Thermal Analysis: methods, principles, application

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Lecture on Thermal analysis

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Heat

$$Q = \Delta U + \int_{V_0}^{V_f} p\,dV = \int_{T_0}^{T_f} C_p\,dT = \Delta H = [J] = [W \cdot s]$$

Heat Capacity

$$C = Q/\Delta T, \quad [J/mol/K]$$

$$C_p = \left(\frac{\partial Q}{\partial T}\right)_p = \left(\frac{\partial H}{\partial T}\right)_p$$

Thermal conductivity

$$\lambda = a \cdot C_p \cdot \rho = [J/s/m/K] = [W/m/K]$$

a – thermal diffusivity, m^2/s

Definition of TA

Group of physical-chemical methods which deal with studying materials and processes under conditions of programmed changing's of the surrounding temperature.

Differential Heat equation

$$\frac{\partial T}{\partial t} = \frac{\lambda}{\rho \cdot C_p} \cdot \left(\frac{\partial^2 T}{\partial z^2} + \frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \cdot \frac{\partial T}{\partial r} + \frac{1}{r^2} \cdot \frac{\partial^2 T}{\partial \varphi^2}\right) + \frac{Q}{\rho \cdot C_p} \cdot \frac{\partial \alpha}{\partial t}$$

Main Thermo-physical properties of materials

Property/Characteristic	Mathematical expression	Unit	Method
Thermal conductivity	$\lambda(T)=a \cdot C_p(T) \cdot \rho(T)$	W/(m*K)	LFA
Thermal linear expansion	$\varepsilon=1/r*(dr/dT)$	%/K	DIL
Enthalpy	$dQ/dt=m \cdot C_p \cdot (dT/dt)$	J/g	DSC
Weight/Composition/ Conversion	$\alpha=(m_o-m_i)/m_o$	%	TG

r, φ - polar coordinates

z - applicate

λ – Thermal conductivity , J/(cm*s*K)

C_p – Thermal capacity, J/(g*K)

ρ– density, g/(cm^3)

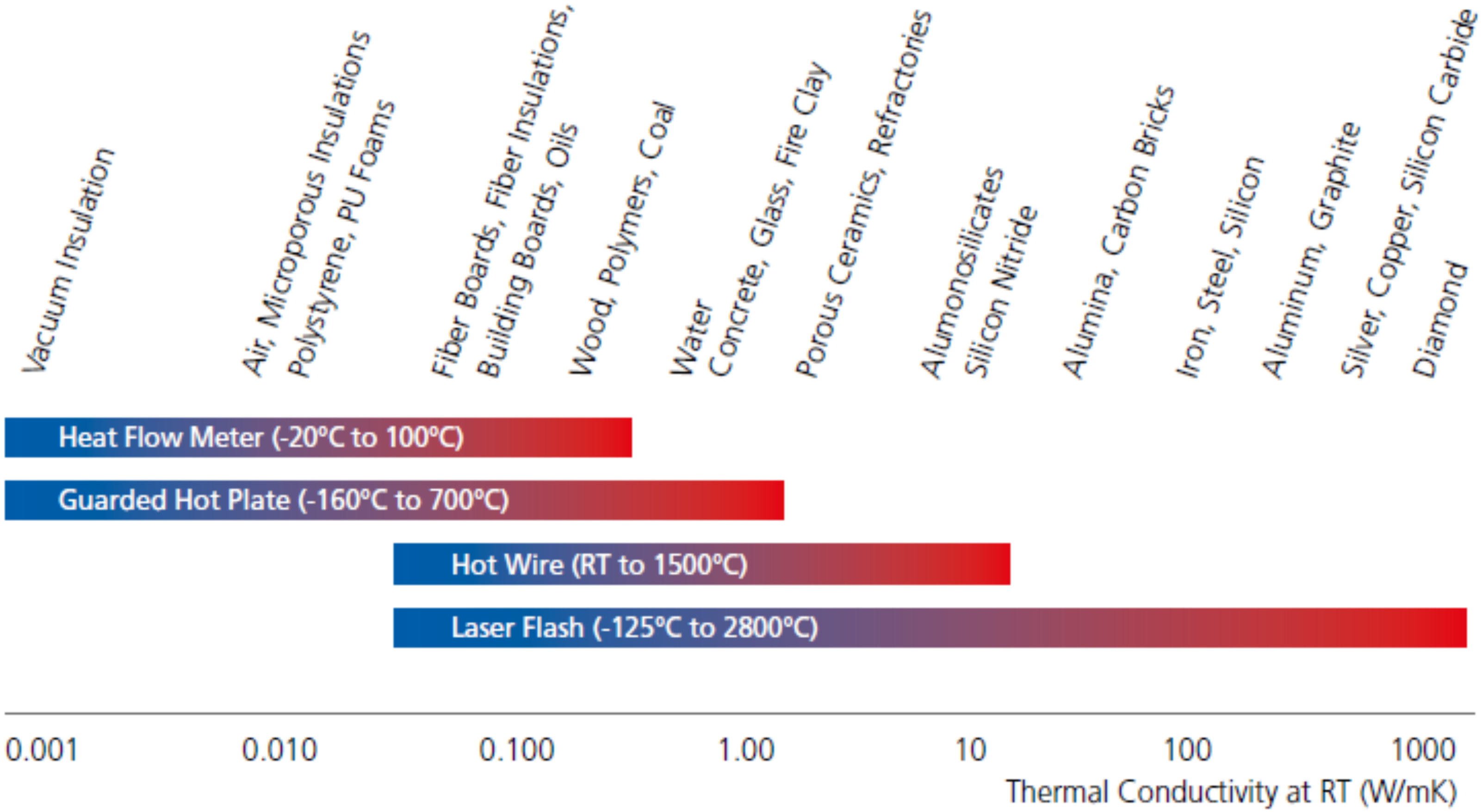
Q – heat of the process (reaction)

α – degree of conversion

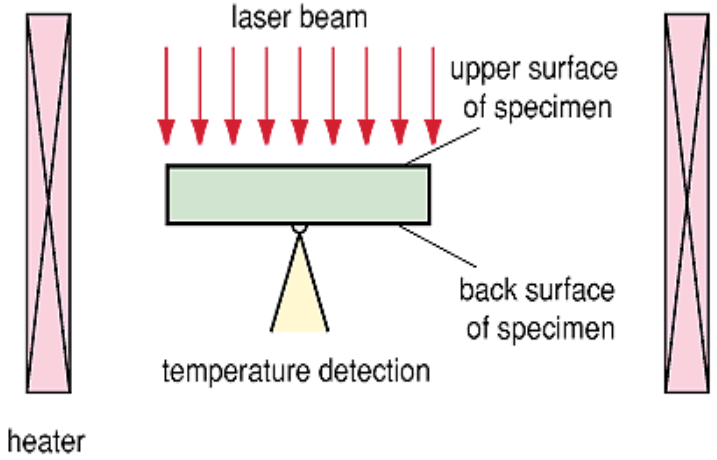
$$a = \frac{\lambda}{\rho C_p}$$

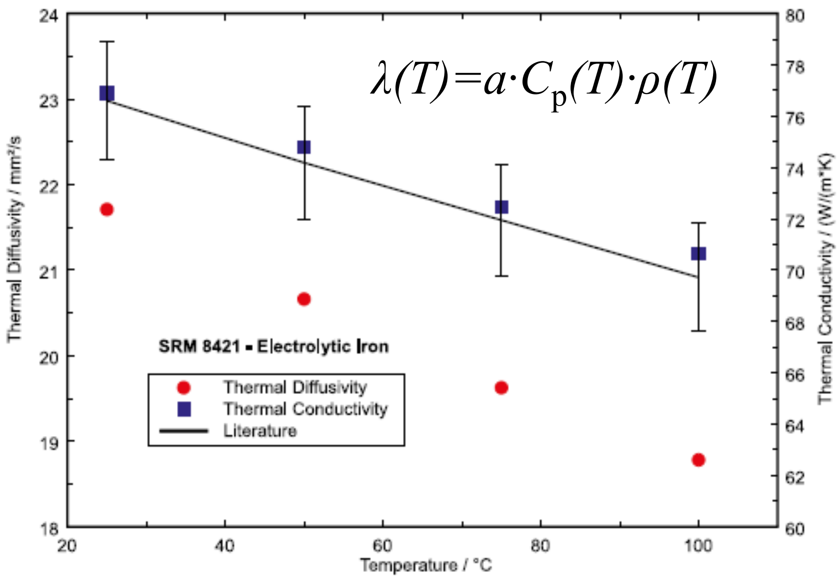
a – thermal diffusivity, cm^2/s

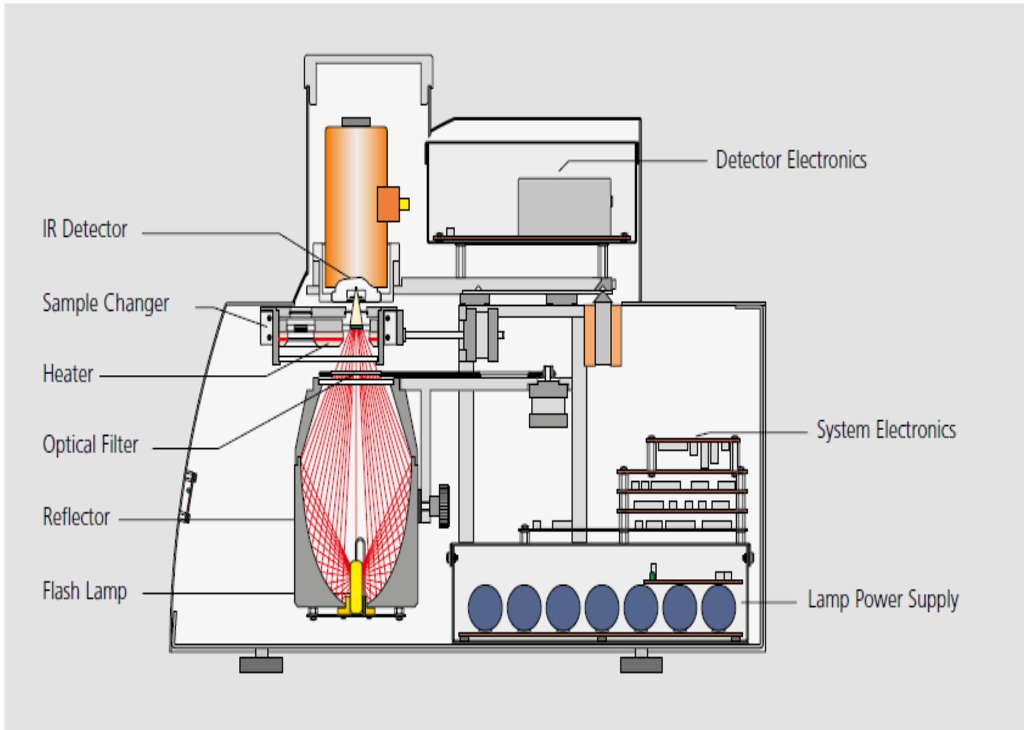
Thermal conductivity, thermal diffusivity

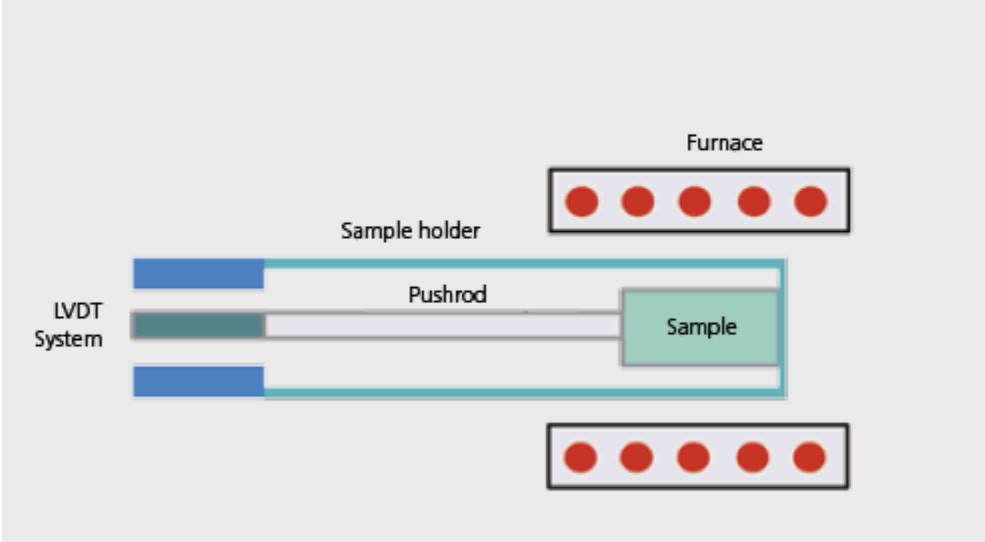


Laser Flash Method (LFA)







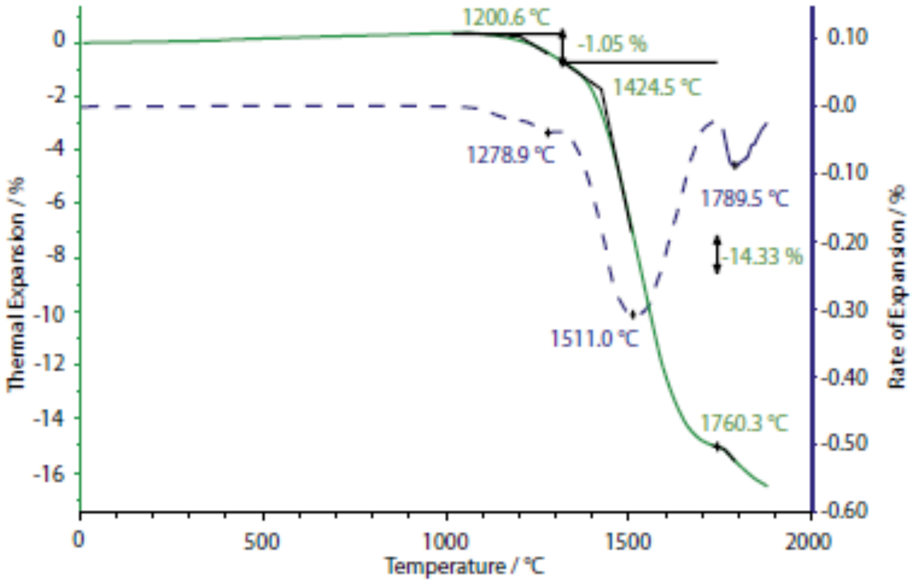


$$\varepsilon = 1/r*(dr/dT)$$

ε – thermal expansion coefficient
r – sample length

DIL Measurement Information

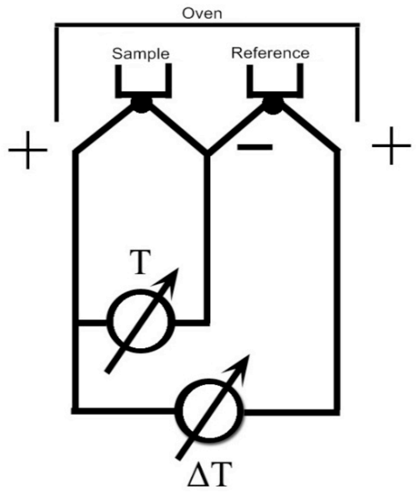
- Linear thermal expansion
- Determination of coefficient of thermal expansion
- Sintering temperatures
- Softening points
- Phase transitions



SiN thermal shrinkage

Principle of combined thermocouple

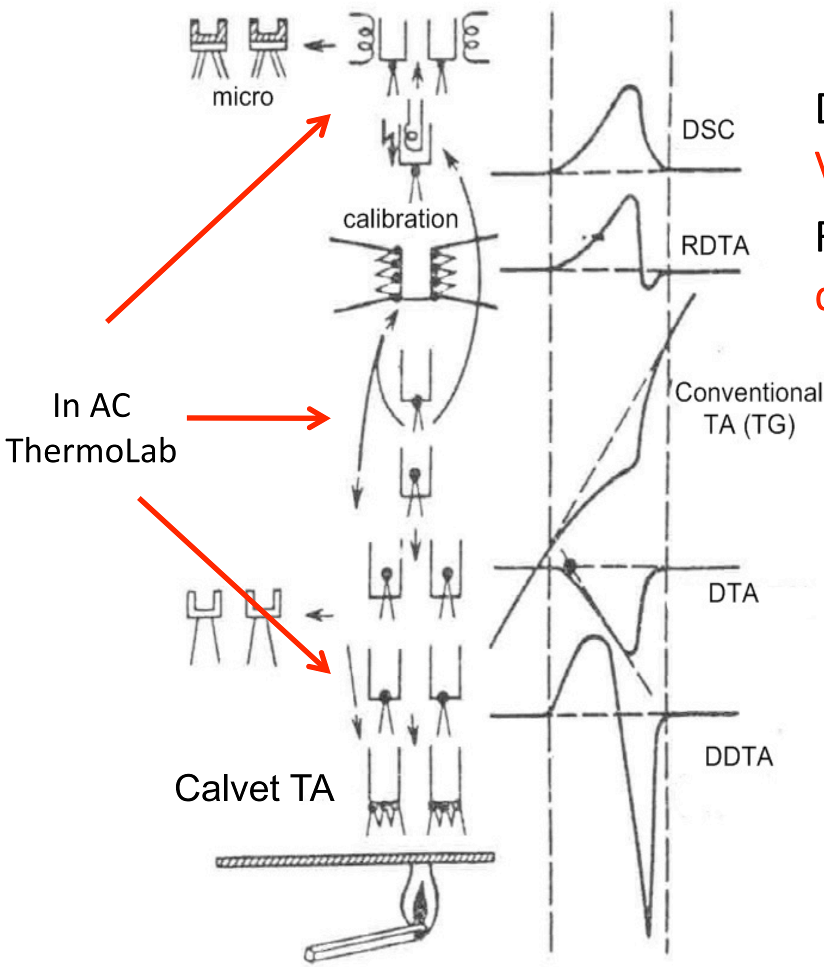
Registration the temperature of the object and temperature difference between sample and reference



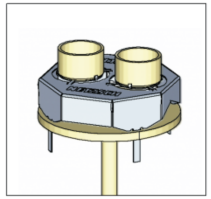
Consequence

Depending on the engineering design, measuring cell construction and the way of data representation, variety of methods has been arisen: DTG, DTA, DSC, STA etc.

