**Thermal Analysis: Dynamic Methods**

“Measurement of a physical property of a substance as a function of temperature, using a controlled temperature program”

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Measurements at Elevated Temperatures

Different possible routes:

- Equilibration at elevated temperature followed by quenching and investigation at room temperature
  ⇒ Determination of properties that are preserved during quenching: crystal structure, phase composition, microstructure etc.

- In situ investigation at high temperatures
  ⇒ Determination of physical properties like electric, thermoelectric, magnetic, mechanical or thermochemical properties etc. than can not be quenched

- Dynamic measurement: following a property while the sample is subject to a temperature program
  ⇒ Determination of reactions occurring during heating and cooling, by following the change of selected physical properties with the temperature.
**DTA - Differential Thermal Analysis**

Historically developed from the simple evaluation of cooling curves:

- Massive Samples
- Slow experiment
- No control of parameters (free cooling)

Exothermic effect (e.g. crystallization)

**DTA: Difference Measurement**

- Temperature program for furnace
- Measurement of $\Delta T = T_R - T_S$
  
  $\Rightarrow$

- Small samples
- Fast experiment
- Controlled temperature program

Diagram:
- Sample
- Reference
- Furnace ($T_F$)
- $T_S$
- $T_R$
Thermal Reactions

All thermal reactions are connected with the exchange of heat

### Pure Substances:
- First order transition
  - (discontinuous in $H$, $V$, $S$)
- Second order transition
  - (discontinuous in $c_p$)
  - solid-solid transition
  - magnetic transformation
  - order/disorder transf.
  - martensitic transformation
  - glass transition
Thermal Reactions – Multi Component Systems

Gibbs Phase Rule:

\[ P + F = C + 2 \]

\( P \)…number of phases, \( F \)…degrees of freedom, \( C \)… number of components

Degrees of freedom: \( T, p, \) composition parameters as variables
the pressure is usually fixed in the measurement system

\[ \Rightarrow P + F = C + 1 \]

Types of reactions:
Invariant reactions: \( F = 0; \) \( T \) is fixed to a certain value during the reaction
Other reactions: \( F > 0; \) the reaction occurs within a temperature interval
The DTA Signal

Idealized Curves of $T(t)$ and $\Delta T(t)$ for the determination of an invariant reaction

$\Rightarrow$ the simplest case
Factors Influencing the Shape of the DTA Signal

Real DTA curves are influenced by a number of factors: instrumental setup * heating rate * sample & reference properties * crucible properties * kind of reaction * kinetics * etc….

These factors influence the shape of the signal and thus the way the data have to be evaluated.
Heat Flow in the Instrument

DTA is a dynamic method. Heat is transferred between furnace, crucible, sample (reference) and thermocouple during the whole experiment.

Three mechanisms: convection, radiation and conduction of heat

Due to the dynamic character of the experiment, the temperature distribution is never completely homogenous. The temperature is not measured in the sample, but at the bottom of the crucible.
Relaxation

Exponential decline to the baseline after the thermal effect

\[ \frac{d\Delta T}{dt} = -A \cdot \Delta T \]

"Newton's law" behavior

The constant "A" reflects the experimental setup

DTA: separated crucibles ⇒ slow relaxation ⇒ optimized sensitivity for the detection of small effects, less effective for separation of succeeding effects.
Influence of Heating Rate

Calculated temperature distribution for spherical sample at different heating rates

Temperature distribution within the sample
($R_i = 0.4 \, \text{cm}, \, k_S = 10^{-7} \, \text{m}^2/\text{s}$)

Radial heat transfer from the surface to the core of the sample:

Inhomogeneous temperature distribution within the sample!

