Thermal Analysis
Information for Users

Dear Customer,

We are very pleased to receive more and more articles from you for publication in UserCom. Thanks to new techniques and better performance, thermal analysis is being used in an ever-increasing number of scientific fields. Hyphenated techniques such as evolved gas analysis, microscopy and chemiluminescence yield much more information about samples and very often greatly simplify the interpretation of measurement results.

We think this issue of UserCom will once again give you ideas for applications in new and interesting areas using the multitude of techniques now available.

Choosing the right baseline

Dr. Rudolf Riesen

Choosing the correct baseline is crucial for the determination of the enthalpy of a transition or a reaction. The baseline represents the DSC curve that would be measured if no transition or reaction occurred. The examples described in this article illustrate how to choose the right baseline for a particular evaluation.

Introduction

In thermal analysis, baselines are mostly used in connection with the integration of peaks. The peak area is determined by integrating the area between the measurement curve and a virtual or true baseline. In the same way, the peak temperature is defined as the point on the curve where the distance to the baseline is greatest. Extrapolated baselines are important for the determination of glass transition temperatures

Contents 1/2007

METTLER TOLEDO

and the onset temperatures of effects. In the literature and in standards, the term "baseline" is sometimes defined differently, or different terms are used for the same thing. The terms most frequently encountered have therefore been summarized together with some brief comments. A number of application examples are then discussed to illustrate the rules governing the choice of baselines and that show which type of baseline should be used for the optimum evaluation of a particular DSC curve.

Terminology

The terms used in thermal analysis are summarized and explained in various standards.

However, since the definitions are not always the same, the terms used have been summarized below for the discussion of baselines that follows. Further definitions can be found in the book by Höhne [1] as well as in the standards mentioned (ISO [2], DIN [3], ASTM [4, 5]). The preferred terms are highlighted, but other terms are also included.

Blank, blank curve, zero line [3], instrument baseline [2]: A thermal analysis curve measured under the same conditions as the sample but without the sample; the mass of the crucibles used must be the same. Blank curves are essential for specific heat capacity determinations. Comment: In some cases, the zero line [1] is also understood as a curve measured without the sample or crucibles.

Sample blank: A curve that is obtained from a "fully converted" sample. This is usually the second heating run of the same sample under the same conditions. The effect measured in the first heating run no longer appears.

Baseline (also sample baseline [2]): Part of the curve that does not exhibit any transitions or reactions.

This is an isothermal baseline if the temperature is held constant. A dynamic baseline is obtained when the temperature is changed through heating or cooling.

The baseline depends on the heat capacity of the sample (with an empty reference crucible) and the blank curve.

Comment: In practice, the term is also used to mean the virtual baseline used for integration.

Virtual baseline [2]: An imaginary line in the region of a reaction or transition that the DSC curve would show if no reaction or transition enthalpy were produced.

Interpolated baseline [1]: This is a line that joins the measured curve before and after the peak.

Extrapolated baseline: This is a line that extends the measured curve before or after the thermal effect.

The types of virtual baselines normally used are explained in the applications.

True baseline: In the region of the transition or reaction, the baseline can be calculated according to physical data or even measured.

Factors influencing the baseline

The influence of measurement conditions on the DSC curve and the baseline should always be taken into account when interpreting curves and evaluating numerical data. Furthermore, the course of the blank curve and its reproducibility should be known.

Possible important parameters that can change during a transition are [1]:
1. Mass, shape and structure of the sample, e.g. powder or film;
2. Thermal conductivity and contact of the sample with the bottom of the crucible, e.g. a powder liquefies during melting;
3. Heat transfer from the crucible to the sensor, e.g. deformation of the crucible due to an increase in the internal pressure or through products escaping from the crucible;
4. Heating rate, e.g. when it changes from dynamic to isothermal;
5. Thermal history of the sample and measuring system.

If it is difficult to choose the baseline, it often helps to examine the sample and crucible after measurement with regard to the above points.

## Principles for constructing virtual baselines

The basic principle for constructing a virtual baseline can be summarized as follows:

The interpolated baseline for the determination of the transition enthalpy or the reaction enthalpy leaves the DSC curve tangentially before the thermal effect and joins the curve again tangentially after the effect.

