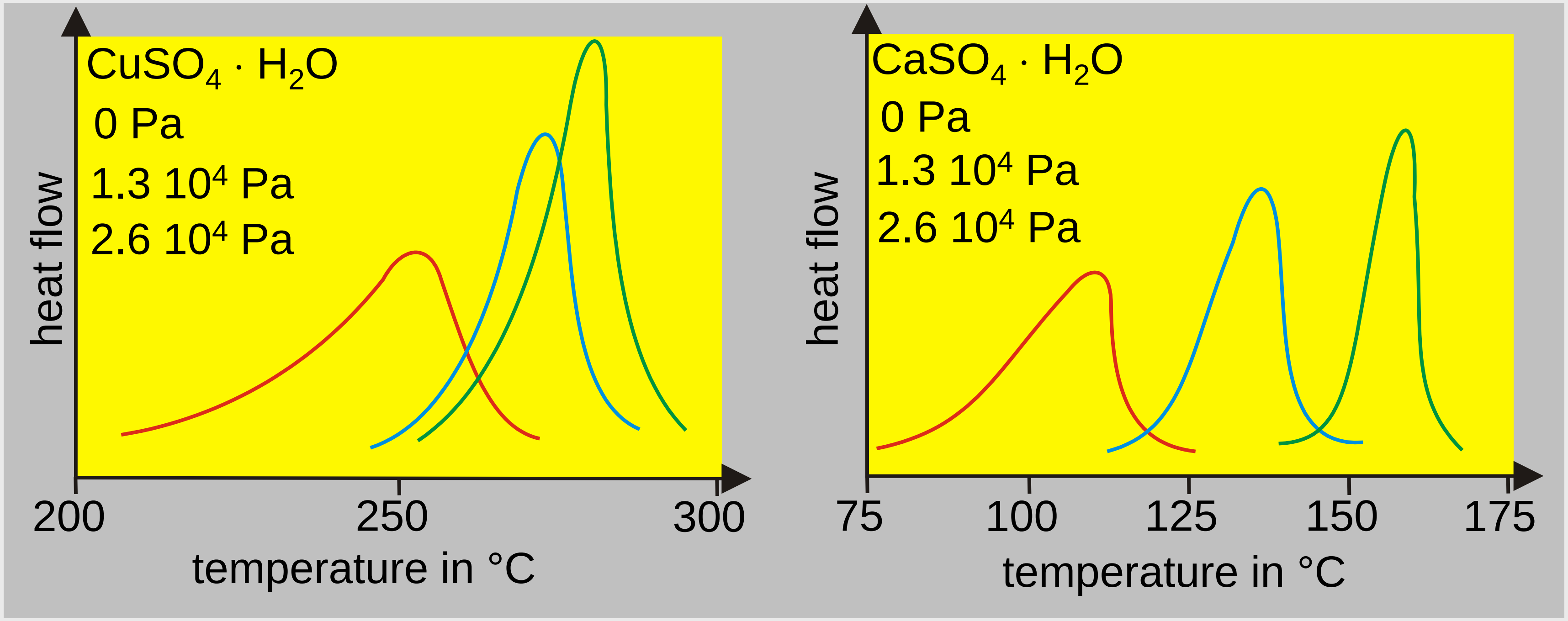
Influence of the gas pressure

If a gaseous product of a reversible reaction is a component of the atmosphere in the sample room, its partial pressure will influence the begin of a reaction

Influence of the water vapor pressure on the decomposition of hydrates

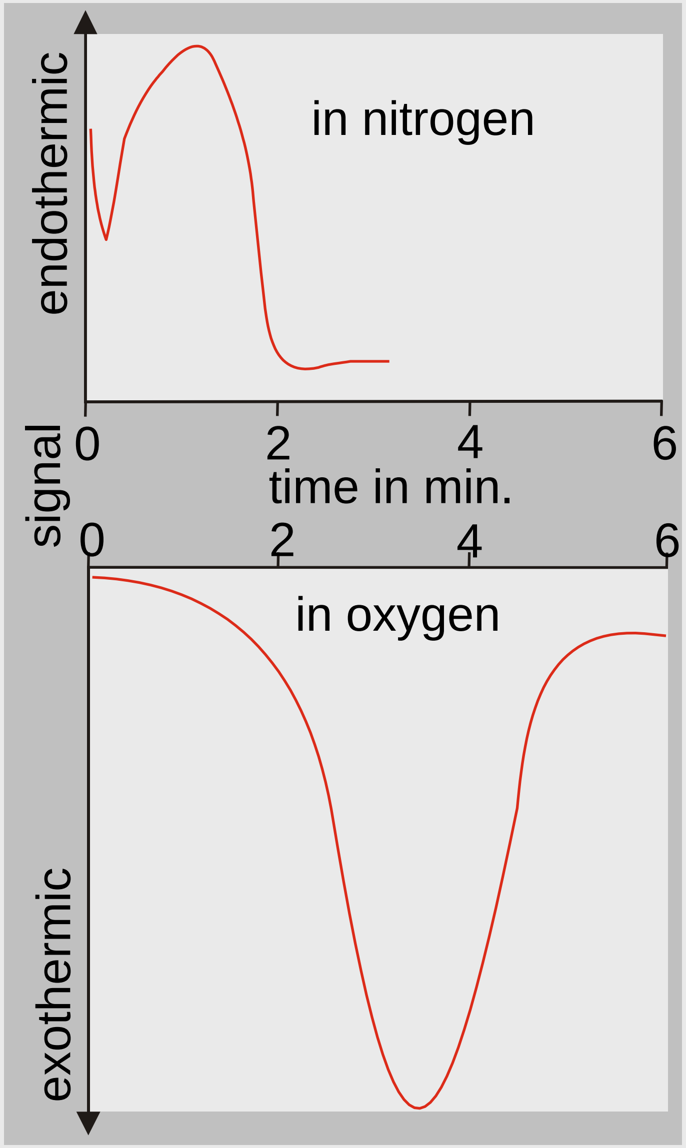
$$CuSO_4 \cdot H_2O \rightarrow CuSO_4 + H_2O\uparrow$$