⇒ virtual shift of effect temperature
⇒ smearing of effect shape

Small heating rate means measurement near equilibrium

[W. Wendland 1986]
# Factors Influencing the Base Line

| **Reference Material:** | Should show **no thermal reactions** and thermal behavior similar to the sample. 
| | different heat capacity $\Rightarrow$ base line drift |
| **Sample Mass:** | Usually between 0.5 and 1000 mg. 
| | resolution $\Leftrightarrow$ sensitivity |
| **Shape of the Sample:** | For good thermal contact $\Rightarrow$ no powder; simple shape |
Example Sample Shape & Base Line

First heating

Second heating

Melting

Temperature /°C
Extrapolated Onset (1,3,4): Invariant effect begins (Heat exchange at constant T)
Onset (2): Non-Invariant effect begins (Heat exchange over a temperature interval)
Step/End (5,7) and Maximum (6): Effect ends (end of heat exchange and return to the base line)
DTA-Curves: Phase Diagram Ag-Sn

[T.B. Massalski 1996]
Good Praxis for DTA Experiments

**Calibration:**
Based on the melting point of pure substances. Crucible, standard material, heating rate, sample mass, atmosphere are kept constant.

**Characterization:**
The composition of samples and the crystal structure have to be investigated separately **before and after** the measurement.

**Combination:**
DTA experiments tell us that something is happening at a specific temperature. They usually do not tell us, what’s happening. Combination with other methods like X-ray diffraction, spectroscopy, microscopic investigation and composition analysis (e.g. Electron probe microanalysis) are required to interpret the results.
DTA: Experimental Setup

- Crucible holder with radiation shielding
- Open Alox crucible arrangement
- Netzsch DTA 404S
From DTA to DSC

Heat flow Differential Scanning Calorimetry (DSC) = Quantitative DTA

Question: Is it possible to evaluate the transferred heat from the temperature difference between sample and reference?

DTA: separated crucibles high sensitivity qualitative

DSC: defined heat flow high reproducibility quantitative

φ...heat flow
R...thermal resistance
O...furnace
P...sample
R...reference
From DTA to DSC

Linear heating rate ⇒ Stationary heat flow \((\phi_{OP}, \phi_{OR})\)
A thermal reaction causes a deviation from stationary conditions

Evaluation possible if reaction heat flow \(\phi_r \sim \Delta T_{PR}\)

Condition: \(\phi_r <\ll \phi_{OP}, \phi_{OR}\).

\[
\phi_r = \frac{dq_r}{dt} = -k(T) \cdot \Delta T_{RP}(T)
\]

\[
q_r = -k(T) \int_{t_1}^{t_2} \Delta T_{RP}(T) dt
\]

\(q_r\)......heat of reaction
\(k(T)\)......calibration constant

\(\phi\)...heat flow
\(R\)...thermal resistance
\(O\)...furnace
\(P\)...sample
\(R\)...reference
DSC-Measurement Modes

1) Determination of reaction temperatures (DTA mode) by evaluation of onset-, kink- and peak-temperatures.
2) Determination of exchanged heat (heat of reaction, heat of fusion) by peak integration
3) Determination of the heat capacity ($C_p(T)$) by base line evaluation
4) Kinetic studies
Evaluation by Peak Integration

Linear heating rate:
\[ T = T_0 + \beta T \]

\[ q_r = -k(T) \int_{t_1}^{t_2} \Delta T_{RP}(T) \, dt \]
\[ q_r = -\int_{T_1}^{T_2} \frac{k(T)}{\beta} \Delta T_{RP}(T) \, dT \]

\( q_r \)......heat of reaction
\( k(T) \)......calibration constant

\( K(T) \) has to be determined in a separate calibration experiment
Baseline Correction

Baseline shift connected with thermal effect $\Rightarrow$ correction necessary

a) provisional baseline (linear extrapolation) between onset and maximum

b) conversion (yield) function $\Delta m / m$ calculated

c) use this for second approximation of baseline

etc... (iteration)

[W. Hemminger 1989]
DSC Calibration

$q_R$ (or $\Delta H_R$) is proportional to the integrated peak area. The respective constant $k(T)$ has to be determined by calibration!

Conditions for calibration:
• Fixed geometry and external parameters
• Precise T- measurement
• Control of sample parameters

"Sensitivity Curve" of the Instrument
• measurement of $\Delta H_m$ of standards
• measurement of $c_p$ of standards
• electrical calibration
The heat capacity $c_p$ of a sample can be evaluated from the baseline.

High quality data needed!

1) Empty crucible measurement
2) Calibration substance measurement (e.g. synthetic sapphire, platinum)
3) Sample measurement

All three measurements have to be performed under exactly the same conditions!

