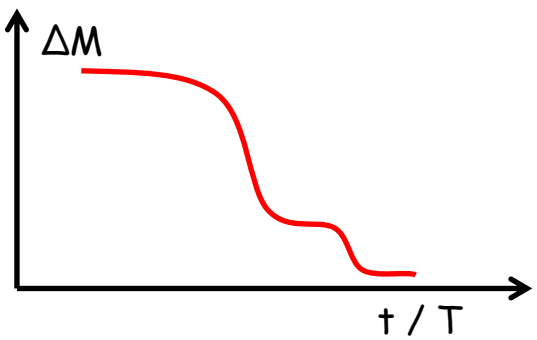
Operando thermal analysis

Andrey Tarasov
8.12.2017

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.

Thermogravimetry

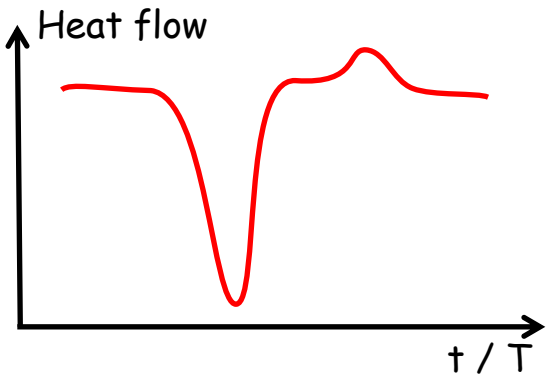


$$r \equiv \frac{dN}{d\tau} = \frac{1}{M} \cdot \frac{dm}{d\tau}$$

$$\Delta m = M \cdot \Delta N$$

A(s)↔ B(g)

Differential Scanning Calorimetry



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

$$\Delta Q = m \cdot C_p \cdot \Delta T$$

A(s)↔B(s)

A(s)↔B(g)

Key parameters:

Course of the reaction, yield of the reaction

Enthalpy of formation/transformation (reaction, phase transition)

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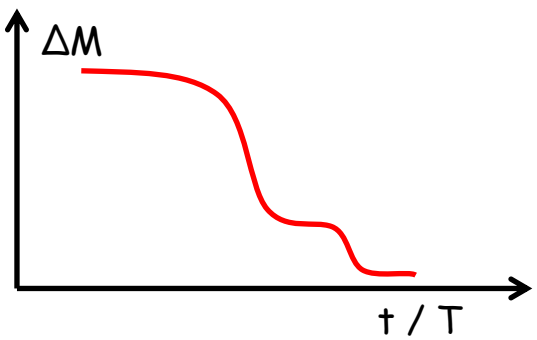
Thermogravimetry



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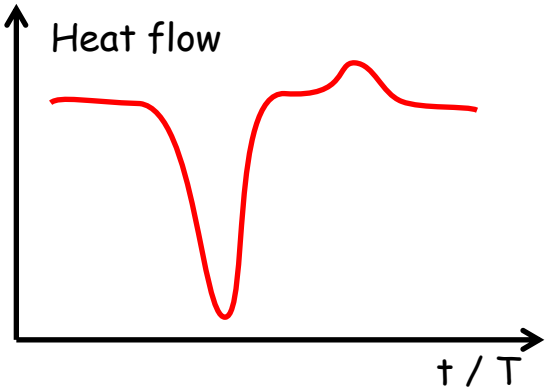


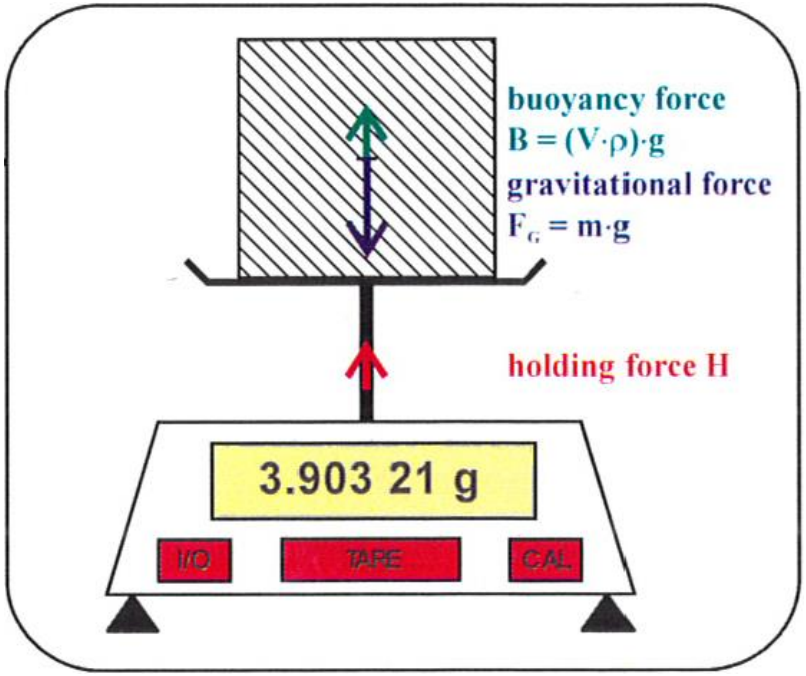
$$\phi \equiv \frac{dQ}{d\tau} = m \cdot C_p \cdot \frac{dT}{d\tau}$$

$$\Delta Q = m \cdot C_p \cdot \Delta T$$

operando≈in-situ – „on site“→in heterogeneous catalysis
„in reaction mixture under operation conditions“

T, P, μ→ conversion/actitvity, mass – transfer conditions

Thermogravimetry: Basic Principle



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)

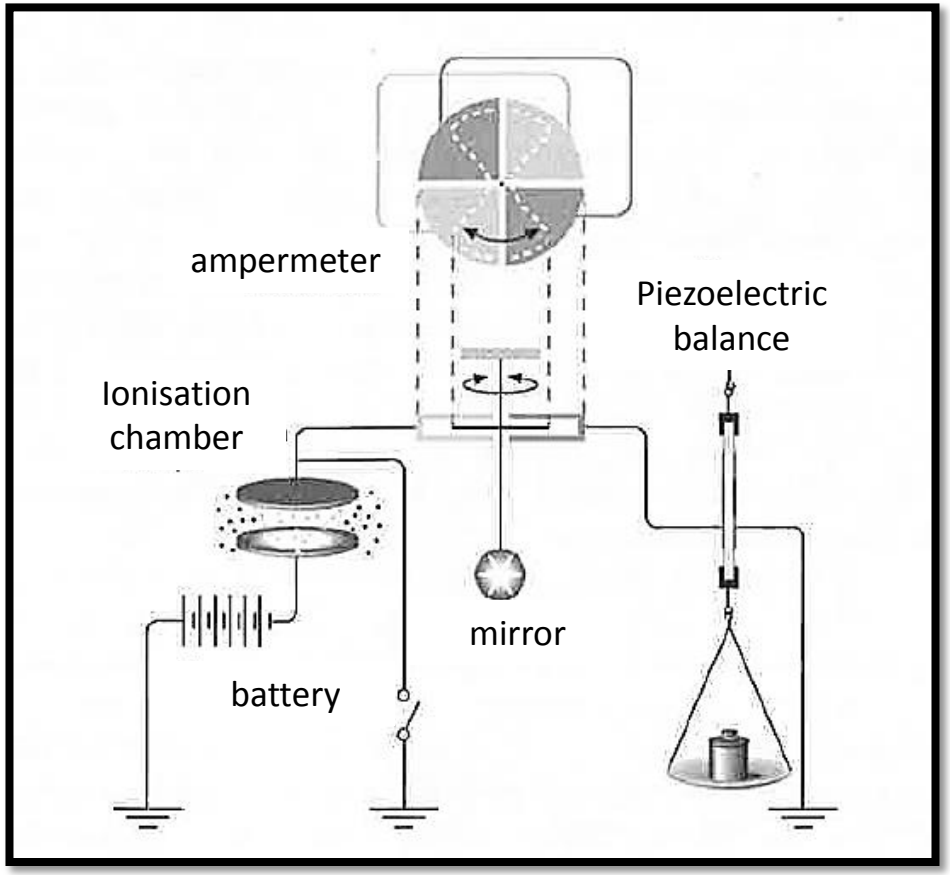
ρ_{gas} - Density of gas, f(T)

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

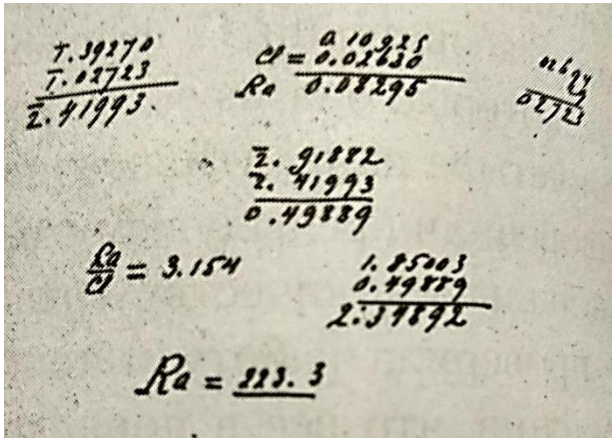
Signal System mass Buoyancy Force

Is it sensitive enough?

1898, Marie Curie “weighted” radioactivity



^{88}Ra, ^{84}Po

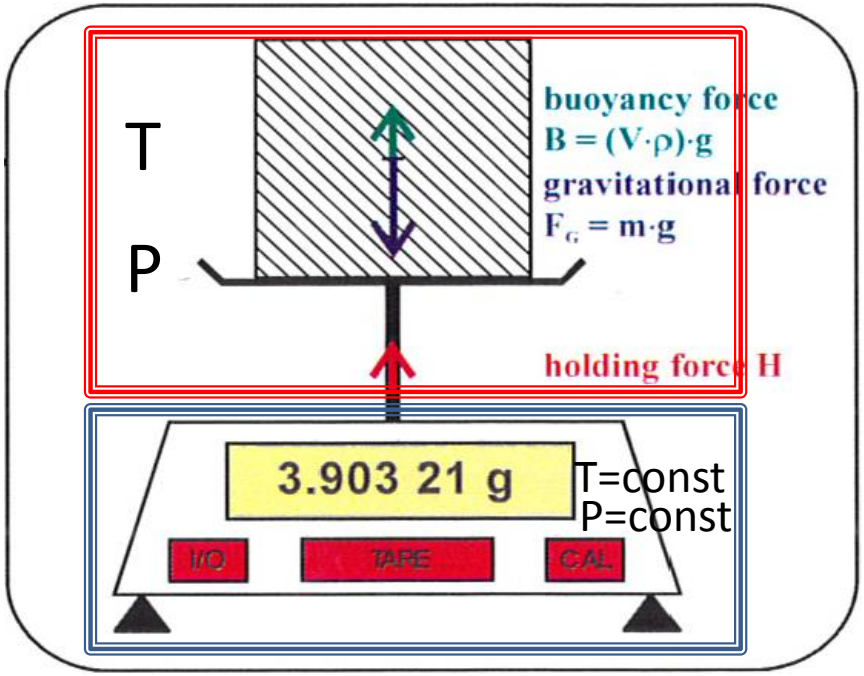


Marie and Pierre Curies diary, 1902. Curie Museum

$Mr(Ra)=225$

1 g earth crust≈10^{-13}g Ra

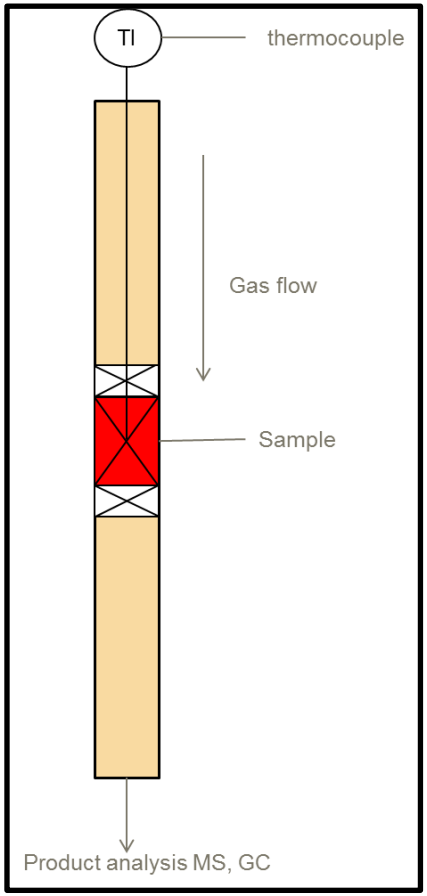
Thermogravimetry: Basic Principle



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

Signal System mass Buoyancy Force

?



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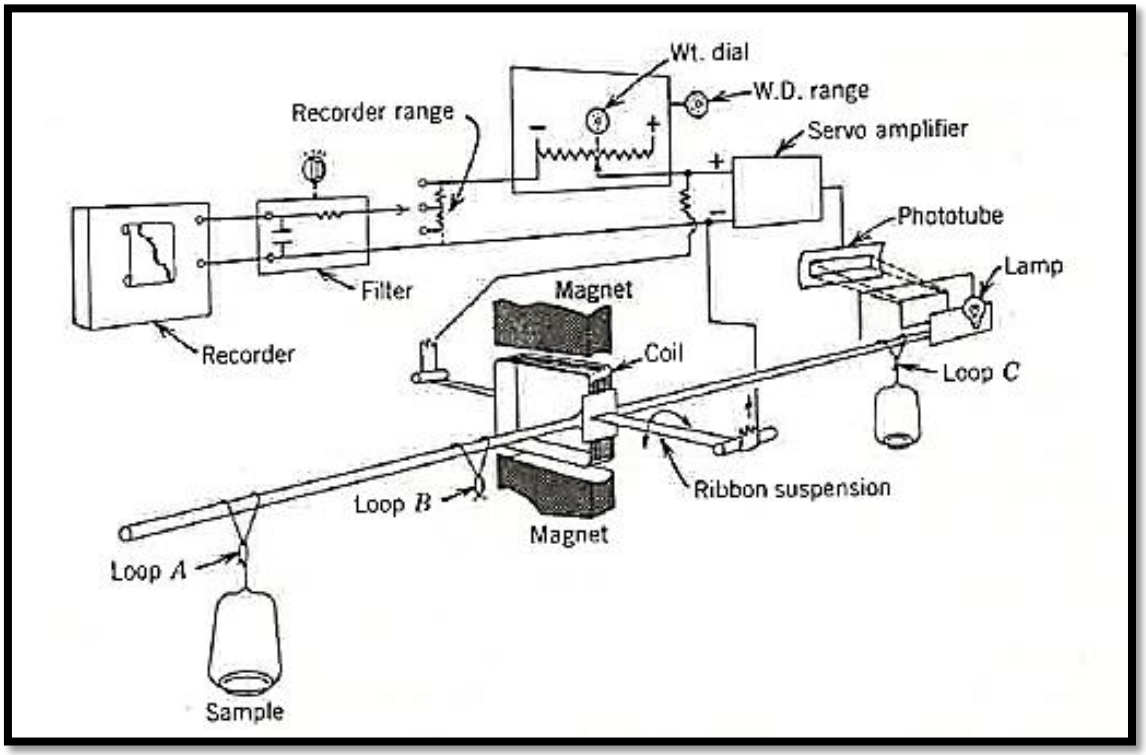
ρ_{gas} - Density of gas, f(T)

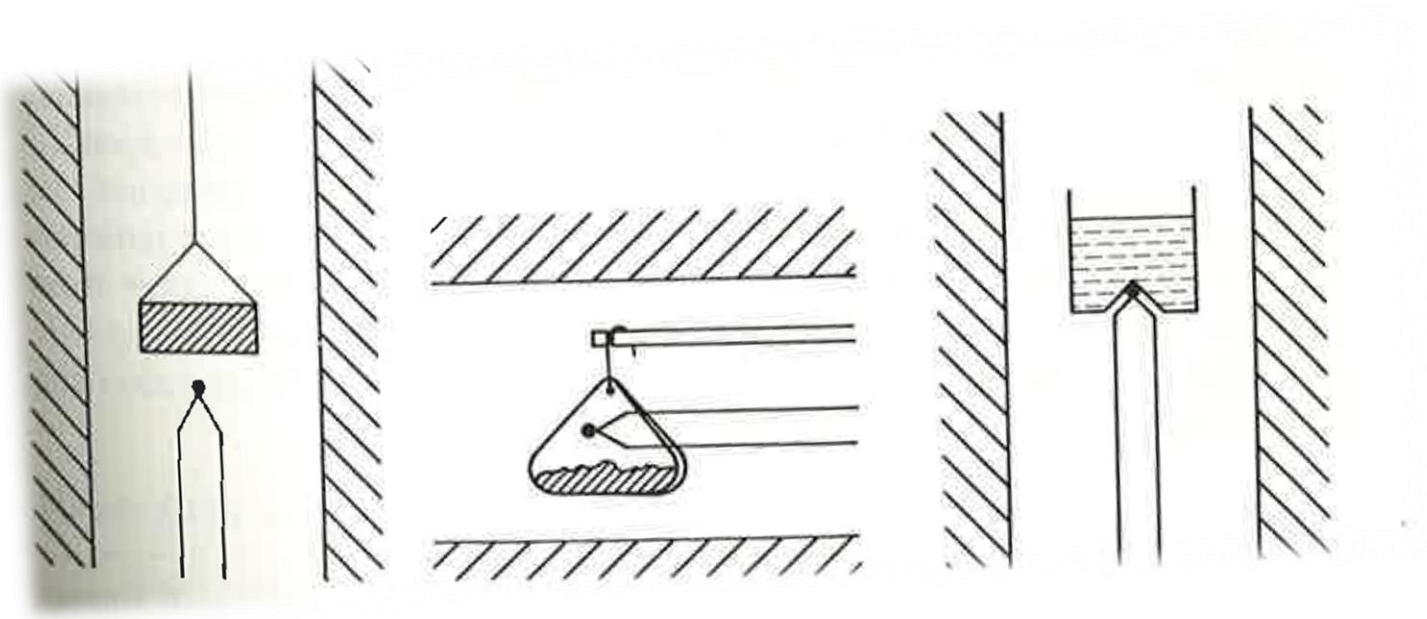
Balance



Schematic diagram of the Cahn Electrobalnce

Commercially available thermobalances employ one of the Cahn-type electromagnetic balance

Temperature detection



No contact | Close proximity | With contact

Sample holders

Sample holders


Al_2O_3 crucibles with different volumes (0.9 ml, 3.4 ml, 5 ml)

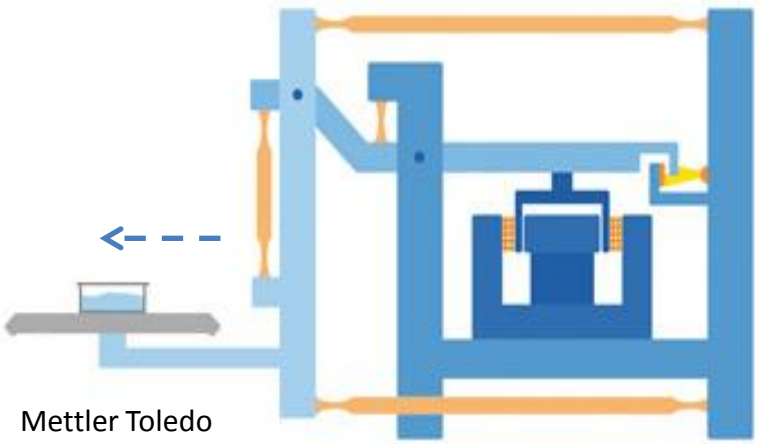

Al_2O_3 slip-on plates (ø 10 mm, 17 mm)


Pt/Ir net-shaped slip-on plates (ø 17 mm, 100/225 meshes/cm²)