A good example to illustrate this is the take-off and landing of an aircraft. In special cases there are some exceptions to this that will be described in the examples. Figure 1 shows how these principles are applied.

a) 1 nonsensical; 2 good (**Line**),
b) 1 unsatisfactory (horizontal straight line); 2 good (integral baseline, possibly **Spline**),

Figure 1.
Drawing interpolated DSC baselines (the endothermic direction is upward).
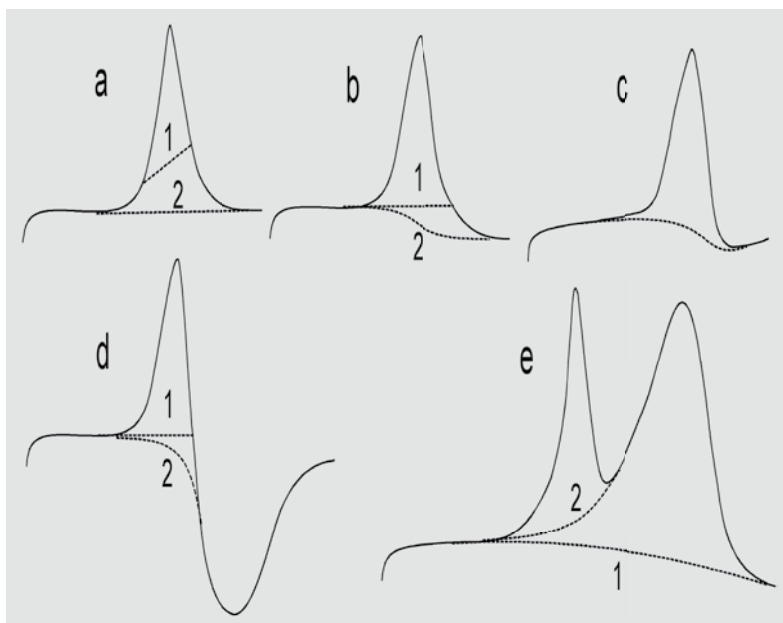
c) good (**Integral tangential**, or possibly **Spline**),
d) melting with exothermic decomposition, 1 good (straight line to the point of intersection with the DSC curve); 2 rather arbitrary because the DSC curve is the sum of simultaneously occurring processes,
e) two overlapping peaks, e.g. eutectic and melting peak of the main component, 1 good for the total integral, 2 good for the integration of the first peak (peak interpreted as sitting on the main peak, **Spline**).

The transition line from one tangent to another can have different shapes and be displayed as a straight line or as a sigmoidal curve (S-shaped function). The type of interpolated baseline chosen depends mostly on the physical conditions or chemical changes involved, for example:

- The specific heat capacity of the sample, c_p, hardly changes during the transition or it changes linearly with temperature.
- The transition is accompanied by a significant change in the heat capacity
- The heat transfer to the sample changes during the transition.

- The mass of the sample changes during the transition.

The ST**A**R^e software provides several different types of baseline to accommodate the changes shown by the DSC curve during a transition.

Table 1 describes the baselines and their typical applications.

The extrapolated virtual baselines are the tangents to the measured curve at the evaluation limits, just as they are used for interpolation with the baselines. Typi-

Baseline type	Description	Typical DSC application
Line	This is a straight line that joins two evaluation limits on the measured curve.	Reactions, without abrupt c_p changes, that exhibit a constant c_p increase or a constant c_p. This baseline is the default setting.
Tangential left	This is the extension of the tangent to the measured curve at the left evaluation limit.	Integration of a melting peak on a measured curve with subsequent decomposition of a substance.
Tangential right	This is the extension of the tangent to the measured curve at the right evaluation limit.	Melting of semicrystalline plastics with significant c_p temperature function below the melting range.
Horizontal left	This is the horizontal line through the point of intersection of the measured curve with the left limit.	Peak integration when substances decompose.
Horizontal right	This is the horizontal line through the point of intersection of the measured curve with the right limit.	Isothermal reactions, DSC purity determination.
Spline	The **Spline** baseline is the curve obtained using a flexible ruler to manually interpolate between two given points (known as a Bezier curve). It is determined as a 2nd order polynomial through the tangents at the evaluation limits. This bow-shaped or S-shaped baseline is based on the tangents left and right.	With overlapping effects.
Integral tangential	Starting with a trial baseline, the integral baseline is calculated using an iterative process. The conversion calculated from the integration between the evaluation limits on the measured curve is normalized. Like the **Spline** curve, this bow-shaped or S-shaped baseline is based on the tangents left and right.	Samples with different c_p temperature functions before and after the effect. The **Line** baseline would possibly cross the DSC curve and lead to large integration errors depending on the limits chosen.
Integral horizontal	This baseline is calculated using an iterative process like the **Integral tangential** baseline. This S-shaped baseline always begins and ends horizontally.	Samples whose heat capacity changes markedly, e.g. through vaporization and decomposition. The **Line** baseline would possibly cross the DSC curve and lead to large integration errors depending on the limits chosen.
Zero line	This is the horizontal line that intersects the ordinate at the zero point. It requires a blank curve subtraction.	Determination of transition enthalpies including sensible heat.
Polygon line	The baseline can be determined through a curved line or a straight line from individually chosen points. The polygon line is then first subtracted from the measured curve and the resulting peak integrated using a straight baseline.	In special cases.