$$CaSO_4 \cdot H_2O \rightarrow CaSO_4 + H_2O\uparrow$$



Influence of the nature of the gas

Thermal decomposition of $NiC_4O_4 \cdot H_2O$



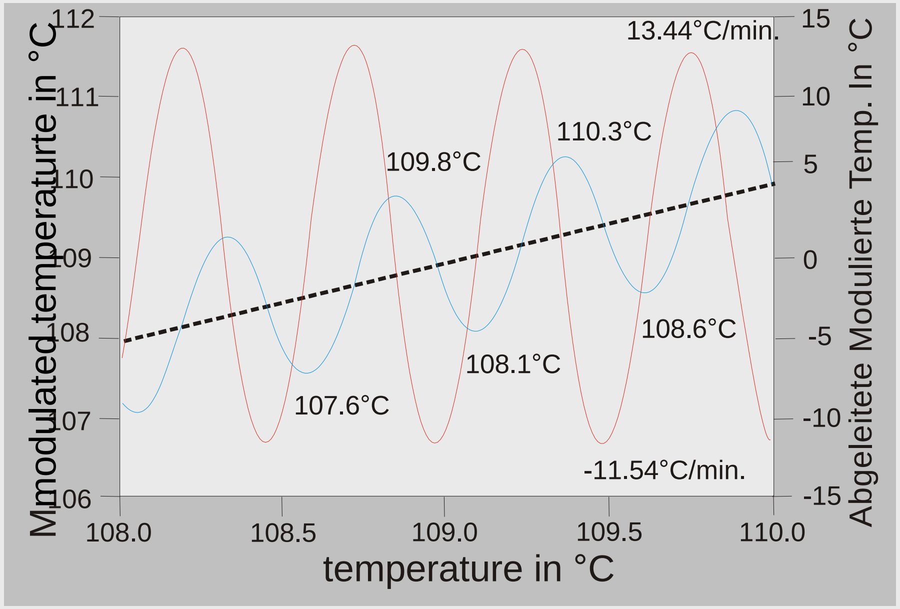
In nitrogen endothermic decomposition into Ni, CO and water

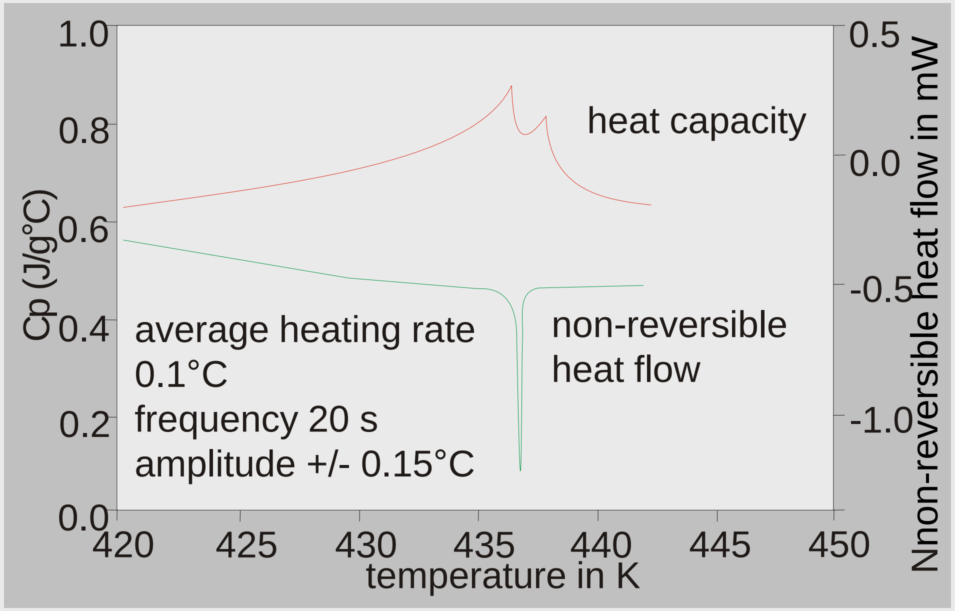
In oxygen exothermic decomposition because of oxidation of CO into CO_2

Modulated differential scanning calorimetry

Differences to conventional DSC:

Instead of a linear heating rate a sinusoidal modulated heating rate is used

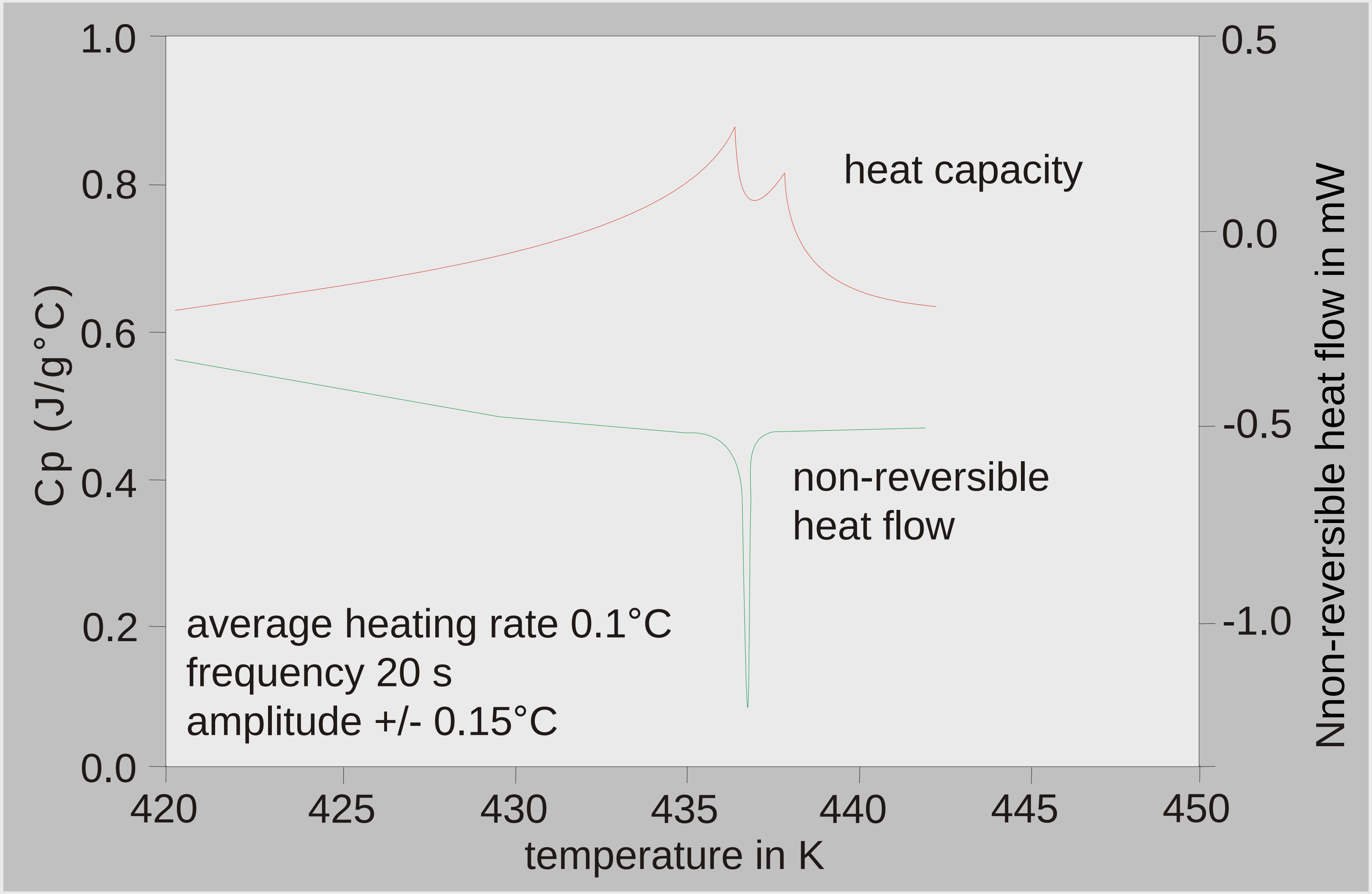




Advantegous

- ❖ Increased sensitivity and resolution
- ❖ Separation of complex transition is much easier
- ❖ Directe determination of heat capacity and heat flow within one experiment
- ❖ **Reversible and irreversible reactions can be separated in one measurement (two different curves are achieved)**

Phase transitions in sodium nitrate



Special instrumentation: High Speed and High Pressure DSC

High Speed DSC (HDSC)

At slower heating rates the resolution becomes better but the sensitivity is reduced!
Solution: Usage of high speed DSC (Heating rate from 50 to 500 C/min).

Example:

Detection of very small amounts of amorphous content because on fast heating rate the glass transition becomes visible, which cannot be detected at low heating rates.

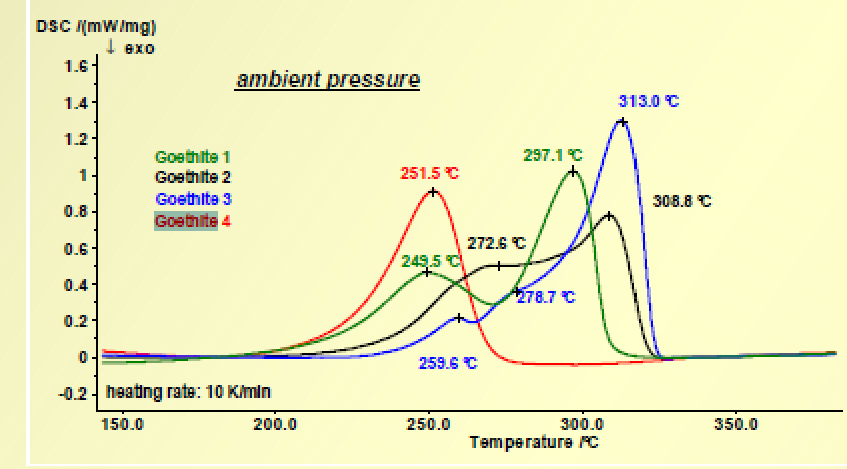
High Pressure DSC (HPDSC)

DSC measurements up to 1000 bar are possible

Examples:

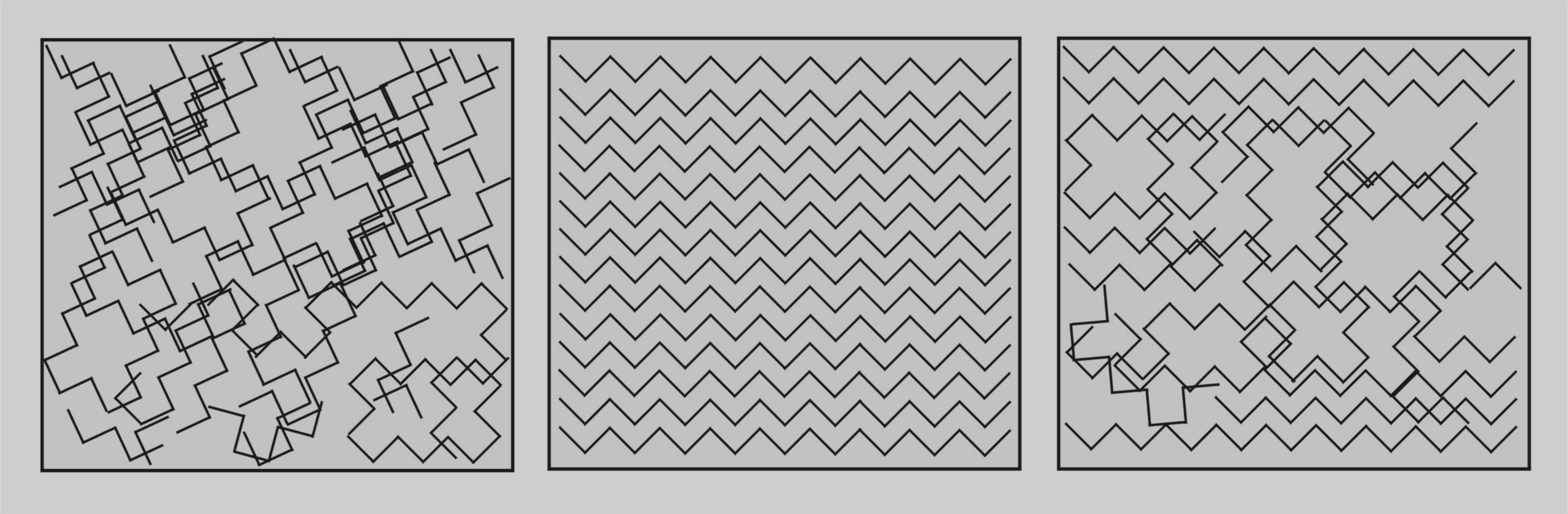
Formation and dissociation of gas hydrates
Investigations under gas supercritical conditions
Investigations on dehydration of goethite to Hematite under high pressure (right)

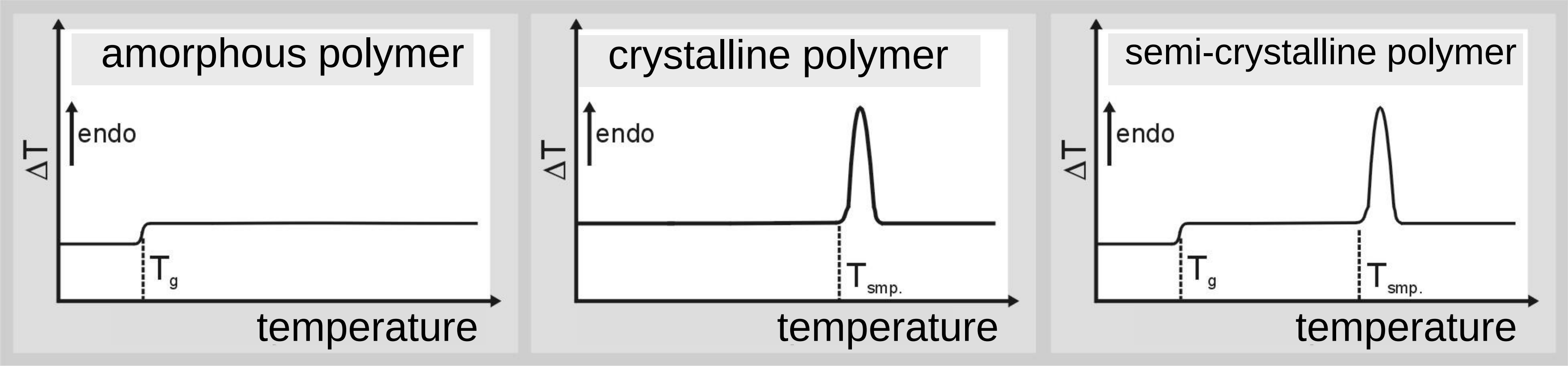
$$\mathbf{2\ \alpha\text{-FeOOH} \longrightarrow \alpha\text{-Fe}_2\text{O}_3 + H_2O}$$



Example: determination of the glass temperature and crystallinity

glass transition: transition of e.g. a polymer from the glassy state into the rubbery-elastic state





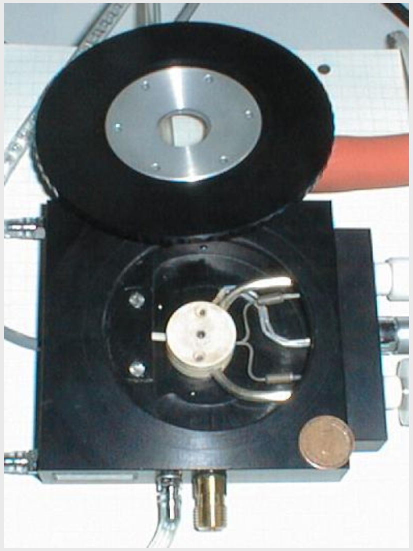
Question: determination of the crystallinity or amorphous content

What is needed for the quantitative determination of the crystallinity (amount of crystalline content) of a semi crystalline compound?

Button	Antwort
1A	melting point of a sample with 100% amorphous content
2B	melting enthalpy of a sample with 100% crystallinity
3C	melting point of a sample with 100% crystallinity
4D	heat capacity of a sample with 100% crystallinity
5E	melting enthalpy of a sample with 100% amorphous content
6	freezing point of a sample with 100% crystallinity