Good thermal contact between sample and crucible required!

$$c_{p,s} = \frac{m_c}{m_s} \cdot \frac{\Delta T_s}{\Delta T_c} \cdot c_{p,c}$$
Kinetics: Basics

Heterogeneous Reaction

\[ \alpha: \text{reaction extent}; \quad \alpha = \frac{\xi}{\xi_{\text{max}}} \]

\[ \frac{d\alpha}{dt} = k(T) \cdot f(\alpha) \]

Need:
- Base line correction
- Calibration of Sensitivity
- Deconvolution \( \Rightarrow \) correction for the time constant \( \tau \) of the instrumental setup

Using DSC we determine

\[ \frac{d\alpha}{dt} = \frac{\frac{dH}{dt}}{\Delta H_R} \]

Determination of \( \tau \) using a square test signal:

U

\[ \text{Signal} \]

Response

t
DSC - Instrumental Setup

Integrated Platinum DSC sensors with Alox or glasscarbon-crucibles

Netsch DSC 404 S
Example DTA – Pure Compounds

\[ \text{NH}_4\text{NO}_3, \ 10\text{Kmin}^{-1} \]

1: ortho II ⇒ ortho I
2: ortho I ⇒ tetragonal
3: tetragonal ⇒ cubic
4: cubic ⇒ liquid
5: decomposition

\[ \text{KNO}_3, \ 5\text{Kmin}^{-1} \]

Heating curve:
- polymorphic transformation & melting

Cooling curve:
- supercooling & metastable transformation
Phase Diagrams by DTA (1)

Al\textsubscript{50}Ni\textsubscript{20}Si\textsubscript{30}

Vertical section at 20 at\% Ni

Single measurement:
- evaluation of heating curves
- cooling curves: supercooling, metastable equilibria
- identification of invariant and non-invariant arrests
Phase Diagrams by DTA (2)

Series of measurements:
• Within a section, but with different compositions
• Identification of thermal arrests at different compositions
• Graphical representation

Invariant ↑
Non-Invariant ↑
Liquidus ↑
Liquidus ↓
Phase Diagrams by DTA (3)

- **Combination with other Methods:**
  Identification of the phase composition of the samples by various isothermal methods:
  - X-ray powder diffraction (XRD)
  - Optical microscopy (metallography)
  - Electron probe microanalysis (EPMA)

- **Combination with information on limiting systems**

- **Evaluation according to Phase diagram rules**

- **Additional Sections at other compositions**
Phase Diagrams by DTA (4)

Limiting Binary Al-Ni

Al-Ni-Si Vertical section at 20 at% Ni
Phase Diagrams by DTA (5)

Limiting Binary Ni-Si

Al-Ni-Si
Vertical section at 20 at% Ni

Dynamic Methods
Phase Diagrams by DTA (6)

Isothermal section at 550°C

⇒ Independent experimental determination necessary!
Phase Diagrams by DTA (7)

**Rule of Landau and Palatnik:**

\[ r_1 = r - d^- - d^+ \geq 0 \]

- \( r \): dimension of phase diagram
- \( r_1 \): dimension of the boundary of neighboring phase fields
- \( d^- \): number of phases that disappear
- \( d^+ \): number of phases that appear
Phase Diagrams by DTA (8)

Reaction Scheme / Scheil Diagram:

**Al-Ni-Si**

**Vertical section at 20 at% Ni**

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Dynamic Methods
DTA: Variation of Experimental Parameters

Citric acid / Citric acid monohydrate
Conflicting information on melting point

10 Kmin\(^{-1}\)

1: Dried sample
2: Open crucible
3: Cover with hole
4: Closed crucible
DSC: Evaporation of Water

2.18 mg Water, 10 Kmin⁻¹
Heat of evaporation by simple DSC experiment

\[ \Delta H_{\text{exp}} = 2241 \text{ Jg}^{-1} \]

\[ \Delta H_{\text{lit}} = 2263 \text{ Jg}^{-1} \]

Boiling point determination not possible with this experiment!
DSC: Glass Transition an Crystallization (1)

PETP sample, measurement on heating

Glass transition

Recrystallization

Melting

Endo

[H. Utschik 1996]
DSC: Glass Transition an Crystallization (2)

