Thermal Analysis TGA / DTA

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Outline

- Definitions
- What is thermal analysis?
- Instrumentation & origin of the TGA-DTA signal.
- TGA
- DTA

Basics and applications

- Phase diagrams & Thermal analysis
  - Thermal analysis,an experimental method to determine phase diagrams.

Nomenclature of Thermal Analysis

ICTAC (International Confederation for Thermal Analysis and Calorimetry)

Definition of the field of Thermal Analysis (TA)

Thermal Analysis (TA) is a group of techniques that study the *properties of materials as they change with temperature*

Thermal analysis

- In practice thermal analysis gives properties like; enthalpy, thermal capacity, mass changes and the coefficient of heat expansion.
- Solid state chemistry uses thermal analysis for studying reactions in the solid state, thermal degradation reactions, phase transitions and phase diagrams.

Thermal analysis

... Includes several different methods. These are distinguished from one another by the property which is measured.

- Thermogravimetric analysis (TGA): mass
- Differential thermal analysis (DTA): temperature difference
- Differential scanning calorimetry (DSC): heat difference
- Pressurized TGA (PTGA): mass changes as function of pressure.
- Thermo mechanical analysis (TMA): deformations and dimension
- Dilatometry (DIL): volume
- Evolved gas analysis (EGA): gaseous decomposition products

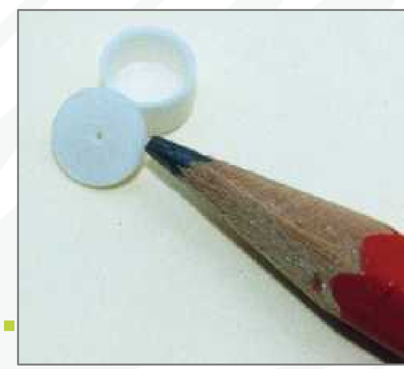
Often different properties may be measured at the same time:

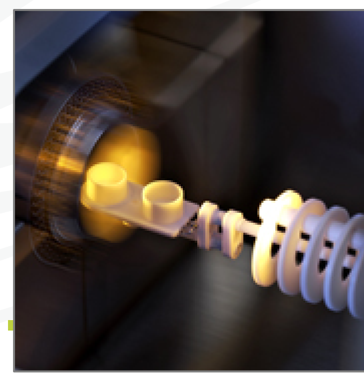
TGA-DTA, TGA-EGA

Instrumentation & origin of the TGA-SDTA signal

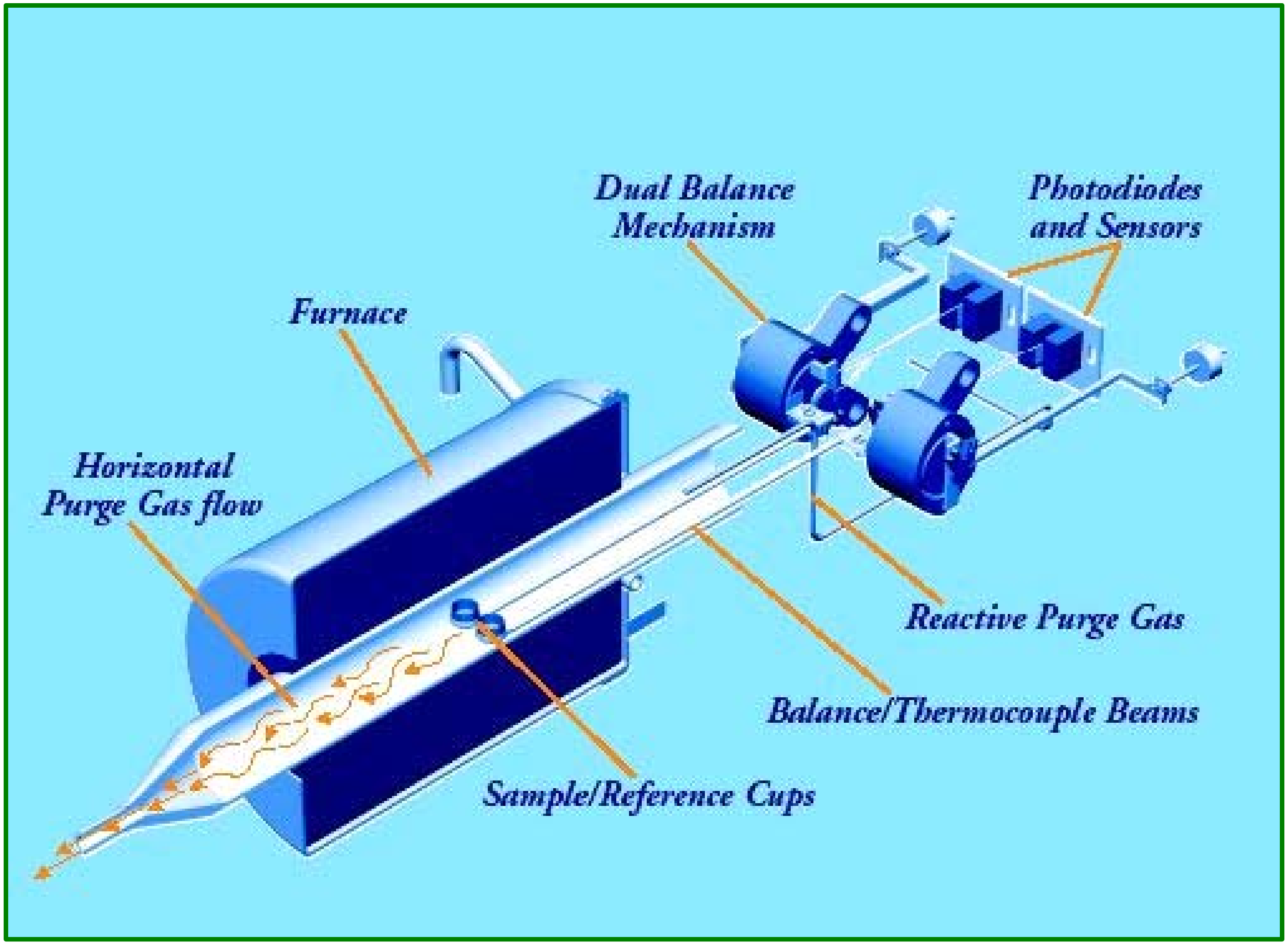
TGA - SDTA

Mettler - Toledo

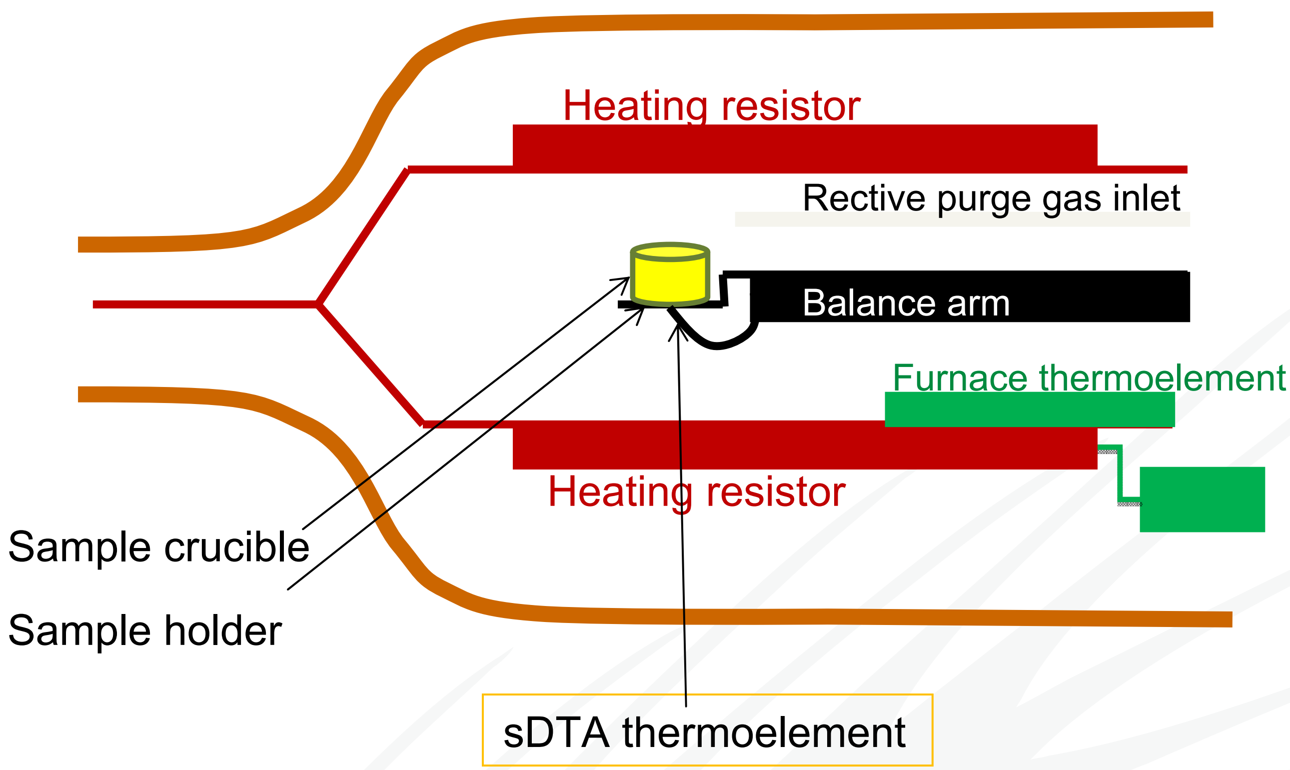




A modern TGA - DTA



Furnace components