TGA-DTA crucibles and slip-on plates

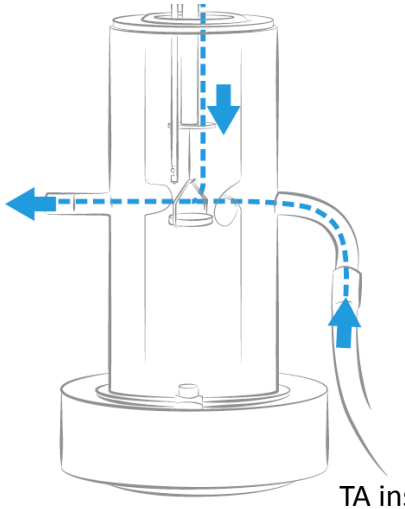
Thermobalance construction geometries

Horizontal, parallel-guided



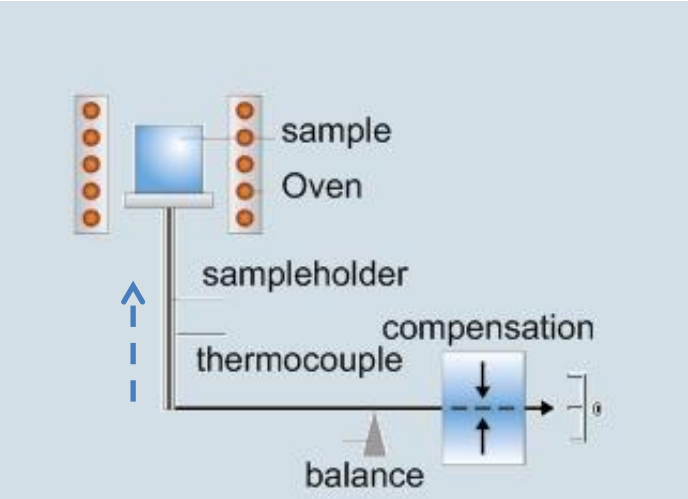
Mettler Toledo

Vertical, free suspended

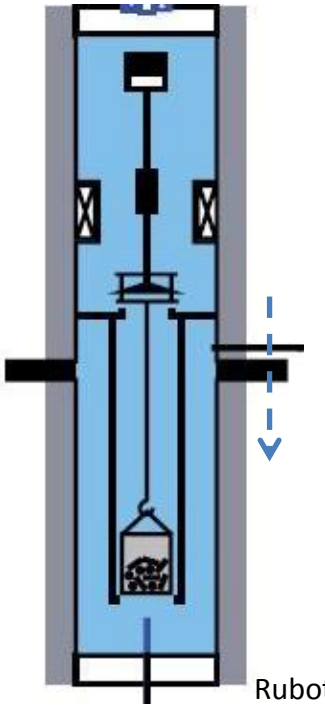


TA instruments

Vertical, top-loader

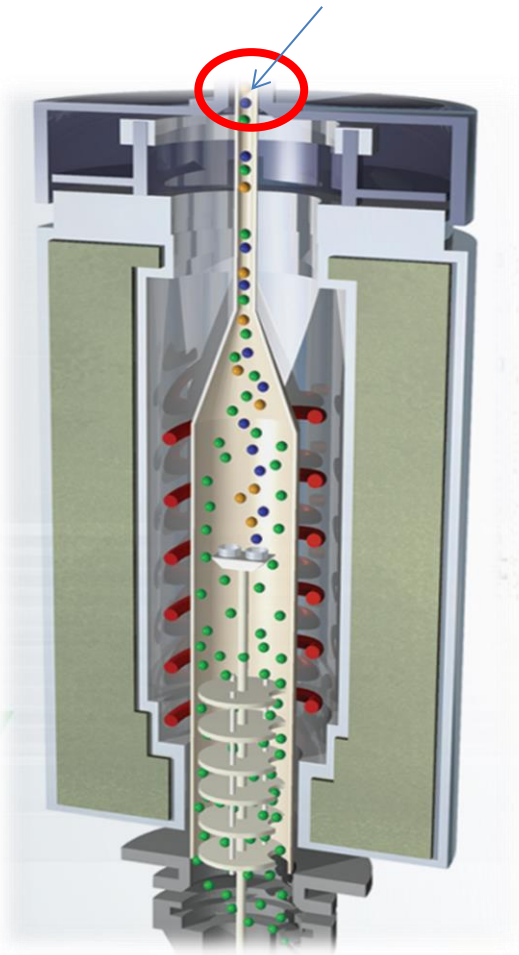


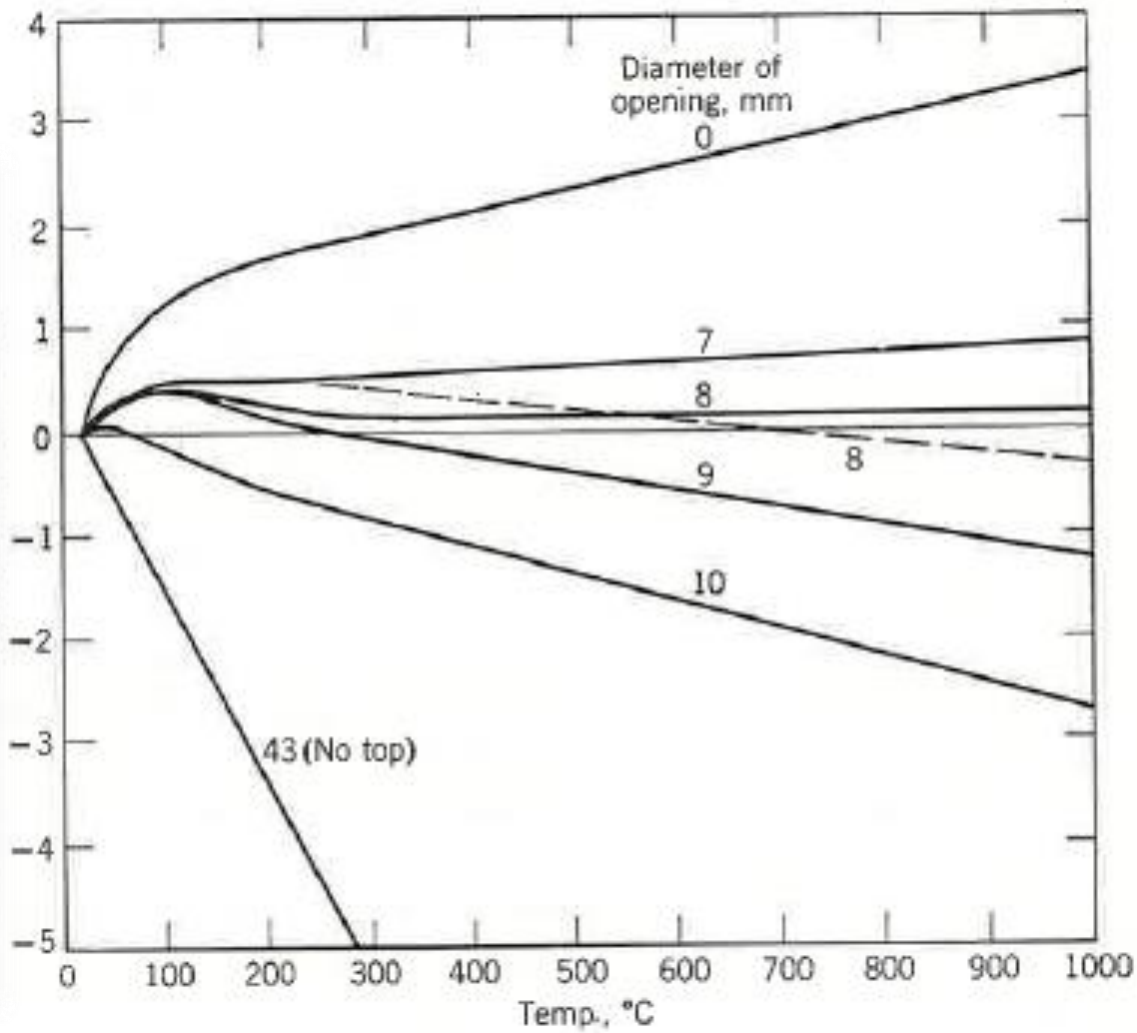
Netzsch, Setaram



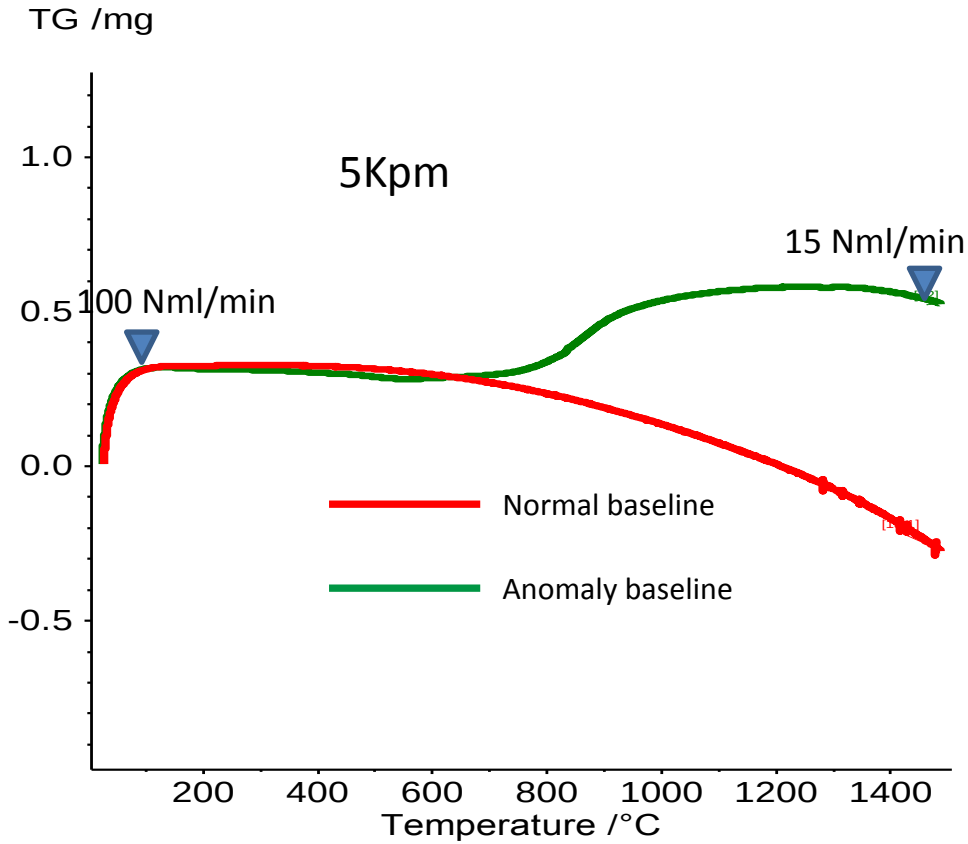
Rubotherm

Furnace Convection Currents and Turbulence



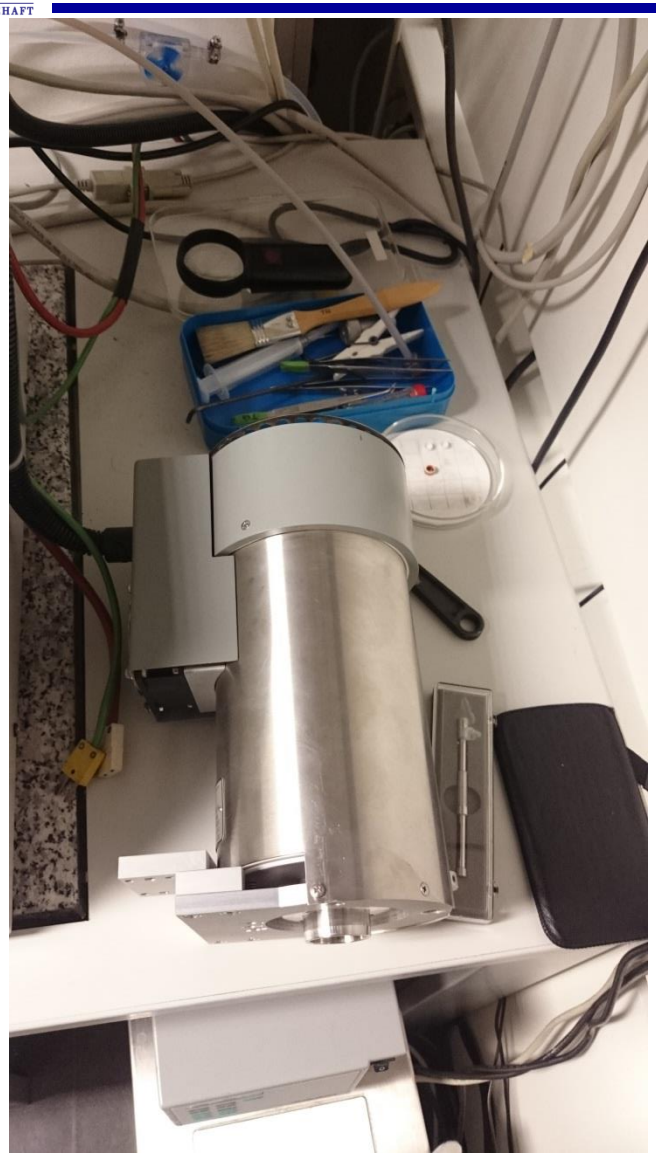


Effect of furnace top opening on apparent mass-change, 5Kpm



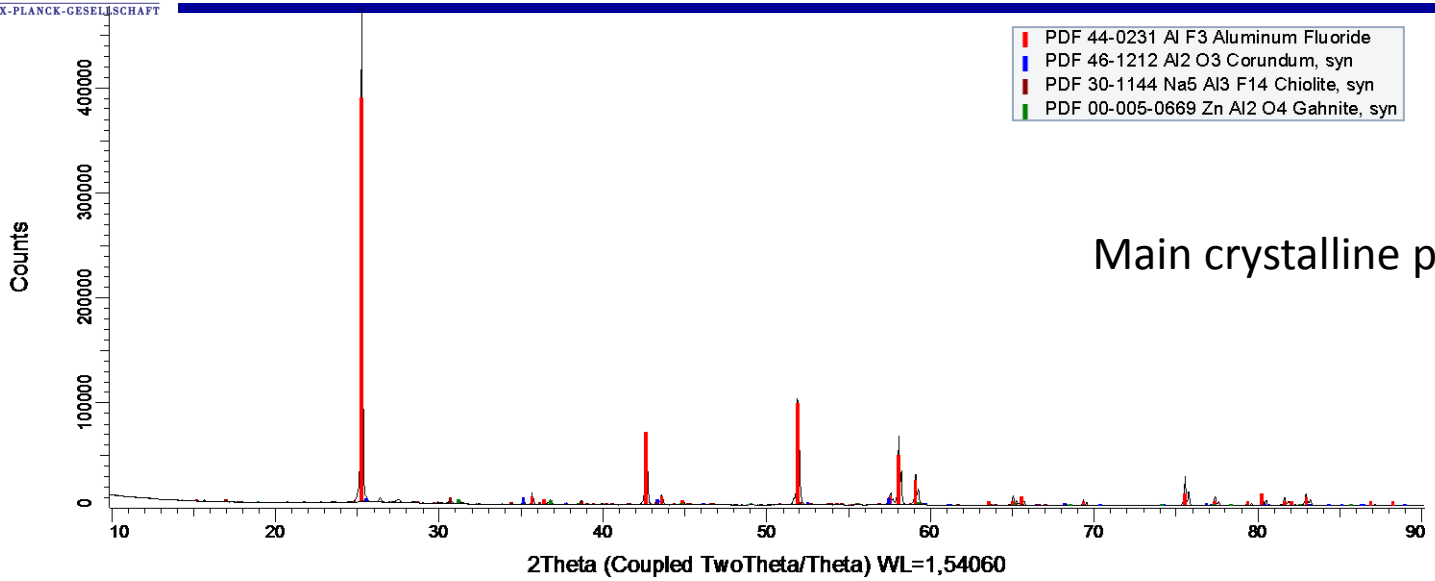
- Reproducible in different gas atmospheres and by different heating rates

gas flow decreases during the heating, starting from 600°C

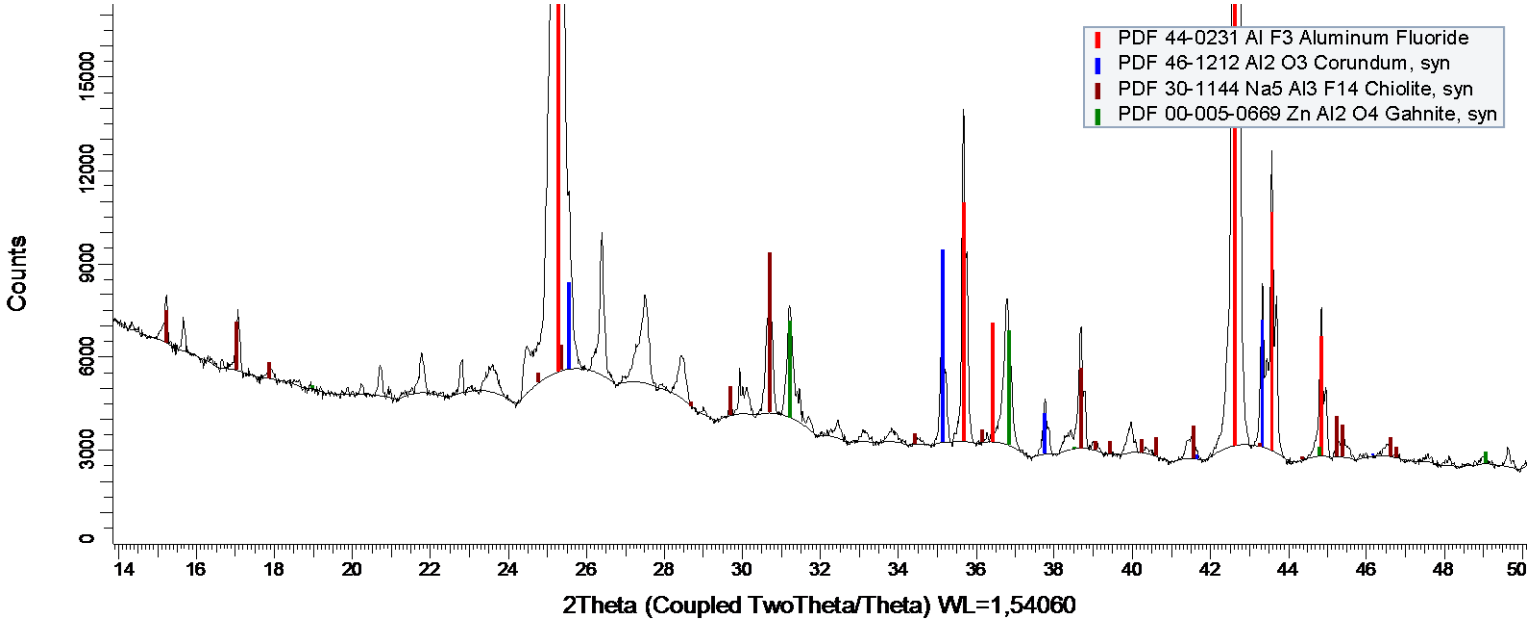


Reassembling the oven
Top part of the tube was plugged with solid material
The material was analyzed by various techniques

XRD



Main crystalline phase is AlF_3



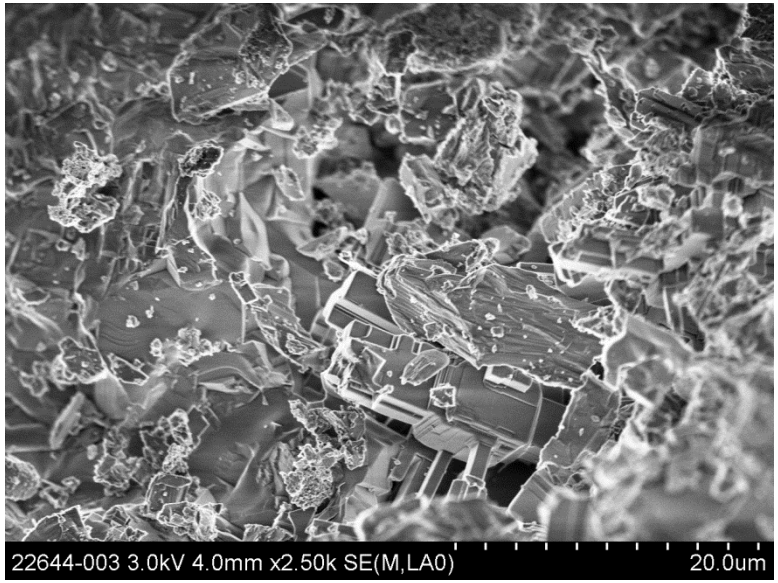
XRF

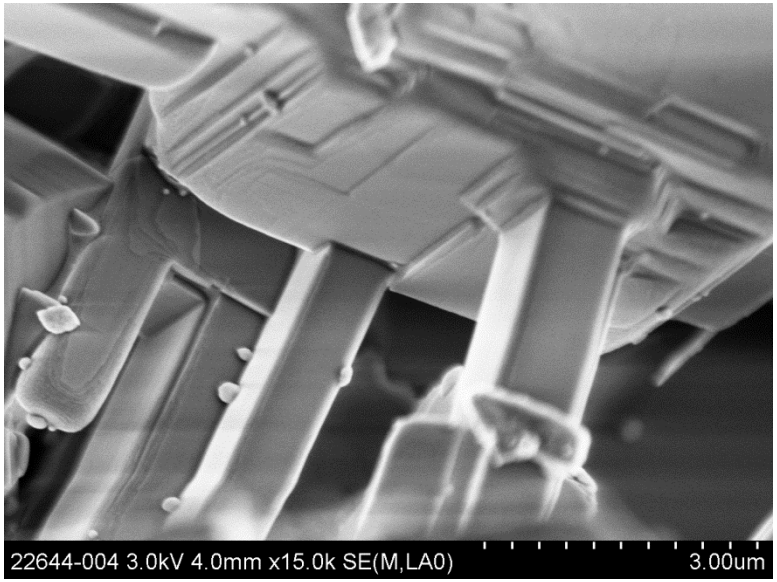
Formula	Concentration, %
AlF3	92.4
Bi2O3	0.45
CaO	0.62
Cr2O3	0.54
CuO	1.17
Fe2O3	1.69
K2O	0.55
MoO3	2.95
NiO	0.16
P2O5	0.33
Ru	0.642
SiO2	1.3
SO3	0.45
WO3	0.33
ZnO	2.21