Thermomicroscopy

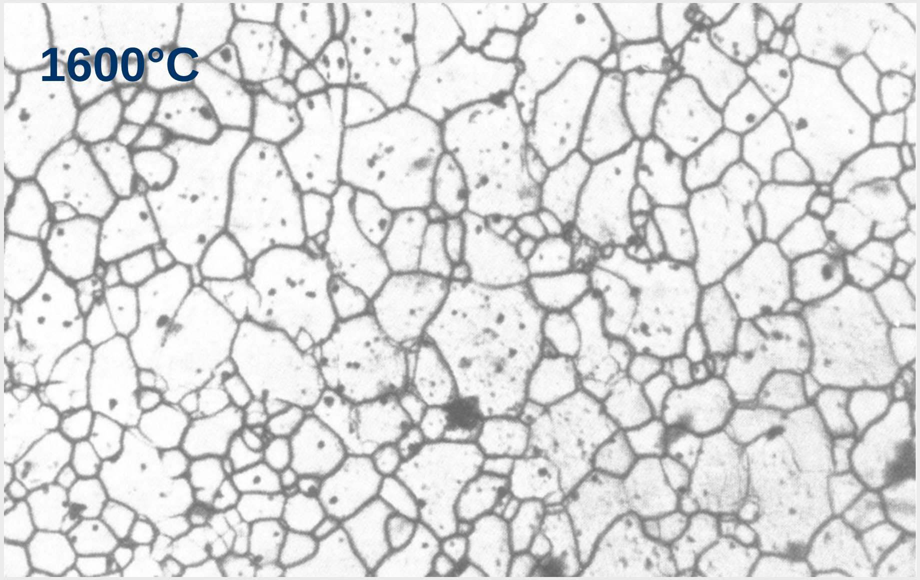
Thermomicroscopy is a method in which a sample is observed using a microscope, applying a controlled temperature time program.



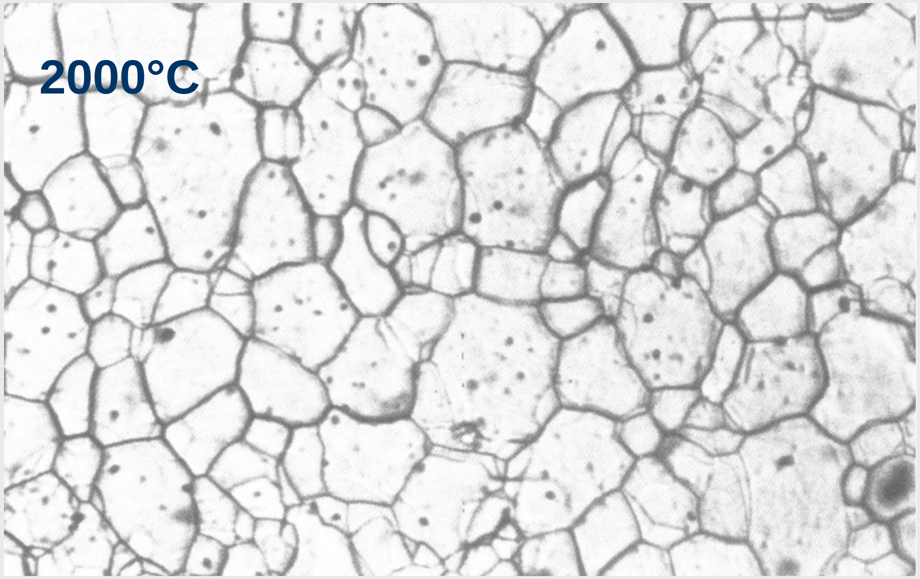
Possible applications

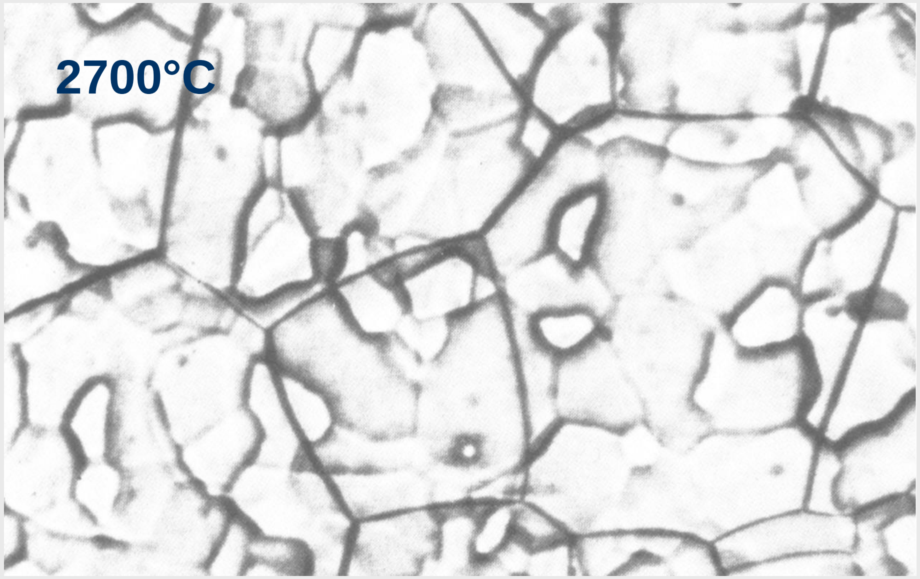
- Investigations on nucleation and crystal growth
- Investigations on the corrosion of materials
- Investigations of phase transitions (e.g. polymorphic phase transitions)
- Investigations on chemical reactions
- Investigations on the phase changes in liquid crystals