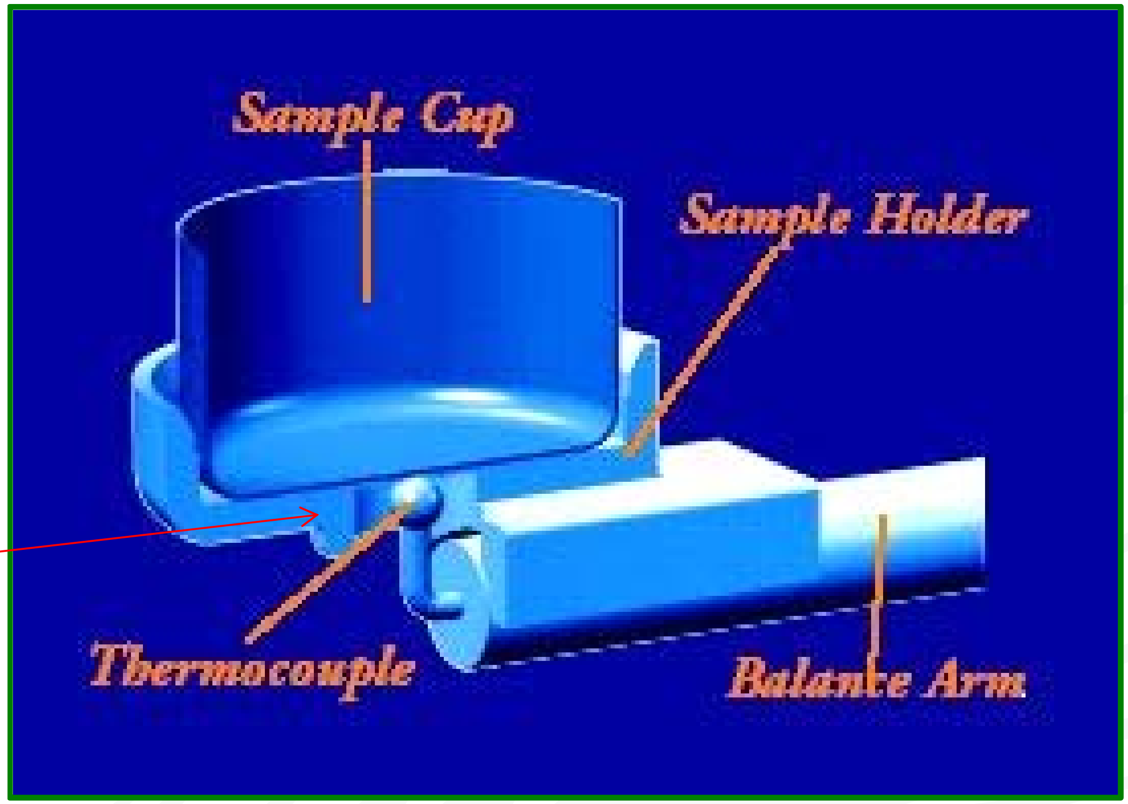
Operating range:
- 200 - 1600 °C

Heating rate:
up to 100 °C/min

Typical heating rate:
10 – 20 °C/min

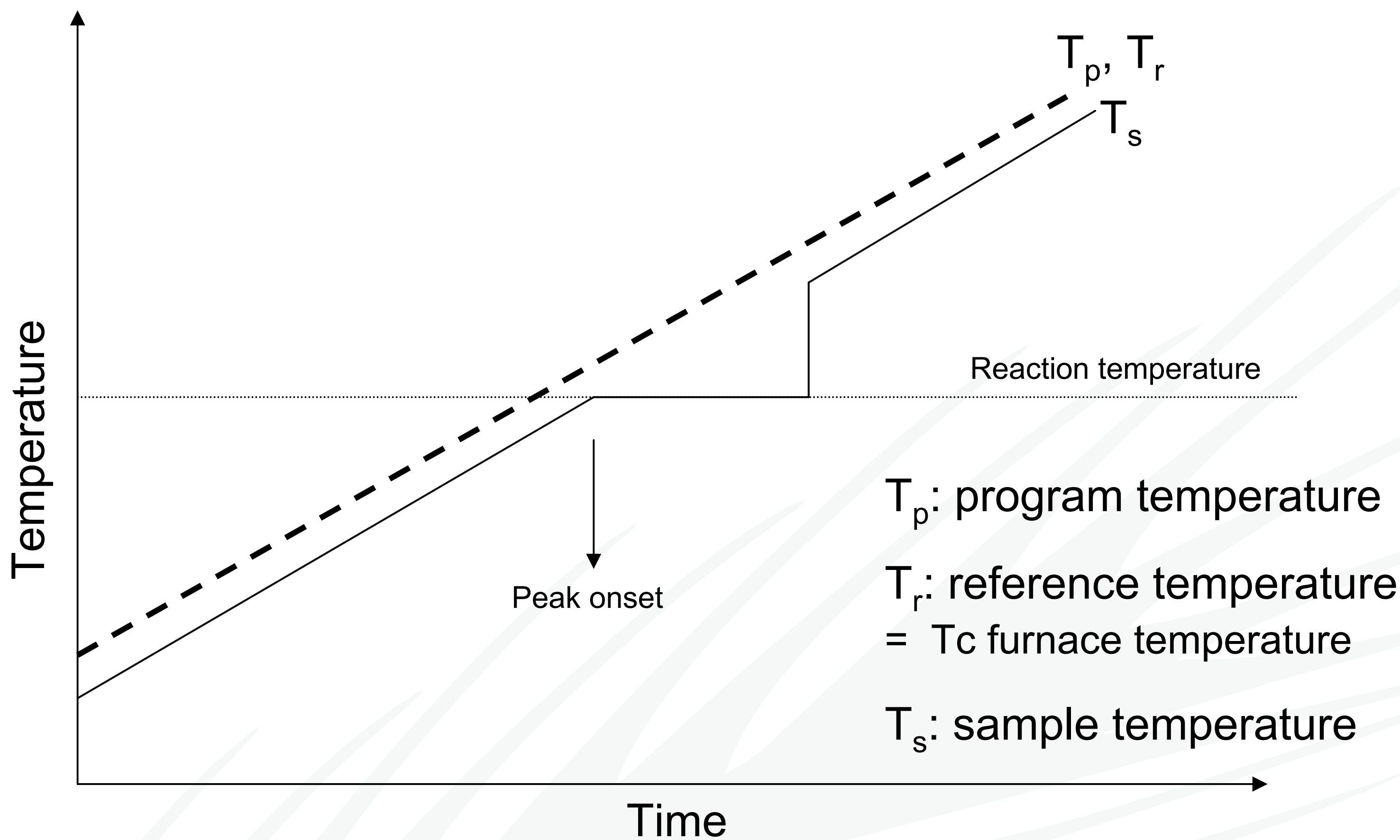
Heat transfer from crucible to recording microbalance & thermo elements

