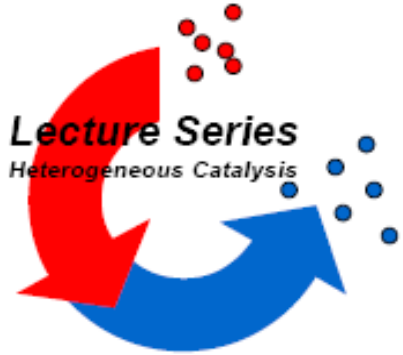
Modern Methods in Heterogeneous Catalysis Research



Thermal analysis methods

Rolf Jentoft

03.11.06

Outline

- Definition and overview
- Thermal Gravimetric analysis
- Evolved gas analysis (calibration)
- Differential Thermal Analysis/DSC
- Kinetics introduction
- Data analysis examples

Definition

Thermal analysis:

the measurement of some physical parameter of a system as a function of temperature.

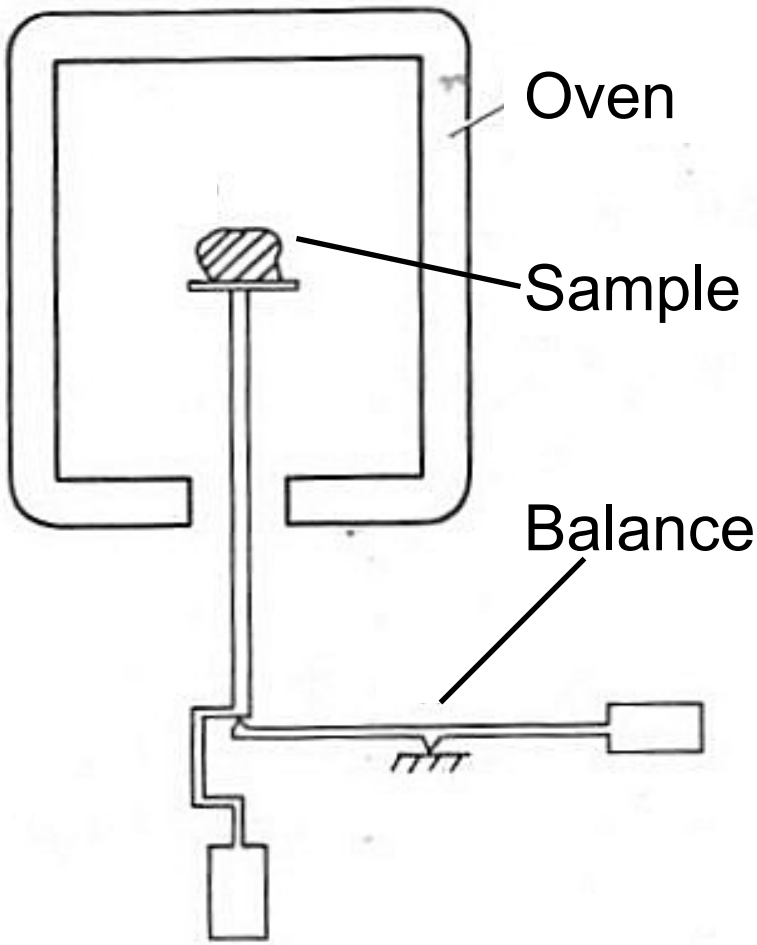
Usually measured as a dynamic function of temperature.

Types of thermal analysis

- TG (Thermogravimetric) analysis: weight
- DTA (Differential Thermal Analysis): temperature
- DSC (Differential Scanning Calorimetry): temperature
- DIL (Dilatometry): length
- TMA (Thermo Mechanical Analysis): length (with strain)
- DMA (Dynamic-Mechanical Analysis): length (dynamic)
- DEA (Dielectric Analysis): conductivity
- Thermo Microscopy: image
- Combined methods

Thermogravimetric

Developed by Honda in 1915



Oven heated at controlled rate

Temperature and Weight are recorded

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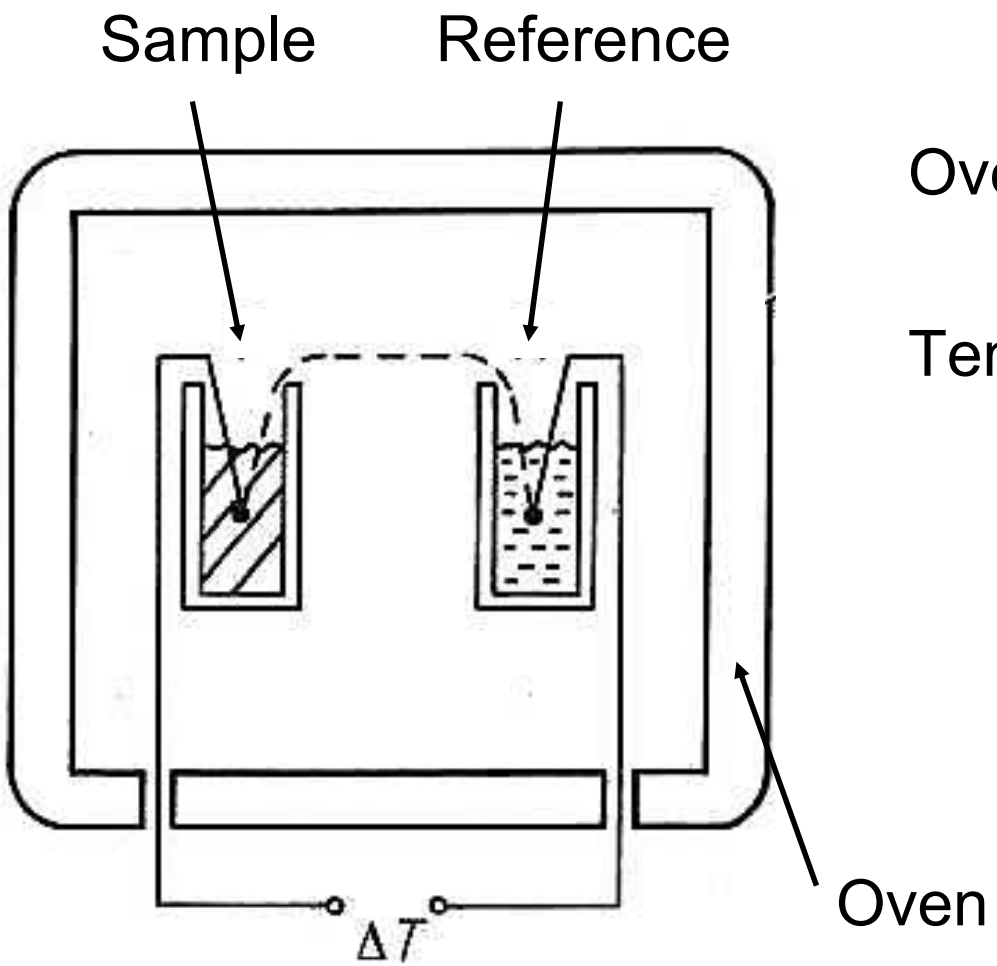
DTA/DSC

First introduced by Le Chatelier in 1887, perfected by Roberts-Austen 1899



Oven heated at controlled rate

Temperature and temperature difference are recorded

Types of thermal analysis

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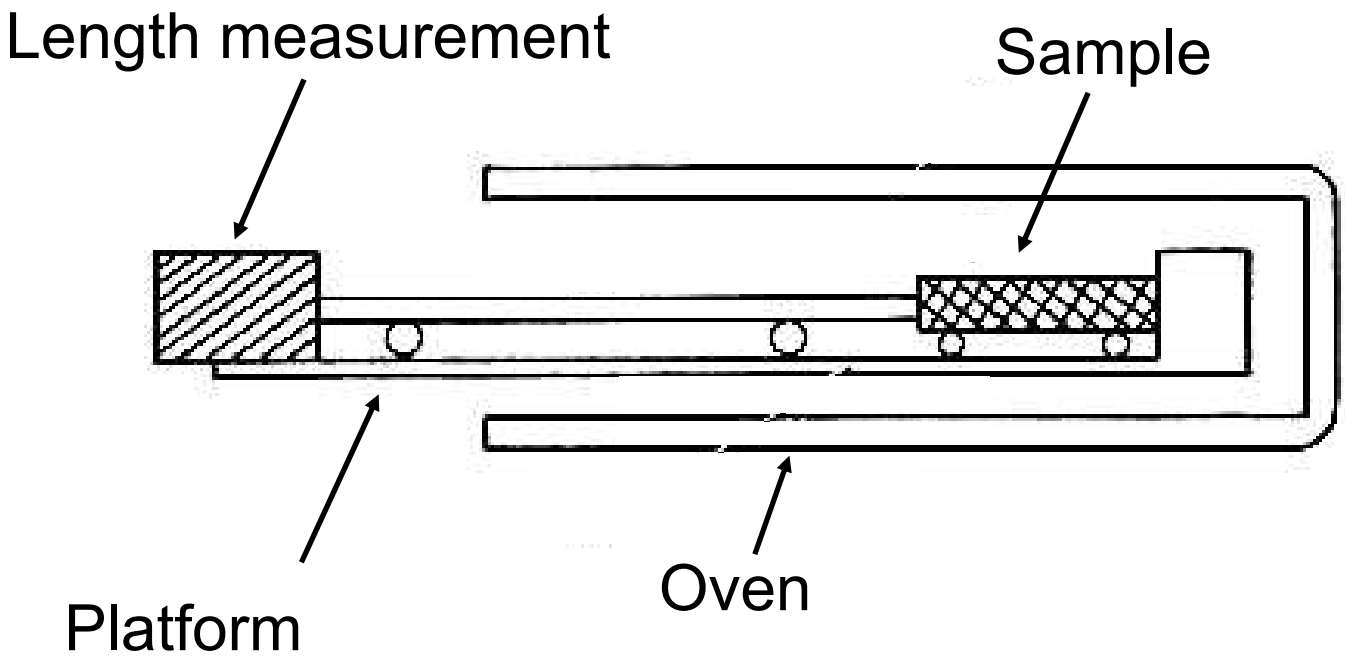
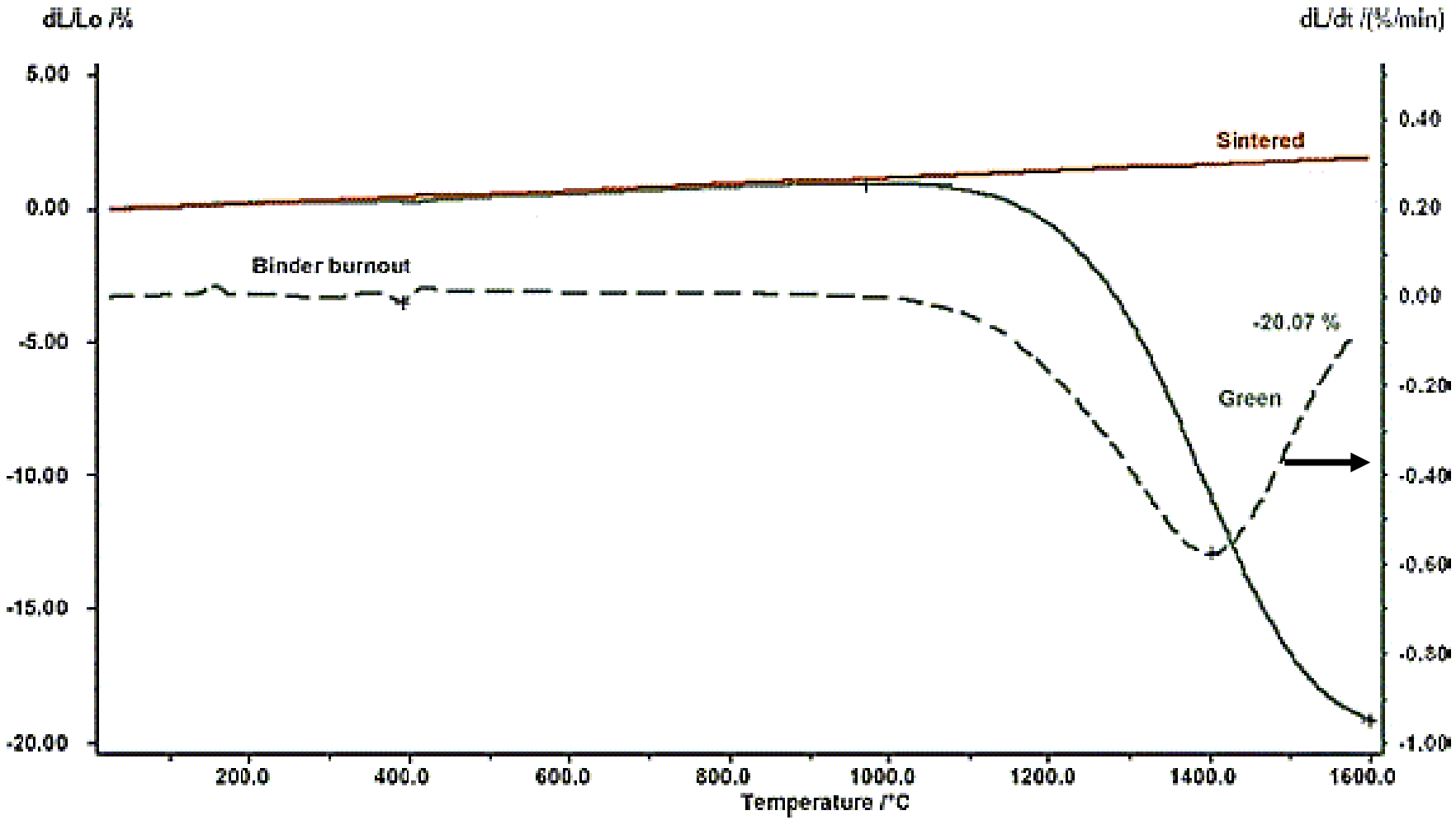
Dilotometry (DIL)