Recrystallisation of a metal


1600°C

Large crystals growth on the costs of the smaller particles

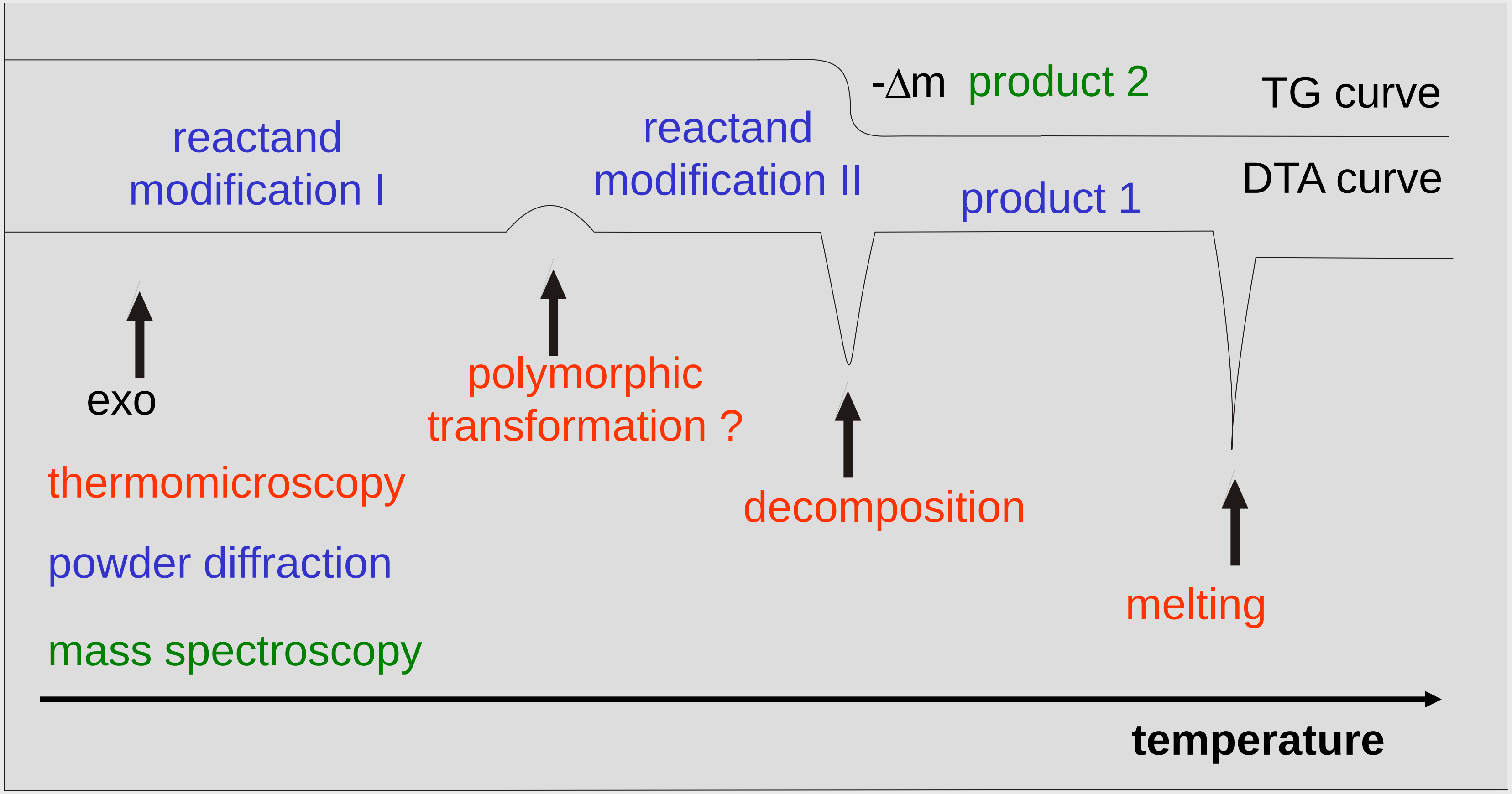

2000°C


2700°C

Critical view on thermoanalytic methods

The result of one single thermoanalytical experiment without any further information about the sample, its reactions and its reaction products has no significant meaning.

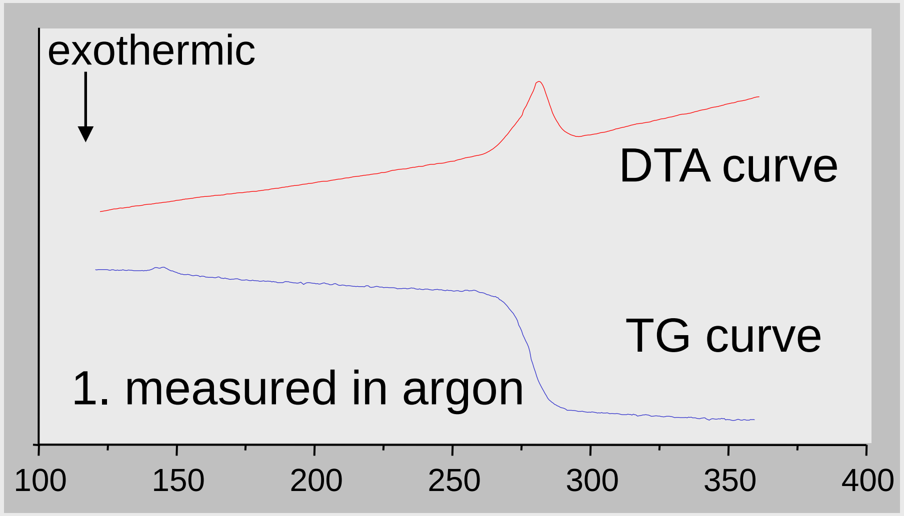
Consequently, different methods should always be combined