platinum

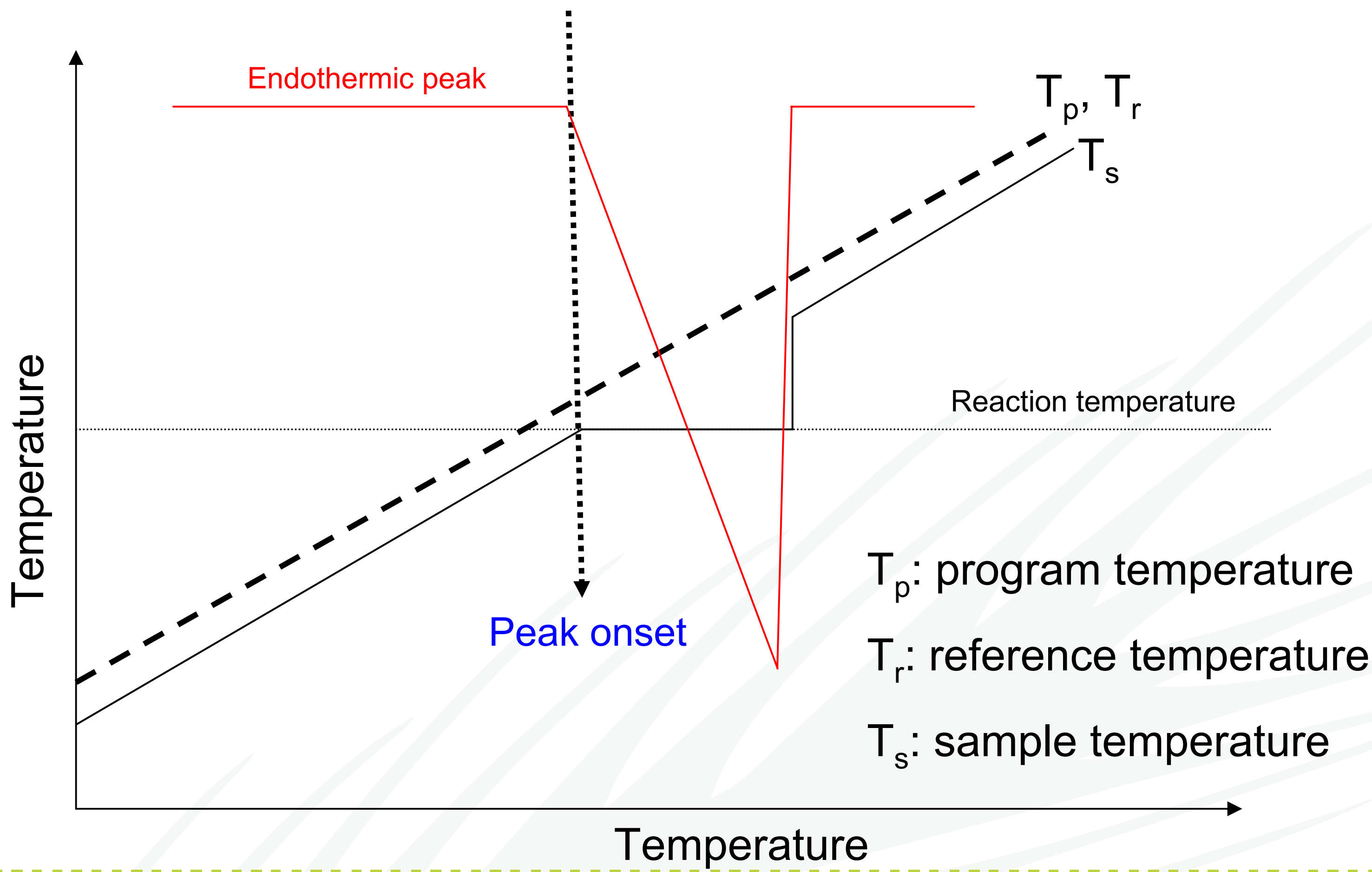


Origin of the TGA-DTA signal

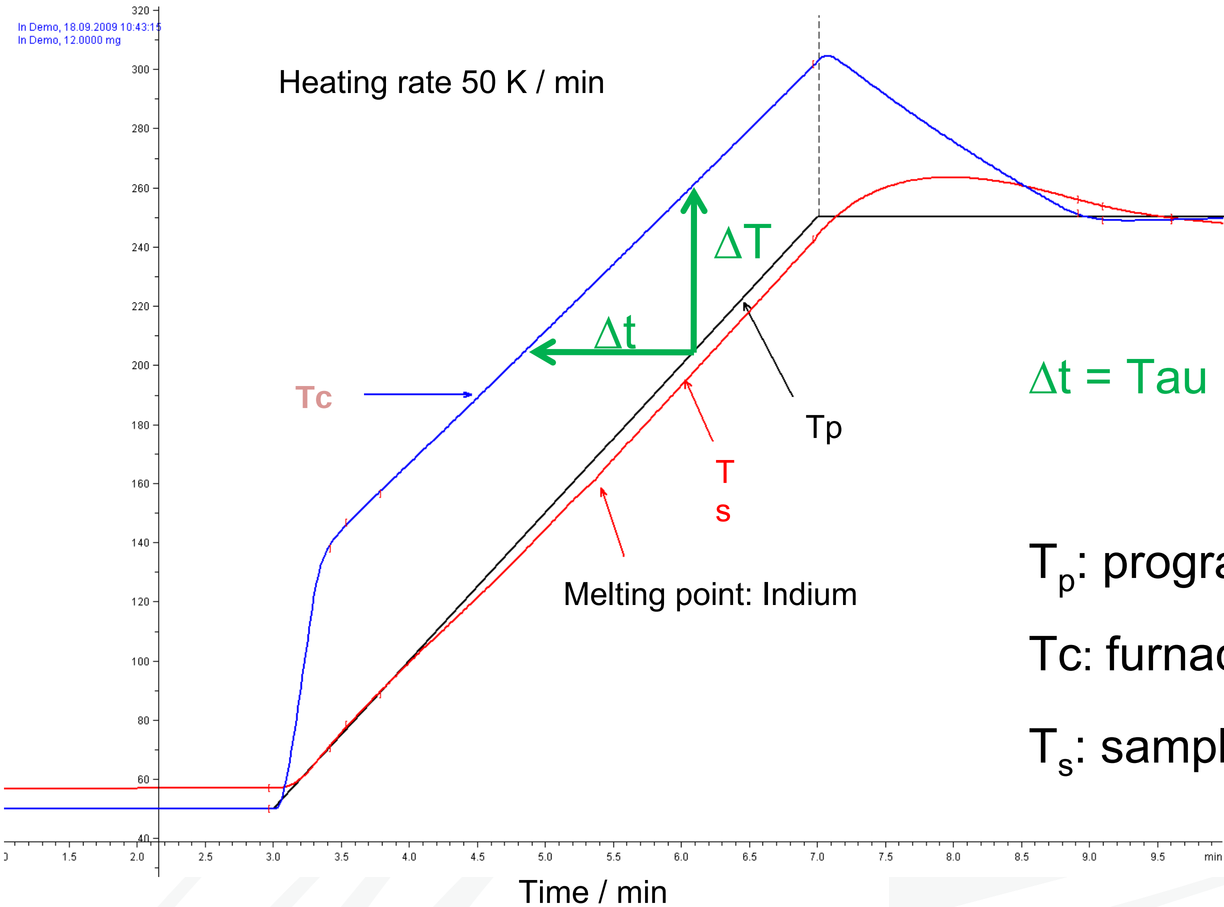
Schematic diagram showing the different temperatures in the DTA during a thermal process.



Origin of the TGA-DTA signal



Origin of the TGA-DTA signal



Δt = Tau lag

T_p: program temperature

Tc: furnace temperature

T_s: sample temperature

TGA

Thermo Gravimetric Analyis

TGA, Basics

Measures changes in weight in relation to changes in temperature.

The measured weight loss curve gives information on:

- changes in sample composition
- thermal stability
- kinetic parameters for chemical reactions in the sample

A *derivative weight loss curve* can be used to tell the point at which weight loss is most apparent

