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Matthias Wagner

Thermal Analysis in Practice

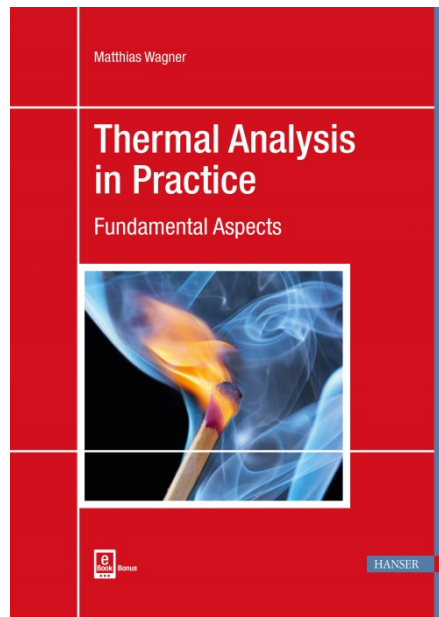Fundamental Aspects

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Sample Pages

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Preface

Thermal analysis is the name given to a group of techniques used to determine the physical or chemical properties of a substance as it is heated, cooled or held at constant temperature. The fascination of thermal analysis lies in its dual character: In addition to its purely analytical functions, it can be used as an engineering tool. Heat treatment applied to a sample in the first measurement may cause physical and chemical changes. Such effects can be investigated by cooling the sample and measuring it a second time in the same instrument.

The aim of *Thermal Analysis in Practice* is to provide practical help to newcomers, inexperienced users or in fact anyone who is interested in learning more about practical aspects of thermal analysis. It gives an overview of the DSC, TGA, TMA, and DMA techniques and shows how they can be used to measure different kinds of thermal events. The work presented in this handbook was performed using METTLER TOLEDO instruments, and the results were evaluated using METTLER TOLEDO's STAR^e software, but since DSC, TGA, TMA, and DMA are industry-standard techniques, readers using equipment from other manufacturers will also benefit greatly from the information presented.

Many modern thermal analysis instruments can be equipped with additional options such as connections to FTIR and MS equipment, humidity generators, UV/VIS light sources, or microscopy. These are covered in this book, as well as more recent developments in instrumentation, such as Flash DSC (fast scanning calorimetry) and connection to GC/MS.

Most of the chapters were written by Georg Widmann. Further contributions were made by Dr. Rudolf Riesen, Dr. Jürgen Schawe, Dr. Markus Schubnell and Dr. Matthias Wagner. We would like to thank everyone involved especially Dr. Vincent Dudler for the chapter on chemiluminescence. We also thank Dr. Angela Hammer for proofreading the original German manuscript. The text was reviewed and translated by Dr. Dudley May, Greifensee, and further reviewed by John Arthur, Australia. I would like to thank Dr. Klaus Könnecke for his contribution to the standards chapter.

Schwerzenbach, April 2017   Dr. Matthias Wagner, Editor

3.6 Polymer Additives

Most polymers contain different types of additives that give them special properties. Some important additives are summarized below.

Fillers such as carbon black are added to rubber to increase the strength and wear resistance of tires or shoe soles. Inorganic fillers in the form of flakes or short fibers improve the mechanical stability of polymers (e.g. polyester mixed with glass fibers). Calcium carbonate, silicate or clay is often used as an extender for large volume polymeric parts of relatively low polymer content.

Pigments serve as additives for coloring polymers. They are usually in the form of fine particles that are dispersed uniformly throughout the polymer mass (e.g. TiO_2 particles for a white color).

Stabilizers counteract the decomposition of polymers under environmental influences (UV-radiation, oxygen, water, heat). For example polyvinylchloride requires heat stabilizers. Otherwise it would lose hydrogen and chlorine atoms even at room temperature with the formation of hydrochloric acid and the polymer would become brittle.

Since most polymers are poor electrical conductors, their surfaces can easily become charged with static electricity. **Antistatic agents** bind moisture from the surroundings, which leads to an increase in the surface conductivity of the polymer.

Most polymers are flammable because they are basically organic materials. **Flame retardants** usually contain chlorine, bromine or metal salts. They prevent the occurrence or the spread of polymer fires.

Plasticizers are molecules of low molecular mass that lower the glass transition temperature. They act as lubricants inside the polymer and so improve its molding properties. Plasticizers are widely used with PVC products to make the PVC soft, for example for water hoses.

3.7 Use of Thermal Analysis to Characterize Polymers

Numerous important properties of polymers can be quantitatively determined using thermoanalytical methods such as DSC, TMA, TGA, DLTMA and DMA. Table 3.3 summarizes the different types of polymer, the thermoanalytical effects, and the techniques that can be used to characterize them.

Polymer type	Effect and corresponding thermoanalytical technique
Thermoplastics	- crystallinity (DSC) - glass transition (DSC, TMA) - melting behavior (DSC) - thermal stability, oxidation stability (DSC, TGA) - elastic behavior (TMA, DLTMA, DMA) - fillers and filler content (TGA-EGA)
Thermosets	- glass transition (often lies in region of decomposition) (DSC, DMA) - curing reaction and determination of the degree of cure (DSC) - thermal expansion coefficients (TMA) - gelation time (DLTMA) - thermal stability, oxidation stability (DSC, TGA) - fillers and filler content (TGA-EGA)

Polymer type	Effect and corresponding thermoanalytical technique
Elastomers	• viscoelastic behavior (TMA, DLTMA, DMA) • thermal stability, oxidation stability (DSC, TGA) • composition (TGA) • vulcanization (DSC) • fillers and filler content (TGA-EGA)

Table 3.3. Polymer types, thermoanalytical effects and the techniques that can be used to analyze them.

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4   Basic Measurement Technology

The aim of this section is to introduce and explain different terms and expressions that a newcomer to thermal analysis might encounter.