Basic Principles and Terminology



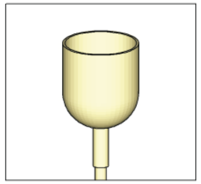
DSC-TG



DSC - (Differential Scanning Calorimetry):
Voltage to keep $\Delta T = T_S - T_R = 0$ vs. T

RDTA (Reverse Differential Thermal Analysis)
dt/dT vs. T

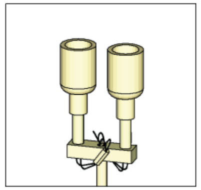
TG



TA – (Thermal analysis)
T_S vs. t

TG – (Thermogravimetric analysis)
Δm vs. T

DTA-TG



DTA - (Differential Thermal Analysis)
$\Delta T = T_S - T_R$ vs. T

Calvet-DSC

DDTA - (Derivative DTA)
$d\Delta T/dt$ vs. T

STA – Simultaneous Thermal Analysis: TG – DSC ; EVA – Evolved gas analysis: MS, FTIR, GC

Hyphenated techniques

Thermocouples

Type	Composition	Temperature range, K		Output voltage (0°C), mV
		T_{min}	T_{max}	
T	Cu /constantan	3	670	20
J	Fe/constantan	70	870	34
E	chromel /constantan	-	970	45
K	chromel /alumel	220	1270	41
S	Pt/PtRh (10)	270	1570	13
R	Pt/PtRh (13)	220	1570	12
C	W/WRe(26)	-	2670	39
N	Nicrosil/Nisil	-	1200	39

Constantan - 58% Cu, 42% Ni

Chromel – 89% Ni, 10% Cr, 1%Fe

Alumel – 94% Ni, 2% Al, 1,5% Si, 2,5 % Mn

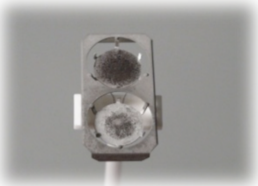
Nicrosil/Nisil – Ni, Cr, Silicon/Ni, Silicon

Cu/Constantan disk sensor on Si(X) waffer.

μ sensor

CuNi disk sensor on Ag plate.

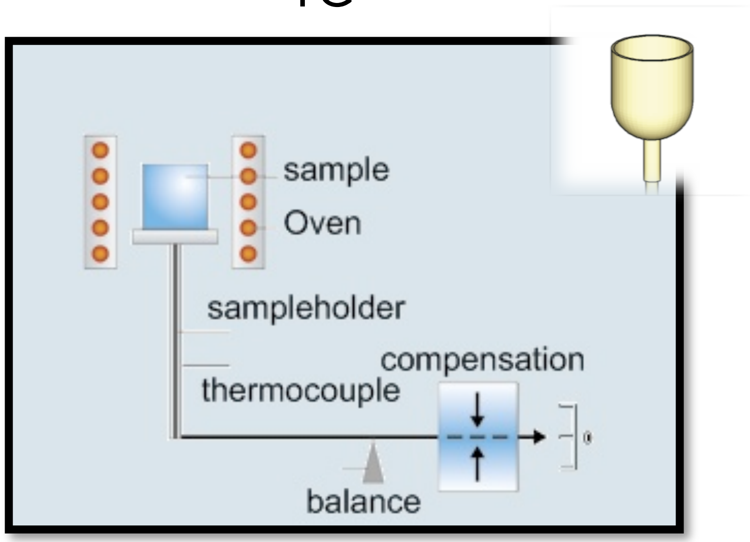
τ sensor



Pt-PtRh(10) diskshaped thermocouple

Basic Principles and Terminology

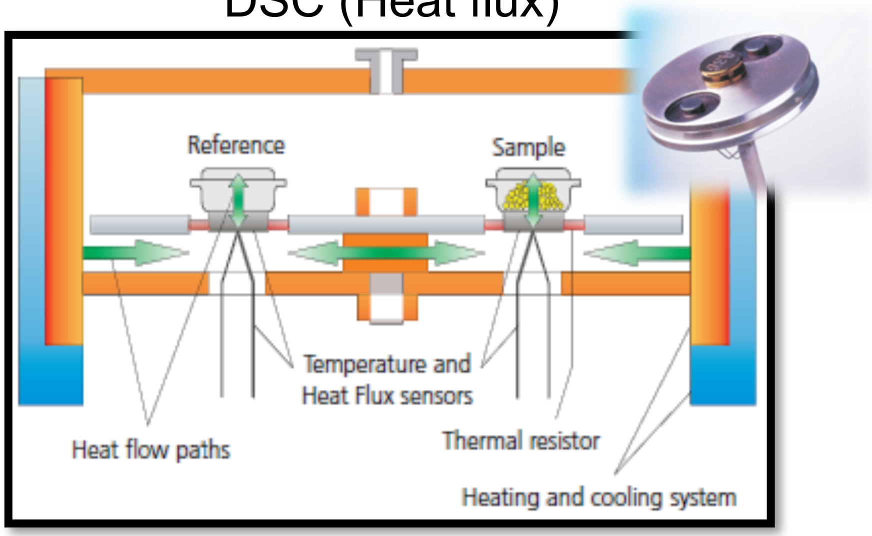
TG



$$S_{MP} \cdot g = ((m_{SC} + m_S + m_A) - \underbrace{(V_{SC} + V_S + V_A) \cdot \rho_{gas}) \cdot g}_{F_B}$$

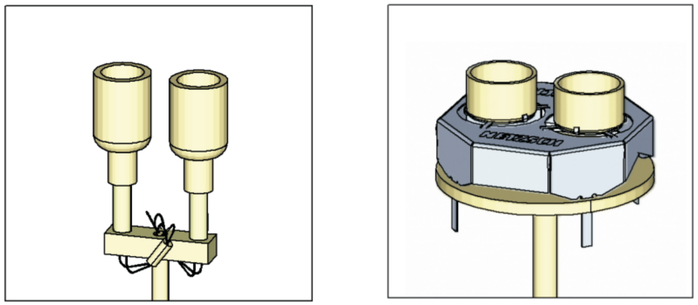
S_{MP} - Measurement signal
F_B - Buoyancy force , f(T)
m_A - Mass of adsorbed gas, f(T)
m_{SC} - Mass of sample container
m_S - Mass of sample , f(T)
V_A - Volume of adsorbed gas , f(T)
V_{SC} - Volume of sample container
V_S - Volume of sample, f(T)
ρ_{gas} - Density of gas, f(T)

DSC (Heat flux)

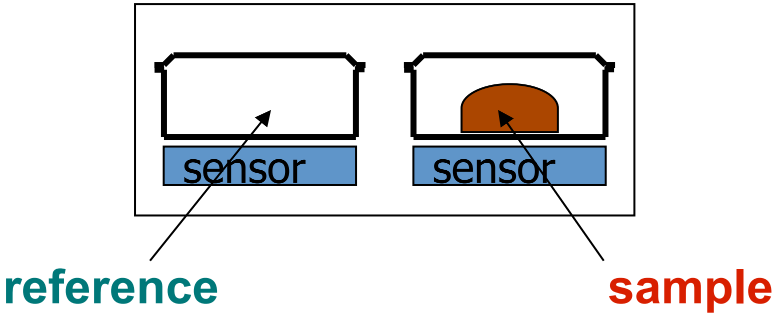


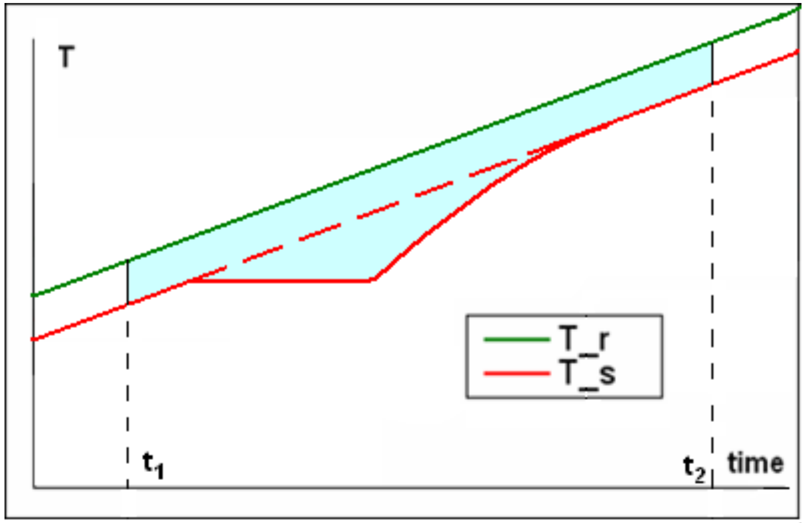
$$\phi \equiv \frac{dQ}{d\tau} = m \cdot C_p \cdot \frac{dT}{d\tau}$$

STA

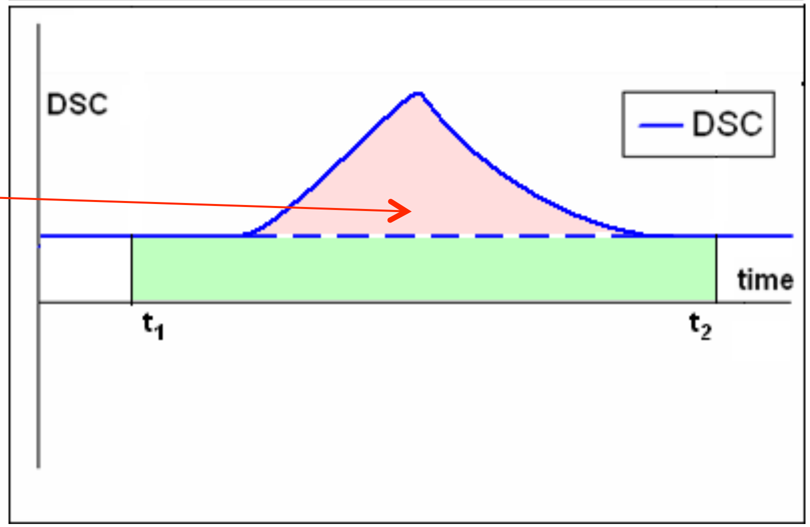


Basic Principles and Terminology





$$\Delta H = \int_{t_1}^{t_2} \left(HeatFlow - Cp \cdot \beta \right) dt$$



General Theory (Heat equation for inert material)

$$\frac{\partial T}{\partial t} = a \cdot \left(\frac{\partial^2 T}{\partial z^2} + \frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \cdot \frac{\partial T}{\partial r} + \frac{1}{r^2} \cdot \frac{\partial^2 T}{\partial \varphi^2}\right)$$

$$a = \frac{\lambda}{\rho C_p}$$

r, φ - polar coordinates

b – heating rate, K/min

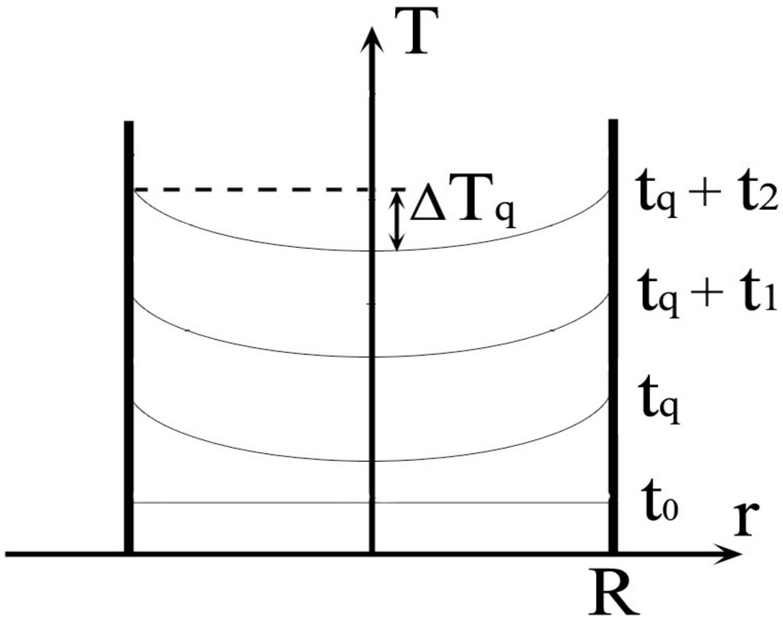
a -Temperature conductivity coefficient, cm^2/s

λ – Thermal conductivity , J/(cm*s*K)

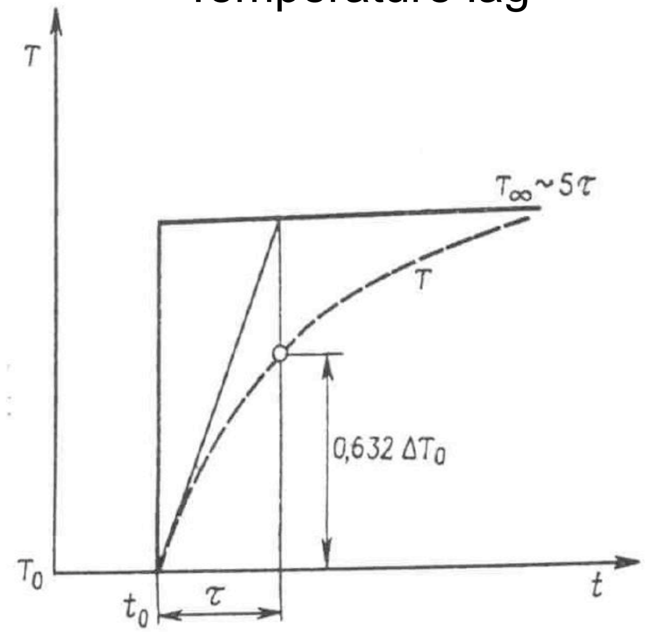
Cp – Thermal capacity, J/(g*K)

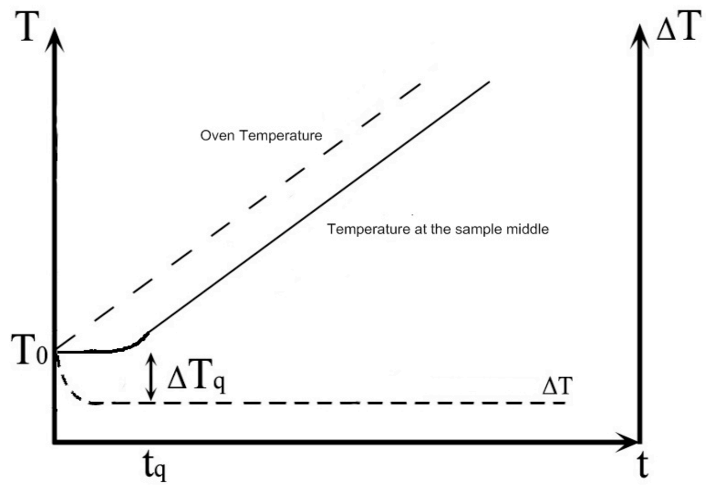
ρ– density, $g/(cm^3)$

$$T(r,t) = T_o + bt - \frac{b(R^2 - r^2)}{4a}$$

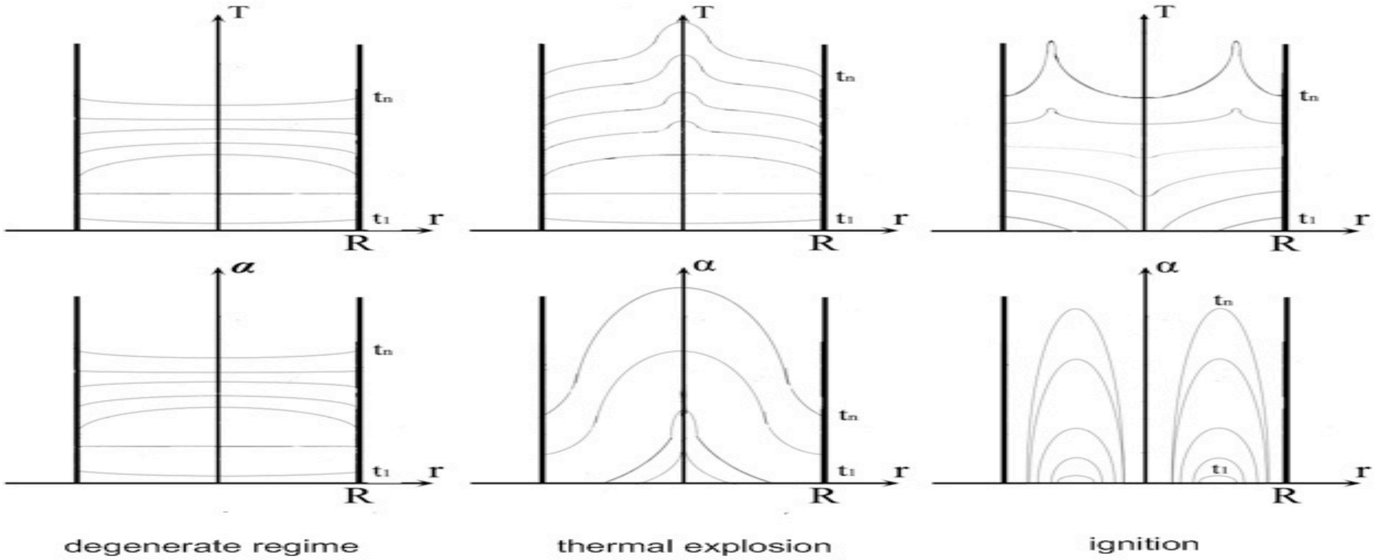


Temperature lag



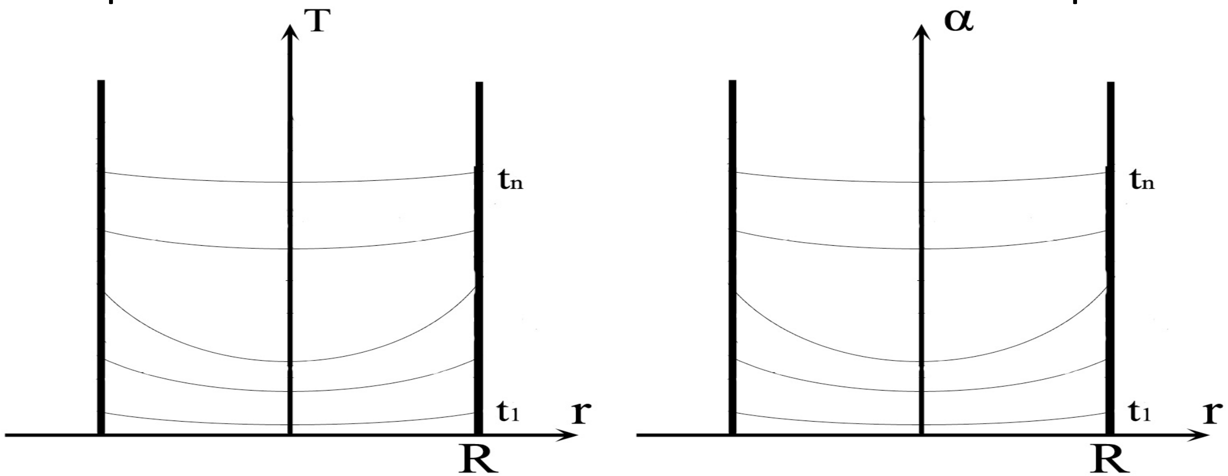


General Theory (Temperature field in active sample)