TGA; Phenomena causing mass changes

Physical

Gas adsorption

Gas desorption

Phase transitions

- Vaporization
- Sublimation

Chemical

Decomposition

Break down reactions

Gas reactions

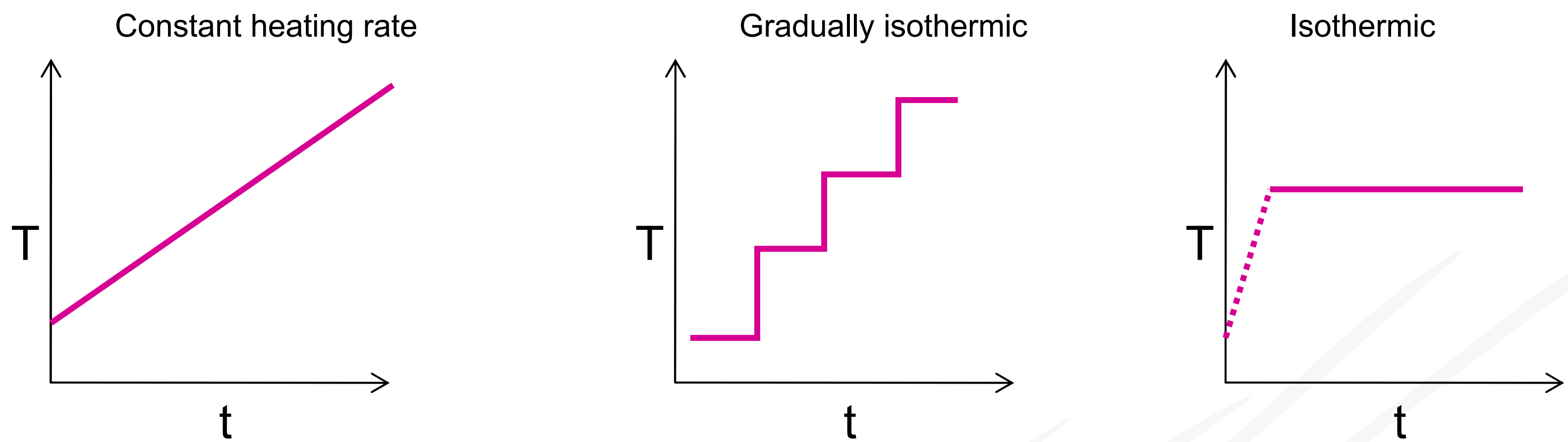
Chemisorption
(adsorption by means of chemical instead of physical forces)

TGA: Applications

- Characterization of
    - Thermal stability
    - Material purity
    - Determination of humidity

- Examination of
    - » Corrosion studies (e.g. oxidation or reactions with reactive gases)
    - » Gasification processes
    - » Kinetic processes

Typical temperature-time programs



Experimental

Sample size: 1 – 100 mg (typically 5 – 20 mg)

Heating / cooling rate: 1 – 50 ºC / min

TGA

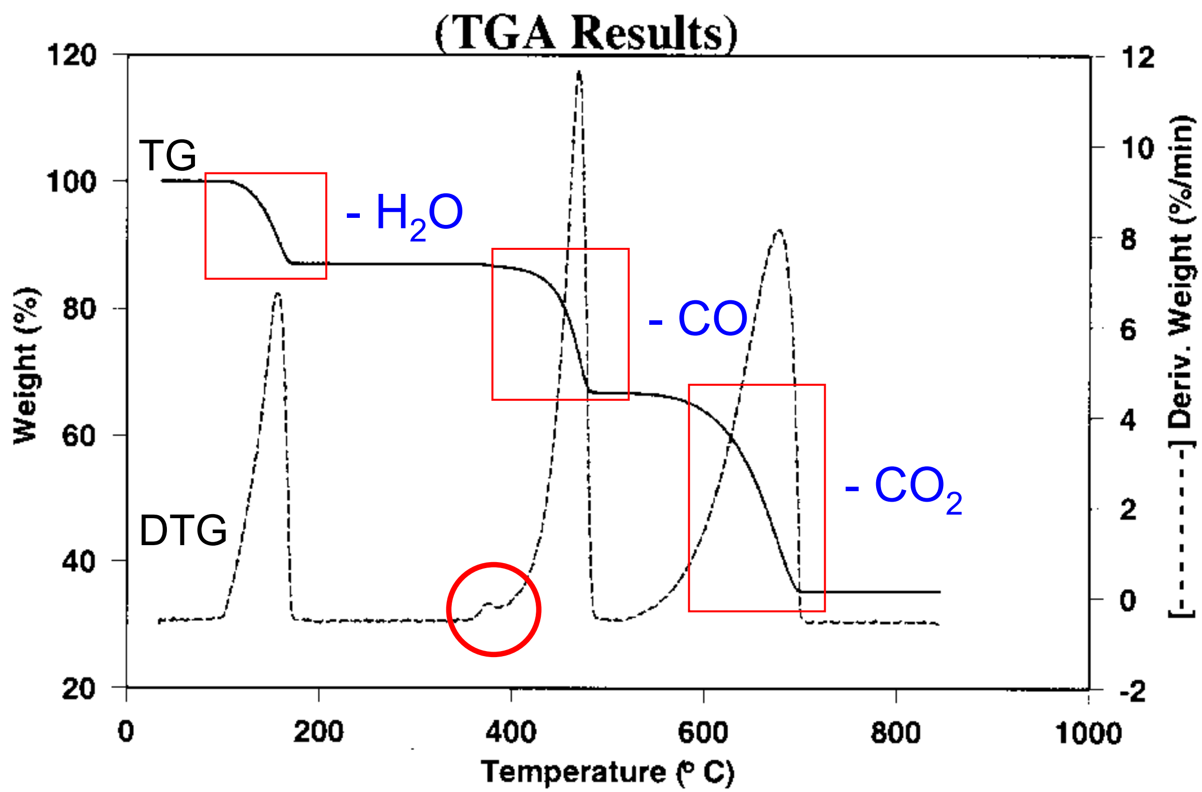
Ex. Decomposition of calcium oxalate monohydrate

- Calcium oxalat monohydrat, a standard material often used to demonstrate TGA performance.
- Exhibits three weight losses with temperature in an inert atmosphere (e.g. N_2).

$$CaC_2O_4 \bullet H_2O \xrightarrow{-H_2O} CaC_2O_4 \xrightarrow{-CO} CaCO_3 \xrightarrow{-CO_2} CaO$$

TGA

Ex. Decomposition of calcium oxalat monohydrate



Absolute confirmation of the decomposition process is possible when the gaseous by products are identified as they evolve, eg. by mass spectrometry (MS).

TGA

Common gaseous components originating from inorganic materials that decompose before the melting point:

H_2O, CO, CO_2, SO_x, NO_x, Cl_2, F_2, CH_3OH, etc.

Also some chemical reactions in solid phase result in gaseous weight loss ex.

$$Na_2CO_3\ (s) + SiO_2\ (s) \rightarrow Na_2SiO_3\ (s) + CO_2\ (g)$$

Factors affecting the TG curve

Heating rate
Sample size

Increases the temperature at which sample decomposition occurs.

Particle size of sample
Packing
Crucible shape
Gas flow rate

Affects the progress of ther reaction

DTA

Differential Thermal Analysis

DTA, Basics

The material under study and an inert reference are made to undergo identical thermal cycles.