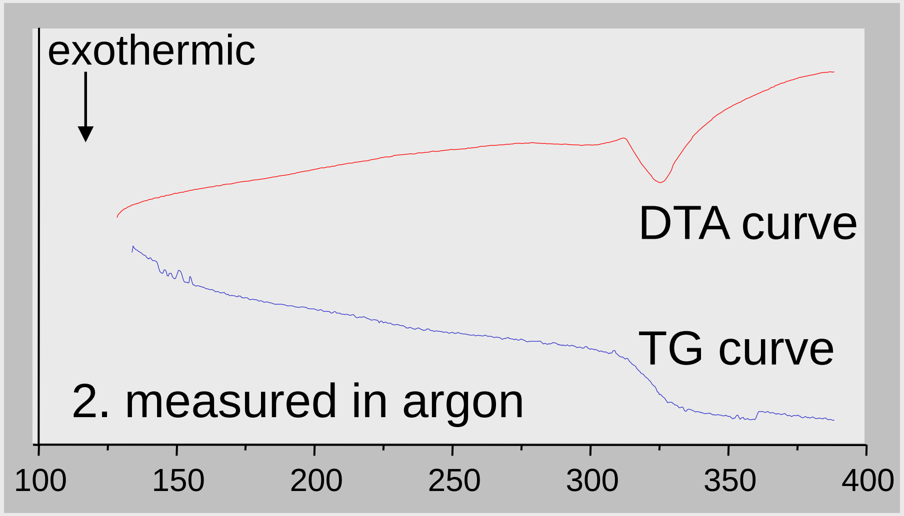


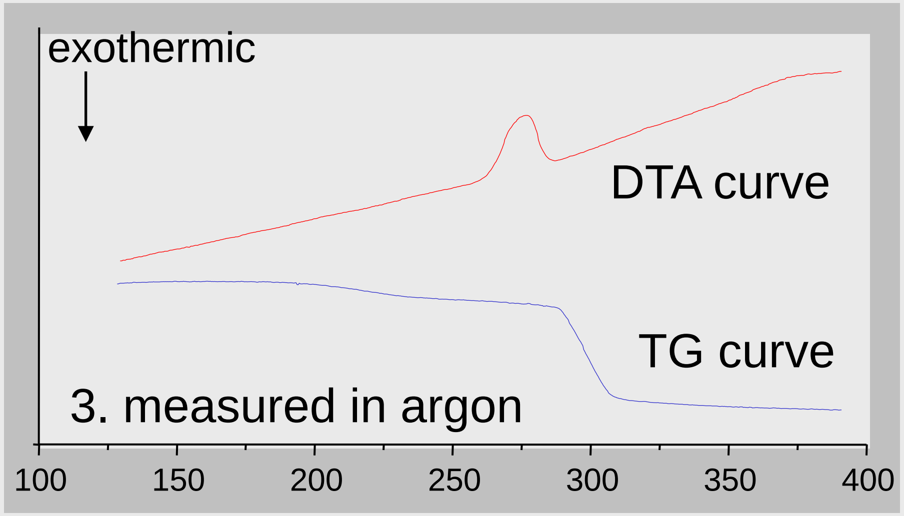
Murphy's law: whatever can go wrong, will go wrong.

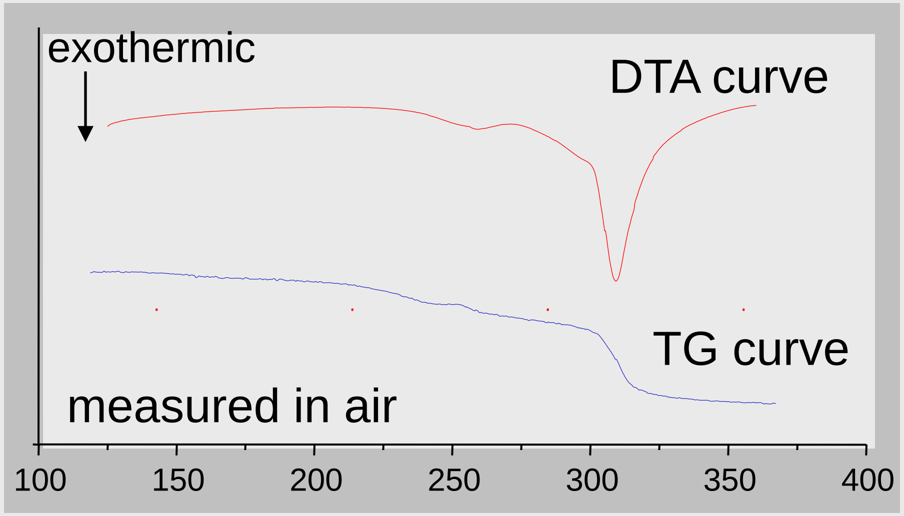
- One measurement is not enough -

Thermogravimetric investigations on $Mn_2Sb_2S_5 \cdot$ ethylamine

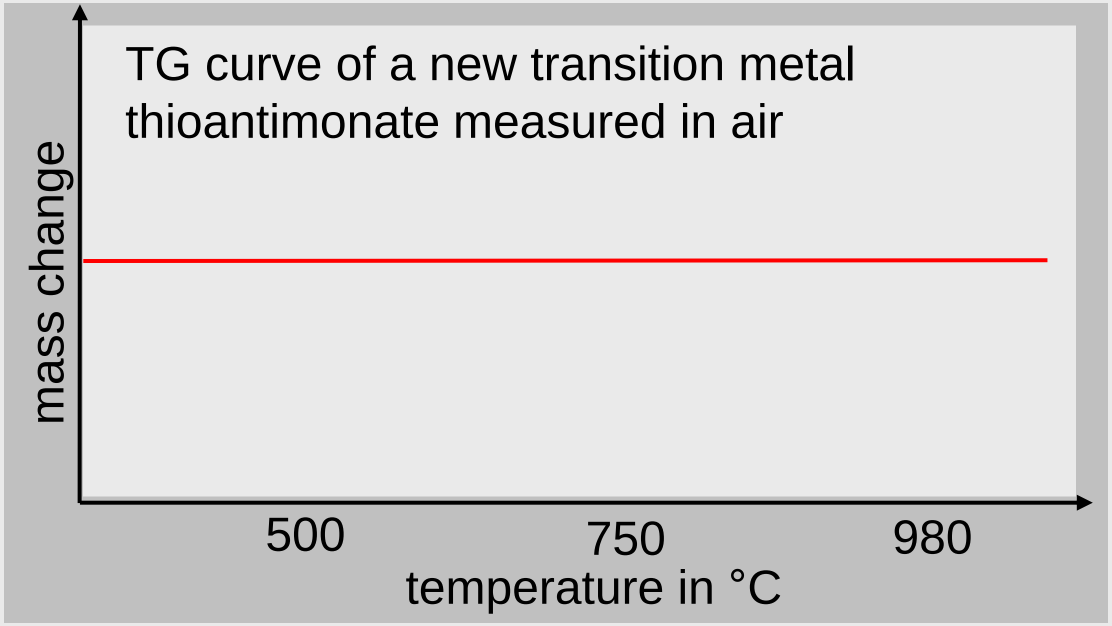








Murphy's law: whatever can go wrong, will go wrong.