Exothermic
ΔQ>0, ΔH<0

Temperature and reaction extent field for exothermic processes



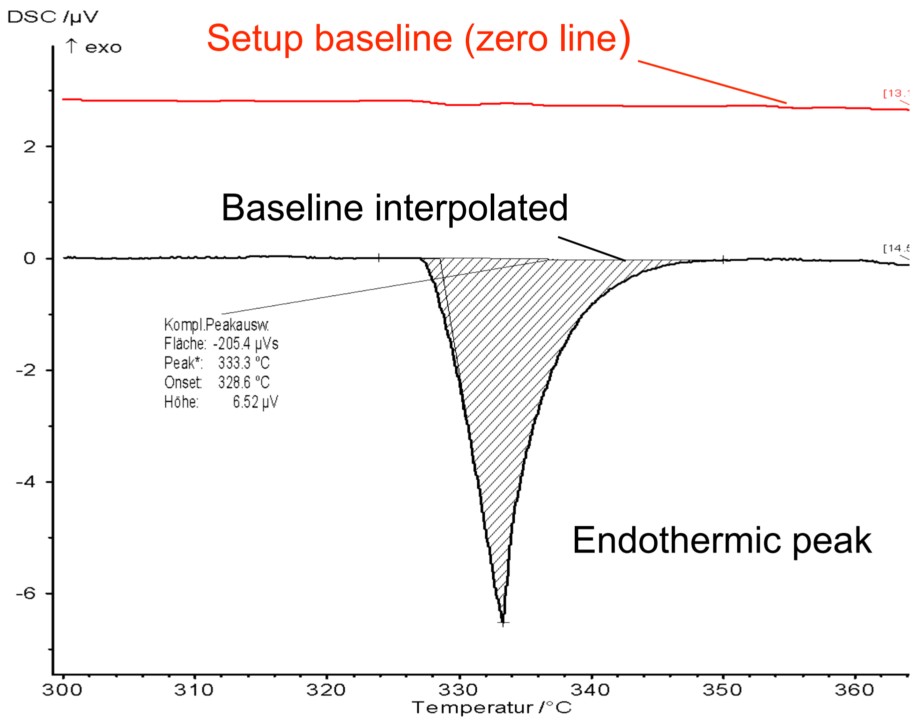
Endothermic
ΔQ<0, ΔH>0

Temperature and reaction extent field for endothermic process

General Theory

DSC

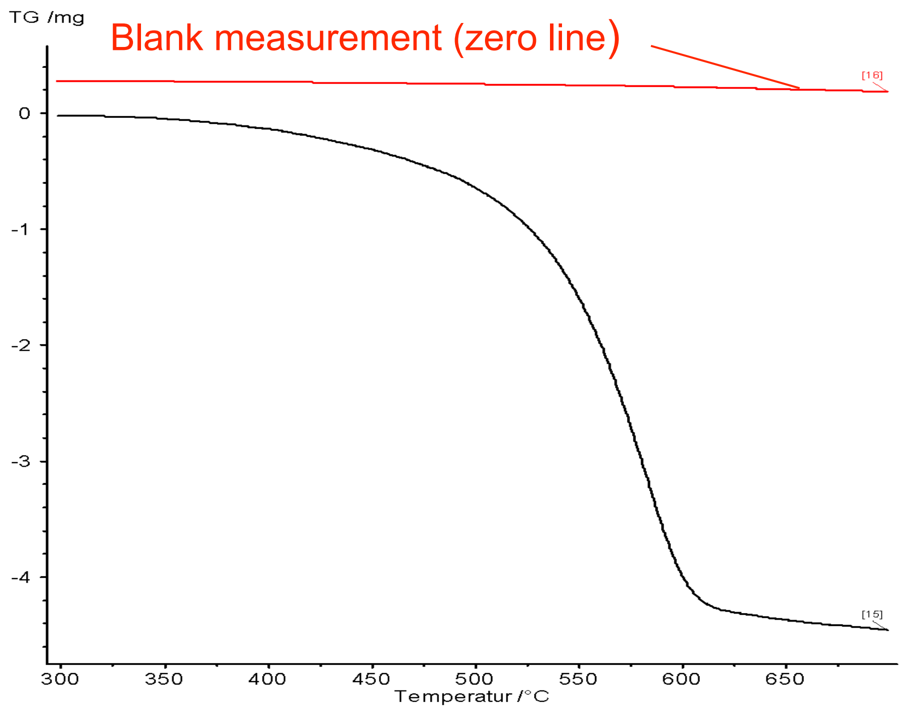
$Pb_{(S)} \rightarrow Pb_{(L)}$, ΔH°_{298}= 5 kJ/mol



Shift of the baseline could appear due to change in thermal resistance of the setup. Position is depending on measuring-history.

TG

$CuO_{(S)}+H_{2(g)} \rightarrow CuO_{(s)}+H_2O_{(g)}$, ΔH°_{298}= -86 kJ/mol



Measurements may have a significant change in weight due to changes in gas density and viscosity.

General Theory

Heat balance

$$Mc\Delta\dot{T} + \Lambda(T)S\Delta T = mQ\dot{\alpha}$$

$\Lambda(T)$ – heat transfer coefficient
c – measuring cell heat capacity
M – mass of the measuring cell
ΔT – generated temperature difference
α - normalized conversion

Heat of the process is determined as follows:

$$Q = \frac{1}{m}\int_0^\infty \Lambda(T)S\Delta T dt + Const$$

S – available surface for heat exchange
m – sample mass
ΔT – generated temperature difference

$$K_{(T)} = \Lambda + 4\Lambda^{rad}T^3 + \lambda_s \equiv K_{DTA}$$

$K_{(T)}$ – instrument constant
Λ^{rad} – radiation energy between oven and sample
λ_s – sample thermal conductivity

$$Q[J/g] \sim K_{DTA} \cdot A[V \cdot s/g]$$

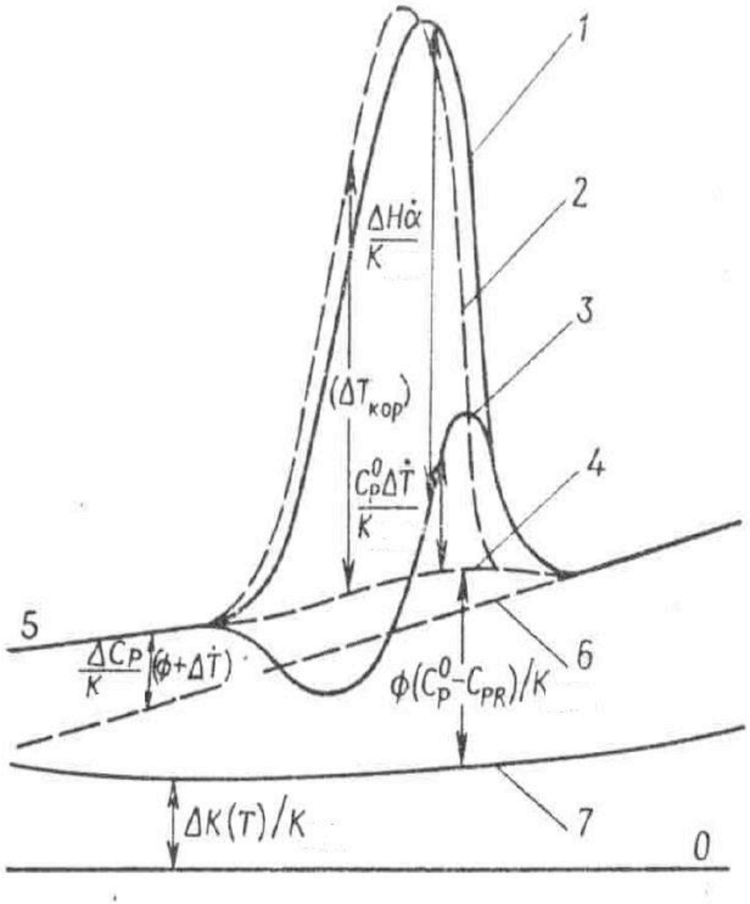
A – DSC peak area

Calibration Standards

Standard	Melting Point,°C	Heat of Fusion, J/g
In	156,6	- 28,6
Sn	231,9	-60,1
Bi	271,4	-53,1
Pb	327,5	-23,0
Zn	419,5	-107,5
Al	660,0	-397,0
Al-Si	577-880	-
Ag	961,8	-104,6
Au	1064,2	
Unalloeyd steels	1147-1536	-
Ni	1455,0	-290,4
Pd	1554,8	-157,3

General Theory (DTA equation)

$$\Delta T = \frac{\Delta K_{(T)}}{K_{DTA}} - \frac{c_s - c_R}{K_{DTA}}\phi - \frac{\Delta c_S}{K_{DTA}}\left(\phi + \Delta \dot{T}\right) - \frac{c_S}{K_{DTA}}\Delta \dot{T} + \frac{Q}{K_{DTA}}\dot{\alpha}$$

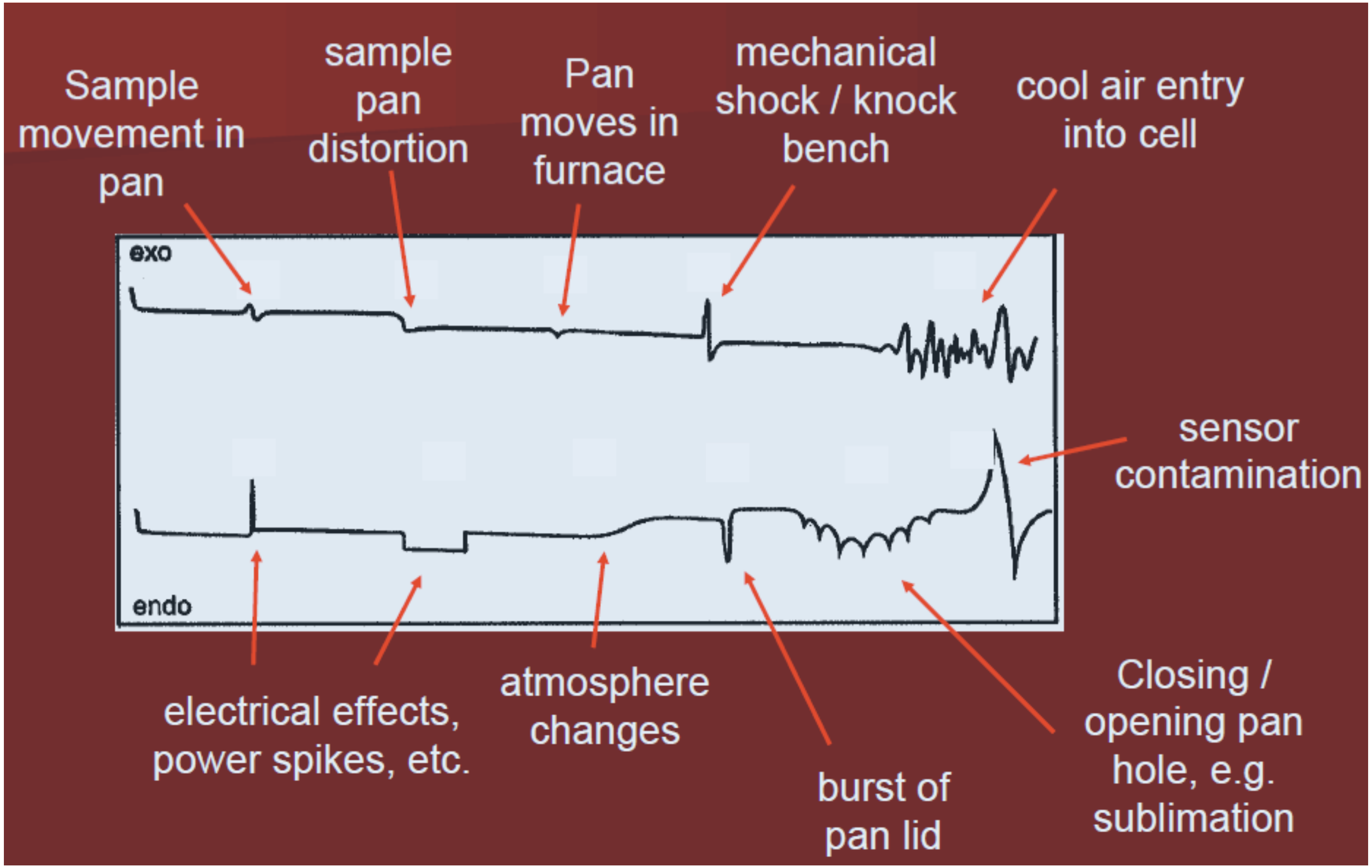


$$K_{(T)} = \Lambda + 4\Lambda^{rad} T^3 + \lambda_s \equiv K_{DTA}$$

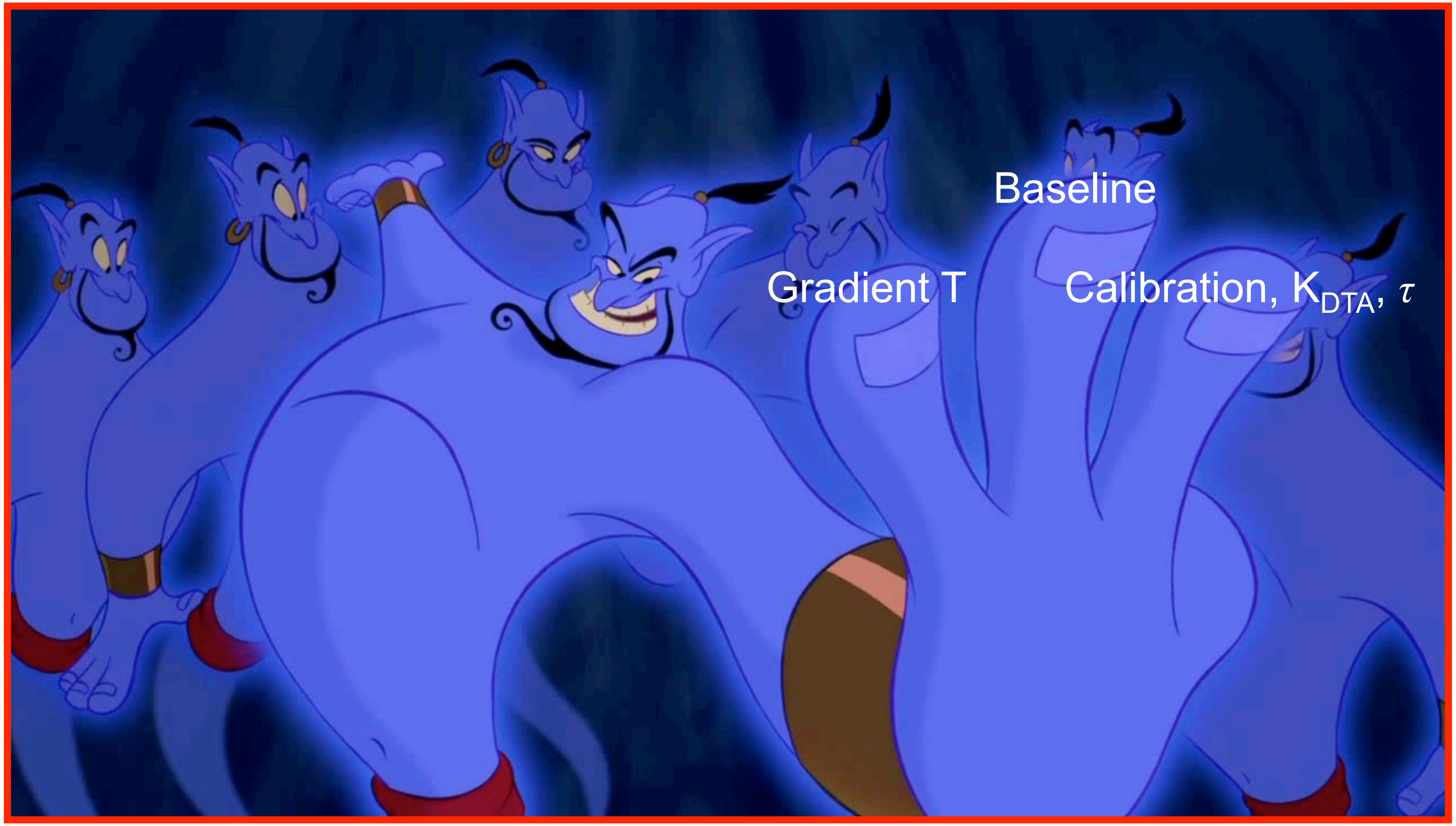
φ – *heating rate, K/min*

1. Experimental DTA curve
2. DTA curve corrected to heat transfer conditions
3. True baseline of DTA curve
4. Interpolated baseline;
5. Experimental baseline;
6. Experimental baseline after process, shifted because of thermal capacity changes.