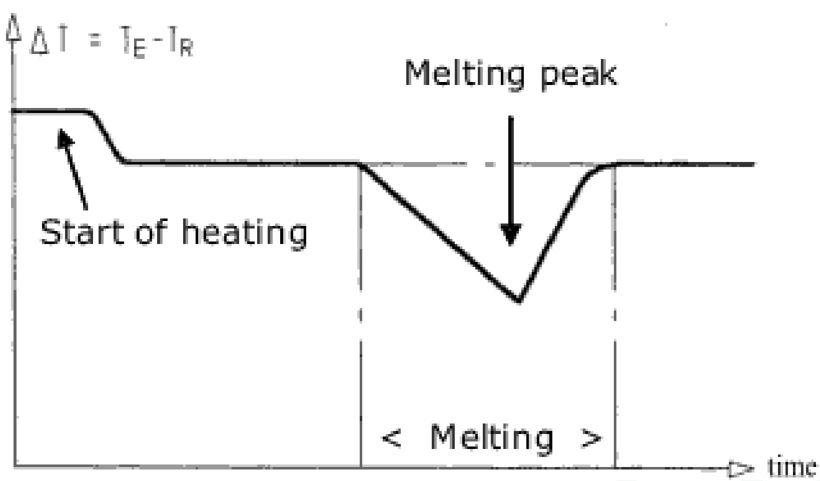
⬇

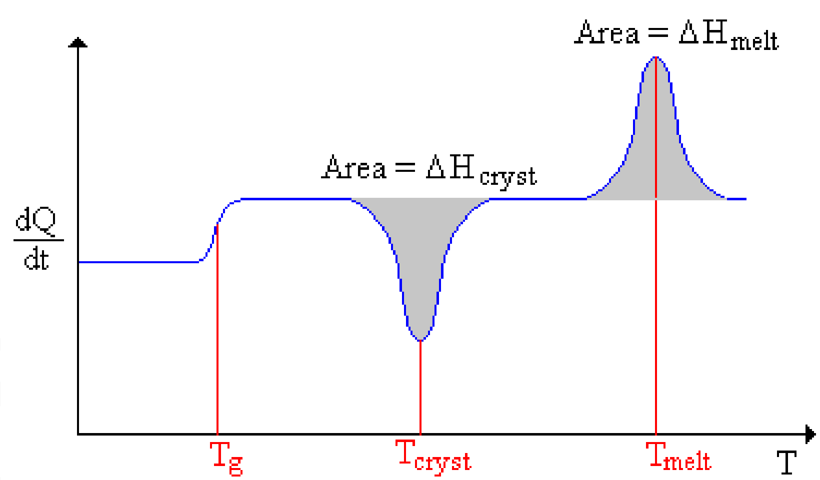
Any temperature difference between sample and reference is recorded.

In this technique the heat flow to the sample and reference remain the same rather than the temperature.

DTA, Basics

➡ The differential temperature is then plotted against time, or against temperature (DTA curve or thermogram).





Crystallization	exothermic	}	Peak orientation ↑↓ in DTA thermogram depends on Instrument manufacturer
Melting	endothermic		

DTA; Phenomena causing changes in heat / temperature

Physical

Adsorption (exothermic)

Desorption (endothermic)

A change in crystal structure (endo – or exothermic)

Crystallization (exothermic)

Melting (endothermic)

Vaporization (endothermic)

Sublimation (endothermic)

Chemical

Oxidation (exothermic)

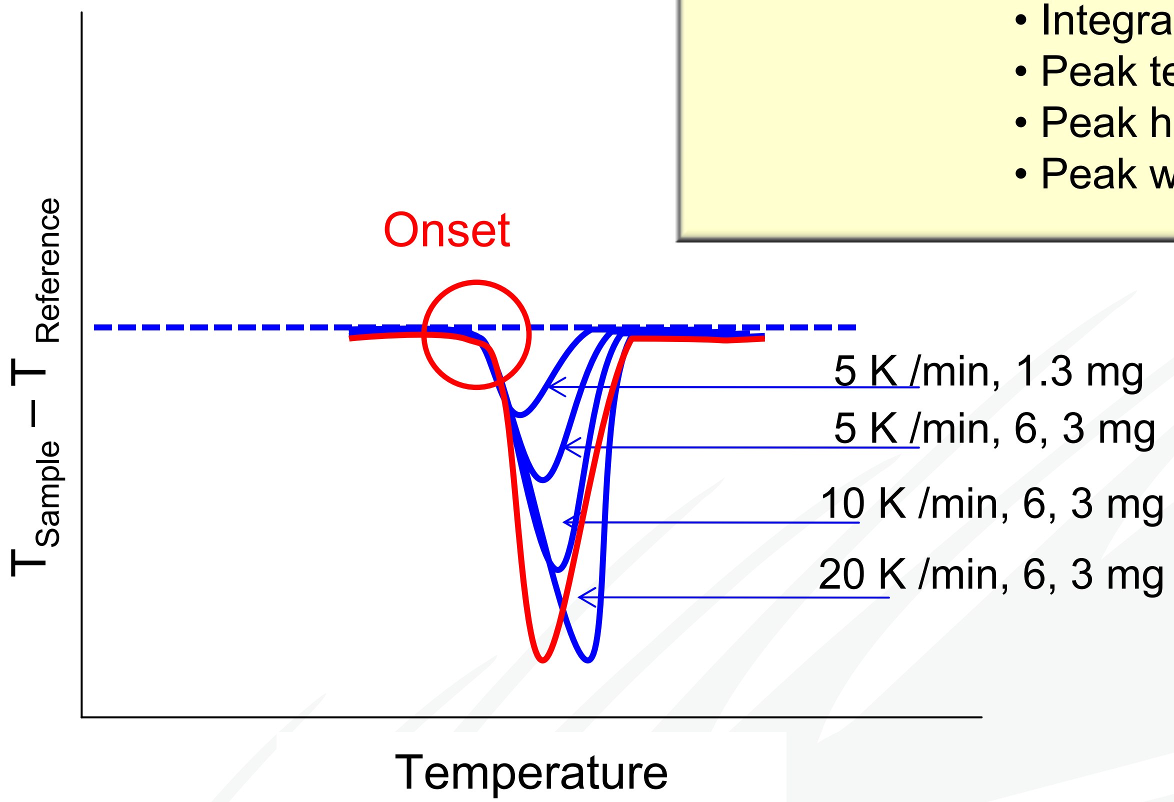
Reduction (endothermic)

Break down reactions (endo – or exothermic)

Chemisorption (exothermic)

Solid state reactions (endo – or exothermic)

Evaluation and interpretation of DTA curves



<u>Typical data obtained from DTA peak evaluation</u>

- Onset - melting
- Endset
- Integral - enthalpy Δh
- Peak temp - melting
- Peak height
- Peak width

Peak temperature is affected by heating rate & sample mass, but not by Δh (enthalpy) and T onset.

