Collected Applications
Thermal Analysis

TUTORIAL KIT

METTLER TOLEDO
Preface

Modern thermal analysis includes a wide range of very sensitive instrumental techniques. These techniques allow the accurate measurement of widely different chemical and physical properties.

The METTLER TOLEDO Thermal Analysis Tutorial Kit includes an application booklet and 14 samples with which you can perform typical experiments. The 22 carefully chosen and well-documented applications cover the main areas of thermal analysis and provide an excellent introduction to this very versatile technique.

The Tutorial Kit is designed to encourage you to experiment with the tutorial samples so that you can discover and become familiar with the possibilities that modern thermal analysis offers. Several samples have been measured and evaluated with different techniques.

We would like to point out that the evaluation results presented here are typical experimental results and should not be treated as scientifically guaranteed data. It is quite possible that some samples undergo slight changes during storage and that the results described here can not be exactly reproduced. We nevertheless hope that this collection of applications will serve as a source of inspiration for your own work.

I would like to thank the Materials Characterization Section of the Marketing Support Group in Schwerzenbach, Switzerland for assistance and Helga Judex for the layout.

Schwerzenbach, August 1998

Dr. Markus Schubnell
## Overview

The METTLER TOLEDO Thermal Analysis Tutorial Kit includes 14 carefully selected samples that enable you to measure many effects that are typically observed in thermal analysis. The following table provides you with an overview of the measurements and evaluations that were performed with these samples for the creation of this collection of applications.

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<td>Aluminum cylinder</td>
<td>Expansion coefficient</td>
<td>TMA</td>
<td>24</td>
</tr>
</tbody>
</table>
1 Melting Behavior of Cocoa Butter

Sample
Cocoa butter

Conditions
Measuring cell: DSC821
Pan: Aluminum standard 40 µl, hermetically sealed
Sample preparation: Press the cocoa butter flakes into the pan with a PTFE rod, 16.971 mg
DSC measurement: Heating from 25 °C to 45 °C at 1 K/min
Atmosphere: Air, stationary environment, no flow

Interpretation
Cocoa butter can consist of different modifications:

<table>
<thead>
<tr>
<th>Modification</th>
<th>Melting range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amorphous</td>
<td>-</td>
</tr>
<tr>
<td>α (metastable)</td>
<td>8 - 15 °C</td>
</tr>
<tr>
<td>β’ (metastable)</td>
<td>15 - 29 °C</td>
</tr>
<tr>
<td>β (stable)</td>
<td>above 29 °C</td>
</tr>
</tbody>
</table>

The relative amounts of the various modifications depend on the thermal history of the sample. The melting temperatures, however, depend on the chemical composition of the glycerides.

Evaluation
The first part of the DSC curve shows the melting of the metastable β’-modification. Then, from about 29 °C onwards, the stable β-modification melts. The percentage amount of cocoa butter melted is shown as a function of temperature in the inserted diagram.
2 Oxidation Stability of Cocoa Butter

Sample Cocoa butter
Conditions Measuring cell: DSC821
Pan: Aluminum standard 40 µl, pierced lid
Sample preparation: Press the cocoa butter flakes into the pan with a PTFE rod
11.546 mg (in an oxygen atmosphere) and 13.665 mg (in an air atmosphere)
DSC measurement: Heating from 100 °C to 250 °C at 10 K/min
Atmospheres: Oxygen 50 cm³/min. Air, no flow

Interpretation
The purpose of this experiment was to investigate the oxidation stability of cocoa butter. The measurements were performed in a stationary air atmosphere and in an atmosphere of oxygen at a flow rate 50 cm³/min. The results show that oxidation in oxygen occurs much more rapidly than in a stationary air atmosphere. In both cases, the temperature of the onset of oxidation was about 190 °C.