Table 1.
List of virtual baseline types for integration.

cal applications of extrapolated baselines are for the determination of the:

- glass transition temperature
- extrapolated onset temperature (also as first deviation from the measured curve)
- step height.

In all evaluations in which extrapolated tangents are used, one must make sure that artifacts on the measured curve or signal noise do not interfere with the determination of the slope of the tangent. This would result in the tangents being in the wrong place.

Application examples

The different types of baseline presented in Figure 1 are illustrated in the follow-ing practical examples. Figure 2 shows the most frequently used virtual base-lines:

a) **Spline**: This is used to determine the reaction enthalpy of a postcuring reaction that is overlapped by the beginning of decomposition.

b) **Horizontal right**: Isothermal curing of an epoxy resin at 140 °C. When the reaction has finished the DSC curve is horizontal. The baseline can be drawn horizontally through the last measured points.

c) **Integral horizontal**: The DSC curve of 1.162 mg water, which on heating evaporates through a 50-µm hole in the crucible lid. The loss of mass causes a change in the sample heat capacity, which is reduced proportion-ally to the amount vaporized. At the end of the measurement the crucible is empty and the DSC signal is practi-cally 0 mW.

d) **Line**: The DSC curve shows a glass transition of the amorphous part of the polyethylene terephthalate (PET) followed by cold crystallization and melting of the crystallites. The straight baseline is the virtual extension of the DSC curve after the glass transition to the curve after the melting and shows the trend of the curve without crystal-lization and melting. The integral of the two effects yields 22.8 J/g as the difference between the exothermic and endothermic processes. This means that crystallites were already present at the beginning of the measurement. In relation to the melting enthalpy of 100% crystalline PET, this shows that the degree of crystallization of the sample was initially about 16% and was therefore not fully amorphous.
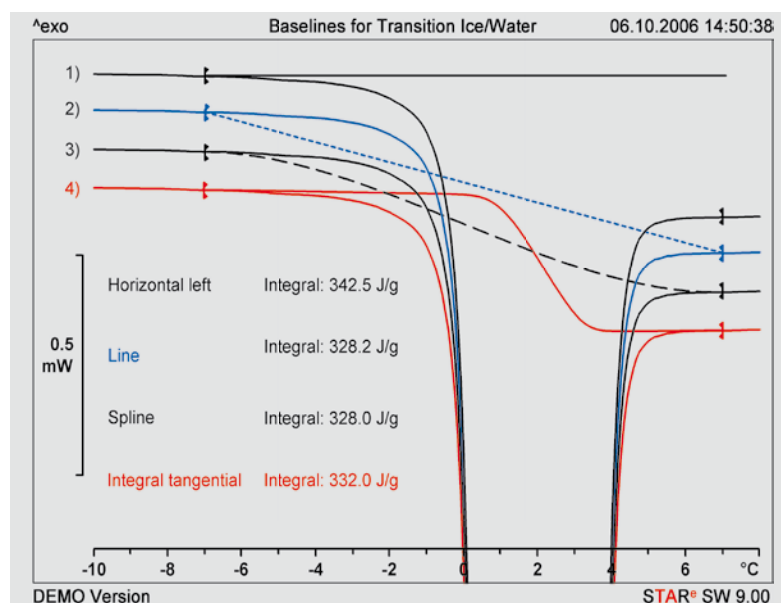
Figure 3 discusses how to draw the interpo-lated baseline if the baselines before and after the peak are at different levels, for example because the specific heat capac-ities of ice (2.1 J/gK) and water (4.2 J/gK) are very different. The figure shows four identical curves of the same part of the DSC melting peak of 1.87 mg water measured at 5 K/min (melting enthalpy 333 J/g). Each curve has a different base-line type.

1) The **Horizontal left** baseline does not take the change in heat capacity in the evaluation range into account and yields a peak area that is too large.

2) The **Line** baseline is clearly unfa-vorable and contradicts the basic principles (no tangents, it crosses the DSC curve). In reality, the change in heat capacity is of course not linear with temperature between the evalua-tion limits as the dotted line wrongly shows.