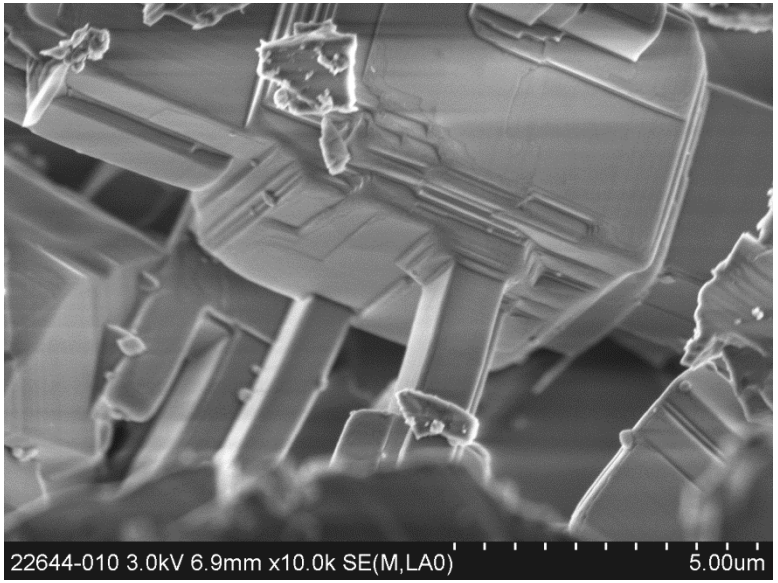
Elemental analysis

SEM_EDX

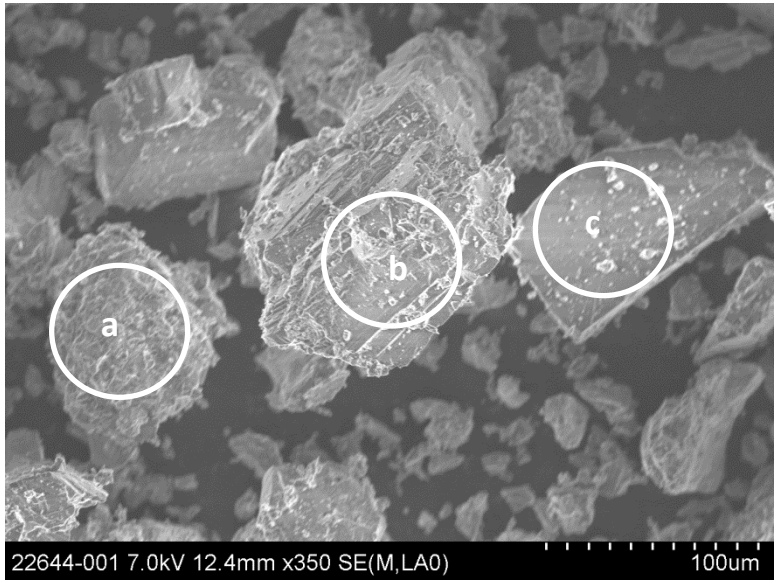
Surface microstructure

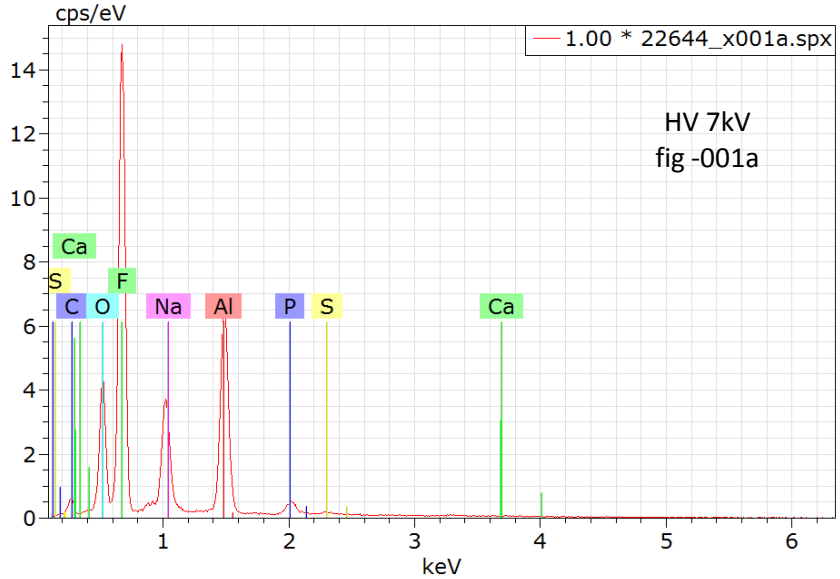


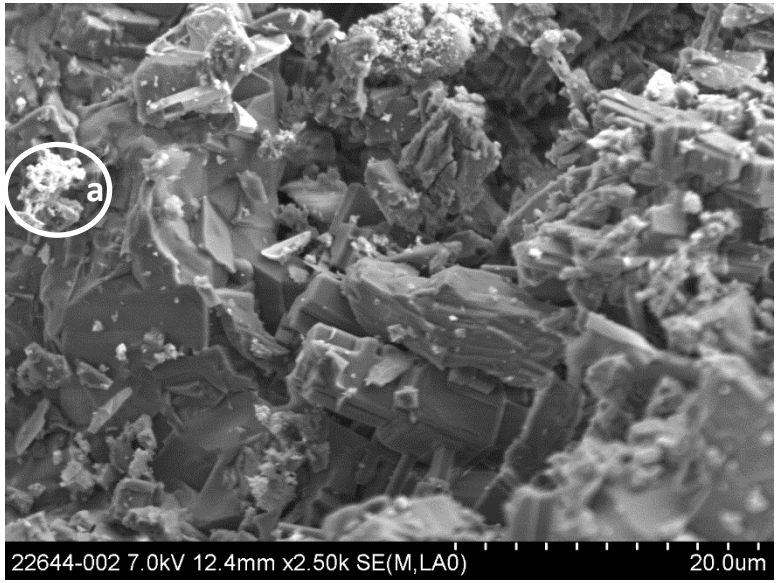


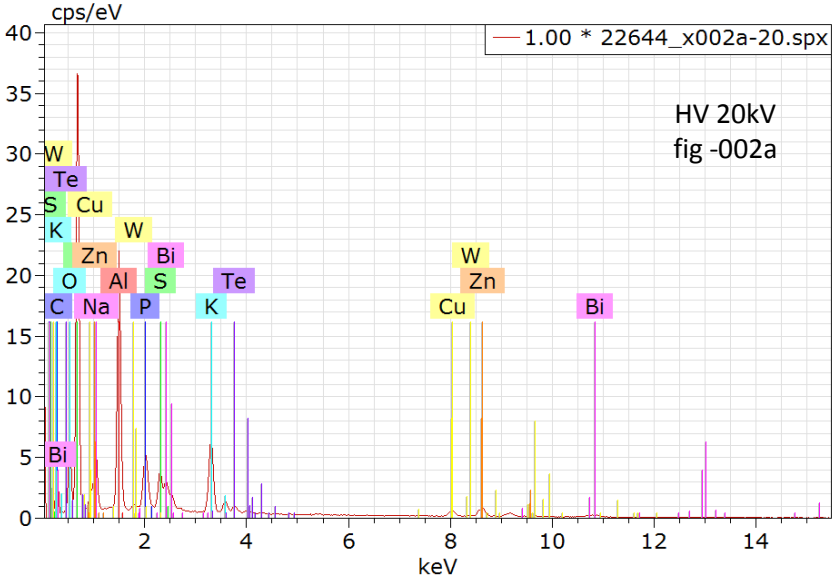


SEM_EDX


a
b
c
22644-001 7.0kV 12.4mm x350 SE(M,LA0)
100um

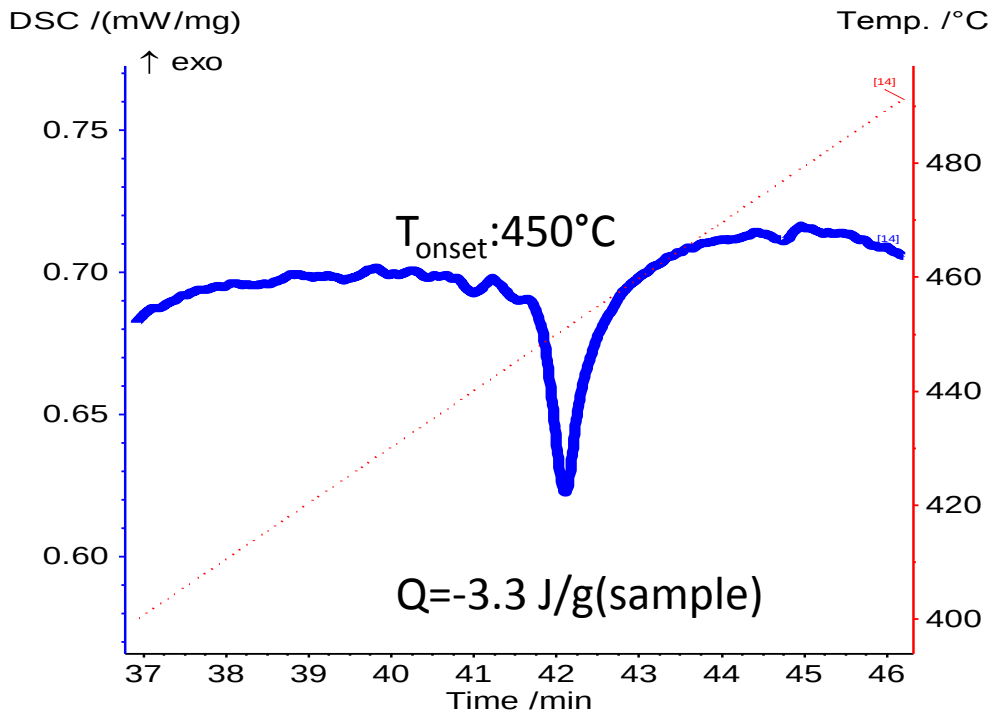

cps/eV
1.00 * 22644_x001a.spx
HV 7kV
fig -001a
Ca
S
F
C
O
Na
Al
P
S
Ca
keV

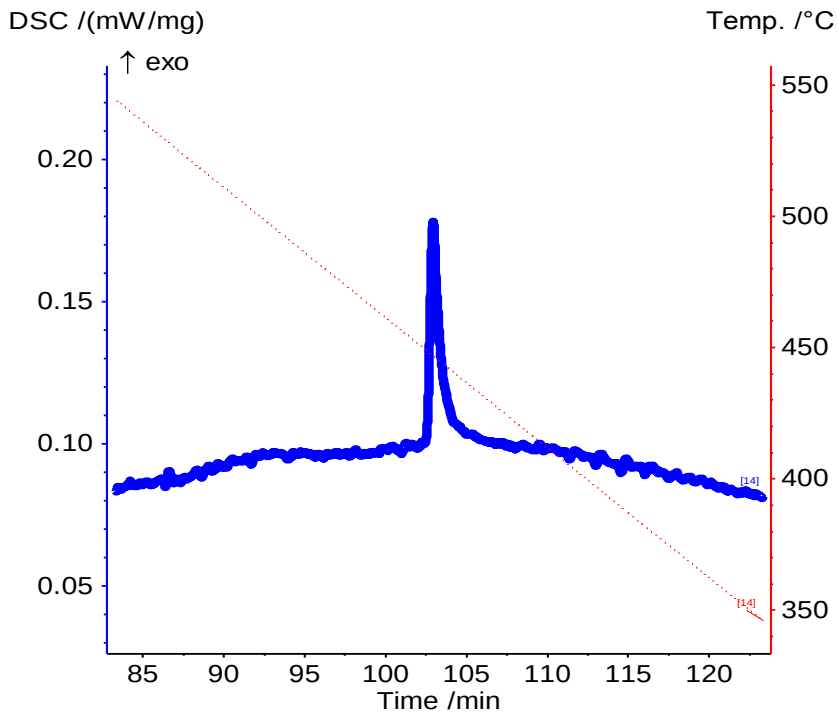

a
22644-002 7.0kV 12.4mm x2.50k SE(M,LA0)
20.0um


cps/eV
1.00 * 22644_x002a-20.spx
HV 20kV
fig -002a
W
Te
S
Cu
K
W
Zn
Bi
W
O
Al
S
Te
Zn
C
Na
P
K
Cu
Bi
Bi
keV

DSC

- Reversible melting point (explains dynamic behaviour of the flow)





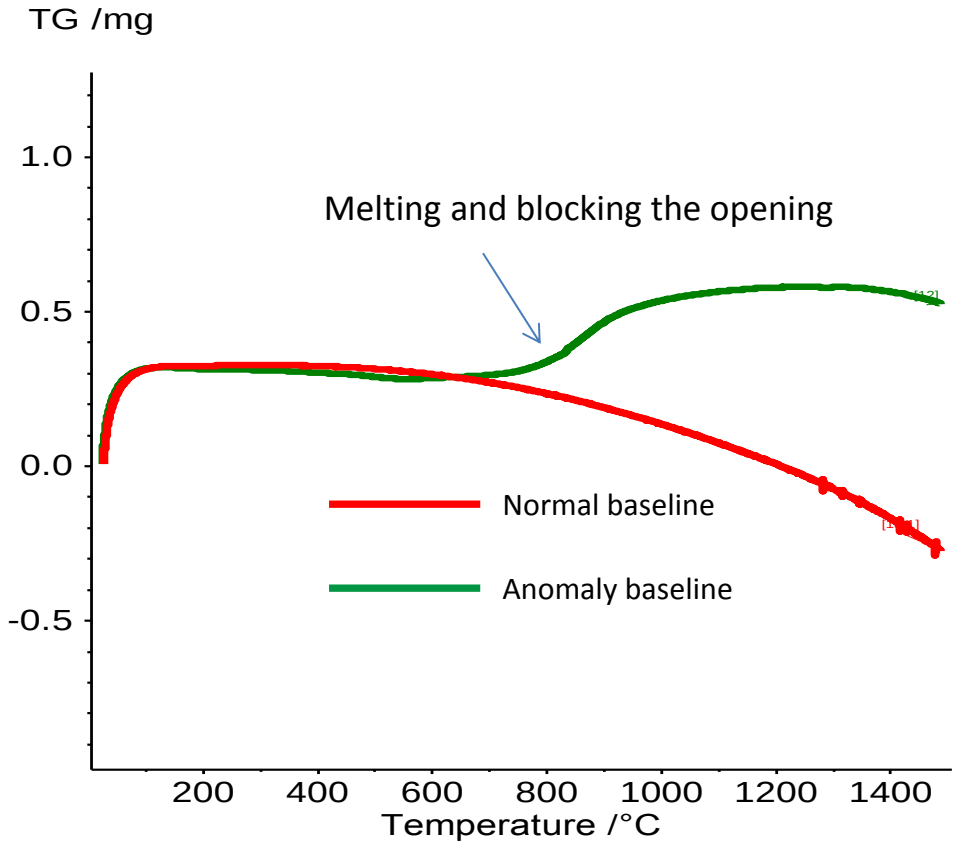
eutectic LiF-NaF-KF (46.5-11.5-42) T_m=454°C