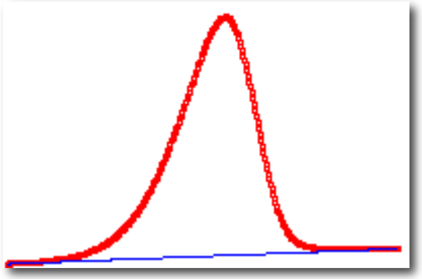
DSC Artifacts



3 major aspects of correct DSC measurement:

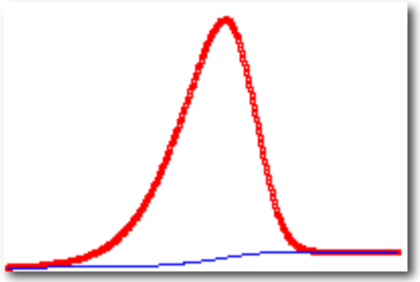


Baseline definition.



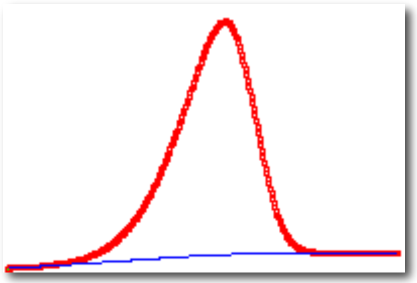
1 *Linear Baseline*

It should be used for measurements in which no significant Cp changes are observed during melting. The linear baseline is generally used.



2 *Sigmoidal Baseline*

This baseline is used when the melting process is accompanied by a notable Cp change.

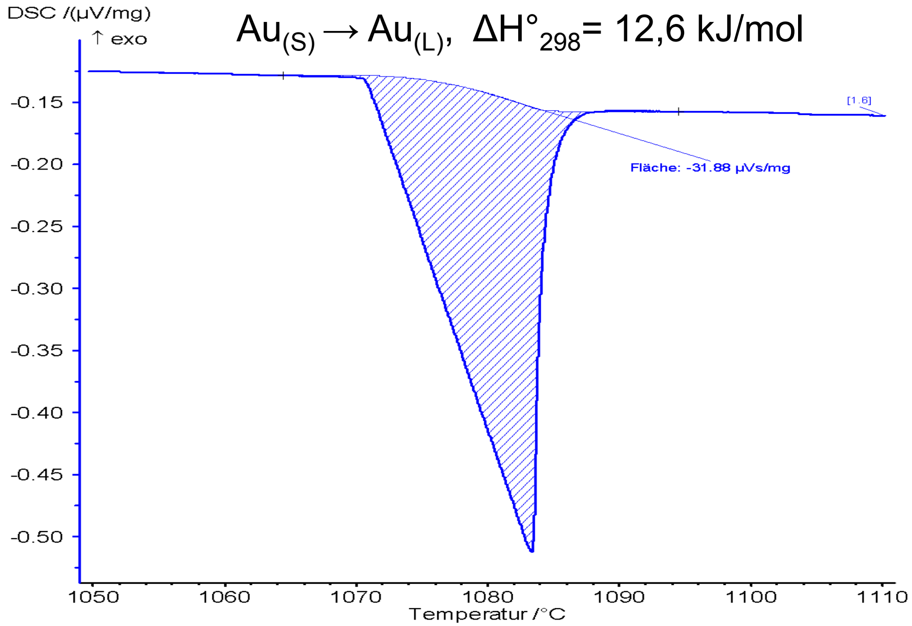


3 *Tangential Area-Proportional Baseline*

This baseline is used when the melting process is accompanied by a notable Cp change and a sloping baseline exists.

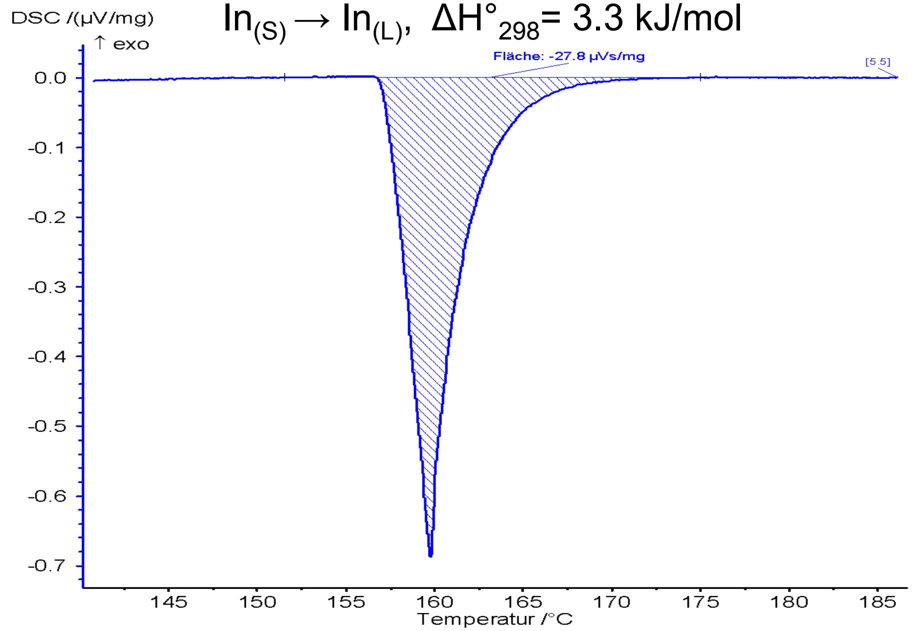
General Theory

$Au_{(S)} \rightarrow Au_{(L)}$, $\Delta H°_{298}$= 12,6 kJ/mol

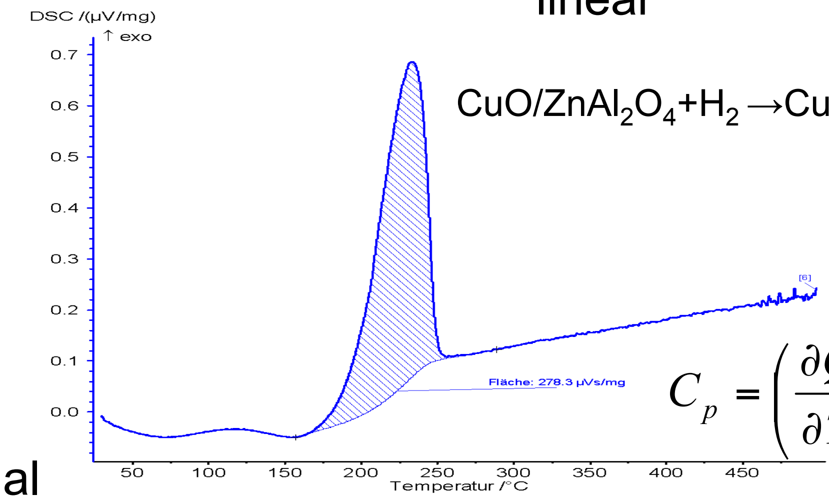


sigmoidal

$In_{(S)} \rightarrow In_{(L)}$, $\Delta H°_{298}$= 3.3 kJ/mol



linear



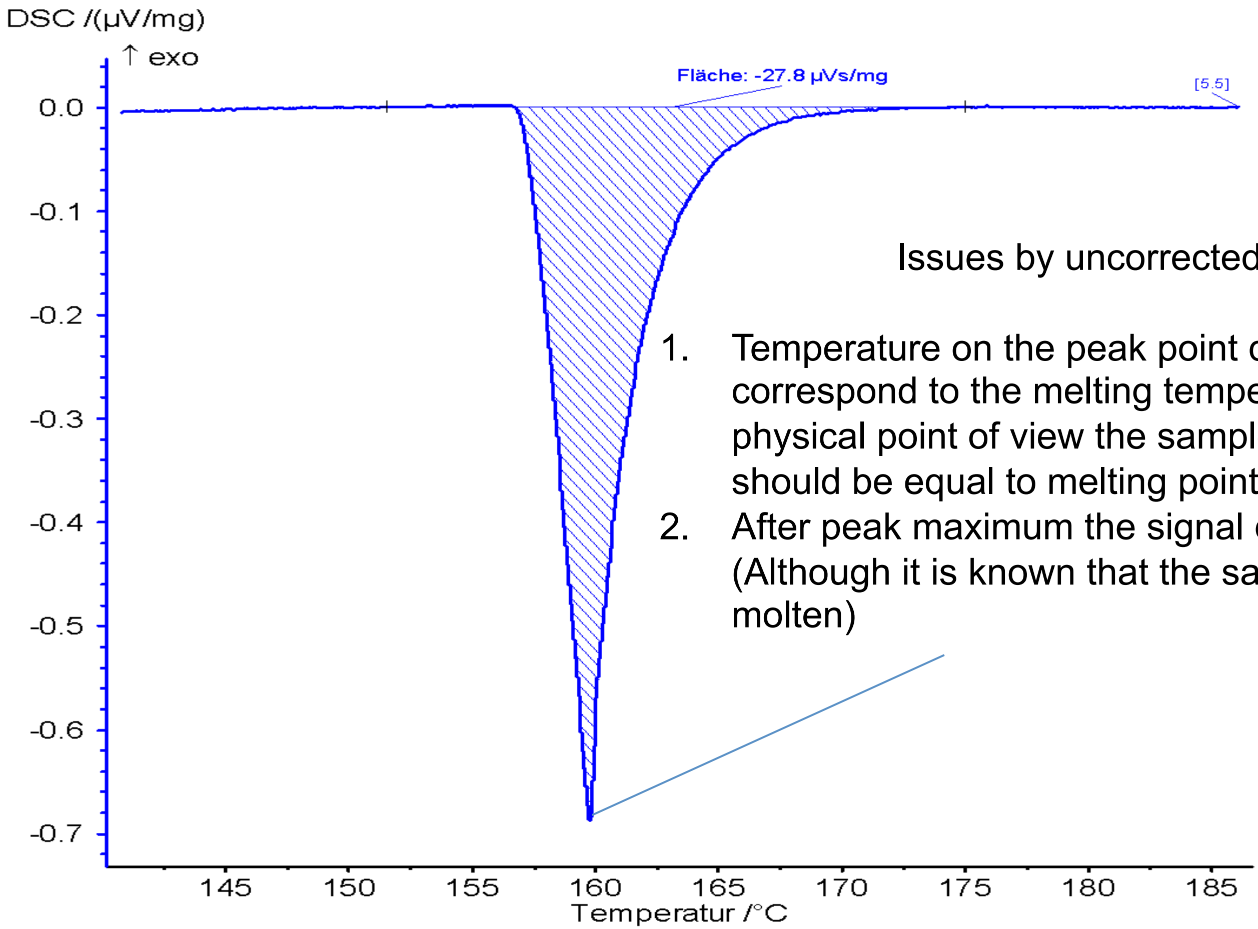
$CuO/ZnAl_2O_4 + H_2 \rightarrow Cu/ZnAl_2O_4 + H_2O$

$$C_p = \left(\frac{\partial Q}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P$$

tangential

DSC peak Correction

$In_{(S)} \rightarrow In_{(L)}$, ΔH°_{298} = 3.3 kJ/mol

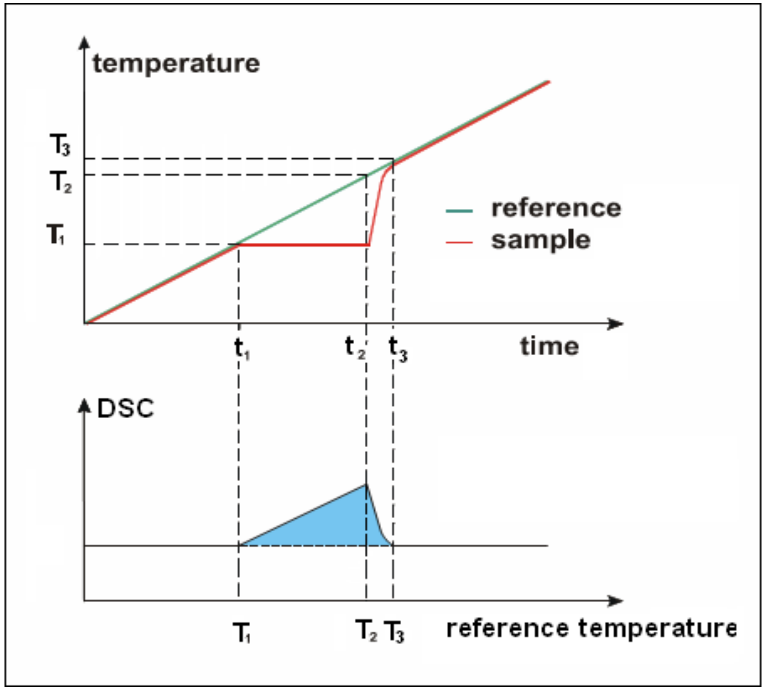


Issues by uncorrected data

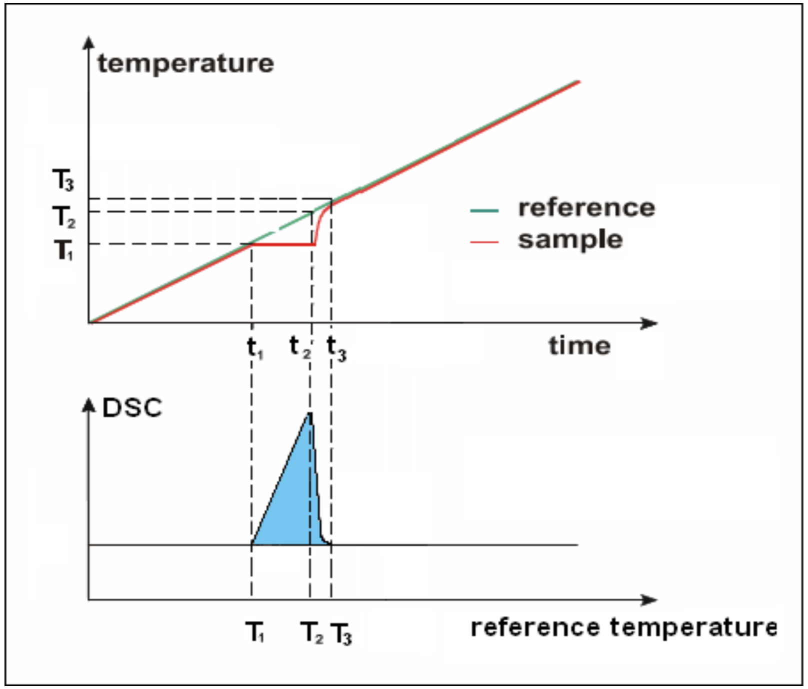
1. Temperature on the peak point does not correspond to the melting temperature (but from physical point of view the sample temperature should be equal to melting point)
2. After peak maximum the signal diminishes slowly. (Although it is known that the sample is completely molten)

Correction on thermal resistance between sample and reference, K_{DTA}

Bad thermal contact
Long melting time
Broad, low peak

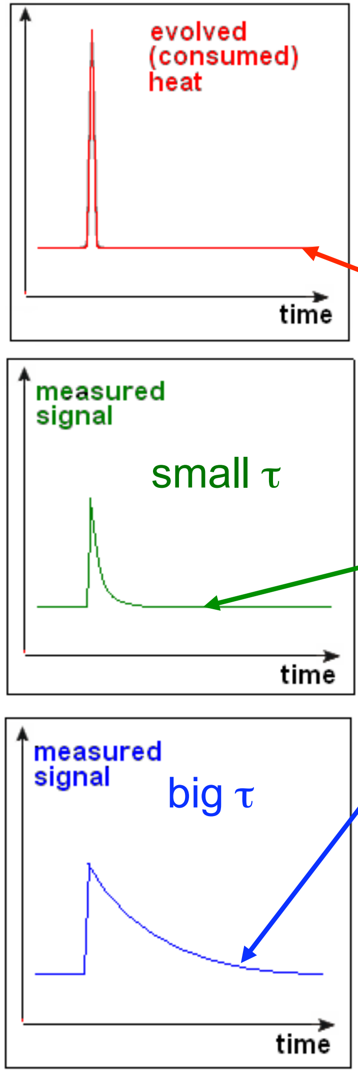


Good Thermal contact
Short melting time
Sharp peak



The slope of the peak left side is depended on thermal resistance
Peak area is the same and equals melting enthalpy.

Correction on time constant τ



$\tau_1 < \tau_2$

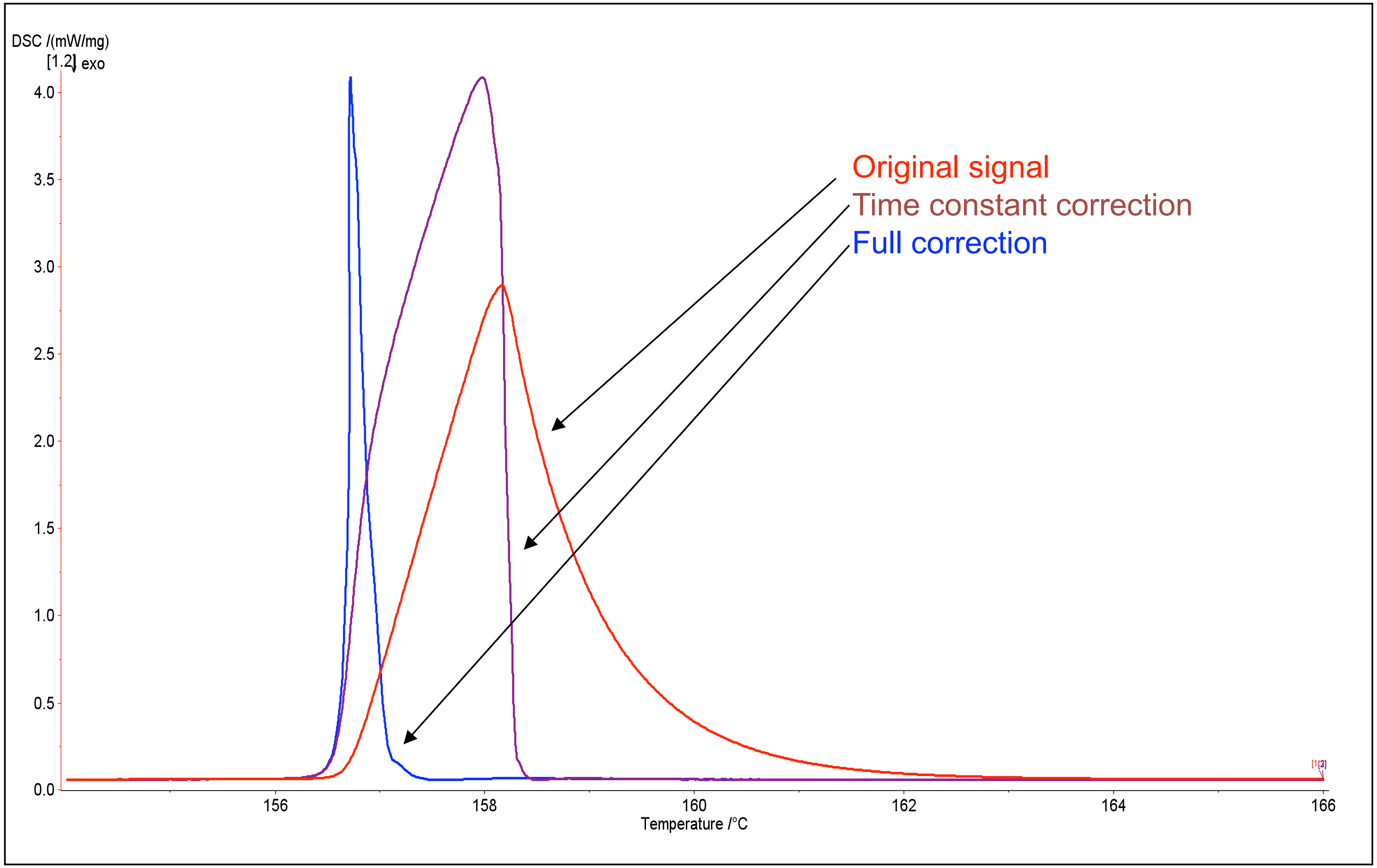
f(t) – evolved heat
F(t) – measured signal
g(t) – response function

$$F(t) = \int_0^t f(t')\, g(t - t')\, dt'$$

$g(t)=\exp(-t/\tau)$

The peak right side is depended on instrument time constant.