Series of samples with different thermal history

[H. Utschik 1996]
DSC: Polymerization Reaction

Sample TEDMA  Polymerization by different methods

1: Thermal Polymerization
2: Peroxo Initiator (25 mmol/l DBPO)
3: Peroxo Initiator (50 mmol/l DBPO)

Full peak integration yields same enthalpy of reaction.

\[ \Delta H_R = -406 \text{ to } -408 \text{ Jg}^{-1} \]

[H. Utschik 1996]
Mixture of LDPE and LLDPE

Melting Behavior:
LDPE: 1 Step, ~105°C
LLDPE: 2 Steps, ~120°C

Concentration determination by area integration

1. Derivation curve used for the separation of areas attributed to LDPE and LLDPE

[H. Utschik 1996]
DSC: Polymer Mixtures (2)

Integration of peak areas yields linear dependence

Different Mixtures

[H. Utschik 1996]
DSC: Purity of Pharmaceuticals (1)

Using van’t Hoff equation

\[ T_0 - T_m = \frac{RT_0^2}{\Delta H_{f,A}} \cdot x_B \]

\[ x_B = \frac{1}{F} \cdot x_B^* \]

\[ T_0 - T_F = \frac{RT_0^2}{\Delta H_{f,A}} \cdot x_B^* \cdot \frac{1}{F} \]

F...molten part of the sample (lever rule!)
The molten part, $F$, is determined by DSC:

Part of the peak area at $T_F$ using the onset angle $\alpha$ for extrapolation plus the respective part of the relaxation curve.

Linearization of raw data, in order to correct for incomplete integration.

Onset angle of the pure substance (calibration!)

Works for enantiomers!

\[ T_0 - T_F = \frac{RT_0^2}{\Delta H_{f,A}} \cdot x_B^* \cdot \frac{1}{F} \]

[W. Hemminger 1989]
TGA: Thermo Gravimetric Analysis

Determination of the mass as a function of temperature ⇒ applicable for all reactions involving the gas phase as one of the reaction partners

- decomposition reactions
- vaporization and sublimation
- desorption
- oxidation and reduction
- corrosion
- etc…

- Small samples
- Gas flow essential
- Different Temperature modes:
  - linear heating
  - isothermal
  - stepwise isothermal

Many commercial instruments available
Usually combined with DTA
TGA: Balance systems

The balance is the most critical part of the instrument
Sample masses: mg – g
Sensitivity: μg to sub - μg range
Constant position required (thermal expansion!)
Effective separation of furnace chamber and balance unit

Balance

Vertical, hanging
e.g. Setaram

Vertical, top-pan
e.g. Netzsch

Horizontal
e.g. Mettler
The TGA Curve (1)

A constant heating rate is usually applied. The change of mass is recorded as a function of temperature.

$\Delta m$: Ideally significant steps. Loss (or gain) of weight according to the stoichiometry of the reaction.

eg.:
- $\text{Ca(COO)}_2 \cdot \text{H}_2\text{O} \rightarrow \text{Ca(COO)}_2 + \text{H}_2\text{O(}g\text{)}$
- $\text{Ca(COO)}_2 \rightarrow \text{CaCO}_3 + \text{CO(}g\text{)}$
- $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2(\text{g})$

Figure 2.15  TG and DTG curves for calcium oxalate monohydrate, 12.65 mg.
Pt crucible, 20 K/min, nitrogen.

[P. Haines 1995]
The TGA Curve (2)

The temperature range belonging to each step strongly depends on experimental parameters.

**Temperature:**
- Evaluation of inflection point (steepest part of the $\Delta m/T$ curve)
- 1st derivative of the $\Delta m/T$ curve (DTG signal)
- Dependent on atmosphere, heating rate, sample mass,....

*Figure 2.15*  TG and DTG curves for calcium oxalate monohydrate, 12.65 mg, Pt crucible, 20 K/min, nitrogen.

[P. Haines 1995]
The Influence of the Gas Phase

Composition of the gas phase and reaction temperature (equilibrium) are fundamentally linked:

Equilibrium constant $K_p$

e.g.: $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \quad K_p = p(\text{CO}_2)$

The local atmosphere determines the reaction:

- Influence of grain size and sample mass.
- Composition of the working gas has to be controlled carefully.
- Flow rate of the gas important!
- Consideration of follow-up reactions!