4.1   Definition

Sensors transform the physical or chemical property being measured into an electrical signal. The signal is usually analog. The term sensor covers a wide range of different measuring devices. Ideally, the measurement signal produced by the sensor should be a unique function of the property it is measuring. Quite often, the function is non-linear (e.g. thermocouple voltage as a function of temperature). If the non-linearity of a sensor is known and is reproducible, it can be easily mathematically modeled using appropriate software.

4.2   Sensitivity

Every sensor has a certain sensitivity. This is defined as the size of the electrical signal per unit of the measured quantity. For example, a copper-constantan thermocouple at room temperature has a sensitivity of about $42\ \mu V/K$. See also detection limit.

The behavior of sensors is normally described using polynomial mathematical models.

$$y = A + Bx + Cx^2 \ldots \tag{4.1}$$

where y is the quantity effectively measured (e.g. the electrical resistance of a resistance thermometer).

A is the ordinate intercept, B the slope (sensitivity of the sensor). C and possibly additional terms are needed to describe the non-linearity of the function. x is the true physical quantity.

4.3   Noise

Signal noise is more important than the sensitivity because modern electronics nowadays allows even very weak signals to be amplified. The noise is however also amplified. There are three main contributions to noise:

1. Real random fluctuations of the quantity (e.g. small fluctuations in temperature),

2. Noise occurring in the sensor (statistical measurement errors), and

3. Amplifier and analog-digital converter noise.

Noise can often be reduced by controlling the environment. For example, with a balance, the first two contributions to noise can be diminished by using a weighing table (dampens building and floor vibrations) and by weighing in a closed weighing room (suppresses air turbulence). A noisy weighing signal can also be smoothed (averaged) in order to obtain a more precise weight value. Weighing of course takes longer because of the time delay before the display stabilizes.

The noise corresponds to an alternating voltage of different frequencies superimposed on the signal. For this reason, as with alternating voltages, the noise is given as the root mean square value (rms) or the peak-to-peak value (pp). The pp/rms ratio is $2\sqrt{2} = 2.82$ for a sinusoidal oscillation, and about 4 to 5 for random noise.

Example: The noise of a temperature measurement device with a copper-constantan thermocouple is 0.5 μV pp (i.e. 0.1 μV rms), or 0.01 °C pp (i.e. 0.002°C rms).
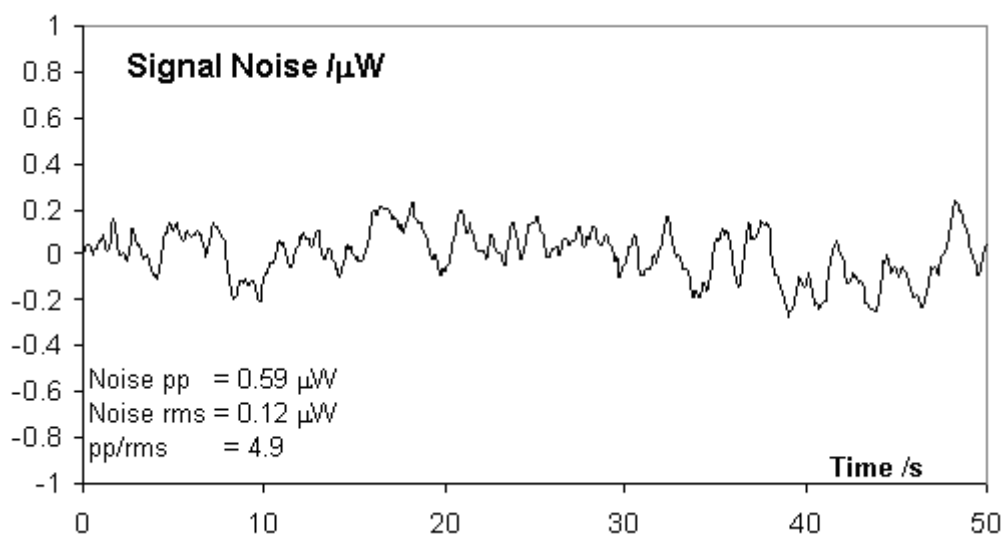
Figure 4.1. Calculation of peak-to-peak (pp) and root-mean-square (rms) values from random noise.

The effective rms value can be calculated from the equation:

$$\text{rms} = \sqrt{\frac{1}{n} \sum (x_i - \bar{x})^2} \qquad (4.2)$$

where n is the number of values, x_i the individual signal values, and $\bar{x}$ the mean value of the signal.

4.4 Detection Limit

The detection limit (often incorrectly called the "sensitivity") refers to the smallest change in the measurement signal that can be detected with reasonable certainty. The detection limit must of course be clearly larger than the background noise, for example 10 times the rms value (equal to about twice the pp noise). See also TAWN sensitivity.

4.5 Drift

When measurements are performed over long periods of time, the slow drift of the measurement signal becomes important, not just the statistical noise. This drift is given in units of the measurement quantity per hour or day. For a balance, the drift can be significantly reduced by thermostating.

If the drift of a measurement curve is reproducible, the curve can be saved as a "blank" curve and subtracted from the measurements that follow.

4.6   Time Constant, Limiting Frequency

In thermal analysis, physical quantities are usually displayed as measurement curves. The signal produced by a sensor cannot follow changes in the measurement quantity infinitely quickly. For example, any thermocouple has a certain heat capacity, C, and is connected to the medium to be measured via a thermal resistance, R_{th}. The product $R_{th} \cdot C$ corresponds to the time constant, τ (tau), of this sensor:

$$\tau = R_{th}\, C \qquad\qquad (4.3)$$

The thermal resistance is given in K/mW and the heat capacity in mJ/K (= mW·s/K) in order to obtain the time constant in seconds. The time constant is sometimes called the response time.
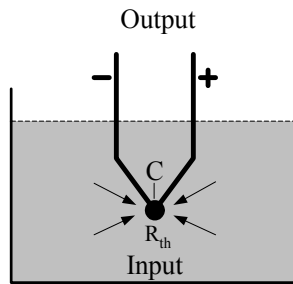
Figure 4.2. A thermocouple attempts to measure the true temperature of a water bath. The heat flows from the water across a thermal resistance R_{th} to the soldered junction, which has a certain heat capacity, C.