DSC peak Correction



The properties of the system «sample-sensor» strongly influence the experimental TA curves

Features of TA Setup	Characteristics of the sample
a)Reaction Atmosphere	a) Particle size
b)Size and shape of the oven	b) Thermal conductivity
c)Sample holder material	c) Thermal capacity
d)Sample holder geometry	d) Packing density of particles (powder, pill, tablet)
e)Heating rate	e) Sample expansion and shrinking
f)Thermocouple (wire diameter)	f) Sample mass
g)Thermocouple location	g) Inert filler
h)Response time	h) Degree of crystallinity

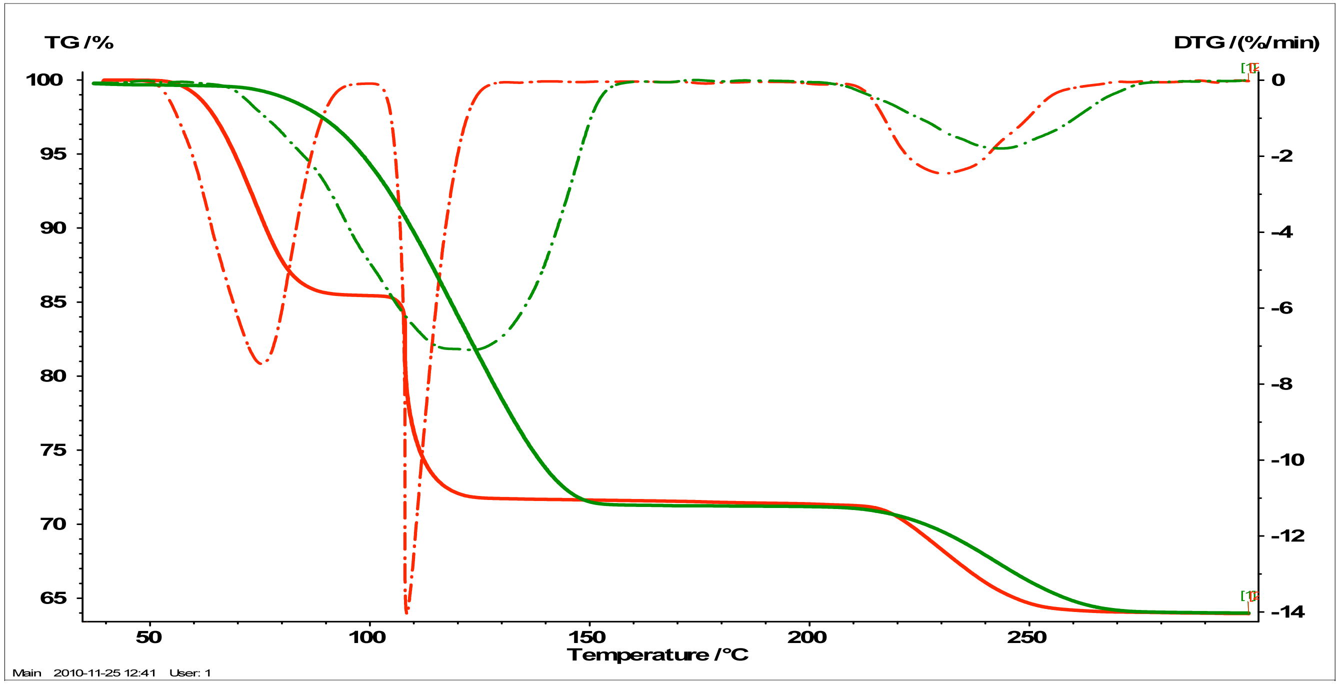
Information obtained depends on procedure
Not fundamental property

Influence of external gas flow

Setup: Netzsch – STA Jupiter

$CaC_2O_4 \cdot nH_2O \rightarrow CaC_2O_4 + nH_2O \rightarrow CaCO_3 + 1/2\ CO_2 \rightarrow CaO + CO_2$

1 stage 2 stage 3 stage

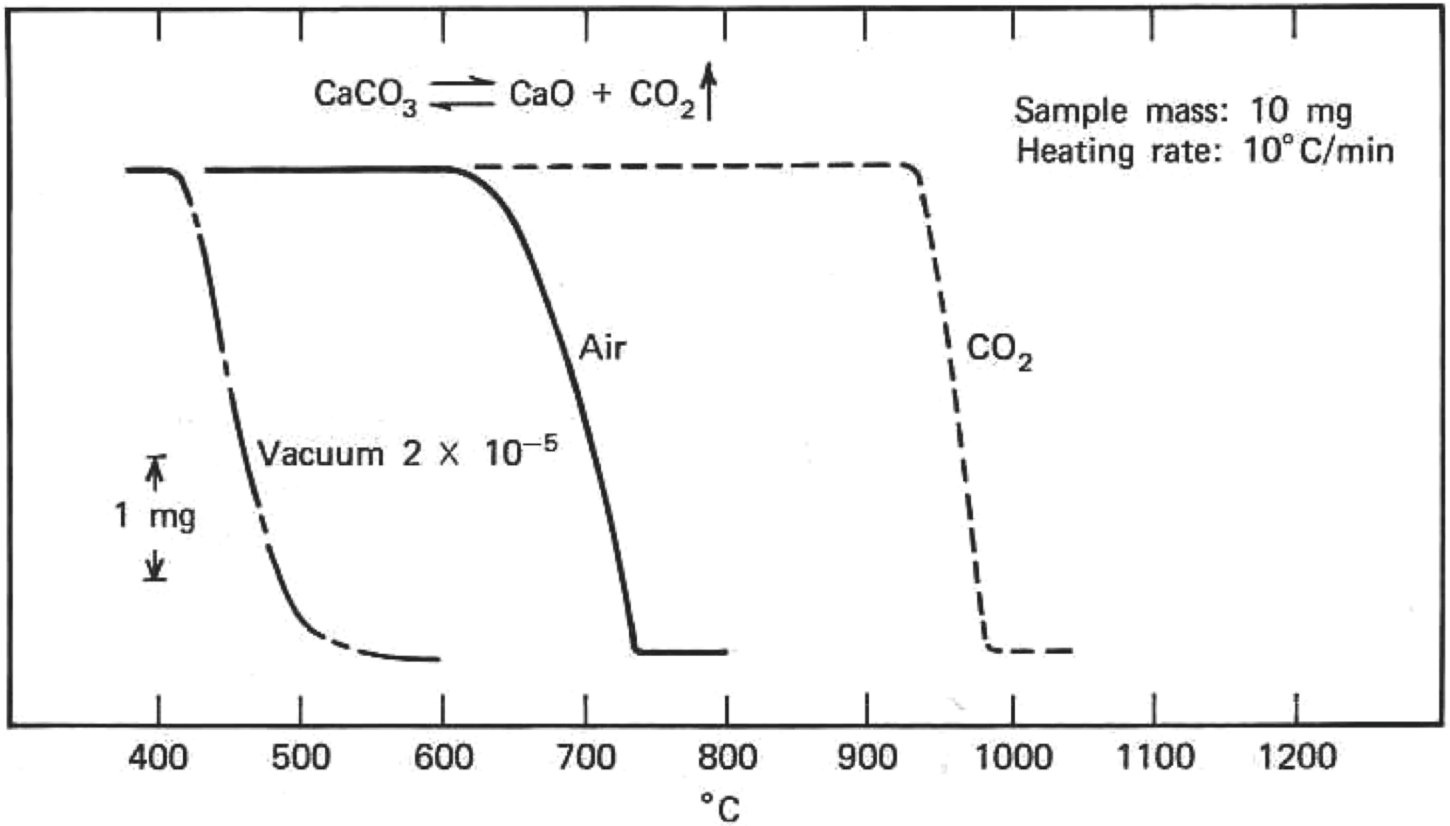


Dehydration of $CaC_2O_4 \cdot nH_2O$ in an open crucible in a dry air flow (red curve) and in a static atmosphere (green curve).

Influence of external atmosphere

Setup: Netzsch – STA Jupiter

TG

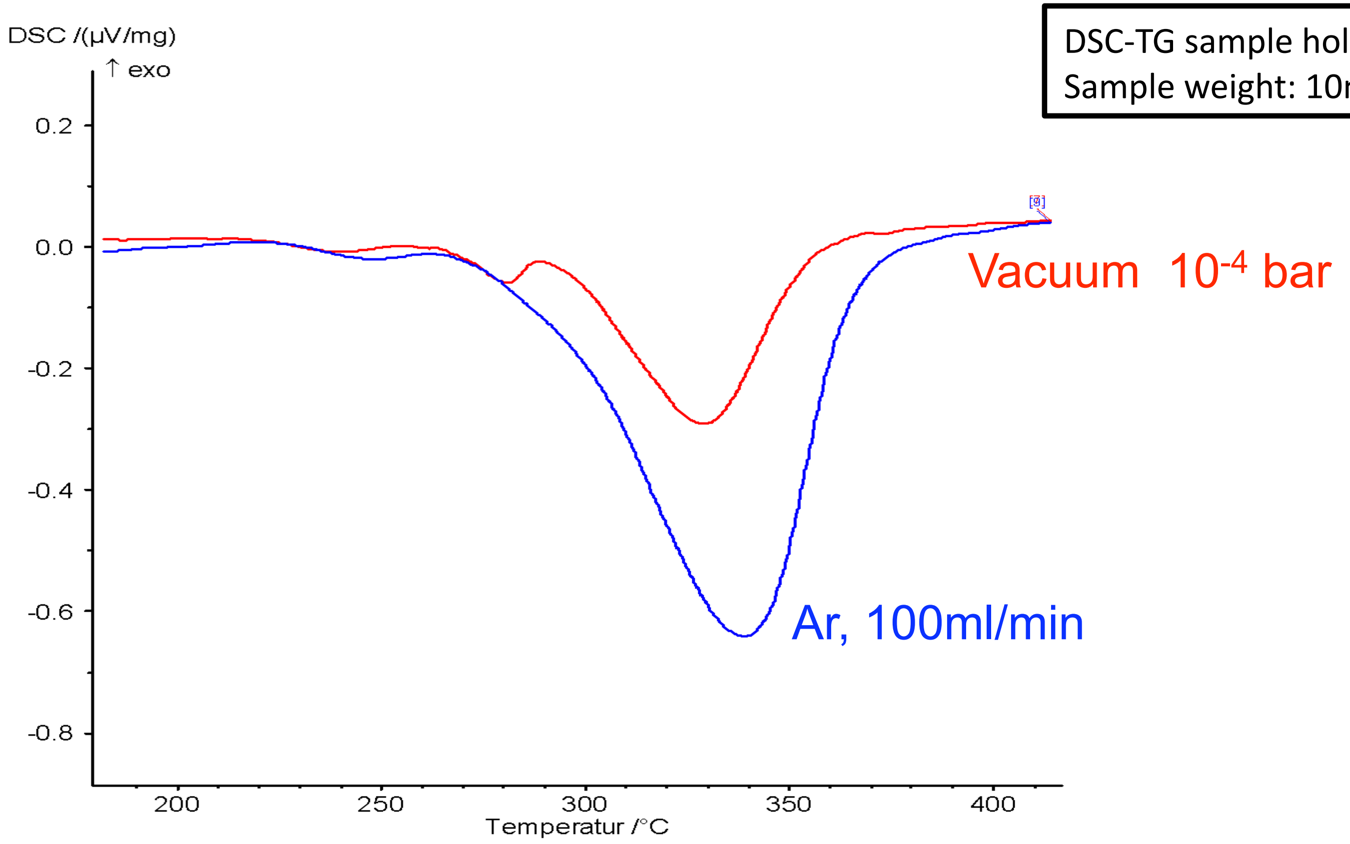


Influence of external atmosphere

$$M_5(OH)_6(CO_3)_{2(s)} \xrightarrow{k1} 5MO_{(s)} + 2CO_{2(g)} + 3H_2O_{(g)}$$

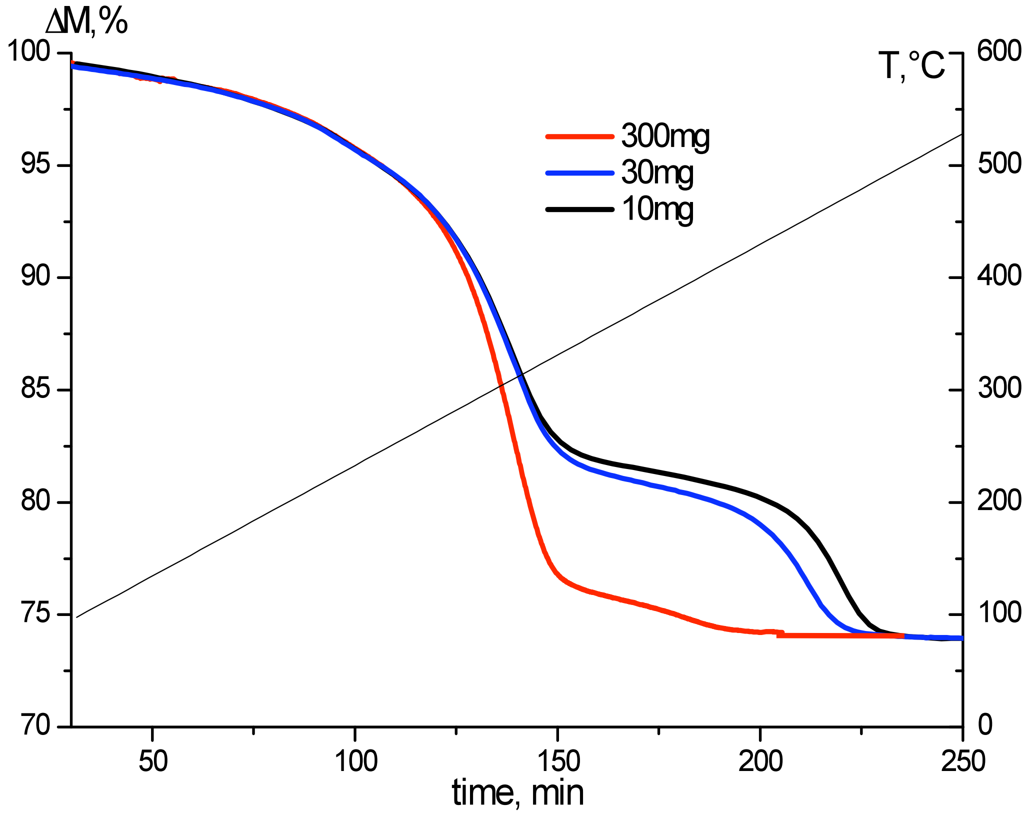
$M = Cu_xZn_{1-x}$

DSC-TG sample holder,
Sample weight: 10mg



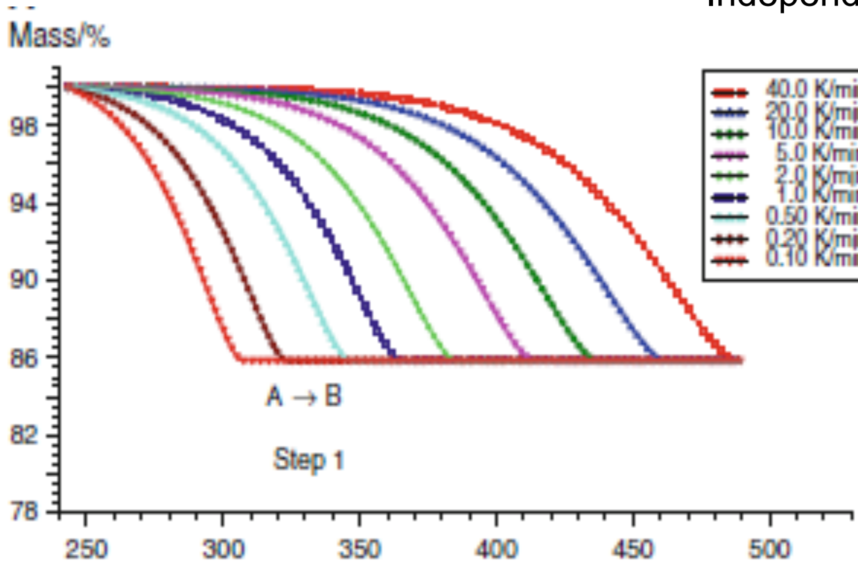
Influence of sample mass

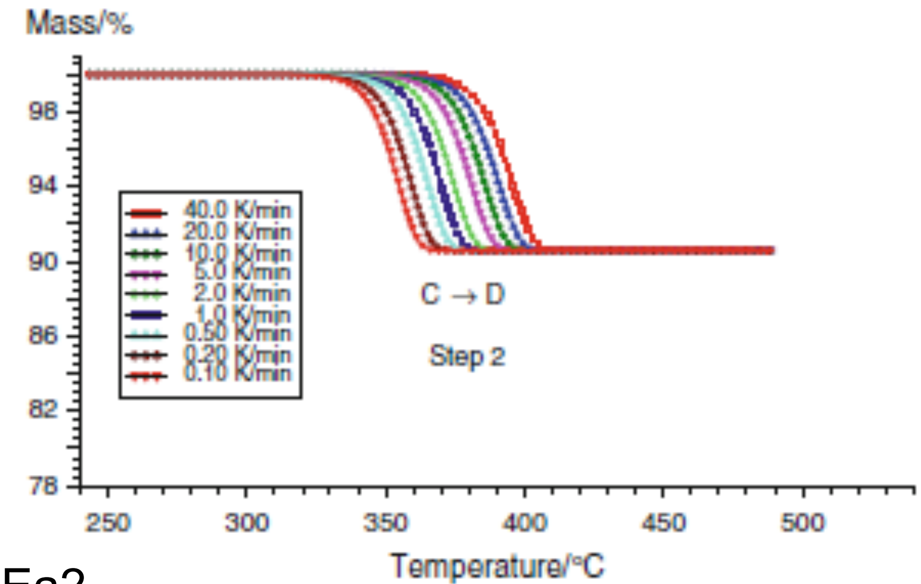
$$M_5(OH)_6(CO_3)_{2(s)} \xrightarrow{k1} 5MO_{(s)} + 2CO_{2(g)} + 3H_2O_{(g)}$$