$K_{1-3}AlF_{4-6}$, $CsAlF_4$ (NOCOLOK ®) T_m=560-570°C

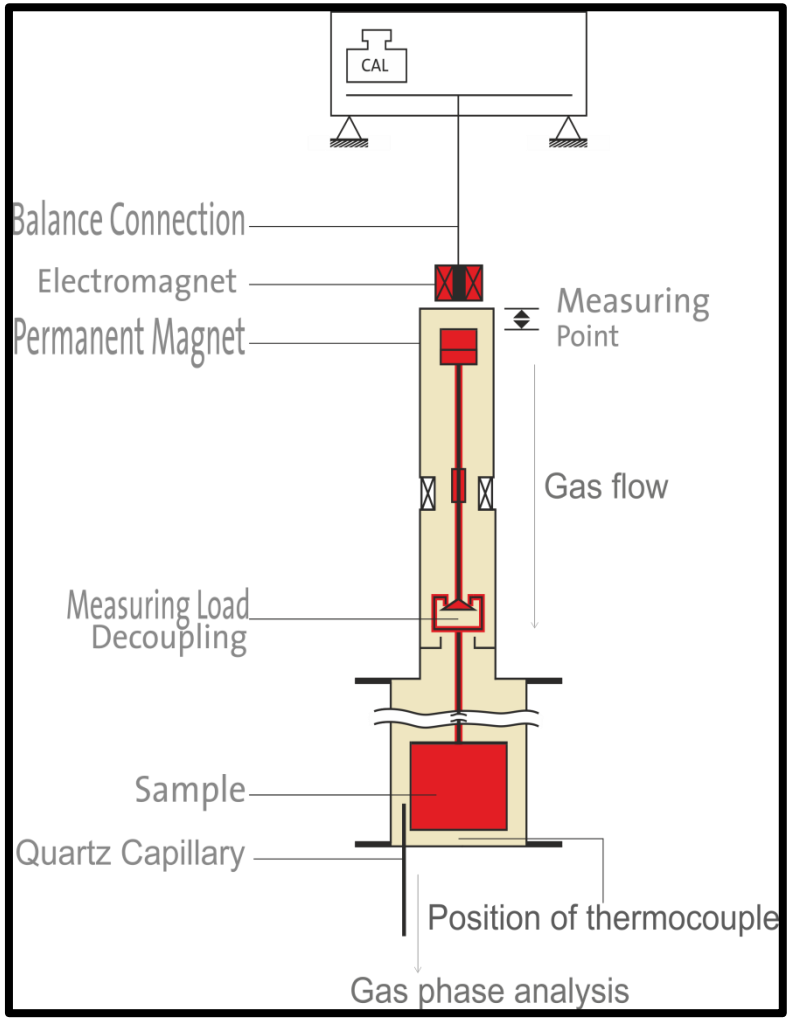
AgF T_m=435°C

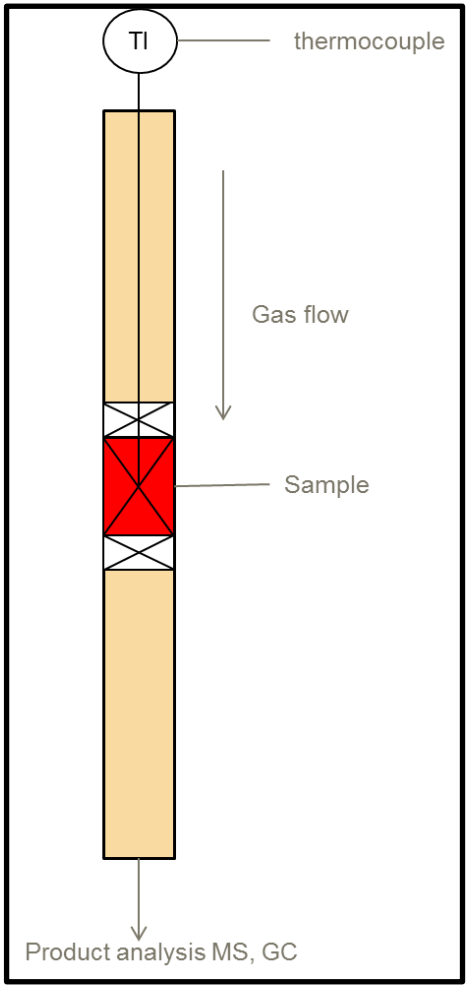
Zn T_m= 419°C

Ammount of the phase undergoes melting 1.5-3%

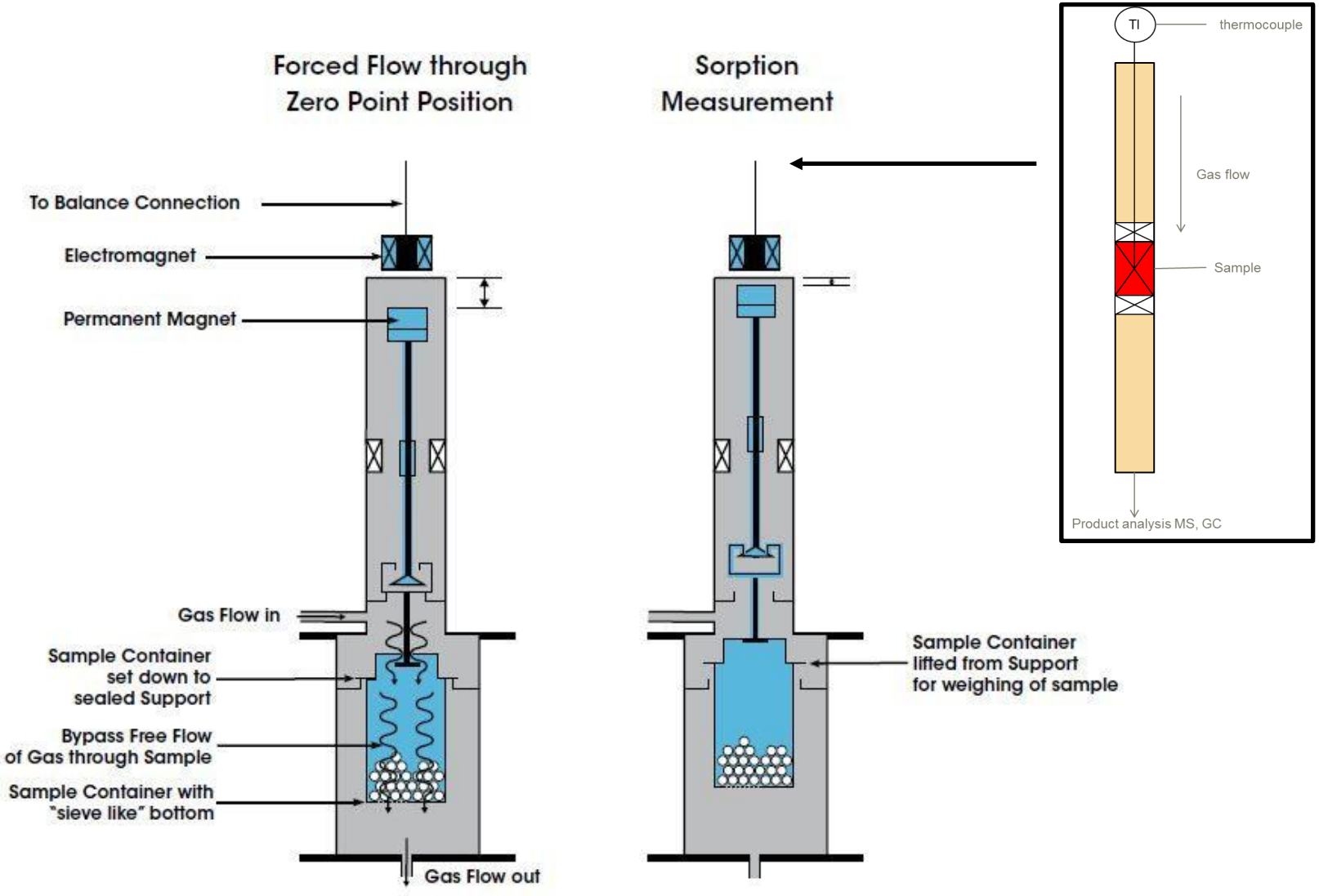

TG /mg
1.0
0.5
0.0
-0.5
Melting and blocking the opening
Normal baseline
Anomaly baseline
200
400
600
800
1000
1200
1400
Temperature /°C

Nearing the plug flow conditions

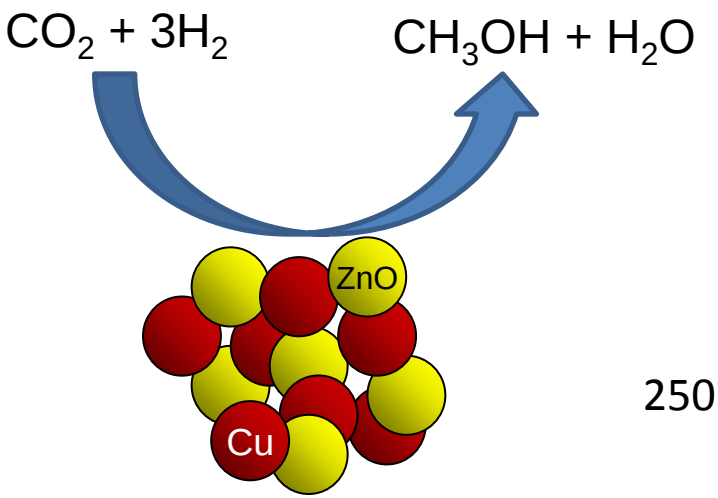




Nearing the plug flow conditions



Case Study: Methanol Synthesis



250°C, 30bar

$$CO_2 + \boxed{3H_2} \longrightarrow \boxed{CH_3OH} + H_2O \qquad \Delta H = -53 kJ/mol$$

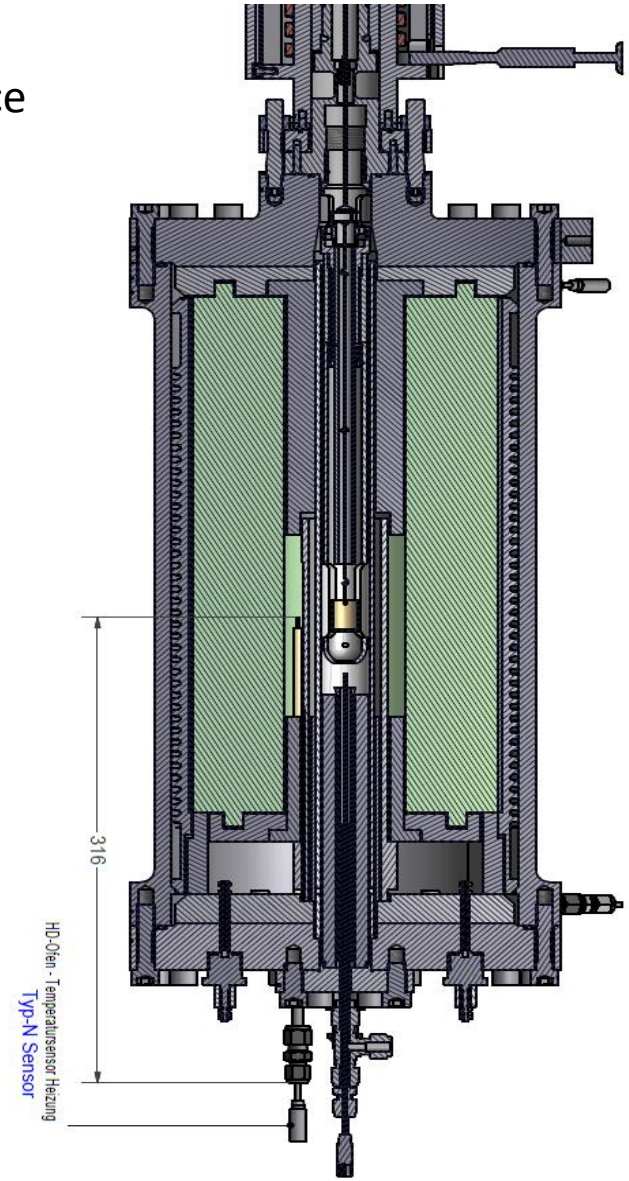
$$CO_2 + H_2 \longrightarrow CO + H_2O \qquad \Delta H = 41 kJ/mol$$

$$CO + 2H_2 \longrightarrow CH_3OH \qquad \Delta H = -95 kJ/mol$$

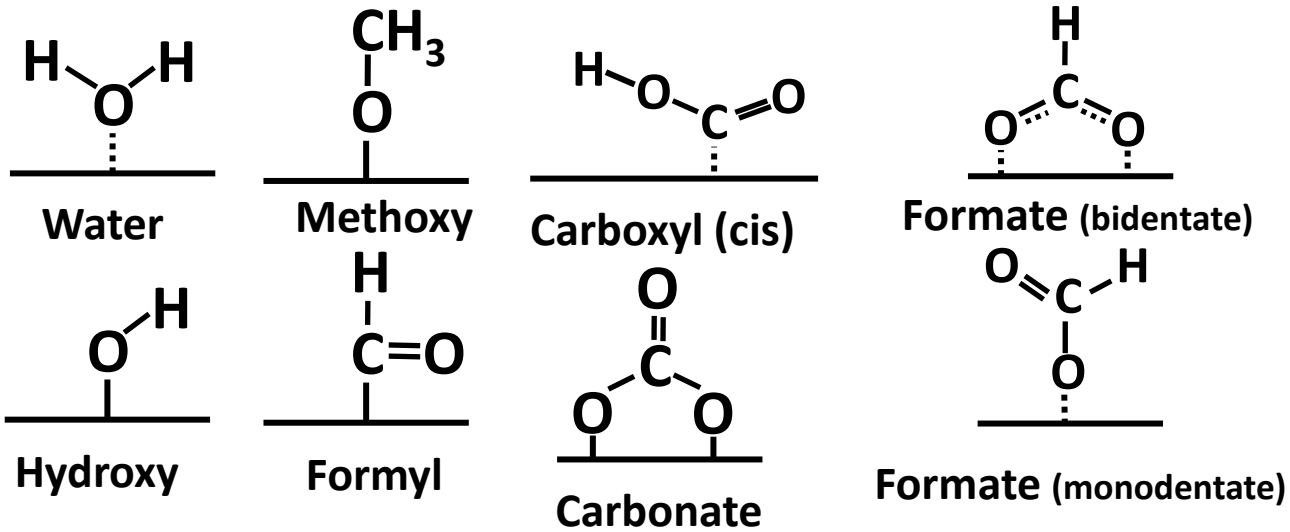
What is the surface composition during the operation?

Case Study: Methanol Synthesis

High Preasure Thermobalance



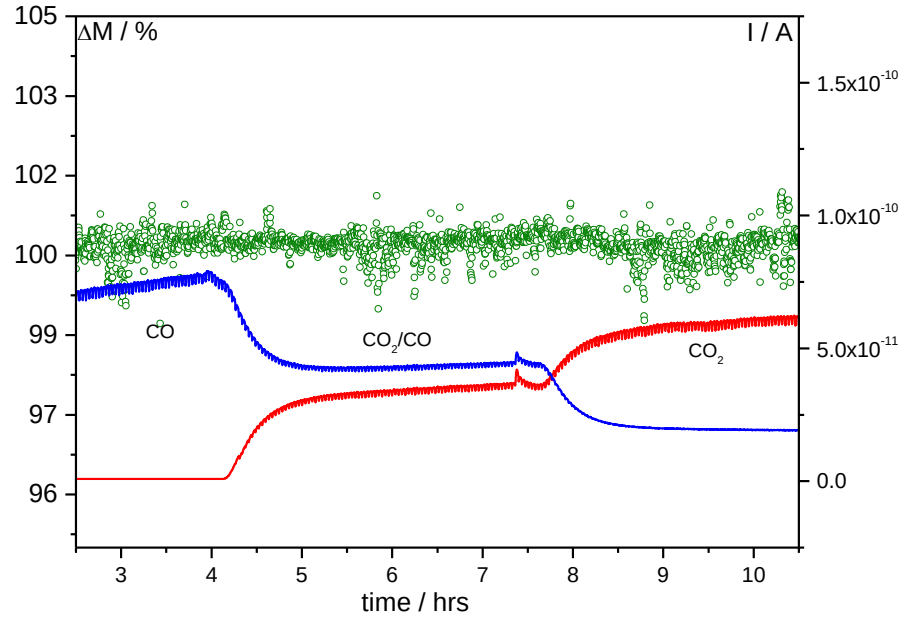
Reaction intermediates and spectators:



Case Study: Methanol Synthesis

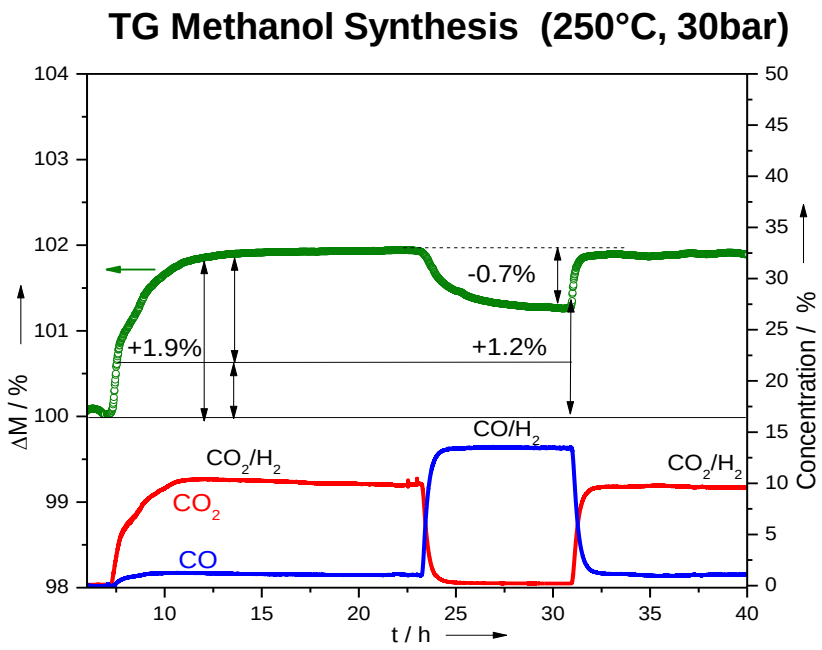
Gas	Density (kg/m^3)
$CO/CO_2/H_2/He(6/8/59/27)$	0.33
$CO/Ar/H_2/He(14/4/59/23)$	0.34
$CO_2/He/H_2$ (12.4/28.8/58.8)	0.35

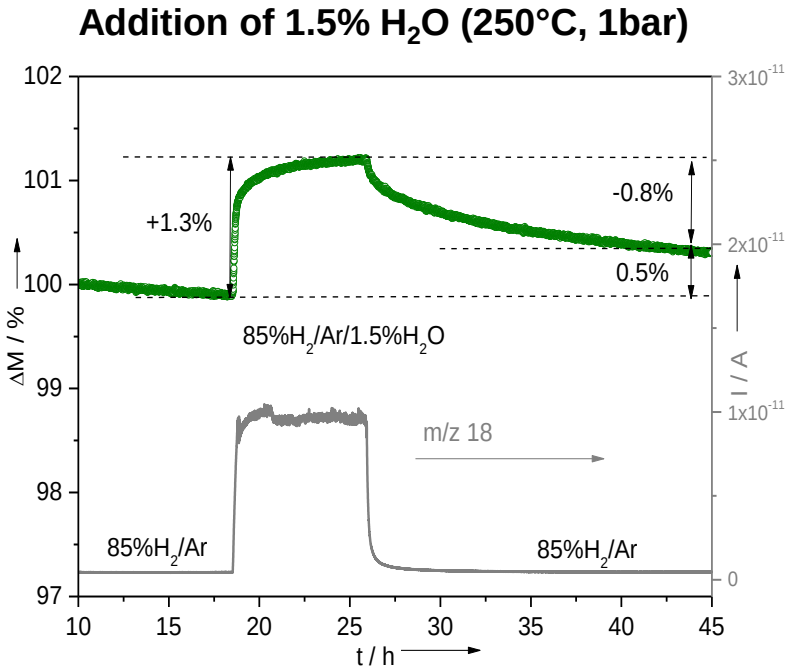
Density alignment



400mg SiO_2, 30 bar, 250°C, feed gas flow 120 ml/min

Case Study: Methanol Synthesis





Case Study: Methanol Synthesis

Cu sites – 400 µmol g(cat)$^{-1}$
ZnOx sites – 273 µmol g(cat)$^{-1}$

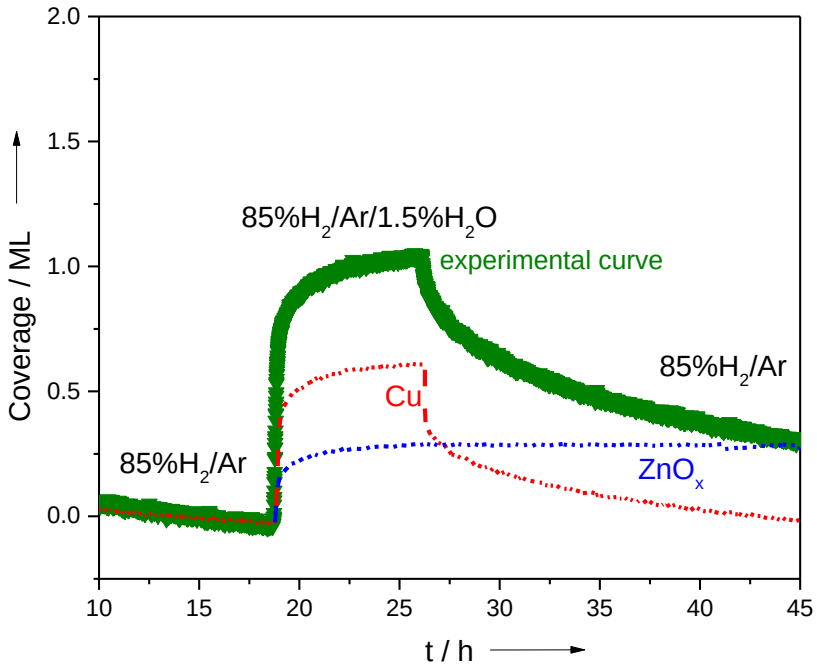
Schumann et al. ACS Catalysis, 2015, 5
Schumann et al. ChemCatChem, 2014, 6

Theoretical mass increase of the catalyst under estimation of ***full covered surface*** with one type of species

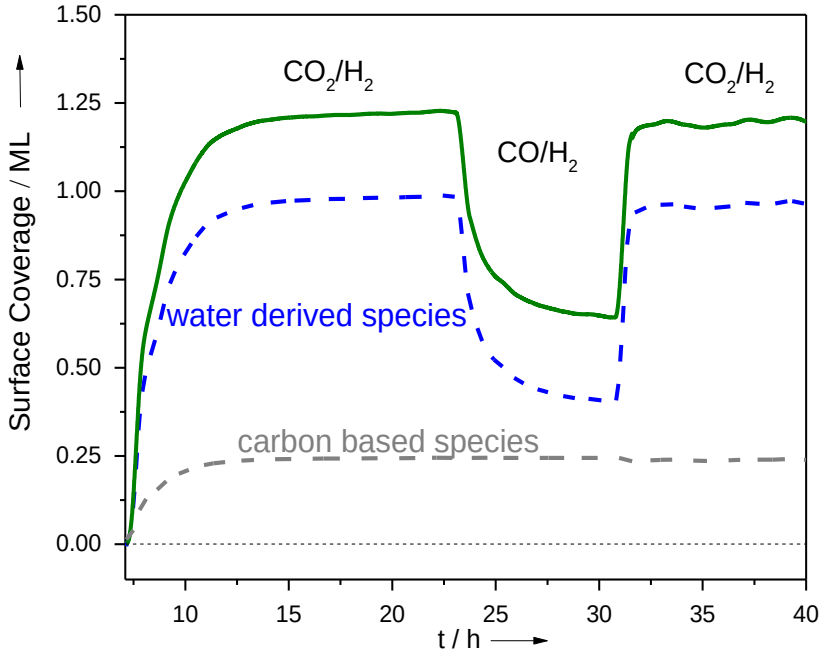
Group/M, gmol^{-1}	Surface stoichiometry	ΔM, % (Cu sites)	ΔM, % (ZnO sites)	Full ΔM,% (Cu/ZnO$_x$ sites)
H_2O/18 water	*1*	*0.72*	*0.49*	***1.21***
OH/17 hydroxy	*1*	*0.68*	*0.46*	***1.14***
OCH_3/31 methoxy	*1*	*1.24*	*0.85*	***2.09***
CHOO/45 formate	***2/1***	***1.8/0.9***	***1.2/0.6***	***3/1.5***