As the following figure shows, the measured signal approaches the true value asymptotically, provided the value remains constant. If the true value increases linearly, the measured signal lags behind by an amount given by the time constant. ("to lag" means to fall behind.)
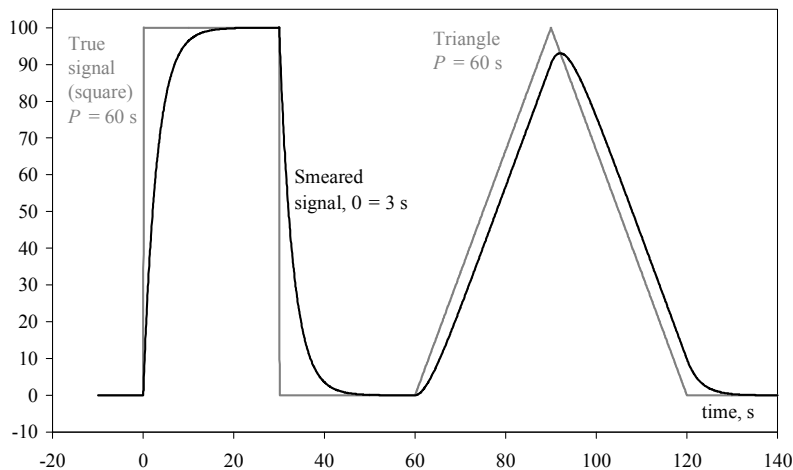
Figure 4.3. The true signal at the input is shown gray (left rectangular, right triangular, both with a period of 60 s; the output signal (black) of the RC element is somewhat smeared with a time constant of 3 s. The limiting frequency in this setup is 0.05 Hz, the limiting period 19 s.

The reciprocal value of the time constant is called the limiting frequency, ω_g (angular frequency, $\omega = 2\pi f$):

$$\omega_g = 1/\tau \quad \text{or} \quad f_g = \frac{1}{2\pi\tau} \qquad\qquad (4.4)$$

So that the limiting period is given by

$$P_g = 2\pi\tau \hspace{5cm} (4.5)$$

The expression "limiting frequency" does not mean that a signal is completely damped above this frequency or that the signal is not deformed below this frequency. Higher frequency signal changes are increasingly damped and are therefore no longer "resolved". This means that close-lying events are not properly separated:
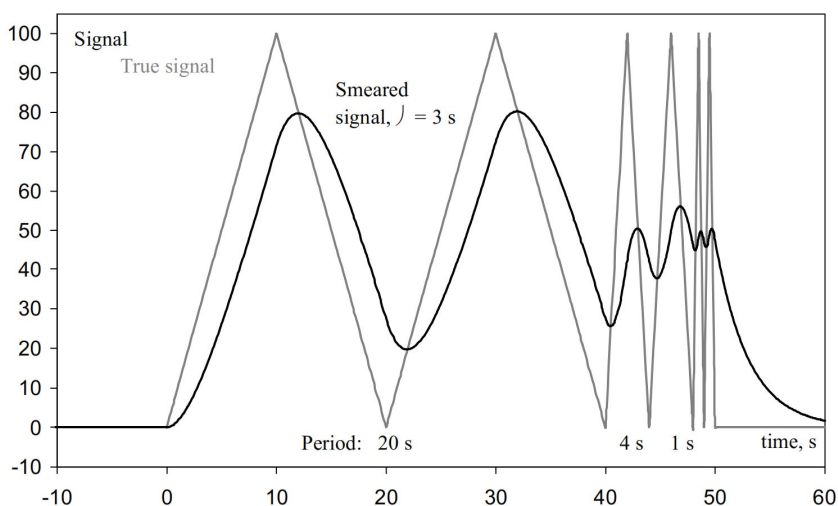
Figure 4.4. The two triangular input signals of 0 to 40 s corresponding to the limiting period of this sensor. They are well resolved and hardly damped. Those with significantly shorter periods (4, and 1 s) are strongly damped and the amplitude is reduced to about 5%.

4.7   Digital Resolution and Sampling Interval

Analog sensor signals are digitized so that they can be numerically displayed and electronically processed. The digital resolution of the ordinate is chosen so that the last decimal place displayed is somewhat noisy. The user can then monitor whether the sensor is functioning properly (e.g. no noise at all or excessive noise are important alarm signals). In the case of the copper-constantan thermocouple, a sensible resolution would be 0.01 K. It would, for example, be nonsense to resolve the noise 100 times for the sole purpose of obtaining impressive values (0.1 mK!) for technical data for the digital resolution of the instrument.

The analog signal is usually sampled at equidistant time intervals. The shorter the time constant of a sensor, the shorter the sampling interval must be to prevent the loss of information. An interval that is 3 to 10 times shorter than the time constant of the measurement setup is optimal. Shorter intervals result in unnecessarily large data files. If no abrupt changes of the measured quantity are expected, the sampling interval can be increased without losing information (especially with very long measurements).

4.8   Calibration and Adjustment of Sensors

Sensors must be calibrated at regular intervals. The calibration procedure checks whether the measurement deviation or measurement error is within acceptable, individually specified error limits. If the error is larger, the measurement system must be adjusted, that is, instrument parameters must be changed so that the error is smaller or eliminated.

Calibration requires reference materials with accurately known properties, that is, either

- a property that defines the scale concerned (e.g. according to the International Temperature Scale, ITS90, pure indium melts at 156.5985 °C, or the water-ice equilibrium at 0 °C) or

- a certified reference substance (e.g. a mass standard of 100 mg ± 5 μg). If no such reference material is available, other possibly less accurate "standards" recommended by experts in the field concerned are used.

The temperature is a measure of the mean kinetic energy of molecules, atoms or ions. It follows from this that there is an absolute zero temperature below which it is impossible to go and at which the kinetic energy of molecules, atoms and ions is a minimum.