Evaluation
<table>
<thead>
<tr>
<th>Atmosphere</th>
<th>Onset temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>oxygen</td>
<td>192 °C</td>
</tr>
<tr>
<td>air</td>
<td>190 °C</td>
</tr>
</tbody>
</table>
3 Determination of the Crystallinity of High Density Polyethylene

**Sample**
High density polyethylene film (PE-HD)

**Conditions**
- Measuring cell: DSC821°
- Pan: Aluminum standard 40 µl, hermetically sealed
- Sample preparation: 2 disks of PE-HD, total weight 2.530 mg
- DSC measurement: Heating from 50 °C to 160 °C at 10 K/min
  - Cooling from 160 °C to 50 °C at 10 K/min
- Atmosphere: Air, stationary environment, no flow

**Interpretation**
The crystalline regions in the PE-HD are destroyed on melting. The amount of heat required for the melting process is proportional to the initial crystallinity. The percentage crystallinity of a sample can therefore be determined by comparing the heat of fusion of the sample with that of a 100% crystalline sample.

**Evaluation**
The heat of fusion for 100% crystalline PE-HD is about 290 J/g. For the tutorial kit sample, values for the crystallinity of 72.2% (heating) and 71.6% (cooling) were obtained from the measured heats of fusion.

The peak temperature of 132 °C on heating is characteristic for PE-HD.
4  Purity of Artificially Contaminated Dimethyl Terephthalate

Sample  Contaminated dimethyl terephthalate (DMT)

Conditions  Measuring cell: DSC821
Pan: Aluminum standard 40 µl, hermetically sealed
Sample Preparation: Several crystals, total weight 4.751 mg
DSC measurement: Heating from 130 °C to 150 °C at 1 K/min
Atmosphere: Air, stationary environment, no flow

^exo  Purity of Dimethyl Terephthalate

Interpretation  The determination of purity is based on the van’t Hoff equation. The STAR® software algorithm not only calculates the purity, but also yields the melting point of the sample as well as the melting temperature at which 10% of the sample has melted. If the melting process is observed visually, this "melting temperature" corresponds to the temperature at which a change in the appearance of the sample can first be seen. The melting point of the pure substance is obtained by extrapolation of the 1/F plot.

Evaluation  Purity  99.4 %
Melting point  140.8 °C
Melting temperature (10% melted)  138.3 °C
Melting point of the pure DMT  141.1 °C
5 Polymorphism of Phenylbutazone

**Sample**
Phenylbutazone

**Conditions**

Measuring cell: DSC821°

Pan: Aluminum standard 40 µl, hermetically sealed

Sample preparation: Phenylbutazone, pressed into the pan with a PTFE rod, total weight 9.006 mg

DSC measurement: Heating from 30 °C to 150 °C, cooling to 30 °C and a second heating run to 150 °C;
All heating and cooling runs at 5 K/min

Atmosphere: Air, stationary environment, no flow

Interpretation
Phenylbutazone can exist in stable and metastable modifications (polymorphism). The stable form melts at about 106 °C (upper curve). On cooling, the melt solidifies to a glassy state. On heating again, the amorphous sample begins to crystallize at about 50 °C to the metastable modification (lower curve, exothermic peak). The metastable form melts at about 93 °C. At the same time, the stable modification crystallizes from the resulting melt (endothermic peak followed by an exothermic peak). The stable modification melts afterwards at about 104 °C. The smaller melting peak area in comparison with that of the first measurement indicates incomplete crystallization.

Evaluation
Heat of fusion of the crystallized stable modification 94 J/g
Heat of crystallization of the metastable modification 67 J/g
Melting temperature of the stable modification (onset) 106 °C
Crystallization temperature of the metastable modification (onset) 49 °C
Melting temperature of the metastable modification (onset) 93 °C
6 Glass Transition of a Printed Circuit Board (DSC Measurement)

**Sample**
Printed circuit board, glass fiber epoxy

**Conditions**
- Measuring cell: DSC821°
- Pan: Aluminum standard 40 µl, pierced lid
- Sample preparation: Disks, 52.964 mg, smooth side facing downwards in the pan (for better thermal conductivity)
- DSC measurement: Heating from 40 °C to 150 °C at 10 K/min
- Atmosphere: Air, stationary environment, no flow

**Interpretation**
If the sample is measured without any thermal pretreatment (first run), the glass transition is masked by relaxation effects. If the same sample is measured again (or measured after thermal pretreatment, e.g. tempering for 1 minute at 130 °C), then the glass transition can be clearly observed (second run). During the glass transition, a sharp increase in the specific heat occurs (see the inserted diagram).