Case Study: Methanol Synthesis

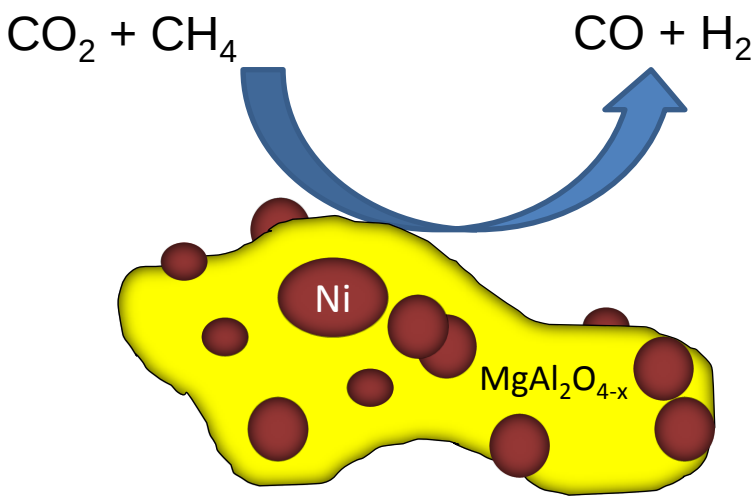
Addition of 1.5% H_2O (250°C, 1bar)



TG Methanol Synthesis (250°C, 30bar)



Case Study: Dry Reforming of methane



Target Reaction Dry reforming (DRM): $CO_2 + CH_4 \rightleftharpoons 2\ CO + 2\ H_2$ $\Delta H^0 =$ 247 kJ/mol

Side reactions (⇨ catalyst deactivation because of **coking**):

- Boudouard reaction: $2\ CO \rightleftharpoons \mathbf{C} + CO_2$ $\Delta H^0 =$ -171 kJ/mol
- Methane pyrolysis: $CH_4 \rightleftharpoons \mathbf{C} + 2H_2$ $\Delta H^0 =$ 75 kJ/mol

Suppression of side reactions:

- high reaction temperature (900 °C)

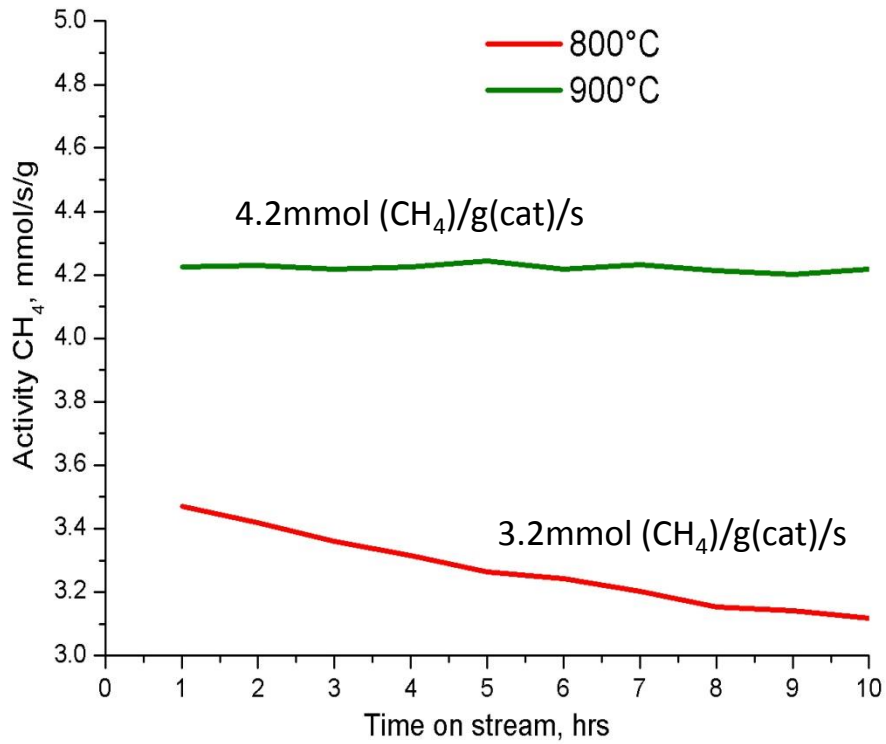
⇨ high temperature stable, long term active, non coking materials required

⇨ ⇨ $Ni/MgAl_2O_4$ catalyst

Case Study: Dry Reforming of methane

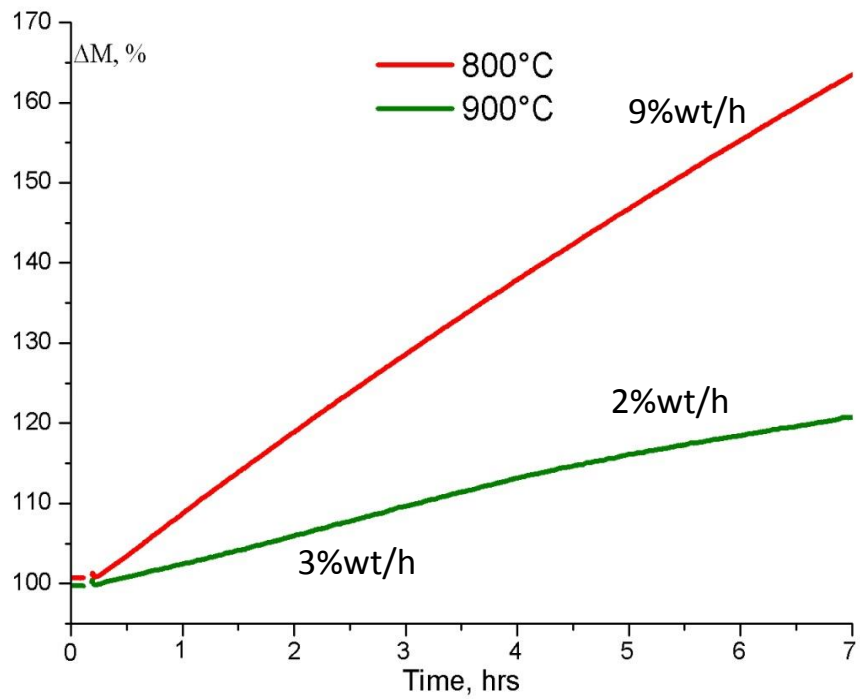
$CO_2 + CH_4 \rightleftharpoons 2\ CO + 2\ H_2$ $\Delta H^0 = 247$ kJ/mol

Activity



- Better performance at higher temperatures

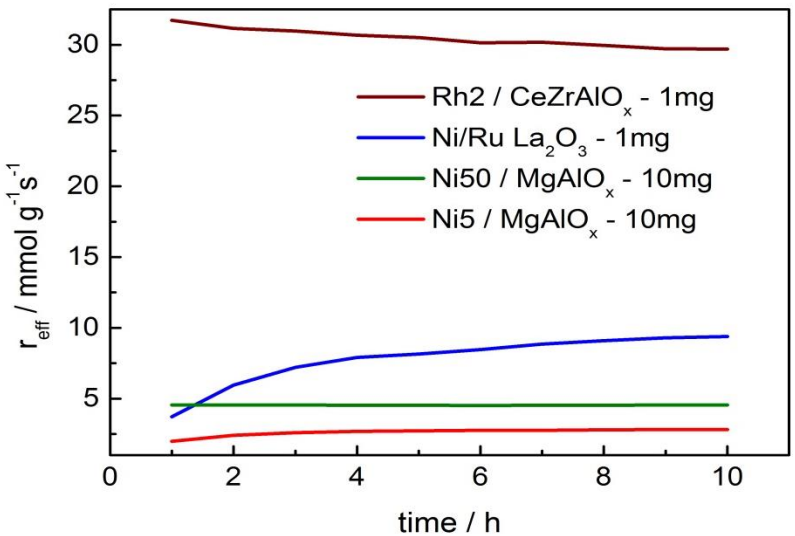
Weight change



- Continuous coke formation

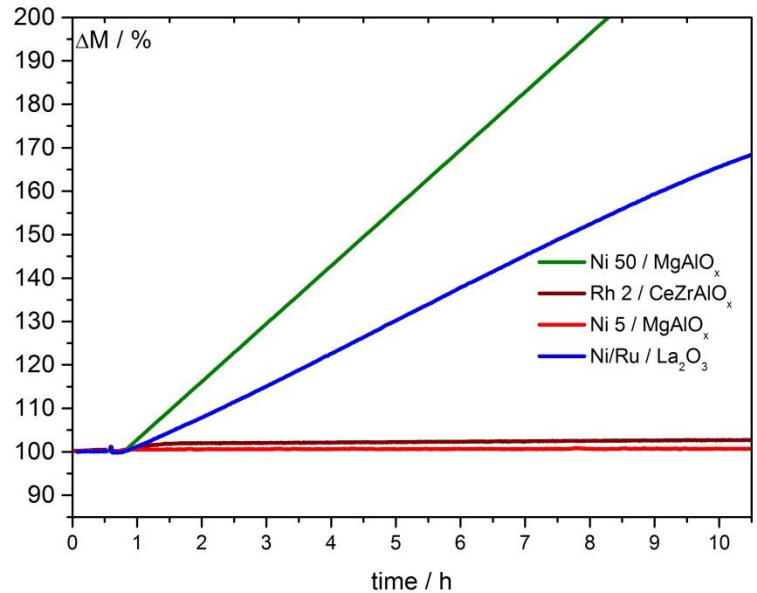
Case Study: Dry Reforming of methane

Activity in DRM



- Continues coking process
- Less coking at lower Ni concentrations

Carbon formation

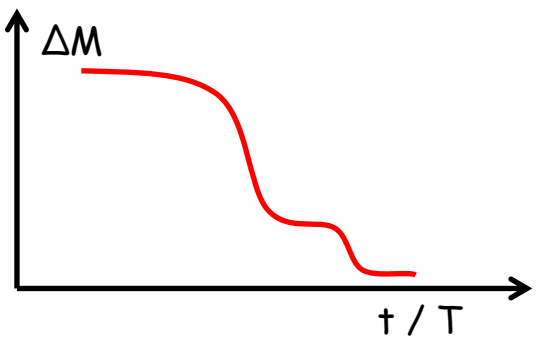


Tarasov et al., Chem. Ing. Tech., **2014**, 86, 1916-1924

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.

Thermogravimetry

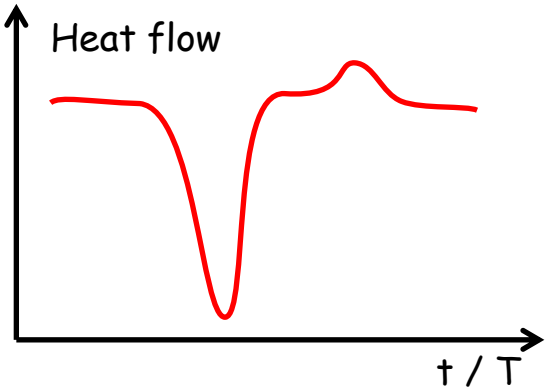


$$r \equiv \frac{dN}{d\tau} = \frac{1}{M} \cdot \frac{dm}{d\tau}$$

$$\Delta m = M \cdot \Delta N$$

A(s)↔ B(g)

Differential Scanning Calorimetry



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

$$\Delta Q = m \cdot C_p \cdot \Delta T$$

A(s)↔B(s)

A(s)↔B(g)

Key parameters:

Course of the reaction, yield of the reaction

Enthalpy of formation/transformation (reaction, phase transition)

Differential Scanning Calorimetry (DSC) –

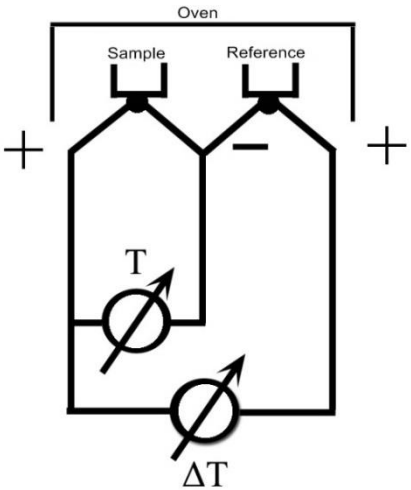
experimental methods for measuring thermal effects
(heat evolution and consumption)

- in extended range of temperatures;
- with improved productivity;
- with higher temporal resolution

Differential – permanently compared to reference

<u>Principle of combined thermocouple</u>

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



Differential Scanning Calorimetry (DSC) –

experimental methods for measuring thermal effects
(heat evolution and consumption)

- in extended range of temperatures;
- with improved productivity;
- with higher temporal resolution

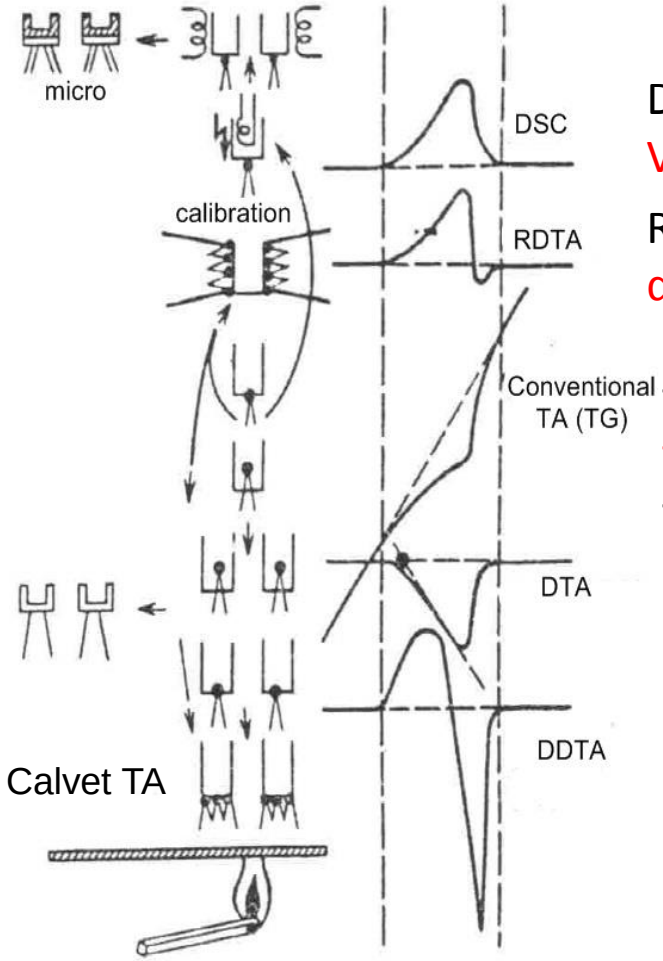
Differential – permanently compared to reference

Scanning – varied (programmed) temperature (permanently and/or stepwise)

Calorimetry – `near calorimetric´ (although reduced) precision (typically, 1-2% of measured thermal value) – as a rule satisactory for a wide range of applications

Based on different technical principles and schemes but fundamentally same physical background: heat transfer and balance

Basic Principles and Terminology



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

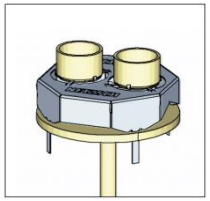
TA – (Thermal analysis)
T_S vs. t

TG – (Thermogravimetric analysis)
Δm vs. T

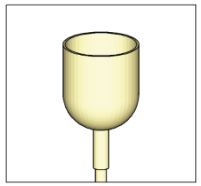
DTA - (Differential Thermal Analysis)
$\Delta T = T_S - T_R$ vs. T

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

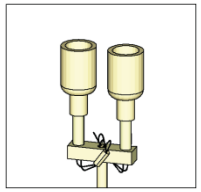
DSC-TG



TG



DTA-TG

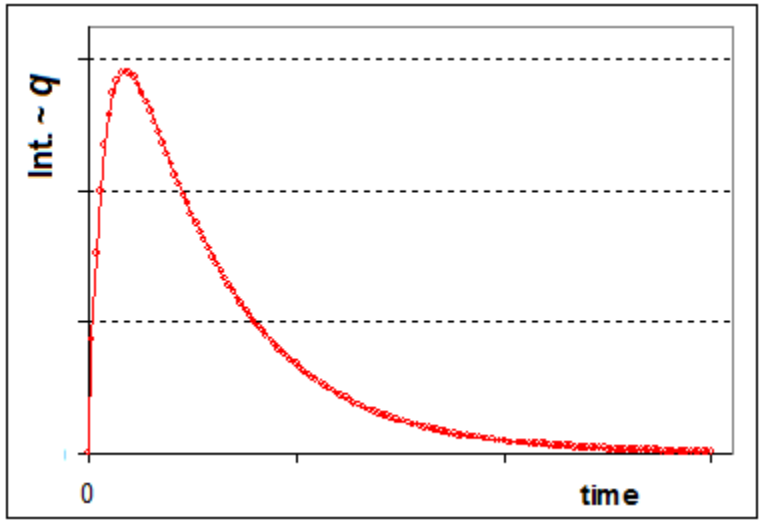


Calvet-DSC

Basic Principles and Terminology

Based on different technical principles and schemes but fundamentally same physical background: heat transfer and balance

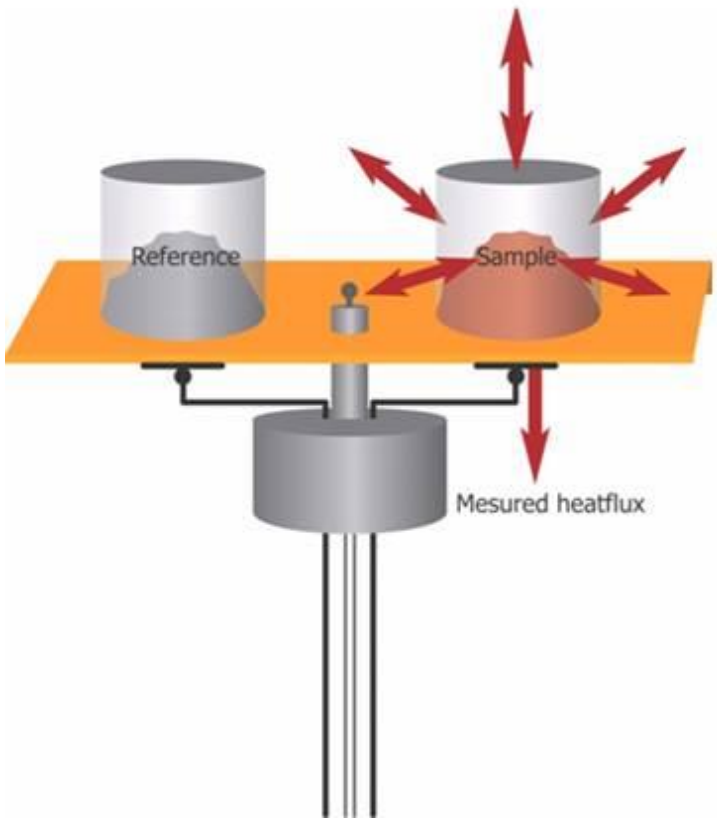
$q = k\Delta T + C(dT/dt)$ – *heat removal and stortage*



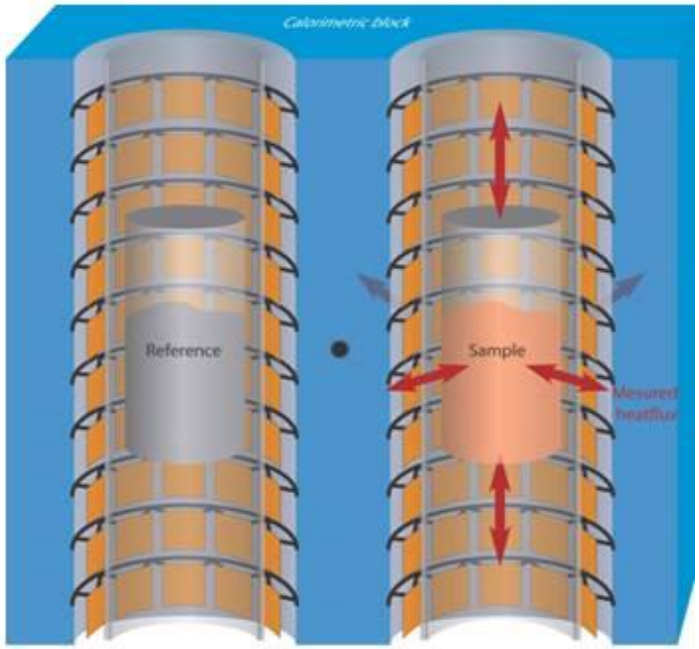
$$Q = \int_0^\infty q\,dt$$

DSC Heat flux

(a)



(b)



Disk shaped, ´Quantitative TA´

Calvet cell

1. ‘Quantitative TA’