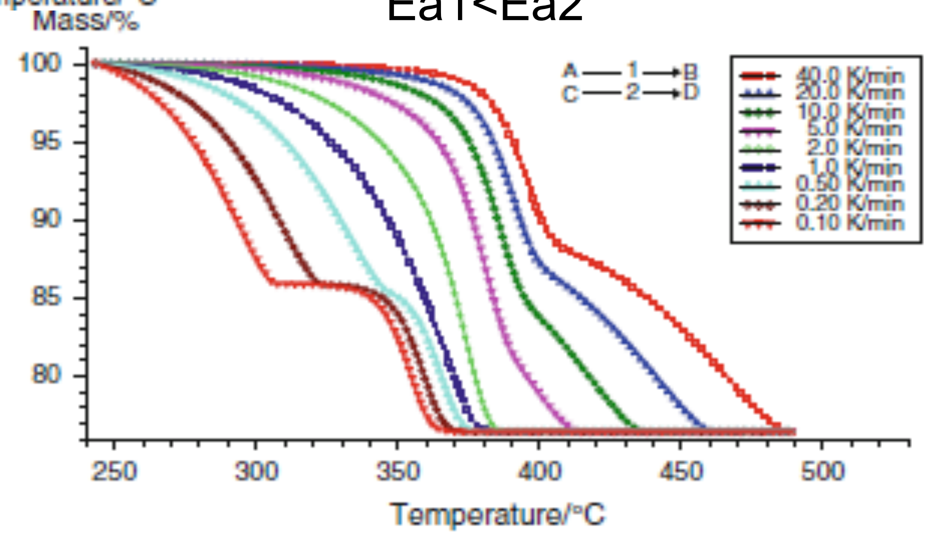
Influence of heating rate

Independent processes



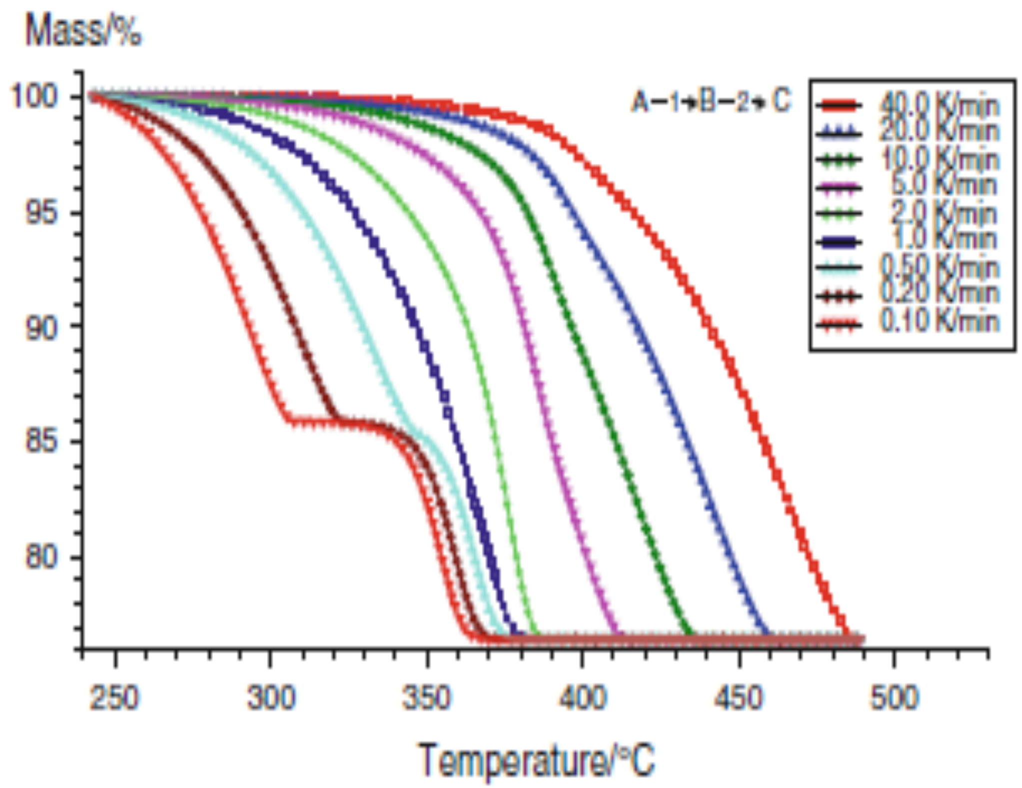


Ea1<Ea2



Influence of heating rate

Subsequent processes

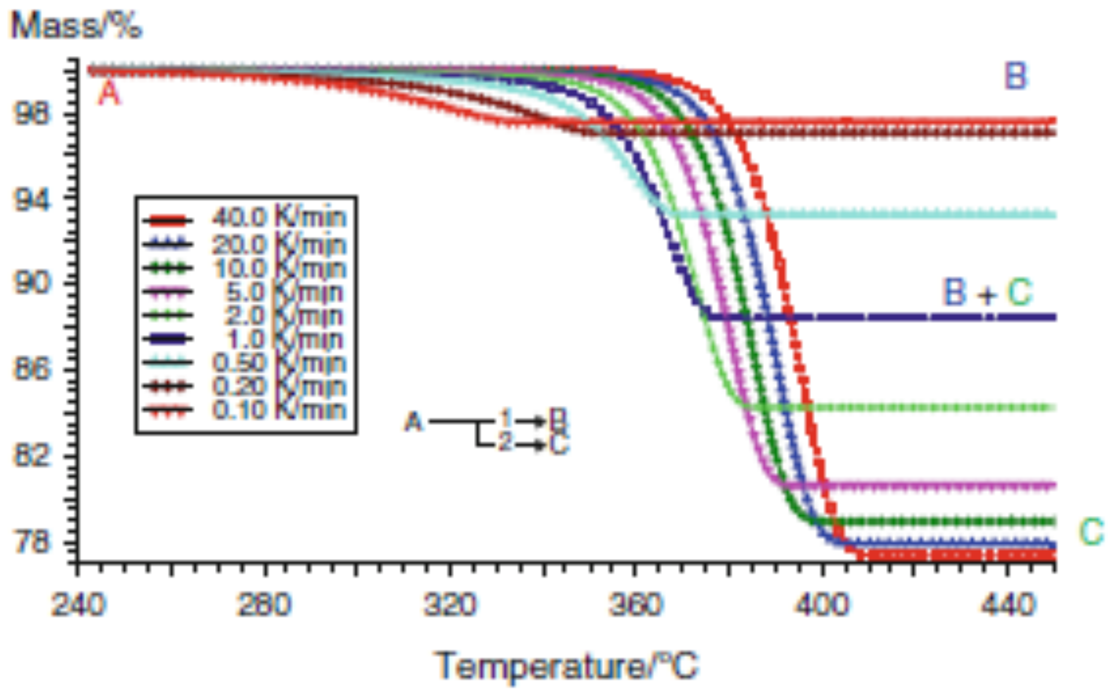


$La(OH)_3 \rightarrow LaOOH + H_2O$

$LaOOH \rightarrow La_2O_3 + H_2O$

Influence of heating rate

Competitive process processes



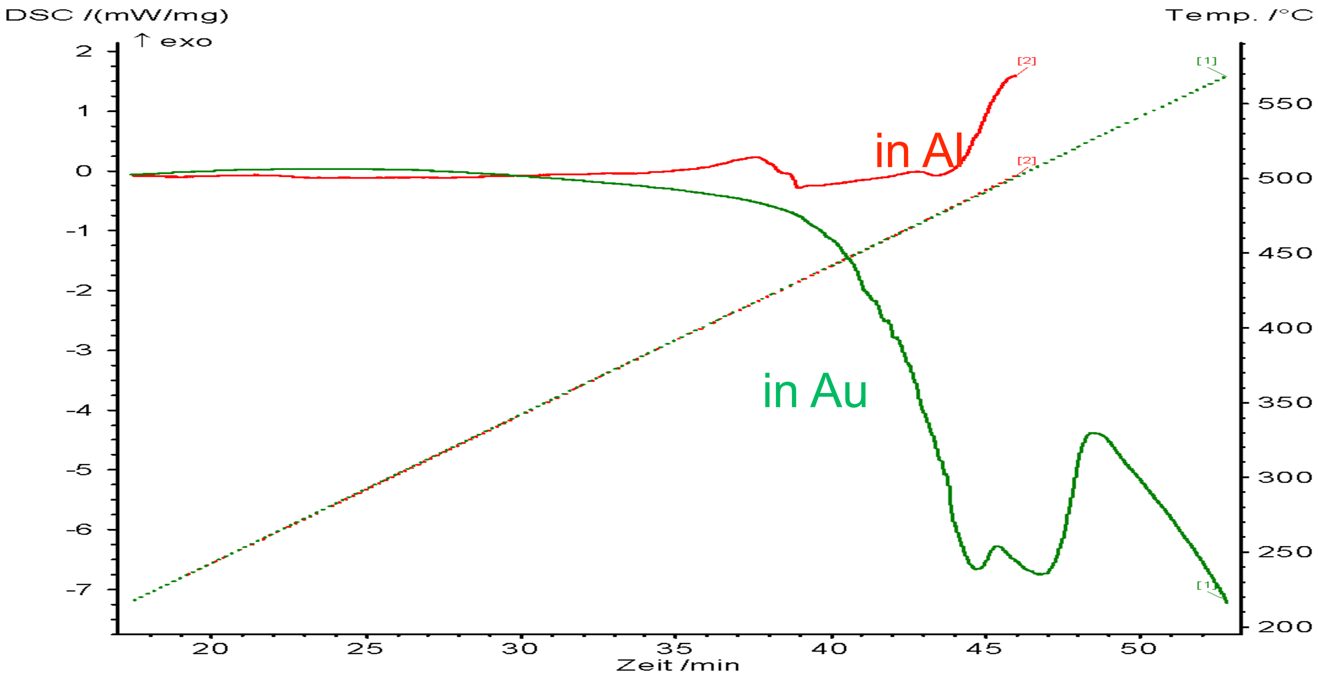
Ea1<Ea2

Influence of the pan material

Setup: Netzsch – STA Jupiter

Al Pt Al_2O_3 Ni Cu Quartz

Pyrolisis of Fluoropolymer: TFE-VDF, -$\{C_2F_4\}_n$ - $\{C_2H_2F_2\}_m$, F42 – in Al an Au pans



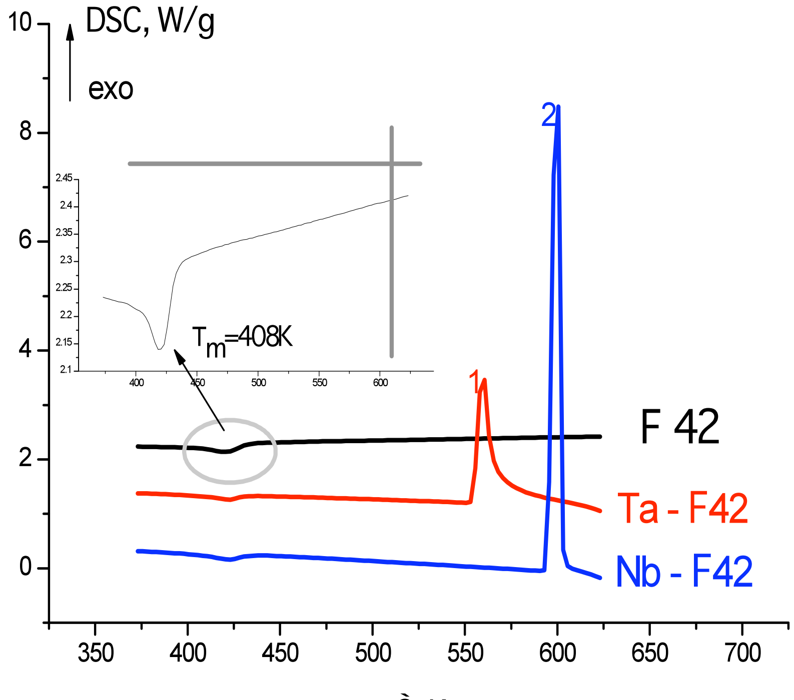
10Kpm, Ar, 100ml/min

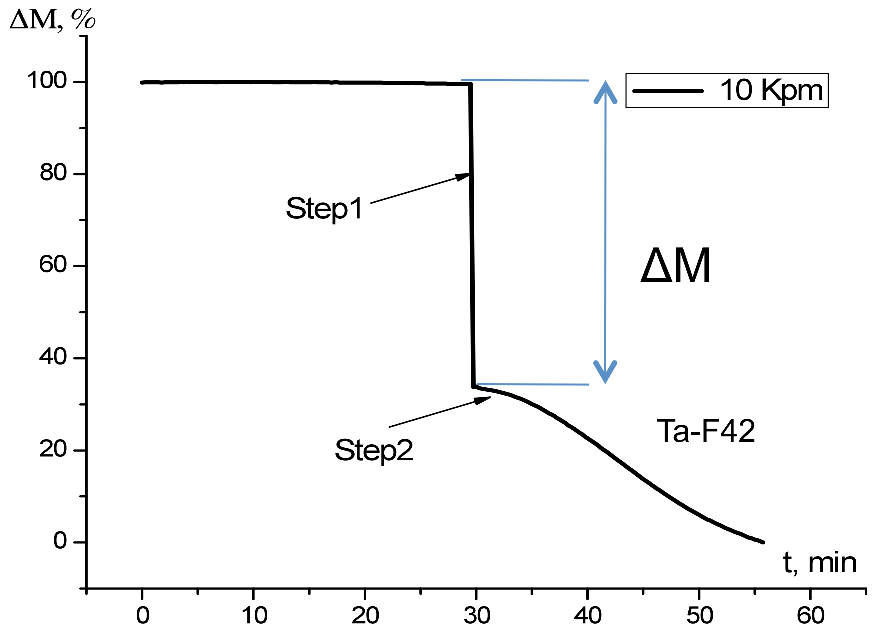
Strong exothermic reactions

Setup: Netzsch – STA Jupiter

Interaction of Ta and Nb with Fluoropolymer: TFE-VDF, -$\{C_2F_4\}_n$ - $\{C_2H_2F_2\}_m$ -, F42

with A. Alikhanjan, and I. Arkhangelsky (2009)





$$Ta_{(s)} + \frac{1}{n}(C_{33}H_{25}F_{43})_{n(s)} \rightarrow TaF_{5(g)} + X_{1(s)}$$

$$\Delta_r H_1^0 \geq -295 \pm 16 kJ/mol$$

$$Nb_{(s)} + \frac{1}{n}(C_{33}H_{25}F_{43})_{n(s)} \rightarrow NbF_{5(g)} + X_{1(s)}$$

$$\Delta_r H_2^0 \geq -240 \pm 13 kJ/mol$$

-strong heat evolution, narrow ΔT

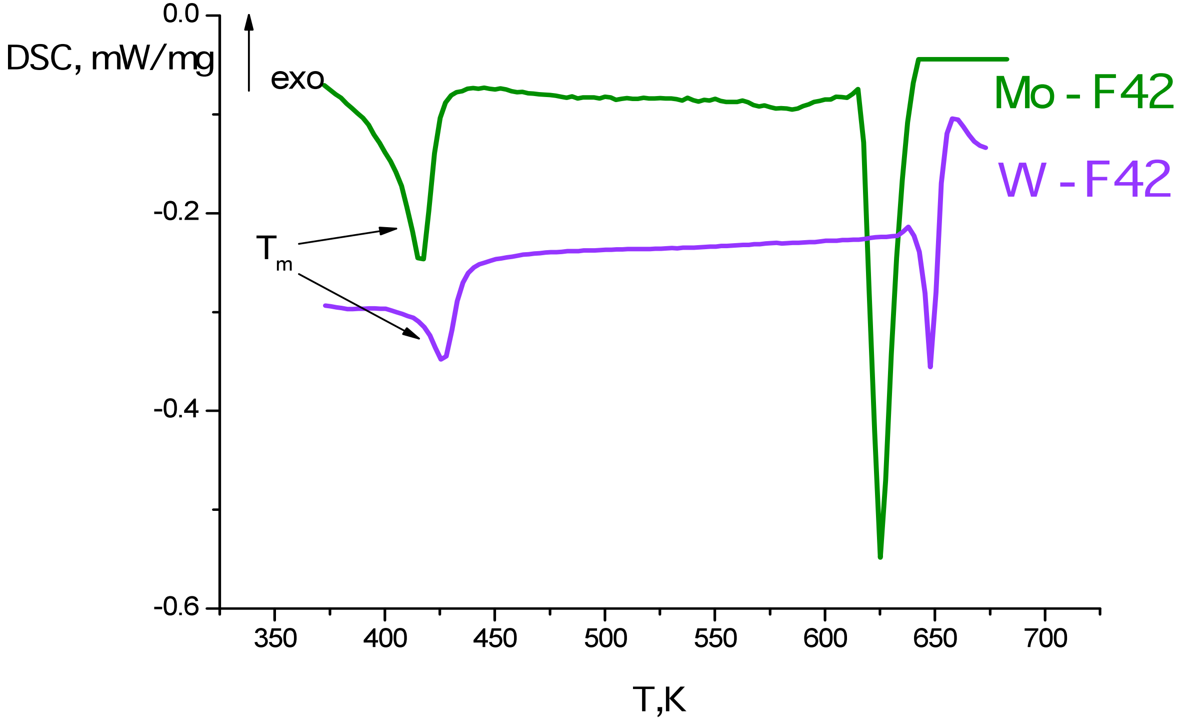
-2 stages by interaction

-sharp weight loss due to reaction between two solid interfaces.