**Evaluation**
- Glass transition temperature (onset) 91 °C
- Glass transition temperature (midpoint) 97 °C
- Change of the specific heat during the glass transition 0.15 J/(g K)
- In comparison: onset with ADSC 91 °C
  - onset with TMA 95 °C
7 Glass Transition of a Printed Circuit Board (ADSC Measurement)

**Probe**
- Printed circuit board, glass fiber epoxy

**Conditions**
- Measuring cell: DSC821
- Pan: Aluminum standard 40 µl, pierced lid
- Sample preparation: Disks, 53.354 mg, smooth side facing downwards in the pan (for better thermal conductivity)
- The sample was preheated with the DSC program (40 °C to 150 °C at 10 K/min) to obtain conditions similar to those of the classical DSC measurement.
- ADSC measurement: Heating from 40 °C to 150 °C at 1 K/min, period 1 min, amplitude 1 °C
- Atmosphere: Air, stationary environment, no flow

**Interpretation**
- The evaluation of an ADSC measurement yields a number of additional results. The measurement of the Total Heat Flow is that which is most comparable with a conventional DSC experiment. The corresponding curve (colored green) shows a glass transition at about 91 °C. The glass transition can also be observed in the curves of the phase angle, the complex heat capacity (c<p> complex) as well as the reversing heat flow (reversing).

**Evaluation**
- Glass transition temperature (onset, reversing heat flow) 91 °C
- In comparison: onset with conventional DSC measurement 91 °C
- onset with TMA 95 °C
8 Glass Transition of a Printed Circuit Board  
(TMA Measurement)

**Sample**
Printed circuit board, glass fiber epoxy, thickness 1.519 mm

**Conditions**
- Measuring cell: TMA/SDTA840
- Probe: 3 mm ball-point probe
- Load: 0.1 N
- Sample preparation: Smooth the surface with a fine abrasive paper; place a quartz glass disk between the sample and the probe.
- TMA measurement: Heating from 30 °C to 250 °C at 10 K/min
- Atmosphere: Air, stationary environment, no flow

**Interpretation**
The glass transition can also be determined in a TMA experiment. The glass transition is observed as a marked change in the expansion coefficient (second run). The result of the measurement yields a glass transition temperature of 95 °C (onset).

If the sample is measured without any thermal pretreatment (first run), the glass transition is masked by relaxation effects.

**Evaluation**
- Glass transition temperature (onset) 95 °C
- In comparison: onset with DSC 91 °C
- Onset with ADSC 91 °C
9 Melting Behavior and Phase Transition of Azoxydianisole

**Sample** 4,4-Azoxydianisole

**Conditions**
- Measuring cell: DSC821
- Pan: Aluminum standard 40 µl, hermetically sealed
- Sample preparation: Several crystals, total weight 5.834 mg
- DSC measurement: Heating from 100 °C to 150 °C at 5 K/min
- Atmosphere: Air, stationary environment, no flow

Interpretation
When a solid melts, its crystal lattice structure is destroyed and a liquid is formed. There is then only a relatively weak interaction between neighboring molecules. In contrast to the isotropic properties of normal liquids, liquid crystals also exhibit a certain degree of spatial orientation even in the liquid state. Depending on the liquid crystal, one can distinguish between a smectic (2 dimensional orientation) and a nematic (1 dimensional orientation) phase. 4,4-azoxydianisole is a substance that exists in the form of a nematic liquid crystal after melting. The liquid crystal properties are however lost above 132 °C.

Evaluation
- Heat of fusion of azoxydianisole 110 J/g
- Melting point (onset) 117 °C
- Isotropic liquid a temperature of 132 °C
- Heat of transition nematic-isotropic 2.8 J/g
10 Thermal Behavior of Polyethylene Terephthalate

**Sample**
Polyethylene terephthalate (PET)

**Conditions**
- Measuring cell: DSC821°
- Pan: Aluminum standard 40 µl, lid pierced with several holes
- Sample preparation: PET disks, smooth side facing downwards in the pan (for better thermal conductivity) 10.190 mg (in nitrogen)
- DSC measurement: Heating from 30 °C to 300 °C at 8 K/min
- Atmosphere: Nitrogen, 50 cm³/min

**Interpretation**
PET exhibits a glass transition accompanied by noticeable thermal relaxation. The sample then crystallizes (exothermic peak) and finally melts at about 230 °C. The slight slope of the baseline is caused by a gradual increase in the specific heat.

