Thermal Analysis
TGA / DTA

Linda Fröberg
Outline

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

- Sample Cup
- Sample Holder
- Thermocouple
- Balance Arm
- Platinum
Origin of the TGA-DTA signal

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

- \( T_p \): program temperature
- \( T_r \): reference temperature
- \( T_s \): sample temperature

\( T_p \): program temperature
\( T_r \): reference temperature
\( T_s \): sample temperature

Peak onset
Refection temperature

Time
Temperature
Origin of the TGA-DTA signal

Temperature

Peak onset

Endothermic peak

Tp, Tr

Ts

Tp: program temperature
Tr: reference temperature
Ts: sample temperature

Reaction temperature
Origin of the TGA-DTA signal

Heating rate 50 K / min

Melting point: Indium

$T_p$: program temperature

$T_c$: furnace temperature

$T_s$: sample temperature

$\Delta t = \text{Tau lag}$
TGA

Thermo Gravimetric Analysis
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

Constant heating rate

Gradually isothermic

Isothermic

Experimental

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

Heating / cooling rate: 1 – 50 °C / 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. N₂).

\[
\begin{align*}
\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O} & \rightarrow \text{CaC}_2\text{O}_4 \\ 
\text{CaC}_2\text{O}_4 & \rightarrow \text{CaCO}_3 \\ 
\text{CaCO}_3 & \rightarrow \text{CaO}
\end{align*}
\]
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).
Common gaseous components originating from inorganic materials that decompose before the melting point:

\[ \text{H}_2\text{O}, \text{CO}, \text{CO}_2, \text{SO}_x, \text{NO}_x, \text{Cl}_2, \text{F}_2, \text{CH}_3\text{OH}, \text{etc.} \]

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

\[ \text{Na}_2\text{CO}_3 (s) + \text{SiO}_2 (s) \rightarrow \text{Na}_2\text{SiO}_3 (s) + \text{CO}_2 (g) \]
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 the 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
Melting endothermic

Peak orientation ↑↓ in DTA thermogram depends on Instrument manufacturer
**DTA**: Phenomena causing changes in heat / temperature

<table>
<thead>
<tr>
<th>Physical</th>
<th>Chemical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption (exothermic)</td>
<td>Oxidation (exothermic)</td>
</tr>
<tr>
<td>Desorption (endothermic)</td>
<td>Reduction (endothermic)</td>
</tr>
<tr>
<td>A change in crystal structure (endo – or exothermic)</td>
<td>Break down reactions (endo – or exothermic)</td>
</tr>
<tr>
<td>Crystallization (exothermic)</td>
<td>Chemisorption (exothermic)</td>
</tr>
<tr>
<td>Melting (endothermic)</td>
<td>Solid state reactions (endo – or exothermic)</td>
</tr>
<tr>
<td>Vaporization (endothermic)</td>
<td></td>
</tr>
<tr>
<td>Sublimation (endothermic)</td>
<td></td>
</tr>
</tbody>
</table>
Evaluation and interpretation of DTA curves

Typical data obtained from DTA peak evaluation

- Onset - melting
- Endset
- Integral - enthalpy $\Delta h$
- Peak temp - melting
- Peak height
- Peak width

Peak temperature is affected by heating rate & sample mass, but not by $\Delta h$ (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

<table>
<thead>
<tr>
<th>Crucible</th>
<th>Sample</th>
<th>Atmosphere</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
<td>Mass</td>
<td>Mass</td>
</tr>
<tr>
<td>Mass</td>
<td>Heat capacity</td>
<td>Heat capacity</td>
</tr>
<tr>
<td>Volume</td>
<td>Heat conductivity</td>
<td>Heat conductivity</td>
</tr>
</tbody>
</table>
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

- Melting point of pure A
- Eutectic point
- Liquidus
- Melting point of pure B

Temperature

100 % A  Composition  100 % B
Constructing phase diagrams by experimental methods:

A) from cooling curves

Method:
Constructing phase diagrams by experimental methods:
B) from DTA curves
Summary

- Thermal analysis gives information about changes in material properties as a function of temperature.

- Several different TA methods exist; focus on TGA - DTA

- Combining the two techniques (TGA-DTA) - comprehensive study of a material's thermal behaviour.

  - While TG only measures changes caused by mass loss, DTA also registers changes in material where no mass loss occur, e.g. crystal structure changes, melting, glass transition, etc.

- Carefulness required with performance of the experimental procedure to obtain correct weight loss curves and thermograms (e.g. sample preparation, choice of crucible, choice of thermal program)

- Origin of TG-DTA signal good to know for better understanding of measured data.