Since all physical and chemical processes are more or less temperature dependent, temperature is a very important measurement quantity. For practical reasons, temperature measurement is based on comparison with a defined temperature scale.

The **International Temperature Scale** of 1990 (**ITS-90**) is based on 14 primary fixed points. These include for example

- the triple point of water (0.01 °C),
- the melting point of indium (156.5985 °C),
- the melting point of aluminum (660.323 °C) and
- the melting point of gold (1064.18 °C).

The two temperature scales in common use in the SI system differ in their zero point.

- The **Kelvin scale, known as the absolute temperature scale** or the **thermodynamic scale of temperature,** begins at 0 K, zero Kelvin. The unit is the Kelvin.
  The temperature of the triple point of water is assigned to the value 273.16 K. 1 K is the 273.16th part of the triple point temperature of water.
- The **Celsius scale** begins at the melting point of water at normal pressure (273.15 K) and has the same scale division as the Kelvin scale, i.e. a 1 K rise in temperature is the same as a 1 °C rise in temperature.

Two-point and multi-point calibrations are particularly recommended because they improve the modeling of the sensitivity function of the sensor.

If all the measured values deviate from the reference value by about the same amount, it is sufficient to shift the ordinate intercept of the function (one-point adjustment). If the deviation increases with increasing values, the slope must also be adjusted. If sufficient calibration points are available (if possible distributed over the whole measurement range), non-linearity can also be adjusted. In the sensor polynomial,

$$y = A + Bx + Cx2 \ldots \hspace{4cm} (4.1)$$

y is the effectively measured quantity (electrical value) or the physical quantity of interest (e.g. the measured temperature) still subject to errors.

A, B, C and possibly other terms are sensor parameters. x is the true physical quantity (e.g. the melting temperature of a reference substance).

For example, we want to calibrate an electronic thermometer using a thermocouple as a sensor. The reference substance is distilled water in a test tube. For the first measurement, the water contains ice crystals (0 °C) and for the second the water is boiling (at normal pressure 100 °C). We hold the thermocouple in the middle of the ice-water mixture and read off the temperature as soon as it is constant. Afterward we boil the water above a Bunsen burner using boiling stones to promote boiling. When the water boils, we hold the thermocouple slightly above the boiling water in the vapor phase and read off the temperature as soon as it is constant.

Ideally, the measured temperatures are 0.0 and 100.0 °C, as in Case 1 in the diagram. In practice, Case 2 with values of 1.6 and 102.2 °C or Case 3 with -2.5 °C and 103.7 °C are more likely to occur. The observed deviations are then plotted against temperature.

7.2.3   The Shape of the Melting and Crystallization Peak

Let us consider an imaginary experiment with a sample (a pure material, non-polymeric, not polymorphous), for example, indium, water, or dimethyl terephthalate:

An isothermal segment below the melting point of the sample is for temperature equilibration of T_r and T_s. We now add a dynamic heating segment. Because of the temperature advance (not shown for simplicity), T_r immediately increases linearly with time. T_s lags somewhat behind due to the heat capacity of the sample. When the sample reaches its melting temperature, T_f, the temperature remains constant until the sample has completely melted. At this point, no more enthalpy of fusion has to be supplied and the temperature increases rapidly until it once again lags slightly behind T_r. Another short isothermal segment is included to achieve temperature equilibration. This is followed by a cooling segment in which T_s once again lags slightly behind T_r. The sample shows a certain degree of supercooling and only starts to crystallize below T_f. The enthalpy of crystallization associated with this process causes the sample temperature to increase and in this particular case to reach the melting point. After complete crystallization, T_s again lags slightly behind T_r.

The sensor signal is equal to $T_s - T_r$. The shape of the melting peak is triangular and finally approaches the baseline asymptotically. The crystallization peak resembles a trapezium that begins almost vertically and ends asymptotically.
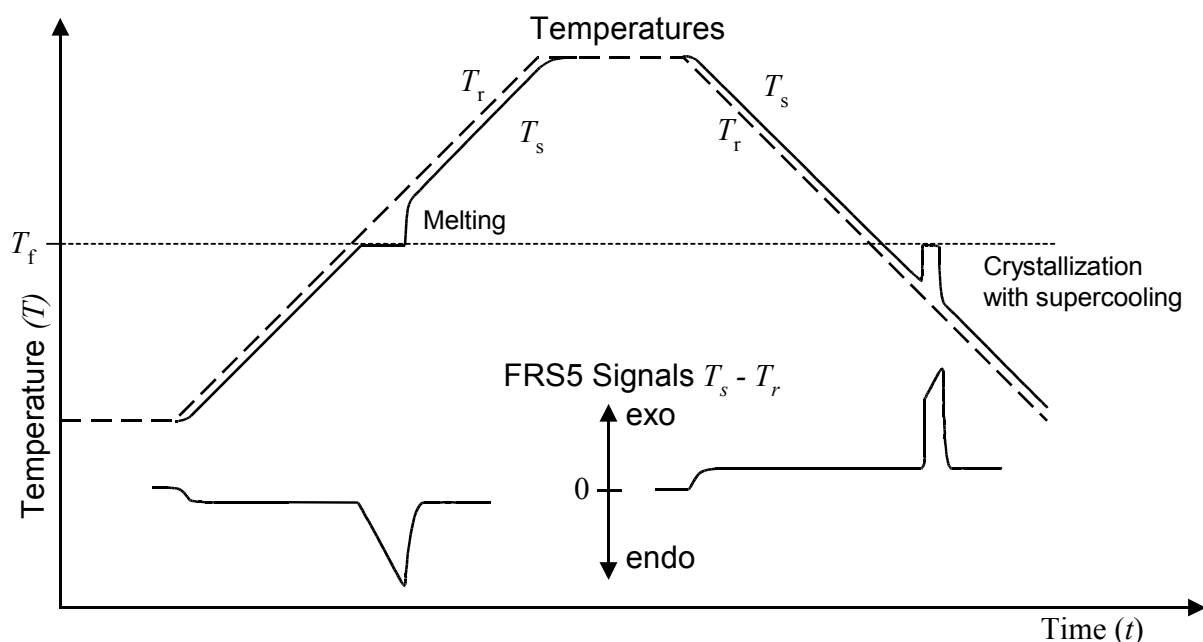
Figure 7.7. Top: The upper diagram shows the course of T_s and T_r on heating a sample with a melting point T_f (left), and on cooling the sample (right). The liquid sample does not crystallize on reaching the melting point but exhibits supercooling. As soon as crystallization begins, the temperature increases and reaches the melting point if the sample mass is sufficiently large. With small samples, the enthalpy of crystallization is not sufficient to heat the sample and the crucible to T_f. Bottom: The resulting sensor signals $T_s - T_r$ are plotted; in accordance with ICTAC rules, $T_s - T_r$ is positive for exothermic processes (exo) and negative for endothermic (endo) processes.