**Evaluation**

<table>
<thead>
<tr>
<th>Effect</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass transition temperature (onset)</td>
<td>74.2 °C</td>
</tr>
<tr>
<td>Crystallization temperature (onset)</td>
<td>132 °C</td>
</tr>
<tr>
<td>Melting &quot;point&quot; (peak)</td>
<td>254 °C</td>
</tr>
<tr>
<td>Heat of crystallization</td>
<td>27.8 J/g</td>
</tr>
<tr>
<td>Heat of fusion</td>
<td>44 J/g</td>
</tr>
<tr>
<td>Δc_p Glass transition</td>
<td>0.30 J/(g K)</td>
</tr>
</tbody>
</table>
11 Elastic Behavior of Polyethylene Terephthalate

**Sample**
Polyethylene terephthalate (PET) disks, 0.4407 mm thick

**Conditions**
Measuring cell: TMA/SDTA840
Probe: 1 mm² flat end probe
Load: 0.01 N / 0.1 N, period 12 s
TMA measurement: Heating from 30 °C to 200 °C at 10 K/min
Atmosphere: Air, stationary environment, no flow

**Elastic Properties of PET**

**Interpretation**
At the glass transition the flat probe penetrates more and more into the material and the sample reacts flexibly to the periodic change of load. The amplitude maximum occurs at about 96 °C. Crystallization of the material initiates the start of the curing process ("physical curing"), which leads to a noticeable decrease in the amplitude. The crystallization process is completed by about 130 °C and the sample is again hard. The contraction of the sample as a result of the glass transition is only 6.3 µm. The curing of the sample leads to an appreciably larger contraction.

**Evaluation**
Glass transition (onset) 76.3 °C
In comparison: onset from DSC (see page 12) 74.1 °C
Contraction at the glass transition 6.3 µm
Contraction as a result of curing 89.3 µm
12 Curing of an Epoxy Powder

Sample
- Epoxy powder

Conditions
- Measuring cell: DSC821
- Pan: Aluminum standard 40 µl, pierced lid
- Sample preparation: Fine powder, 10.268 mg
- DSC measurement: Heating from 30 °C to 300 °C at 10 K/min
- Atmosphere: Air, stationary environment, no flow

Interpretation
The epoxy powder liquefies at about 65 °C (glass transition with marked thermal relaxation). The curing of the resin occurs above about 160 °C. The very small exothermic peak that is hardly noticeable in the curing peak is caused by the melting of dicyandiamide (a constituent of the accelerator). After curing, the epoxy resin is a glassy mass; correspondingly a glass transition at 104 °C (onset) can be observed in the second heating run. In this case also, a weak thermal relaxation effect is visible.

Evaluation
- Glass transition 65 °C
- Thermal relaxation 8.4 J/g
- Curing begins at 160 °C
- Heat of curing 49.4 J/g
- Glass transition (onset) of the cured resin 104 °C
- $c_p$ change during the glass transition 0.23 J/(g K)
### 13 Kinetics of Curing of an Epoxy Powder

**Sample**  
Epoxy powder

**Conditions**

<table>
<thead>
<tr>
<th>Measuring cell:</th>
<th>DSC821°</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pan:</td>
<td>Aluminum standard 40 µl, pierced lid</td>
</tr>
<tr>
<td>Sample preparation:</td>
<td>Fine powder, various sample weights</td>
</tr>
<tr>
<td>DSC measurement:</td>
<td>Heating from 30 °C to 300 °C at heating rates of 2, 5 and 10 K/min</td>
</tr>
<tr>
<td>Atmosphere:</td>
<td>Air, stationary environment, no flow</td>
</tr>
</tbody>
</table>

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#### Interpretation

In order to determine the kinetics of a chemical reaction several preliminary experiments are run at different heating rates. The activation energy can then be determined on the basis of the conversion curves using the model free kinetics program.

The kinetic parameters determined in this way can be checked with an isothermal experiment. To do this, the sample at room temperature is put into the DSC821° module that has already been heated up to the desired isothermal temperature. The conversion curve is calculated from the measurement curve and is then compared with the results of the experiment with model free kinetics.