Mass loss: reflects the available metal surface which is in contact with polymer.

Strong exothermic reactions

Setup: Netzsch – STA Jupiter



$$\begin{cases} W_{(s)} + \frac{1}{n}(C_{33}H_{25}F_{43})_{n(s)} \rightarrow WF_{6(g)} + X_{(s)} & \text{Exothermic} \\ WF_{6(g)} + H_2 0_{(l)} \rightarrow WOF_{4(g)} + 2HF_{(g)} & \text{Endothermic (due to water traces)} \end{cases}$$

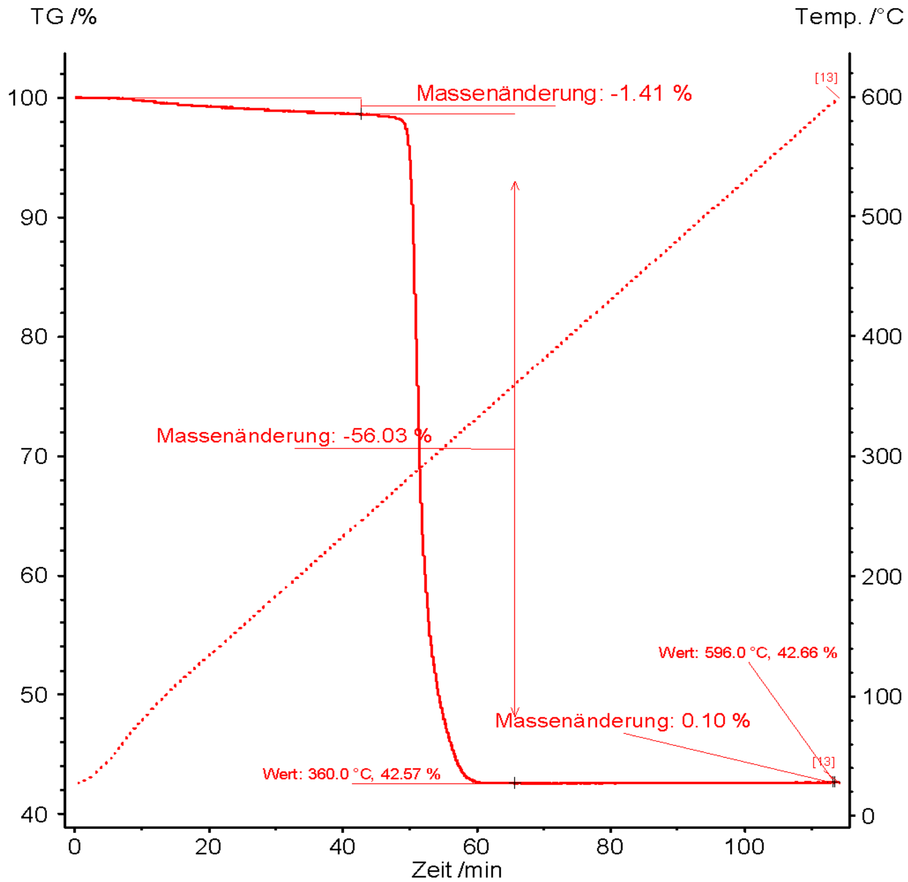
Two effects coinsides resulting in endothermic effect.

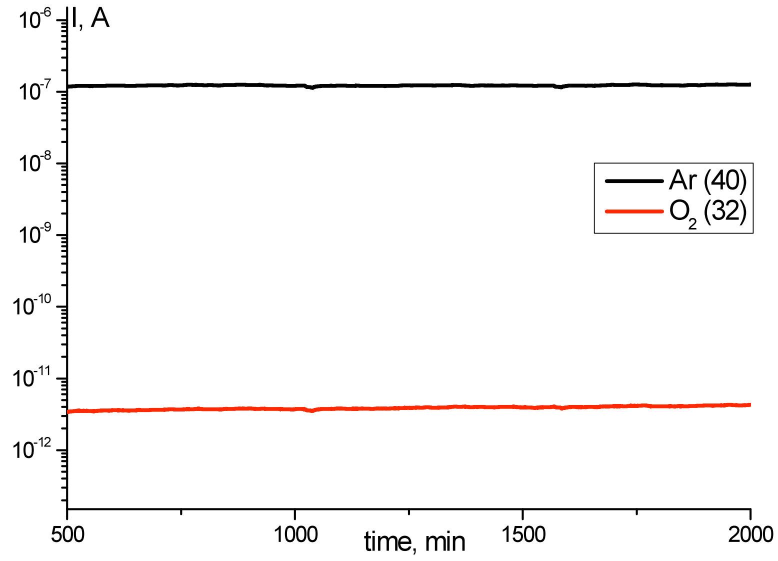
Measurement in inert. Is the system oxygen free?

Setup: Netzsch – STA Jupiter

$CuC_2O_4{\cdot}0.5H_2O \rightarrow Cu + 2CO_2$

$Cu + 1/2O_2 \rightarrow CuO$





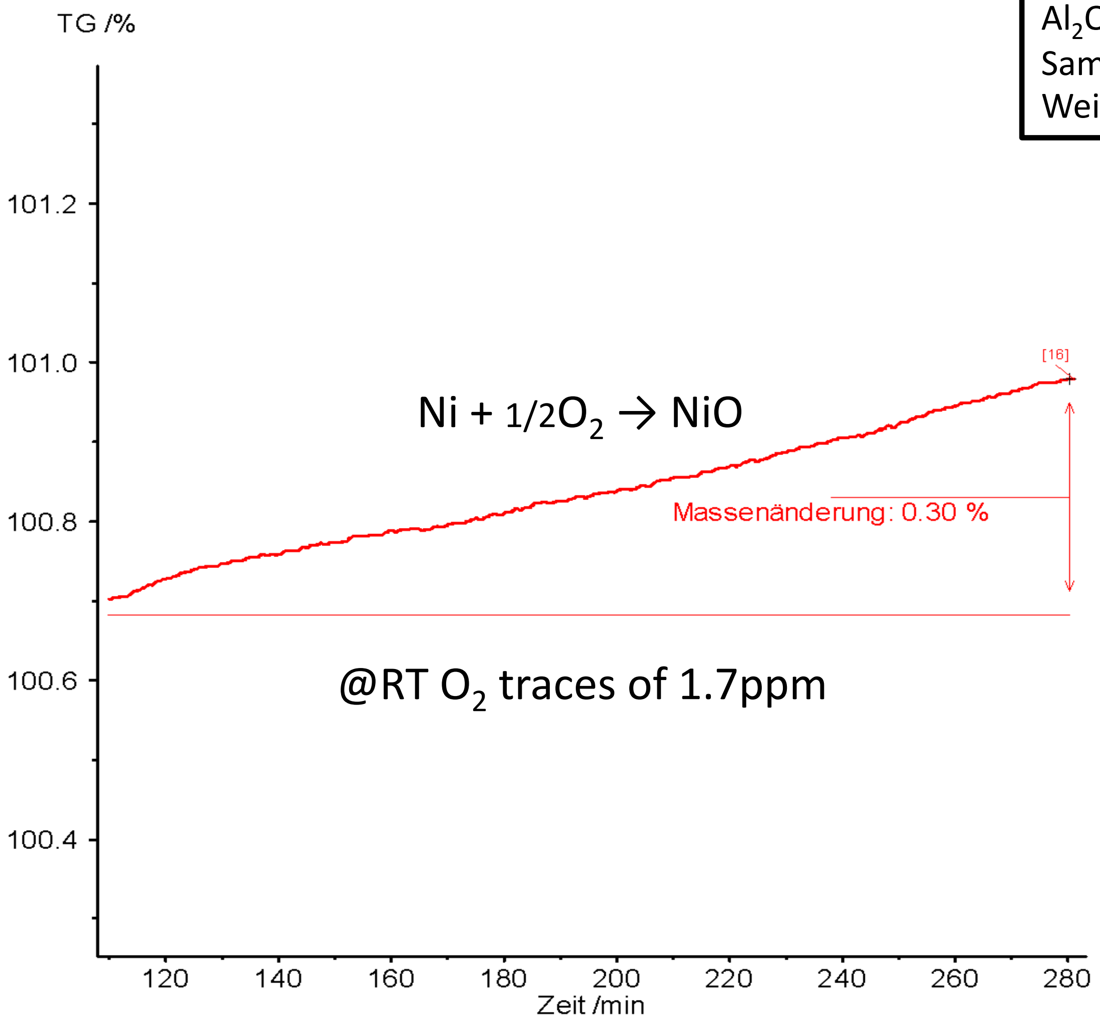
O_2 traces of 0.25ppm

DSC-TG sample holder,
Al_2O_3 pan, Ar 100ml/min
Sample: $CuC_2O_4{\cdot}0.5H_2O$
Weight: 9.1mg

Measurement in inert. Is the system oxygen free?

Setup: Netzsch – STA Jupiter

DSC-TG sample holder,
Al_2O_3 pan, Ar 100ml/min
Sample: $Ni/MgAl_2O_4$
Weight: 14.1mg



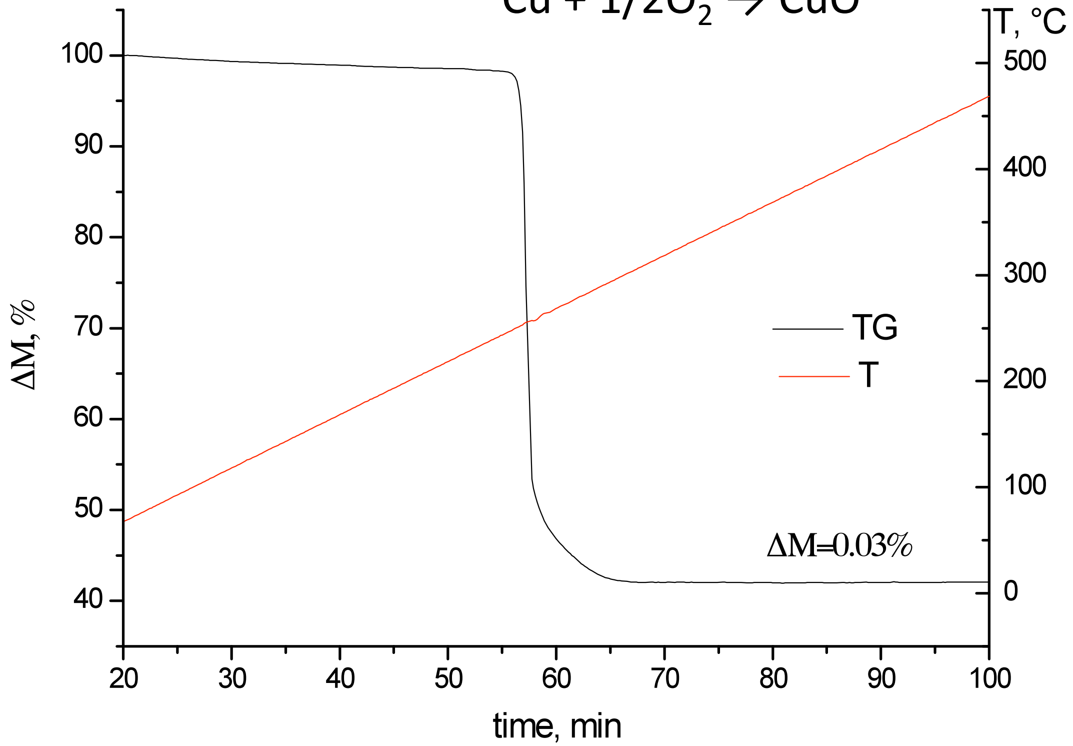
Measurement in inert. Is the system oxygen free?

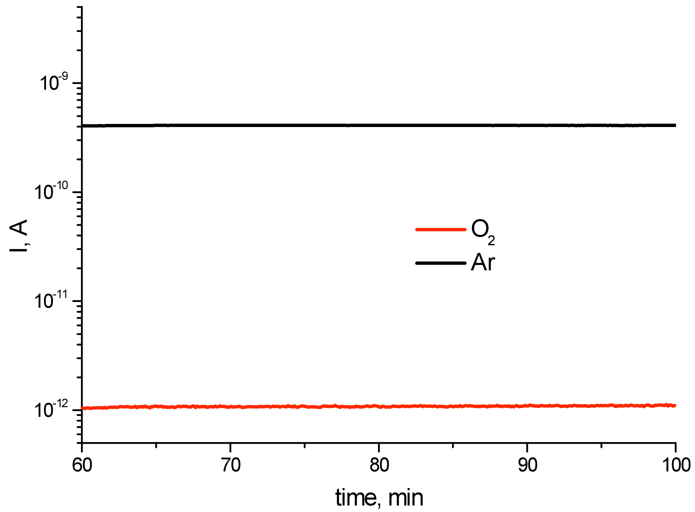
Setup: Rubotherm – MSB

$CuC_2O_4 \cdot 0.5H_2O \rightarrow Cu + 2CO_2$

$Cu + 1/2O_2 \rightarrow CuO$

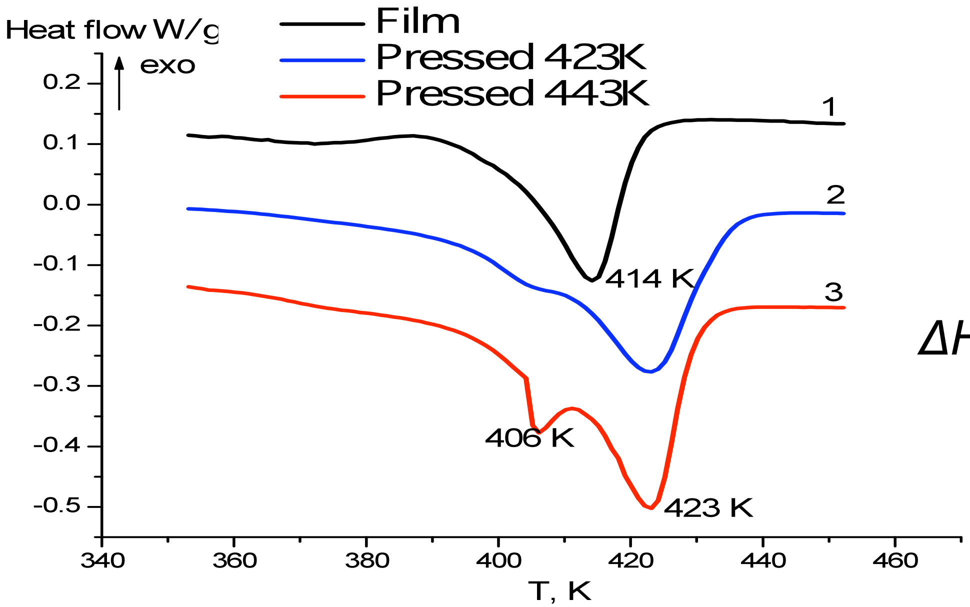
TG sample holder,
Al_2O_3 pan, Ar 250ml/min
Sample: $CuC_2O_4 \cdot 0.5H_2O$
Weight: 301.8mg





O_2 traces of 7ppm

Determination of crystallinity degree



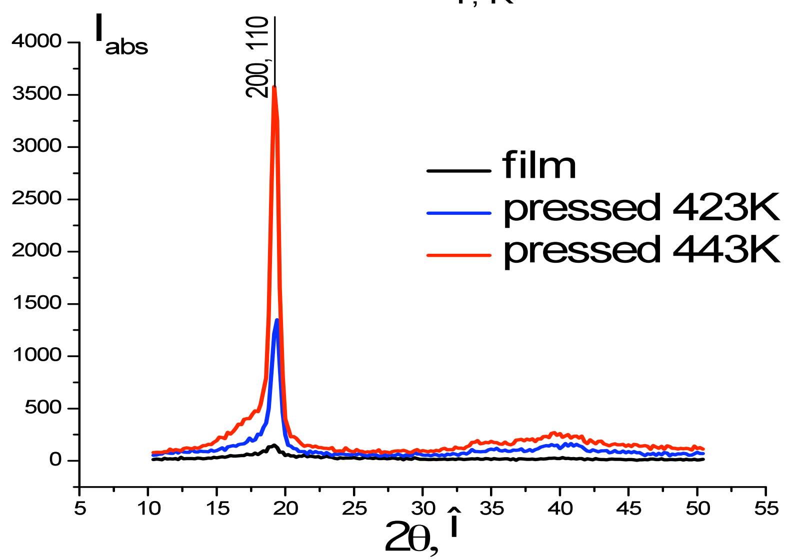
TFE-VDF, -{C_2F_4}$_n$ - {$C_2H_2F_2$}$_m$ -, F42