3) The **Spline** baseline is somewhat bet-ter, but also crosses the DSC curve.

4) In this case, the **Integral horizontal** baseline is optimal. It draws the baseline proportional to the peak area from the level before the peak to the level after the peak and so takes into account the change in heat capacity.

Figure 2.
Examples of fre-quently used types of baseline.

Figure 3.
Example for the change of the heat capacity during the transition ice/water.

In the first three cases, the result of the integration can be improved by choosing better limits, but even so, the virtual baselines do not correspond to the physical facts.

Overlapping thermal effects are usually the most difficult with regard to choosing a realistic virtual baseline.

Figure 4 shows how a second heating run of the reacted sample helps to locate the exact position of the baseline. An epoxy resin was partially cured at 100 °C for 80 min, causing the material to vitrify [6]. The DSC curves shown in Figure 4 were then measured at 5 K/min. The postcuring reaction begins at the glass transition (curve 1). Curve 2 shows the DSC second measurement of the same, fully cured, sample. The straight line 3 (dotted) describes the course of the DSC curve after complete curing above the glass transition. It therefore represents the baseline for the integration and serves as a tangent for the determination of the glass transition temperature. It can be assumed that the behavior of the heat capacity above the glass transition during postcuring is about the same as that of the fully cured sample.

The postcuring enthalpy is determined as follows: The dotted line (curve 3) is subtracted from curve 1 yielding curve 4. The peak in this curve is integrated using the **Zero line** baseline type within the limits shown. Separation of the partially overlapping peaks could also be achieved using temperature-modulated DSC.

The purpose of the example in Figure 5 is to show how important correct interpretation of the DSC curve is. The choice of the integration limits and the baseline type should be good enough to obtain results that provide consistent information for further investigations.

Figure 5 shows the DSC curve of a 40% solution of sucrose in water measured at 5 K/min after slow cooling. The glass transition occurs at about −45 °C and the ice that had crystallized out melts in the sucrose solution in the range −37 °C to 0 °C. Integration from −29 °C (dotted
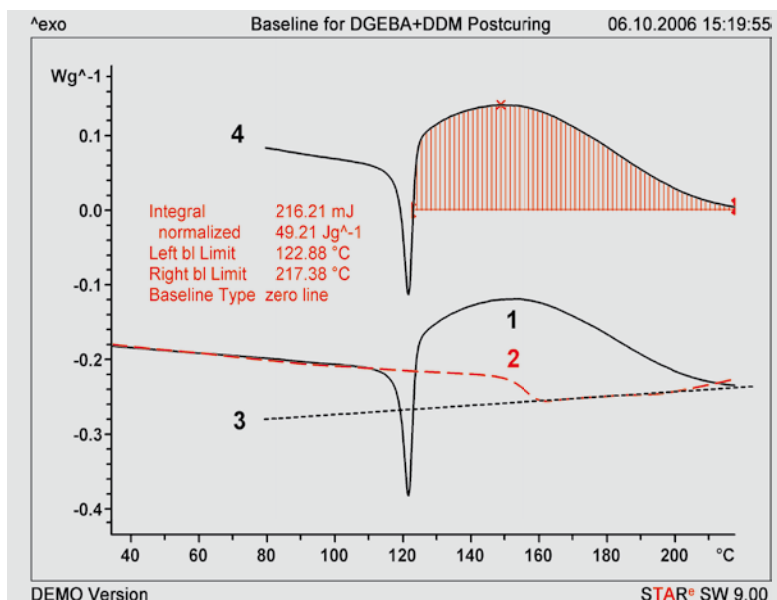

Figure 4.
Example showing a special baseline (Polygon using just two points, X) to determine the postcuring reaction. The **Zero line** baseline was used to integrate the peaks in curve 4.
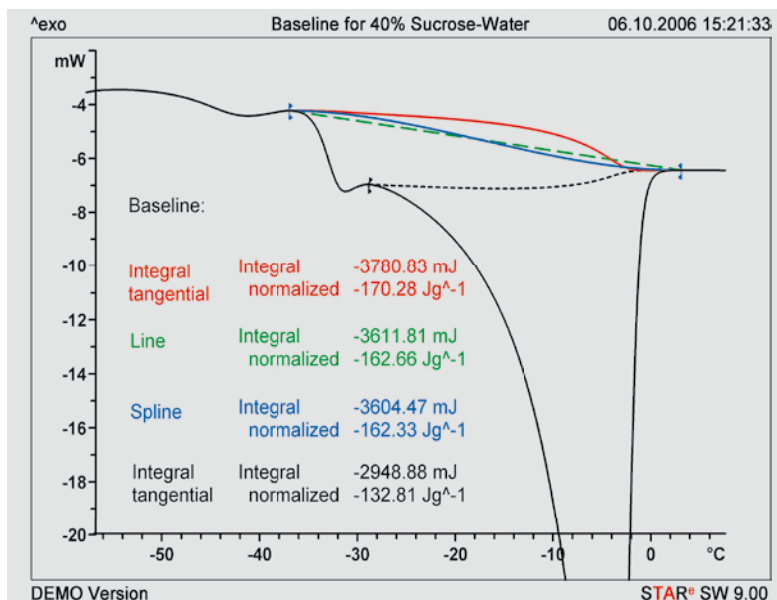