Finally, the sensor signal is converted to the DSC signal using eq 7.1. At the same time, the sign is set correctly (ICTAC: exothermic in the upward direction, or anti-ICTAC: endothermic upward). Although the calorimetric sensitivity is temperature dependent, the appearance of the curve hardly changes over the small temperature region observed so we can do without another diagram with the DSC signal.

Note: The DSC curves in this handbook are displayed with exothermic changes in the upward direction.

Dynamic DSC measurements are usually plotted against temperature rather than against time. If the reference temperature is chosen as the abscissa, the curve remains linear with time and does not change in appearance. DSC curves are, however, distorted if they are plotted with respect to sample temperature.
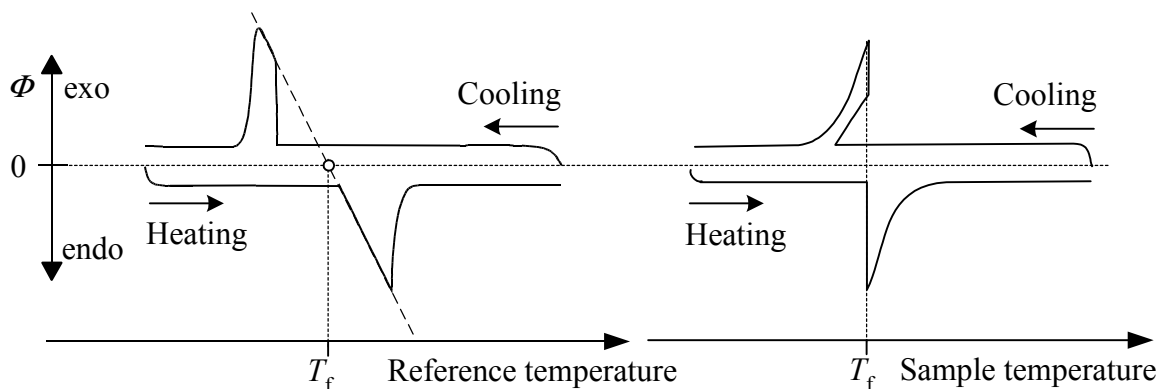
Figure 7.8. Left: The two DSC curves are plotted against the reference temperature. Comparison with Figure 7.7 immediately shows that all sample temperatures on the dashed line must be identical. The slope of this line is $-1/R_{th}$. Right: The DSC curves are plotted against sample temperature. Here the peak areas do not correspond to quantities of heat. Crystallization curves in particular look rather unusual.

In Figure 7.8, lines showing the same sample temperature have been drawn. In the right diagram, the line is vertical, but not in the left diagram. This has to do with the fact that the reference temperature continues to increase during isothermal melting of the sample. Let us assume that $T_s - T_r$ is just -1 K. In this case, according to eq 7.1,

$$\Phi_l = \frac{T_s - T_c}{R_{th}}$$

(7.1)

the heat flow is -1 K$/R_{th}$. The slope of the line of constant sample temperature (the slope of the pure melting peak) is therefore $-1/R_{th}$.

An important evaluation procedure is derived from this line of constant sample temperature, namely the "extrapolated starting temperature", more usually known as the "onset". This method evaluates sample temperature at the intersection of the tangent before the effect (i.e. the "baseline") and the tangent drawn to the peak.
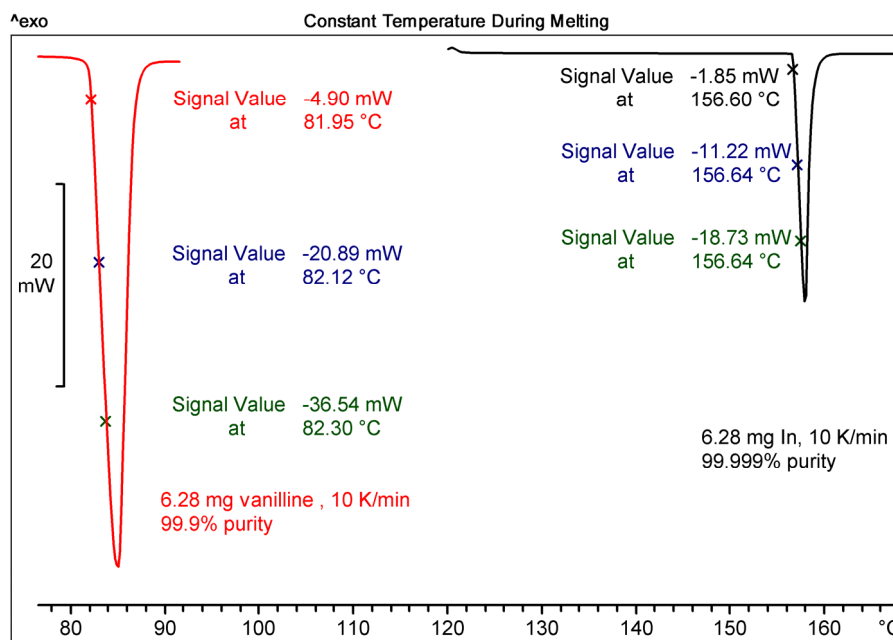
Figure 7.9. The sample temperature of the melting peak of indium remains constant at 156.6 °C (right) while the reference temperature increases from 156.6 to 167.4 °C (not visible from the figure). Only extremely pure non-polymeric materials exhibit a constant (sample) temperature during melting. With increasing impurity levels, the temperature increases more and more during melting. As the vanillin melting peak (left) shows, the increase at 99.9% purity is already 0.35 K.