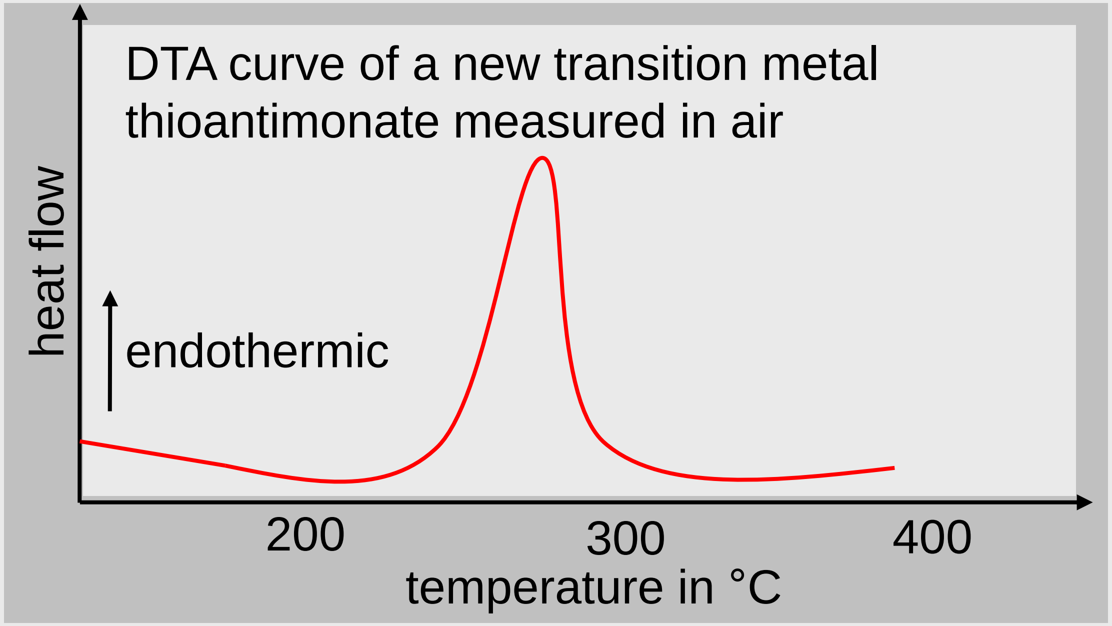


Problem

TG curve surprising because of the unusual high stability of the material

Solution

balance was locked by accident



Problem

Reaction should be exothermic

Solution

sample and reference was exchanged by accident, which change the sign of the signal

Supplemental

Additional methods

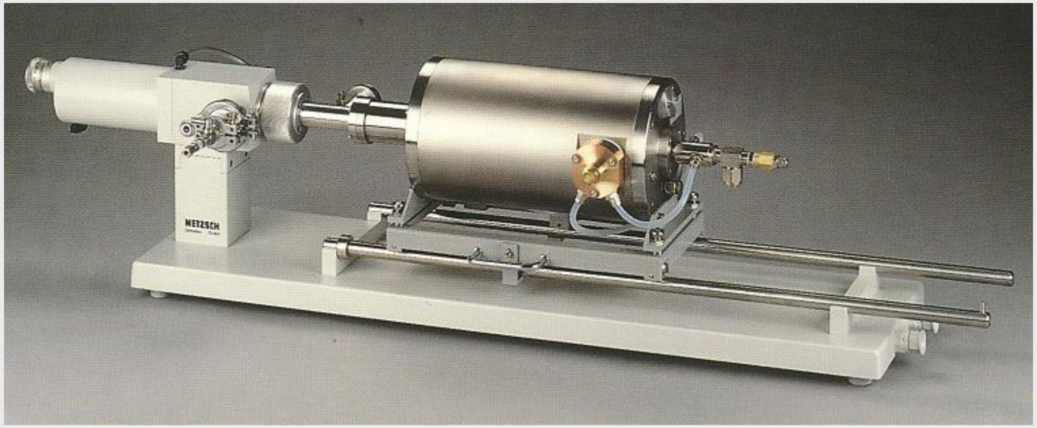
Dilatometry (**DIL**)

Thermo**m**echanical **A**nalysis (**TMA**)

Dynamic **M**echanical **A**nalysis (**DMA**)

Dilatometry (DIL)

Dilatometry is a method in which changes in volume of a compound are measured applying a controlled temperature time program.



Possible applications

- Determination of the coefficient of expansion (lengths, volume)
- Investigations of first order phase transition (this method is very sensitive against changes in volume)
- Investigations on the sintering behaviour of e.g. ceramcis
- Measurement of the change in volume during a magnetic transition
- Investigations on the swelling behaviour of e.g. paper

Thermomechanical (TMA) and dynamic mechanic analysis (DMA)

Thermomechanometry is the measurement of a change of a dimension or a mechanical property of a sample while the sample is subjected to a controlled temperatur time program and a constant force.

When the force is changed with a frequency and amplitude, this method is called Dynamic mechanical analysis.

Possible applications

- ❖ Determination of the storage modulus and the loss modulus
- ❖ Determination of transition temperatures at viscoelacity behaviour
- ❖ Determination of the glass temperature (much more sensitive than e.g. DSC)
- ❖ Investigations on the compatibility of sandwich materials
- ❖ Investigations on curing processes
- ❖ Fatigue testing and determination of the brittleness temperature