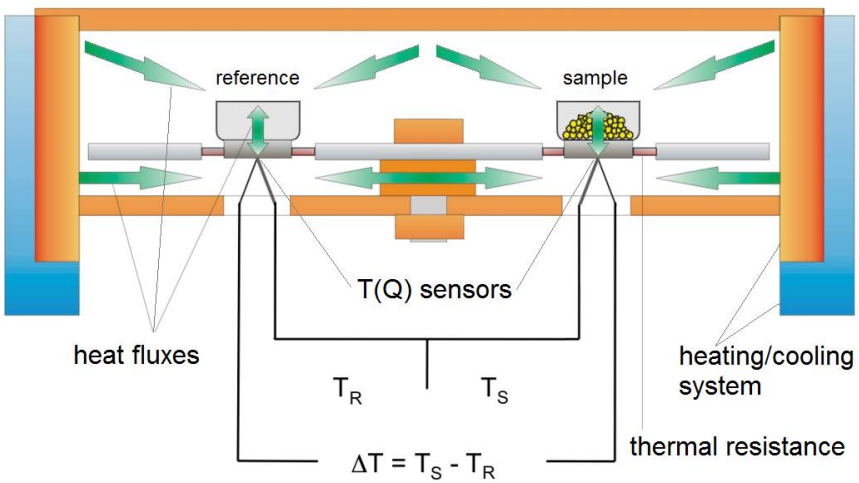
– multiple sensors

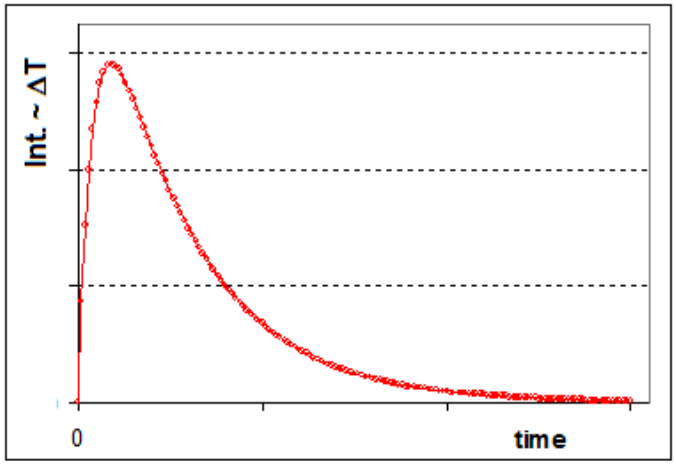
– tight contact between sensors and holders

– rapid heat removal from the sample

$C(dT/dt) \approx 0$ *and*

$q \approx k\Delta T$





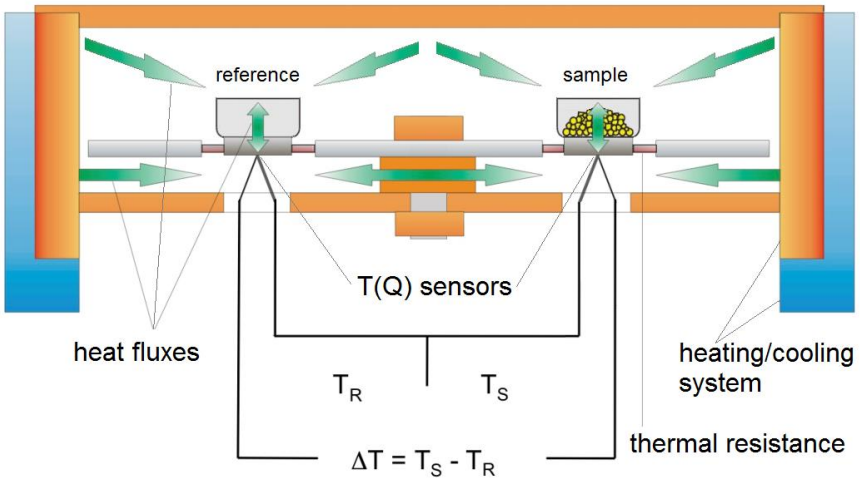
$$Q \approx \int_0^\infty \Delta T dt$$

1. ‘Quantitative TA’

– multiple sensors

– tight contact between sensors and holders

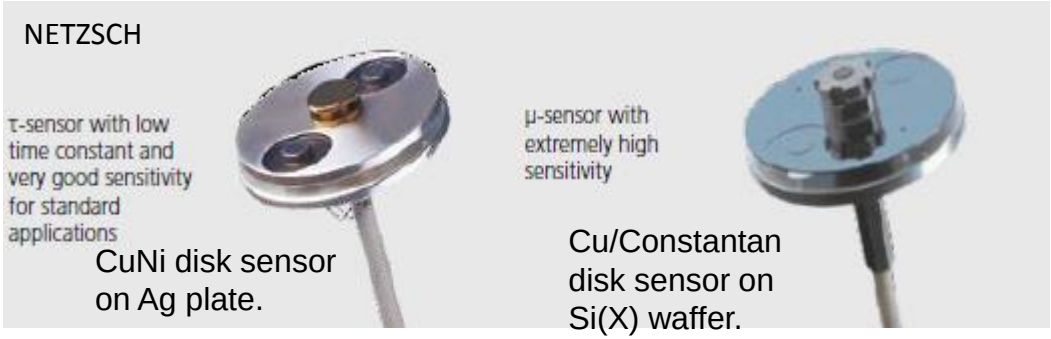
– rapid heat removal from the sample



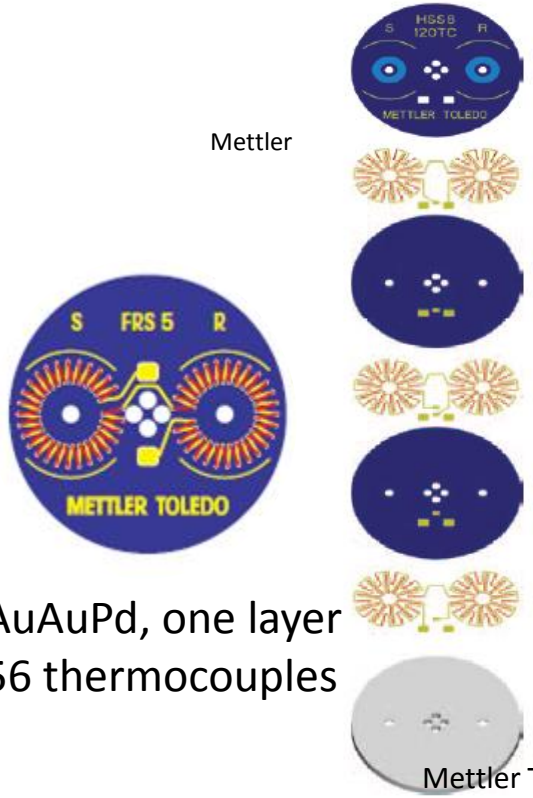
- relatively simple design;
- wide range of T’s;
- compatible with other methods (e.g. TG)

- calibration is critical and can vary from sample to sample;
- gas-solid diffusion

DSC sensors



Mettler



AuAuPd, one layer
56 thermocouples

Mettler Toledo

Methods and Instruments

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
P	Platinel/AuPd	500	1400	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

Platinel – 55% Pd, 31% Pt, 14% Au

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

μ sensor

CuNi disk sensor on Ag plate.

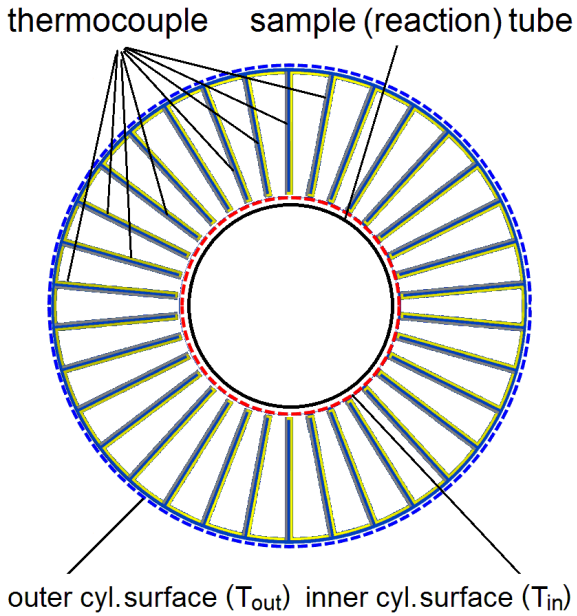
τ sensor

Pt-PtRh(10) diskshaped thermocouple

2. 'Heat-flux', or 'heat-conductive', or Calvet-type DSC

– heat flux is measured outside of the sample assuming that it is proportional to the ΔT on different distances from it

Calvet sensor (top view)



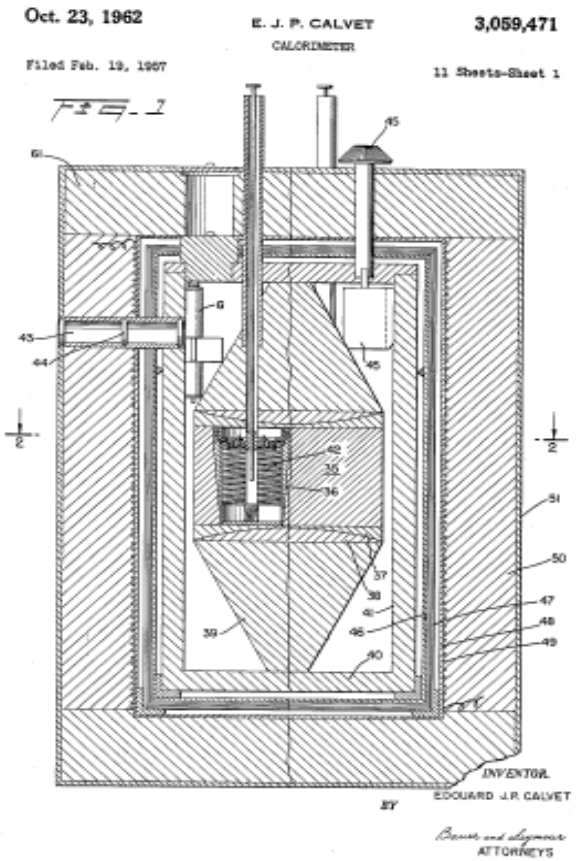
$q \sim (T_{in} - T_{out})$

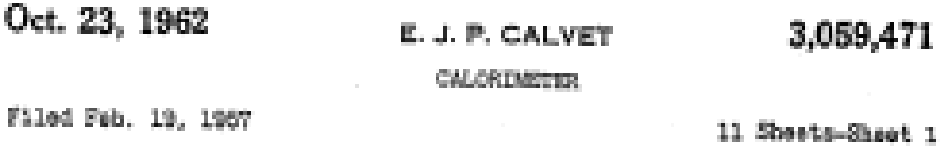
Calvet calorimetry (incl. DSC):

- none of the TC's measures the temperature of the sample (!!!);
- the DSC signal is formed as ΔT between two cylindrical surfaces (inner and outer) on different distances from the sample

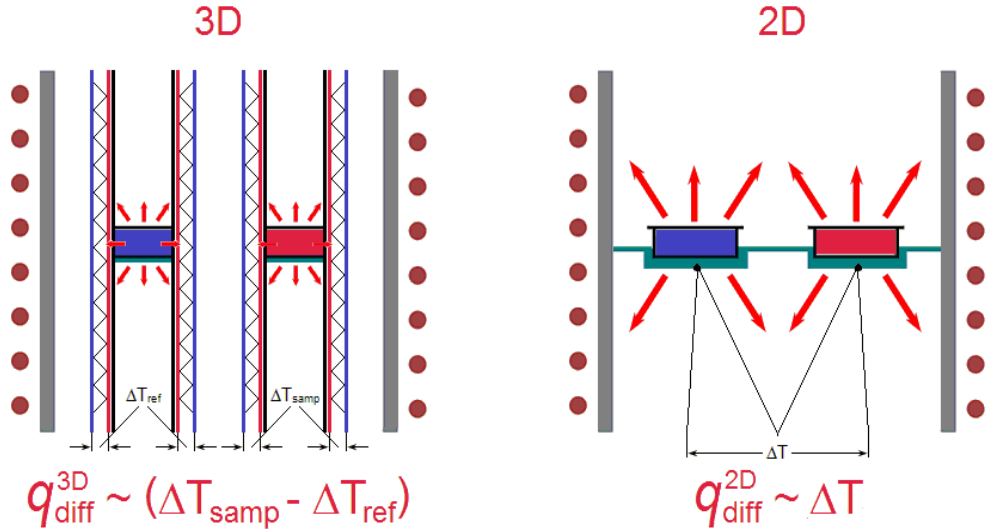
2. ‘Heat-flux’, or ‘heat-conductive’, or Calvet-type DSC

– heat flux is measured outside of the sample assuming that it is proportional to the ΔT on different distances from it





Side view: Calvet (3D) vs. TA (2D) sensing



the sample does not play the role of 'thermal resistance';

– no tight contact between sample (and reference) holder(s) and the sensor is required;

– 3D heat sensing;

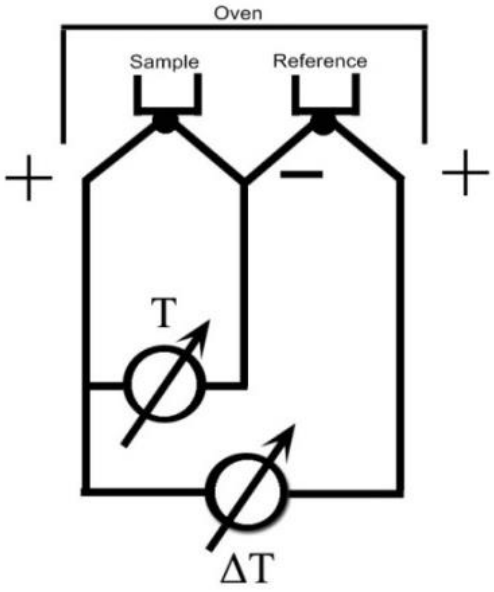
– good gas-solid mass-transfer conditions;

– high compatibility (e.g. with TGA)

– relatively low temporal resolution

3D vs. 2D sensing: more efficient (complete) capturing of heat fluxes from/to the sample – lower sensitivity to the sample properties !!!

Concept

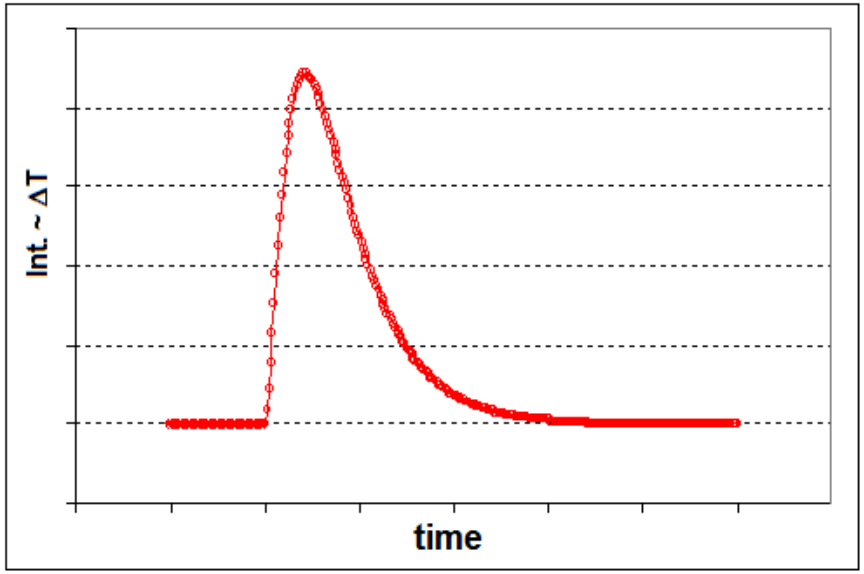


$$q = K \cdot \Delta T + C \cdot \frac{\partial T}{\partial t} \approx K\left[\Delta T + \tau\left(\frac{d\Delta T}{dt}\right)\right]$$ - Tian equation

heat removal and storage

q – heat flux at every moment of time
K – specific thermal conductivity
C – specific thermal capacity
τ- K/C characteristic time constant

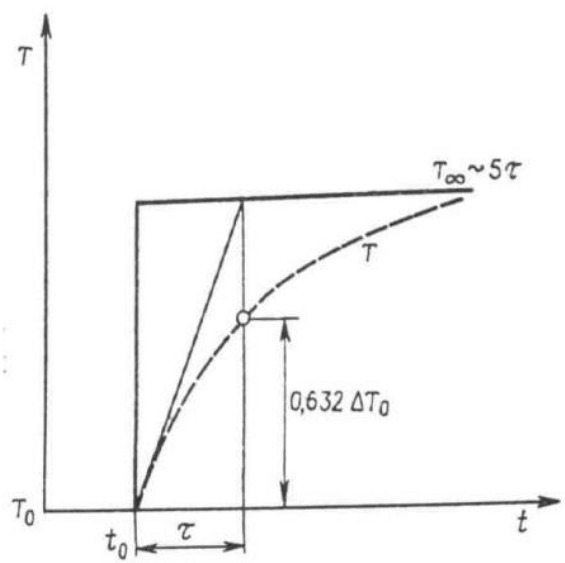
Concept



$$Q = \int_0^\infty q\,dt \simeq a\int_0^\infty \Delta T\,dt$$

$q = k\Delta T + C(dT/dt) \approx k\Delta T + C(d\Delta T/dt) = k[\Delta T + \tau^*(d\Delta T/dt)]$

$\tau^* = C/k$ – time constant of fluxmeter

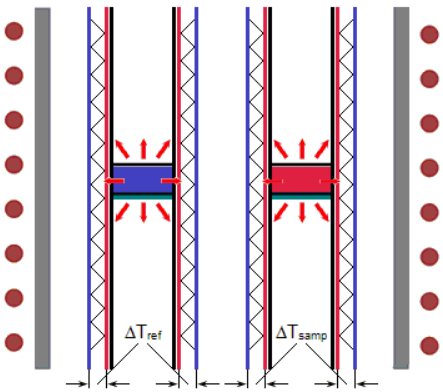


Time constant is depended on design, construction and materials of the calorimetric cell.