Thermal Analysis in Practice **Fundamental Aspects**

7.3 Sample Preparation

Sample preparation is of utmost importance for achieving optimum measurement quality. Besides the right crucible, attention must also be given to

1. good thermal contact between the sample and crucible so that thermal effects are not smeared,
2. the prevention of contamination of the outer surfaces of the crucible either with sample or with its decomposition products, and
3. the influence of the atmosphere surrounding the sample.
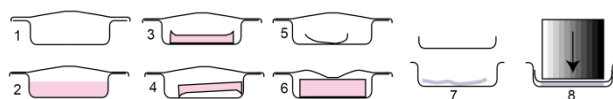
Figure 7.10. (1): Standard 40-μL aluminum crucible with lid before sealing. (2) to (6): After hermetically sealing through cold welding. (2): Liquid or powder sample of ideal geometry. (3): Punched-out sample with the flat side facing downward. (4): Bad example, with irregular side facing downward. (5): Originally flat plastic film that curves upward on heating. (6): Sample with deformed lid pressed downward. (7) and (8): Light aluminum crucible with a sample of irregular shape, for example a soft film, before sealing (7) and after sealing (8). The rubber punch adapts the lid to the shape of the sample.

Thermal contact:

Poor thermal contact results in large temperature gradients in the sample. Effects that are in reality sharp become smeared. Small temperature gradients give sharp effects. This increases the repeatability of results and improves the separation of neighboring peaks.

Small temperature gradients in the sample crucible are obtained by using samples of low mass and through good thermal contact between the sample and crucible:

- Flat disks, dense powders, and liquids are ideal.
- Irregularly shaped samples, for example plastic parts, are optimized by sawing and grinding flat the side in contact with the bottom of the crucible.
- Brittle substances are ground to a fine powder in a mortar. The powder is then added to the crucible using a funnel and compacted by means of a Teflon rod. Even paste-like samples can be pressed down into the crucible with a Teflon rod. Deformation of the bottom of the crucible can be prevented by placing the crucible on a flat surface (if necessary with a hole in it to accommodate the center pin).
- Samples that have been punched out: any burrs (ragged or rough edges) should be removed or the sample is placed in the crucible with the burrs facing upward.
- Liquids: Dip a spatula into the sample. The drop on its end is transferred by touching the sample crucible. Alternatively a small syringe can be used (be careful because plastic parts may be attacked by solvents).
- Fibers: If the fibers are sufficiently thick, they can be cut into small lengths that lie flat in the crucible (covering with a layer of heat conducting powder is sometimes advantageous).
  Thin fibers can be packed into a bundle in a small piece of degreased aluminum foil that is then pressed flat using the Teflon rod. The packet is then placed in the crucible with the flat side facing downward.
- Plastic films that often curve upward during melting can be held down flat against the bottom of the standard aluminum crucible using a light aluminum lid.
- Strongly exothermic reactions can be measured by mixing (diluting) the sample with relatively coarse aluminum oxide or glass powder. This also facilitates the diffusion of gases from the sample. The substance used to dilute the sample must be dry and must not react with the sample.
- If samples sublime, the crucible volume should be as low as possible (use light aluminum crucibles or the lid of a light aluminum crucible as a "filler").

The base of the crucible should always be flat, not indented or bow-shaped - otherwise heat transfer is poor.

External contamination of the crucible:

The crucible must not be contaminated with any sample residues once it has been prepared! This could prevent proper operation of the sample changer. Furthermore, sample material should never come into direct contact with the DSC sensor. A contaminated sensor can produce artifacts (effects due to the contaminant) and cause poor heat transfer. Organic sensor contamination can be removed by heat cleaning (at 600 °C for 10 min using air as purge gas). Water-soluble contamination can be carefully removed using a moistened cotton bud followed by heat cleaning.

Certain samples tend to creep up the walls of an open crucible during the measurement and contaminate the DSC sensor. This can be prevented by using a crucible lid (with a hole).

Influence of the atmosphere:

- An **open crucible** without a lid allows the atmosphere of the measuring cell to come into contact with the sample (free exchange of gas). The measurement is then performed under isobaric conditions (i.e. under the practically constant pressure of the surrounding atmosphere). There is of course the danger that substances that creep out of the crucible or that sputter can damage the measuring cell. This can be prevented by covering the crucible with a lid with a hole.
Restricted gas exchange (**self-generated atmosphere**) is necessary to determine the boiling point of a liquid. It prevents the sample from prematurely evaporating. The self-generated atmosphere is obtained by sealing the crucible using a lid with a small hole. The hole is made by placing the lid on a relatively hard surface, for example, the crucible box, and piercing it with a sharp needle. If possible, the diameter of the hole (20 to 100 µm) should be examined under a microscope. To check whether in fact there is a hole, the lid can be held in front of a source of light. We recommend the use of lids with the pre-punched 50-µm hole.