Dilometry: change in length with temperature

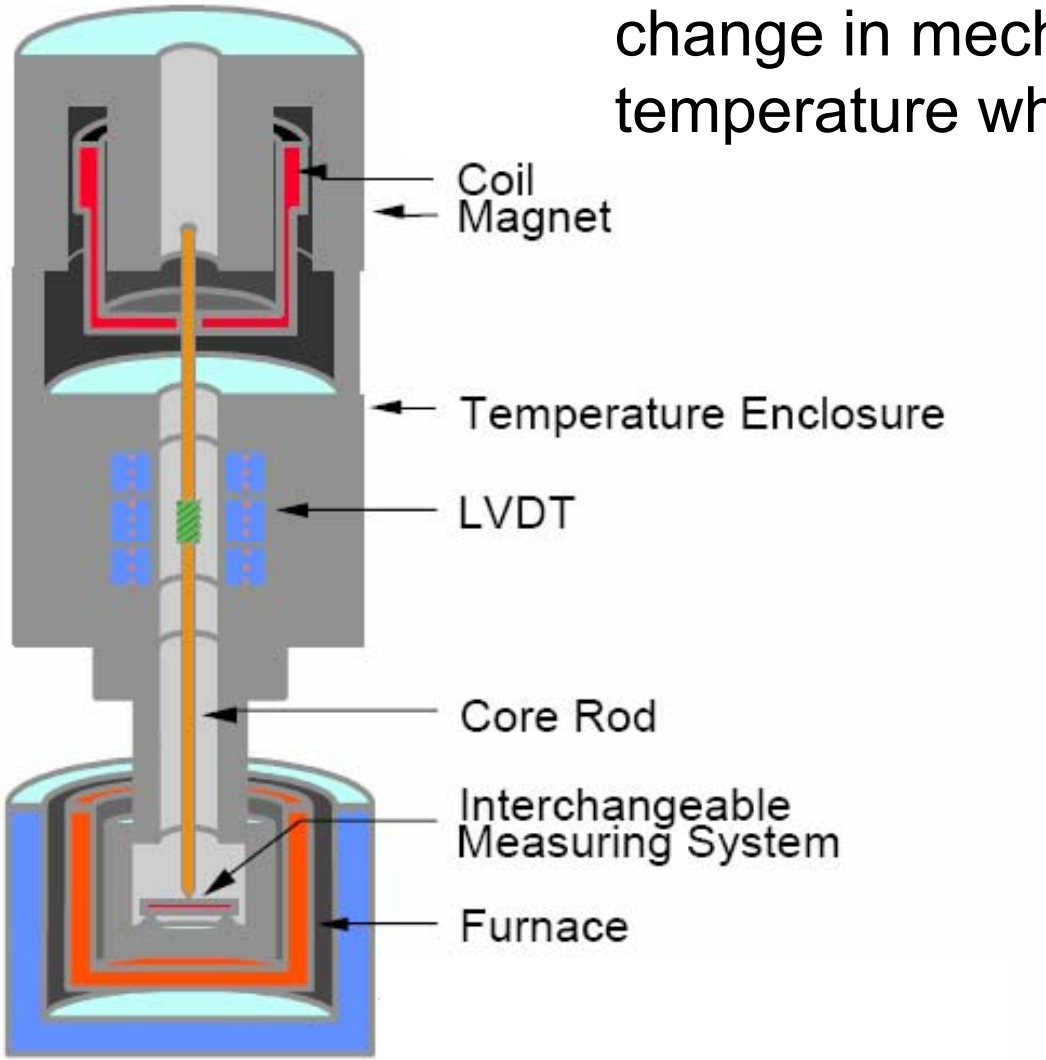


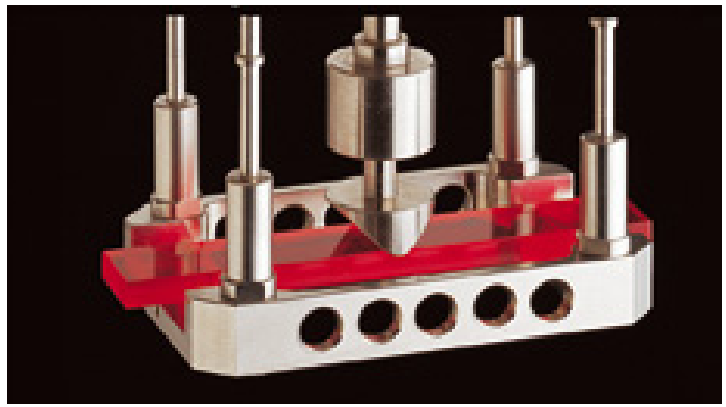
DIL of “Green” and Sintered Yttria-stabilized Zirconia

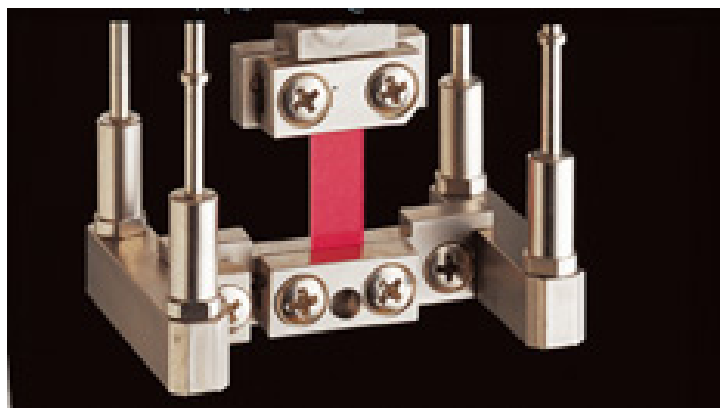


TMA and DMA

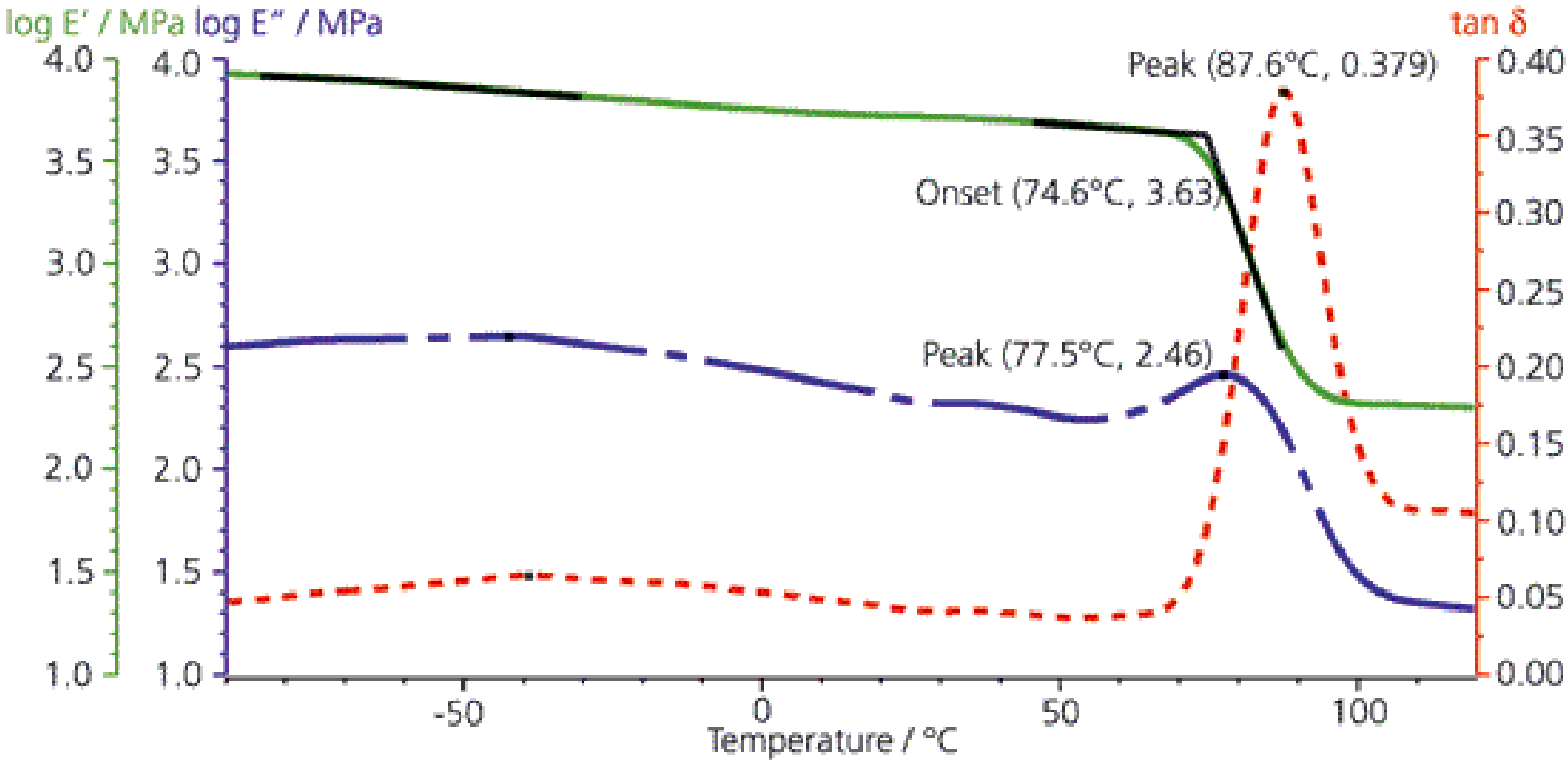
Dynamic mechanical analysis:
change in mechanical properties with temperature while under dynamic stress







DMA of polyester fiber



Glass transition starts at 75°C.
The storage modulus decreased from
approx. 4,200 MPa to 200 MPa.