---

#### Evaluation

The conversion curve of the sample of epoxy powder run isothermally at 185 °C agrees quite well with the results obtained from model free kinetics. It is now possible to estimate the time needed to cure the epoxy powder at 190 °C. The table shows that the curing time has been reduced by roughly 4 minutes (for 95% curing).
14 Specific Heat Capacity \((c_p)\) of Corundum

**Sample**
Corundum (aluminum oxide powder, alumina)

**Conditions**
Measuring cell: DSC821
Pan: Aluminum standard 40 µl, pierced lid
Sample preparation: Aluminum oxide powder, 33.13 mg; the powder was heated at 120 °C for 1 minute before weighing, in order to remove any moisture
DSC measurement: Isothermal for 2 min at 40 °C
Heating from 40 °C to 150 °C at 10 K/min
Blank curve corrected
Atmosphere: Air, stationary atmosphere, no flow

\[^\text{exo}\] Specific Heat of Alumina

**Interpretation**
The \text{STAR}\textsuperscript{e} software offers two different procedures for performing \(c_p\) measurements: a direct method and the so called sapphire method. The direct method determines \(c_p\) from the blank curve corrected DSC signal. In contrast, the sapphire method determines \(c_p\) by making a direct comparison with the heat capacity of sapphire.

<table>
<thead>
<tr>
<th>Evaluation</th>
<th>Temperature</th>
<th>(c_p) Sapphire</th>
<th>(c_p) Direct</th>
<th>(c_p) Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>60 °C</td>
<td>842 mJ/(g K)</td>
<td>853 mJ/(g K)</td>
<td>844 mJ/(g K)</td>
</tr>
<tr>
<td></td>
<td>80 °C</td>
<td>876 mJ/(g K)</td>
<td>877 mJ/(g K)</td>
<td>877 mJ/(g K)</td>
</tr>
<tr>
<td></td>
<td>100 °C</td>
<td>908 mJ/(g K)</td>
<td>908 mJ/(g K)</td>
<td>907 mJ/(g K)</td>
</tr>
<tr>
<td></td>
<td>120 °C</td>
<td>935 mJ/(g K)</td>
<td>942 mJ/(g K)</td>
<td>934 mJ/(g K)</td>
</tr>
<tr>
<td></td>
<td>140 °C</td>
<td>961 mJ/(g K)</td>
<td>974 mJ/(g K)</td>
<td>959 mJ/(g K)</td>
</tr>
</tbody>
</table>
## 15 Phase Transition of Quartz Sand (DSC Measurement)

### Sample

- Quartz sand

### Conditions

- Measuring cell: DSC821
- Pan: Aluminum standard, 40 µl, pierced lid
- Sample preparation: Quartz sand, 16.435 mg
- DSC measurement: Heating from 400 °C to 640 °C at 10 K/min
- Atmosphere: Air, stationary environment, no flow

### Interpretation

α-quartz or crystalline silicon dioxide is a widely occurring mineral. The α-modification, which is stable at room temperature, changes to β-quartz at 575 °C (solid-solid phase transition). The transition enthalpy is 7.5 J/g. The phase change is also accompanied by a change in specific heat.

### Evaluation

- Phase transition (onset) 574.0 °C
- Enthalpy 7.51 J/g
- $c_p$ change as a result of the phase change 0.17 J/(g K)
16 Phase Transition of Quartz Sand (TMA Measurement)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Quartz sand, single grain, 40 µg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conditions</td>
<td>Measuring cell: TMA/SDTA840</td>
</tr>
<tr>
<td></td>
<td>Probe: 3 mm ball-point probe</td>
</tr>
<tr>
<td></td>
<td>Load: 0.3 N</td>
</tr>
<tr>
<td></td>
<td>TMA measurement: Heating from 400 °C to 650 °C at 10 K/min</td>
</tr>
<tr>
<td></td>
<td>Blank curve corrected</td>
</tr>
<tr>
<td></td>
<td>Atmosphere: Air, stationary environment, no flow</td>
</tr>
</tbody>
</table>

**Interpretation**

α-quartz or crystalline silicon dioxide is a widely occurring mineral. The α-modification, which is stable at room temperature, changes to β-quartz at 575 °C (solid-solid phase transition). This phase change leads to a very marked expansion. The expansion coefficient of the β-modification is slightly negative, i.e. the quartz sand grain gradually contracts.