- If a sample is **hermetically sealed** in the crucible, no work of expansion occurs (e.g. endothermic evaporation). Since the sample is subjected to increasing pressure from its decomposition products, the onset of decomposition shifts to higher temperatures. This isochoric type of measurement is limited by the pressure limits of the crucible (aluminum standard crucible withstands about 200 kPa overpressure). The high-pressure crucibles have proven useful for such measurements.
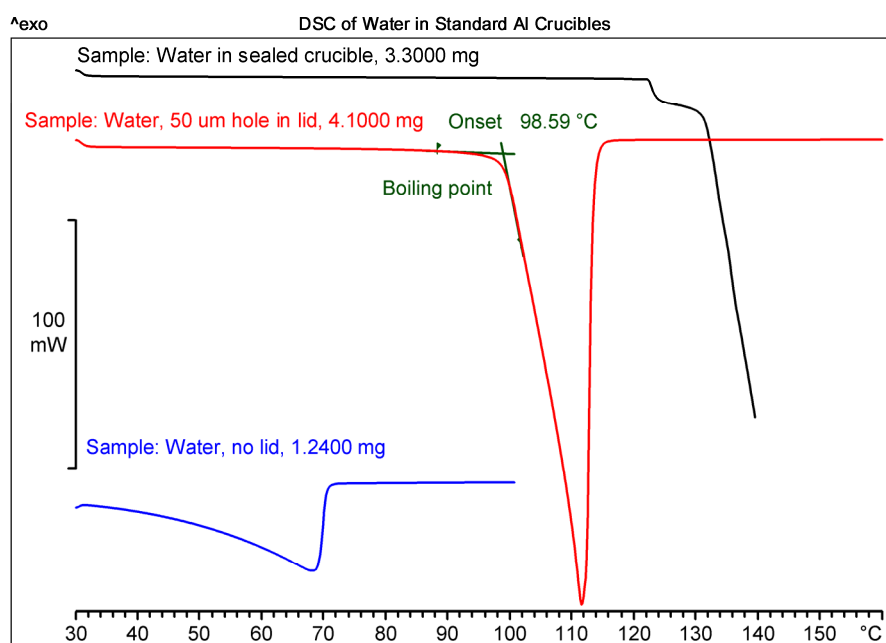

Figure 7.11. DSC curves of water. Above: In a hermetically sealed crucible, there is no boiling point. The effect at about 125° C is due to the crucible bursting. Middle: In a self-generated atmosphere, the boiling point can be measured as the onset. Below: In an open crucible, water evaporates before the boiling point is reached.

7.4 Performing Measurements

7.4.1 The Purge Gas in DSC Measurements

To protect the DSC measuring cell and to achieve good reproducibility, we recommend purging the cell using a gas flow rate of about 50 mL/min. This applies to all measurements. When open crucibles or crucibles with a hole in the lid are used, the sample is exposed to the atmosphere of the measuring cell.

Nitrogen is inert in the temperature range up to about 600 °C and is therefore the standard atmosphere for DSC measurements. Many measurements are performed in **air** because most samples do not react with the oxygen of the air below 100 to 200 °C. **Oxygen** is normally used for studies involving oxidative behavior.

Helium is completely inert and has excellent thermal conductivity. This property lowers the DSC time constant, which is why it is sometimes used instead of nitrogen to obtain better separation of close-lying peaks.

Further notes on atmosphere can be found in Chapter 6, General Measurement Methodology.

7.4.2 Crucibles for DSC Measurements

General information on crucibles can be found in Chapter 6, General Measurement Methodology. Crucibles serve as sample containers and protect the DSC sensor against contact with the sample. They should normally be inert with respect to the sample, that is, they should not react with it in any way.

The most important crucibles used for DSC are:

- **Aluminum crucibles**. Aluminum is largely inert. It is however attacked (dissolved) by sodium hydroxide and many acids. In some cases, metal samples can form low melting alloys with aluminum. Solution: heat the aluminum crucible at 400 °C for 10 minutes in air to enhance the protective oxide layer.
  Under pressure, aluminum crucibles made of pure aluminum can be cold-welded and hermetically sealed.
  The METTLER TOLEDO **standard 40-μL aluminum crucible** with lid is the crucible most often used. There are also special lids that are pierced with a fine needle by the sample changer directly before measurement. This prevents gas exchange occurring before analysis while the sample waits on the sample turntable.
  The **light aluminum crucible** for films and powdered samples gives improved peak separation due to its very short time constant. Liquid samples should not be measured with this crucible because they are often squeezed out when the lid is closed.

- **High-pressure crucibles** are mostly used for safety investigations of chemicals and reaction mixtures. The advantage of these crucibles is that the sample remains completely inside the crucible and really does reach the reaction temperature. In an aluminum crucible, it would evaporate (depending on the vapor pressure) and be swept out of the measuring cell by the purge gas without undergoing the reaction.
  METTLER TOLEDO offers pressure crucibles of different types. They are sealed by pressing or screwing the lid onto the crucible.

Crucibles made of platinum, gold, copper, sapphire or glass are also available for special purposes but are less frequently used.

8 Fast Scanning Calorimetry

8.1 Introduction

The great strength of today's DSC is that complex information about physical transitions, the structure of materials, the kinetics and enthalpies of chemical reactions and other transformations can be obtained quickly and easily. Conventional DSC has therefore developed into a widely used standard method.

Modern conventional DSC instruments have a signal time constant around one second. Scanning rates are typically between 0.1 K/min to 300 K/min and cover almost 3.5 decades. To analyze solidification processes, a wide range of cooling rates are also possible.

However, these rates are not sufficient to model technical production processes (e.g. casting techniques) because cooling rates between 1 K/s and 10,000 K/s are used. The materials (polymers, aluminum alloys, metallic glasses etc.) resulting from such industrial processing can be in the form of super-saturated solid solutions, nano-structures, polymorphic phases, glasses or other metastable structures. These metastable materials can also show diffusion or reorganization effects at low heating rates, which can lead to misinterpretation of conventional DSC measurements. As a result, there is a need for dynamic calorimeters, which can be used to analyze processing cooling rates. The impact of cooling rates, on the material properties can be studied through the analysis of reorganizations during heating and the kinetics of fast transformations [1, 2, 3]. The need for widening the scanning rate range for dynamic calorimetry, to allow a more detailed investigation of meta-stable materials, was one of the motivators in the development of fast scanning calorimetry (FSC).

Flash DSC revolutionizes the well-known DSC technology. The instrument can analyze reorganizational processes that were previously impossible to measure. The Flash DSC is complementary to conventional DSC. Heating rates now cover a range of more than 7 decades.