E‘ is storage modulus
E“ is loss modulus
δ is the phase lag

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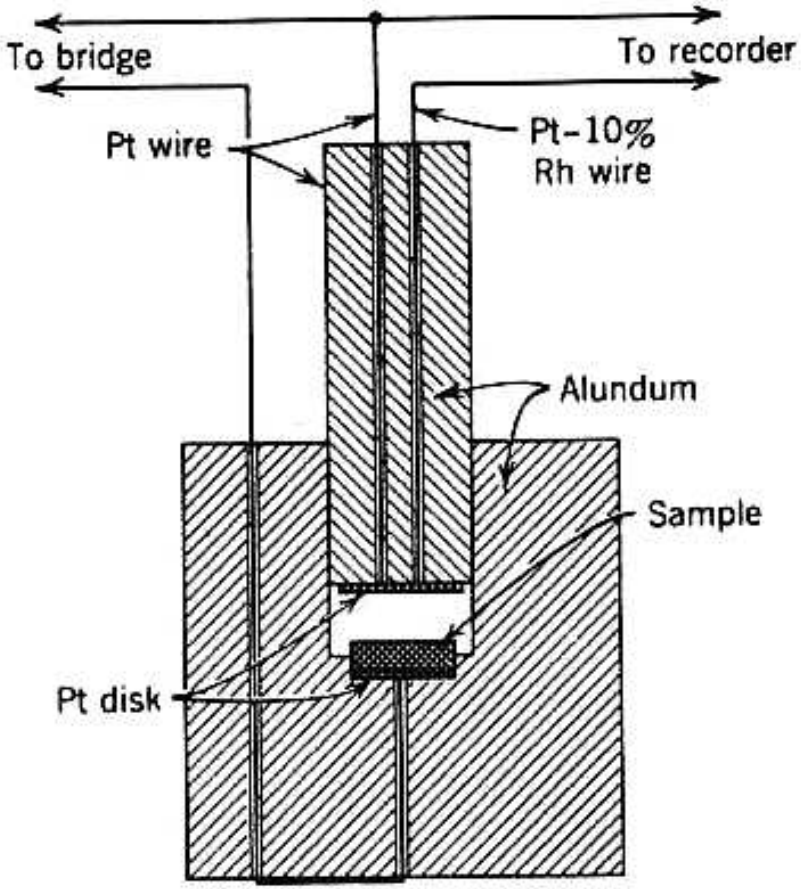
Dielectric analysis

Change in conductivity with temperature



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Sintering of W 1600-2700 °C

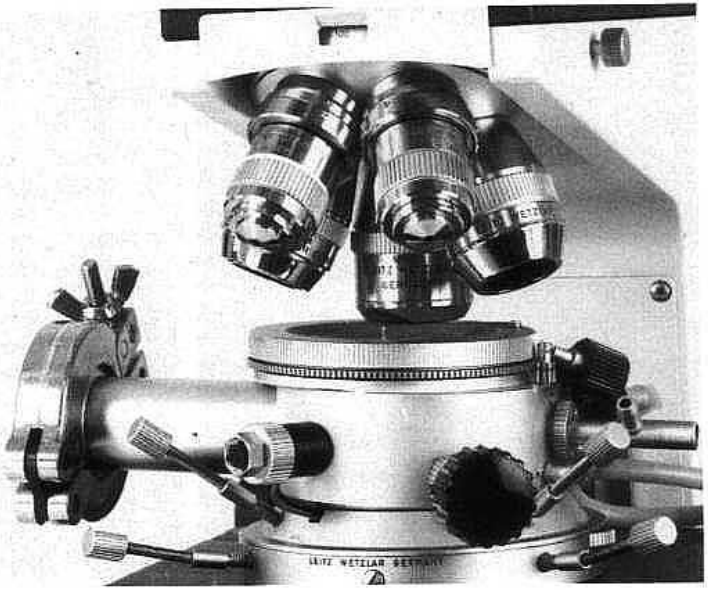
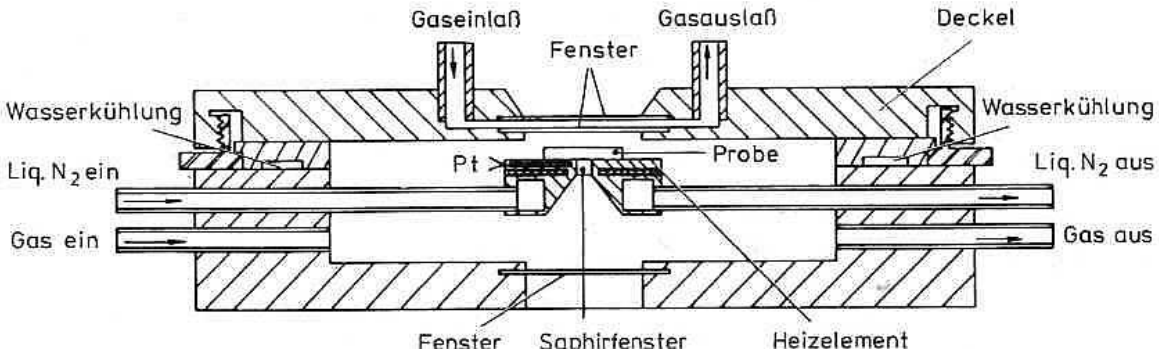
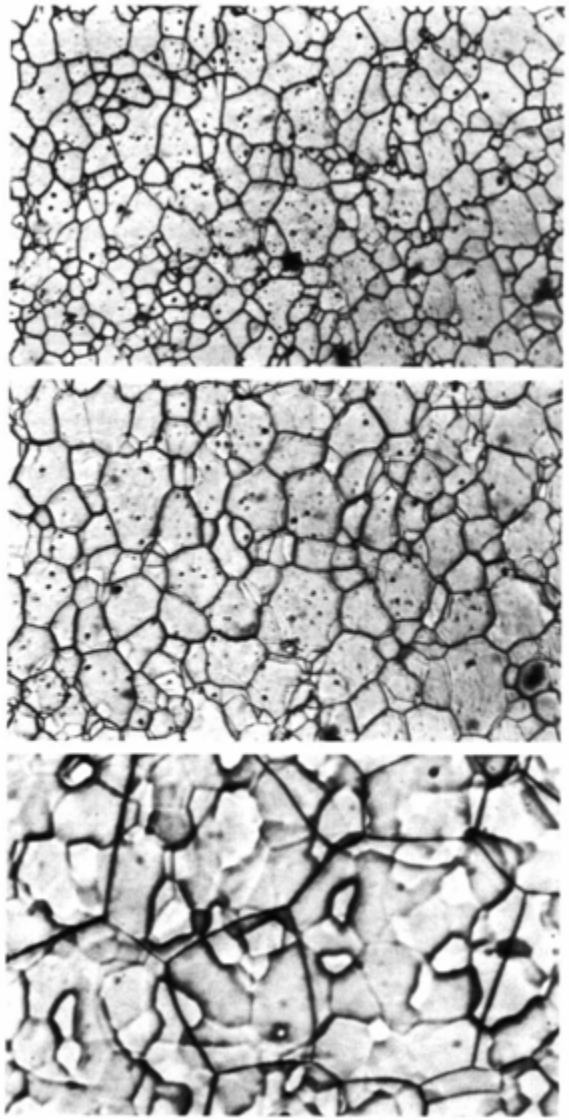


Abb. 7.6. Heizkammer 1750 au
Mikroskopobjekttisch. Für Ar
beiten in Gasatmosphäre ode
unter Vakuum. (Photo: Fa. Leitz





TGA with Optical Window

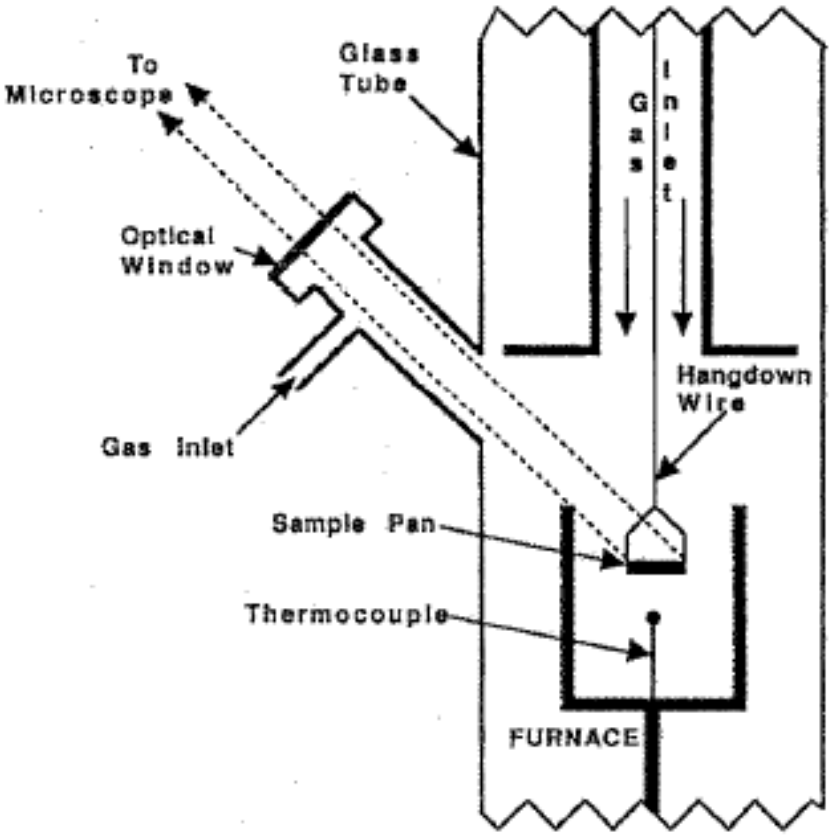


FIG. 2. Detail showing the TGA furnace, its side tube, and the optical window that allows direct observation of reacting particles placed in the sample pan.

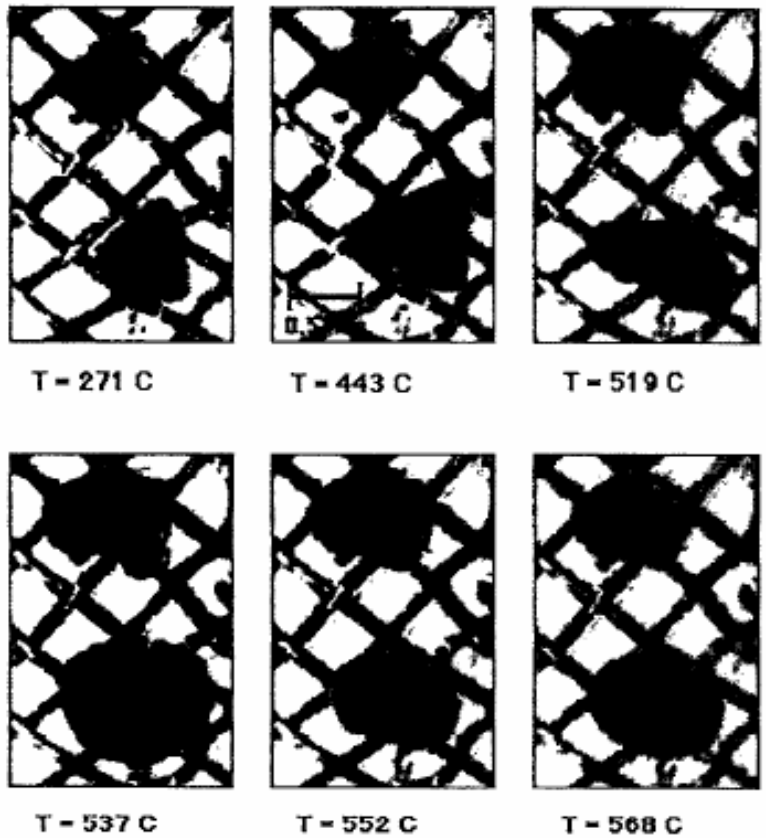


FIG. 7. Sequence of digital images showing the size and shape changes of two pyrolyzing coal particles at several reactor temperatures. The particles are separated on the pan by a platinum wire mesh.