Concept

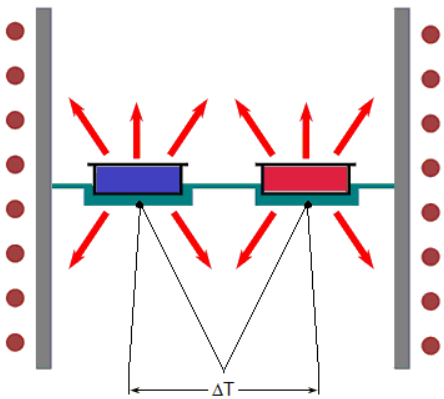
Side view: Calvet (3D) vs. TA (2D) sensing

3D



$q_{diff}^{3D} \sim (\Delta T_{samp} - \Delta T_{ref})$

2D



$q_{diff}^{2D} \sim \Delta T$

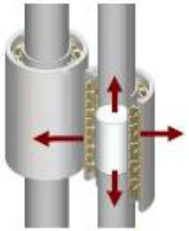
$q = k[\Delta T + \tau^*(d\Delta T/dt)]$

$k\downarrow \Rightarrow \tau^* (\approx C/k)\uparrow$

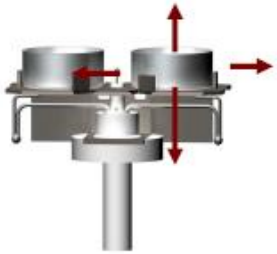
$\langle q \rangle \uparrow @ \tau^*\uparrow$

$k\uparrow \Rightarrow \tau^* (\approx C/k)\downarrow$

$\langle q \rangle \downarrow @ \tau^*\downarrow$



Example of 3D calorimetric sensor



Example of plate-shape DSC sensor (2D)

All Heat convection, conduction and radiation is measured

Only heat conducted directly through the bottom of the vessel is measured

Concept

Three ranges of characteristic times of the process should be considered:

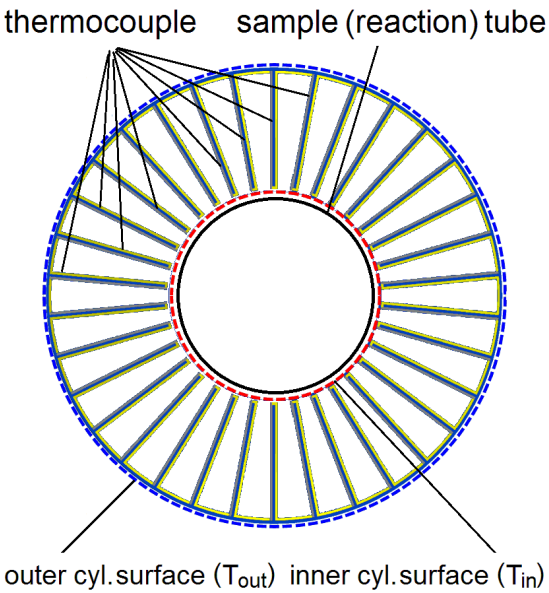
$\tau_\Theta < 0.1\ \tau$ Thermal inertia of the registration system completely shades the kinetics

$\tau_\Theta > \tau$ When the kinetics may rather accurately be determined using Tian equation

$0.1\ \tau < \tau_\Theta < \tau$ When the available methods give kinetics that is somewhat distorted by the thermal inertia of a sample

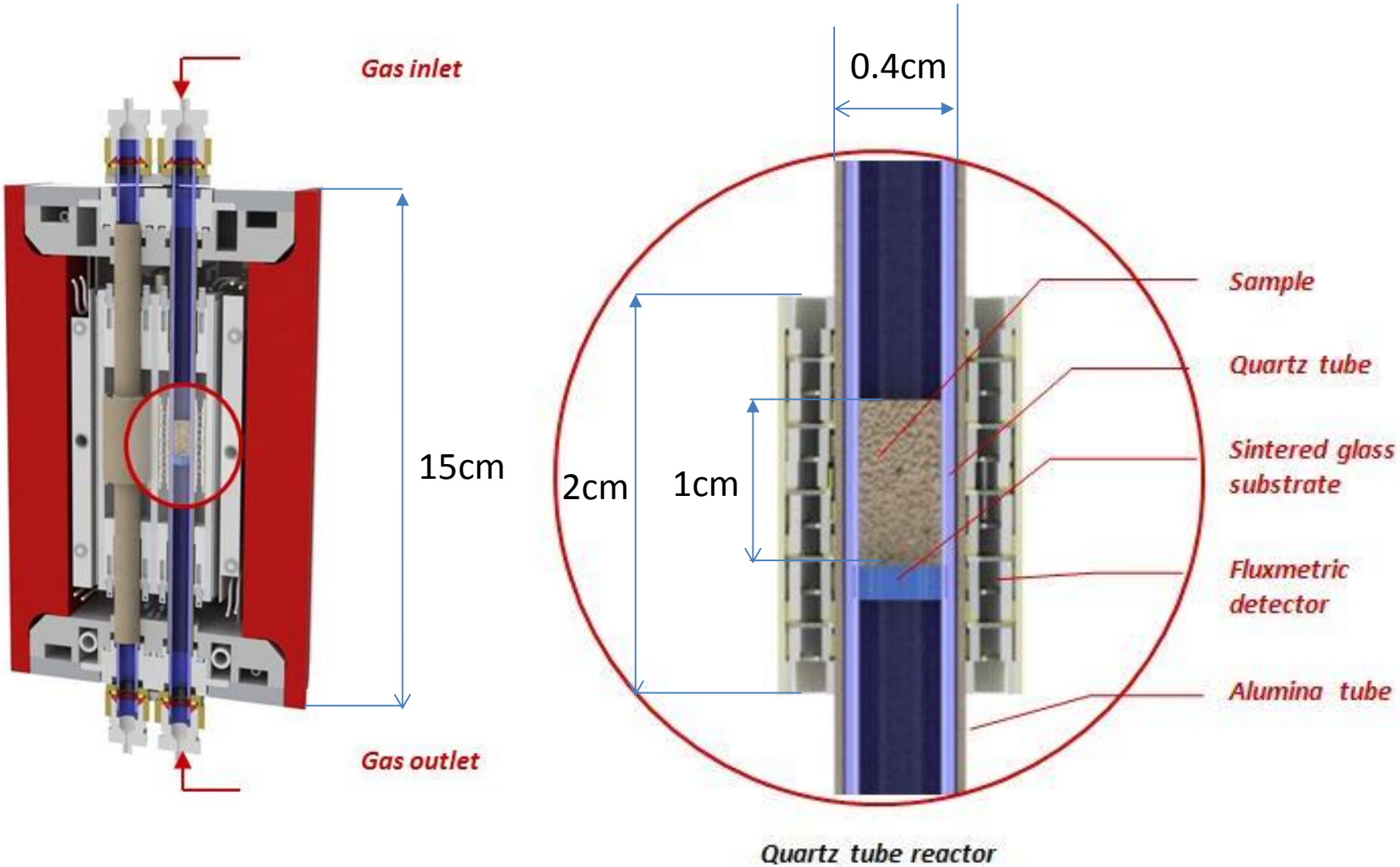
In-situ DSC

Calvet sensor (top view)

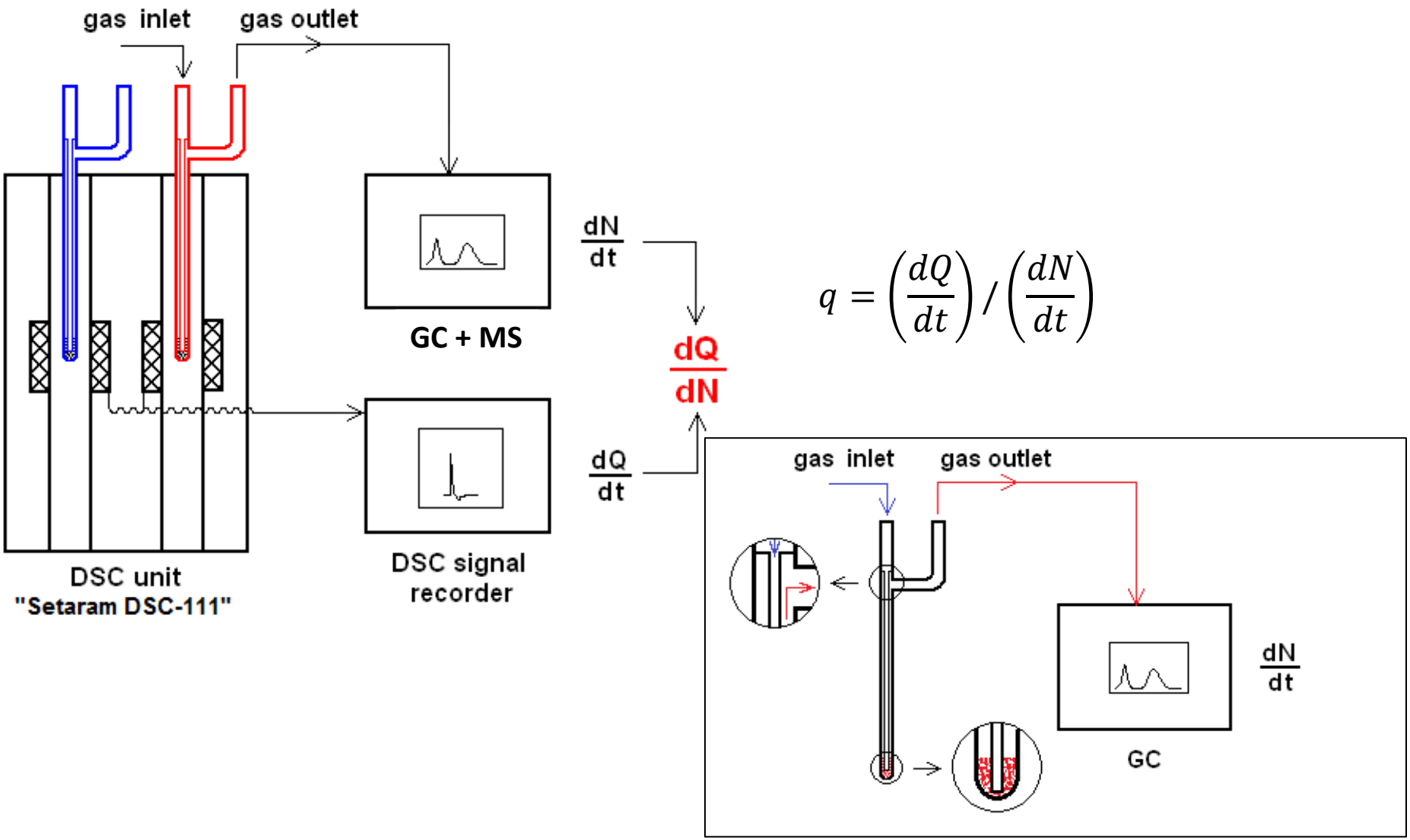


$q \sim (T_{in} - T_{out})$

In-situ DSC setup



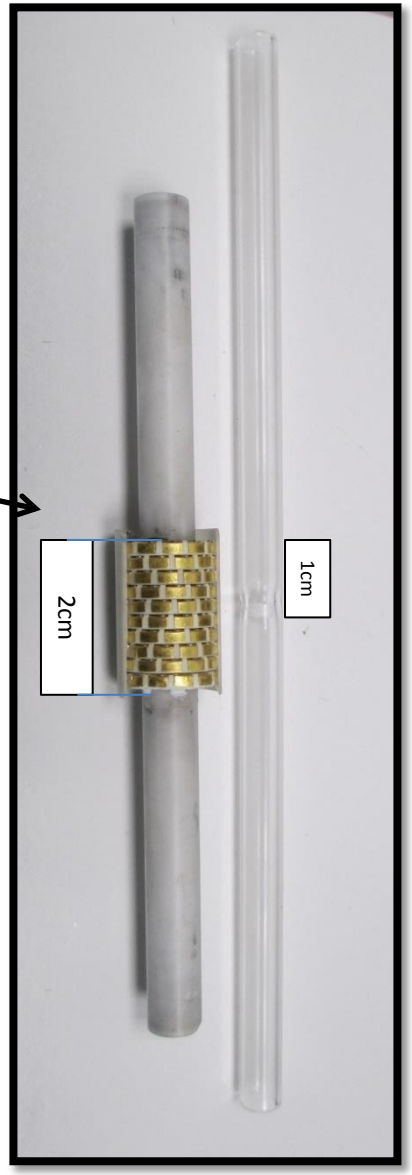
In-situ DSC setup



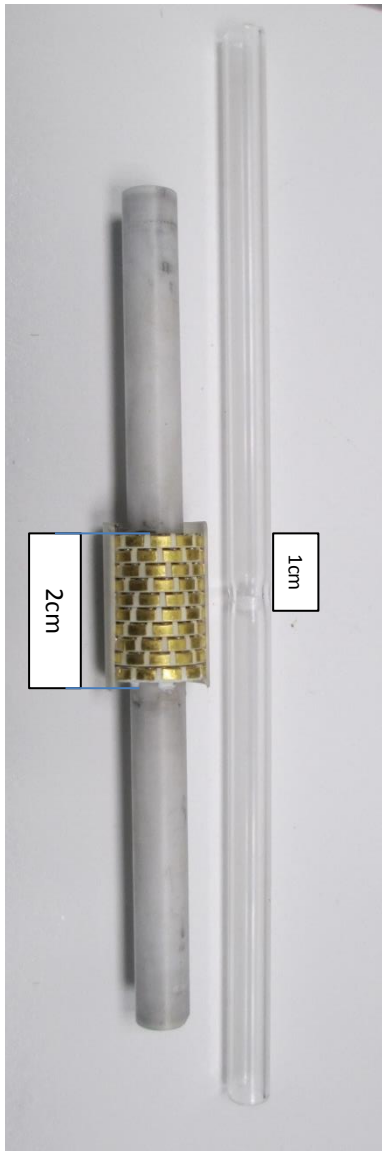
$$q = \left(\frac{dQ}{dt}\right) / \left(\frac{dN}{dt}\right)$$

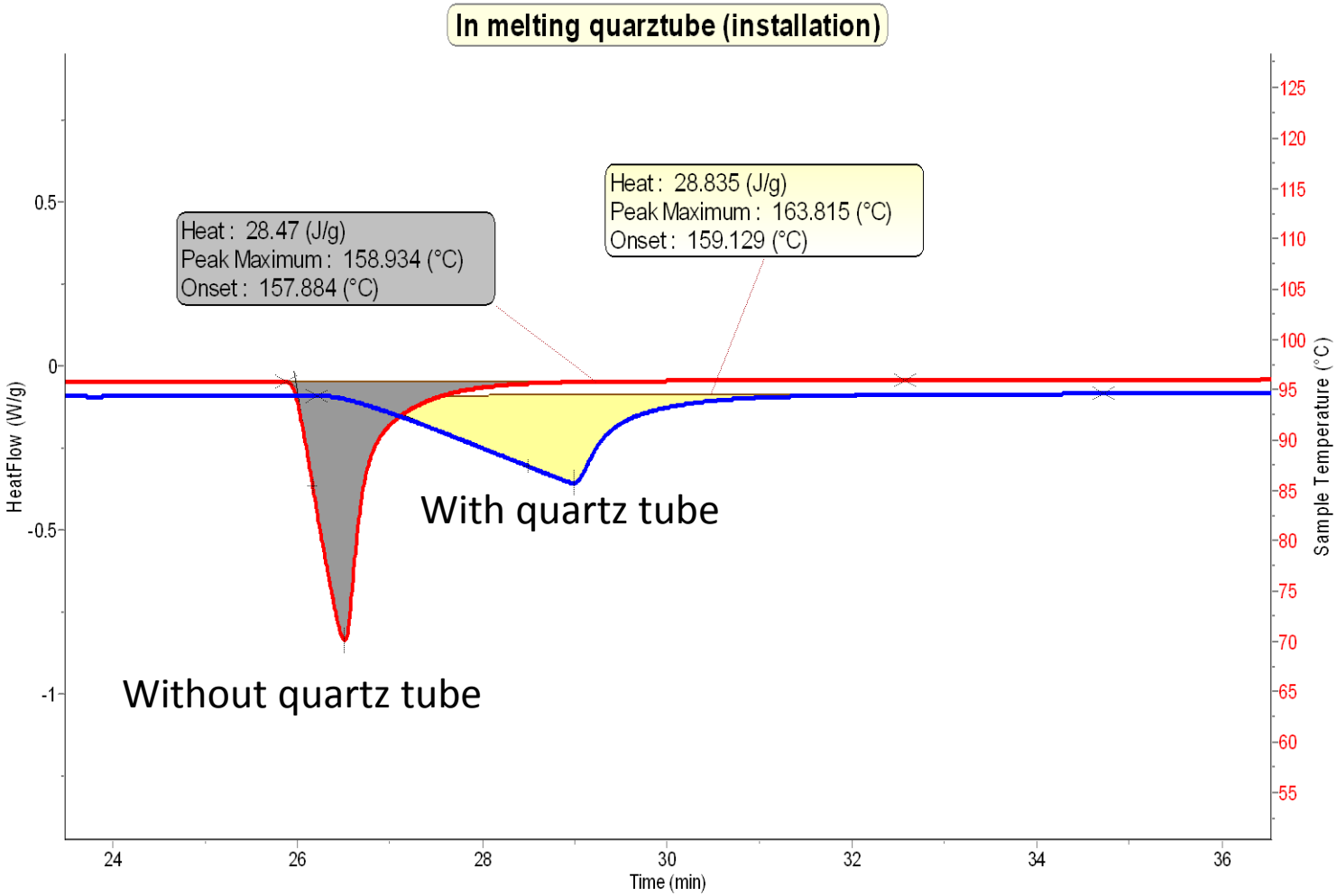
Sinev et al.

In-situ DSC setup

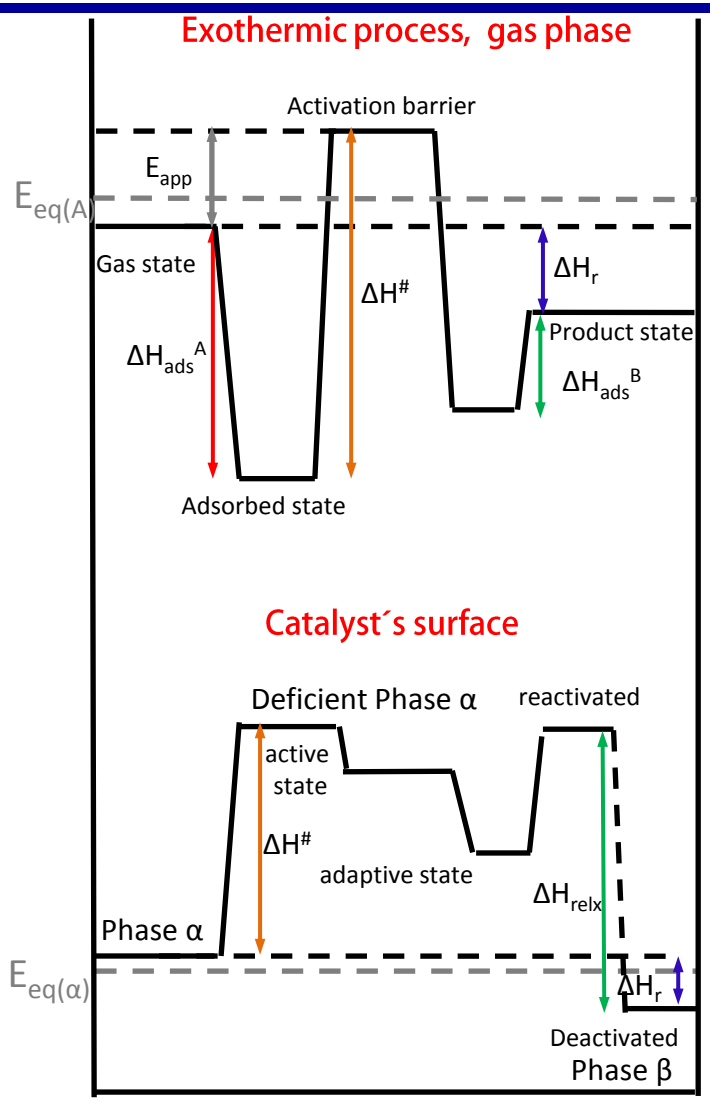


In-situ DSC setup





What can we measure?