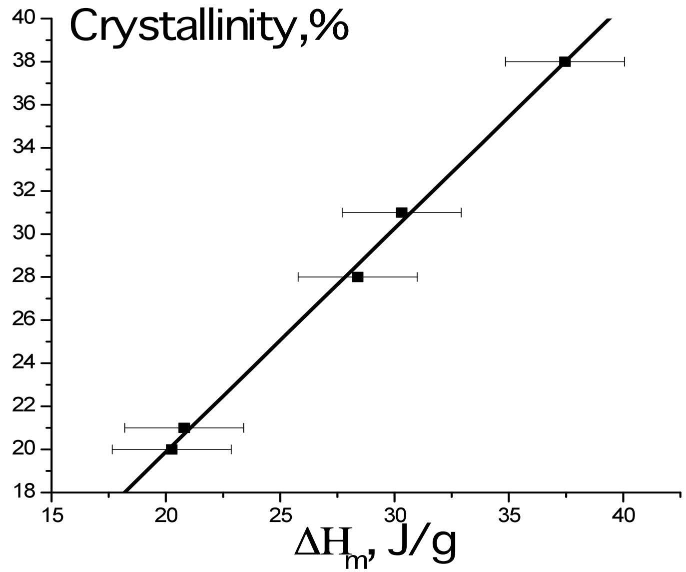
$X = \Delta H_f / \Delta H_f^o$

X-degree of crystallinity

ΔH_f^o – *enthalpy of polymer with 100% degree of crystallinity*

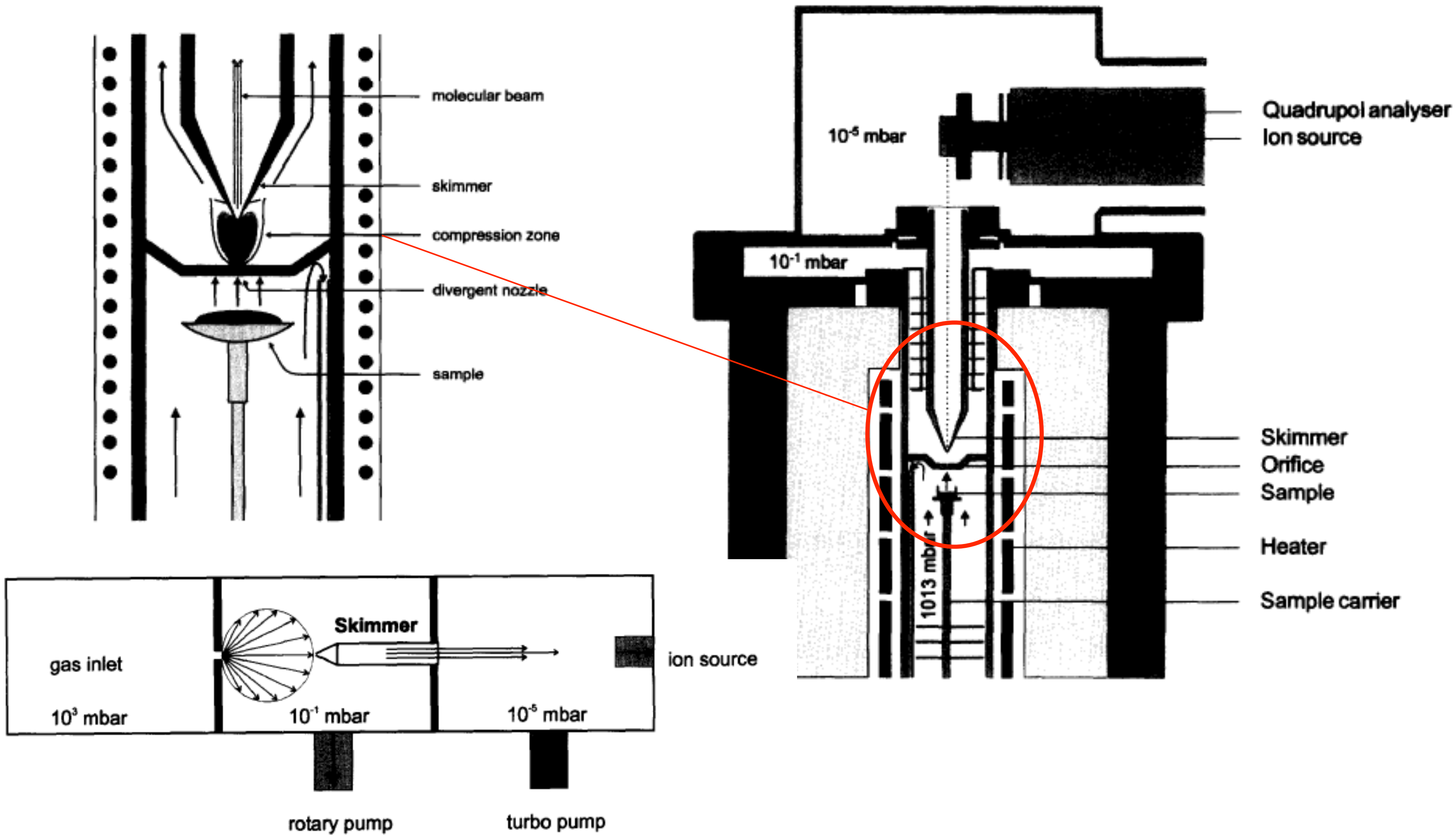
ΔH_f^o = 99.3J/g



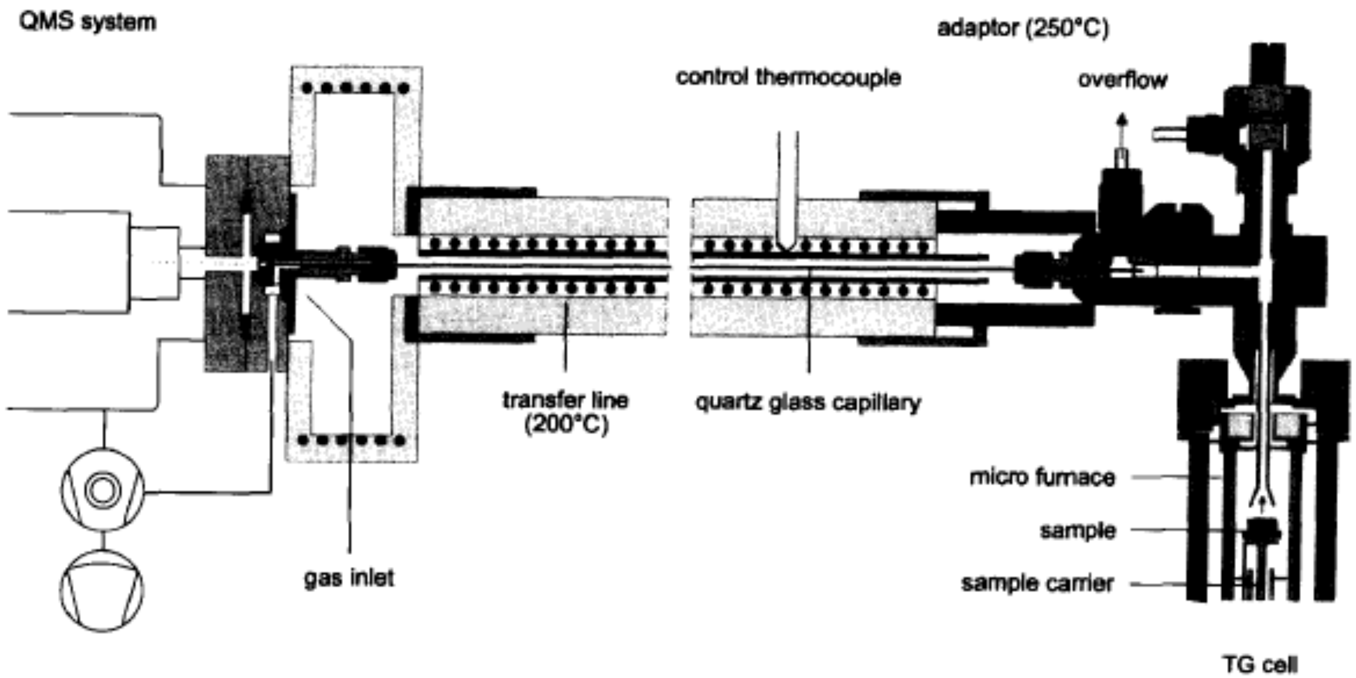


TA-MS Coupling systems

Skimmer coupling system



Capillary coupling system



Main Problems of TA-MS coupling system

- Pressure reduction

  10^3mbar → 10^{-5}mbar

- Condensation and secondary reactions

  Unfalsified gas transfer

  Different viscosity – Demixing

- Attribution of a fragment to a chemical process

  Pyrolysis or evaporation

  MS fragmentation or sample behavior

- Overlapping of thermal processes

  hydrolysis and oxidation due to rest water and oxygen background in the feed.

Disadvantages: shock sensitive, no direct MS inlet.

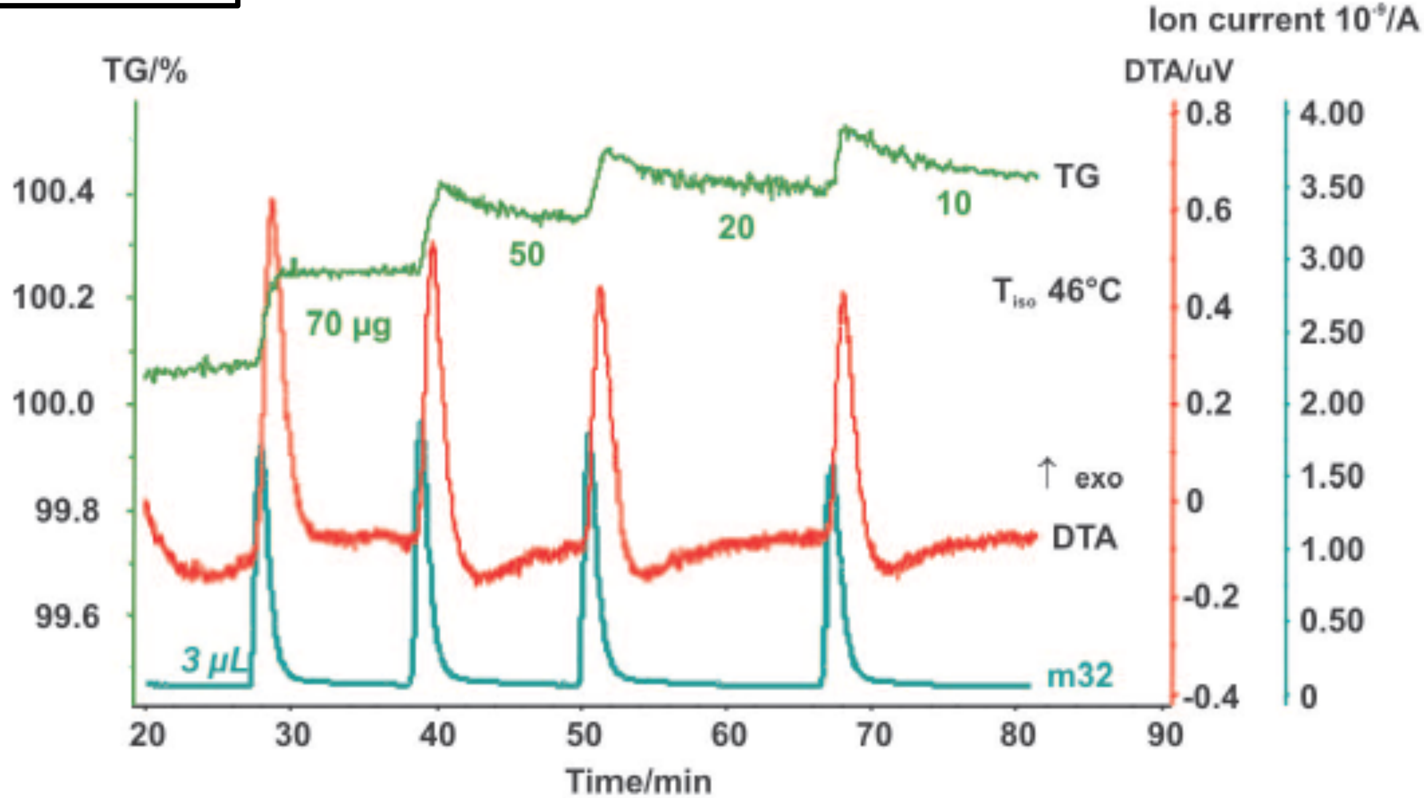
Kaiserberger (1999)

(PulseTA®) Adsorption of Methanol on β-AlF_3

M. Feist et. al. 2010

Sample: β- AlF3
Sample weight: 43.81 mg
Δm=0.15mg,
N2 - 70ml/min

Determining Lewis acidity

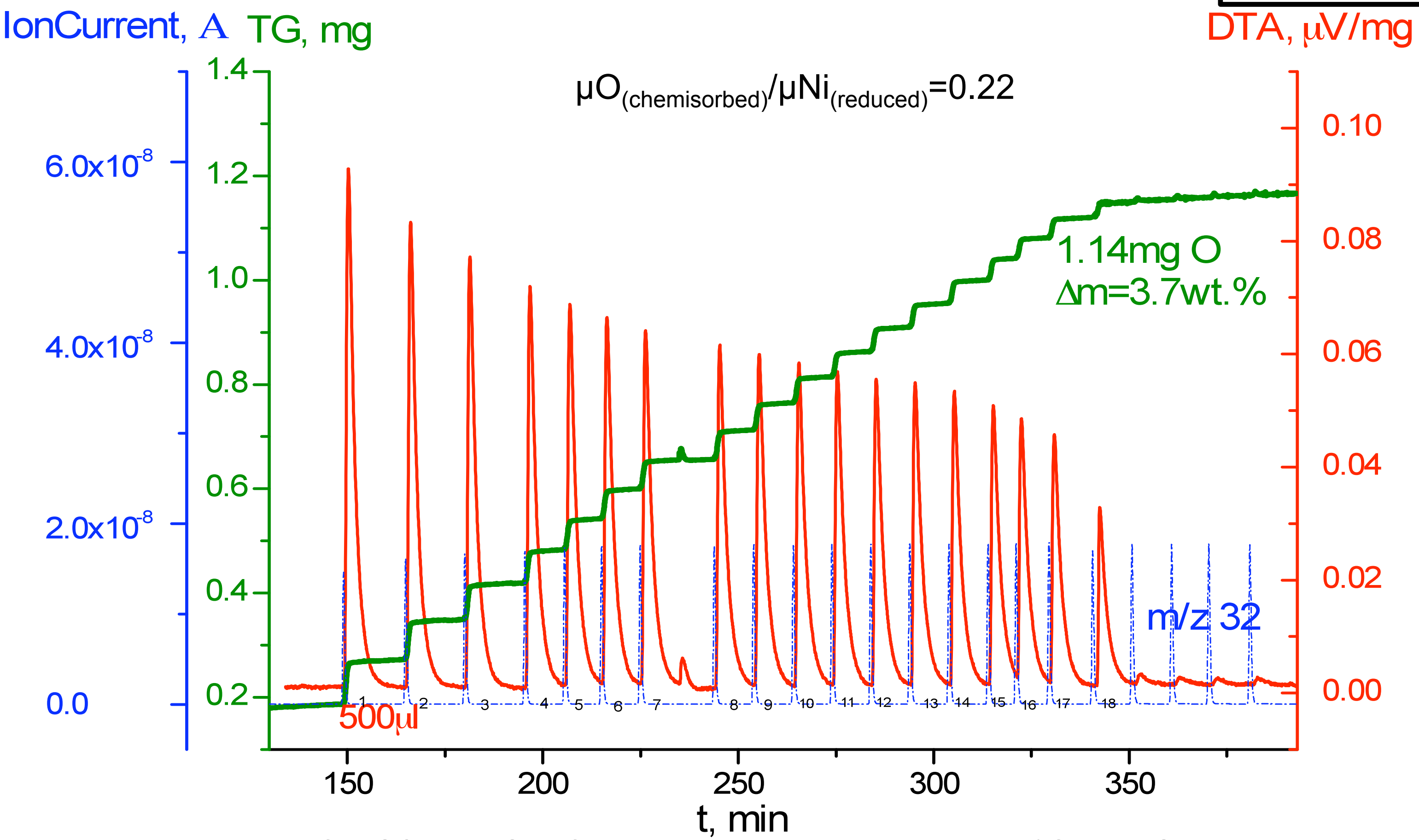


TA-MS curves for a PulseTA® experiment on pretreated (2 h, 250 °C; vacuum)

(PulseTA®) Titration of Ni surface with O_2

** Assuming O/Ni=2, dNi=9nm in agreement with TEM

Sample: $Ni/MgAl_2O_4$
Sample weight: 30.8 mg
Δm=1.14mg,
Ar - 100ml/min



PTA curves of $NiO/MgAl_2O_4$ after reduction, isothermal at 45°C with O_2 injections, Interupted by a H_2 pulse

Resources

- J. Sestak, Thermophysical properties of solids (Academia, Prague, 1984)
- G. Höhne, W. Hemminger, H.-J.Flammersheim, Differential Scanning Calorimetry (Springer, Berlin, 1996)
- E. Moukhina, J. Therm Anal. Calorim. (2012) 109: 1203-1214
- http://www.netzsch.com

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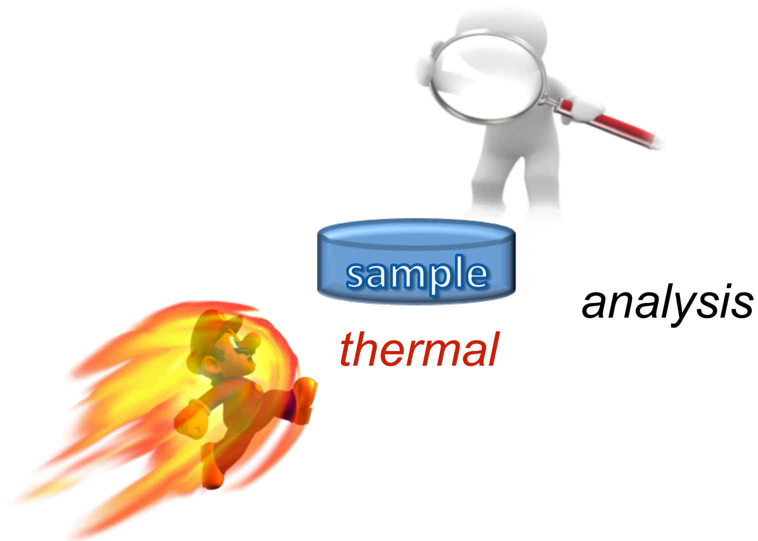
- Dr. Alexander Dunaev, MSU Moscow



MAX-PLANCK-GESELLSCHAFT

Thank you!