TGA- DTA
Keys for successful experimental practice

- Raw materials should be of high purity.
- Fine -grained powder should be used to achieve greater contact area and better equilibrium conditions.
- The time at any temperature must be sufficiently long in order to permit completeness of reactions.

TGA- DTA
Keys for successful experimental practice

Factors affecting the heat transfer, Tau lag & signaling

Crucible	**Sample**	**Atmosphere**
Material	Mass	
Mass	Heat capacity	
Volume	Heat conductivity	
Heat capacity		

Phase diagrams & Thermal analysis

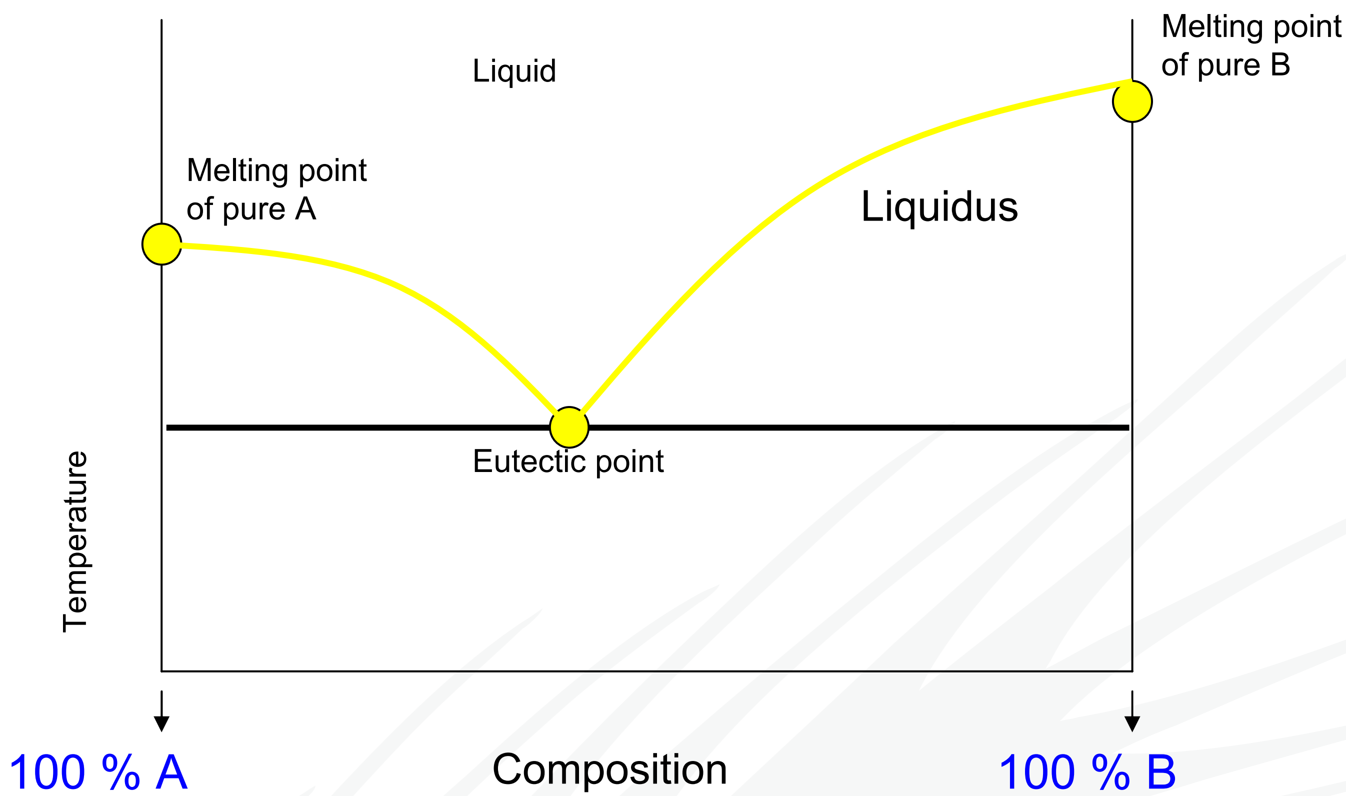
Phase Diagram

- A phase diagram show conditions at which thermodynamically distinct phases can occur at equilibrium.
- It is determined experimentally by recording cooling rates over a range of compositions.
- Phase transitions occur along lines of equilibrium (=phase boundaries).
  - Solidus = Temp. below which the substance is stable in the solid state.
  - Liquidus = Temp. above which the substance is stable in a liquid state.