Matzakos and Zygourakisa Rev. Sci. Instrum. 64 (6), June 1993, 1541-48

TG analysis

Thermolysis curve

Pyrolysis curve

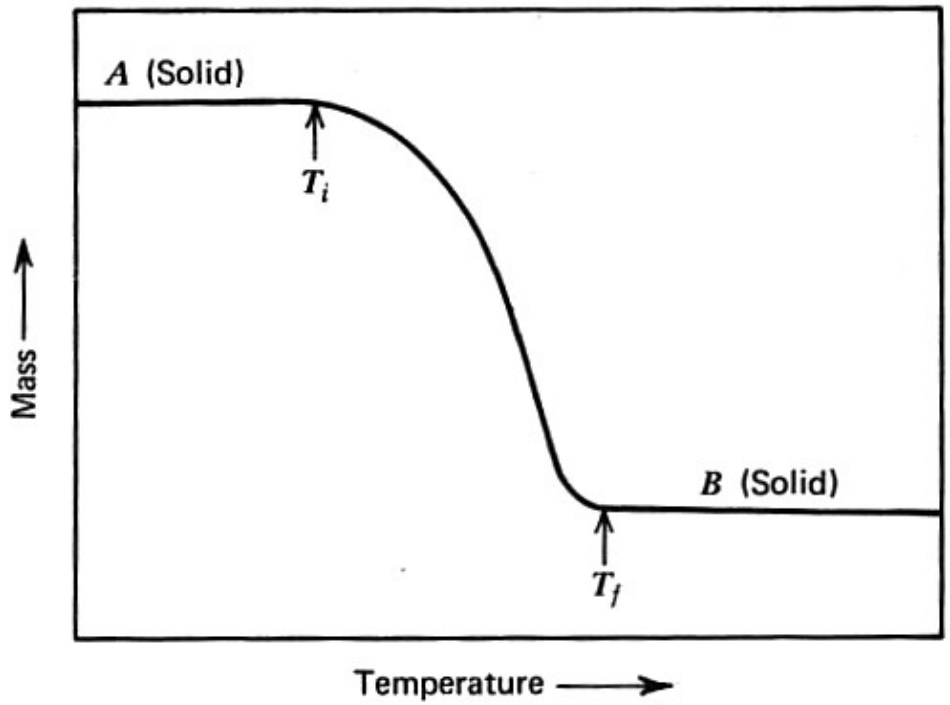
Thermogram

Thermogravimetric curve

Thermogravigram

Thermogravimetric analysis curve

TG curve



A (Solid) → B (Solid) + C (Gas)

Information obtained depends on procedure

Not fundamental property

TG analysis: uses

1) Thermal decomposition of substances (calcination and heat treatment and polymer stability)
2) Corrosion of metals
3) Determination of moisture, volatiles, and ash content
4) Evaporation rates and sublimation
5) Distillation and evaporation of liquids
6) Reaction kinetics studies
7) Compound identification
8) Heats of vaporization and vapor pressure determinations

TG curve: Instrumental effects

Furnace heating rate

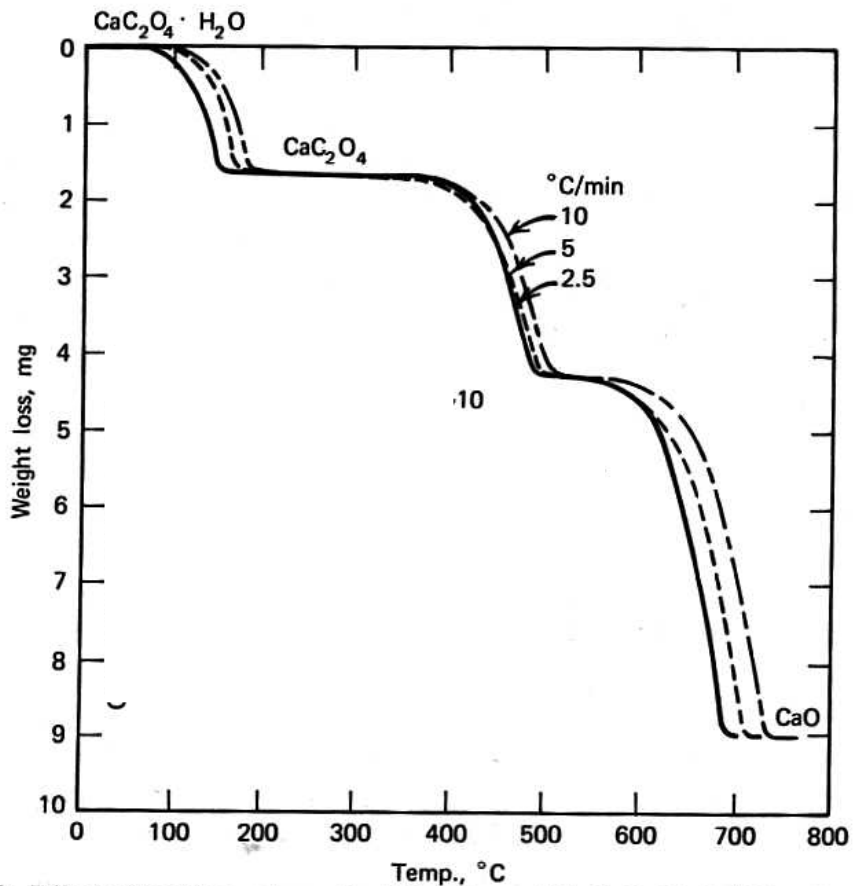


Figure II.2. Effect of heating rate on the TG curves of $CaC_2O_4 \cdot H_2O$ (15). Sample 14.8 mg; dynamic He atmosphere at 150 ml/min.

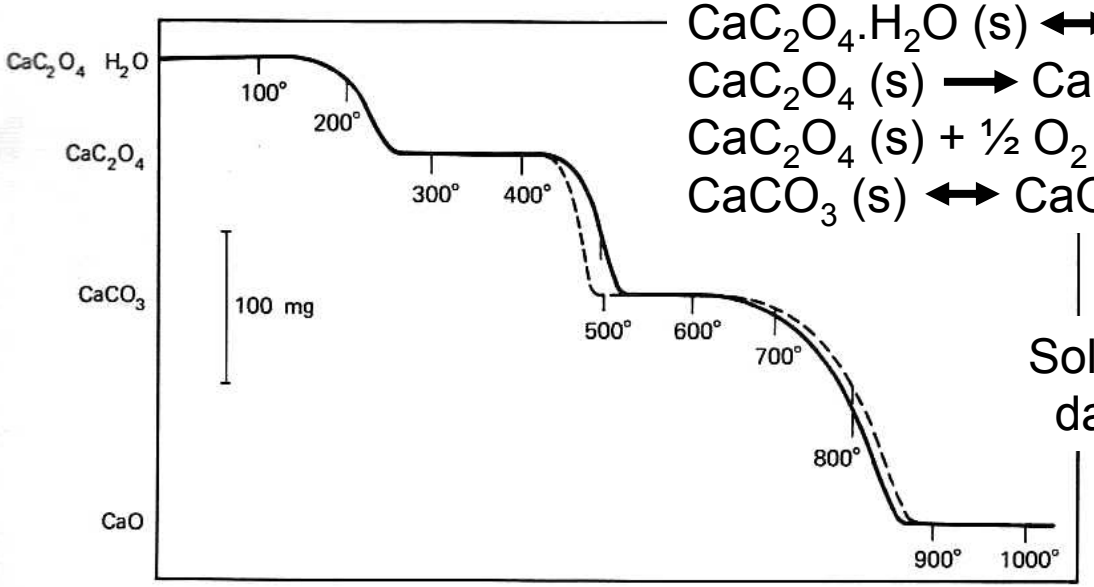
Slower heating =
better resolution

Usually,
Higher heating rate =
shift to higher temperature

TG curve: Instrumental effects

Furnace gas atmosphere

A (solid) → B (solid) + C (gas)
A (solid) ↔ B (solid) + C (gas)
A (solid) + B (gas) → C (solid)
A (solid) + B (gas) ↔ C (solid)
A (solid) + B (gas) → C (solid) + D (gas)
A (solid) + B (gas) ↔ C (solid) + D (gas)

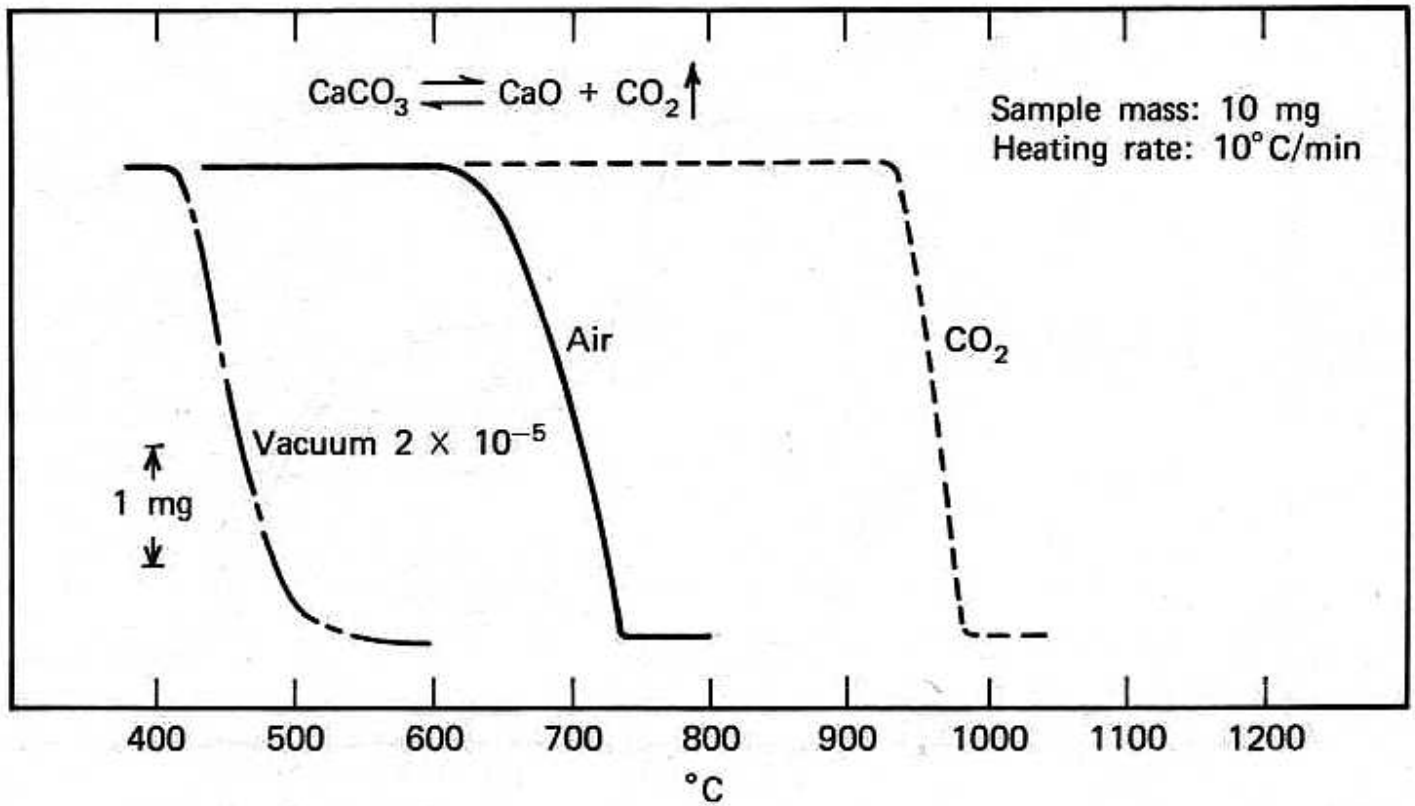


$CaC_2O_4.H_2O$ (s) ↔ CaC_2O_4 (s) + H2O (g)
CaC_2O_4 (s) → $CaCO_3$ (s) + CO (g) (in N_2)
CaC_2O_4 (s) + ½ O_2 (g) → $CaCO_3$ (s) + CO_2 (g) (in O_2)
$CaCO_3$ (s) ↔ CaO + CO_2 (g)