[W. Hemminger 1989]
Quasi-Isothermal Mode

**Problem:** Lack of selectivity and bad separation of different steps.

**Approach:** Stepwise experiment to avoid kinetic effects

Different solutions are implemented in different commercial instruments: “Controlled rate” or “Autostep” mode

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**Graphical Representation:**

- **dm/dT (DTG) threshold value triggers the begin and end of quasi-isothermal mode.**
- **E.g.: Decomposition of Ni(NH$_3$)$_6$Cl$_2$**

[P.Haines, 1995]
Quasi-Isothermal DTA

In case of DTA, separation of effects is often a difficult problem. Systematic errors occur for non-invariant effects.

Q-DTA (“Smith DTA”):
\[ \Delta T \text{ (furnace – sample)} \text{ is kept constant } \Rightarrow dQ/dT \text{ constant} \]
Near equilibrium method \( \Rightarrow \) no “overheating” observed
Switch signal: 1\textsuperscript{st} derivation of DTA signal

Not included in commercial instruments

e.g.: liquidus in the vicinity of a eutectic point
TGA – Instrumental Setup

TGA sample holders

Combined TGA / DTA sample holders

Setaram Setsys Evolution
Example: Decomposition of Rubber

Example for a standardized procedure used for quality control

Steps:
1) evaporation of volatile components
2) pyrolytic decomposition
3) oxidation of carbon and filler material
4) partial decomposition of inorganic filler material

Working gas: N₂ (<600°C), O₂ (>600°C)

[H. Utschik 1996]
Example: Quality Characterization of Coal

Standard procedure for the quality control of raw materials

Stepwise isothermal mode with change of working gas at 900°C

Characteristic steps:
• H₂O
• Volatiles
• Carbon
• Ash

[P.Haines, 1995]
TGA - Combinations

**Combination with DTA/DSC**
- Identification of intermediate reactions
- Determination of reaction temperatures
- Temperature calibration of the instrument

**Evolved Gas Analysis (EGA)**
- Analysis of the chemical composition of the evolved gas by means of spectroscopic methods
- Better understanding of complex decomposition reactions

Coupling with FT-IR:
Determination of specific bands (e.g. C=O, CH₃, etc.)

Coupling with MS or GC-MS:
For detailed analysis of complex gas mixtures

Heated gas transfer system required!
Summary Dynamic Standard Methods

DTA, DSC and TGA are **standard methods** for the characterization of the thermal behavior of materials. Many commercial Instruments are available.

The use in industry is focused on **quality control and characterization**.

Scientific use is focused on the **investigation of phase diagrams**, the **analysis of thermal reactions** and the **measurement of thermodynamic properties**.

Usually, the **combination with other methods** is required for an unambiguous interpretation of results.
Dilatometry

Measurement of the thermal expansion of solid samples. Thermal expansion coefficient $\alpha$

$$\alpha = \frac{1}{l_0} \left( \frac{dl}{dT} \right)_p$$

Investigation of:
- Thermal Expansion of Polycrystalline and single crystalline material
- Phase transitions
- Change of microstructure
- Recrystallization
- Thermal treatment of lattice distortions and stress
- Manufacturing processes (sintering etc.)

Measurement modes: isothermal or temperature program
Dilatometry – Experimental Setup

Thermal expansion of pushrod $\Rightarrow$ correction of raw data required
Example: Sintering Barium Zirconate

Heating: 10 Kmin⁻¹, 1Kmin⁻¹, isothermal 1590 °C
Atmosphere: air

Pressed powder pellet with binder ("green body")

- binder burning
- shrinkage due to sintering process
- start of grain growth

Optimum density at 3.5 hours
Determination of expansion coefficient

Accurate thermal expansion studies are challenging due to sample material:
- porosity
- anisotropic behavior ⇒ microstructure dependent

For the study of thermal expansion, high-temperature X-ray diffraction is a good alternative method:
⇒ Measurement of lattice parameters as a function of composition
Thermomechanical Analysis TMA

TMA includes many different mechanical testing operations.

• isothermal or dynamic temperature program
• constant or oscillating load

Netzsch TMA 402
Thermomechanical Analysis TMA

Standardized testing procedures for the industry.