Experimental methods for determining phase diagrams

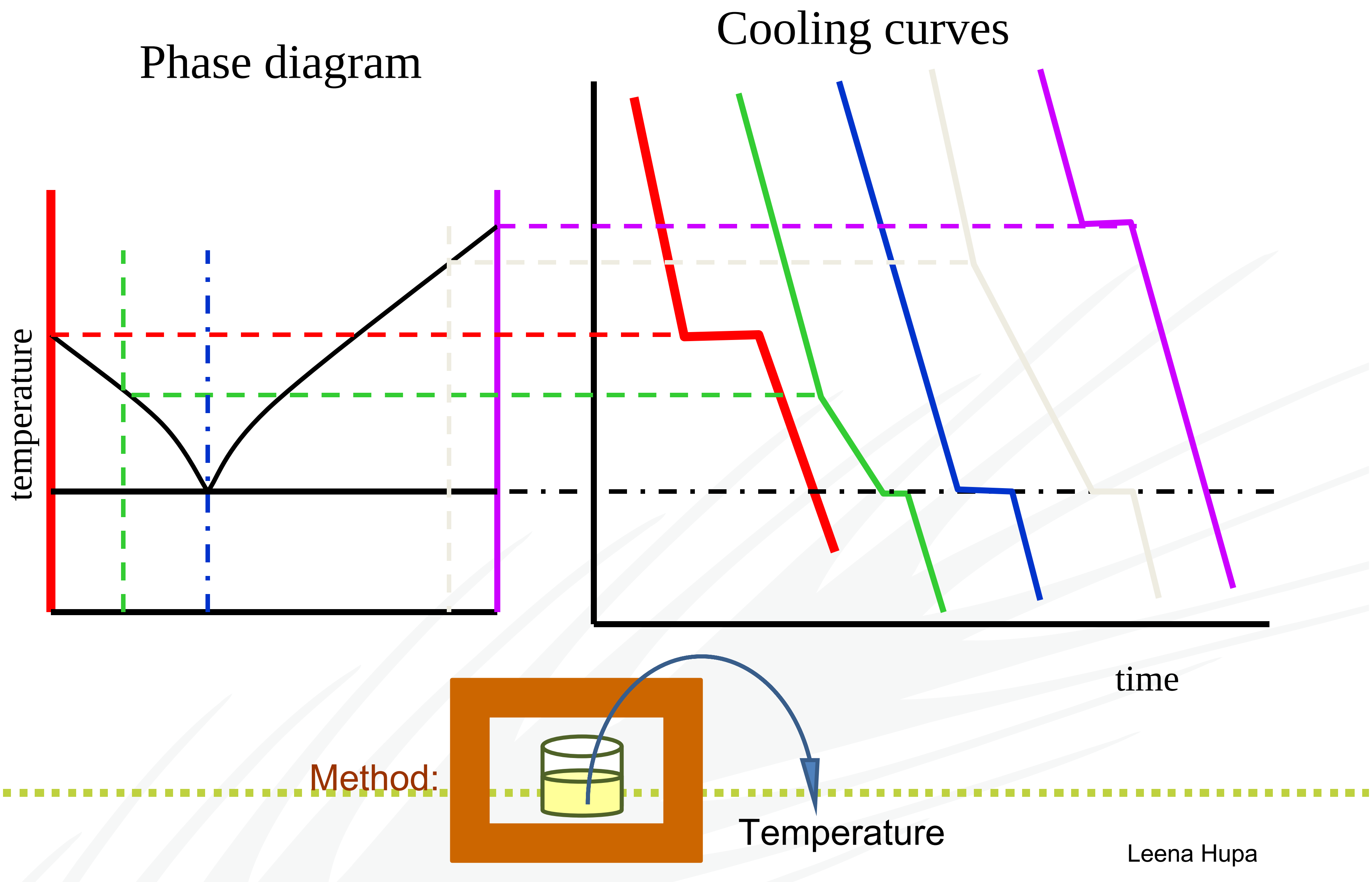
- Thermal analysis
- High temperature microscopy
- High temperature X-ray diffraction
- Measurement of electrical conductivity as function of temperature.
  - Salt mixtures: solid salts have low conductivity, melts have high.

How to build a phase diagram



Constructing phase diagrams by experimental methods:

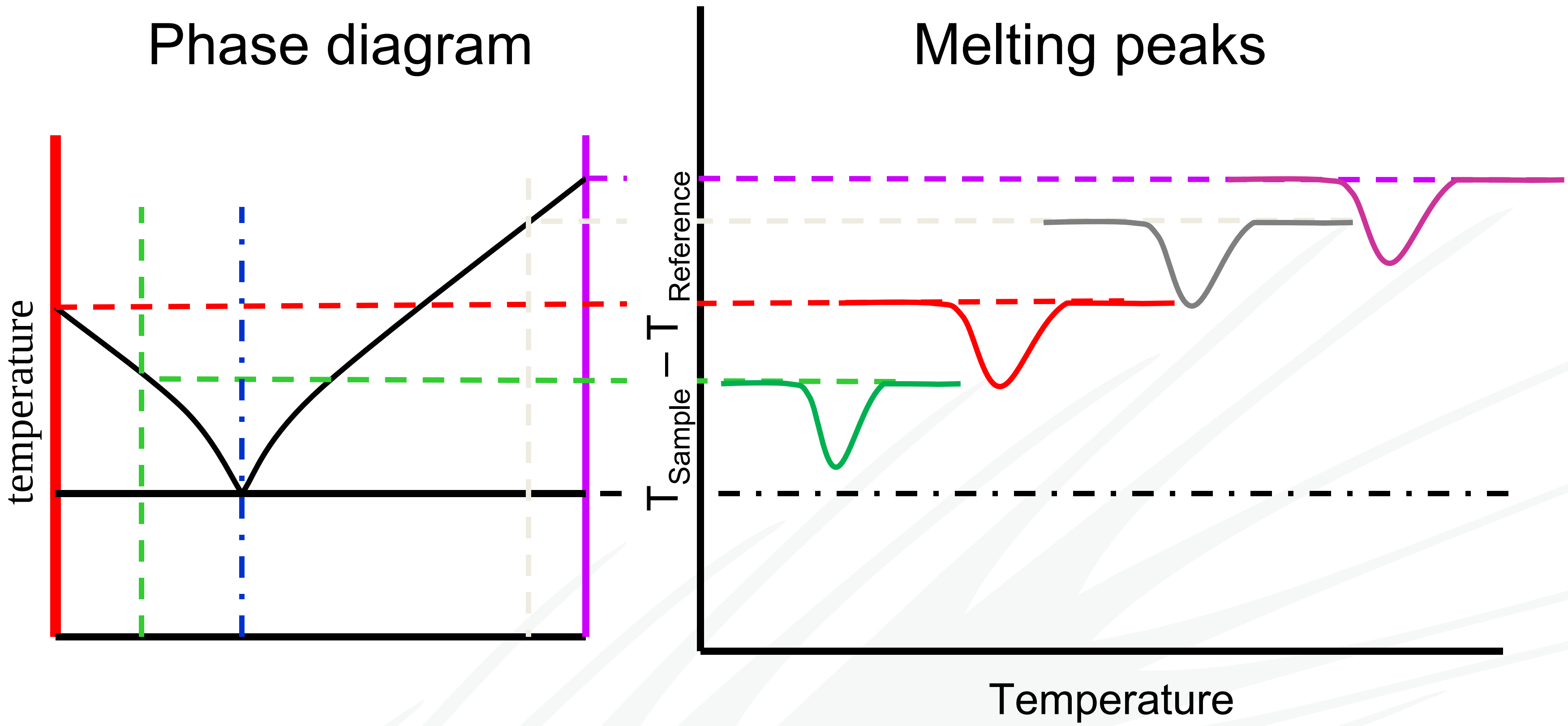
A) from cooling curves



Leena Hupa

Constructing phase diagrams by experimental methods:

B) from DTA curves



Summary

- Thermal analysis gives information about changes in material properties as function of temperature.
- Several different TA methods exist; focus on TGA - DTA
- Combining the two techniques (TGA-DTA) - comprehensive study of a materials thermal behaviour.
  - While TG only measures changes caused by mass loss, DTA also register changes in material where no mass loss occur, e.g. *crystal structure changes, melting, glass transistion*, etc.
- Carefullenes required with performance of the experimental procedure to obtain correct weight loss curves and thermograms (e.g. sample preaparation, choice of crucible, choice of thermal program)
- Origin of TG-DTA signal good to know for better understanding of measured data.