Solid line in nitrogen,
dashed line in oxygen

TG curve: Instrumental effects

Furnace gas atmosphere



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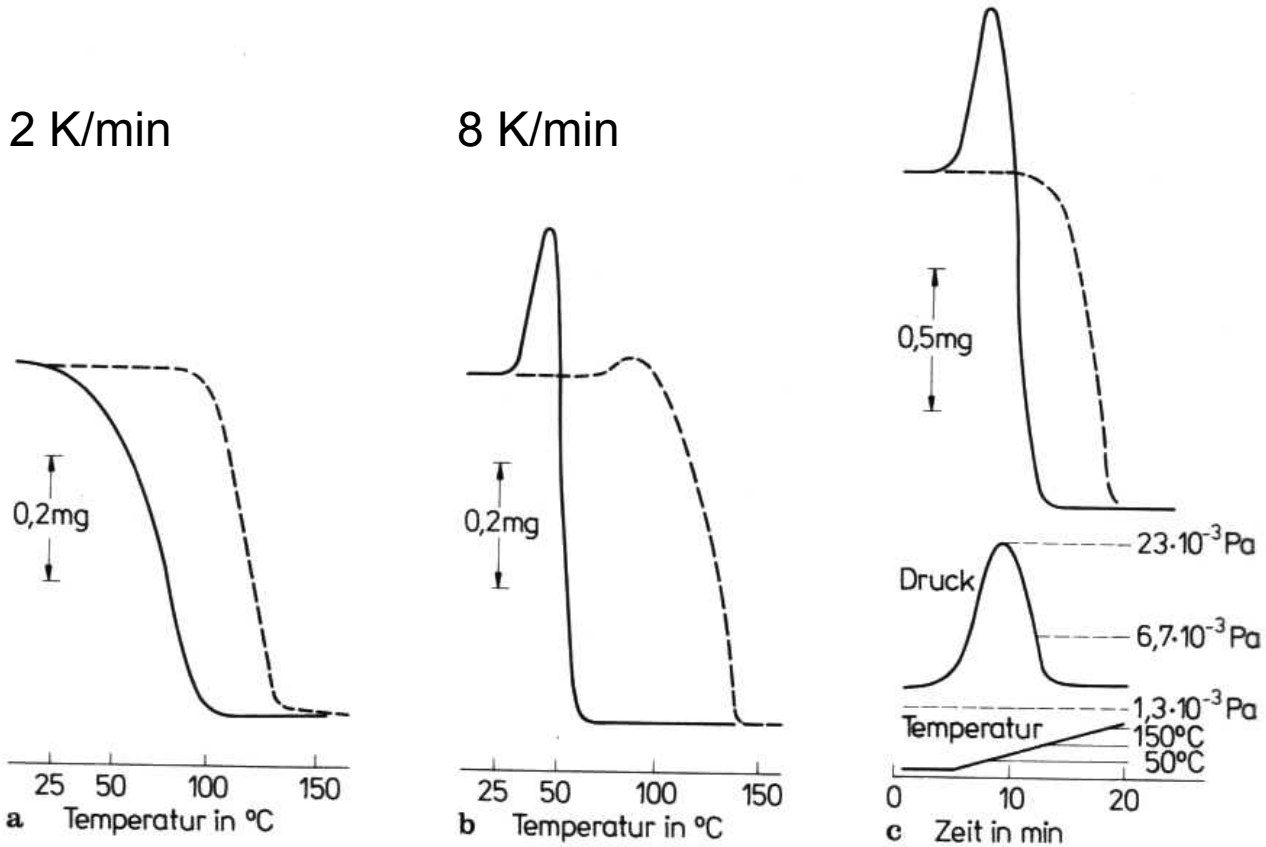
TG curve: Instrumental effects

Furnace configuration

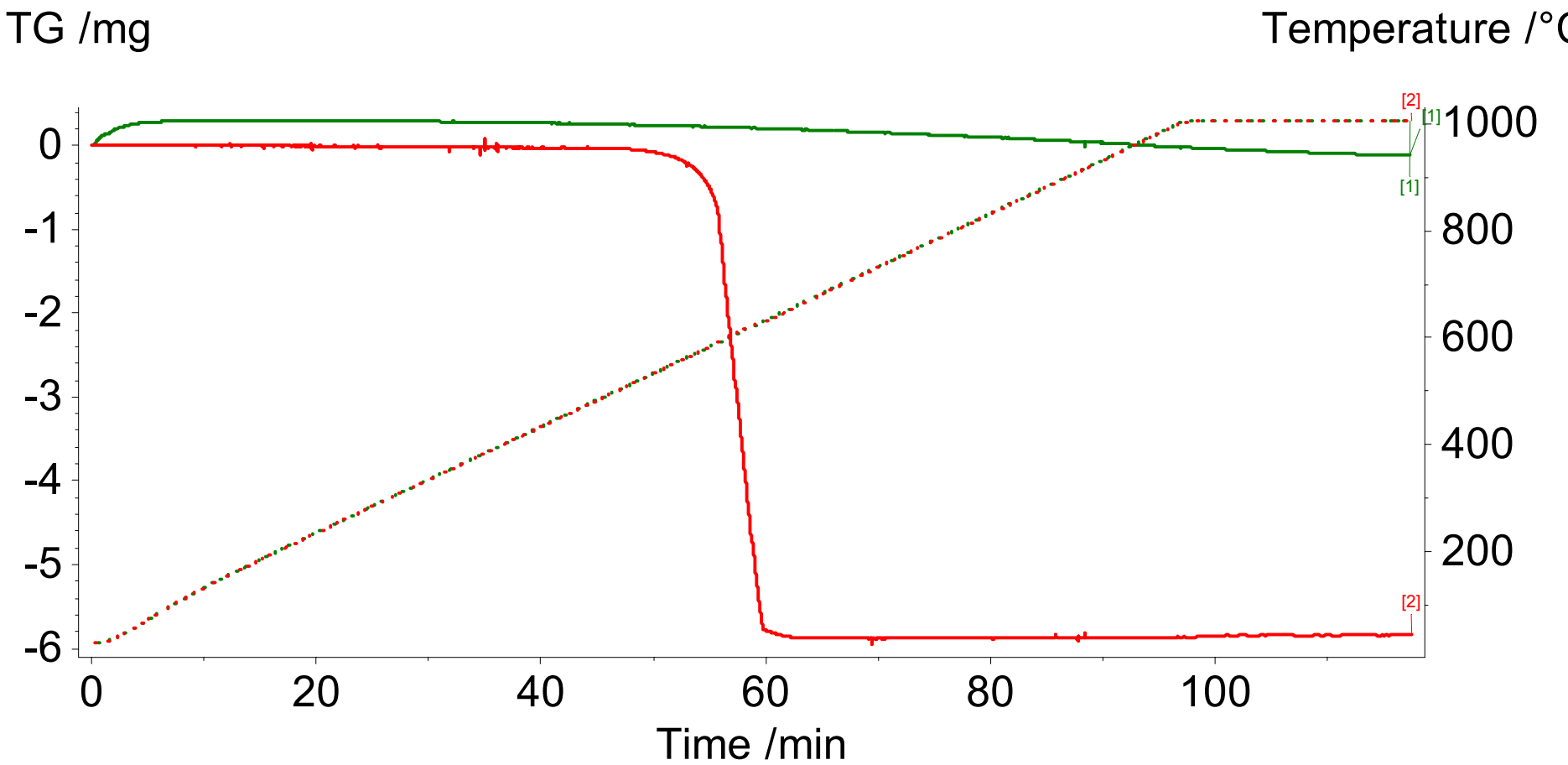


Dehydration of $CaC_2O_4.H_2O$, (dashed line, single crystal)

TG curve: Instrumental effects

Correction file

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



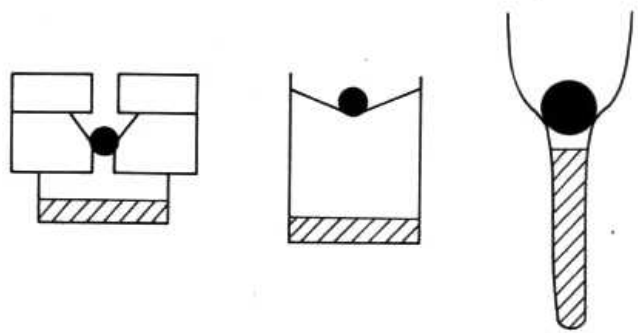
TG curve: Sample effects

Crucible type

Mass transport by flow (ΔP) and diffusion (ΔC)

A (solid) → B (solid) + C (gas)
A (solid) + B (gas) → C (solid)
A (solid) + B (gas) → C (solid) + D (gas)

- Thin layer vs. Large amount of sample
- Detection limit vs. Diffusion limitation
- Self generated atmosphere

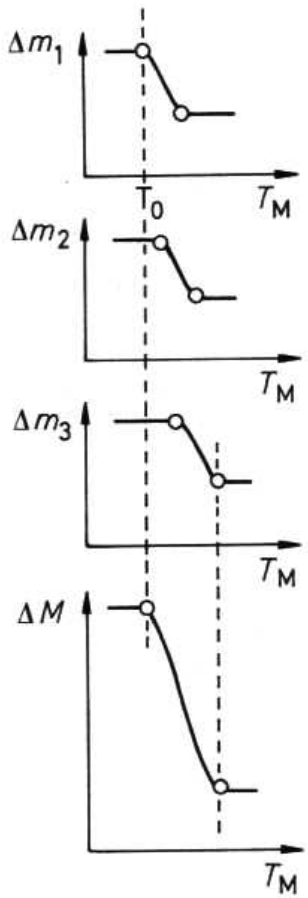


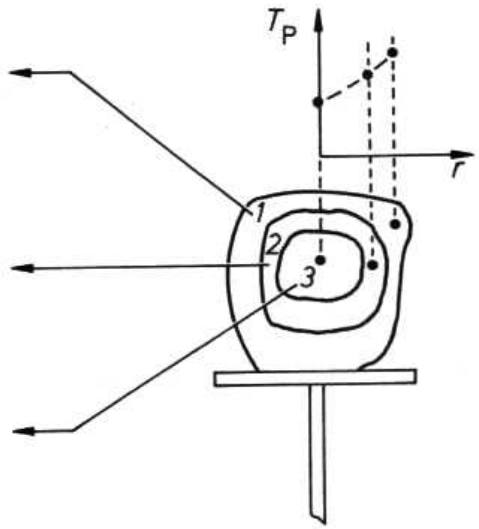
TG curve: Sample effects

Thermal conductivity and particle size

Large particles and low thermal conductivity can effect results

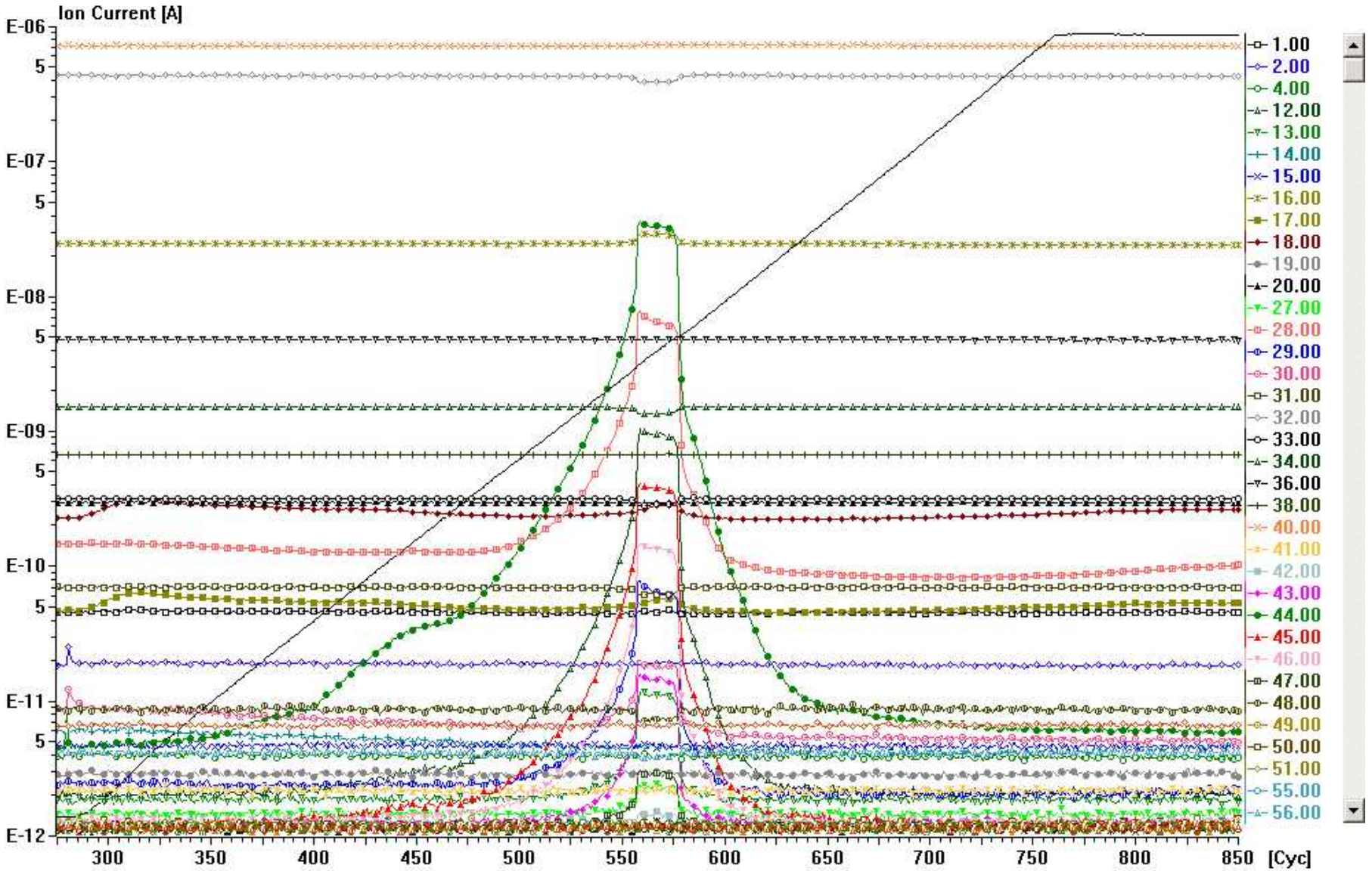
	λ
Reine Metalle	30–400
Legierungen	14–160
Al_2O_3 (gesintert)	25–35
Pulverschüttungen	0,1–0,8
(Korngröße: 0,1 bis 0,4 mm)	
Gläser	0,7–1,4
Pyrex-Glas	1,12
Kunststoffe	0,15–0,35
Flüssigkeiten	0,1–0,6
Wasser	0,6
Gase (anorganisch)	0,01–0,17
Luft	0,02