Simplified schematic representation

Transformation of gas phase molecules

- Information on reaction kinetics (Ea)
- Simulation of different conditions in-situ
- Adsorption - desorption enthalpies

Transformation in solid state

- Redox dynamics
- Effects of oxygen diffusion into subsurface
- Redestribution of bulk and surface oxygen
- Oxygen binding energy (oxides)
- Thermochemistry of defects formation

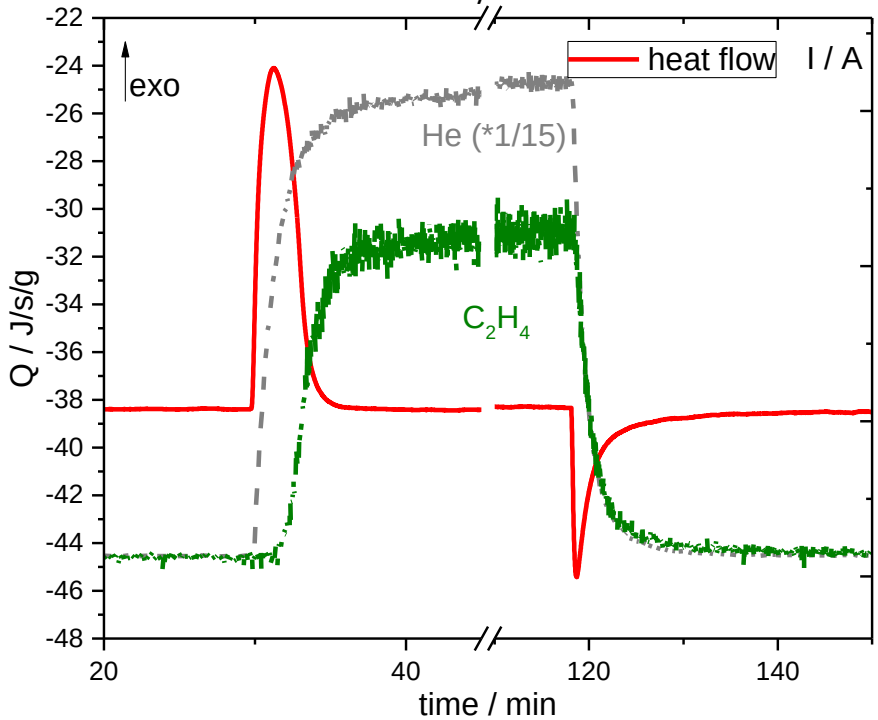
Adapted using: van Santen, R. A., Modern Heterogeneous Catalysis, Wiley, 2017 and Schlögl, R., Introduction to Heterogeneous Catalysis, Lecture, FHI Berlin, 2017

Case study: Validation, C_2H_4 adsorption on Ag catalyst

5%Ag/SiO2, Max Lamoth

In-situ DSC

30°C, total flow 30mlm, Ptotal 1,15bar
12 hours SynAir 300°C



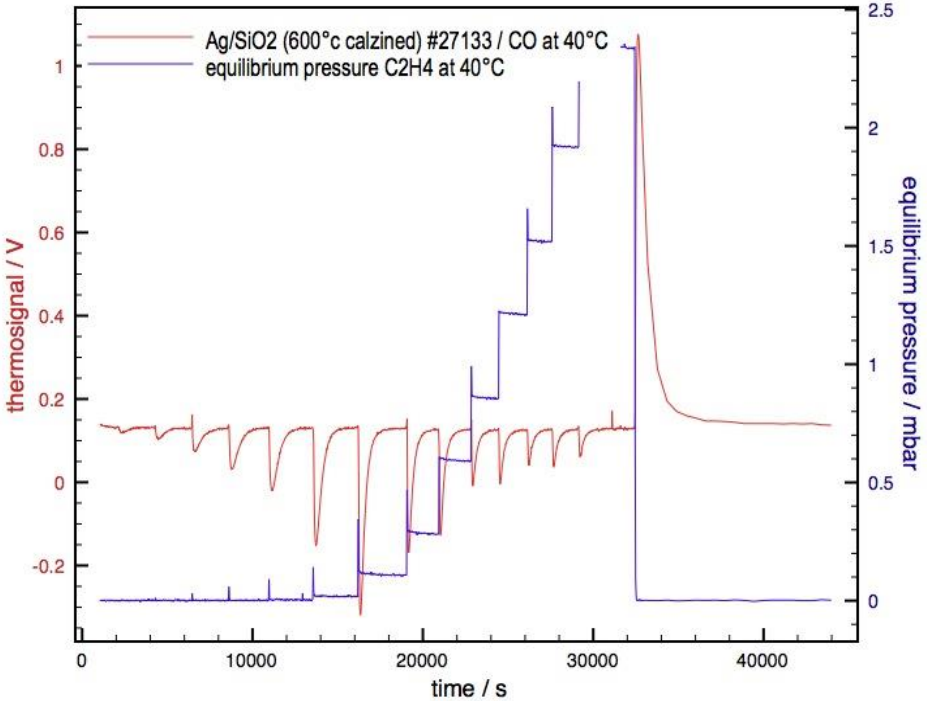
ΔH_{ads}=-94kJ/mol(C_2H_4)

N(C_2H_4)=26µmol/g(cat)

reversible

Microcalo

40°C, Prange 0-3mbar
3 hours SynAir 300°C



ΔH_{ads}=-87-33kJ/mol(C_2H_4)

N(C_2H_4)=33µmol/g(cat)

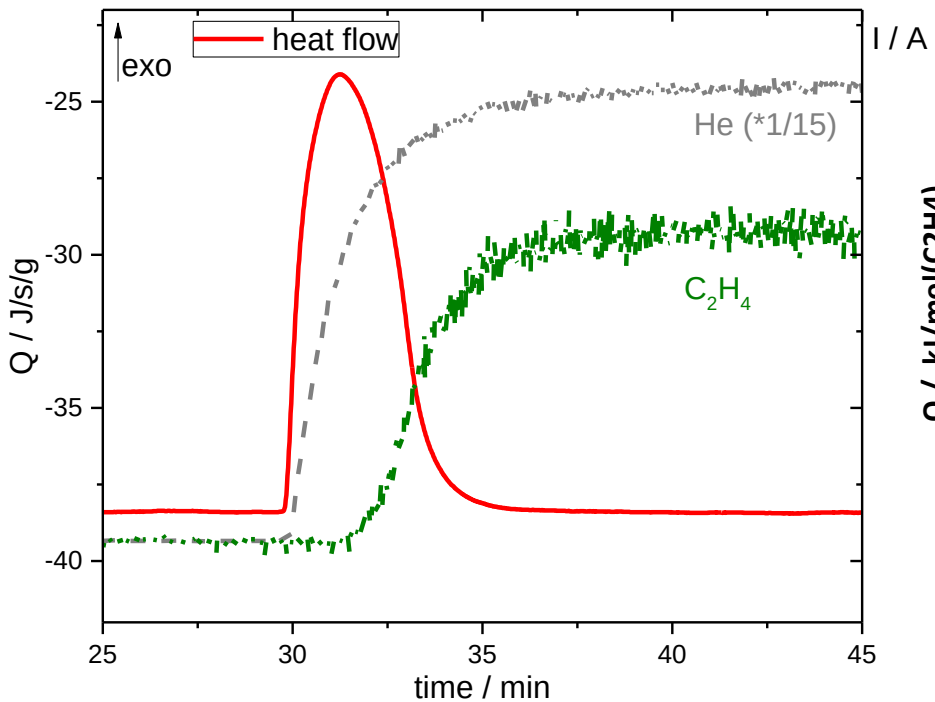
reversible

Case study: Validation, C_2H_4 adsorption on Ag catalyst

5%Ag/SiO2, Max Lamoth

In-situ DSC

30°C, total flow 30mlm, P_{total} 1.15bar, P_{C2H4}0.6mbar
12 hours SynAir 300°C



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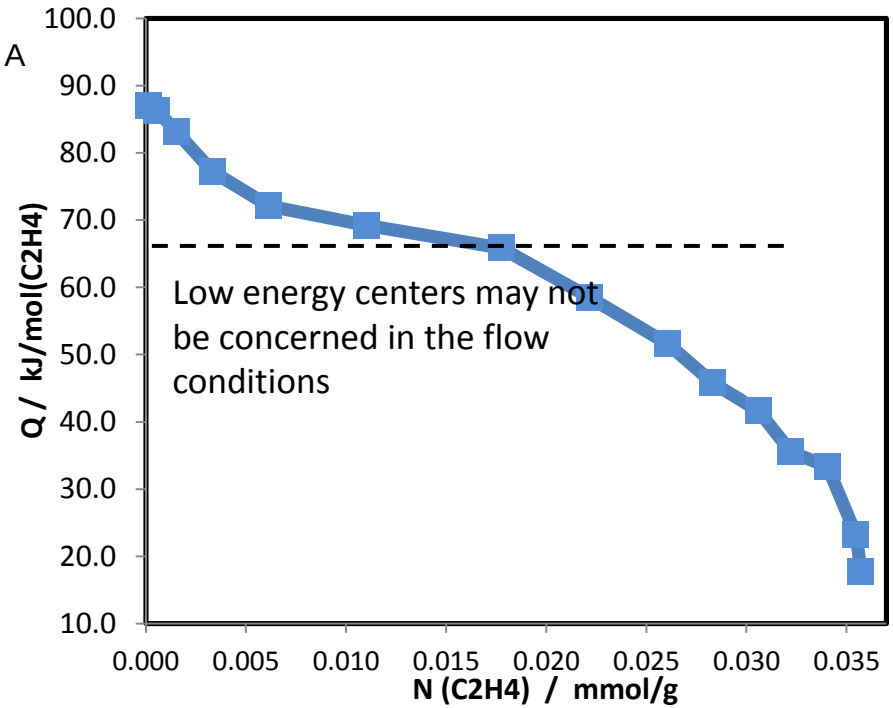

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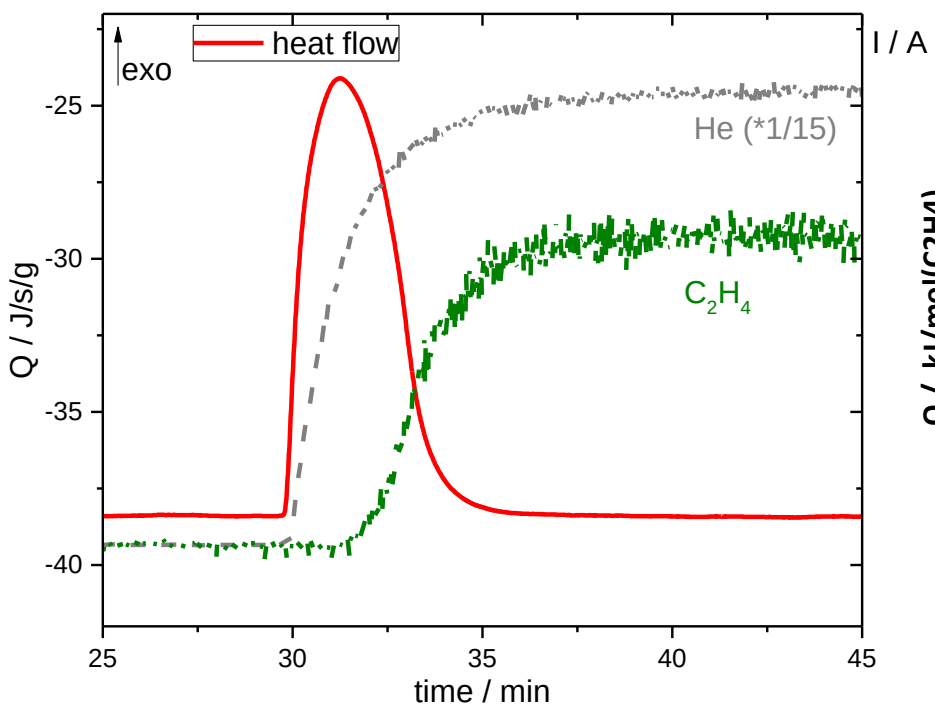
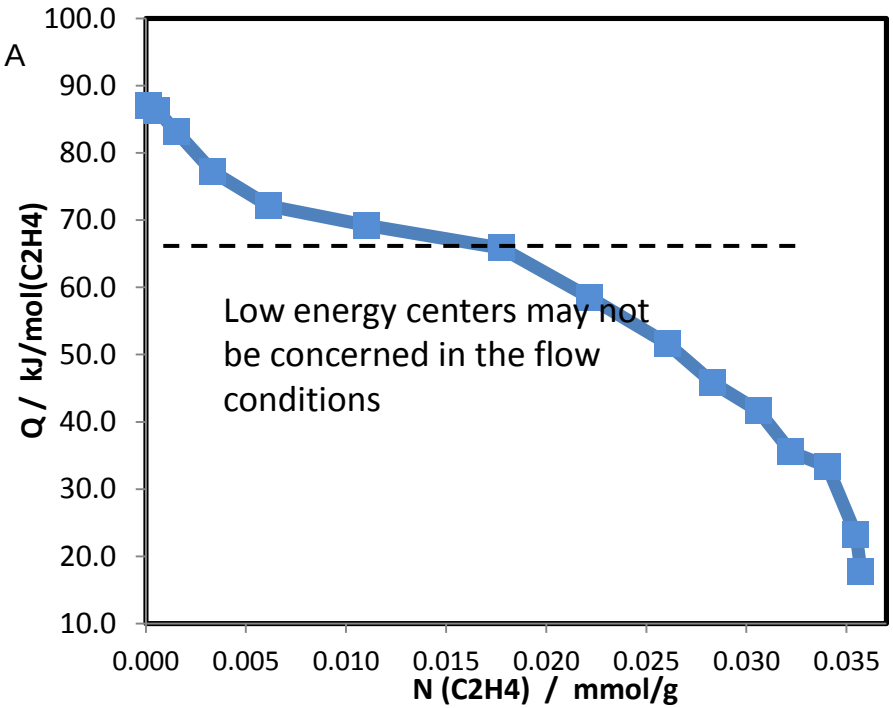
30°C, total flow 30mlm, P_{total} 1.15bar, P_{C2H4}0.6mbar
12 hours SynAir 300°C



Microcalo

40°C, Prange 0-3mbar
3 hours SynAir 300°C



Desorption and readsorption are occurring simultaneously with diffusion

In UHV systems diffusion takes part in a very limited extent, while readsorption can be avoided using sufficiently high pumping speed

Case study: alkane ODH over VSb/Al2O3

$C_nH_{2n+2} + ½\ O_2 \rightarrow C_nH_{2n} + H_2O$

$C_nH_{2n+2} + zO_2 \rightarrow nCO_X + (n+1)\ H_2O$

Catalysts – V-containing bulk and supported oxides

'Classical' Red-Ox Kinetics over V-containing catalysts –
Mars-van-Krevelen* or oxygen rebound-replenish (ORR) mechanism

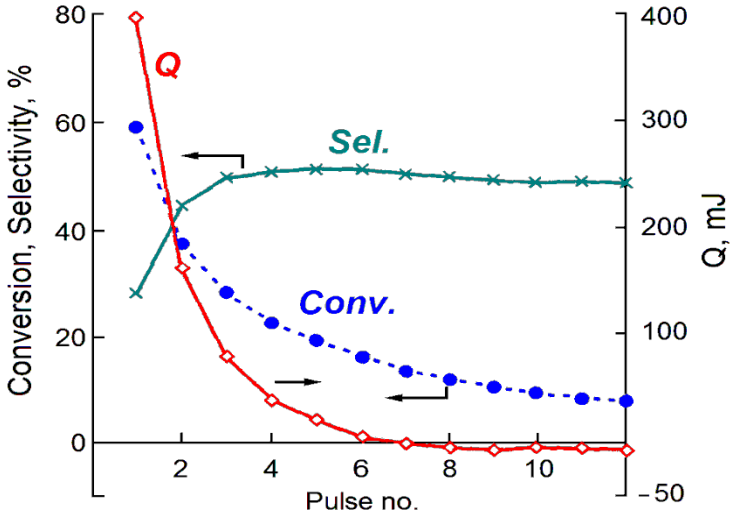
$$[O]_S + A \rightarrow [\ ]_S + AO$$

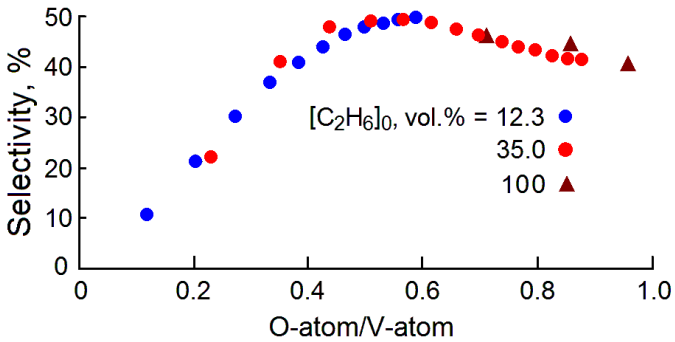
$$[\ ]_S + O_2 \rightarrow \ldots \rightarrow [O]_S$$

Sinev et al.

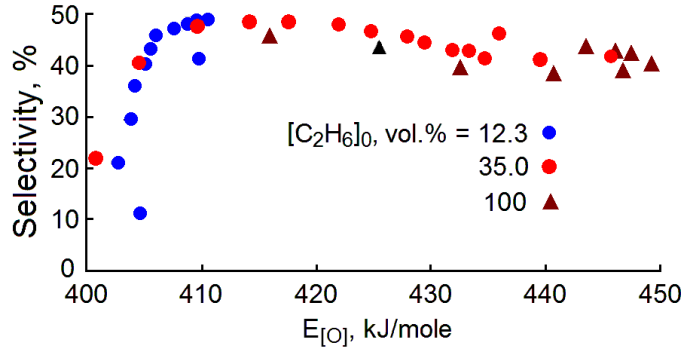
Case study: alkane ODH over VSb/Al2O3

$C_nH_{2n+2} + ½ O_2 \rightarrow C_nH_{2n} + H_2O$





V(4+) state is optimal for high selectivity to ethylene



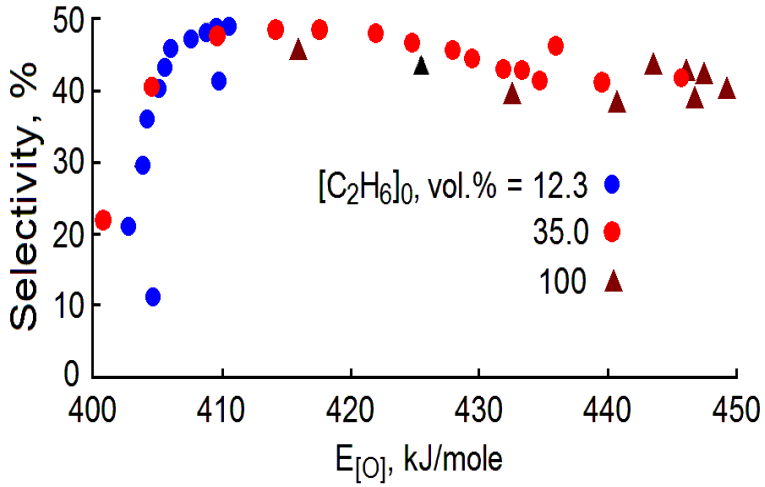
V(5) → V(4+) – jump of S @ small variations of $E_{[O]}$;

V(4+) → (V3+) – slow decrease of S in a wide range of $E_{[O]}$ variation

🔑 'Chemical' factor (i.e. state of surface sites and their interaction with HC's) is more important than 'energy' one

Sinev et al.

Case study: alkane ODH over VSb/Al2O3

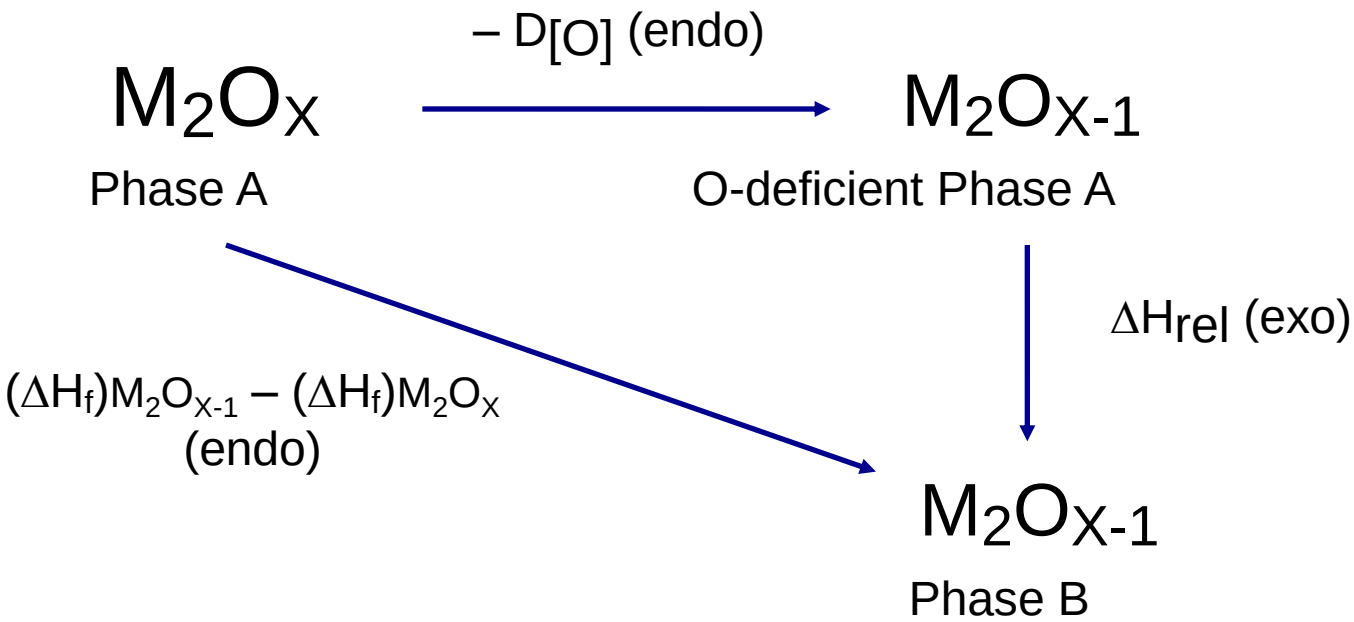


$(\Delta H_f)_{M2OX-1} - (\Delta H_f)_{M2OX} \approx E_{[O]}$

$Sb_2O_5 \rightarrow Sb_2O_4 + ½\ O_2$	-171 kJ/mole O_2
$Sb_2O_4 \rightarrow Sb_2O_3 + ½\ O_2$	-383 kJ/mole O_2
$V_2O_5 \rightarrow V_2O_4 + ½\ O_2$	-224 kJ/mole O_2
$V_2O_4 \rightarrow V_2O_3 + ½\ O_2$	-442 kJ/mole O_2
$V_2O_3 \rightarrow 2VO + ½\ O_2$	-710 kJ/mole O_2

Is $E_{[O]} \approx (\Delta H_f)_{M2OX-1} - (\Delta H_f)_{M2OX}$???

Sinev et al.



$D_{[O]}$ – O-binding energy (in 'phase homogeneity' range);

$(\Delta H_f)_{M_2O_X}$, $(\Delta H_f)_{M_2O_{X-1}}$ – standard (tabulated) values;

ΔH_{rel} – enthalpy of relaxation (elimination of vacancies, lattice re-organization, etc.)

$$|(\Delta H_f)M_2O_{X-1} - (\Delta H_f)M_2O_X| < |E_{[O]}| < |D_{[O]}|$$

Sinev et al.

Experimentally measured value