**Evaluation**

Phase transition (onset) 570 °C
Expansion of the grain of quartz sand at the phase transition 490 nm
17 Dehydration of Copper Sulfate Pentahydrate

Sample
Copper sulfate pentahydrate (CuSO₄ • 5 H₂O)

Conditions
Measuring cell: DSC821
Pan: Aluminum standard 40 µl, pierced lid
Sample preparation: Copper sulfate, finely ground, 12.424 mg
Copper sulfate crystals, 11.184 mg,
DSC measurement: Heating from 40 °C to 300 °C at 10 K/min
Atmosphere: Nitrogen, 50 cm³/min

Interpretation
When copper sulfate pentahydrate is heated, it loses its water of crystallization. This dehydration process occurs in three steps at different temperatures according to the following equations:

CuSO₄ • 5 H₂O ⇔ CuSO₄ + 2 H₂O (I)
CuSO₄ • 3 H₂O ⇔ CuSO₄ + 2 H₂O (II)
CuSO₄ • H₂O ⇔ CuSO₄ + 1 H₂O (III)

If the copper sulfate crystals are ground, the first two dehydration steps can be clearly separated. The same degree of separation cannot be obtained at this heating rate with crystals that have not been ground.

Evaluation
The average energy of the bond between the water of crystallization and the CuSO₄ can be estimated from the enthalpy values. If the temperature independent values of 4.186 J/(g K) and 2253 J/g are assumed for the specific heat and the heat of evaporation of water respectively, then a value of 224 J/(g water of crystallization) is obtained for the average bond energy of the water of crystallization.
18 Thermal Decomposition of Copper Sulfate Pentahydrate

Sample  
Copper sulfate pentahydrate, (CuSO₄ • 5 H₂O)

Conditions  
Measuring cell: TGA/SDTA850  
Pan: Alumina 70 µl, open  
Sample preparation: Finely ground, 31.5 mg  
TGA measurement: Heating from 25 °C to 1000 °C at 10 K/min, blank corrected  
Atmosphere: Nitrogen, 50 cm³/min

Thermal Decomposition of Copper Sulfate Pentahydrate

Interpretation  
As previously described (see page 19), hydrated copper sulfate loses its water of crystallization in several steps. The resulting anhydrous copper sulfate then decomposes in 3 further reaction steps:

\[
2 \text{CuSO}_4 \Leftrightarrow \text{Cu}_2(\text{SO}_4)_2 \text{O} + \text{SO}_3 \quad (I)
\]

\[
\text{Cu}_2(\text{SO}_4)_2 \text{O} \Leftrightarrow \text{CuO} + \text{SO}_3 \quad (II)
\]

\[
2 \text{CuO} \Leftrightarrow \text{Cu}_2 \text{O} + \text{O}_2 \quad (III)
\]

Evaluation  
<table>
<thead>
<tr>
<th>Reaction step</th>
<th>Δm stoichiometric</th>
<th>Δm measured</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dehydration (total)</td>
<td>36.1 %</td>
<td>35.8 %</td>
</tr>
<tr>
<td>Reaction I+II</td>
<td>32.1 %</td>
<td>32.1 %</td>
</tr>
<tr>
<td>Reaction III</td>
<td>3.2 %</td>
<td>3.2 %</td>
</tr>
</tbody>
</table>
19 Dehydration of Copper Sulfate Pentahydrate (TGA)

Sample
Copper sulfate pentahydrate, (CuSO₄ • 5 H₂O)

Conditions
Measuring cell: TGA/SDTA850
Pan: Alumina 70 µl, open
Sample preparation: Finely ground crystals, 33.025 mg
TGA measurement: Heating from 25 °C to 1000 °C with MaxRes
Atmosphere: Nitrogen, 50 cm³/min

Dehydration of Copper Sulfate Pentahydrate

Interpretation
Without the use of MaxRes, the first two dehydration steps can not be clearly separated (see previous page). The MaxRes option automatically adjusts the heating rate to the rate of change of the sample weight; a rapid weight loss leads to a reduction of the heating rate, a very gradual weight loss to an increase of the heating rate. The TG curve shows that with MaxRes the first two dehydration steps are clearly separated. No blank curve correction can of course be made with MaxRes because of the variable heating rate. In addition, the experiment usually lasts appreciably longer than a “conventional” TG experiment at a typical heating rate of 10 K/min.