TG curve: Sample effects

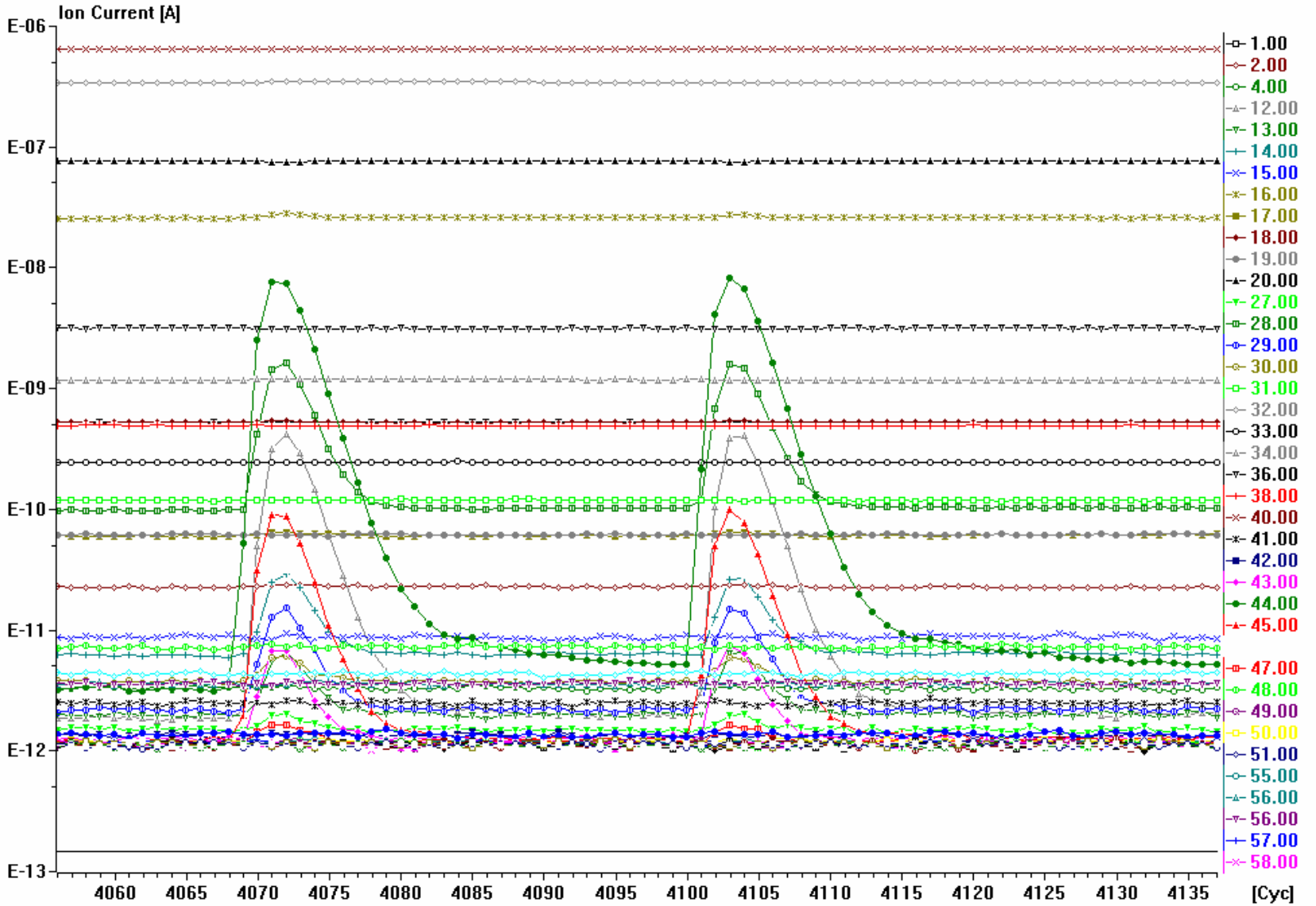
Diffusion limitation



Evolved gas analysis

- Single thermal analysis method may not be sufficient to understand changes in sample
- Control of gas phase requires analysis of gas phase
- Mass spectrometry and Infra-red analysis
- Transfer of gas to analytical instrument
- Calibration of the gas analysis technique

Evolved gas analysis: Pulse Calibration



Thermal analysis: crucibles

The best type of crucibles are disposable crucibles

Crucible selection criteria (size and material):

- Temperature range
- Chemical compatibility
- Detection limits
- Gas exchange characteristics

Crucible cleaning

Mechanical cleaning not recommended

Thermal analysis: crucibles

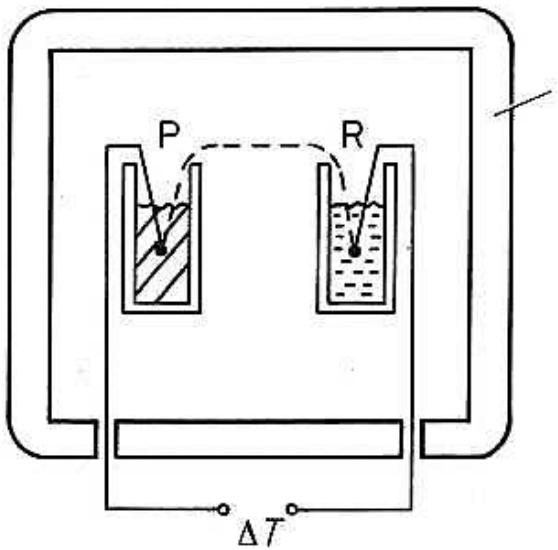
Table 4.8 Compatibility between calibration substances and crucible materials (according to Cammenga et al., 1993)

Crucible material \ Calibration substance	Cyclopentane	Water	Gallium	Indium	Tin	Lead	Zinc	Lithium sulfate	Aluminum	Silver	Gold
Corundum, Al_2O_3	□	□	+	+	+	+	+	+	+	+	+
Boron nitride, BN	□	□	+	+	+	+	+	+	+	?	?
Graphite, C	□	□	+	+	+	+	+	+	+	+	–
Silicate glass	+	+	+	+	+	+	?	+	–	×	×
Quartz glass, SiO_2	+	+	+	+	+	+	+	+	–	+	+
Aluminum, Al	+	·	–	+	–	+	–	+	×	×	×
Aluminum, oxidized	+	+	+	+	+	+	+	+	×	×	×
Silver, Ag	+	+	–	–	–	–	–	?	–	×	×
Gold, Au	+	+	·	·	–	–	–	+	–	–	×
Nickel, Ni	+	+	·	·	·	·	·	?	–	+	–
Iron, Fe	+	·	·	+	·	+	–	?	–	+	–
Stainless steel	+	+	·	+	·	+	–	?	–	+	–
Platinum, Pt	+	+	·	·	–	–	–	+	–	–	–
Molybdenum, Mo	+	+	·	?	·	?	·	?	?	?	–
Tantalum, Ta	+	+	?	+	?	?	?	+	–	+	–
Tungsten, W	□	□	·	?	?	·	+	?	·	+	+

+ : No solubility and influence on melting temperature to be expected.
– : Melt dissolves crucible material, greater change of melting temperature.
· : Partial solution processes possible with negligible change of melting temperature.
× : Crucible melts.
? : Compatibility unknown.
□: Combination cannot be realized.

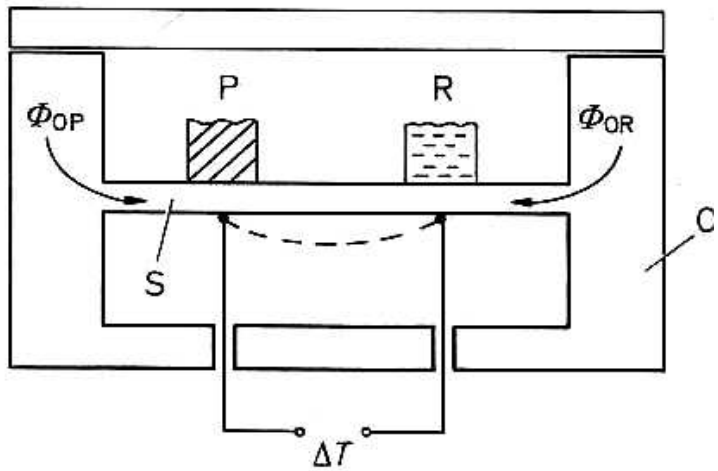
DTA/DSC

DTA



Measure temperature difference between sample and reference while they are being heated.

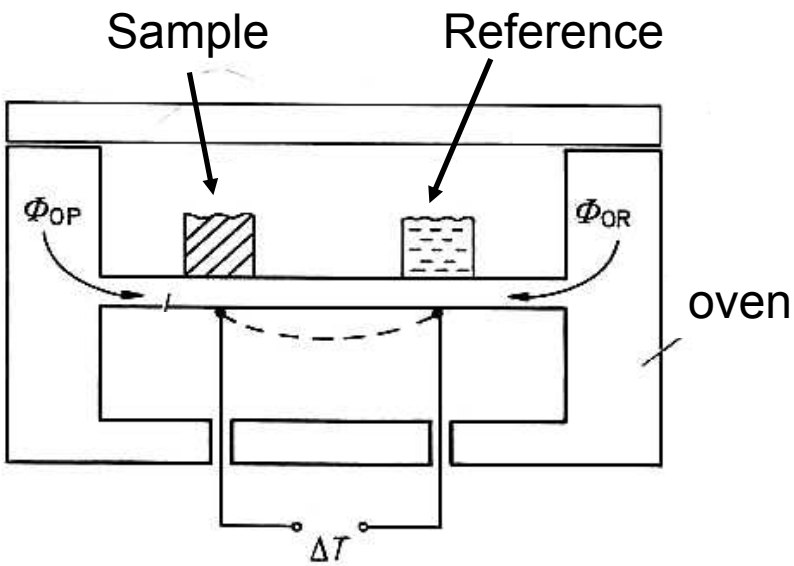
DSC



Measure difference in heat flow to sample and reference while they are being heated.