Figure 5.
Curve interpretation and the choice of integration limits and baselines.

line) would assume that the specific heat capacity decreases, which is not the case here. The **Line** and **Spline** baselines yield enthalpy values that are 5% too low. Only the **Integral tangential** baseline from −37 °C gives the correct value that can be used for a consistent quantitative evaluation.

Although one thinks mostly about interpolated baselines, extrapolated baselines are in fact just as important.
This is shown in the examples in Figure 6:
a) Oxidation induction time (OIT) of a mineral oil, measured at 180 °C at an oxygen pressure of 3.5 MPa.
b) Melting point of benzoic acid determined as the extrapolated onset.

c) Glass transition temperature of polystyrene determined as the midpoint according to how the tangents are constructed (depends on the particular standard).
d) At the glass transition, the specific heat capacity, c_p, increases leading to a step in the c_p curve. The step height is characteristic of the amorphous content of the sample.

Conclusions

Whenever possible, physical changes must be taken into account when choosing the optimum baseline for an integration or onset determination.

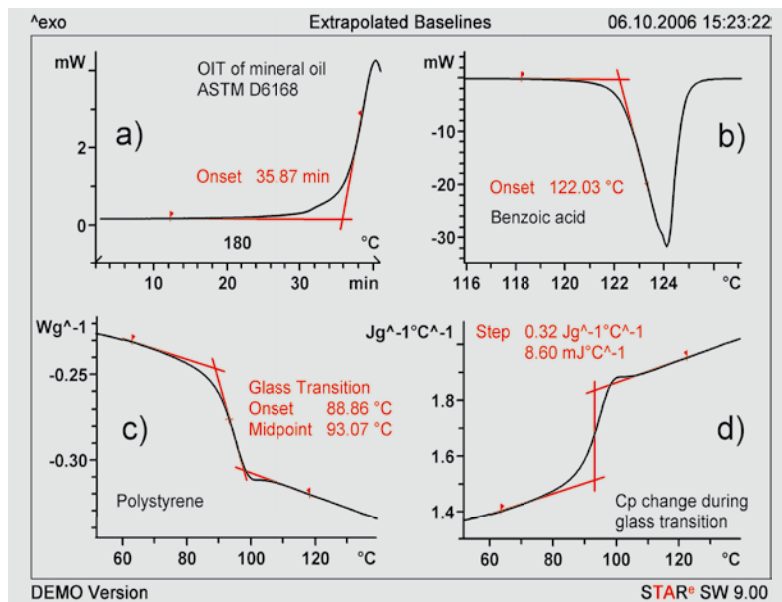Since jumps in heat capacity rarely occur, a virtual baseline should be con-

Figure 6.
Examples of extrapolated baselines.

structed that is smooth and free from any irregularities or discontinuities.

The correct choice of baseline assumes that the curve has been properly and consistently interpreted [7]. Furthermore, the integration limits must be carefully chosen depending on the information required.

The rules and types of baseline discussed here using DSC measurements as examples can be applied to other TA measurement techniques, e.g. for the integration of peaks from SDTA, DTG analyses and other mathematically derived measurement curves.

Literature
[1] G. W. H. Höhne, W. Hemminger and H.-J. Flammersheim: Differential Scanning Calorimetry, Springer Verlag, 1996. Chapter "The DSC Curve"
[2] ISO 11357-1 (1997) Plastics – DSC. General principles
[3] DIN 51005 Thermal analysis; Terms
[4] ASTM E473 Standard Terminology Relating to Thermal Analysis and Rheology
[5] ASTM E 2161 Standard Terminology Relating to Performance Validation in Thermal Analysis
[6] J. Schawe, METTLER TOLEDO UserCom 14, 17
[7] METTLER TOLEDO UserCom with articles on curve interpretation: DSC, UserComs 11 and 12; TGA, UserCom 13