Figure 8.1. Formation of sample structures using different cooling rates.
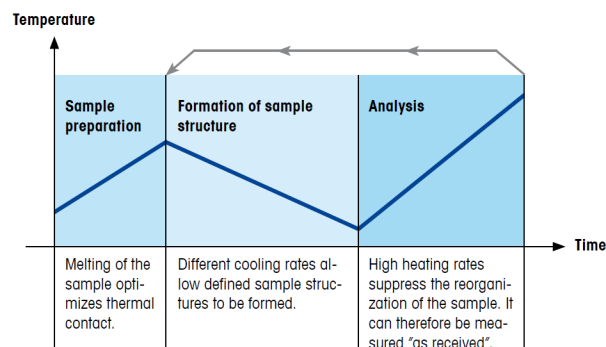
The Flash DSC allows you to prepare samples with defined structures, such as those that occur during rapid cooling in injection molding processes. The application of different cooling rates, as shown in Fig. 8.1, influences the crystallization behavior and structure of the sample. The use of high heating rates enables materials to be analyzed without interference from reorganization processes – there is no time for such processes to occur. The Flash DSC is also the ideal tool for studying crystallization kinetics.

8.2 Design and Measurement Principle

8.2.1 The Calorimeter
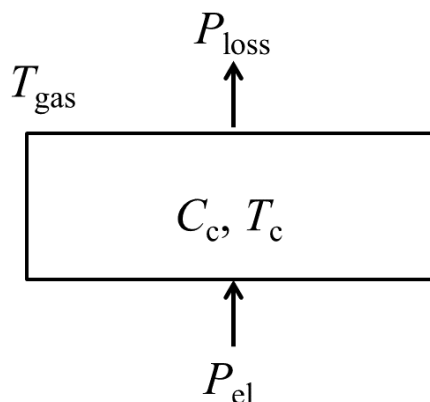
Figure 8.2. Simplified model of a calorimeter

In order to understand some main aspects of a fast scanning calorimeter, the simplified model shown in Fig 8.2 is used. The calorimeter with the heat capacity C_c and at a temperature T_c is surrounded by a gas, with the temperature $T_{gas} \leq T_c$. The temperature of the calorimeter is controlled by the electric power, P_{el}, of the heater. The calorimeter loses energy due to the heat flow between the calorimeter and the surrounding, P_{loss}.

$$P_{loss} = -\frac{\Delta T}{R_{CG}} \tag{8.1}$$

where ΔT is the temperature difference between the calorimeter and the surrounding gas and R_{CG} is the thermal resistance between the calorimeter and gas. These parameters depend on the type of the gas, the pressure and the size of the calorimeter.

For this simple model, the equation is balanced by defining P_{el} as:

$$P_{el} - \frac{\Delta T}{R_{CG}} = C_c \, \beta \tag{8.2}$$

where $\beta = \dfrac{\mathrm{d}T_c}{\mathrm{d}t}$ is the scanning rate.

Eq. (8.2) shows the basic requirements of a fast scanning calorimeter:

- For $P_{el} \geq P_{loss}$ the calorimeter is heated or kept isothermal; otherwise the calorimeter is cooled.
- To reach high heating rates, the heat capacity of the calorimeter must be small.
- To reach high cooling rates, the surrounding gas should be at low temperature and the thermal resistance must be sufficiently small.

This means that the calorimeter must be small (low C_c). For high cooling rates, it is necessary for the calorimeter to be surrounded by a cold gas. The maximum cooling rate increases with decreasing gas temperature and with increasing heat conductivity of the gas (low R_{CG}). This requires a sufficiently high heating power.

To achieve a small heat capacity of the calorimeter, C_c, the related volumes have to be as low as possible. Therefore, the calorimeter usually consists of a thin Si_3N_x - membrane with the electronic components for the heater and temperature sensor. The chip sensors are made using integrated circuit fabrication technology [4]. More detailed aspects of fast scanning calorimeters are discussed by Schick et al. [5, 6]. An overview of different chip sensors for calorimeters is given in [7].

8.2.2   The Sample

The sample has to fulfill several requirements:

- In order to follow the fast temperature changes, the sample must have good thermal contact to both the calorimeter and the surrounding gas. The heat capacity must be sufficiently small.

- If the bulk behavior of the sample should be measured, surface induced effects must be suppressed. This requires sufficiently large sample volumes.

- Good thermal contact between the calorimeter and the sensor is also necessary to measure the sample temperature.

- Small temperature gradients inside the sample require sufficiently thin samples.

8.2.3   Design of the Flash DSC

The Flash DSC from METTLER TOLEDO (Fig. 8.3) is a commercial Fast Scanning DSC. The behavior of the instrument depends on the sensor used. For the UFS1 sensor, the signal time constant is less than one millisecond. This allows very high heating and cooling rates to be achieved. Even with such short time constants, the sensitivity of the DSC is excellent. Therefore, measurements can also be performed at relatively low heating rates.

The typical heating rates extend from 0.5 K/s to 40,000 K/s (30 K/min to 2,400,000 K/min) and depend on the experimental conditions, the temperature range and the sample properties. Therefore, there is a region in which the lower heating and cooling rates of the Flash DSC and the higher heating and cooling rates of a conventional DSC overlap. The Flash DSC complements a conventional DSC. The combination of both instruments makes the accessible heating and cooling rate range more than 7 decades. This allows new information to be obtained on structure formation and reorganization processes in materials.

Figure 8.3. The METTLER TOLEDO Flash DSC

The Flash DSC is operated by the **STA**Rᵉ Software from METTLER TOLEDO. This software includes numerous features specially designed for the Flash DSC. These include:

- Use of different sensor types.

- Creation of temperature programs containing up to 200 segments.

- The possibility to improve the sample temperature accuracy by calibration after the measurement.

- Flexible evaluation procedures for large sets of measured curves (e.g. subtraction of one curve from a set of curves).

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