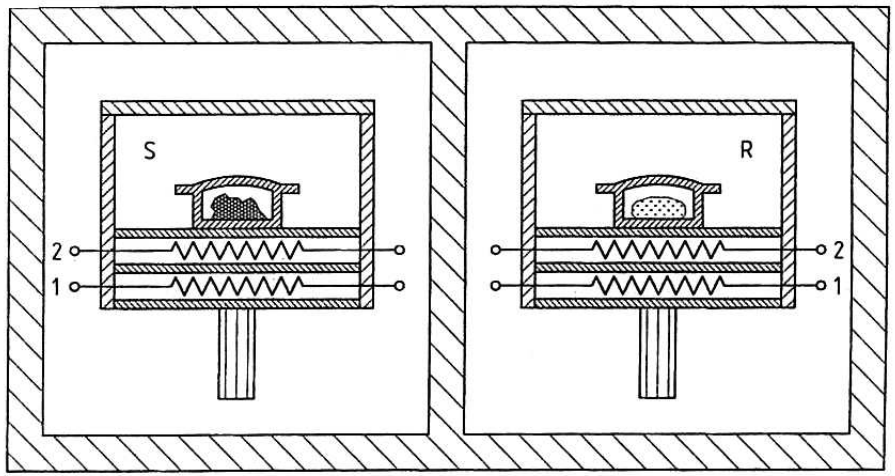
DSC

Heat flux DSC



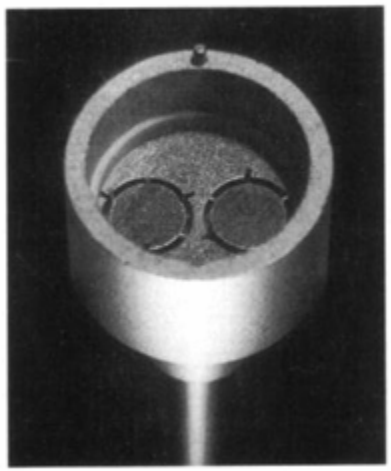
- Heat flows through disk
- Temperature of disk measured
- Heat transfer through disk greater than through gas phase

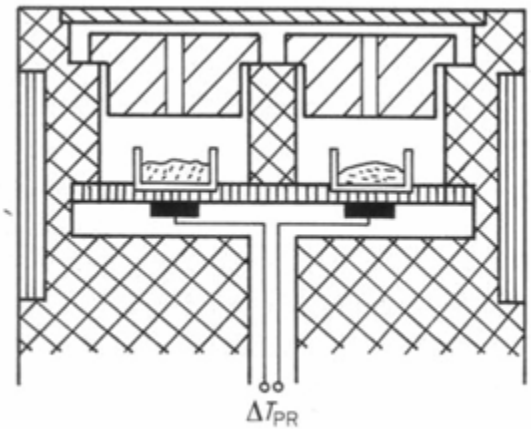
Power compensating DSC



- Each sample has own heater
- Temperature of samples controlled independently
- Less power required with endotherm

DSC





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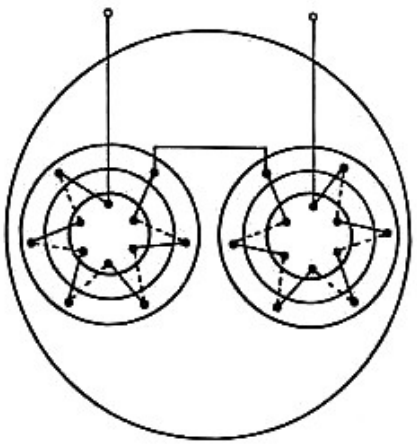
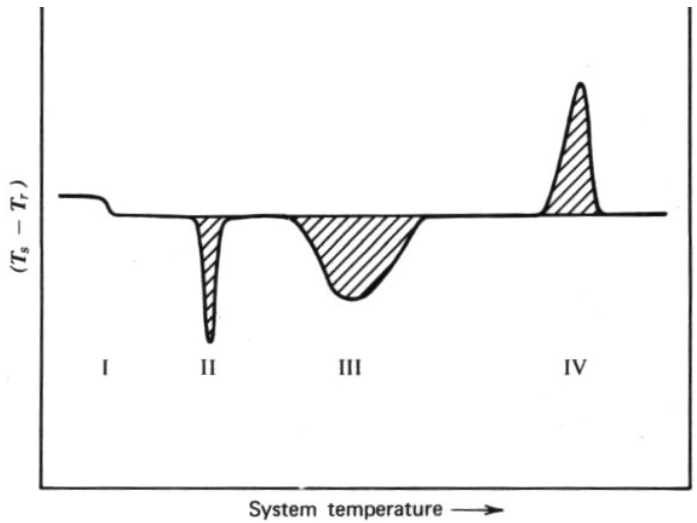




DTA/DSC :Reference

Reference should have same physical properties as sample

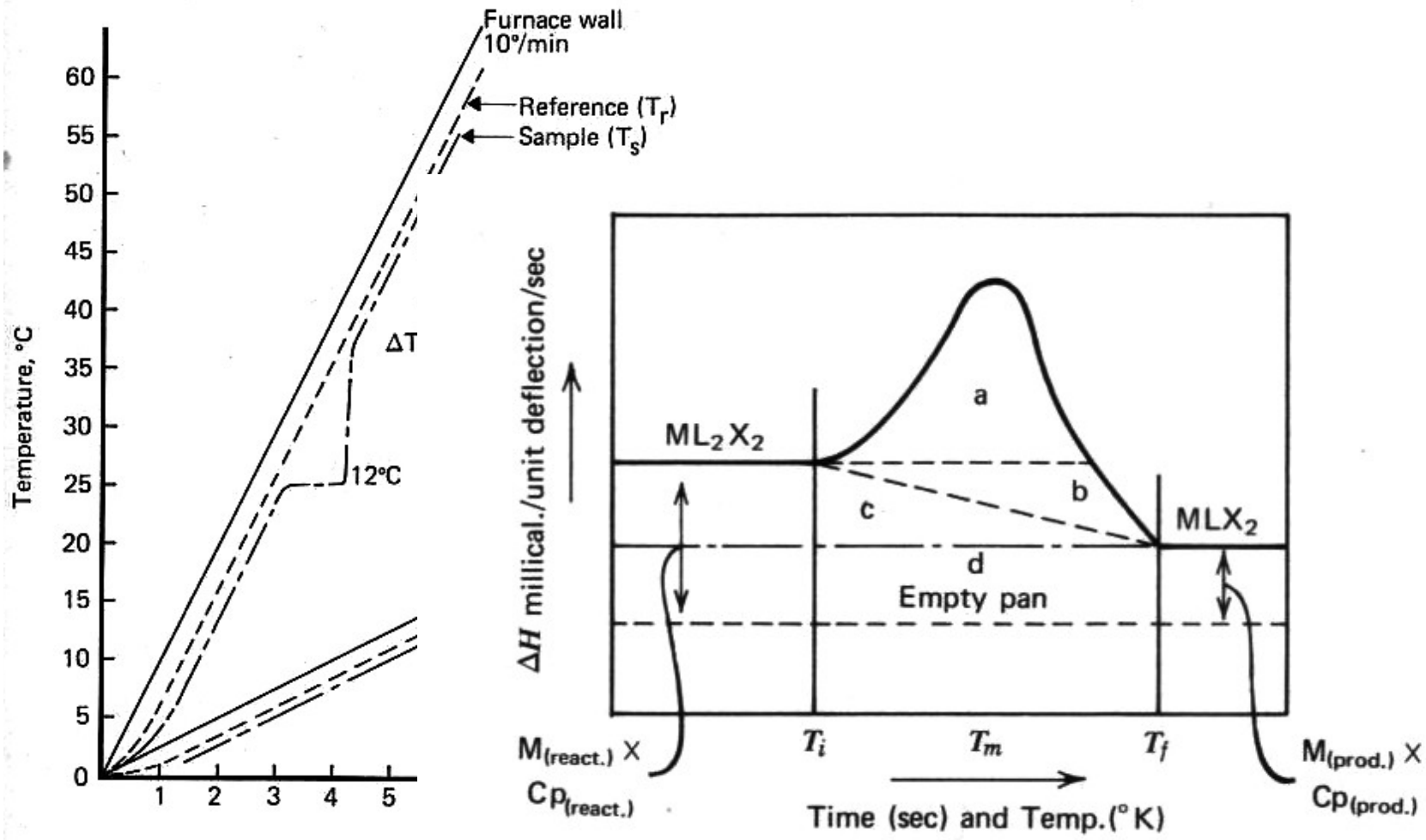
Reference should not have any transformations during heating

Reference for sample which looses weight?

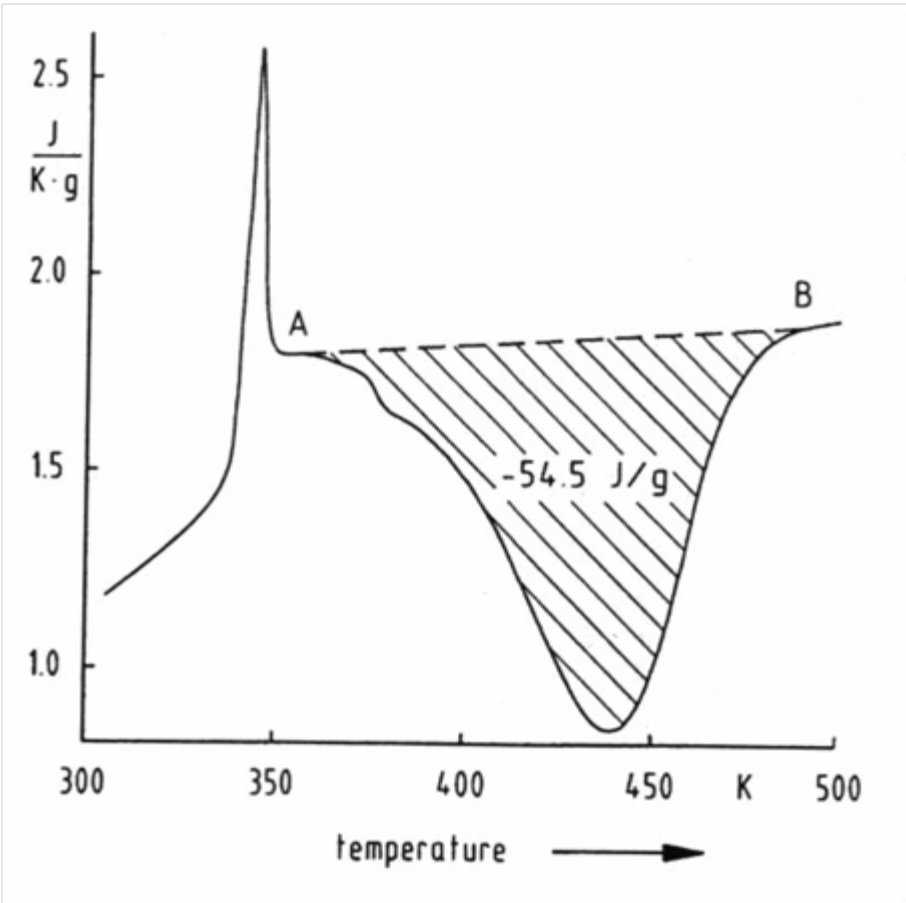
Commonly used, SiC, Al_2O_3, empty crucible