Evaluation
Copper sulfate pentahydrate loses 2 molecules of water in each of the first two dehydration steps. This leads to a weight loss of 14.4% for each step. The measured weight losses were 14.3% and 14.2% without MaxRes and 14.4% and 14.0% with MaxRes.
20 Thermal Decomposition of Calcium Oxalate Monohydrate

Sample
Calcium oxalate monohydrate, CaC₂O₄ • H₂O

Conditions
Measuring cell: TGA/SDTA850
Pan: Alumina 70 µl, open
Sample preparation: CaC₂O₄ • H₂O powder, 19.45 mg
TGA measurement: Heating from 30 °C to 1000 °C at 15 K/min
Blank curve corrected
Atmosphere: Nitrogen, 20 cm³/min

Interpretation
Above about 120 °C, CaC₂O₄ • H₂O loses its water of crystallization. The anhydrous oxalate then decomposes in 2 reaction steps:

\[ \text{CaC}_2\text{O}_4 \quad \Rightarrow \quad \text{CaCO}_3 + \text{CO} \quad (I) \]

\[ \text{CaCO}_3 \quad \Leftrightarrow \quad \text{CaO} + \text{CO}_2 \quad (II) \]

The onset temperatures of the individual reaction steps can be determined from the TGA signal (not evaluated in this example), the first derivative of the TG signals (DTG curve) or the SDTA signal.

Evaluation

<table>
<thead>
<tr>
<th>Reaction step</th>
<th>( \Delta m ) (stoichiometry)</th>
<th>( \Delta m ) (measured)</th>
<th>Onset (SDTA/DTG)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dehydration</td>
<td>-12.3%</td>
<td>-12.7%</td>
<td>144 / 144 °C</td>
</tr>
<tr>
<td>Reaction (I)</td>
<td>-19.18%</td>
<td>-19.2%</td>
<td>484 / 481 °C</td>
</tr>
<tr>
<td>Reaction (II)</td>
<td>-30.14%</td>
<td>-30.9%</td>
<td>715 / 713 °C</td>
</tr>
</tbody>
</table>
21 Thermomechanical Behavior of Enameled Copper Wire

Sample
Insulated copper wire, 7 mm long, diameter 0.317 mm

Conditions
Measuring cell: TMA/SDTA840
Probe: 3 mm ball-point probe
Load: 0.1 N
TMA measurement: Heating from 30 °C to 360 °C at 20 K/min
Atmosphere: Oxygen, 20 cm³/min

Stability of Enamel on Copper Wire

Interpretation
The coating of the copper wire softens at about 85 °C (glass transition). It begins to decompose at about 200 °C. The thickness of the coating is 21 µm (half of the total step). The diagram also shows the degree of decomposition of the sample as a function of temperature. Decomposition is complete by about 310 °C.

Evaluation
Glass transition temperature (onset) 86 °C
Decomposition of the coating begins at (from conversion) ≈200 °C
Original thickness of the coating 21 µm
22 Expansion Coefficient of Aluminum

Sample
Aluminum cylinder, 4.652 mm long

Conditions
Measuring cell: TMA/SDTA840
Probe: 3 mm ball-point probe
Load: 0.1 N
TMA measurement: Heating from 30 °C to 200 °C at 10 K/min
Blank curve corrected
Atmosphere: Air, stationary environment, no flow
**Interpretation**

The expansion coefficient $\alpha$ is defined as the relative change in length of a sample when its temperature is increased:

$$\alpha = \frac{dL}{dT} \frac{1}{L_0}$$

Often, the so-called average expansion coefficient,

$$\alpha_{\text{mean}} = \frac{\Delta L}{\Delta T} \frac{1}{L_0},$$

is used, where $\Delta L$ refers to the length $L_0$ at room temperature, and $\Delta T$ to the temperature difference between the sample temperature and room temperature. In general, the coefficient of linear expansion is dependent on the direction of measurement.

**Evaluation**

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>Expansion coefficient [ppm/K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>23.4</td>
</tr>
<tr>
<td>120</td>
<td>25.6</td>
</tr>
<tr>
<td>180</td>
<td>26.1</td>
</tr>
</tbody>
</table>