DTA/DSC: Temperatures

Temperature of oven, reference and sample during measurement

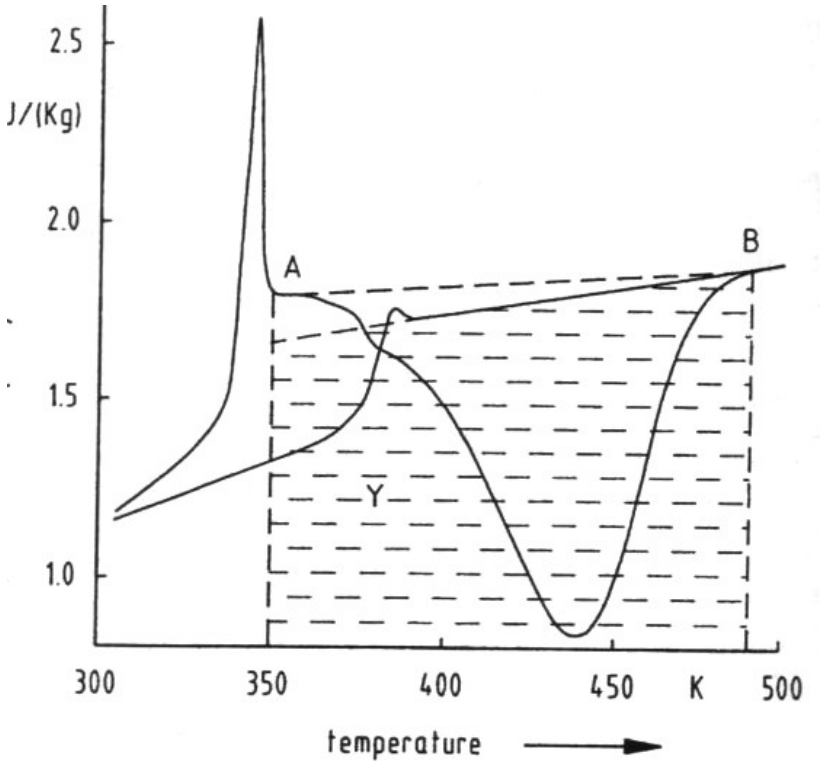


Heat integration

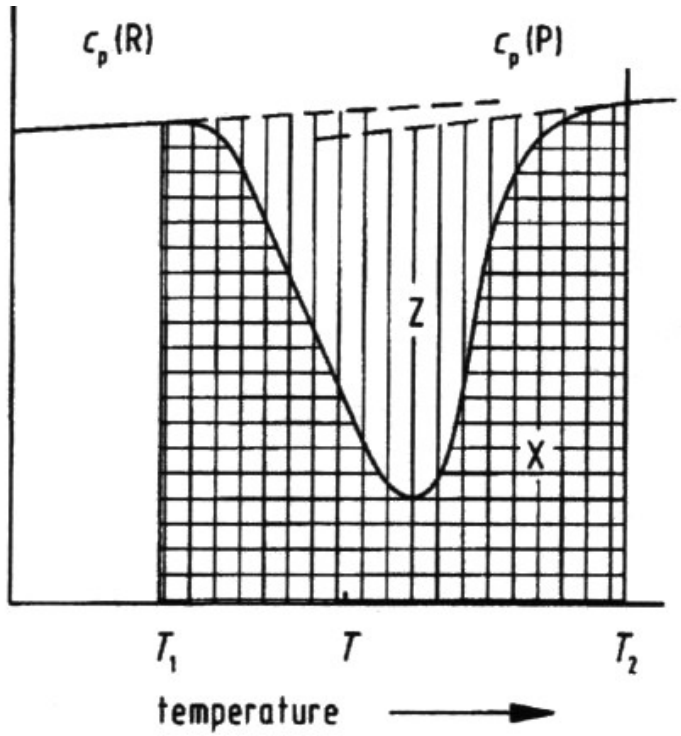


Curing a epoxy resin,
Simple linear baseline

Heat integration

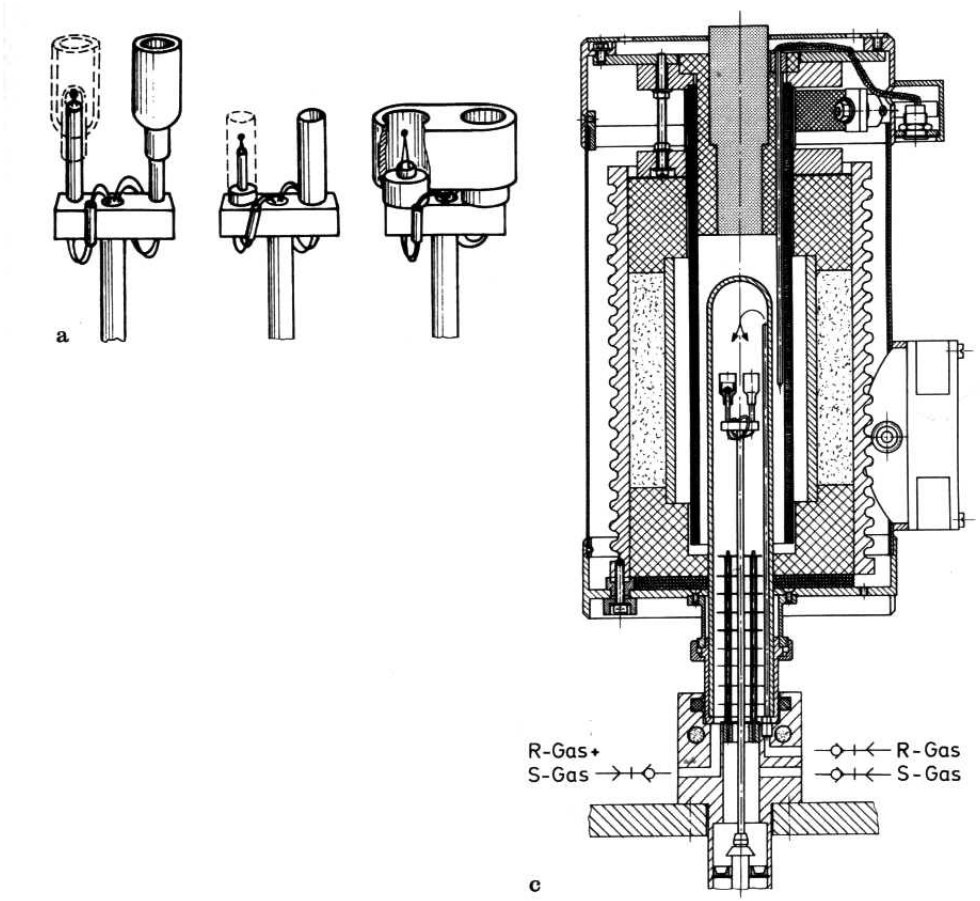


Re-heat cured resin to measure baseline (heat capacity) at end of reaction



TG analysis: combined methods

Thermal analysis methods are more powerful when combined



Analysis Methodology

- VxOy Characterization

V_xO_y Nanoparticles

- Model catalyst for partial oxidation of butane
  - Alkoxide/benzyl alcohol route*
- Catalytic properties
  - At 473 K mainly acetic acid

    (C-C bond clevage)
  - At 573 and 673 K mainly malaic anhydride (oxidation)
- Previous knowledge
  - From EELS and XPS V oxidized from mix of V^{+3} and V^{+4} to V^{+4} and V^{+5}

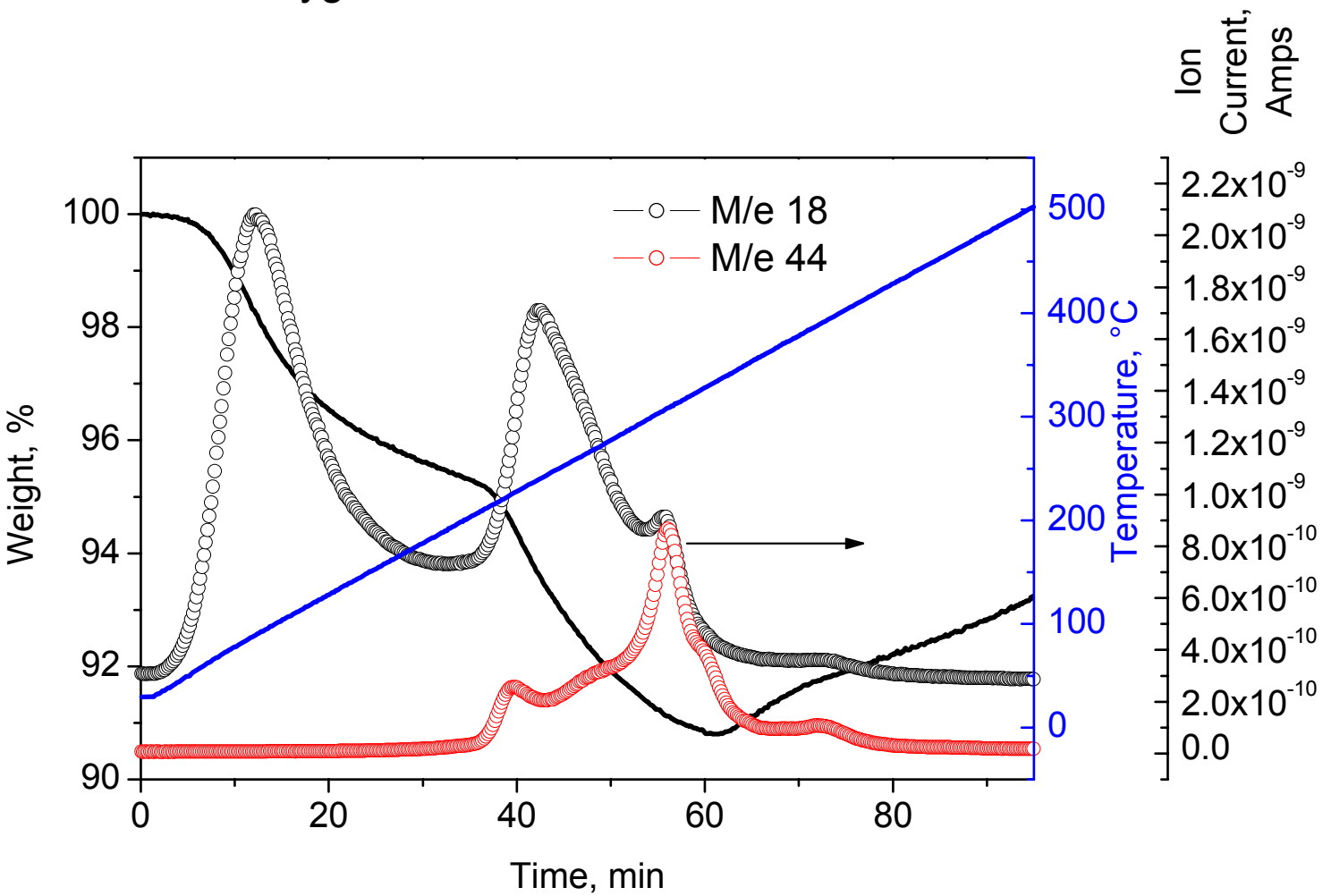
N. Pinna, M. Antoneitti, M. Niederberger, Colloids Surf. A 250 (2004) 211.

V_xO_y Nanoparticles

- From TEM, EELS, and XPS vanadium is oxidized from V^{+3} and V^{+4} to V^{+4} and V^{+5}
- What causes the change in selectivity?
- What can TGMS tell us about the material?
- Only several milligrams of material available!

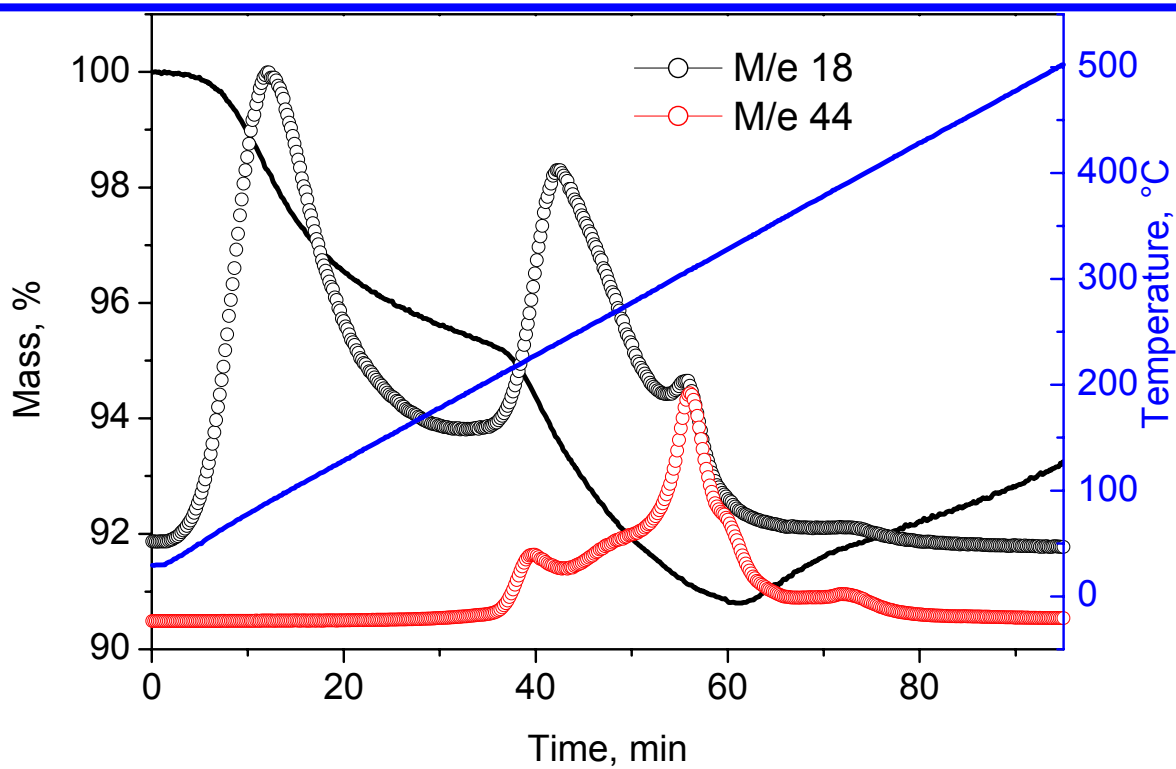
TGMS of V_xO_y particles

Conditions: 21 % oxygen, 5 K/min to 773K



TGMS of V_xO_y particles

- Calibrate MS:
  - H_2O ($CuSO_4$*$4H_2O$)
  - CO_2 (pulse valve)
- First M/e 18: 0.94mg



- Dehydration and combustion (assume C:H = 1:1) = 1.92 mg
- Weight loss of only 1.77mg suggests simultaneous re-oxidation
- Prolonged re-oxidation produces V_2O_5: basis for valence calculation of 4.5 at 340°C.

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Ice Calorimeter by Lavoisier